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Д.В. Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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SYNTHESIS OF NANOCRYSTALLINE COMPLEX OXIDES IN SUPERCRITICAL ALCOHOLS

Abstract. An intensive search for solid electrolytes with high proton conductivity is being continued over the past few decades, which is primarily due to the high practical significance of these systems. Proton conductors are widely used as components of electrochemical devices such as gas sensors, electrolyzers, fuel cell membranes, etc. The variety of currently known solid proton conductors can be classified by operating temperature parameters, with the allocation of low, medium and high temperature regions. Each class, from the point of view of its practical use, has a number of advantages, but at the same time, specific disadvantages that hinder practical implementation. In this regard, the material science goal - the synthesis of new materials with functional properties, remains relevant.

For the first time, complex oxides – lanthanum niobates – were synthesized using alcohol solutions of salts of the corresponding metals by the solvothermal method in a flow reactor in a supercritical isopropanol medium. This method allows one to obtain single-phase lanthanum orthioniobate oxides, the phase composition, structure and morphology of which is characterized by X-ray phase analysis (XRD), Raman spectroscopy (Raman spectroscopy), scanning and transmission electron microscopy (SEM and TEM).

Key words: synthesis in supercritical alcohols, complex oxides, lanthanum orthoniobate.

Proton-conducting electrolytes for H^+ - SOFC were discovered by Iwahara et al. [1,2] in the early 1980s. They indicated that niobates and tantalates of rare earth metal are a group of compounds with interesting properties, both from scientific and practical point of view. The study of the properties of these ceramic materials was based on the study of their optical and, in particular, fluorescent properties [3-4].

The structural properties of this ceramic were studied in [5,6]; It turned out that lanthanum niobate at 490 to 525°C undergoes a phase transition (of the second kind) from a monoclinic phase with a fergusonite structure to a tetragonal one with scheelite structure. This phase transition is accompanied by a large thermal expansion, and in turn, it was determined that the high-temperature phase has a higher proton conductivity.

A number of works were devoted to the search for doping cations capable of stabilizing the high-temperature phase. It was shown that in the case of introduction of cations into the lanthanum sublattice, the transition temperature changes only slightly, whereas in the case of substitution of niobium into the sublattices, it changes appreciably (up to room temperature in the case of doping with antimony or vanadium) [7, 8].

The introduction of lanthanides with a smaller ionic radius into the lanthanum position does not affect significantly the phase transition temperature, but strongly changes the optical and electrical properties of rare-earth niobates, in particular, enhances the luminescent properties [9].

Rare-earth metal orthiobates are a new class of high-temperature proton conductors with the ABO_3 perovskite structure [10,11], having proton conductivity of the order of 10^{-4} Ohm^{-1} Sm^{-1} at temperatures above 700°C and high stability in a humid and CO_2 enriched environment. However, $LaNbO_4$ has a rather low conductivity [12].

Since the presence of oxygen vacancies is the main factor responsible for the appearance of proton defects, the value of proton conductivity is directly related to the defectiveness of the complex oxide. Numerous efforts have been made to improve conductivity by single- or multi-element doping of perovskite sublattices with cations having a lower valency and a larger ionic radius, including monovalent (Na^+, K^+), divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}) or trivalent cations (Fe^{3+}, Gd^{3+}, La^{3+}), as well as perovskite B-sublattices with cations having high valency with a small ionic radius, such as W^{5+}, Ce^{4+}, Zr^{4+} , Mn^{3+}, Co^{3+}, Yb^{3+}, and Y^{3+} [13,14].

According to Hausgrund and Norby [11], when doping lanthanum niobate with calcium cations ($La_{0.99}Ca_{0.01}NbO_4$), the proton conductivity in wet hydrogen increases sharply and is about 10^{-3} C/cm at 900°C, while it is two orders of magnitude lower in the case of undoped material

Various methods are used to synthesize rare-earth metal orthioiobates: the preparation from salts melts [15, 16], solid-phase synthesis [11,15,16,17], the sol-gel method [18,19,20], spray pyrolysis (thermal decomposition of aerosol solutions) [12], coprecipitation [21] and mechanochemical synthesis [21,22]. Most of the above methods are multi-stage, time-consuming and require large time and energy spending. In contrast, synthesis using supercritical fluids (SCS) is characterized by simplicity and high productivity.

Aymonie [23] emphasizes that the supercritical fluid technology used to produce oxide materials makes it possible to control the synthesis process by varying the operating parameters and provides an understanding of how each parameter, affecting the synthesis process, allows controlling the material characteristics in terms of size , morphology, structure.

The aim of this work is to obtain proton-conducting materials using alcohol solutions of salts of the corresponding metals by the solvothermal method in a flow reactor in a supercritical isopropanol medium. During the study, the complex oxides $LaNbO_4$ and $La_{0.99}Ca_{0.01}NbO_4$ were synthesized and characterized by a complex of physicochemical methods.

Experimental part. Samples of complex oxides were synthesized by solvothermal synthesis using supercritical isopropanol in a flow-type reactor; installation scheme is shown in figure 1. Samples of lanthanum niobates were synthesized using alcohol solutions of salts of the corresponding metals. The precursors used were $La(NO_3)_3*6H_2O$ (VECTON, 99.99%), $Ca(NO_3)_2$ (REAHIM, 99.5%), $NbCl_5$ (LLC NPP Methim, 99.90%). Precursor solutions were prepared by dissolving in isopropanol . The resulting mixture was injected into the mixer with a syringe pump at a rate of 5 ml/min. A preheated alcohol was injected continuously with a plunger pump in the same mixer at a rate of 9 ml/min. The synthesis was carried out at 400^0C and 120-130 atm. After exiting the reactor and depressurizing the product was cooled in a heat exchanger and collected in a storage tank. The decantation method was used to separate the solid product from the mother liquor. The resulting precipitates were dried and calcined at $700\text{-}1300^0$C for 4 hours.

To obtain a dense ceramic based on a sample doped with calcium, the compressed tablet was calcined in air for 4 hours at 1300°C. Its density was estimated using data on its weight and geometric dimensions.

The phase composition of the samples was studied using a BrukerAdvance D8 diffractometer with CuKα radiation. Diffraction patterns were obtained by scanning in the angle range 15 - 90 (2Θ) with a scan step of 0.05 (2Θ). The obtained phases were identified using an ICDD X-ray file cabinet. The coherent scattering region (CSR) was determined by the diffraction reflection (004) for the tetragonal $La_{0.99}Ca_{0.01}NbO_4$ [PDF 50-0919] and (-121) for the monoclinic [PDF 22- 1125] phases.

IR spectra of the samples were recorded on IR Fourier spectrometer Cary 660 FTIR spectrometer (Agilent Technologies) and PIKE Technologies Gladi ATR in the range of 4000-250 cm^{-1}, with a scanning step of 32. Electron microscopic studies were performed on a JSM-6460 LV scanning electron microscope (JEOL, Japan).

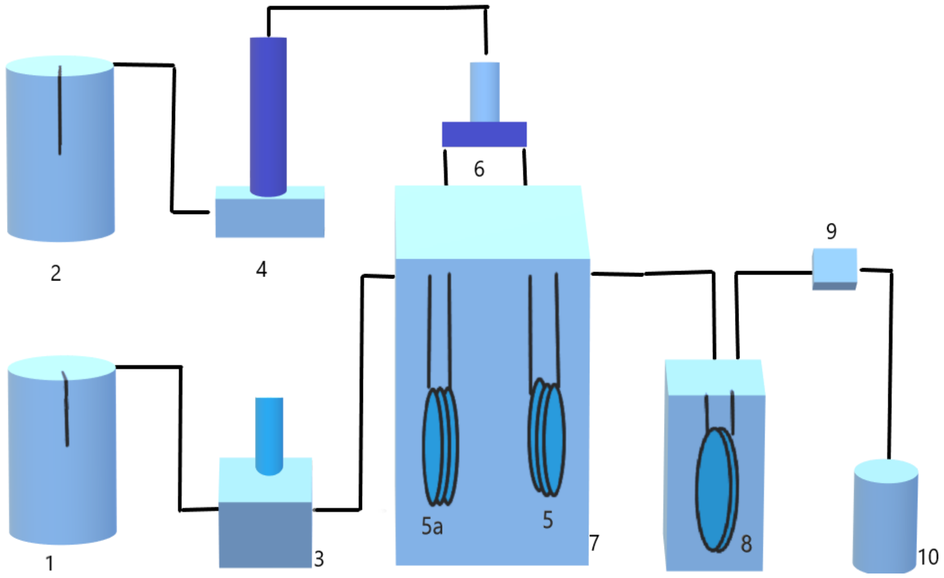
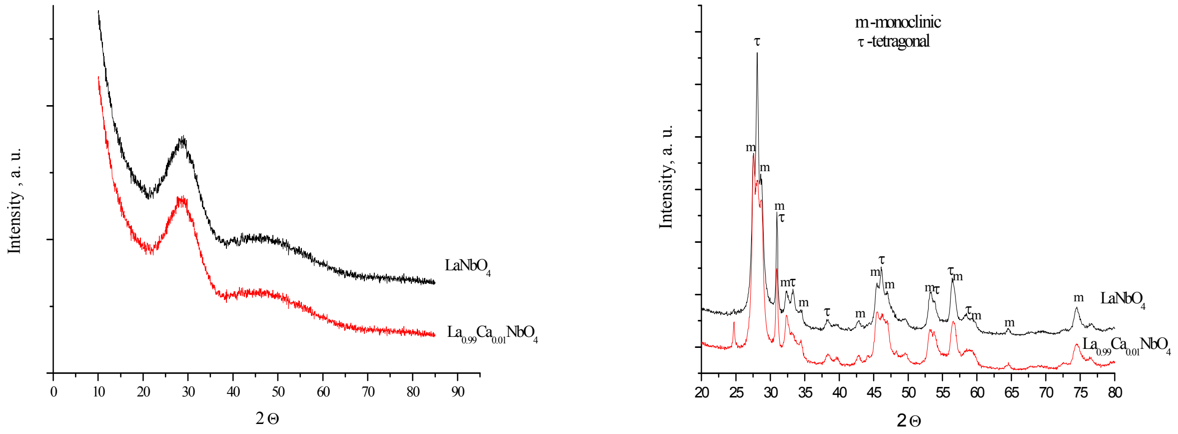


Figure 1 - Laboratory installation for supercritical synthesis 1 - a tank with alcohol, 2 - a tank with a solution of metal salts, 3 - a plunger pump, 4 - a syringe pump, 5 - a reactor, 5a - a flow heater for alcohol, 6 - a mixer, 7 - a furnace, 8 - a heat exchanger, 9 - back pressure valve, 10 - storage tank

Results and discussion. According to the X-ray diffraction pattern (figure 2a), after supercritical synthesis, the initial lanthanum orthoniobate and the calcium doped sample are X-ray amorphous materials. After calcination at 700°C in both samples, lanthanum orthoniobate is formed in two phase modifications: low-temperature monoclinic [01-083-1911] and high-temperature tetragonal [00-050-0919]



a

b

Figure 2 - X-ray diffraction patterns of lanthanum orthoniobate samples a) after SCA and b) after calcination at 700°C

According to the XRD data (figure 2b), $La_{0.99}Ca_{0.01}NbO_4$ is a mixture of two phases — monoclinic and tetragonal, whose peaks are broadened, indicating that the sample obtained during the synthesis is an ultrafine material with a primary particle size of the nanometer range. With an increase of the calcination temperature (figure 3), the crystallization of both phases increases, and the phase ratio changes in the direction of increase of the monoclinic phase $La_{0.99}Ca_{0.01}NbO_4$. After calcination at 1300°C, the tetragonal phase is retained in very small quantities.

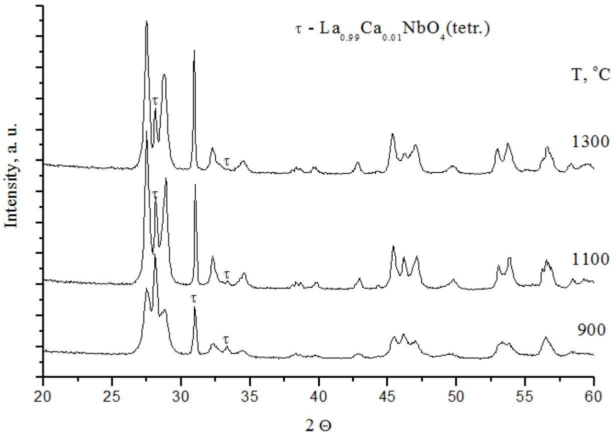


Figure 3 - Diffraction patterns of $La_{0.99}Ca_{0.01}NbO_4$ after calcination at 900–1300°C

As follows from the data in Table. 1, the domains of both phases remain in the nano-region even at high calcination temperatures. It should be noted that the size of the monoclinic phase domains decreases with an increase in the calcination temperature, which may be related to the specific dynamics of the transformation process of the tetragonal phase into the monoclinic one, which does not proceed to the end even at 1300°C. In this case, a decrease in the specific surface with increasing annealing temperature indicates an increase in the average particle size of the sample and, therefore, an increase in the density of domain walls with which the channel of rapid diffusion of oxygen ions and protons can be associated [19].

Table 1 - Characteristics of $La_{0.99}Ca_{0.01}NbO_4$ after calcination at 700-1300ºC

№	Calcination temperature, ^{0}C	Coherent scattering region, nm		S_{BET}, m^2/g
		Tetragonal phase	Monoclinic phase	
1	700	23.8	-	20
2	900	35.4	42.3	16
3	1100	52.9	27.9	4
4	1300	66.0	27.5	0.2

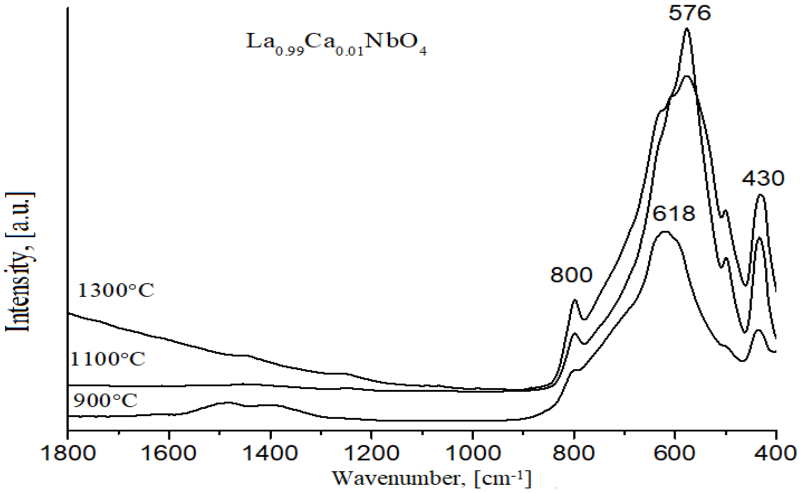


Figure 4 - IR spectra of lanthanum orthoniobates after calcination at 900–1300°C

According to IR spectroscopy, the absorption bands in the range of 1500–1400 cm^{-1} for the low-temperature sample correspond to carbonates (figure 4). The spectral absorption regions of Nb-O groups in the [Nb^{5+} O_4] $^{3+}$ tetrahedron are in the region of 600 cm^{-1}. Oscillations in the regions of 800 and

430 cm^{-1} correspond to the monoclinic phase $La_{0.99}Ca_{0.01}NbO_4$, which is in good agreement with the XRD data. The intensities of these peaks increase with annealing temperature.

The relative density of $La_{0.99}Ca_{0.01}NbO_4$ tablet calcined at 1300°C for 4 hours was ~ 90%, which indicates good sinter ability of the materials obtained by this method due to their disorder. Indeed, for samples obtained by the method of high-temperature solid-phase synthesis, such a density is achieved only at higher temperatures of ~ 1500°C [15-17]. The fine-grained structure of ceramics with the grain size 1-5 microns also should be noted (figure 5).

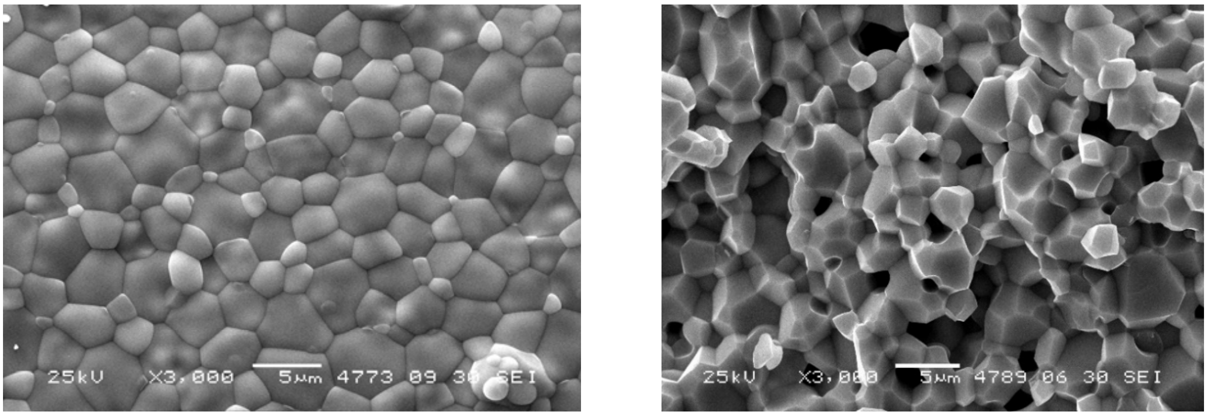


Figure 5 - SEM images taken from the surface (a) and from the cleavage (b) of the $La_{0.99}Ca_{0.01}NbO_4$ ceramic sample

Conclusions. Thus, in this work, the complex oxides $LaNbO_4$ and $La_{0.99}Ca_{0.01}NbO_4$ were obtained by solvothermal methods in a flow reactor in a supercritical isopropanol environment for the first time. According to XRD and IR spectroscopy of lattice vibrations, the structure of the samples is a mixture of monoclinic and tetragonal phases, the ratio of which varies with increasing calcination temperature. Preservation of nanocrystallinity even in the high-temperature $La_{0.99}Ca_{0.01}NbO_4$ sample can play a large role in its transport characteristics.

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НАНОКРИСТАЛДЫ КҮРДЕЛІ ОКСИДТЕРДІ ЖОҒАРЫ КРИТИКАЛЫҚ СПИРТТЕ СИНТЕЗДЕУ

Аннотация. Протон өткізгіші бар қатты электролиттерді интенсивті қарастыру жұмысы бірнеше ондаған жылдар бойы жалғасуда және бұл, ең алдымен, мұндай жүйелердің жоғары практикалық маңыздылығына байланысты. Газ датчигі, электролизатор, отынның жасушалық мембранасы және т.б. протон өткізгіші электрохимиялық құрылғылардың компоненті ретінде кеңінен қолданылады. Қазіргі уақытта белгілі протон өткізгіштерінің жұмыс температурасына байланысты төмен, орташа және жоғары температуралы протон өткізгіштер болып жіктеледі. Әрбір кластың практикалық қолдану тұрғысынан алғанда, бірқатар артықшылығы бар, сонымен бірге олардың сәтті коммерциялануына кедергі болатын нақты кемшіліктері де кездеседі. Осыған байланысты материалтану ғылымының негізгі міндеті – функционалды қасиеттері бар жаңа протон өткізгіш қасиеті бар нанокомпозиттерді синтездеу.

Протон өткізгіш қасиеті бар электролиттерді 1980 жылдардың басында Ивахара және басқа да ғалымдар зерттей бастады. Ғалымдар сирек кездесетін қосылыс – ниобаттар мен танталдардың ғылыми тұрғыдан да, практикалық тұрғыдан да маңызды қасиеттері бар қосылыстар тобы екенін көрсетті. Бұл керамикалық материал қасиетін зерттеу, олардың оптикалық қасиетін, атап айтқанда, люминесцентті зерттеуге негізделді. Лантан ортониобатының құрылымдық қасиетін зерттегенде 490-ден 525°С-қа дейінгі температурада фергусонит құрылымы бар моноклиндік фазадан, шеелит құрылымы бар тетрагональды фазаға ауысуы байқалады.

Лантан ортониобаты – жоғары температуралы протон өткізгіш қасиеті бар ABO_3 перовскит құрылымды күрделі оксид, жоғары температурада 700°С протон өткізгіші 10^{-4}Ом$^{-1}$см$^{-1}$, ал ылғалды және байытылған CO_2 ортасында тұрақты болып келеді.

Жалпы формуласы ABO_3 перовскит құрылымды күрделі оксидтер тұрақтылығына байланысты электролиттің ең қолайлы материалы. А перовскит катионына төмен валентті сілтілік металдар (Na^+, K^+), еківалентті сілтілік жерметалдар (Ca^{2+}, Sr^{2+}, Ba^{2+}) және үшвалентті (Fe^{3+}, Gd^{3+}, La^{3+}) катиондар орналасуы мүмкін. Керісінше, перовскит В катионы W^{5+}, Ce^{4+}, Zr^{4+}, Mn^{3+}, Co^{3+}, Yb^{3+} және Y^{3+} сияқты кішкентай иондық радиусы бар жоғары валентті катиондармен қамтамасыз етіледі. Көптеген перовскит құрылымды күрделі оксидтердің протон өткізгіштік қасиеті бар.

Сирек кездесетін металдар лантан ортониоттарды синтездеу үшін келесідей түрлі әдістер қолданылады: балқытпалардан тұз дайындау, қатты фазалы синтез, золь-гель әдісі, спрей пиролизі (аэрозольдің термиялық ыдырау), бірге тұну және механохимиялық синтез. Жоғарыда аталған әдістердің көпшілігі көпсатылы, ұзақ уақыт пен энергияны қажет етеді. Керісінше, жоғары критикалық сұйықтықты қолдана отырып синтездеу әдісі қарапайым және жоғары өнімді болып келеді. Aymonie еңбектерінде оксидті материалды өндіруде қолданылатын жоғары критикалық сұйықтық технологиясы зерттелетін материал морфологиясы, құрылымы жағынан параметрлерін өзгертіп, синтез үдерісін бақылауға және синтез үдерісіне әсер ететін әрбір параметрдің мөлшері мен материалдық сипаттамаларын басқаруға болатындығын айтты.

Сондықтан, бұл жұмыста алғаш рет жоғары критикалық ортада изопропанол қатысында $LaNbO_4$ мен $La_{0.99}Ca_{0.01}NbO_4$ күрделі оксидтер синтезделініп алынды. Алынған $LaNbO_4$ мен $La_{0.99}Ca_{0.01}NbO_4$ күрделі оксидтердің күйдіру температурасына байланысты физико-химиялық қасиеттері зерттелді.

Жұмыс нәтижесінде алынған $LaNbO_4$ мен $La_{0.99}Ca_{0.01}NbO_4$ құрамды күрделі оксидтер қазіргі уақытта сутегі энергия саласында қарқынды зерттеуге байланысты үлкен сұранысқа ие. Сондықтан протон өткізгіш қасиеті бар нанокомкомпозиттер әлі де үлкен зерттеулерді талап етеді.

Түйін сөздер: жоғары критикалық спритте синтездеу, күрделі оксидтер, лантан ортониобаты, құрылымдық сипаттамалар.

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СИНТЕЗ НАНОКРИСТАЛЛИЧЕСКИХ СЛОЖНЫХ ОКСИДОВ В СВЕРХКРИТИЧЕСКИХ СПИРТАХ

Аннотация. Интенсивный поиск твердых электролитов с высокой протонной проводимостью продолжается на протяжении последний нескольких десятилетий, что обусловлено в первую очередь высокой практической значимостью данных систем. Протонные проводники находят широкое применение в качестве компонентов электрохимических устройств, таких как газовые сенсоры, электролизеры, мембраны топливных элементов и др. Многообразие известных в настоящее время твердых протонных проводников может классифицироваться по параметрам рабочих температур, выделяя низко-, средне- и высокотемпературные области. Каждый класс, с точки зрения их практического использования, обладает рядом достоинств, но и в то же время специфическими недостатками, сдерживающими их практическое внедрение. В этой связи, материаловедческая задача − синтез новых материалов с функциональными свойствами, остается актуальной.

Протонпроводящие электролиты для Н + -ТОТЭ были обнаружены Iwahara и соавт. в начале 1980-х годов. Они указали, что ниобаты и танталаты редкоземельных металлов представляют собой группу соединений с интересными свойствами как с научной, так и с практической точки зрения. Изучение свойств этих керамических материалов базировалось на исследовании их оптических свойств, и, в частности флуоресцентных. Структурные свойства этой керамики были изучены и оказалось, что ниобат лантана при температуре от 490 до 525°C претерпевает фазовый переход (второго рода) из моноклинной фазы со структурой фергусонита в тетрагональную со структурой шеелита. Ортониобаты редкоземельных металлов являются новым классом высокотемпературных протонных проводников со структурой перовскита ABO_3, имеют протонную проводимость порядка 10^{-4} $Ом^{-1}$ $См^{-1}$ при температурах выше 700 °C и высокую устойчивость во влажной и обогащенной CO_2 среде. Однако $LaNbO_4$ обладает достаточно низкой проводимостью. Поскольку наличие вакансий кислорода является основным фактором, ответственным за появление протонных дефектов, то величина протонной проводимости напрямую связана с дефектностью сложного оксида. Многочисленные усилия были предприняты для улучшения проводимости путем одно- или многоэлементного допирования как A-подрешетки перовскита катионами, имеющими более низкую валентность и больший ионный радиус, включая одновалентные (Na^+, K^+), двухвалентные катионы (Ca^{2+}, Sr^{2+}, Ba^{2+}) или трехвалентные катионы (Fe^{3+}, Gd^{3+}, La^{3+}), так и B-подрешетки перовскита катионами, имеющих высокую валентность с небольшим ионным радиусом, таким как W^{5+}, Ce^{4+}, Zr^{4+}, Mn^{3+}, Co^{3+}, Yb^{3+} и Y^{3+}. Согласно Hausgrund и Norby, при допировании ниобата лантана катионами кальция ($La_{0.99}Ca_{0.01}NbO_4$) протонная проводимость во влажном водороде резко увеличивается и составляет около 10^{-3} С/см при 900ºC, в то время как в случае недопированного материала проводимость на два порядка ниже.

Для синтеза ортониобатов редкоземельных металлов используют различные методы: получение из расплавов солей, твердофазный синтез, золь-гель метод, спрей-пиролиз (термическое разложение аэрозоля растворов), соосаждение и механохимический синтез. Большинство из перечисленных выше методов являются многостадийными, трудоемкими и требуют больших временных и энергетических затрат. В отличие от них синтез с использованием сверхкритических флюидов (СКС) характеризуется простотой и высокой производительностью. В работе Aymonie подчеркивается, что технология сверхкритических флюидов, применяемая для получения оксидных материалов, дает возможность управлять процессом синтеза путем варьирования рабочих параметров и дает понимание того, как каждый параметр, влияющий на процесс синтеза, позволяет контролировать характеристики материала с точки зрения размера, морфологии, структуры.

Целью данной работы является получение протонпроводящих материалов с использованием спиртовых растворов солей соответствующих металлов сольвотермальным методом в проточном реакторе в сверхкритической среде изопропанола. В ходе работы были синтезированы сложные оксиды $LaNbO_4$ и $La_{0.99}Ca_{0.01}NbO_4$ и охарактеризованы комплексом физико-химических методов.

Таким образом, в данной работе впервые получены сложные оксиды $LaNbO_4$ и $La_{0.99}Ca_{0.01}NbO_4$ сольвотермальном методам в проточном реакторе в среде сверхкритического изопропанола. По данным РФА и ИК-спектроскопии колебаний решетки, структура образцов представляет собой смесь моноклинной и тетрагональной фаз, соотношение которых изменяется с ростом температуры прокаливания. Сохранение нанокристалличности даже у высокотемпературного образца $La_{0.99}Ca_{0.01}NbO_4$ может играть большую роль в его транспортных характеристиках.

Ключевые слова: синтез в сверхкритических спиртах, сложные оксиды, ортониобат лантан.

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IMPACT OF HUMIC ACID ON GROWTH, DEVELOPMENT AND PRODUCTIVITY OF CORN HYBRID UNDER CONDITIONS OF NORTHERN KAZAKHSTAN

Abstract. The biological activity of humic acids is proven on various types of crops. Domestic preparation "Kazuglegumus" is a fertilizer proposed for increasing crop yields, containing water-soluble organometallic chelate complexes with free C – O, C – O, C-NH functional groups. The authors present the results of a study of the effectiveness of the use of domestic organic fertilizer obtained from oxidized brown coal on the growth and productivity of corn hybrids in the northern regions of Kazakhstan. The agrochemical properties of the soil were studied, phenological observations were carried out on the phases of plant development, taking into account the yield of green mass during harvesting, zootechnical analysis of feed. Field experiments were carried out at «North Kazakhstan Research Institute of Livestock and Crop Production» LLP in 2019 on Hungarian selection hybrids MV 170 and MV 270. Phenological observations on the phases of maize development showed that the use of potassium humate with trace elements has a stimulating effect on the growth and development of maize hybrids, increasing its productivity and yield in the forest steppe conditions of North Kazakhstan. The optimal effective dose of "Kazuglegumus" humate fertilizer was determined for pre-sowing treatment of corn seeds and subsequent extracorporeal feeding.

Key words: foliar top dressing, potassium humate, corn, pre-sowing seed treatment, productivity, fertilizer, coal.

Introduction. For many years, corn has remained an important agricultural crop in Kazakhstan. According to the National Agency for Statistics, in the Republic of Kazakhstan in 2019, corn was grown on an area of more than 252 thousand hectares, which is 3.5 thousand hectares more than in 2018. The largest number of cultivated areas in Akmola, Turkestan, Kostanai and Zhambyl regions. The main exporters of Kazakh corn are Uzbekistan, Russia, Turkmenistan, Afghanistan and Tajikistan. In 2019, Kazakhstan exported about 50 thousand tons of corn, of which 45 942 tons - to Uzbekistan. Currently, relations are being established with the China on the export of agricultural products, including corn [1]. In the light of existing achievements and emerging prospects, the need to maintain soil productivity and soil health becomes apparent. It should be noted that in recent years there has been an increase in interest in "environmentally friendly" soil fertilization in agriculture. A wide range of commercial humic products are used as soil additives to increase crop yields, as well as to increase the efficiency of nutrient utilization by plants. [2]. A qualitative analysis of the soil, seeds, processing technologies, the use of fertilizers to increase productivity - all these issues are quite relevant in obtaining high yields of corn. The properties of Russian-made peat humates are widely studied, and the need for their use in growing corn is scientifically proven. Thus, the studies conducted by the authors on the experimental field of the Belgorod Scientific Research Institute of Agriculture in many years of field experience in the Central Chernozem region on the use of potassium humate growth regulator for spraying vegetative plants of medium early corn hybrid tillage in the range of 8.51-8.57 t/ha [3]. The effectiveness of the joint use of mineral fertilizers and plant growth regulator potassium-sodium humate with trace elements produced by the "Force of Life" in the cultivation of corn on grain was studied on the irrigated chestnut soils of the Volgograd. Its composition includes (in %): humic acid - 20; other organic acids - 10; nitrogen – 10; phosphorus – 1.0; potassium – 2.0; sodium – 1.0; sulfur – 0.5; magnesium – 0.5; iron – 0.5; copper – 0.5; manganese – 0.5; pine forest – 0.5; zinc – 0.5; molybdenum – 0.01; cobalt – 0.005.

The advantage of fertilized plants in development was noted already in the phase of 3-5 leaves and remained until the end of the growing season. It should be noted that the Russian humate of potassium sodium with microelements was used on irrigated chestnut soils, which allowed the authors to obtain results on increasing plant growth by 20% in height, dry ground mass accumulation in the 3-5 leaf phase by 43-48%, in phase of full wax ripeness 53-56% [4]. In the forest-steppe zone of the Republic of North Ossetia-Alania, studies were conducted on the use of preparations derived from humic substances in order to combat weed vegetation and reduce the stress effect on corn plants of Russian selection hybrids. The authors found that the most effective in the forest-steppe zone is the use of the drug «potassium humate 80». Its use in concentrations of 0.01-0.02% allowed to increase the content of chlorophyll in corn leaves by 7.7-17.6% in comparison with the control. At the same time, the authors note that increased concentrations of "potassium humate" have a depressing effect on the intensity of corn photosynthesis [5]. Various methods of applying humate fertilizers. So, in a study to determine the effect of the use of K-Humate on dry matter, elemental composition and absorption of nutrients by corn plants, the drug was applied to the soil or leaves at doses of 150, 300 and 450 g/day when growing plants in pots. The soil used in this study was loamy (38.4% clay, 39.9% water and 21.7% sand), slightly alkaline (pH 7.8), moderate in organic matter (2.90%) and rich in content CaCOa (11.5%). [6,-9]. According to the analysis, the fertilizer contains the following forms of nutrients available for plants: HA- 53-59%, K - 12.53%, N - 1.1%, O - 16.57%, Si - 17.61% [10, 11].

The aim of the research is to analyze the effectiveness of the use of organic fertilizer “Kazuglegumus” on the growth and productivity of maize hybrids in the northern regions of Kazakhstan.

Materials and methods. The object of research is the corn hybrids of the Hungarian selection MV 170 and MV 270. Hybrid corn MV 170 - a hybrid of Hungarian selection with a short growing season of 85-100 days, FAO group 170, height 150-170 cm. The color of the leaves is dark green with the number on the main stem 11-14. The spadix is long, narrow, well covered with a wrapper, length is 14-17 cm. The mass of 1000 grains is 250-280 g. The type of grain is round. The grain yield when threshing 80-84%. Resistant to cold, tolerates drought.

Hybrid corn MV 270 - a hybrid of Hungarian selection with a growing season of 90-105 days, FAO group 300, 160-180 cm high. The color of the leaves is dark green with 11-14 on the main stem. The ear is thick with deeply embedded grains, 15-18 cm long. The mass of 1000 grains is 270-300 g. The type of grain is tooth-like has increased adaptability. Field experiments were conducted in 2019 at «North Kazakhstan Research Institute of Livestock and Crop Production» LLP. The soil of the experimental plot is typical for black earths of forest steppe of North Kazakhstan - black earth is plain, medium-sum medium-weight, heavy and medium-carb.

Gross reserves of basic food elements in the black-earth soils of North Kazakhstan are high, however, most of them (especially phosphorus) are in a difficult state for plants. The soil of the test site is poorly provided with mobile phosphorus, medium - nitrogen, exchange potassium - high. Agrochemical properties of the soil of the test site are characterized by the following indicators (table 1)

Table 1 - Agrochemical characteristics of the soil of the experimental plot

Soil layer, cm	Humus content, %	PH (H_2O)	gross, %			Movable mg / kg		
			nitrogen	phosphorus	potassium	N-NO_3	P_2O_5	K_2O
0-20	5,7	7,0	0,31	0,18	2,51	15,8	29	415
20-40	5,1	7,3	0,27	0,19	2,12	17,8	28	380
40-60	4,3	7,6	0,21	0,10	1,96	15,2	18	325
60-80	3,7	7,7	0,18	0,09	1,87	12,6	13	310
80-100	3,6	7,8	0,14	0,07	1,85	11,9	11	300

The climate of the region where the experiments were carried out is characterized by sharp continentality. The region is characterized by severe, long winters and hot, short summers. The average long-term temperature of July is + 20.2 °C, of January - 25.4 °C. The frost-free period lasts from 110 to 130 days. The sum of positive temperatures above 10 °C, at which the normal growth and development of annual herbs is observed, is in the range of 2100 °C. The duration of the period with daily average temperatures above 10 °C during 139 days. The average annual rainfall in the region ranges from 280-340 mm. During the growing season, May - August, 180-200 mm falls. This area is characterized by early spring drought, exacerbated by strong winds, which leads to severe desiccation of the soil. The following analyzes were used in the experiments: observations of meteorological conditions, analysis of soil moisture every 10 cm of the 0-100 cm layer during the sprouting period, phenological observations of the phases of plant development, plant density during the sprouting period by counting all plants from 3 meters to four internal rows on two non-adjacent replicates, the dynamics of the height of plants before harvesting by measuring 10 plants on four internal rows, on two non-adjacent replicates, taking into account the yield of green mass during harvesting, by cutting 15 cm all corn plants with 3 meters in four inner rows on each plot.

One field experiment was laid in 2-fold repetition with a total plot area of 240 m^2. The following were determined in soil samples: humus – according to Tyurin in the modification of Simakov; pH of an aqueous extract on a pH meter; total nitrogen - according to Kjeldan; nitrate nitrogen - by ion-selective method; phosphorus and potassium - according to Machigin (before sowing).

The initial moisture was determined in an oven at a temperature of 60-65 °C, moisture moisture - at 105 °C, crude fiber - according to Genneberg-Shtoman; crude fat - according to S.V. Rushkovsky; crude ash - ashing method at a temperature of 450-500 °C; total nitrogen - photocolorimetric method using the reaction of indophenol greens; phosphorus - vanadium molybdate method; potassium oxide - on a flame photometer; carotene in freshly collected Zirrel samples. The content of feed units was calculated according to chemical analyzes.

The soil of the experimental plot was treated according to the type of early winter fall as a flat-cutter with a KPG-2.2 deep-ripper to a depth of 20-22 cm. In winter, double snow retention was carried out, in spring - early spring harrowing in 2-3 traces to close moisture. Before sowing, soil treatment was carried out with the SZS-2.1 seeder and rolling with ZKK-6A ring-spur rollers.

Presowing treatment of corn seeds was carried out with liquid humate fertilizer "Kazuglegumus" in doses of 1 ml / kg, 3 ml / kg, 10 ml / kg according to the following scheme (table 2).

Table 2 - The Impact of humate fertilizer "Kazuglegumus" on the productivity of corn hybrids

Fertilizer dose	Hybrid corn	
	MV 170	MV 270
Control	+	+
Kazuglegumus 1 ml / kg + 1 l / ha + 1 l / ha	+	+
Kazuglegumus 3 ml / kg + 1.5 l / ha + 1.5 l / ha	+	+
Kazuglegumus 10 ml / kg + 2 l / ha + 2 l / ha	+	+
Note: 1 dose - seed treatment, 2 dose - the first foliar top dressing, 3 dose - the second foliar top dressing		

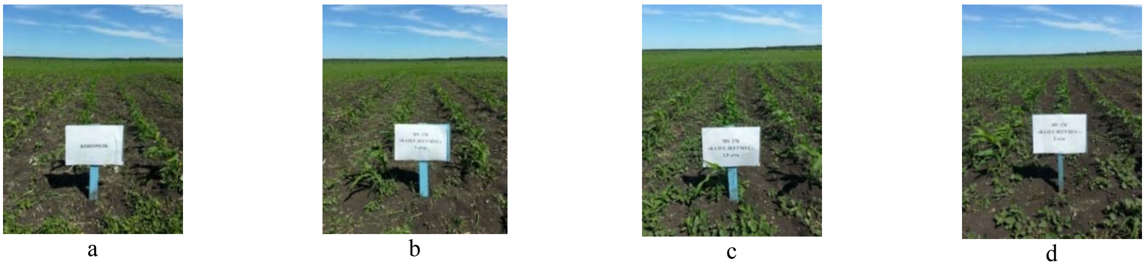
At the time of sowing (May 20, 2019), the supply of productive moisture in the meter soil layer was 95-101 mm. Corn was sown with the SON-2.8A seeder with 70 cm aisle. Seeding depth of 5-6 cm, seeding rate - 75 thousand seeds / ha. After sowing, the plot was rolled in for better contact of the seeds with the soil. To destroy germinating weeds and destroy the soil crust, pre-emergence and post-emergence harrowing was carried out with light harrows across the rows at a low tractor speed. With the appearance of 5-7 leaves, inter-row processing of corn was carried out to a depth of 5-6 cm to further destroy weeds.

The first foliar treatment was carried out in the phase of 6-8 leaves, the second - in the phase of sweeping corn plants. Foliar treatment of corn with a backpack sprayer was carried out by spraying with fertilizer "Kazuglegumus" in doses of 1, 1.5 and 2 l/ha.

Results and discussion. Field germination of seeds was 64.8-78.1%.

Phenological observations on the phases of the development of corn showed that the use of potassium humate with trace elements had an effect when used at a dose of 3.0 and 10.0 ml/kg for seed treatment, and at a dose of 1.5 and 2.0 l/ha at the first and second foliar treatment.

The emergence of seedlings of corn plants of the hybrid MV 170 was noted in the control, in the second and third experiments on May 31, in the version with a maximum dose of 10 ml/kg, 2 l/ha, 2 g / ha on May 30, full germination in the control, in the second and third options - June 3, and in the fourth experiment a day earlier - June 2 (figure 1).



a b c d

Figure 1 - Seedlings of corn plants of the hybrid MV 170 when treated with different doses of fertilizer:
a - control, b) 1 l / ha, c) 1.5 l / ha, d) 2 l / ha

The emergence of seedlings of corn plants of the hybrid MV 270 was noted in the control, in the second and third experiments - on June 1, and in the fourth experiment two days earlier - on May 31, full seedlings in the control and in the second and third variants - June 6, and in the fourth experience - June 4 (figure 2).

a b c d

Figure 2 - Seedlings of corn plants of the hybrid MV 270 when treated with different doses of fertilizer:
a - control, b) 1 l / ha, c) 1.5 l / ha, d) 2 l / ha

General data on the results of phenological observation of corn plants of the hybrid MV 170 in experiments on the use of fertilizer "Kazuglegumus" are presented in table 3.

Table 3 - Phenological observations of the growth and development of corn plants of the hybrid MV 170

Hybrid name	Sowing	shoots		Sweeping	Bloom	Ripeness		
		beginning	full			dairy	wax	full
Control	20/05	31/05	03/06	24/07	7/08	07/09	-	-
Kazuglegumus1 ml / kg + 1 l / ha + 1 l / ha	20/05	31/05	03/06	24/07	7/08	07/09	-	-
Kazuglegumus3 ml / kg + 1.5 l / ha + 1.5 l / ha	20/05	31/05	03/06	23/07	7/08	07/09	-	-
Kazuglegumus 10 ml / kg + 2 l / ha + 2 l / ha	20/05	30/05	02/06	21/07	5/08	04/09	-	-

As can be seen from table 3, the phase of emergence of the corn hybrid of MV 170 into the tube of plants of corn was noted in the control and second experiment – June 29, in the third experiment – one day, and in the fourth experiment – three days earlier. The sweeping phase of this hybrid in the control and second experiment was recorded on July 24, in the third experiment - a day earlier, in the fourth experiment - three days earlier. The flowering phase was observed on August 7 in the control, the second and third experiment, and in the fourth experiment two days earlier. The phase of dairy ripeness was noted on September 7 in the control, the second and third experiment. In the fourth experiment, where the maximum dose of humate fertilizer was used, this phase occurred three days earlier.

Generalized data on the results of phenological observation of corn plants of the hybrid MV 270 in experiments on the use of fertilizer "Kazuglegumus" are shown in table 4.

Table 4 - Phenological observations of the growth and development of corn plants of the hybrid MV 270

Hybrid name	Sowing	shoots		Sweeping	Bloom	Ripeness		
		beginning	full			dairy	wax	beginning
Control	20/05	01/06	04/06	28/07	13/08	13/09	-	-
Kazuglegumus 1 ml / kg + 1 l / ha + 1 l / ha	20/05	01/06	04/06	28/07	13/08	13/09	-	-
Kazuglegumus 3 ml / kg + 1.5 l / ha + 1.5 l / ha	20/05	01/06	04/06	28/07	13/08	13/09	-	-
Kazuglegumus 10 ml / kg + 2 l / ha + 2 l / ha	20/05	31/05	03/06	25/07	9/08	11/09	-	-

The sweeping phase of this hybrid in the control, second and third variants were observed on July 28, in the fourth experiment - three days earlier. The flowering phase was noted on August 13 in the control; in the second and third experiments, this phase occurred one day, and in the fourth experiment, four days earlier. The onset of the phase of milk ripeness was recorded on September 15 in the control, in the second and third experiments - in two, and in the fourth experiment, where the maximum dose of humate fertilizer was used, - four days earlier.

At the time of harvesting, corn plants in all experimental plots, incl. and control, were in the phase of milk ripeness, which is associated with prolonged precipitation, which prevented the achievement of the phase of wax ripeness.

When determining the standing density of seedlings of corn plants MV 170 and MV 270, the presence of a relationship and a direct dependence of the dose of fertilizer on the standing density of plants during seedlings were revealed (table 5).

Table 5 - The density of the corn plant during the germination period, depending on the dose of fertilizer

Fertilizer dose	MV 170		MV 270	
	standing density pcs / m^2	± to control, %	standing density pcs / m^2	± to control, %
Control	6,9	-	6,8	-
Kazuglegumus 1 ml / kg + 1 l / ha + 1 l / ha	7,1	2,8	6,8	-
Kazuglegumus 3 ml / kg + 1.5 l / ha + 1.5 l / ha	7,1	2,8	6,9	1,4
Kazuglegumus 3 ml / kg + 1.5 l / ha + 1.5 l / ha	7,2	4,2	7,1	4,2

As can be seen from table 5, the best indicator of plant stand density for seedlings of the hybrid MV 170 for seedlings is 7.2 pcs / m^2, and for the hybrid of MV 270 - 7.1 pcs / m^2, with a fertilizer dose of 10 ml / kg, 2 l / ha and 2 l / ha, which exceeds the control by 4.2%.

A direct correlation was also found between the increase in the dose of fertilizer and the indicator of the height of corn growth (table 6).

Table 6 - Plant height of corn hybrids depending on the dose of fertilizer "Kazuglegumus"

Fertilizer dose	hybrid MV 170			hybrid MV 270		
	height	± to control		height	± to control	
		cm	%		cm	%
Control	164,8	-	-	179,3	-	-
Kazuglegumus 1 ml / kg + 1 l / ha + 1 l / ha	171,2	6,4	3,9	189,8	10,5	5,8
Kazuglegumus 3 ml / kg + 1.5 l / ha + 1.5 l / ha	172,7	7,9	4,8	193,2	13,9	7,7
Kazuglegumus 10 ml / kg + 2 l / ha + 2 l / ha	177,5	12,7	7,7	198,5	19,2	10,7

As can be seen from table 6, the hybrid MV 170 has the highest indicator of plant height in the fourth embodiment. It is equal to 177.5 cm, the difference with the control is 12.7 cm. Hybrid MV 270 the best indicator of height is also noted in the experiment with the maximum dose of potassium humate. It was 198.5 cm, which is 19.2 cm higher than the benchmarks

Analysis of the yield of feed units per hectare of sown area showed that according to this indicator, the best results were revealed according to the results of the fourth experiment, where doses of fertilizer “Kazuglegumus” were applied at 10.0 ml / kg for seed treatment, and 2.0 l / ha during the first and second foliar treatment (table 7).

Table 7 - The output of feed units of corn hybrids depending on the dose of humate fertilizer

Fertilizer dose	MV 170			MV 270		
	productivity green m., c / ha	Sod. in 100 kg green m., feed. units	feed output. units, t / ha	productivity green m., c /ha	Sod. in 100 kg green m., feed. units	feed output. units, t / ha
Control	216,5	23,1	50,9	247,3	23,5	61,7
Kazuglegumus 1 ml / kg + 1 l / ha + 1 l / ha	246,4	23,4	58,7	275,5	23,6	70,5
Kazuglegumus 3 ml / kg + 1.5 l / ha + 1.5 l / ha	263,6	23,6	63,0	294,0	23,9	76,3
Kazuglegumus 10 ml / kg + 2 l / ha + 2 l / ha	275,6	23,5	65,7	301,9	23,7	80,3

As can be seen from table 7, a higher yield of feed units per hectare was obtained in the fourth version of the experiments on both hybrids, which amounted to 65.7 c / ha for the hybrid MV 170, and 80.3 c / ha for the MV 270 hybrid.

Conclusion. The Kazuglegumus fertilizer had a positive effect on the productivity of maize hybrids. The highest yield of green mass of the hybrid MV 170 of 275.6 c / ha was obtained in the fourth group, where the plants were treated with fertilizer at a dose of 10 ml / kg, 2 l / ha, 2 l / ha. The same regularity was also observed in the hybrid MV 270, where the maximum green mass yield was 301.9 c / ha. The high dry solids in both maize hybrids was positively influenced by the dose of humate fertilizer at 3 ml / kg 1.5 l / ha, 1.5 l / ha. In the MV 170 hybrid, it was 34.5, and in the MV 270 hybrid 34.7%.The highest yield of feed units per hectare was obtained for both maize hybrids in the fourth experimental version when treating plants with Kazuglegumus fertilizer at a dose of 10 ml / kg, 2 l / ha, 2 l / ha and amounted to 65.7 c / m in the hybrid MV 170 ha, the hybrid MV 270 - 80.3 c / ha.

It is worth noting the fact that corn plants of both hybrids during the growing season were not susceptible to any diseases inherent in this type of plant, although corn was also the precursor. In the course of the experiments, the optimal effective dose of humate fertilizer was determined: for pre-sowing treatment of corn seeds - 10 ml / kg, for the next two foliar dressings - 2 l / ha and 2 l / ha, respectively. The use of potassium humate with trace elements in the form of humate fertilizer "Kazuglegumus" stimulates plant immunity and prevents the death of corn plants from specific diseases

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СОЛТҮСТІК ҚАЗАҚСТАН ӨҢІРІНДЕ ЖҮГЕРІ БУДАНДАРЫНЫҢ ӨСІМІНЕ, ДАМУЫНА ЖӘНЕ ӨНІМДІЛІГІНЕ ГУМИН ҚЫШҚЫЛЫНЫҢ ӘСЕРІН ЗЕРТТЕУ

Аннотация. Гумин қышқылдарының биологиялық белсенділігі ауылшаруашылығы дақылдарының алуан түрінде дәлелденген. «Казуглегумус» отандық препаратының құрамында С–О, С–О, С-NH функционалды топтар мен суда еритін металл органикалық хелатты кешендері бар, ауылшаруашылығы дақылдарының өнімділігін арттыру үшін ұсынылған тыңайтқыш. Авторлар Қазақстанның солтүстік аймағындағы жүгері будандарының өсімі мен өнімділігіне, тотыққан қоңыр көмірден алынған отандық органоминералды тыңайтқыштарды қолданудың тиімділігін зерттеу нәтижелерін ұсынған. Топырақтың агрохимиялық қасиеттері зерттелді, өсімдіктердің даму фазалары бойынша фенологиялық бақылау жүргізілді, егін жинау кезеңінде жасыл массаның шығымдығы есепке алынды, жемге зоотехникалық талдау жүргізілді. Егіс тәжірибесі 2019 жылы «Солтүстік Қазақстан малшаруашылығы және өсімдікшаруашылығы ҒЗИ» ЖШС-де MV 170 және MV 270 Венгр селекциясы буданында жүргізілді. Жүгерінің даму фазасы бойынша фенологиялық бақылау микроэлементтері бар калий гуматын қолданылу, жүгері буданының өсімі мен дамуына, өнімділігі мен шығымдығын арттыруға ынталандырушы әсер ететінін көрсетті.

Жүгері тұқымын себу алдында өңдеу үшін «Казуглегумус» гуматты тыңайтқыштың оңтайлы тиімді дозасы және одан кейінгі тамырдан тыс қоректендіру анықталды. «Казуглегумус» сауда маркасындағы отандық калий гумат препараты – ауылшаруашылығы дақылдарының өнімділігін арттыру үшін ұсынылатын ісіну және шетелдік тыңайтқыштар тізбегіндегі жаңа бренд. Фульв қышқылы және гумин қышқылымен күрделі комбинацияда тірі ағзаны сауықтыру бойынша биожетімді кешен құрайды. Құндылығы 70-тен астам түрлі компонентті минерал, 20-дан астам амин қышқылы, витамин, табиғи полисахарид, стерин, гормон, майлы қышқыл, өсімдік пигменттері (флавоноид) және табиғи антиоксиданттарға (катехиндер) байланысты.

Осы кешен құрамында табиғитекті стероидты емес фитоэстрагендер – изофлавоноидтар, сондай-ақ хинонды антибиотиктерінің қасиеттері бар және басқа да пайдалы компоненттер табылды. Биологиялық белсенді заттардың мұндай концентрациясы гумин қышқылдарының тірі организмдерге оң әсерінің алуан түрлілігін тудырады.

«Казуглегумус» калий гуматы негізіндегі отандық органоминералды тыңайтқыш (ОМУ) – қоңыр көмірді тотықтыру арқылы алынған қара қоңыр түсті субстанциясы. Тыңайтқыштарды өндіру технологиясын «Көмір химиясы және технология институты» ЖШС авторлық ұжымы және «Казтехноуголь» ғылыми-өндірістік бірлестігі» ЖШС өндірушісі әзірледі.

Бұл технология ультрадисперсті мицеллаларды алуға мүмкіндік беретін ультрадыбыс және ауа оттегінің Б2 маркалы тотыққан қоңыр көмірге бірлескен әсеріне негізделген. Алынған өнім бөлшектерінің мөлшері өсімдіктердегі кеуектердің өлшемінен әлдеқайда аз, бұл өсімдіктер ағзасына тез енуге ықпал етеді. Осылайша алынған калий гуматы құрамында С–О,С–ОН, с - NH функционалды топты суда еритін металл органикалық хелатты кешендері бар.

Түйін сөздер: тамырдан тыс қоректендіру, калий гуматы, жүгері, казуглегумус, тұқымды алдын ала өңдеу, өнімділік, тыңайтқыш, көмір, фенологиялық бақылау.

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ВЛИЯНИЕ ГУМИНОВОЙ КИСЛОТЫ НА РОСТ, РАЗВИТИЕ И ПРОДУКТИВНОСТЬ ГИБРИДОВ КУКУРУЗЫ В УСЛОВИЯХ СЕВЕРНОГО КАЗАХСТАНА

Аннотация. Биологическая активность гуминовых кислот доказана на различных видах сельскохозяйственных культур. Отечественный препарат «Казуглегумус» – удобрение, предлагаемое для повышения урожайности сельскохозяйственных культур, содержащее водорастворимые металлоорганические хелатные комплексы со свободными С–О,С–ОН, С-NH функциональными группами. Авторами представлены результаты изучения эффективности применения отечественного органоминерального удобрения, полученного из окисленного бурого угля, на рост и продуктивность гибридов кукурузы в северных регионах Казахстана. Изучены агрохимические свойства почвы, проведены фенологические наблюдения по фазам развития растений, учет урожайности зеленой массы в период уборки урожая, зоотехнический анализ кормов. Полевые опыты проводились в 2019 году в ТОО «Северо-Казахстанский НИИ животноводства и растениеводства» на гибридах венгерской селекции MV 170 и MV 270. Фенологические наблюдения по фазам развития кукурузы показали, что применение гумата калия с микроэлементами оказывает стимулирующий эффект на рост и развитие гибридов кукурузы, повышение ее продуктивности и урожайности в условиях лесостепи Северного Казахстана.

Определена оптимальная эффективная доза гуматного удобрения «Казуглегумус» для предпосевной обработки семян кукурузы и последующих внекорневых подкормок. Отечественный препарат гумата калия под торговой маркой «Казуглегумус» – новый бренд в линейке отечественных и зарубежных удобрений, предлагаемый для повышения урожайности сельскохозяйственных культур. В сложной комбинации с фульвовой кислотой, гуминовые кислоты образуют биодоступный комплекс по оздоровлению живого организма. Его ценность обусловлена наличием более 70 различных компонентов из минералов, более 20 аминокислот, витаминов, природных полисахаридов, стеринов, гормонов, жирных кислот, растительных пигментов (флавоноиды), природных антиоксидантов (катехины).

В составе данного комплекса обнаружены нестероидные фитоэстрагены натурального происхождения – изофлавоноиды, а также, обладающие свойствами антибиотиков хиноны и прочие полезные компоненты. Такая концентрация биологически активных веществ обуславливает многообразие положительного влияния гуминовых кислот на живые организмы.

Отечественное органоминеральное удобрение (ОМУ) на основе гумата калия «Казуглегумус» – субстанция темно-коричневого цвета, полученная путем окисления бурого угля. Технология производства удобрения разработана авторским коллективом ТОО «Институт химии угля и технологии» и производителем ТОО «Научно-производственное объединение «Казтехноуголь».

Технология основана на совместном воздействии на окисленный бурый уголь марки Б2 ультразвука и кислорода воздуха, приводящем к получению ультрадисперсных мицелл. Размеры частиц полученного продукта намного меньше, чем размеры пор в растениях, что способствует к быстрому проникновению в организм растений. Полученный таким образом гумат калия содержит себе водорастворимые металлоорганические хелатные комплексы со свободными С–О,С–ОН, С- NH функциональными группами.

Ключевые слова: внекорневые подкормки, гумат калия, кукуруза, казуглегумус, предпосевная обработка семян, продуктивность, удобрение, уголь, фенологические наблюдения.

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BIOSYNTHESIS AND DYNAMICS OF ACCUMULATION OF SESQUITERPENE LACTONES IN *ARTEMISIA GLABELLA* KAR. ET KIR.

Abstract. The study of biosynthetic processes in plant cells and methods for their regulation is an important aspect in the development of biotechnological methods for the production of valuable medicinal compounds. The identification and establishment of enzyme structures involved in the formation of secondary metabolites in plants by using molecular genetic methods is one of the relevant ways in the study of their biosynthesis. For a successful search, it is necessary to use plant organs with their quantitative accumulation.

In this work for the first time, a quantitative assessment of the content of sesquiterpene lactones arglabin and argolide in CO_2-extracts of *Artemisia glabella* Kar. et Kir. individual organs were performed at different stages of the growing period (start of regrowth, end of regrowth, budding, flowering, fruiting); using electron scanning microscopy, the leaves surface morphology was determined. It was found that the quantitative accumulation of arglabin is observed during budding stage and its amounts are 1.90% in leaves and 1.56% in buds. On the surface of leaves *Artemisia glabella* Kar. et Kir., there are capitate glandular trichomes of an oval shape, the sizes of which vary between 70-80 microns in length and 33-38 microns in width.

Based on the obtained experimental data, we assume that the leaves and buds of intact plant *Artemisia glabella* Kar. et Kir. during the budding stage will be the optimal samples to search for genes involved in the biosynthesis of sesquiterpene lactones.

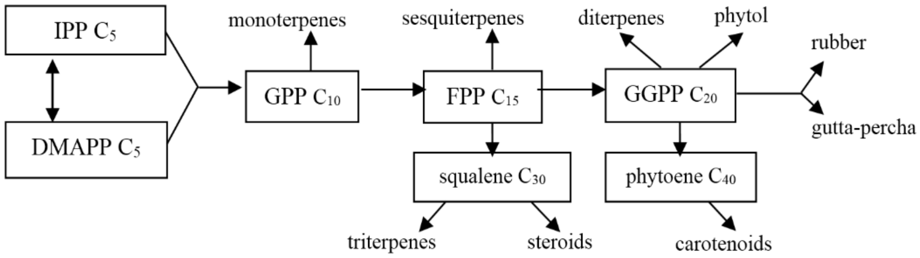
Key words: sesquiterpene lactones, arglabin, biosynthesis, trichomes, supercritical fluid extraction, *Asteraceae*, *Artemisia glabella* Kar. et Kir.

Introduction. The study of biosynthetic processes of plant cells and methods of their regulation is one of the current trends in biological chemistry. The biosynthesis of isoprenoids, a very large group of natural compounds that are diverse in structure and function, has been studied by many foreign researchers [1-15]. It was established that the biosynthetic pathway of all isoprenoids begins with two branched phosphorylated precursors – isopentenyl pyrophosphate and dimethylallyl pyrophosphate (figure 1), which are formed in living organisms along one of two pathways [1]:

1) *mevalonate pathway (classic, Bloch-Lynen pathway, MVA-pathway)* - from mevalonic acid, occurring under the action of enzymes located in cytosol;

2) *non-mevalonate pathway (alternative, Rohmer pathway, MEP- pathway)* - from methylerythritol phosphate occurring under the action of enzymes localized in plastids.

Under the action of isopentenyl pyrophosphate isomerase enzyme, a double bond shift occurs in isopentenyl pyrophosphate (IPP) and an isomeric compound, dimethylallyl pyrophosphate (DMAPP), is formed. Further formation of terpenes occurs by attaching IPP residues to a DMAPP molecule to produce geranyl pyrophosphate or to a growing chain of isoprenoid with the formation of farnesyl pyrophosphate, etc. (figure 1).



IPP – isopentenyl pyrophosphate; DMAPP – dimethylallyl pyrophosphate;
GPP – geranyl pyrophosphate; FPP – farnesyl pyrophosphate; GGPP – geranylgeranyl pyrophosphate

Figure 1 – The main pathways of terpenoids formation

It should be noted that the cytoplasmic (MVA) and chloroplast (MEP) pathways differ only in the early stages: since the formation of the C_5-unit of IPPP, there are no differences in the stages of biosynthesis [2, 3]. In addition, higher plants and some microorganisms are characterized by the use of both pathways of isoprenoid biosynthesis, and although both pathways in the plant cell function simultaneously, they are physically isolated from each other [1].

To date, the biosynthetic pathways of the formation of individual sesquiterpene lactones in a number of plants of the *Asteraceae* family have been studied (costunolide in *Cichorium intybus* L. [4], *Helianthus annuus* L. и *Lactuca sativa* L. [5]; parthenolide in *Tanacetum parthenium* (L.) Sch. Bip. [6]; artemisinin in *Artemisia annua* L. [7, 8, 9] and in some others). The key to determining biosynthetic genes in many studies has been the identification of plant organs in which quantitative accumulation of sesquiterpene lactones occurs [9, 10]. On the surface of most of them, there are exogenous specialized terpenoid-containing secretory structures - glandular trichomes [11], which show the highest concentration of sesquiterpene lactones and quantitative content of TpGAS synthase (a gene encoding the first stage of germacranolide biosynthesis) [8, 9, 12]. Their presence and morphological diversity for a number of plants *Asteraceae* family are confirmed by electronic scanning microscopy [13, 14, 15]. It was glandular trichomes that were used in many studies to isolate RNA and its sequencing in order to determine the nucleotide sequences of genes encoding the structures of terpenoid biosynthesis enzymes in plants.

The aim of this work was the quantitive evaluation of the content of sesquiterpene lactones in individual organs of *Artemisia glabella* Kar. et Kir. at different stages of the growing period and determining the size of glandular trichomes on their surface in order to select optimal samples for the search for genes involved in biosynthesis of arglabin.

Materials and methods of the research. The object of research in this work was the plant of the flora of Kazakhstan *Artemisia glabella* Kar. et Kir. of *Asteraceae* family. Aerial parts of *Artemisia glabella* Kar. et Kir. were collected in the Karkaraly district of the Karaganda region in accordance with the phenospectrum for the main stages of growing season of the plant: start of regrowth – 01.06.2018; end of regrowth – 22.06.2018; budding – 18.07.2018; flowering – 15.08.2018; fruiting – 18.09.2018). Plant samples were placed in the herbarium fund of the laboratory of botany and biotechnology of JSC “IRPH “Phytochemistry”.

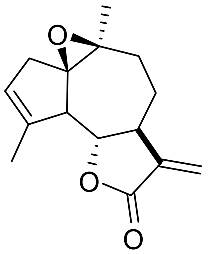
The collected raw materials were divided into individual organs (stems, leaves were separated and, depending on the developmental stage, buds/flowers/fruits), also whole shoots were left for study. All plant sampes were dried by the air-shadow method.

The extraction of secondary metabolites from the aerial part and individual organs of the plant was carried out on a supercritical fluid extraction unit USFE-5/2 [16] with the following parameters (for all types of raw materials): pressure 16 MPa; temperature 60^0C; duration 180 minutes. For each extraction, 100 g of raw material collected in 2018 during the corresponding growing period was used.

The quantitative content of components in the CO_2 extracts was determined by high-pressure reversed-phase HPLC with a UV-detector on a Hewlett Packard Agilent 1100 Series chromatograph in isocratic mode. Analysis conditions: analytical column 4.6×150 mm, Zorbax SB-C18 sorbent with a particle size of 5 μm, column temperature - room temperature, mobile phase acetonitrile:water mixture (1:1), mobile phase velocity 0.5 ml/min, injection load 20 μl, detection at a wavelength of 204 nm. Data was calculated using ChemStation software.

The study of surface morphology of individual plant organs was carried out using optical microscopy methods. MBR-1A biological microscope was used to inspect the surface. Scanning electronic microscope of high-spatial resolution Mira 3 LMU Tescan was used to detect the size of terpenoid-containing structures. Air-dried samples of *Artemisia glabella* Kar. et Kir. leaves with a sputtering of 25 nm thick gold were prepared for analysis.

Results and discussion. Among secondary metabolites of *Artemisia glabella* Kar. et Kir., there are sesquiterpene lactones arglabin (1) and argolide (2) - biologically active compounds with a proven pharmacological effect and promising for chemical modifications, as well as dihydroargolide (3).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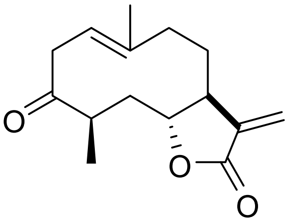
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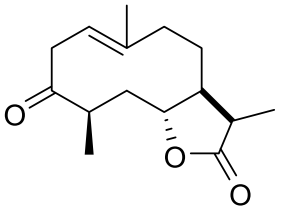
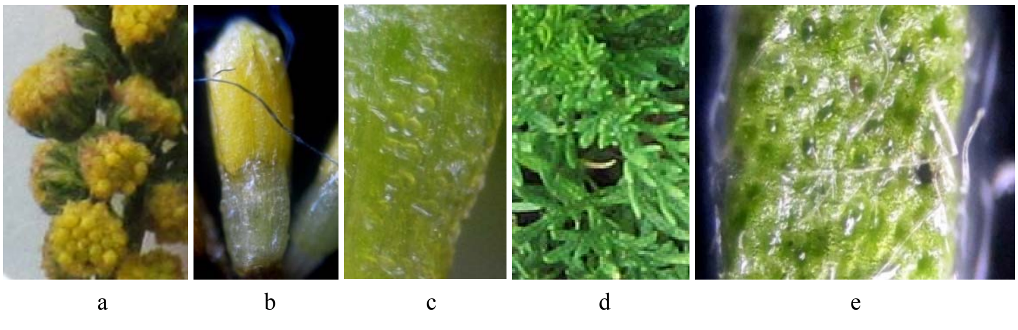

(3)

The major component of the *Artemisia glabella* extract is sesquiterpene lactone arglabin - 1(10)-epoxy-5,7α,6β(H)-guaia-3(4),11(13)-dien-12,6-olide, the average content of which is 1.49% for air-dry raw materials, the rate of recovery by supercritical fluid extraction reaches 92.4% [17]. It has an inhibitory effect on a number of transplantable tumors (Pliss's lymphosarcoma, Walker's carcinosarcoma, RMC-1 breast cancer, alveolar liver cancer, P-388 and D-1120 leukemia), as well as on tumor strains resistant to standard chemotherapeutic drugs (fluorouracil, sarcolysin, prospidin, rubomycin), is used as an immunomodulating agent [18]. There was also revealed its hypolipidemic effect in hepatoma cells [19]. The water-soluble derivative of dimethylaminoarglabin hydrochloride [18] is the active substance in the unique antitumor drug "Arglabin", which, according to a number of characteristics, has no analogues in the world, has passed clinical studies and is used in antitumour therapy. Arglabin is promising for chemical modification; more than 70 derivatives are obtained on its basis [20].

Microscopic examination of the surface of *Artemisia glabella* Kar. et Kir. organs allowed us to establish that the epidermal glandular structures (trichomes) of the aerial parts *Artemisia glabella* (figure 2) are represented by two forms: glandular hairs and capitate glandular trihomes (both are multicellular). On both sides of the leaves and on the lower part of flower *Artemisia glabella*, glandular trichomes predominate (Figure 2c, 2d), which have an oval in shape. The size of glandular trichomes on the leaves surface varies between 70-80 microns in length and 33-38 microns in width (figure 3).



a – anthodium of *Artemisia glabella*; b – flowers from anthodium;
c – lower part of the flower; d – leaves on the stem; e – leaf (view from above)

Figure 2 – The presence of terpenoid-containing structures on the surface of aerial parts *Artemisia glabella* Kar. et Kir.

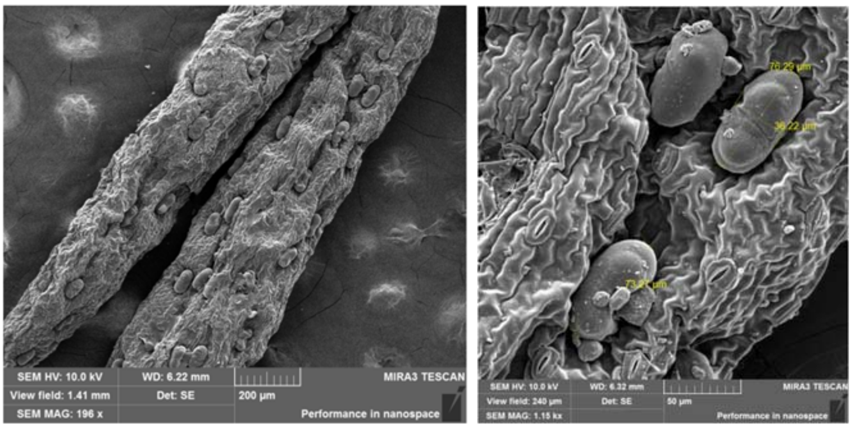


Figure 3 – Size of glandular trichomes on the surface of *Artemisia glabella* Kar. et Kir. leaves

To study the dynamics of accumulation of sesquiterpene lactones in individual organs of *Artemisia glabella* Kar. et Kir. a series of CO_2-extraction of raw materials collected at different stages of the growing period was carried out. The results of chromatographic analysis of the obtained CO_2-extracts are presented in table 1.

Table 1 – Results of HPLC analysis of the quantitative content of arglabin and argolide in CO_2-extracts of *Artemisia glabella*

№	Type of plant raw material	Extract mass	Content, % per extract		Content, % on air-dry materials	
			arglabin	argolide	arglabin	argolide
1	2	3	4	5	6	7
I	*SR – start of regrowth (raw material collection 01.06.2018)*					
1	whole shoots	7,05	15,98	1,95	1,12	0,14
II	*ER – end of regrowth (raw material collection 22.06.2018)*					
2	whole shoots	5,71	13,75	3,86	0,78	0,22
3	shredded stems	1,85	11,74	2,91	0,21	0,05
4	leaves	9,58	13,13	3,71	1,26	0,35
III	*B - budding (raw material collection 18.07.2018)*					
5	whole shoots	7,15	20,76	5,56	1,50	0,40
6	shredded stems	2,90	13,91	2,91	0,40	0,08
7	leaves	7,44	25,56	6,83	1,90	0,51
8	buds	8,28	18,84	4,65	1,56	0,39
IV	*FL – flowering (raw material collection 15.08.2018)*					
9	whole shoots	6,25	8,73	2,09	0,55	0,13
10	shredded stems	2,50	7,83	1,69	0,20	0,04
11	leaves	5,70	8,12	1,72	0,46	0,10
12	inflorescences	6,60	10,25	2,32	0,68	0,15
13	young whole shoots (regrowth)	8,18	9,37	1,93	0,77	0,16
V	*FR– fruiting (raw material collection 18.09.2018)*					
14	whole shoots	3,57	11,12	2,31	0,39	0,08
15	shredded stems	1,66	8,04	1,26	0,13	0,02
16	leaves	7,35	15,43	3,29	1,13	0,24
17	multiple fruit + leaves	7,00	12,86	3,15	0,90	0,22
18	young whole shoots (regrowth)	7,40	15,96	3,41	1,18	0,25

At the *start of regrowth* stage, the yield of CO_2-extract from whole shoots (leaves and stems) is 7.05% on air-dry materials with an average concentration of arglabin of 1.12% on air-dry materials.

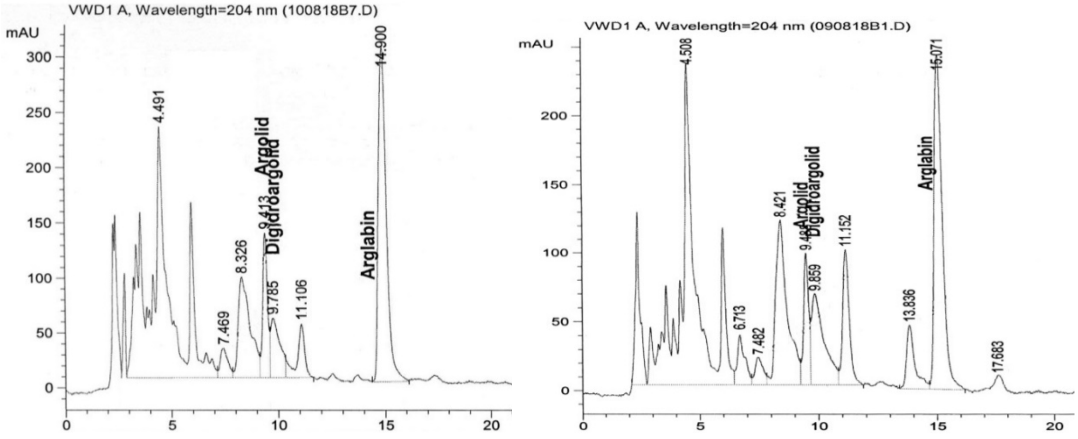
At the *end of regrowth* stage, there is a slight decrease in the yield of extract to 5.70% on air-dry material, which is most likely due to the relative increase in the proportion of stems in the total weight of the raw material, the extract yield of which (as can be seen from the data in Table 1) is insignificant and is 1.85% on air-dry material. Also, in this phase, an increase in argolide concentration is observed by almost 2 times (up to 3.86 in the extract and 0.22 on air-dry materials) with a slight decrease in the concentration of arglabin (from 1.12% to 0.78%).

A quantitative yield of CO_2-extract is observed during *budding* stage (on average, within 7.15% on air-dry material). During this stage, the highest concentration of arglabin and argolide in the obtained extracts was noted. Thus, the highest content of arglabin was recorded in the leaves (25.56% in the extract and 1.90% on air-dry material), it is slightly lower in buds (18.84% in the extract and 1.56% on air-dry material). This fact is completely correlated with the presence on the surface of precisely these *Artemisia glabella* organs of capitate glandular trichomes - structures where the formation and accumulation of terpenoid nature substances occur.

The chromatogram of the CO_2-extract of raw material *Artemisia glabella* collected during budding stage shows the presence of three additional peaks of components with retention times of 6.7139, 13.836 and 17.683 min, which form and accumulate in buds (figure 4b).

During the *flowering* stage, the yield of the extract decreases to 6.25% on air-dry material, there is an almost three-fold decrease in the concentration of arglabin and argolide (up to 0.55% and 0.13% on air-dry material respectively).

For the *fruiting* stage, the extract yield is minimal (3.57% on air-dry material) and the content of sesquiterpene lactones arglabin and argolide in whole shoots is 0.39 and 0.08% on air-dry material.



а

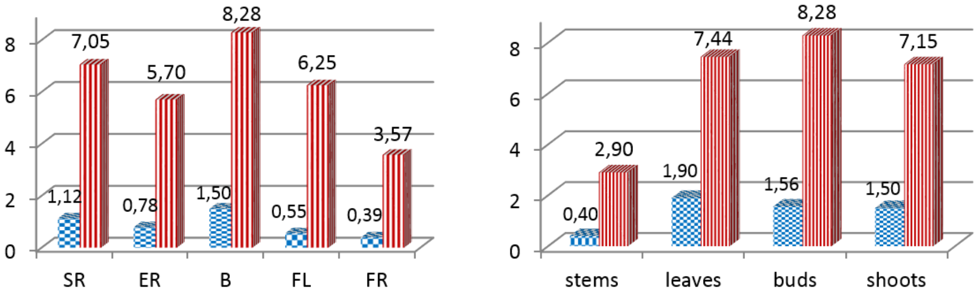
б

a – leaves extract; b – buds extract

Figure 4 – Chromatograms of the component composition of the CO_2-extract of individual organs of *Artemisia glabella* during budding stage

From the data in table 1 it is also seen that the biosynthesis of arglabin continues in young whole shoots even with the repeat regrowth, which is observed in the 2-3rd decade of August. Moreover, the content of arglabin in them remains quite high (1.18% on air-dry material during the fruiting stage).

Comparative data on the content of target component (arglabin) for different stages of the growing period and in individual organs at the budding stage are presented on diagrams (figure 5).



a

b

a – in whole shoots along the stages of growing period; b - in individual organs in the budding stage; blue chessboard pattern - yield of extract, % on air-dry material; red stripe pattern - arglabin content, % on air-dry material

Figure 5 – Arglabin content and CO_2-extract yield on dried raw materials of *Artemisia glabella* Kar. et Kir.

The results of an experiment on CO_2-extraction of secondary metabolites from raw materials of *Artemisia glabella* correlate with previously obtained by chloroform extraction data on the quantitative accumulation of sesquiterpene lactones precisely at the budding stage in leaves and buds [21, p. 79, 89]. It should be noted that the percentage content of arglabin in the *Artemisia glabella* population growing in the natural habitat (Karkaraly district) is almost 3 times higher. However, this difference can also be associated with the use of various methods for its extraction from plant materials (chloroform and supercritical fluid extraction).

Conclusion. As a result of the studies, it was found that the presence of sesquiterpene lactone arglabin is observed in all individual organs of *Artemisia glabella* Kar. et Kir. and during all stages of the growing period. Terpenoid-containing organs are leaves and buds, in which its quantitative accumulation during budding stage is noted (within 1.56–1.90% according to HPLC analysis of CO_2 extracts). On the surface of these organs there are specialized terpenoid-containing structures - glandular trichomes, in which the biosynthesis and accumulation of sesquiterpene lactones and other terpenoids under the action of sesquiterpene synthases occur. According to electronic scanning microscopy data, the glandular trichomes on the surface of *Artemisia glabella* Kar. et Kir. leaves have an oval shape, their sizes vary between 70-80 microns in length and 33-38 microns in width. Thus, we assume that the leaves and buds of an intact plant are optimal samples to search for genes involved in the biosynthesis of sesquiterpene lactones.

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ARTEMISIA GLABELLA KAR. ET KIR. ӨСІМДІГІНДЕГІ СЕСКВИТЕРПЕНДІ ЛАКТОНДАРДЫҢ ЖИНАҚТАЛУ ДИНАМИКАСЫ ЖӘНЕ БИОСИНТЕЗІ

Аннотация. Жұмыстың мақсаты – арглабин биосинтезіне қатысатын гендерді іздеу үшін оңтайлы үлгілерді таңдау мақсатында вегетациялық кезеңнің түрлі сатысында *Artemisia glabella* Kar. et Kir. өсімдігінің жекелеген мүшелеріндегі сесквитерпенді лактондардың мөлшерін сандық бағалау және олардың бетіндегі безді трихомалардың көлемін анықтау.

Бұл жұмыста алғаш рет вегетациялық кезеңнің түрлі сатысында (өсу үдерісінің басы, аяғы, бүрлеу, гүлдеу, жеміс беру) *Artemisia glabella* Kar. et Kir. өсімдігінің жекелеген мүше CO_2-сығындысындағы арглабин мен арголид сесквитерпенді лактондарының мөлшеріне сандық бағалау жүргізілді; электронды сканерлеу микроскопия әдісімен жапырақ бетінің морфологиясы анықталды.

Зерттеу нәтижесінде арглабин сесквитерпенді лактоны *Artemisia glabella* Kar. et Kir. өсімдігінің барлық мүшесінде және вегетациялық кезеңнің барлық сатысында байқалады. Оның сандық жинақталуы бүрлеу кезеңінде айқындалды және жапырақта 1,90%, гүлшанақта 1,56% көрсетті. Арглабин биосинтезі тамыз айының 2-3-онкүндігінде байқалатын жас өскіннің қайта өсу үдерісінде де жалғасады. Бұл ретте олардың құрамындағы арглабиннің мөлшері салыстырмалы түрде жоғары болады (жеміс беру сатысында 1,18%).

Artemisia glabella Kar. et Kir. өсімдігінің жерүсті бөлігінде терпеноидты құрылымдардың екі түрі анықталды: безді түкше және бас тәрізді безді трихома. Тықыр жусан жапырақтарының екі жағында және гүлдің төменгі бөлігінде бас тәрізді безді трихомалар басым келеді. Электронды сканерлеу микроскопиясының деректері бойынша тықыр жусан жапырақтарының бетіндегі безді трихомалар сопақ пішінді болып келеді, өлшем ұзындығы 70-80 мкм және ені 33-38 мкм шегінде өзгереді.

Алынған эксперименттік деректердің негізінде сесквитерпенді лактондардың биосинтезіне қатысатын гендерді іздеу үшін оңтайлы үлгілер ретінде бүрлен фазасындағы *Artemisia glabella* Kar. et Kir. интактілі өсімдігінің жапырағы мен гүлшанағы таңдалды.

Түйін сөздер: *Asteraceae*, *Artemisia glabella* Kar. et Kir., сесквитерпенді лактондар, арглабин, биосинтез, трихомалар, жоғары критикалық флюидті экстракция.

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БИОСИНТЕЗ И ДИНАМИКА НАКОПЛЕНИЯ СЕСКВИТЕРПЕНОВЫХ ЛАКТОНОВ В *ARTEMISIA GLABELLA* KAR. ET KIR.

Аннотация. Цель работы – количественная оценка содержания сесквитерпеновых лактонов в отдельных органах *Artemisia glabella* Kar. et Kir. на разных стадиях вегетационного периода и определение размеров железистых трихом на их поверхности при выборе оптимальных органов растения для поиска генов, участвующих в биосинтезе арглабина.

Впервые проведена количественная оценка содержания сесквитерпеновых лактонов арглабина и арголида в CO_2-экстрактах отдельных органов *Artemisia glabella* Kar. et Kir. на разных стадиях вегетационного периода (начало отрастания, конец отрастания, бутонизация, цветение, плодоношение). Методом электронной сканирующей микроскопии определена морфология поверхности листьев – одного из основных органов биосинтеза сесквитерпеновых лактонов.

Установлено, что присутствие сесквитерпенового лактона арглабина наблюдается во всех органах *Artemisia glabella* Kar. et Kir. и на всех стадиях вегетационного периода. Количественное его накопление отмечается в период бутонизации и составляет 1,90% в листьях и 1,56% в бутонах. Биосинтез арглабина продолжается и при повторном отрастании молодых побегов, которое наблюдается во 2-ой - 3-ей декадах августа. При этом содержание арглабина в них остается сравнительно высоким (1,18% в период плодоношения).

На поверхности листьев и бутонов *Artemisia glabella* Kar. et Kir. установлено наличие двух форм терпеноидсодержащих структур: железистых волосков и головчатых железистых трихом. На обеих сторонах листьев и нижней части цветка у полыни гладкой преобладают головчатые железистые трихомы. По данным электронной сканирующей микроскопии, железистые трихомы на поверхности листьев полыни гладкой имеют овальную форму, размеры варьируются в пределах 70-80 мкм в длину и 33-38 мкм в ширину.

На основании полученных экспериментальных данных в качестве оптимальных органов для поиска генов, участвующих в биосинтезе сесквитерпеновых лактонов, выбраны листья и бутоны интактного растения *Artemisia glabella* Kar. et Kir. в фазе бутонизации.

Ключевые слова: *Asteraceae*, *Artemisia glabella* Kar. et Kir., сесквитерпеновые лактоны, арглабин, биосинтез, трихомы, сверхкритическая флюидная экстракция.

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LANGMUIR-BLODGETT FILMS BASED ON SUPERHYDROPHOBIC SOOT

Abstract. In this paper it was produced Langmuir-Blodgett films based on superhydrophobic soot by Nima CD installation (England). Chloroform was used because it has a low boiling point and is not miscible in water. Consequently, the dispersion can be dropped onto the surface of the water in the Langmuir-Schaefer trough. The superhydrophobic soot was obtained at the Institute of Combustion Problems (Almaty, Kazakhstan) by combustion propan-butan mixture by applying an electric filed. To establish complete information about the structure of the soot obtained, studies were conducted by Raman spectroscopy and a transmission electron microscope (TEM). An analysis of the results of Raman spectra shows that two modifications of carbon are present in the obtained samples - amorphous carbon 1350 cm^{-1} (D - amorphous) and 1590 cm^{-1}, a graphitized carbon phase. As a result, it was found that the produced Langmuir-Blodgett films have a nanostructure, since soot has a nanoscale (20-60 nm), which is confirmed by electron microscopic and Raman studies.

Key words: film, superhydrophobic soot, surface.

Introduction. A Langmuir-Blodgett (LB) film is a nanostructured system formed when Langmuir films - or Langmuir monolayers (LM) - are transferred from the liquid-gas interface to solid supports during the vertical passage of the support through the monolayers. LB films can contain one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing the solid substrate into the liquid. A monolayer is adsorbed homogeneously with each immersion or emersion step, thus films with very accurate thickness can be formed. This thickness is accurate because the thickness of each monolayer is known and can therefore be added to find the total thickness of a Langmuir–Blodgett film. The gorgeous feature of Langmuir-Blodgett films is the internal control of the internal layer structure down to the molecular level and the exact control over the obtaining film thickness. Sophisticated LB troughs let us to treat several materials with different functionalities and offer the opportunity to setup the layer architecture according to the requirements of the desired molecularly engineered organic thin film setup [1].

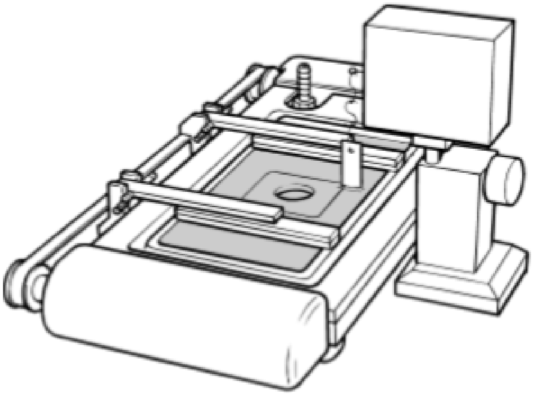
In work [2-5] transparent superhydrophobic films with TiO_2 photocatalysts, cobalt nanoparticle Langmuir-Schaefer films on ethylene glycol subphase, some methodologies based on technique to build thin films of graphene oxides, Quantum Dots and silver nanowires were studied. Surface roughness and morphology of the films are changed with rising concentration of TiO_2, which was attributed the size difference of the starting materials. The wetting angle of the resulting film which contain 2 wt % TiO_2 was higher than 140° even after UV illumination with the intensity of 1.7 mW/cm^2 for 800 h. The film with 2 wt % TiO_2 maintained higher wetting angles than the film with 0 wt % TiO_2 after 1800-h out door exposure. The obtained films in this work are the first ones that satisfy the demands of transparency, superhydrophobicity and long lifetime contemporaneously [2]. The possibility of modification of surface wettability is particularly eligible in implantology. This effect is reached by coating a given material with thin films containing nanoparticles of different chemical properties [6]. This work reports on the fabrication, optimization and characterization of ultrathin films containing submicrometer particles (sMPs) of the hydrophilic and water stable UiO-66-COOH(Zr) metal organic framework (MOF). It was established that the presence of MOF particles significantly enhances the surface roughness and allows ultrathin, hydrophobic coverage to be obtained. It has been shown that the crystallinity and the porosity of the MOF remains almost unaltered in MOF/ODP films [7].

Langmuir-Schaefer deposition is a scalable process for forming a percolating film based on graphene platelets which can be applied for electronic gas sensing [8-10] and LB films can find application in many area [11].

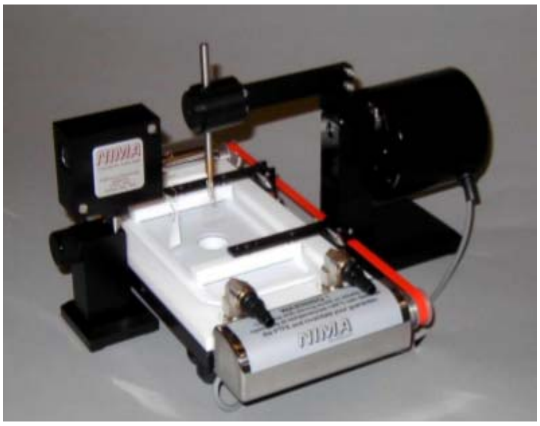
In the presented work it was created LB films based on superhydrophobic soot obtained by combustion propan-butan mixture. For the first time kind of soot having superhydrophobic properties was synthesized at the Institute of Combustion Problems (Almaty, Kazakhstan), which was obtained by applying an electric filed [12].

Experimental part. The Nima software uses Microsoft Sans Serif fonts, as our software is compatible with all versions of Windows from 95 to XP you may need to load the specific MS Sans Serif font onto your PC. Copies are on the Nima CD. When the required number of layers have been deposited, the dipper will stop. Data can be viewed also in the (pressure & area) -time and dipper - area axes, selected from the Graph Menu.

A typical LB film deposition instrument (Nima CD) shown in figure 1.



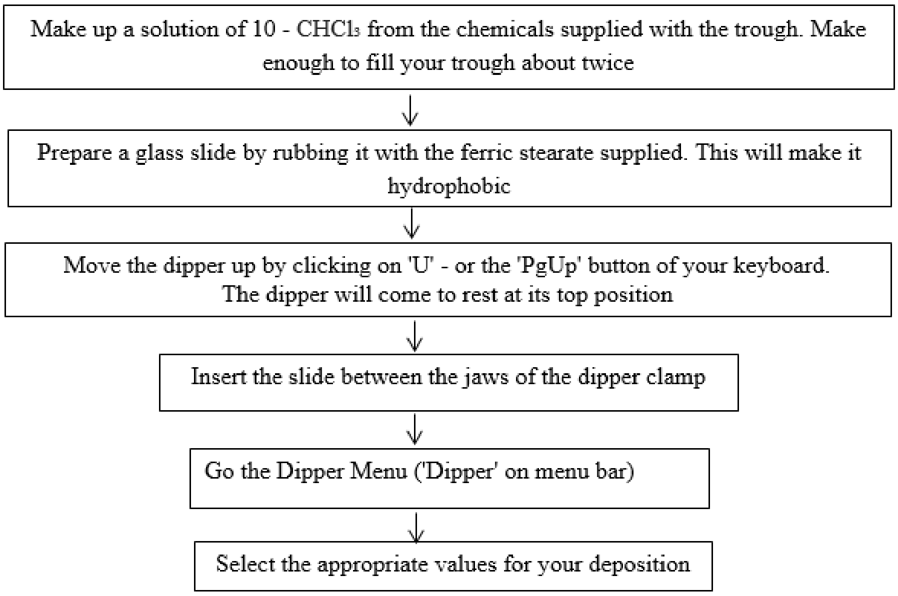
a – scheme



b – photo

Figure 1 - A typical LB film deposition instrument (Nima CD)

A typical multi-layer deposition (conventional dipper) was obtained by following stages which are shown in the scheme below.



Make up a solution of 10 - $CHCl_3$ from the chemicals supplied with the trough. Make enough to fill your trough about twice

Prepare a glass slide by rubbing it with the ferric stearate supplied. This will make it hydrophobic

Move the dipper up by clicking on 'U' - or the 'PgUp' button of your keyboard. The dipper will come to rest at its top position

Insert the slide between the jaws of the dipper clamp

Go the Dipper Menu ('Dipper' on menu bar)

Select the appropriate values for your deposition

Typical values are: Dipper Speed: 20 mm/min; Target pressure: 25 mN/m; Top End: 5 mm; Bottom End: 20 mm; Number of Layers: 10.

Then, spread the monolayer and select 'Pressure Control' from the Barrier menu of Installation of Nima CD. The film will be compressed to its target pressure. If pressure control is unstable, reduce the 'Feedback Gain' value. A value of 1.0 is good for almost all conditions.

After, select 'Program Dip' from the “Dipper menu”. The dipper will be run down and up under the selected conditions.

Results and discussions. Thus, to produce thin films of superhydrophobic soot, 10 mg of the powder was dissolved in 10 mL of chloroform. Chloroform must be used because it has a low boiling point and is not miscible in water. Consequently, the dispersion can be dropped onto the surface of the water in the Langmuir-Schaefer trough.

The chloroform quickly evaporates and the hydrophobic soot is left sitting at on the water. This floating layer is reducing the surface tension of the water, as measured by the pressure sensor at the surface.

As more dispersion is deposited, the surface tension at the surfaces decrease while the surface pressure due to the material increases.

When the surface is sufficiently covered, the floating 'islands' of hydrophobic soot can be compressed into a continuous film.

The barriers are moved to reduce the area occupied by the soot and force the islands to come together.

As it is compressed, the surface pressure increases - which leads to the pressure-area graph in the attached file.

When completely compressed, the film can be deposited by lowering the substrate attached to the vacuum pump.

The software is used to bring the substrate into contact with the surface and the film will be deposited, as it shown in figure 2.

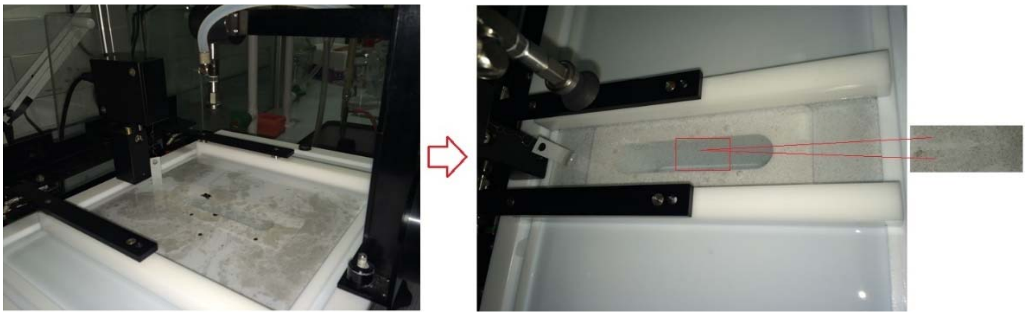


Figure 2 - Creation film on the water surface

When the film is nearly fully compressed (like the attached data), it may rearrange on the surface. This can be controlled by using less dispersion or compressing to lower surface pressures, figure 3.

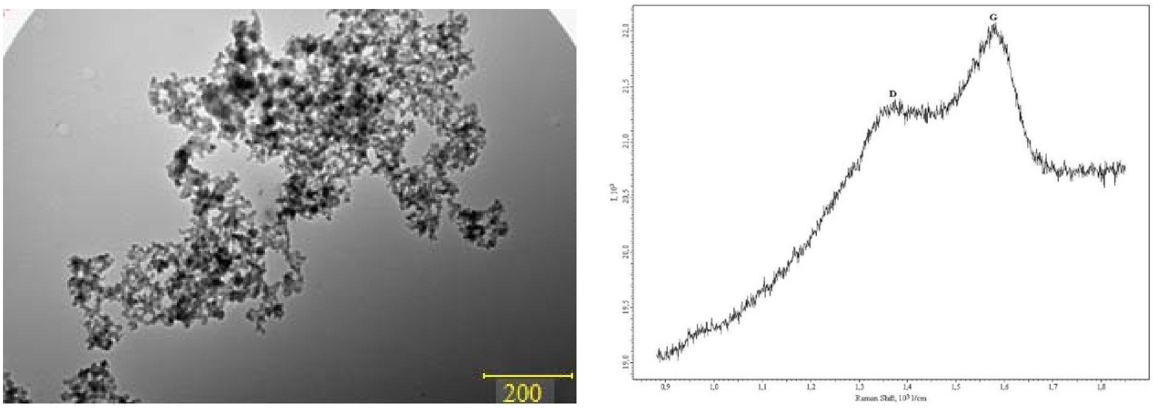
It is known that, the air/water interface possesses excess free energy originating from the difference in environment among the surface molecules and those in the bulk. This interfacial free energy is approachable by measurements of the surface tension. The surface tension of water is about 72 mN/m at 20°C which is an exclusively high valuation in comparison with other liquids and accordingly makes water a perfect sub phase for monolayer studies.

The overall way to transportation an amphiphile to the surface is to dissolve it in a volatile non-polar solvent and then using a micro syringe to deposit onto the surface. The solution spreads rapidly to cover the available area. As far as the solvent evaporates, a monolayer is formed. When the available area for the monolayer is large the distance between adjacent molecules is enormous and their interactions are weak. The monolayer can then be regarded as a two-dimensional gas. Under these conditions, the monolayer has less impact to the water surface tension. If the available surface area of the monolayer is reduced by a barrier system, the molecules start to exert a repulsive force on each other.

Figure 3 - Hydrophobic soot film

Surface pressure curve recorded during the LB monolayer assembly from computer. The most important indicator of the monolayer properties of an amphiphilic material is obtained by measuring the surface pressure as a function of the area of water surface available to each molecule. Thus, final surface pressure reached 50 mN/m.

The soot applied for creating LB films was investigated by transmission electron microscope (TEM) and Raman spectroscopy, figure 4. The obtained spectra are shown in figure 4, b.



a b

Figure 4 - Results of investigation methods of soot samples: a – TEM images; b – Raman spectra

As it can be seen from TEM images, the superhydrophobic soot has nanospherical chain structure, in the form of pearls with varying degrees of branching, which have a diameter in the range of from 20 up to 60 nm.

Analysis of the Raman spectra shows that in the samples obtained there are two peaks 1350 cm^{-1} (D - amorphous) and 1590 cm^{-1} (G - graphite), corresponding to the phase of amorphous carbon (figure 4, b).

Conclusion. In this article, the LB film preparation technique was discussed. Langmuir-Blodgett technique was used to assemble monolayers of superhydrophobic soot. Films were deposited using the vertical (LB) deposition methods onto glass substrates. However, soot films do not completely cover the water surface, probably due to the dissolution of into the aqueous subphase. As a result, it was found that the obtained Langmuir-Blodgett films has a nanostructure, since soot has a nanoscale from 20 to 60 nm, which is confirmed by electron microscopic and Raman studies.

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ПЛЕНКИ ЛЕНГМЮР-БЛОДЖЕТТ НА ОСНОВЕ СУПЕРГИДРОФОБНОЙ СУТКИ

Аннотация. Область исследований наноразмерных эффектов показывает, что гидрофобные свойства поверхностей основаны на правильной структуре частиц, выступов или вершин субмикронного и нанометрового размера, расположенных на поверхности упорядоченным образом. Поверхности, имеющие гидрофобные свойства, могут быть получены химическим или методом выращивания наноразмерных материалов. Такой эффект существует в дикой природе. Ярким примером является поверхность листьев лотоса, усеянная многочисленными микроскопическими выступами, придающими поверхности листьев исключительные супергидрофобные свойства.

Эти исследования показывают, что сажа, синтезируемая при сжигании углеводородного топлива в определенных условиях, обладает супергидрофобным свойством и может быть использована в качестве наполнителя при создании гидрофобных покрытий.

Супергидрофобная сажа получена при сжигании пропан-бутановой смеси при наложении электрического поля в лаборатории синтеза углеродных наноматериалов в пламени Института проблем горения (Алматы, Казахстан).

Для установления полной информации о структуре получаемой сажи проведены исследования просвечивающим электронным микроскопом (ПЭМ), методом спектроскопии комбинационного рассеяния.

Результаты ПЭМ показали, что супергидрофобная сажа имеет наносферическую цепную структуру в форме жемчуга с разной степенью разветвления, диаметр которой находится в диапазоне от 20 до 60 нм.

Анализ результатов спектров комбинационного рассеяния света показывает, что в полученных образцах присутствуют две модификации углерода - аморфный углерод 1350 см$^{-1}$ (D - аморфный) и 1590см$^{-1}$ (G - графитизированная углеродная фаза).

В данной работе были изготовлены пленки Ленгмюра-Блоджетт на основе супергидрофобной сажи на установке Nima CD (Англия). Для получения тонких пленок 10 мг супергидрофобной сажи растворяли в 10 мл хлороформа. Хлороформ следует использовать, поскольку он имеет низкую температуру кипения и не смешивается с водой. Следовательно, дисперсия может быть сброшена на поверхность воды в корыте Ленгмюра-Шефера.

Хлороформ быстро испаряется, а гидрофобная сажа остается на воде. Этот плавающий слой уменьшает поверхностное натяжение воды, измеряемое датчиком давления на поверхности.

По мере осаждения большего количества дисперсии поверхностное натяжение на поверхностях уменьшается, а поверхностное давление из-за материала увеличивается.

Когда поверхность достаточно покрыта, плавающие «островки» гидрофобной сажи могут быть спрессованы в непрерывную пленку.

Барьеры перемещаются, чтобы уменьшить площадь, занятую сажей, и заставить острова объединиться. По мере сжатия давление на поверхность увеличивается, что приводит к графику области давления в прикрепленном файле. После полного сжатия пленка может быть нанесена путем опускания подложки, прикрепленной к вакуумному насосу. Пленка будет сжата до целевого давления. Если контроль давления нестабилен, уменьшите значение «Усиление обратной связи». Значение 1,0 хорошо для почти всех условий.

После этого необходимо выбрать «Dipper menu», затем меню «Program Dip». Ковш будет опускаться и подниматься при выбранных условиях.

Таким образом, были получены пленки Ленгмюра-Блоджетт на основе сажи, обладающей супергидрофобными свойствами. В результате было обнаружено, что полученные пленки Ленгмюра-Блоджетт имеют наноструктуру, которые подтверждаются электронно-микроскопическими и рамановскими исследованиями.

Ключевые слова: пленка, супергидрофобная сажа, поверхность.

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АСАГИДРОФОБТЫ КҮЙЕ НЕГІЗІНДЕ ЛЕНГМЮР-БЛОДЖЕТ ҚАБЫҚШАЛАРЫН АЛУ

Аннотация. Наноөлшемді эффектілерді зерттеу саласы беттің гидрофобты қасиеттері бөлшектердің дұрыс құрылымына, беткейге реттелген субмикронды және нанометр өлшемдерінің шыңдарына негізделгенін көрсетеді. Гидрофобты қасиеттері бар беттерді химиялық жолмен немесе наноөлшемді материалдарды өсіру әдісімен алуға болады. Мұндай әсер табиғатта бар. Жарқын мысал ретінде, жапырақтардың бетіне ерекше асагидрофобты қасиет беретін, көптеген микроскопиялық шығыңқы сызықтармен ерекшеленетін лотос жапырақтарының беткі қабатын алуға болады.

Бұл зерттеулер көмірсутекті отындарды жағу арқылы синтезделген күйенің белгілі бір жағдайда асагидрофобты қасиетке ие екендігін және гидрофобты жабынды жасау барысында толтырғыш ретінде пайдаланылатындығын көрсетті.

Пропан-бутан қоспасын жағу барысында алынған асагипрофобты күйе электр өрісін беру арқылы жану проблемалары институтының жалында көмірсутекті наноматериалдарды синтездеу зертханасында алынды (Алматы, Қазақстан).

Алынған күйенің құрылымы туралы толық ақпарат алу үшін күйе үлгілері жарықтандырғыш электронды микроскоп (ЖЭМ) және комбинациялық шашырау спектроскопиясы арқылы зерттелді.

ЖЭМ нәтижелері көрсеткендей, асагидрофобты күйенің диаметрі 20-дан 60 нм-ге дейінгі диапазонда болатын түрлі дәрежедегі інжу түріндегі наносфералық тізбекті құрылымдардан тұрады.

Комбинациялық шашырау спектроскопиясы нәтижелерін талдау алынған үлгілерде көміртектің екі үлгісі – 1350 см$^{-1}$ (D - аморфты) және 1590 см$^{-1}$ (G - графиттелген көміртегі фазасы) бар екендігін көрсетті.

Жұмыста Нима CD қондырғысында (Англия) асагидрофобты күйе негізінде Ленгмюр-Блоджетт қабықшалары алынды. Жұқа қабықшаларды алу үшін 10 мл хлороформда 10 мг асагидрофобты көміртекті күйе ерітілді. Хлороформның қайнау температурасы төмен және сумен араласпайтындықтан қолданылды. Сондықтан дисперсияны Лангмюр-Шефер ыдысындағы судың бетіне ағызуға болады.

Хлороформ тез буланып, гидрофобты күйе суда қалады. Бұл қалқымалы қабат су қысымының сенсорымен өлшенетін судың кернеуін азайтады.

Дисперсия көп болған сайын, беттердегі кернеу азаяды және материалдың әсерінен беткі қысым жоғарылайды.

Табақшаның беткі қабаты жеткілікті түрде жабылған кезде, гидрофобты күйенің қалқып жүрген «үшкір бөлшектері» үздіксіз қабықшаға қысылады.

Кедергілер күйенің алып отырған ауданын азайтуға және үшкір бөлшектерді бір-біріне жақындатуға мәжбүр етеді.

Сығылған сайын бетіндегі қысым жоғарылайды, бұл тіркелген файлдағы қысым аймағының графигіне әкеледі. Толық сығылғаннан кейін, қабықшаны алу мақсатында вакуумдық насосқа бекітілген табақшаны төменге түсіру арқылы қолдануға болады. Қабықша мақсатты қысымға дейін қысылады. Егер қысымды басқару тұрақсыз болса, «кері байланыс өсімі» мәнін азайту қажет. 1.0 мәні барлық жағдайға тиімді болып саналады.

«Dipper мәзірін», одан кейін «Program Dip» мәзірін таңдаңыз. Ожау таңдалған жағдайда төмендейді және көтеріледі.

Осылайша күйе негізіндегі асагидрофобты қасиеті бар Ленгмюр-Блоджетт қабықшалары алынды. Нәтижесінде алынған Ленгмюр-Блоджетт қабықшаларының наноқұрылымды екендігі анықталды, бұл жарықтандырғыш электрондық және раман спектроскопиясы арқылы расталды.

Түйін сөздер: қабықша, асагидрофобты күйе, бет.

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TESTING OF MO-CONTAINING CATALYSTS APPLIED TO AL-, AL/ZR-PILLARED CLAYS DURING THE OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE

Abstract. The development of an alternative method for the oxidative dehydrogenation of ethane to ethylene is an important task in the presence of a suitable catalyst. Mo-containing catalyst systems applied to Al-, Al/Zr-columnar clays were prepared. The textural characteristics of the synthesized Al-, Al/Zr-columnar clays differ from the textural properties of natural clay with an increase in their specific surface from ~54 m^2/g to ~215 m^2/g. The LaNbMo and VMoTeNb catalyst systems applied to l-, Al/Zr-columnar clays showed higher activity and selectivity for oxidative dehydrogenation of ethane (ODH). A detailed characterization was achieved using XRD, adsorption of N_2, SEM, BET to study the texture properties of the synthesized catalysts. The highest activity and ethylene selectivity were shown by 10% VMoTeNb/PILCs and 20% VMoTeNb/PILCs catalysts. The lowest ethylene selectivity was exhibited by 10% LaNbMo/PILCs and 20% LaNbMo/PILCs catalysts. The results obtained indicate that the application of LaNbMo and VMoTeNb polyoxide active phases to Al-, Zr-columnar clays can improve the physical and mechanical properties of these types of catalysts due to changes in both the nature of the crystalline phase and the catalytic properties in oxidation reactions.

Keywords: oxidative dehydrogenation; ethane ethylene; mechanism ethylene production.

1. Introduction

In recent years natural gas reserves and their rational use have been of great interest. Partly, natural gas can be attributed to renewable natural resources, since methane emission begins immediately with rotting biomass of animal and vegetable origin, and they renew faster than oil.

Currently, natural gas is widely used in the power industry and much less in the chemical industry due to some inertness of the gas. That is, many chemical reactions that have an industrial sense require too high costs to be economically viable [1, 2]. For example, the process of dehydration of light alkanes also presents a significant problem associated with their low reactivity, high energy consumption, and low selectivity [3-5].

One of the ways to intensify the dehydrogenation of alkanes is their oxidative dehydrogenation (ODE). In the case of oxidative dehydrogenation of ethane (ODE), these reactions are as follows:

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O\ \Delta H_{298} = -105\ \mathrm{kJ/mol},$$

$$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O\ \Delta H_{298} = -1428\ \mathrm{kJ/mol},$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 3H_2O\ \Delta H_{298} = -1323\ \mathrm{kJ/mol}.$$

Despite the widespread use of steam cracking, fluid catalytic cracking, and catalytic dehydrogenation in the synthesis of olefins, intensive research is underway to develop oxidative dehydrogenation (ODH) catalysts for alkanes. This approach can significantly reduce the temperature of this process, which leads to higher selectivity and less coking of the catalysts [1, 3]. A number of catalysts have been proposed to improve ethane conversion and ethylene selectivity [6-10].

Ethane ODE is performed on a solid catalyst in which ethane reacts with an oxidizing agent, usually oxygen. When comparing the ODH of ethane with existing commercial processes, a number of advantages are noted: there is no thermodynamic limitation (ΔGR, 298K^{o}=-128 kJ/mol); the reaction is exothermic (ΔHR, 298K^{o}=-106 kJ/mol), which eliminates the need for energy; a limited number of reaction products (COx and ethylene) is observed; catalyst deactivation with coke does not occur due to the presence of oxygen in the reaction medium [8]. Therefore, the development of an alternative method for the oxidative dehydrogenation of ethane to ethylene in the presence of a suitable catalyst has become an urgent task.

Based on this, the goal of this study is to develop new catalytic systems applied to columnar clays in order to obtain an environmentally friendly and economically viable catalyst, designed to increase ethane conversion and ethylene selectivity.

2. Experimental part

2.1 Catalytic synthesis

Research objects are polyoxide catalyst systems deposited on columnar clays capable of catalyzing the process of oxidative dehydrogenation of ethane to ethylene.

2.1.1 Mechanical activation of natural clays

To activate natural kaolinite clays, the AGO-2 high-voltage planetary mill was used. The grinding was carried out with steel balls with a diameter of 8 mm and a total weight of 200 g in 150 ml water-cooled steel drums. The ratio of balls' mass to the mass of mixture (M) was 20:30. The rotational speed of the drums was 1200 rpm (40g). To ensure a low level of powder contamination in the steel grinding medium, the natural lining of the working surface of drums and balls, obtained by preliminary activation of a similar mixture, leading to the coating of the surface of the balls and the inner surface of the drums with the processed composition, was used [11].

2.1.2 Synthesis of columnar clays

Pre-cleaned and ground natural clays with particle diameters up to 0.25 mm were incubated for 24 hours at room temperature for complete hydration., Aluminum and zirconium hydroxocomplexes were used as intercalating solutions (hydrolysis of aqueous solutions of aluminum chloride (0.2 M) and zirconium chloride (0.2 M) in aqueous NaOH solution (0.5 M)). Pillarization was carried out by slowly adding intercalating agent to clay samples, followed by washing of chlorine ions. The obtained Al-, Zr-columnar clays were dried for one day at room temperature, then they were calcined at 500 ^{0}C for 5 hours.

2.1.3 Preparation of catalysts

Mixed oxides LaNbMo and MoVTeNb with nominal atomic ratios La:Nb:Mo=1:0.8:0.2 and V:Mo:Te:Nb=0.3:1:0.23:0.12 were prepared. The synthesis of the catalysts included the following stages: 1) an aqueous solution containing ammonium paramolybdate (Merck, 99%), telluric acid (Sigma-Aldrich, 98%) and ammonium metavanadate (Sigma-Aldrich, 99.5%), was prepared with constant stirring at 80 °C FROM; separately 2) an aqueous solution of niobium oxalate (ABCR Laboratories, 99%) was also prepared at 80 °C. 3) then, a solution of niobium oxalate was added to a mixture containing ammonium paramolybdate, telluric acid and ammonium metavanadate with vigorous continuous stirring. The resulting mixture turned into a suspension, which was cooled to room temperature. Using the impregnation method, the prepared polyoxide system was applied onto the surface of Al-, Al/Zr-columnar clays by the volume of moisture capacity. Then, the catalyst samples were dried at 50 °C for gradual evaporation of water. The catalysts were first thermally treated at 310 °C for 1 h, then they were calcined at 700 °C for 3 h in a stream of nitrogen.

2.2 Characterization of catalysts

2.2.1 Study of physico-chemical properties of the catalysts

The texture characteristics of columnar clays were studied using nitrogen adsorption and desorption isotherms using the BET method (Brauner-Emmett-Teller) on a SORBTOMETR-M device (Russia). The change in the phase composition of the catalysts was monitored using x-ray phase analysis on a general-purpose diffractometer DRON-4-0.7 with CuKα radiation (Russia).

2.2.2 Statistical processing of data

Statistical analysis was performed with a help of SPSS Statistical Program (version 16, Chicago, Illinois, USA) using semi-logarithmic regression analysis Graphpad PRISM Software (San Diego, California, USA).

2.3 Catalytic test

2.3.1 Reactor plant with on-line chromatographic analysis

Catalytic experiments were carried out in an automated laboratory flow reactor with on-line chromatographic analysis of the components of the reaction mixture. A quartz tube reactor with an internal diameter of 10 mm and 200 mm in length was equipped with two thermocouples, one of which showed the temperature of the wall of the reactor, and the other measured the temperature of the catalyst layer. All runs were performed by feeding a mixture, consisting of ethane (C_2), oxygen (O_2) and nitrogen (N_2) as a diluent in the ratio C_2H_6:O_2:N_2 = 10:10:80, into the reactor. The purity of ethane, oxygen, and nitrogen used in this work was 99.7 vol. %, 99.996 vol. %, and 99.999 vol. %, respectively. The gas flow rate was quantified using independent mass flow temperature controllers.

2.3.2 Reaction conditions

For a typical experiment, 0.60 g of a heat-treated catalyst with an average particle size of 150 μm was charged to the reactor. Before carrying out the reaction, the composition of the gas mixture was checked using GC, and was preheated to 140 °C. A blank experiment, conducted at 480 °C, confirmed the absence of transformations of both ethane and oxygen in the absence of a catalyst.

The reaction was carried out for 6 hours. In all experiments, the carbon balance was in the range of 100% ± 2.0%. For systematical study of the effect of temperature and contact time on the catalytic behavior of LaNbMo and VMoTeNb catalysts, the first series of experiments were carried out in accordance with the factorial design of the experiment. The partial pressures of ethane, oxygen, and nitrogen at the inlet were fixed at 7.0, 5.5, and 65.5 kPa, respectively.

3. Results and discussion

3.1 Texture characteristics of columnar clays

The specific surface of Al-, Al/Zr-columnar clays was determined using indicators of nitrogen adsorption and desorption isotherms by the BET method on a SORBTOMETR-M device (Russia) (table 1).

Table 1 - Textural characteristics of Al-, Al/Zr-columnar clays

№	Compound	S_{BET}, m^2/g	$V_{pore\ ads}$, cm^3/g	$V_{pore\ des}$, cm^3/g	$V_{micropore}$, cm^3/g	Average pore diameter, A	$D_{pore\ ads}$, A	$D_{pore\ des}$, A
1	glina MM	53.7097	0.115297	0.119158	0.002722	95.0805	139.1295	117.4108
2	Al-PILCs	173.1012	0.048405	0.061924	0.049691	26.6481	111.0876	51.2044
3	Al/Zr-PILCs	216.3813	0.046253	0.061939	0.063175	24.3099	105.5924	48.1946

Note: V pore ads/des – by method BJH;
Average pore diameter: 4V/A BY BET;
BJH adsorption/desorption average pore diameter: 4V/A.

The textural properties of the synthesized Al-, Al/Zr-columnar clays are shown in table 1. The specific surface of natural clay treated with intercalating agents increased from ~54 m^2/g to ~215 m^2/g.

It can be seen from Figure 1 that the specific surface (SBET, m^2/g) of natural clay grows when it is pillared with intercalating agents of aluminum and zirconium. The average pore diameter of Al-, Al/Zr-columnar clays gradually decreases compared to natural clay. In this case, the average micropore volume (Vmicropore, cm^3/g) in all the studied samples remains unchanged.

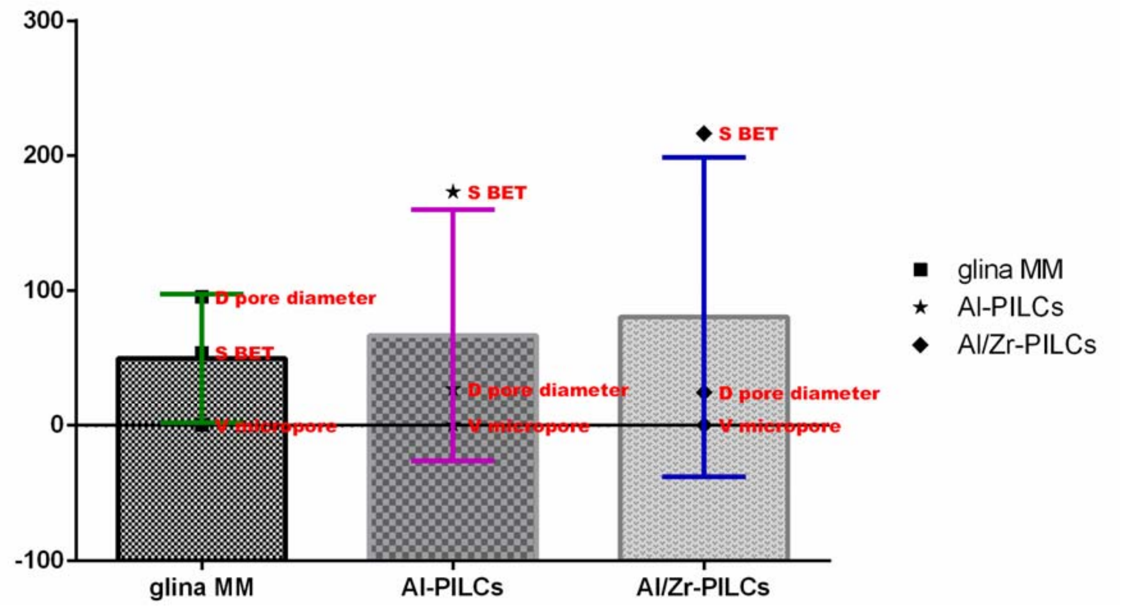

Figure 1 - Comparison of the texture properties of natural clay with Al-, Al / Zr-columnar clays

3.2. Catalytic testing

Catalytic properties of the polyoxide LaNbMo and VMoTeNb catalysts applied to Al-, Zr-columnar clays in the oxidative dehydrogenation reaction of ethane (ODE) were studied. The synthesized samples were tested in a flow reactor with on-line chromatographic analysis of the reaction mixture components. The test results are shown in table 2 and in figure 2.

Table 2 - Catalytic properties of polyoxide catalysts LaNbMo and VMoTeNb applied to columnar clays in the oxidative dehydrogenation of ethane

№	Sample	Tp., °C	t, c	X, %	Selectivity,%	
					C_2H_4	CO_x
1	10% LaNbMo/PILCs	400	5,52	10,2	36,1	63,9
		430	5,52	14,6	35,3	64,7
		460	5,52	21,0	35,3	64,7
2	20% LaNbMo/PILCs	400	3,36	0,8	34,1	65,9
		430	3,36	1,5	38,0	62,0
		460	3,36	2,6	44,7	55,3
3	10% VMoTeNb/PILCs	420	5,52	49,3	91,9	8,1
		441	5,52	65,3	87,7	12,3
		461	5,52	79,6	81,3	18,7
4	20%VMoTeNb/PILCs	417	5,52	47,4	90,9	9,1
		440	5,52	62,9	87,6	12,4
		460	5,52	80,6	78,8	21,2

Note: PILCs – Al/Zr-pillared clays

For the initial reaction mixture (vol. %) the components (table 2, figure 2) were taken in the following ratios $C_2H_6:O_2:N_2 = 10:10:80$.

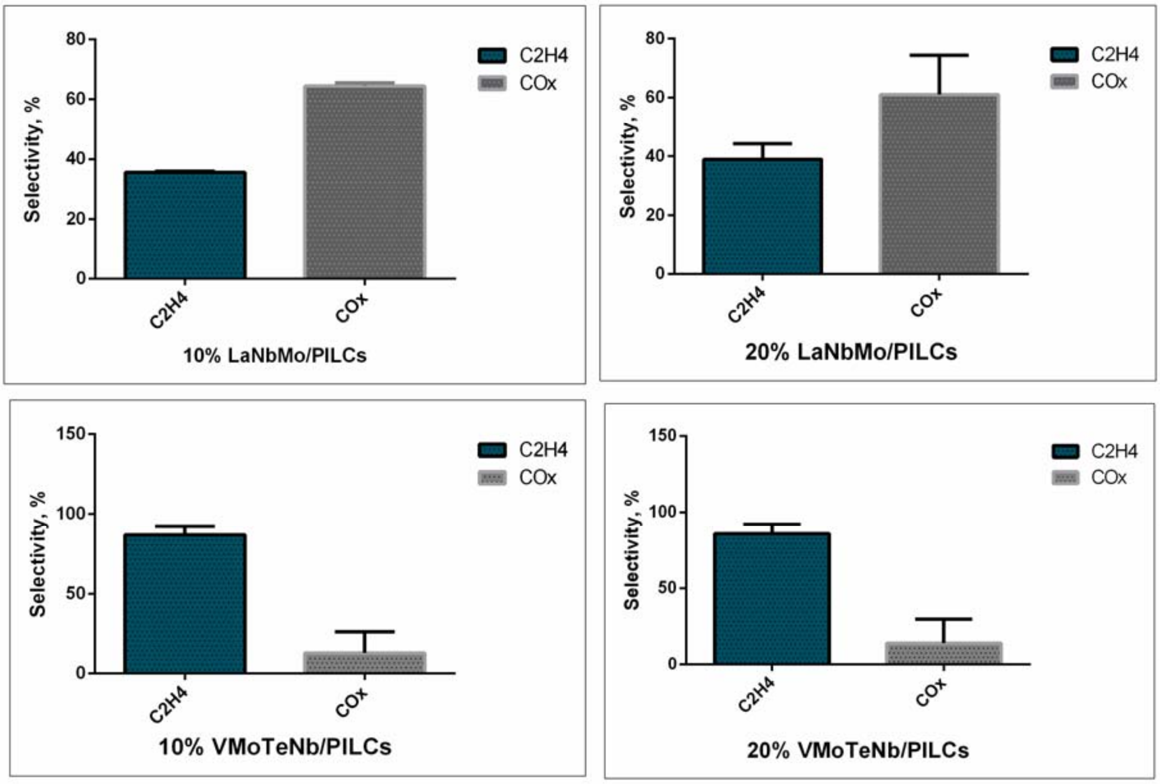

Figure 2 - Oxidative dehydrogenation of ethane to ethylene with LaNbMo and VMoTeNb polyoxide catalysts

The results of catalytic tests of the polyoxide LaNbMo and VMoTeNb catalysts (Figure 2) applied to Al-, Al/Zr-columnar clays showed that catalysts with the chemical composition of VMoTeNb have high selectivity during the oxidative dehydrogenation of ethane to ethylene, despite the active mass in them.

Mixed metal oxides MoVTeNbO have low surface area, which limits their potential industrial use. The inclusion of metal oxides on the substrate improves the mechanical properties of the catalysts and, as a rule, modifies their catalytic behavior, which can adversely affect the catalytic activity [10, 12].

It is known [10, 13] that Mo-containing catalysts applied to natural supports (alumina, modified clays, zeolites) have a higher reactivity than alumina.

Conclusions. The results obtained indicate that the deposition of LaNbMo and VMoTeNb polyoxide active phases on Al-, Zr-columnar clays can improve the physical and mechanical properties of these types of catalysts by changing the nature of the crystalline phase, as well as catalytic properties in oxidation reactions

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Al-, Al/Zr-БАҒАНАЛЫҚ САЗБАЛШЫҒЫНА ОТЫРҒЫЗЫЛҒАН Mo-ҚҰРАМДЫ КАТАЛИЗАТОРЛАРДЫ ЭТАНДЫ ЭТИЛЕНГЕ ТОТЫҚТЫРА ДЕГИДЛЕУ ҮДЕРІСІНДЕ СЫНАУ

Аннотация. Олефиндер синтезінде бу, сұйық каталитикалық крекингтің және каталитикалық дегидрогенизацияның кеңінен қолданылуына қарамастан, алкандарды тотықтыра дегидрлеу (ODH) катализаторларын құру бойынша қарқынды зерттеулер жүргізілуде. Этанды тотықтыра дегидрлеу (ЭТД) қатты катализаторда орындалады, онда этан тотықтырғышпен, яғни оттегімен әрекеттеседі. Этанды этиленге дейін тотығу арқылы дегидрлендіруді жүзеге асыру үшін жоғары селективті катализатор дайындау басты міндет болып саналады.

Осылайша қоспалар құрамы: La:Nb:Mo = 1:0.8:0.2 және V: Mo:Te:Nb = 0.3:1: 0.23:0,12 болатын Al-, Al/Zr-бағаналы сазбалшықтарға отырғызылған LaNbMo және MoVTeNb катализаторы дайындалды. Бағаналы саздың құрылымдық сипаттамасы BET әдісін қолдана отырып, азот адсорбциясы және десорбция изотермаларының көрсеткіші негізінде зерттелді. Синтезделіп алынған Al-, Al/Zr-бағаналық сазбалшықтың құрылымдық сипаттамасы табиғи сазбалшық құрылымынан үстіңгі қабытының ~54 м^2/г-ден 15215 м^2/г дейін өсуі арқылы ерекшеленеді.

Автоматтандырылған online хроматографиялық анализ орнатылған зертханалық ағынды реакторда каталитикалық тәжірибе жүргізу барысында Al-, Al/Zr-бағаналық сазбалшық бетіне отырғызылған LaNbMo және VMoTeNb каталитикалық жүйелері этанның тотықтыра дегидрленуіне (ЭТД) қатысты өте жоғары белсенділік пен селективтілік танытты.

Синтезделген катализаторлардың құрылымдық қасиеттері XRD, N$_2$, SEM, BET адсорбция әдістері негізінде сипатталды. Ең жоғары белсенділік пен этилен селективтілігін 10% VMoTeNb/PILCs және 20% VMoTeNb/PILCs катализаторлары көрсетті. Этиленнің ең төмен селективтілігін LaNbMo/PILC 10% және LaNbMo/PILCs 20% катализаторлары көрсетті.

Al-, Al/Zr-бағаналы сазбалшықтарға отырғызылған LaNbMo және VMoTeNb катализаторларының каталитикалық сынақ нәтижесін сараптауда химиялық құрамы VMoTeNb катализаторының этиленге тотығу арқылы дегидрлену үдерісінде құрамындағы белсенді массалардың мөлшеріне қарамастан жоғары селективті екендігін көрсетті.

Аралас металл оксидтері MoVTeNb аз көлемді үстіңгі бетке ие, бұл олардың өнеркәсіптік қолданылуын шектейді. Металл оксидтерін субстратқа қосу катализатордың механикалық қасиетін жақсартады және, әдетте, каталитикалық белсенділікке теріс әсер етуі мүмкін каталитикалық әрекетті өзгертеді.

Алынған нәтижелер Al-, Zr-бағаналы сазбалшықтарға отырғызылған полиоксидтік белсенді фазалы LaNbMo және VMoTeNb катализаторларының тотығу реакциясындағы кристалл фаза мен каталитикалық қасиеттерінің жақсаратындығын көрсетті.

Түйін сөздер: тотықтыра дегидрлеу, этан, этилен, механизм, этилен өндірісі.

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ИСПЫТАНИЕ МО-СОДЕРЖАЩИХ КАТАЛИЗАТОРОВ, НАНЕСЕННЫХ НА Al-, Al/Zr-СТОЛБЧАТЫЕ ГЛИНЫ, В ПРОЦЕССЕ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ ЭТАНА В ЭТИЛЕН

Аннотация. Несмотря на широкое использование парового крекинга, флюид-каталитического крекинга и каталитического дегидрирование при синтезе олефинов, ведутся интенсивные поиски по разработке катализаторов окислительного дегидрирования (ODH) алканов. ОДЭ этана выполняется на твердом катализаторе, в котором этан реагирует с окислителем, обычно кислородом. Разработка альтернативного способа окислительного дегидрирования этана в этилен является актуальной задачей в присутствии подходящего катализатора.

Таким образом, были приготовлены катализаторы – смешанные оксиды LaNbMo и MoVTeNb с номинальными атомными отношениями La:Nb:Mo=1:0,8:0,2 и V:Mo:Te:Nb=0,3:1:0,23:0,12, нанесенные на Al-, Al/Zr-столбчатые глины. Были изучены текстурные характеристики столбчатых глин по показателям изотерм адсорбции и десорбции азота по методу БЭТ. Результаты данного исследования показали, что текстурные свойства синтезированных Al-, Al/Zr-столбчатых глин отличаются от текстурных свойств природной глины с увеличением их удельной поверхности от ~54 м^2/г до ~215 м^2/г.

При проведении каталитических экспериемов на автоматизированном лабораторном проточном реакторе с on-linexроматографическим анализом каталитические системы LaNbMo и VMoTeNb, нанесенные на Al-, Al/Zr-столбчатые глины проявляли более высокую активность и селективность в отношении окислительного дегидрирования этана (ODH).

Детальная характеристика была достигнута с использованием XRD, адсорбции N$_2$, SEM, БЭТ для изучения текстурных свойств синтезированных катализаторов. Наибольшую активность и селективность по этилену показали 10% VMoTeNb /PILCs и 20% VMoTeNb /PILCs катализаторы. Наименьшей селективностью по этилену обладали 10% LaNbMo/PILCs и 20% LaNbMo/PILCs катализаторы.

Результаты каталитических испытаний полиоксидныхLaNbMo и VMoTeNb катализаторов, нанесенных на Al-, Al/Zr-столбчатые глины, показали, что при окислительном дегидрировании этана в этилен высокую селективность имеют катализаторы с химическим составом VMoTeNb, несмотря на содержание в них активной массы.

Смешанные оксиды металлов MoVTeNb имеют низкую площадь поверхности, что ограничивает их потенциальное промышленное применение. Включение оксидов металлов на подложку улучшает механические свойства катализаторов и, как правило, модифицирует их каталитическое поведение, что может оказывать неблагоприятное влияние на каталитическую активность.

Полученные результаты исследования свидетельствуют о том, что нанесение на Al-, Zr-столбчатые глины полиоксидных активных фаз LaNbMo и VMoTeNb может улучшить физические и механические свойства катализаторов этих типов за счет изменения как природы кристаллического фазы и каталитические свойства в реакциях окисления.

Ключевые слова: окислительное дегидрирование; этан; этилен; механизм; производства этилена.

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ON THE PRODUCTION OF PURIFIED DIAMMONIUM PHOSPHATE FROM EXTRACTION PHOSPHORIC ACID BASED ON OFF BALANCE ORES OF THE KARATAU BASIN

Abstract. The problem of utilization of man-made waste from the mining complex has not lost its relevance since the end of the last century. The amount of waste only in the «Central» mine quarry of the Zhanatas field, is about 22 million tons of phosphate-silicon raw materials (PSRM). More than 12 million tons after flotation enrichment were used for acid processing and as commercial phosphates for electro thermal processing. When refining the Zhanatas quarries to the working depth, at least 18-19 million tons of PSRM will be formed [1].

Off-balance ores of internal overburden are represented by three special dumps of the mines "Kokjon", "Koksu", "Tjesay", "Aksay", the volume of which is more than 3.2 million tons with a content of up to 20% P_2O_5.

Mineral fertilizers in the agro-industrial sector of the economy play a key role in improving crop productivity and quality. Given the export orientation of the phosphorus industry, it cannot be considered outside of macroeconomics, as its situation remains complex and unstable.

The practical importance of innovative research to develop technological foundations and technical solutions for the production of diammonium phosphate (DAP) [7], derived from wet-process phosphoric acid (PSRM)balance Karatau phosphorite is no doubt also compiled the original data on the establishment of a pilot plant and the calculated techno-economic assessment of innovative industrial production.

Our proposed technology will reduce the economic costs of processing off-balance raw materials and increase the range of phosphorus-containing products to 10-15%; increase the production of PSRM and DAP to 20-25%; create additional jobs.

The results of innovative scientific research are applicable to the chemical enrichment of man-made waste for target products, which are urgently needed by the agro-industrial complex, to improve the environmental and economic indicators of industrial regions and the welfare of the population of Kazakhstan.

Keywords: Off-balance phosphorites, Karatau basin, diammonium phosphate, extraction phosphoric acid, drum granulator dryer, neutralization, evaporated and non-evaporated PSRM.

Introduction. In world practice, the trademark diammonium phosphate 18:46 has long been established, with a mass fraction of total nitrogen of at least 18 %, and total P_2O_5 of at least 46 %, exported fertilizers usually meet these requirements. In addition, export contracts more strictly regulate the granulometric composition [8]. This requires normalization of the proportion of the size of DAP granules from 2 to 4 mm or from 2 to 5 mm, produced by the largest producers of Russia-JSC "PhosAgro-Cherepovets" and LLC "Balakovskaya mineral fertilizers", which are part of the holding company "PhosAgro" and contain at least 95% of granules from 2 to 5 mm (in practice, from 97 to 100 %) [2].

The composition of the fertilizer DAP includes diammonium phosphate $(NH_4)_2HPO_4$ and monoammonium phosphate $NH_4H_2PO_4$, as well as impurities whose content depends on the chemical composition of the initial phosphoric acid [3].

Diammonium phosphate fertilizer (diammophos, DAP) - a complex fertilizer containing two main nutrients-nitrogen and phosphorus. In accordance with the technical conditions, diammonium phosphate fertilizer, according to its physical and chemical parameters, must meet the technical requirements of TU-113-08-556-93 [4,5].

Commercial innovative product is fire-and explosion-proof. Hazard class-4, maximum permissible concentration (MPC) of DAP dust in the air of the working area-10 mg/m^3 [6].

Compared with ammophos, which contains the predominant amount of monoammonium phosphate (MAP) and diammonium phosphate per unit of P_2O_5 contains twice as much nitrogen, despite the fact that the total content of nutrients in MAP and DAP is the same (about 64 %), in addition, more concentrated fertilizers can be obtained on the basis of DAP [5,14].

In the process of innovative production of DAP, the extraction phosphoric acid is subjected to deeper ammonification, due to the introduction of the cheapest and one of the most concentrated nitrogen – containing components-ammonia-into the fertilizer.

This makes it possible to use a smaller amount of more expensive nitrogen-containing production components (ammonium nitrate or urea) for nutrient balancing [16], which makes it more economically feasible to obtain DAP and fertilizers based on it.

Especially important role of DAP plays in the process of blending. Due to the high concentration of nutrients, its use leads to savings in financial resources for transportation, storage and application of DAP-based fertilizers to the soil [1,12].

Currently, ammonium phosphates with a nutrient concentration (P2O5+N) of more than 60% are obtained in the CIS countries from Apatite concentrates and high-quality phosphorites of North Africa.

Production of highly concentrated fertilizers from phosphorites of the Karatau basin of the Republic of Kazakhstan requires deeper enrichment, with the production of concentrates containing more than 30% P_2O_5 and MgO less than 1% [3,7], or additional purification of extraction phosphoric acid from impurities, and especially from magnesium and fluorine, since iron and sulfur can play the role of micro-fertilizers.

The production of phosphorus and other mineral fertilizers in Kazakhstan is mainly carried out by three enterprises: - «Kainar» LLP, with a capacity of 240 thousand tons per year (Shymkent) and the «KazAzot» LLP plant (Aktau), where there are production facilities nitrogen fertilizers and liquid ammonia with a capacity of 1600 thousand tons per year, Taraz branch of «Kazphosphate» LLP mineral fertilizer plant (MFP), with a capacity of 150 thousand [19] tons per year. However, they do not fully satisfy the need of the Republic of Kazakhstan for fertilizers.

Therefore, establishing the mechanism of the influence of impurities, in particular compounds of fluoride and magnesium on the physico-chemical and physico-mechanical properties of purified DAF are necessary conditions for the creation of a hardware-technological scheme of the innovative technology of obtaining the target product (DAP) from natural phosphate rock of the Karatau basin and industrial wastes [16], stored in the dumps of the Zhanatas, Aksay and Kokjon mines.

In the course of research on the innovative process of obtaining DAP, the main attention is paid to the chemistry, kinetic dependencies and hardware design of the main technological stages, as well as to the quality of the finished product: such as caking, granule strength, and dust formation [18]. In the literature, the influence of the concentration of phosphoric acid, the impurities contained in it, and the hardware design of the process on the properties of the finished product, as well as the mechanism and chemise of this influence are not sufficiently developed, which is the goal of an innovative research work [8], which has relevance.

The difference between the innovative technology offered by us and the existing ones is the use of evaporated and unpaired extraction phosphoric acid from raw resources of domestic balance and off balance ores.

The production of mineral fertilizers from local raw materials will allow involving low-grade phosphorites and man-made waste in the new technology of enrichment.

DAP, obtained using phosphoric acid with a lower concentration than traditional technology, has lower physical and mechanical properties, increased hygroscopicity and traceability [10]. To preserve the quality of DAF during transportation and storage the moisture content of the finished product shall be not more than 2.0 %; for this purpose– exposure of the product to produce at least 2 hours and the temperature of the shipment is maintained in accordance with the requirements of normative technical documentation.

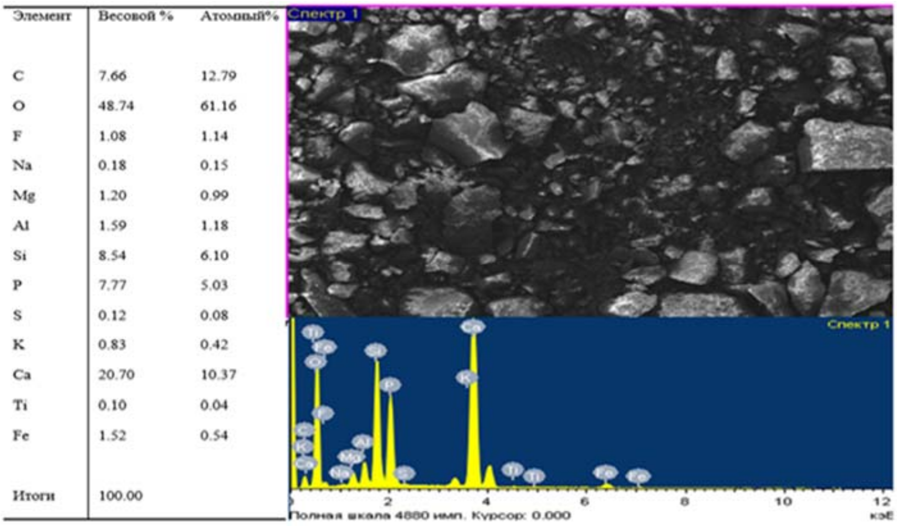
Materials and Methods. In connection with the rise of the economy of the Republic of Kazakhstan on the basis of innovative and industrial development and its transfer from a raw material to a competitive commodity-producing state, there is a need to develop new and improve existing technologies in all sectors of the economy [7].

Experimental research is traditionally the most objective method. Therefore, the main method of the proposed work is a free associative instrumental method of experiment, one of the most accessible and effective ways to develop a number of scientifically based physical, chemical, technological and technical solutions for the synthesis of competitive domestic DAP with an optimal ratio of paired and non-paired PSRM [9,11].

This will ensure compliance with the principles of scientific ethics and their use in the creation of technology for the synthesis of DAP in BGS using unpaired and evaporated PSRM and ammonia gas [17].

To conduct experiments, samples of phosphate raw materials from various deposits "Chulaktau", "Zhanatas" and "Kokjon" were studied on a raster electron microscope (SEM) for the content of P_2O_5 . The results of the study are shown in figures 2,4 and 6.figures 1,3 and 5 show the appearance of a large and crushed sample of phosphorites taken for experiments.

Figure 1 - Coarse and crushed phosphorite sample taken from «Chulaktau» field



Элемент	Весовой %	Атомный%
C	7.66	12.79
O	48.74	61.16
F	1.08	1.14
Na	0.18	0.15
Mg	1.20	0.99
Al	1.59	1.18
Si	8.54	6.10
P	7.77	5.03
S	0.12	0.08
K	0.83	0.42
Ca	20.70	10.37
Ti	0.10	0.04
Fe	1.52	0.54
Итоги	100.00	

Figure 2 - Elemental composition and electronic image by electron microscopic examination of a phosphorite sample taken from the «Chulaktau» deposit

Figure 3 - A large and crushed phosphorite sample taken from the «Zhanatas» field

Элемент	Весовой %	Атомный%
C	19.55	28.42
O	43.65	49.38
Mg	8.06	5.79
Al	0.49	0.32
Si	1.53	0.95
P	8.18	7.10
K	0.20	0.09
Ca	17.93	7.81
Fe	0.41	0.13
Итоги	100.00	

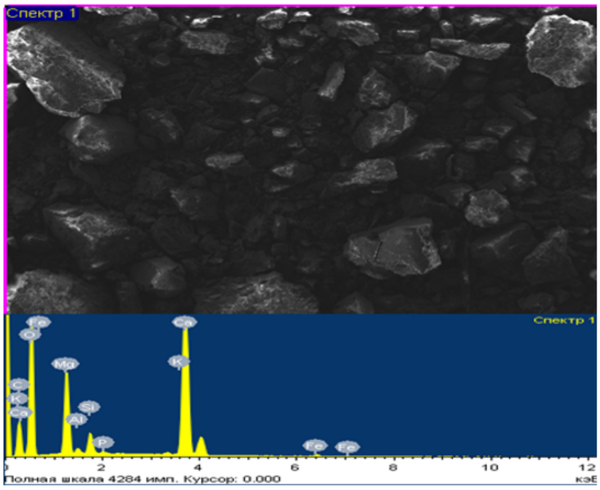


Figure 4 - The elemental composition and the electronic image are shown according to the results of an electron microscopic study of a phosphorite sample taken from the «Zhanatas» deposit

Figure 5. Coarse and crushed phosphorite sample taken from «Kokjon» deposit.

Элемент	Весовой %	Атомный%
C	12.53	20.00
O	47.31	56.70
F	2.22	2.24
Na	0.21	0.17
Mg	4.26	3.36
Al	0.67	0.48
Si	2.90	1.98
P	6.13	3.79
S	0.21	0.13
K	0.17	0.09
Ca	22.40	10.72
Mn	0.17	0.06
Fe	0.81	0.28
Итоги	100.00	

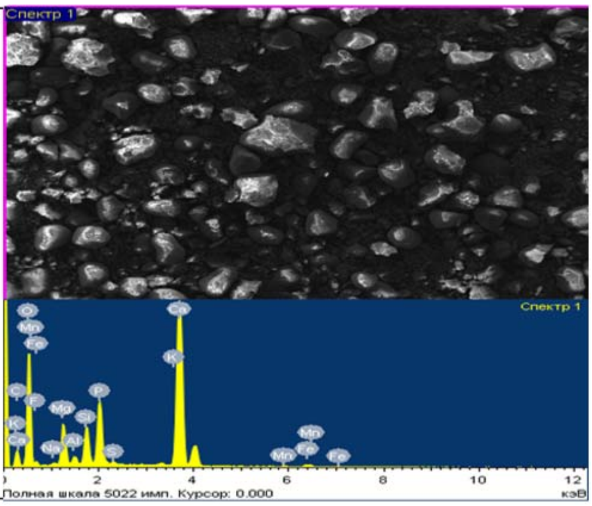


Figure 6 - The elemental composition and the electronic image are shown according to the results of electron microscopic examination of a phosphorite sample taken from the «Kokjon» deposit

Results and discussion. The chosen method, with its own individuality of the Association process, has common reference points of contact between individual participants of collective research, as well as with respondents offering various DAP production technologies [13].

Table 1 shows the content of P_2O_5 (%) in the phosphate feedstock of the «Chulaktau», «Zhanatas» and « Kokjon» deposits.

Table 1 - P_2O_5 content (%) in the phosphate feed of the «Chulaktau», «Zhanatas» and « Kokjon» deposits

Type of phosphate material	Content P_2O_5,%	
	Weight %	Atomic %
Chulaktau	7,77	5,03
Zhanatas	8,18	7,10
Kokjon	6,13	3,79

Comparison of the results of research of samples of phosphate raw materials from various deposits «Chulaktau», «Zhanatas» and «Kokjon» for the content of P_2O_5 shows that the best quality is characterized by the phosphorite of the Deposit "Zhanatas", containing P2O5 -8.18% [12].

The presence of harmful impurities and low P_2O_5 content make it necessary to enrich the phosphorous ore [1,15]. To do this, in our opinion, it is possible to use the flotation method of enrichment. At present, fine - milled fosmuka is obtained from carbonate ores and flotation phosphorous concentrate is obtained from it. Flotation phosphate concentrate is usually used as a raw material for the production of phosphorous-containing and complex mineral fertilizers, phosphoric acid.

Conclusion. Experimental data and technological schemes can be used to obtain diammonium phosphate from substandard phosphate raw materials. The aim of the research is to develop and create an innovative technology for obtaining high-quality diammonium phosphate in a drum granulator dryer from a mixture of evaporated and unpaired extraction phosphoric acid with a predominant share of unpaired EFC extracted from off-balance phosphorites of the Karatau basin. From the conducted research of samples of phosphate raw materials of various deposits, «Chulaktau», «Zhanatas» and «Kokjon», the best was the phosphorite of the" «Zhanatas» Deposit, containing P_2O_5 - 8.18%.

Scientific research and experimental work was carried out using modern laboratory equipment equipped with computer technology. The analysis of the raw materials, the resulting product and materials was performed using physical and physico-chemical methods of research on modern raster microscope JSM 6390 LV, DRONE, IR spectroscopy, etc., and comparative analysis was performed using mathematical processing of research results [4.19].

The results of the conducted research of bidit are applied in the development of technological bases and technical solutions for the innovative process of diammonium phosphate production using BGS from unpaired extraction phosphoric acid obtained from phosphorites of the Karatau basin.

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ҚАРАТАУ БАССЕЙНІНІҢ БАЛАНСТАН ТЫС КЕНДЕРІ НЕГІЗІНДЕ ЭКСТРАКЦИЯЛЫҚ ФОСФОР ҚЫШҚЫЛЫНАН ТАЗАРТЫЛҒАН ДИАММОНИЙФОСФАТ АЛУ

Аннотация. Тау-кен өндіру кешенінің техногендік қалдығын пайдаға жарату мәселесі өткен ғасырдың соңынан бастап өзектілігін жоғалтпай келеді. Жаңатас кен орны «Центральный» карьеріндегі қалдық мөлшері 22 млн. тоннаға жуық фосфат-кремний шикізатын (ФКШ) құрайды. Флотациялық байытудан кейін 12 млн. тоннадан астам қышқылды өңдеу үшін электротермиялық өңдеуде тауарлық фосфорит ретінде пайдаланылған. «Жаңатас» карьерін жұмыс тереңдігіне дейін жетілдіру кезінде кемінде 18-19 млн. тонна ФКШ пайда болады [1].

Ішкі аршыма тау жыныстарының баланстан тыс кендері «Көкжон», «Көксу», «Тьесай», «Ақсай» сынды үш арнайы үйінді арқылы ұсынылды, көлемі 3,2 млн. тоннадан астам, құрамында 20% P2O5 бар.

Экономиканың агроөнеркәсіптік секторында минерал тыңайтқыштар ауылшаруашылығы дақылдары-ның өнімділігі мен сапасын арттыруда маңызды рөл атқарады. Фосфор саласының экспорттық бағытын ескере отырып, оны макроэкономикадан тыс қарастыруға болмайды, өйткені оның жағдайы күрделі және тұрақсыз болып қалады.

Диаммонийфосфат (ДАФ) өндірісінің технологиялық негізі мен техникалық шешімін әзірлеу бойынша инновациялық зерттеулердің практикалық маңыздылығы [7], Қаратау теңгерімдік фосфориттерінен экстракциялық фосфор қышқылынан (ЭФК) алынатын, сондай-ақ тәжірибелік-өнеркәсіптік қондырғы құруға бастапқы деректер жасалған және өнеркәсіптік инновациялық өндірісті техникалық-экономикалық бағалау жұмысы есептелген.

Біз ұсынып отырған технология теңгерімнен тыс шикізатты қайта өңдеуге, экономикалық шығынды азайтуға және құрамында фосфор бар өндірілетін өнім сұрыптамасын 10-15%-ға, ЭФК және ДАФ өндіріс көлемін 20-25%-ға дейін жоғарылатуға, қосымша жұмыс орындарын құруға мүмкіндік береді.

Инновациялық ғылыми зерттеулер нәтижесі агроөндірістік кешен аса қажетті, мақсатты өнімдерге техногендік қалдықтарды химиялық байытуда, өнеркәсіптік аймақтардың экологиялық-экономикалық көрсеткіштерін және ҚР халқының әл-ауқатын жақсартуда қолданылады.

Түйін сөздер: баланстан тыс фосфориттер, Қаратау бассейні, диаммонийфосфат, экстракциялық фосфор қышқылы, барабанды түйіршіктегіш кептіргіш, бейтараптандыру, буланған және буланбаған ЭФК.

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О ПОЛУЧЕНИИ ОЧИЩЕННОГО ДИАММОНИЙ ФОСФАТА ИЗ ЭКСТРАКЦИОННОЙ ФОСФОРНОЙ КИСЛОТЫ НА ОСНОВЕ ЗАБАЛАНСОВЫХ РУД БАССЕЙНА КАРАТАУ

Аннотация. Проблема утилизации техногенных отходов горнодобывающего комплекса не теряет свою актуальность с конца прошлого столетия. Количество отходов только по карьеру «Центральный», месторождения Жанатас составляет около 22 млн. тонн фосфатно-кремниего сырья (ФКС). Более 12 млн. тонн после флотационного обогащения использовано для кислотной переработки и как товарные фосфориты при электротермической переработке. При доработке карьеров «Жанатас» до рабочей глубины образуется не менее 18-19 млн. тонн ФКС [1].

Забалансовые руды внутренней вскрышной породы представлены тремя спецотвалами рудников «Кокжон», «Коксу», «Тьесай», «Аксай», объем которых составляют более 3,2 млн. тонн с содержанием до 20% P_2O_5.

Минеральные удобрения в агропромышленном секторе экономики играют ключевую роль в повышении урожайности и качества сельскохозяйственных культур. Учитывая экспортную направленность фосфорной отрасли, ее нельзя рассматривать вне макроэкономики, так как ее обстановка остается сложной и неустойчивой.

Практическая значимость инновационных исследований по разработке технологических основ и технических решений производства диаммонийфосфата(ДАФ)[7], получаемого из экстракционной фосфорной кислоты (ЭФК) балансовых фосфоритов Каратау не вызывает сомнений, также составлены исходные данные на создание опытно-промышленной установки и рассчитана технико-экономическая оценка промышленного инновационного производства.

Предлагаемая нами технология позволит снизить экономические затраты на переработку забалансового сырья и увеличить ассортимент выпускаемых фосфорсодержащих продуктов до 10-15%; увеличить объем производства ЭФК и ДАФ до 20-25%; создать дополнительные рабочие места.

Результаты инновационных научных исследований применимы при химическом обогащении техногенных отходов на целевые продукты, в которых остро нуждается агропромышленный комплекс, в улучшении эколого-экономических показателей промышленных регионов и благосостояния населения РК.

Ключевые слова: забалансовые фосфориты, бассейн Каратау, диаммонийфосфат, экстракционная фосфорная кислота, барабанный гранулятор сушилка, нейтрализация, упаренная и неупаренная ЭФК.

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DEVELOPMENT OF TECHNOLOGY OF YOGHURT BY USING ACID WHEY

Abstract. Fermented milk products play an important role in people's nutrition, especially for children, the elderly, and the ill people. The dietary properties of fermented milk products are that they improve metabolism, stimulate the secretion of stomach acid, and stimulate the appetite. The presence of microorganisms in their composition that can survive in the intestines and inhibit putrefactive microflora leads to inhibition of putrefaction processes and the extinction of the formation of toxic protein breakdown products entering the human blood. Among dairy products, dietary fermented milk products are in high demand, especially dietary yogurts with vegetable additives.

Whey is the liquid protein part of milk that remains after the separation of cottage cheese obtained as a result of milk coagulation by acidic or proteolytic enzymes. It has high nutritional and biological value. Even though that the composition of the whey is a valuable secondary product, the question of its rational use is still unresolved.

The purpose of this research is to develop an optimal technology for the production of fermented milk products, namely yogurt by using acid whey. For this study, acid whey was selected, since the amount of produced acid whey more than the production of the amount of cheese whey. Recently, there has also been a growing interest in the possibility of using whey proteins in the development of technology for fermented milk products, but more and more often in these studies, a cheese whey is used. According to GOST 34352-2017 "Milk whey-raw materials" in terms of physical and chemical composition acid whey is not inferior to cheese whey, except for the indicator of titrated acidity, which is much higher in acid whey. Therefore, the use of acid whey in the development of technology for the production of fermented milk products is a time-consuming process that requires careful selection of the primary processing of whey and strict compliance with the processing modes of the main product.

For the fermentation process of yogurt with the addition of whey of different origins, several types of starter cultures were selected, such as starter cultures from Genesis, Vivo, and Yalactis company. To obtain a dense, homogeneous clot of the finished product and to reduce the use of heat treatment, ultrasonic (US) treatment was used before the fermentation process of the mixture, and instead of traditional homogenization and pasteurization processes. And also to intensify the fermentation process of microorganisms by saturating them with oxygen at the beginning of the fermentation process, the samples were rotated around their axis in a shaker incubator for a certain amount of time at a constant fermentation temperature.

The study was based on organoleptic and physicochemical analysis of prepared yoghurt with added whey, as well as a comparative analysis of production technology and physicochemical characteristics of yoghurt added natural whey and whey, produced from the manufacture of cottage cheese from powdered milk. We also studied the optimal ratio of milk and whey to obtain more suitable and attractive for customer organoleptic properties.

Key words: whey, cottage cheese whey, yoghurt, fermented milk products, processing of whey.

Introduction. Reasonable use of milk whey is the main task in the state program for the development of the agro-industrial complex (AIC) of the Republic of Kazakhstan in 2017-2021. In the dairy industry, one of the reserves for improving production efficiency can be the search for suitable directions for processing dairy raw materials using all its components, through the widespread introduction of waste-free technologies developed based on the latest achievements of science and technology. In this regard, it will be profitable to use whey as the main raw material for expanding the range of food products [1].

Because of the high content of organic compounds capable of oxidation, the indicator of biochemical oxygen demand (BOD) of whey is an average of 50,000 mg O_2/l, which is high in amount. In this regard, the ingress of whey into sewage systems, and in emergency cases-directly into reservoirs can cause serious environmental problems. In comparison for the oxidation of organic compounds that contained in 25 tons of whey (a cheese factory of average daily capacity) will require the same amount of oxygen as for the oxidation of household wastewater in a city with a population of 40 thousand people [2].

In recent years the amount of processed milk, likewise the amount of whey, in Kazakhstan has increased. In such countries as France, the United States, Sweden, and Canada, the dairy industry processes 50-95% of dairy by-products [3]. At the same time, the dairy industry in Kazakhstan was processed only about 1/5 of all whey. Some entrepreneurs have begun to send the whey for initial processing, and then for sale. The rest is poured into the sewer, which is an irrational decision in the production of dairy products. It is also impractical for dairies to hold a high wastewater treatment cost that is why companies are looking for alternative solutions to the problem of whey utilization.

Deep processing of whey, as well as its further use in the production of food products as a milk substitute, is a profitable solution, both from an economic and environmental point of view.

Even though whey is the least energetically valuable dairy product, this product has a pronounced property of stimulating the secretion of the gastric digestive glands. Due to the presence of easily digestible proteins, vitamins, carbohydrates, and minerals in it, whey considered as a biologically valuable product [4].

Whey approximately consists of 93.7% water. The remaining 6.3% includes dry substances such as milk sugar (lactose), proteins, macro-and micronutrients. Lactose is a carbohydrate that normalizes the activity of the gastrointestinal tract. Whey proteins regarded as complete ones that contain a balanced composition of essential amino acids. The biological value of whey proteins is very high-112% relative to the standard. Whey proteins are involved in several processes, such as the process of hematopoiesis and the synthesis of liver proteins. Milk whey contains a small amount of milk fat, which has high digestibility and helps to strengthen the activity of enzymes. The whey contains all B vitamins, as well as vitamin C, nicotinic acid, choline, vitamin A, vitamin E, and Biotin. It also contains calcium, magnesium, and probiotic bacteria. This leads to a special interest in whey among specialists from many branches of the food industry [5].

At the moment, whey used in a wide range of products and various forms (liquid, concentrated, or dried). Whey used in the production of products such as baked goods, processed cheese, ready-made dry mixes, infant food, beverages, frozen desserts [6].

Researchers from Kazakh agro technical University studied the concept of innovative technology of waste free processing of dairy products, particularly cottage cheese. The technology of processing cottage cheese, and acid whey were proposed. The opportunity of getting beverages by using acid whey and Saskatoon berries were proved [7].

Fortification of conventional foods with biologically active substances helps to improve health and reduce the risk of disease. However, most bioactive agents with biologically active substances have restrictions of use in food, so they require additional study of the effect of fortifiers on food. Scientists at the University of Lorraine in France have studied the use of curcumin in the production of yogurt. The results of studies have shown that curcumin is adsorbed on the bacterial shells of Lactobacillus bulgaricus and mainly on Streptococcus thermophilus, without suppressing their growth and their acidifying ability [8].

At the University of North Carolina researchers have studied the capability of proteins from cottage cheese whey to reconstruction for future use in yogurt. The results of the tests showed that the yogurt, prepared from cottage cheese whey protein, had a color and titrated acidity similar to those obtained using sweet whey protein. Yogurts with acid and sweet whey proteins differ in sensory characteristics from the control yogurt made from skim milk concentrate. The yogurt, prepared from acid whey, had a lower gel strength, a higher sour taste, and a lower density and viscosity compared to yogurts made from sweet whey [9].

Many food scientists have investigated the feasibility and acceptability of using whey and whey products in beverages and fermented milk products, but not enough research studies conducted on the use of unprocessed, liquid curd whey in foods such as fermented milk drinks, particularly yogurts [10].

The purpose of this research is to investigate the process of production yogurts by addition of acid whey of various source (whey collected from cottage cheese production, that made from natural milk and milk powder), as well as different ratios of whey with the main raw material (milk), to obtain the optimal composition of the finished product with an attractive appearance and useful composition.

Experimental part. (*Materials and methods)* In this research milk is taken as the main raw material, which was examined by GOST 31450-2013. Natural whey and whey, collected from the cottage cheese production by using milk powder, were taken from milk processing plants in the Akmola region of the Republic of Kazakhstan. Also, for the fermentation process, we used starter cultures from Genesis, Vivo, and Yalactis of different composition (5 different types).

The following methods of analyses were used:

- titrimetric method according to GOST 3624-92, GOST 25555.0-82;
- potentiometric method according to Gost25179-90;
- refractometric method according to GOST 25179-90;
- organoleptic method according to GOST 34352-2017, GOST 31981-2013.

Yogurts with the use of whey in different ratios of compositions produced in the experimental production shop for processing dairy products of the S.Seifullin Kazakh agrotechnical University (Nur-Sultan, Republic of Kazakhstan). The research of raw materials and finished products conducted in the laboratory of the Department of food and processing technology, technical faculty, S.Seifullin Kazakh agrotechnical University (Nur-Sultan, Republic of Kazakhstan).

The milk tested according to GOST 31450-2013. The chemical composition of curd whey studied according to GOST 34352-2017, for the content of acidity, density, and proteins. Then the milk mixed with natural whey and whey obtained from reconstituted milk in a ratio of 50/50 and 30/70. The resulting raw material processed with ultrasound (US) waves at a power of 300 W for 5-6 minutes with simultaneous heating of the raw material to 36±10C. Then starter cultures of Genesis, Vivo, and Yalactis of different compositions (5 different types) were added at a dose of 5% of the total weight of the product. Fermentation was carried out at a temperature of 38±10C for 6-8 hours. The flasks were placed in the Orbital shaker-Incubator ES 20/60 incubator, where the first 50 minutes of fermentation performed rotational-vibrational movements of samples to saturate the starter microbiological culture with air.

Results and discussion. The obtained experimental samples examined for organoleptic characteristics and physical and chemical indicators, the results of which shown in tables 1,2 and figures 1,2,3,4.

Table 1 - Organoleptic characteristics of yogurt with the addition of natural whey

Samples of yogurt	Name of characteristics of yogurt		
	Appearance and texture	Taste and smell	Color
Yogurt (ratio of milk and whey 50/50)	Homogeneous, fairly viscous.	Common for fermented milk products, without strange tastes and odors	Milky-white
Yogurt (ratio of milk and whey 30/70)	Heterogeneous, liquid, there is a stratification of the layer of whey from milk.	Acid, with a hint of whey	Milky-white and yellow, common for milk and whey, respectively

Table 2 - Organoleptic characteristics of yogurt using whey obtained
from the production of cottage cheese from milk powder

Samples of yogurt	Name of characteristics of yogurt		
	Appearance and texture	Taste and smell	Color
Yogurt (ratio of milk and whey 50/50)	The clot is uniform, dense and fairly viscous.	Common for fermented milk products, without strange tastes and odors	Milky-white
Yogurt (ratio of milk and whey 30/70)	Heterogeneous, liquid, there is a stratification of the layer of whey from milk.	Acid, with a hint of whey	Milky-white and yellow, common for milk and whey, respectively

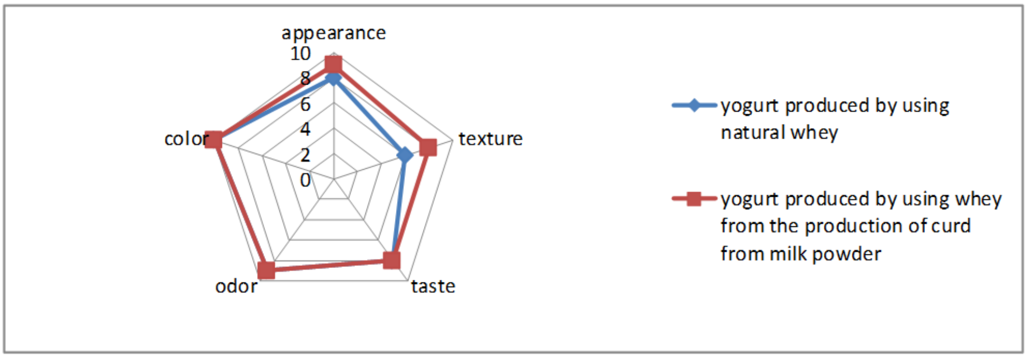

Figure 1 – Sensory characteristics of yogurt produced with the addition 50% of whey

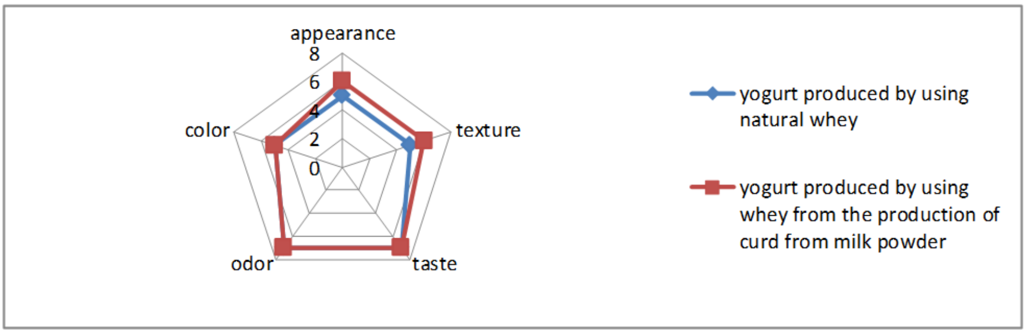

Figure 2 – Sensory characteristics of yogurt produced with the addition 70% of whey

According to organoleptic measures, the results obtained from yogurts, produced using whey collected from cottage cheese from milk powder are on a par with yogurts, produced from natural whey. However, when using whey obtained from the production of cottage cheese from milk powder, more dense and viscous consistency of the product clot can be achieved.

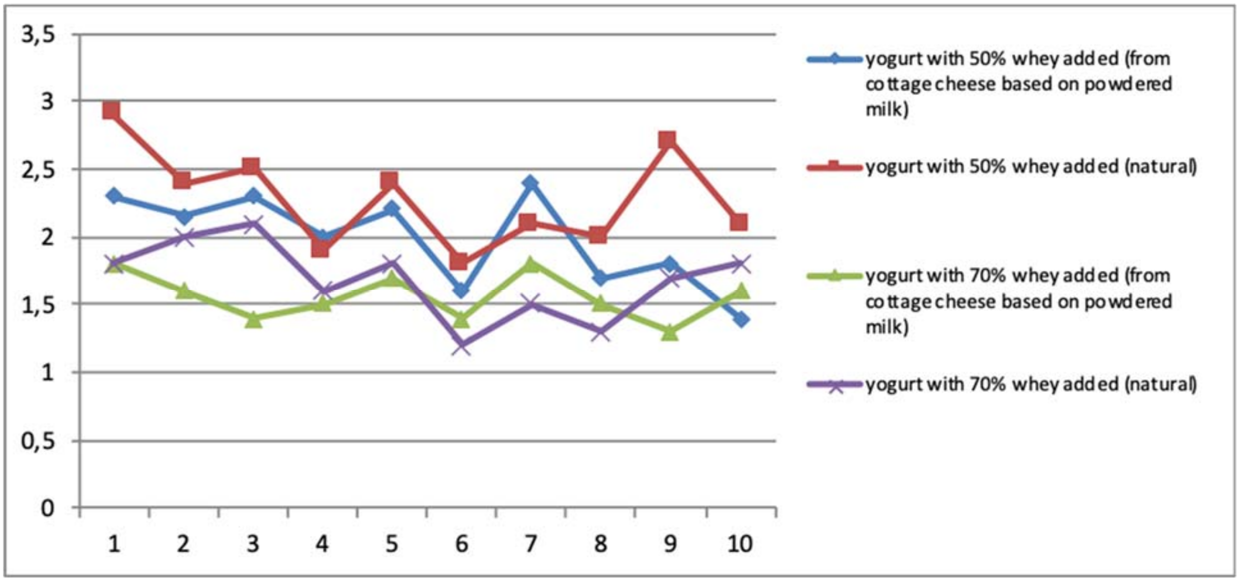

Figure 3 – Protein content of the studied yogurt

According to the given data, the protein content in yogurts, with the addition of natural whey, is higher than in yogurts, with the addition of whey obtained from the production of cottage cheese from milk powder. Furthermore, it can be noted that a greater amount of protein was obtained when the ratio of milk and whey 50/50 used than when the ratio of 30/70. This can be connected to the low acidity of the fermentation mixture used.

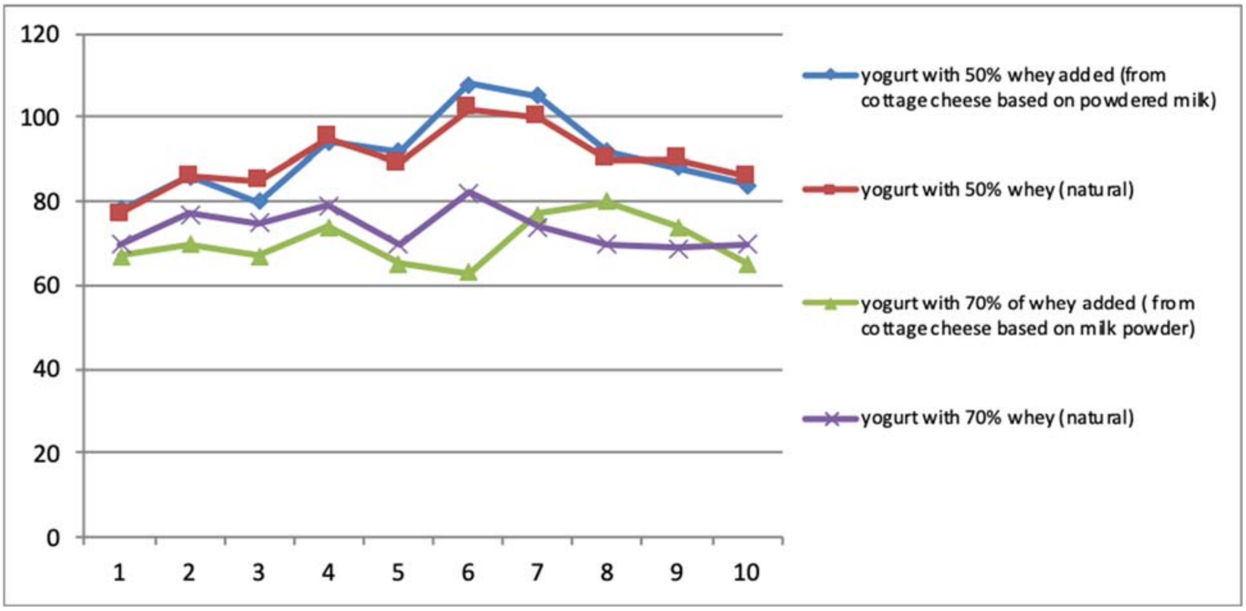

Figure 4 – Acidity content of the studied yogurt

In compliance with the presented data on the acidity of yogurt, it can be seen that the optimal ratio of milk and whey in the production of yogurt is the proportion 50/50. At a ratio of 30/70, due to the high acidity of the resulting mixture, lactic acid bacteria develop very slowly, which consequently impacts to the organoleptic properties of the product.

Conclusion. In the course of the study, the possibility of producing yogurt by using acid whey in equal proportions with milk was proved. Since the acidity of acid whey is higher than that of sweet whey, its use requires compliance with stricter processing regimes. Also, it should be noted that the final composition of the product may be influenced by other factors than those described in the article. Therefore, research work on this topic will continue, and by basing on further research, it will be possible to conclude the advantages of using natural whey, and whey obtained from processed products from milk powder in the production of dairy products.

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САРЫСУДЫ ПАЙДАЛАНУ АРҚЫЛЫ ЙОГУРТ ТЕХНОЛОГИЯСЫН ЖАСАУ

Аннотация. Қышқыл сүт өнімдері адамның, әсіресе балалардың, егде жастағы адамдардың және науқастардың тамақтануы барысында маңызды рөл атқарады. Қышқыл сүт өнімдерінің диеталық қасиеттері зат алмасуды жақсартады, асқазан сөлінің бөлінуін ынталандырады және тамаққа деген тәбетін ашады. Құрамында ішекте сіңуге және шірік микрофлораны басуға қабілетті микроорганизмдердің болуы шіру үдерістерінің тежелуіне және адам қанына түсетін ақуыз ыдырауының әсерінен пайда болатын улы өнім түзілісін тоқтатады. Сүт өнімдерінің арасында диеталық қышқыл сүт өнімдері, әсіресе, өсімдік қоспалары бар диеталық йогурттар үлкен сұранысқа ие.

Сарысу – сүттің қышқыл немесе протеолитикалық ферменттермен ұйыту нәтижесінде алынған сүзбеден бөлгеннен кейін қалған сүттің сұйық ақуыз бөлігі. Ол жоғары тағамдық және биологиялық құндылықтарға ие. Сарысу құрамы бойынша құнды екінші өнім болып саналатынына қарамастан, оны тиімді пайдалану мәселесі әлі күнге дейін шешілмеген.

Зерттеудің мақсаты қышқыл сүт өнімдерін, атап айтқанда сарысу қосылған йогуртты өндірудің оңтайлы технологиясын әзірлеу болып саналады. Осы зерттеуге сүзбе сарысуы таңдалды, өйткені сүзбе сарысуын өндіру көлемі өндірілетін ірімшік сарысуының мөлшерінен асып түседі. Сондай-ақ, соңғы уақытта қышқыл сүт өнімдерінің технологиясын әзірлеуде сарысу ақуыздарын пайдалану мүмкіндігіне қызығушылық артты, алайда осы зерттеуде көбіне ірімшік сарысуы пайдаланады. МЕМСТ 34352-2017 «Сүт сарысуы – шикізат» бойынша сарысудың физика-химиялық құрамы бойынша сүзбе сарысуы ірімшік сарысуында әлдеқайда жоғары титрленетін қышқылдық көрсеткішінен басқа ірімшік сарысуынан кем болмайды. Сондықтан қышқыл сүт өнімдерін өндіру технологиясын әзірлеуде сүзбе сарысуын пайдалану сарысуды бастапқы өңдеуді мұқият іріктеуді және негізгі өнімді қайта өңдеу режимін қатаң сақтауды талап ететін, көп еңбекті қажет ететін үдеріс болып саналады.

Сарысу қосылған йогуртты ашыту үдерісіне түрлі текті ашытқы дақылдарының бірнеше түрі, атап айтқанда Genesis, Vivo және Yalactis фирмасының ұйытқысы таңдап алынды. Дайын өнімнің тығыз, біртекті ұйыған қоюын алу мақсатында және жылумен өңдеуді пайдалануды азайту үшін дәстүрлі гомогендеу мен пастерлеудің орнына қоспаны ұйыту үдерісінің алдында ультрадыбыстық (УЗ) өңдеу қолданылды. Сондай-ақ ашыту үдерісінің басында микроорганизмдерді оттегімен қанықтыру арқылы ферментациялау үдерісін байыту үшін сынаманы шейкер-инкубаторда өз осінің айналасында ұйытудың тұрақты температурасы кезінде белгілі бір уақыт мөлшерінде айналдырылды.

Зерттеу барысында құрғақ сүттен дайындалған сүзбе сарысуы мен табиғи сарысу қосылған дайын йогурттың негізгі органолептикалық және физикалық-химиялық көрсеткішіне салыстырмалы талдау жүргізілді. Осы көрсеткіштермен қатар, өнімнің органолептикалық көрсеткіші бойынша тұтынушыға арналған қолайлы және қызықтыратын өнім алу алу үшін сүт пен сарысудың оңтайлы арақатынасы зерттелді.

Түйін сөздер: сарысу, сүзбе сарысуы, йогурт, сүтқышқылды өнімдер, сарысуды қайта өңдеу.

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РАЗРАБОТКА ТЕХНОЛОГИИ ЙОГУРТА С ИСПОЛЬЗОВАНИЕМ СЫВОРОТКИ

Аннотация. Кисломолочные продукты играют важную роль в питании людей, особенно детей, лиц пожилого возраста и больных. Диетические свойства кисломолочных продуктов заключаются в том, что они улучшают обмен веществ, стимулируют выделение желудочного сока и возбуждают аппетит. Наличие в их составе микроорганизмов, способных приживаться в кишечнике и подавлять гнилостную микрофлору, приводит к торможению гнилостных процессов и прекращению образования ядовитых продуктов распада белка, поступающих в кровь человека. Среди молочных продуктов большим спросом пользуются диетические кисломолочные продукты, особенно диетические йогурты с растительными добавками.

Сыворотка – это жидкая белковая часть молока, которая остается после отделения творога, полученного в результате свертывания молока кислотными или протеолитическими ферментами. Она обладает высокой пищевой и биологической ценностью. Несмотря на то, что по составу сыворотка является ценным вторичным продуктом вопрос о рациональном ее использовании до сих пор стоит нерешенным.

Целью данного исследования является разработка оптимальной технологии производства кисломолочных продуктов, а именно йогурта с добавлением сыворотки. Для данного исследования была выбрана творожная сыворотка, так как количество производства сыворотки творожной превышает количество производимой подсырной сыворотки. Также в последнее время вырос интерес в возможности использования сывороточных белков при разработке технологии кисломолочных продуктов, однако все чаще в этих исследованиях используют подсырную сыворотку. Согласно ГОСТу 34352-2017 «Сыворотка молочная – сырье» по физико-химическому составу сыворотка творожная не уступает сыворотке подсырной, за исключением показателя титруемой кислотности, которая намного выше в творожной сыворотке. Поэтому использование творожной сыворотки при разработке технологии производства кисломолочных продуктов является трудоемким процессом, который требует тщательного подбора первичной переработки сыворотки и строгое соблюдение режимов переработки основного продукта.

Для процесса заквашивания йогурта с добавлением сыворотки разных происхождений были выбраны несколько видов заквасочных культур, а именно закваски фирмы Genesis, Vivo, и Yalactis. С целью получения плотного, однородного сгустка готового продукта и для уменьшения употребления тепловой обработки была использована ультразвуковая (УЗ) обработка перед процессом заквашивания смеси вместо традиционной гомогенизации и пастеризации. А также для интенсификации процесса ферментации микроорганизмов путем насыщения их кислородом в начале процесса заквашивания пробы вращали вокруг своей оси в шейкер-инкубаторе определенное количество времени при постоянной температуре заквашивания.

В ходе исследования были проведенны базовые органолептические и физико-химические анализы готового йогурта с добавлением творожной сыворотки, а также был проведен сравнительный анализ технологии производства и физико-химических показателей йогурта с применением сыворотки натуральной и сыворотки, полученной в результате производства творога из сухого молока. Наряду с этими показателями было исследовано оптимальное соотношение молока и сыворотки для получения более подходящего и привлекательного для потребителя по органолептическим показателям продукта.

Ключевые слова: сыворотка, творожная сыворотка, йогурт, кисломолочные продукты, переработка сыворотки.

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ABOUT THE PRODUCTION OF FERTILIZER MIXTURE WITH THE USE OF TECHNOGENIC WASTE

Abstract. Coal is one of the oldest fuels, and was the main source of energy until the middle of the XX century. Now, despite the active use of oil, gas, and uranium, the share of coal in global electricity production is about 40% (in China – 78%, in the US – 50%, in Russia – 19%). However, coal does not burn without a trace. In the process of its combustion, not only energy is generated, but also waste [1-2].

According to B. Tarchevsky's classification [3,4], ash dumps by origin belong to the group of garbage dumps. By addition, ash dumps can be either loose or tightly-tiled.

The average size of ash deposits changes significantly only near the place where the pulp is released, and the size change is small in the rest of the ash dump [2]. After the end of operation of this container, ash dumps pollute the atmosphere, water, and soil.

The situation that has developed in the world and domestic markets for mineral fertilizers and fertilizer mixtures makes a number of technological and technical requirements for obtaining high-quality products of the agro-industrial complex, is relevant, which formed the basis for the development and creation of an environmentally safe mixtures.

The technology will allow you to:

- to obtain a new nomenclature of fertilizer mixture containing magnesium and other micronutrients, as well as to develop a technological scheme for obtaining fertilizer mixture containing magnesium and other micronutrients;

The results of innovative research will be used in the agricultural sector of the economy and in farms of the Republic of Kazakhstan.

Keywords: fertilizer mixture, prolonged action, mineral fertilizers, ash and slag waste thermal, plants, screening of dolomite ores, trace elements.

Introduction. A prerequisite for the development is the creation of a new range of mineral fertilizers and fertilizer mixture obtained from phosphates, ash and slag waste generated during the processing of brown coal and trace elements based on substandard screenings of dolomite ores [5].

There is a known method for producing fertilizer mixture [8] containing nitrogen, phosphorus and potassium in the form of different components (nitrogen in the form of ammonium nitrate, ammonium sulfate, urea, ammonium phosphates, phosphorus in the form of superphosphates, phosphorous flour; potassium in the form of chloride and sulfate), in which the initial components are mixed in dry form in specified proportions to obtain the necessary fertilizer composition. The disadvantages of this method are dusting and segregation of the resulting mixture.

In the method for obtaining phosphorous fertilizers [3-4], with a high content of P_2O_5 assimilated by plants from non-enriched phosphate raw materials, the stages of separate grinding of the phosphorus-containing raw materials and the mineral additive with their mixing are used.

The method improves the quality of phosphorus-containing mineral fertilizer by increasing the lemon-soluble form of P_2O_5 to 61-78 %.

The disadvantages of the method include separate mechanochemical activation of phosphorus-containing raw materials and mineral additives, which complicates the technological process. In the method for obtaining organomineral humic fertilizers [4], the humate-containing substance (peat, sapropel, brown coal) is treated with a chemical reagent, potassium nitrophosphate, and a nitrogen-containing fertilizer, in the form of urea, is introduced into the resulting mixture. The advantage of this method is the ability to carry out humification processes in a single container.

Therefore, an innovative technology for obtaining a fertilizer mixture from ash and slag waste is the most promising and environmentally and economically feasible. There are a number of ways to obtain a complex organomineral fertilizer containing phosphates, humic acids and moisture-retaining other nutrients based on boron, zinc, copper, sulfur, etc. [12]

The practical significance of ash and slag waste in agriculture, as an environmentally friendly and cost-effective fertilizer or soil amendments, can be established after field experiments for each type of soil, in order to confirm its quality and safety of fertilizer mixture.

The idea is to improve the quality and quantity of agricultural products through the use of innovative technology for obtaining magnesium-containing additives and trace elements.

This is achieved by complex and joint processing of ash and slag waste from a thermal power plant (TPP) and substandard screenings formed during the extraction and preparation and technological processing of dolomite ore.

Materials and Methods. The current situation on the world and domestic markets for mineral fertilizers and fertilizer mixture impose a number of technological and technical requirements in order to obtain high-quality products of the agro-industrial complex, which is also relevant. This formed the basis of an innovative project to develop and create an environmentally safe fertilizer mixture [12-15].

It is known that experimental research with the associative instrumental method is objective and allows us to develop scientifically-based physical, chemical and technological solutions for obtaining various nomenclatures of fertilizers and fertilizer mixtures.

Based on the chosen method, it is possible to develop reliable and technological regulations, identify the optimal parameters of technological processes, technological schemes of various productions, initial data for the design of installations, technical and economic assessments of industrial enterprises for the intended goals and objectives of research. The selected method will allow you to develop time and production schedules, with the justification of optimum parameters of technological process, main equipment and machines to implement their goals and objectives of the study, baseline data for pilot and industrial plant, technical and design documentation, techno-economic assessment of industrial production.

The ash and slag waste contain a significant part of the elements of the periodic table of D. I. Mendeleev: oxides of silicon, aluminum, iron, rare earth metals and is used for extracting useful metals [15-16].

To create a new range of mineral fertilizers-fertilizer mixture obtained from phosphates, ash and slag waste, we took samples of unbalanced phosphorite and dolomite from the «Aksay» deposit for research. figures 2,4,6 shows the result of a study of a sample of phosphate raw materials and dolomite from the «Aksay» deposit.

Figure 1 - A large and crushed sample of unbalanced phosphorite taken from «Aksay» field

Элемент	Весовой %	Атомный%
C	6.05	9.97
O	51.09	63.18
F	0.73	0.76
Na	0.21	0.18
Mg	2.13	1.73
Al	3.11	2.28
Si	16.94	11.94
P	3.59	2.29
K	1.54	0.78
Ca	12.17	6.01
Ti	0.15	0.06
Mn	0.45	0.16
Fe	1.83	0.65
Итоги	100.00	

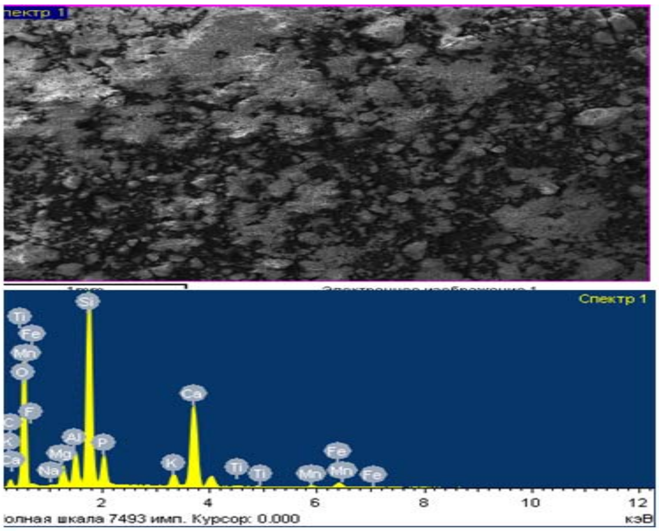

Figure 2 - The element composition and electronic image of the software are shown the results of electron microscopic examination of a sample of unbalanced phosphorite taken from the «Aksay» deposit

Figure 3 - A large and crushed dolomite sample taken from the «Aksay» field.

Элемент	Весовой%	Атомный%
C	13.44	20.30
O	54.72	62.03
Mg	10.77	8.03
Al	0.21	0.14
Si	0.42	0.27
Ca	20.30	9.18
Fe	0.14	0.05
Итоги	100.00	

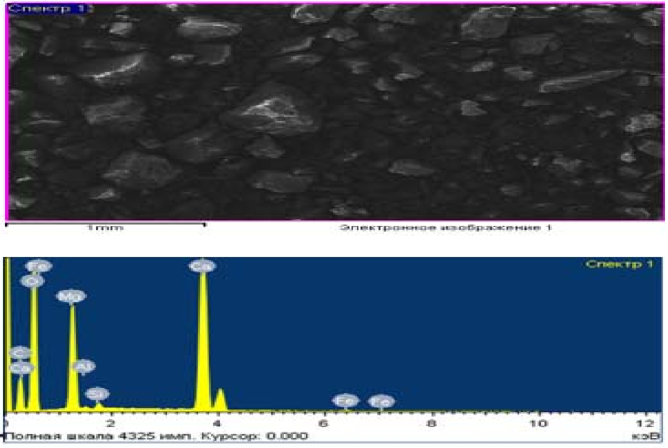

Figure 4. The element composition and electronic image of the software are shown the results of electron microscopic examination of a sample of dolomites taken from the «Aksay» deposit

Results and discussion. The method chosen by us, with its individual process, will allow us to obtain better quality agricultural products and reduce the harmful impact on the health and well-being of the population of our state and on a global scale of man-made ash and slag waste and sifting of dolomite fines.

Table 1. shows the content of microelement Mg (%) in phosphate raw materials and dolomite of the «Aksay» deposit.

Table -1: content of microelement Mg (%) in phosphate raw materials and dolomite of the «Aksay» deposit.

Type of phosphate material	Content Mg %	
	Weight %	Atomic %
Phosphate raw materials of the «Aksay» deposit	2.3	1.73
Dolomite deposits «Aksay»	10.77	8.03

From the samples used for the study of phosphate raw materials and dolomite of the «Aksay» deposit for Mg content, the best result was shown by the dolomite of the «Aksay» deposit, containing Mg-10.77%.

Today, a method for obtaining complex-mixed mineral fertilizer [17], by high-temperature treatment of a charge containing phosphate raw materials, vermiculite and waste from the coal mining industry.

The phosphorous fines are pre-ground to a class less than 0.1 mm, and vermiculite and waste from the coal mining industry to a class 0-1 mm, the resulting charge is moistened to a humidity of 6-8% by weight. water, subjected to high-temperature treatment at 750-9000^{0}C in a rotating drum furnace, cooled to a temperature of 25-40^{0}C and mixed with 8-12% granulated ammonium nitrate.

The process is carried out with the following content of charge components, wt.%: phosphate raw materials-60-72, coal mining waste-8-15, vermiculite-7-16, ammonium nitrate-8-12.

The disadvantage of this method is the high temperature of the process (850-1000^{0}C) and the lack of nitrogen in the product, which increases the quality of mineral fertilizer.

Therefore, an innovative technology for obtaining a fertilizer mixture from ash and slag waste is the most promising and environmentally and economically feasible.

Conclusion. Based on the conducted research, the innovative technology of obtaining a multi-component mineral fertilizer with its wide application in the agro-industrial complex, improving the agrochemical properties of the soil and the cost-effective process of producing mineral fertilizers is of applied significance.

The introduction of the results of innovative research into production will allow to obtain an environmentally safe mix for the agro-industrial sector of the economy of the southern and South-Western regions and the Republic of Kazakhstan as a whole. This will ensure, on the one hand, to increase the efficiency of the use of fertilizers within Kazakhstan, and on the other – to Orient producers to supply fertilizers for export.

The resulting social and economic effect can be attributed to improving the welfare of the country's population through the use of environmentally friendly agricultural products, obtaining a competitive new range of fertilizer mixture containing magnesium and trace elements.

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ТЕХНОГЕНДІ ҚАЛДЫҚТАРДЫ ҚОЛДАНУ НЕГІЗІНДЕ ҚОСПА ТЫҢАЙТҚЫШ АЛУ ӨНДІРІСІ

Аннотация. Көмір – отынның көне түрінің бірі, XX ғасырдың ортасына дейін ол энергияның негізгі көзі болып келді. Қазір мұнай, газ, уран белсенді пайдаланылуына қарамастан, әлемдік электр энергиясындағы көмірдің үлесі шамамен 40% құрайды (Қытайда 78%, АҚШ-та 50%, Ресейде 19%). Алайда көмір қалдық шығарады. Оның жану үдерісінде энергиямен қоса, қалдықтар да пайда болады [1-2].

В.Тарчевский классификациясына сәйкес [3,4], пайда болған күл-шлактары қоқыс тобына жатады. Қосымшаға сәйкес, күл-шлактары бос немесе тығыз тақтайша болуы мүмкін.

Көмірді жағу кезінде минералды компоненттер күл мен шлакқа өтеді, олар күл үйінділерінде энергетикалық өндірістің қалдықтары ретінде жиналады. Қазіргі уақытта жинақталған күл үйінділерінің массасы үлкен. Еліміздің көмір жылу электр станцияларының күл үйінділерінде 20 млрд. т астам күл мен шлак жиналды, ал күл үйінділері орналасқан жердің жалпы ауданы ондаған мың гектарды құрады.

Күл-шлактарының орташа мөлшері тек целлюлоза өндірілетін жерде ғана айтарлықтай өзгереді, ал қалған күл үйінділерінде мөлшері аз болады [2]. Осы резервуарды пайдаланудан шығарғаннан кейін күл үйінділері атмосфераны, суды, топырақты ластайды.

Күл-шлак қалдықтарын (КШҚ) қатты, техногендік қалдықтарды жою мәселесін шеше отырып, тозған топырақ үшін қоректік заттарға әлеуетті қоспа ретінде пайдаланылуы мүмкін. Біздің ойымызша, ЖЭО күлінің құрамында бірегей технологиялық қасиеттері бар, оларды тыңайтқыш ретінде тиімді пайдалануға құрамында кездесетін компоненттер мүмкіндік береді, сонымен қатар КШҚ-да өсімдіктердің қалыпты өсуі мен дамуына қажетті элементтер бар.

Әлемдік және ішкі нарықта қалыптасқан минералды тыңайтқыштар мен тыңайтқыш қоспаға агроөнеркәсіп кешенінің сапалы өнімдерін алу мақсатында бірқатар технологиялық және техникалық талаптар қойылады, бұл сондай-ақ өзекті болып саналады, бұл экологиялық қауіпсіз тыңайтқыш қоспасын әзірлеу және құру жөніндегі жұмыстың негізіне алынды.

Технология мүмкіндігі:

- энерго орталықтың доломитті кенді эксплуатациялау үдерісінде пайда болған ЖЭО күл-шлак түріндегі техногенді қалдықтарын инновациялық технология арқылы жаңа тыңайтқыш қоспа алу үшін пайдалану;
- тыңайтқыш қоспаның жаңа түрін алу өндірісінде ЖЭО-тың күл-шлак қалдықтары мен Қаратау бассейнінің доломитін қолдану арқылы өндіріс аумағындағы экологиялық қауіпті азайту;
- экологиялық қауіпсіз тыңайтқыш қоспасын, құрамында магний және басқа да микротыңайтқыш алуда оңтайлы параметрін анықтау.

Инновациялық ғылыми зерттеуден алынған нәтижелер Қазақстан Республикасының экономиканың аграрлық секторында және фермерлік шаруашылығында пайдаланылады.

Түйін сөздер: тыңайтқыш қоспасы, ұзаққа созылған әсер, минералды тыңайтқыштар, жылу электр орталықларының күлі мен шлак қалдықтары, доломит кенінің кесінділері, микроэлементтер.

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О ПРОИЗВОДСТВЕ ТУКОСМЕСИ С ПРИМЕНЕНИЕМ ТЕХНОГЕННЫХ ОТХОДОВ

Аннотация. Уголь – один из древнейших видов топлива, который вплоть до середины XX века был основным источником энергии. Сейчас, несмотря на активное использование нефти, газа, урана, доля угля в мировом производстве электроэнергии составляет около 40% (в Китае – 78%, в США – 50%, в России – 19%). Однако уголь не сгорает бесследно. В процессе его сжигания образуется не только энергия, но и отходы [1-2].

По классификации В. Тарчевского [3,4], золоотвалы по происхождению относятся к группе мусорных отвалов. По сложению золоотвалы могут быть как рыхлые, так и плотно-плитчатые.

При сжигании углей минеральные компоненты переходят в золу и шлак, которые складируются как отходы энергетического производства в золоотвалах.

Накопленная к настоящему времени масса золоотвалов огромна. На золоотвалах угольных теплоэлектростанций страны было складировано более 20 млрд т золы и шлака, а общая площадь земель, занятых золоотвалами, составляла многие десятки тысяч гектаров.

Средний размер зольных отложений изменяется существенно только вблизи места выпуска пульпы, а на остальной части золоотвала изменение размеров невелико [2]. После прекращения эксплуатации данной емкости золоотвалы загрязняют атмосферу, воду, почву.

ЗШО может использоваться в качестве потенциальной добавки к питательным веществам для деградированных почв, тем самым решая проблему удаления твердых, техногенных отходов.

По нашему мнению, зола ТЭЦ содержит компоненты, обладающие уникальными технологическими свойствами, позволяющими эффективно использовать их в качестве удобрений, так как элементы, которые необходимые для нормального роста и развития растений обнаружено в ЗШО.

Сложившееся на мировом и внутреннем рынках к минеральным удобрениям и тукосмесям положение предъявляет ряд технологических и технических требований для получения качественной продукции агропромышленного комплекса является актуальной, что легло в основу по разработке и созданию экологически безопасной тукосмеси.

Технология позволит:

- использовать техногенные отходы ТЭЦ в виде золошлакового материала, образующего в процессе экслуатации энерго предприятия по переработке доломитовых руд при получении инновационной новой номенклатуры тукосмеси;

- получить новую номенклатуру тукосмеси, содержащей магний и другие микроудобрения, а также разработать технологическую схему получения тукосмеси, содержащей в своем составе магний и другие микроудобрения;

Результаты инновационных научных исследований будут использованы в аграрном секторе экономики и в фермерских хозяйствах Республики Казахстан.

Ключевые слова: тукосмесь, пролонгированное действие, минеральные удобрения, золошлаковые отходы *тепловой электростанции*, отсевы доломитовых руд, микроэлементы.

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Co-Mg-Mn COMPOSITE CATALYSTS FOR PARTIAL OXIDATION OF NATURAL GAS

Abstract. The problem of rational utilization of natural and associated petroleum gases and the cessation of their flaring is one of the acute and unresolved environmental problems. The aim of this work is to develop effective thermally stable catalysts of a new generation for the processes of oxidative conversion of light alkanes of natural and associated gas into synthesis gas. The results of partial oxidation of the methane of natural gas on the catalysts prepared by solution combustion synthesis are presented. Investigation of the activity of catalysts produced from initial mixture of $Co(NO_3)_2$ - $Al(NO_3)_3$ - $Mg(NO_3)_2$ - $Mn(NO_3)_2$ + urea of different composition was carried out for the production of synthesis-gas. It was found that the optimal conditions for producing of synthesis-gas are: CH_4 conversion - 98%, yield of target products: H_2 - 98 - 99% and CO - 40 - 43%, T = 900°C, space velocity - 2500 h^{-1}. The catalysts were studied by X-ray diffraction, transmission electron microscopy, specific surface area, pore volume and average pore diameter. The presence in the catalysts of simple and mixed oxides, metal aluminates and spinel-type structures, the presence of which contributes to the active work of catalysts for oxidative conversion of CH_4, has been established.

Key words: catalytic oxidation, methane, synthesis-gas, cobalt, magnesium.

Introduction. In the twenty-first century, humanity is faced with a global problem – Earth's climate change as a result of an increase in the concentration of greenhouse gases in atmosphere. The problem of greenhouse gases and their reduction is closely related to energy security, the stability of global energy markets and the sustainable development of each state and the world community as a whole. It is generally accepted that full reduction and mitigation of the effects of climate change is currently impossible, but measures must be taken to reduce the emissions of anthropogenic greenhouse gases. The study of the selective oxidative conversion of methane is consistent with Kazakhstan's development priorities in the use of its own hydrocarbons. According to forecasts, saturated hydrocarbons will not only preserve, but also strengthen their position as raw materials for the production of valuable organic compounds and fuel compositions, which will contribute to the revival of the national petrochemical industry. The activation of natural and associated petroleum gas (containing from 65 to 98% methane) for the targeted single-stage synthesis using nanoscale catalysts is one of the most relevant and important tasks in the field of organic catalysis. The gas processing plants of Kazakhstan are currently engaged mainly in the purification of gases from water, impurities of carbon dioxide and hydrogen sulfide for their use in domestic purposes. Therefore, there is a great economic incentive to develop effective catalysts for converting of natural gas into valuable products. So far, the production of synthesis gas is the only economically feasible way of converting methane into more valuable chemicals. The production of synthesis-gas from methane using active and stable catalysts plays an important role in the chemical and petrochemical industries. Prospects for the development of the global gas processing industry are associated with the creation and implementation of new catalytic environmentally friendly technologies for the production of synthesis-gas and hydrocarbons based on the production of fuel mixtures. Often the targeted production of synthesis-gas ($CO + H_2$) as an environmentally friendly modern fuel, as well as expensive olefins, is the first step in converting of natural gas.

For the above processes, oxide catalysts [1-3], their mixtures, and composites based on them [4,5] have been recently used instead of the noble metals [6,7] that were used previously. The method of self-propagating high-temperature synthesis has become widespread in recent years [8], especially its modification - the solution combustion synthesis (SCS) [9-11], as a result of which finely dispersed oxides and spinels are synthesized [12,13].

Previously, we investigated the process of oxidative conversion of light alkanes into synthesis-gas in the presence of oxygen on different types of catalysts: noble metals [14-16], oxides [17,18] and catalysts prepared by solution combustion synthesis [19-23].

The paper presents the data of the activity of the developed SCS catalyst based on Co - Al - Mg - Mn, capable of carrying out the process of oxidative conversion of methane into synthesis-gas.

Experimental

Catalyst preparation

SCS was used to prepare catalysts. A mixture of salts and distilled water was placed in a quartz glass. The content of the glass was heated to 80 - 100°C. Then the beaker with the solution was placed in a preheated muffle furnace, where the catalysts were prepared at various temperatures. At the beginning of the reaction, a large amount of heat is generated, which ensures a rapid spread of the combustion front and a sharp increase in temperature. After several minutes, structural catalysts are formed, the formation of which is one of the reasons for the high activity of the prepared samples.

Characterization techniques

The initial mixture and reaction products were analyzed using a Chromos GC-1000 chromatograph with the Chromos software. Chromatographic peaks were calculated using calibration curves constructed for the corresponding products using the Chromos software for pure substances. The catalysts were studied by XRD on a Siemens Spellman DF3 spectrometer with Cu-Kα (λ = 1.5406E) radiation in steps of 0.03°/1" in the 2θ range from 5° to 100°. For semi-quantitative X-ray analysis, 5% KCl was added to the analyzed samples as an internal standard. Transmission electron microscopy (TEM) was used to determine the morphology of the developed catalysts. The electron-microscopic characteristics of the catalysts were obtained on an EMK-125 K microscope (Sumy, Ukraine) at an accelerating voltage of 75 kV. The specific surface area was determined and the pore distribution in the catalysts was measured by the BET method (Brunauer–Emmett–Teller) using a GAPPV-Sorb 2800 analyzer. Nitrogen (99%) with helium (99%) was used as the carrier gas. Pore volume and average pore diameter were calculated by the BJH method using desorption isotherm curves.

Results and discussion. Catalysts of the Co - Al - Mg - Mn + urea series were prepared in a muffle furnace heated to 500°C. Three thermocouples were installed on top. All thermocouples were in a glass, which was located inside the muffle furnace. The first thermocouple was in the lower layer of the solution, the second thermocouple was in the middle layer and the third thermocouple was in the surface layer of the solution. Two combustion modes are carried out during the synthesis of catalysts by the solution combustion method: volumetric explosion and self-propagating mode. In the volume of the explosive mode, the solution is heated and the water evaporates. The gel is formed after the evaporation of water. The temperature in the muffle furnace gradually rises to a critical temperature. As soon as the temperature reaches critical, an exothermic reaction is carried out throughout the volume of the catalyst. Figure 1 shows the temperature-time profile of the volumetric combustion regime of the system 12.5% $Co(NO_3)_2$ + 12.5% $Al(NO_3)_3$ + 12.5% $Mg(NO_3)_2$ + 12.5% $Mn(NO_3)_2$ + 50% urea.

In the process of synthesis, the solution evaporates at T_o = 100°C and a gel is formed starting from temperature T_1 = 167°C, and a volumetric explosion occurs with T_2 = 270°C. The maximum temperature in the lower part reaches 564°C, in the middle part - up to 825°C, in the upper part reaches 1007°C. Table 1 shows the temperature at different levels of the solution in the synthesis of Al - Co - Mg - Mn catalysts with different contents of active components.

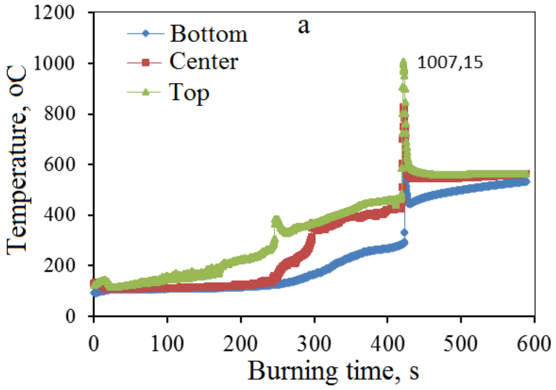

Figure 1 – Temperature-time profile of the volumetric combustion mode of the 12.5% Al - 12.5% Co - 12.5% Mg - 12.5% Mn + 50% urea system

Table 1 – Temperature in various layers during the synthesis of Al - Co - Mg - Mn catalysts with different contents of active components

The initial composition of the catalyst	T_o	T_1	T_2
12.5% $Al(NO_3)_3$ - 12.5% $Co(NO_3)_2$ - 12.5% $Mg(NO_3)_2$ - 12.5% $Mn(NO_3)_2$ + 50% $CO(NH_2)_2$	92.6	286.1	564.2
3% $Al(NO_3)_3$ - 3% $Co(NO_3)_2$ - 41% $Mg(NO_3)_2$ - 3% $Mn(NO_3)_2$ + 50% $CO(NH_2)_2$	97.4	280.4	659.98
3% $Al(NO_3)_3$ - 3% $Co(NO_3)_2$ - 3% $Mg(NO_3)_2$ - 41% $Mn(NO_3)_2$ + 50% $CO(NH_2)_2$	95.9	287.6	755.7
41% $Al(NO_3)_3$ - 3% $Co(NO_3)_2$ - 3% $Mg(NO_3)_2$ - 3% $Mn(NO_3)_2$ + 50% $CO(NH_2)_2$	97.3	284.0	523.6
3% $Al(NO_3)_3$ - 41% $Co(NO_3)_2$ - 3% $Mg(NO_3)_2$ - 3% $Mn(NO_3)_2$ + 50% $CO(NH_2)_2$	100.7	276.0	491.7

Table 1 shows the temperatures in the solution (only the lower part of the solution) during the synthesis of Al - Co - Mg - Mn catalysts with different element contents and shows the initial temperature (T_o), the ignition temperature (T_1), and the adiabatic flame temperature (T_2). The adiabatic flame temperature indicates the maximum combustion temperature achieved under adiabatic conditions.

Study of the activity of 12.5% Al - 12.5% Co - 12.5% Mg - 12.5% Mn + 50% urea catalysts prepared at 300 - 600°C by solution combustion synthesis in a flow catalytic installation was carried out at 900°C, GHSV = 2500 h^{-1}, 34% CH_4 + 17% O_2 + 49% Ar. The results of studies carried out during the synthesis of catalysts at temperatures from 300 to 600°C are presented in Figure 2.

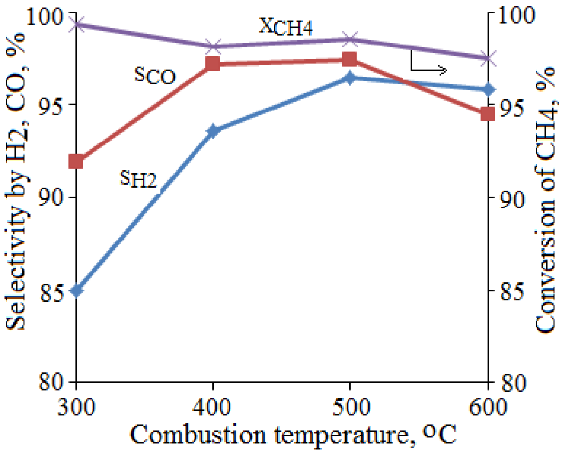

Figure 2 – Dependence of methane conversion and selectivity by H_2 and CO from the catalyst preparation temperature

The catalyst 12.5% Al - 12.5% Co - 12.5% Mg - 12.5% Mn + 50% urea prepared at 500°C showed high selectivity by H_2 (96.5%) and CO (97.4%). The methane conversion was 98.5%. Further, to determine the activity of the samples, the composition of the catalyst was varied. A series of catalysts prepared at 500°C by the solution combustion synthesis was studied using a PKU-1 apparatus. The catalytic reaction was carried out at atmospheric pressure and a temperature of 900°C. The experimental results are presented in Table 2.

Table 2 – Methane conversion and selectivity by H_2 and CO on catalysts of various compositions during the oxidation of methane to synthesis gas

Catalysts	X_{CH4}, %	Selectivity, %	
		H_2	CO
12.5% Al – 12.5% Co – 12.5% Mg – 12.5% Mn + 50% $CO(NH_2)_2$	94.7	95.4	99.4
41% Al - 3% Co - 3% Mg - 3% Mn + 50% $CO(NH_2)_2$	42.1	63.8	74.5
3% Al - 41% Co - 3% Mg - 3% Mn + 50% $CO(NH_2)_2$	99.7	87.9	96.9
3% Al - 3% Co - 41% Mg - 3% Mn + 50% $CO(NH_2)_2$	14.7	19.5	22.6
3% Al - 3% Co - 3% Mg - 41% Mn + 50% $CO(NH_2)_2$	32.4	42.9	46.9

As can be seen from Table 2, as a result of varying the content of elements in Al - Co - Mg - Mn catalysts, it was found that the catalysts exhibit the highest activity in the case of the highest content of aluminum and especially cobalt. Samples of 12.5% Al - 12.5% Co - 12.5% Mg - 12.5% Mn and 3% Al - 41% Co - 3% Mg - 3% Mn possess the maximum catalytic activity, while 41% Al A - 3% Co - 3% Mg - 3% Mn sample has lower activity. As a result of the analysis of the obtained results, a catalyst of the composition 20% Al - 20% Co - 5% Mg - 5% Mn was synthesized.

An analysis of the data indicates that the methane conversion values, as well as the H_2/CO ratios, are almost identical both at 1500 h^{-1} and at 2500 h^{-1}. The methane conversion reaches 94 - 98% in both cases. The $H_2/CO = 2$ is achieved at a space velocity of 1500 h^{-1}, starting from 800°C, which is favorable for syntheses of alcohols and olefins. The ratio slightly exceeds 2 at 2500 h^{-1}. At a space velocity of 2500 h^{-1}, the highest values were obtained for the yields of H_2 and CO. When implementing the process at 1500 h^{-1}, the hydrogen yield is reduced to 80%.

The phase composition of the Al - Co - Mg - Mn series of catalysts was studied by XRD. Figure 3 shows the XRD spectra of the catalysts.

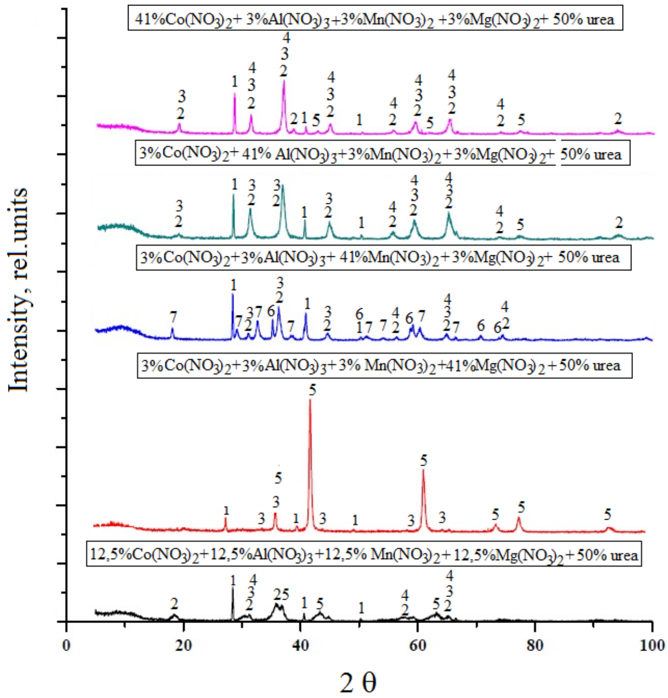

Figure 3 – X-ray phase analysis of catalysts of various compositions based on Al - Co - Mg - Mn + urea. 1 - KCl, 2 – Co_3O_4, 3 – $MgAl_2O_4$, 4 – $CoAl_2O_4$, 5 – MgO, 6 – MnO, 7 – Mn_5O_8

As a result of X-ray phase studies, it was found that the samples contained: Co_3O_4, $MgAl_2O_4$, $CoAl_2O_4$, MgO Periclase, MnO, and Mn_5O_8.

Table 3 presents the texture characteristics of Al - Co - Mg - Mn + urea catalysts with different element contents.

Table 3 – Textural characteristics of Al - Co - Mg - Mn + urea catalysts with different content of elements

Catalysts	Textural characteristics		
	Surface area, m^2/g	Pore volume, cm^3/g	The average pore size, nm
12,5% Al - 12,5% Co - 12,5% Mg - 12,5% Mn + urea	7.6	0.02	11.8
41% Al - 3% Co - 3% Mg - 3% Mn + urea	5.2	0.02	11.4
3% Al - 41% Co - 3% Mg - 3% Mn + urea	6.1	0.02	13.7
3% Al - 3% Co - 41% Mg - 3% Mn + urea	7.8	0.03	16.8
3% Al - 3% Co - 3% Mg - 41% Mn + urea	5.4	0.02	14.3
20% Al - 20% Co - 5% Mg - 5% Mn + 50% urea	22.2	0.03	18.5

The specific surface area of the catalysts is low. This is due to high combustion temperatures during preparation of catalysts. Despite this, the synthesized catalysts have a high specific activity, which allows them to compete even with catalysts of the Pt group.

Electron microscopy studies were carried out for the developed series of catalysts. For example, electron microscopic photographs of 3% Al - 41% Co - 3% Mg - 3% Mn + urea catalyst were obtained (Figure 4). The microdiffraction pattern of particles with a size of 20 - 40 nm, located on a thin film, is represented by reflections and corresponds to a mixture of phases: β-MnO_2, возможно, Co_2O_3. For samples with a size of 30 - 50 nm or more, the microdiffraction pattern is represented by reflections located along the rings and corresponds to a mixture of phases: MgO, (Co, Mg) O, ϵ-MnO_2, $MgH_{0.85}$, CoO.

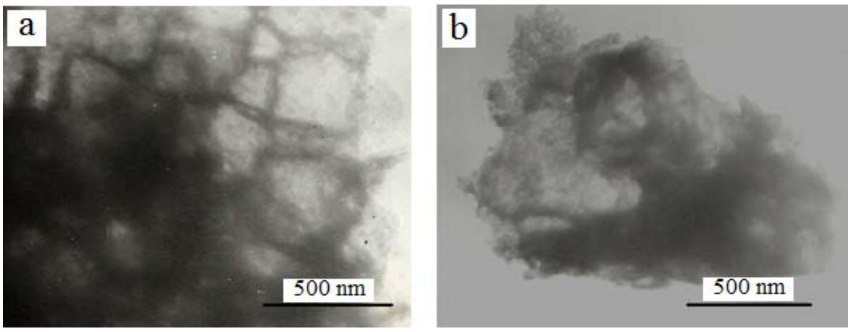

Figure 4 – TEM photographs of 3% Al - 41% Co - 3% Mg - 3% Mn + urea catalysts

From the obtained results it was found that the optimal conditions for producing of synthesis-gas are: CH_4 conversion - 98%, yield of target products: H_2 - 98 - 99% and CO - 40 - 43%, T = 900°C, GHSV = 2500 h^{-1}.

Conclusion. Thus, it was found that the synthesized Al - Co - Mg - Mn + urea catalysts are active in the reaction of partial conversion of methane into synthesis-gas. The optimal conditions for the maximum operation of this catalyst are: a space velocity of 2500 h^{-1} at a temperature of 900°C. The presence in the catalysts of simple and mixed oxides, metal aluminates and spinel-type structures, the presence of which contributes to the active work of the catalysts for the oxidative conversion of methane, has been established.

Acknowledgments

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ТАБИҒИ ГАЗДЫ КОМПОЗИТТІ Co-Mg-Mn КАТАЛИЗАТОРЛАРЫНДА ПАРЦИАЛДЫ ТОТЫҚТЫРУ

Аннотация. Жиырма бірінші ғасырда адамзат атмосферада парниктік газдардың шоғырлану мөлшерінің өсуі нәтижесінде Жердегі климаттың өзгеруінің жаһандық проблемасына тап болды. Парниктік газдар және олардың таралу жағдайын бәсеңдету мәселесі энергетикалық қауіпсіздігі, жаһандық энергетикалық нарықтың тұрақтылығымен және мемлекеттер мен жалпы әлемдік қоғамдастықтың тұрақты дамуымен тығыз байланысты. Қазіргі уақытта климаттың өзгеру салдарын толық қалпына келтіру және оны жеңілдету жеңіл тимейді, дегенмен антропогендік парниктік газ шығарындысын азайту жөніндегі шараларды қабылдау қажет. Метанды талғамды тотықтыра айналдыруды зерттеу Қазақстанның өзіндік көмірсутектерін пайдаланудың даму басымдықтарына сәйкес келеді. Жасалынған болжамдар бойынша қаныққан көмірсутектер шикізат көзі ретінде ғана сақталмай, ұлттық мұнай-химия өнеркәсібін қайта жандандыруға ықпал ететін құнды органикалық қосылыстар мен отын композицияларын алу үшін өзіндік ұстанымдарын нығайтады. Нанөлшемді катализаторларды пайдалана отырып, мақсатты бір сатылы синтез үшін табиғи және мұнайға ілеспе газдарды (құрамында 65-тен 98%-ға дейін метан бар) активтендіру органикалық катализ саласындағы ең өзекті және маңызды міндеттердің бірі. Қазіргі уақытта Қазақстанның газ өңдеу зауыттары негізінен газды тұрмыстық мақсатта пайдалану үшін судан, көмірқышқыл газы мен күкіртсутегі қоспаларынан тазартумен айналысады. Сондықтан табиғи газды құнды өнімдерге айналдыру үшін тиімді катализаторларды әзірлеуге деген үлкен экономикалық қажеттілік бар. Әлі күнге дейін метанды анағұрлым құнды химиялық заттарға айналдырудың жалғыз экономикалық және қолжетімді жолы – синтез-газ өндірісі. Белсенді және тұрақты катализаторларды пайдалана отырып, метаннан синтез-газды алу химия және мұнай-химия өнеркәсібі үшін маңызды рөл атқарады. Әлемдік газ өңдеу өнеркәсібін дамытудың келешегі отын қоспаларын өндіруге негізделген синтез-газ бен көмірсутектерді алудың жаңа экологиялық таза катализдік технологияларын құруға және оны енгізуге байланысты. Қазіргі заманғы экологиялық таза отын ретінде синтез-газды ($CO+H_2$), сондай-ақ қымбат тұратын олефиндерді мақсатты өндіру табиғи газды түрлендірудегі басты қадам болып саналады.

Жоғарыда аталған үрдістер үшін бұрын пайдаланылған асыл металдардың орнына соңғы уақытта оксидті катализатор мен оның қоспалары негізіндегі композиттер қолданылуда. Соңғы жылдары өздігінен таралатын жоғары температуралы синтез әдісі, әсіресе оның модификациясы – ерітіндіде жану әдісі (SCS) арқылы жұқа дисперсті оксидтер мен шпинельдерді синтездеу кеңінен таралуда.

Ерітіндіде жану әдісімен Co - Al - Mg - Mn + несепнәр катализаторларының сериясы муфельдік пеште дайындалды. Катализаторларды ерітіндіде жану әдісімен синтездеу үрдісінде жанудың екі режимі жүзеге асырылады: көлемдік жарылыс және өздігінен таралу режимі. Көлемдік жарылыс режимі кезінде ерітінді алдымен біртіндеп қызады және құрамындағы су буланады. Су буланғаннан кейін гель пайда болады. Муфель пешіндегі температура біртіндеп шектік температураға дейін жоғарылайды. Температура шегіне жеткенде экзотермиялық реакция катализатордың барлық көлемі бойынша жүзеге асырылады.

Ерітіндіде жану әдісі арқылы 300 - 600^{o}C температурада дайындалған 12,5% Al - 12,5% Co - 12,5% Mg - 12,5% Mn + 50% несепнәр катализаторларының белсенділігі ағымды катализдік қондырғыда зерттелді. Реакцияның шарты: 34% CH_4 + 17% O_2 + 49% Ar, көлемдік жылдамдық 2500 сағ$^{-1}$, ал реакцияның температурасы – 900^{o}C. Температура 500^{o}C кезінде дайындалған 12,5% Al - 12,5% Co - 12,5% Mg - 12,5% Mn + 50% несепнәр катализаторы H_2 (96,5%) және CO (97.4%) бойынша жоғары селективтілікті көрсетті. Метанның конверсиясы 98,5% көрсетті. Одан әрі дайындалған үлгілердің белсенділігін анықтау үшін катализатор құрамына түрлендіру жүргізілді. Құрамындағы элементтерді түрлендіру нәтижесінде дайындалған Al-Co-Mg-Mn катализаторларда ең көп мөлшерде алюминий, сонымен қатар кобальттың мөлшері көп болған жағдайда катализаторлар ең жоғары белсенділік танытатыны анықталды.

Синтез-газ алу үшін оңтайлы жағдай: T = 900^{o}C пен W = 2500 сағ$^{-1}$ болғанда, CH_4-тің конверсиясы 98%, ал мақсатты өнімдердің шығымы: H_2 - 98 - 99% және CO - 40 - 43%, болатыны айқындалды. Сондай-ақ, катализатор құрамында метанның тотыға айналу жұмысына белсенді ықпал ететін қарапайым және аралас оксидтердің, металл алюминаттары мен шпинель түріндегі құрылымдар анықталды.

Түйін сөздер: катализдік тотығу, метан, синтез-газ, кобальт, магний.

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Co-Mg-Mn КОМПОЗИТНЫЕ КАТАЛИЗАТОРЫ ПАРЦИАЛЬНОГО ОКИСЛЕНИЯ ПРИРОДНОГО ГАЗА

Аннотация. В двадцать первом веке человечество сталкивается с глобальной проблемой изменения климата Земли в результате роста концентрации парниковых газов в атмосфере. Проблема парниковых газов и их сокращение тесно связаны с энергетической безопасностью, стабильностью глобальных энергетических рынков и устойчивого развития каждого государства и мирового сообщества в целом. Принято считать, что полное восстановление и смягчение последствий изменения климата в настоящее время невозможно, но необходимо принять меры по сокращению выбросов антропогенных парниковых газов. Изучение селективного окислительного превращения метана соответствует приоритетам развития Казахстана в использовании собственных углеводородов. По прогнозам, насыщенные углеводороды не только сохранят, но и укрепят свои позиции в качестве сырья для получения ценных органических соединений и топливных композиций, которые будут способствовать возрождению национальной нефтехимической промышленности. Активация природного и попутного нефтяного газа (содержащего от 65 до 98% метана) для целевого одностадийного синтеза с использованием наноразмерных катализаторов является одной из наиболее актуальных и важных задач в области органического катализа. Газоперерабатывающие заводы Казахстана в настоящее время занимаются в основном только очисткой газов от воды, примесей углекислого газа и сероводорода для их использования в бытовых целях. Поэтому существует большой экономический стимул в разработке эффективных катализаторов для превращения природного газа в ценные продукты. До сих пор единственным экономически доступным путем преобразования метана в более ценные химические вещества является производство синтез-газа. Получение синтез-газа из метана с использованием активных и стабильных катализаторов играет важную роль в химической и нефтехимической промышленности. Перспективы развития мировой газоперерабатывающей промышленности связаны с созданием и внедрением новых каталитических экологически чистых технологий получения синтез-газа и углеводородов, основанных на производстве топливных смесей. Первым шагом в преобразовании природного газа часто является целевое производство синтез-газа ($CO+H_2$) как экологически чистого современного топлива, а также дорогостоящих олефинов.

Для вышеперечисленных процессов в последнее время используют оксидные катализаторы, их смеси, композиты на их основе вместо благородных металлов, которые использовали ранее. Метод самораспространяющегося высокотемпературного синтеза получил распространение в последние годы, особенно его модификация – метод растворного горения (SCS), в результате которых синтезируются тонкодисперсные оксиды и шпинели.

Катализаторы серии Co - Al - Mg - Mn + мочевина были приготовлены в муфельной печи методом растворного горения. В процессе синтеза катализаторов методом горения в растворе осуществляется два режима горения: объемный взрыв и самораспространяющийся режим. В объеме взрывного режима раствор нагревается и вода испаряется. После испарения воды образуется гель. Температура в муфельной печи постепенно растет до критической температуры. Как только температура доходит до критической, экзотермическая реакция осуществляется по всему объему катализатора.

Было проведено исследование активности 12,5% Al - 12,5% Co - 12,5% Mg - Mn + 50% мочевина катализаторов, приготовленных при 300 - 600°C методом горения в растворе, в проточной каталитической установке. Условия реакции: 34% CH_4 + 17% O_2 + 49% Ar, объемная скорость 2500 $ч^{-1}$, температура реакции - 900°C. Катализатор 12,5% Al - 12,5% Co - 12,5% Mg - 12,5% Mn + 50% мочевина, приготовленный при 500°C, показал высокие селективности по H_2 (96,5%) и CO (97.4%). Конверсия метана составила 98,5%. Далее для определения активности образцов было проведено варьирование состава катализатора. В результате варьирования содержания элементов в Al - Co - Mg - Mn катализаторах было установлено, что в случае наибольшего содержания алюминия и в особенности кобальта катализаторы проявляют наивысшую активность.

Оптимальными условиями для получения синтез-газа являются: 98% конверсия CH_4, выход целевых продуктов: H_2 - 98 - 99% и CO - 40 - 43%, T = 900°C и W = 2500 $ч^{-1}$. Установлено присутствие в катализаторах простых и смешанных оксидов, алюминатов металлов и структур шпинельного типа, присутствие которых способствует активной работе катализаторов окислительного превращения метана.

Ключевые слова: каталитическое окисление, метан, синтез-газ, кобальт, магний.

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CHEMICAL CONSTITUENTS OF LIPOSOLUBLE EXTRACT OF *SPIRAEA HYPERICIFOLIA* L.

Abstract. The genus *Spiraea* L., spirea, represents deciduous shrubs of the family *Rosaceae Juss*., subfamily *Spiraeoideae* Focke. The genus is widespread in the temperate and the subtropical zone of the northern hemisphere having more than 100 species. *S. hypericifolia* L. has the most extensive Eurasian range and is considered one of the most evolutionarily advanced representatives of the genus. In the leaves of *S. hypericifolia* L. detected, p-hydroxybenzoic, coffee, ferulic, chlorogenic acid, flavones apigenin, luteolin and 5-glucosides of flavonols isoquercitrin and avicularin. In this study, chemical constituents of liposoluble extract of *Spiraea hypericifolia* L. were determined for the first time. The components isolated from liposoluble extract of the aerial part of medicinal plant of *S. hypericifolia* L. were analyzed using the GC-MS method. In total, sixty-three compounds were isolated from hexane part and their relative content was determined by normalizing the peak area, in which the main components are octacosanol (9.59%), docosene-1 (8.57%), squalene (8.12%), and n-hexadecanoic acid (7.50%) separately. These compounds have high biological activites, namely anti-inflammatory, antimicrobial, antitumor, antibacterial.

Key words: *S. hypericifolia* L., hexane extract, liposoluble components, GC-MS.

Introduction. The development of medicinal flora and intensive search for new sources of biologically active substances with a wide range of pharmacological effects are very relevant for the development of the pharmaceutical industry. Among the promising sources of plant raw materials are representatives of the genus *Spiraea* L. (*Rosaceae Juss*.).

Species of the genus *Rosaceae Juss* are of considerable interest as plants used in folk medicine and have a great resource potential. Phenolic compounds with high biological activity were found in *Spiraea:* flavonols, flavones, flavans, and phenol-carboxylic acids. Saponins, essential oils and steroid glycosides have been found in various parts of plant species of the genus *Rosaceae Juss.* In Chinese medicine, they are used as medicinal plants with analgesic, antipyretic and anti-inflammatory properties. In modern studies, the biological activity of plant species of the genus *Rosaceae Juss,* associated with the presence of phenol-carboxylic acid derivatives-antimicrobial, phytotoxic [1], has been well studied. Antitumor activity of flavans was detected [2].

Meadowsweet (*Spiraea hypericifolia* L.) is a perennial shrub with a height of 50-150 cm.The leaves are 10-25 mm long and 1.5 - 1.8 mm wide, glabrous or short-pubescent when young, back-oval or lanceolate, whole-edged [3, 4]. In *S. hypericifolia* L., p-oxybenzoic, coffee, ferulic, chlorogenic acids, flavones-apigenin, luteolin and their 5-glucosides, flavonols - isocvercitrin and avicularin, catechins, carotenoids, aromatic carboxylic acids, and vitamin C were found [5-6]. Plants of the genus *Spiraea* are used as a means to relieve headaches of various types, as well as rheumatic joint pain, gastrointestinal diseases, helminthiasis, gynecological diseases. Powerful antibacterial and antiviral action leads to the use with colds and flu, and herpes. The literature does not contain information about the liposoluble composition of species *S. hypericifolia* L., which grows in the Almaty region of Kazakhstan.

The experience of our research group has previously conducted similar studies on the different medicinal plants [7-10]. The purpose of this work is to qualitative and quantitative determine chemical constituents of liposoluble extract of meadowsweet from the Almaty region.

Materials and methods. *Plant material.* The aerial part of the plant material *S. hypericifolia* L. was collected in the Almaty region of Kazakhstan in October 2018. The aerial part of *S. hypericifolia* L. dried in air was cut into small pieces and stored at room temperature.

Extraction and isolation. Naturally dried aerial parts of *S. hypericifolia* L. (100 g) were ground, then extracted with 90% ethyl alcohol (1:8) three times (seven days each time) at room temperature. After evaporation of the solvent at low pressure, the residue was dissolved in water, subsequently the resulting solution was sequentially separated with hexane, dichloromethane, ethyl acetate and n-butanol to obtain the corresponding extracts. The resulting hexane extract was analyzed by GC-MS.

Experimental part. The liposoluble components in the hexane extract of the medicinal plant were analyzed using the GC-MS method. The work was carried out on a gas chromatograph with mass selective detector Agilent 7890A -5975C. Used capillary column HP-5MS length 30 m, internal diameter 0.25 mm, film thickness of stationary phase 0.25 µm. Chromatography conditions: carrier gas-helium; flow rate 1 ml / min; column temperature: initial temperature of 50°C (10 min), temperature rise from 10°C / min from 50°C to 300°C, final temperature of 300°C (40 min), scanning range of 30-1000 AU, electronic shock mode at 70eV. The temperature of the ion source is 230°C. 1 µl of the sample was injected Into the chromatograph evaporator. Samples were introduced by splitting with a 5: 1 split ratio.

Identification of the compounds: Identification of compounds was done by comparing the NIST and Wiley library data of the peaks and mass spectra of the peaks with those reported in literature. Percentage composition was computed from GC peak areas on HP-5MS column without applying correction factors [11].

Results and discussion. In the study, sixty-three chemical components were identified from the hexane part of the aboveground part of *S. hypericifolia* L. plants using the GC-MS method. Their relative content was determined by normalizing the peak area. The GC-MS chromatogram of fat-soluble components from the aboveground part of *S. hypericifolia* L. is shown in figure 1.

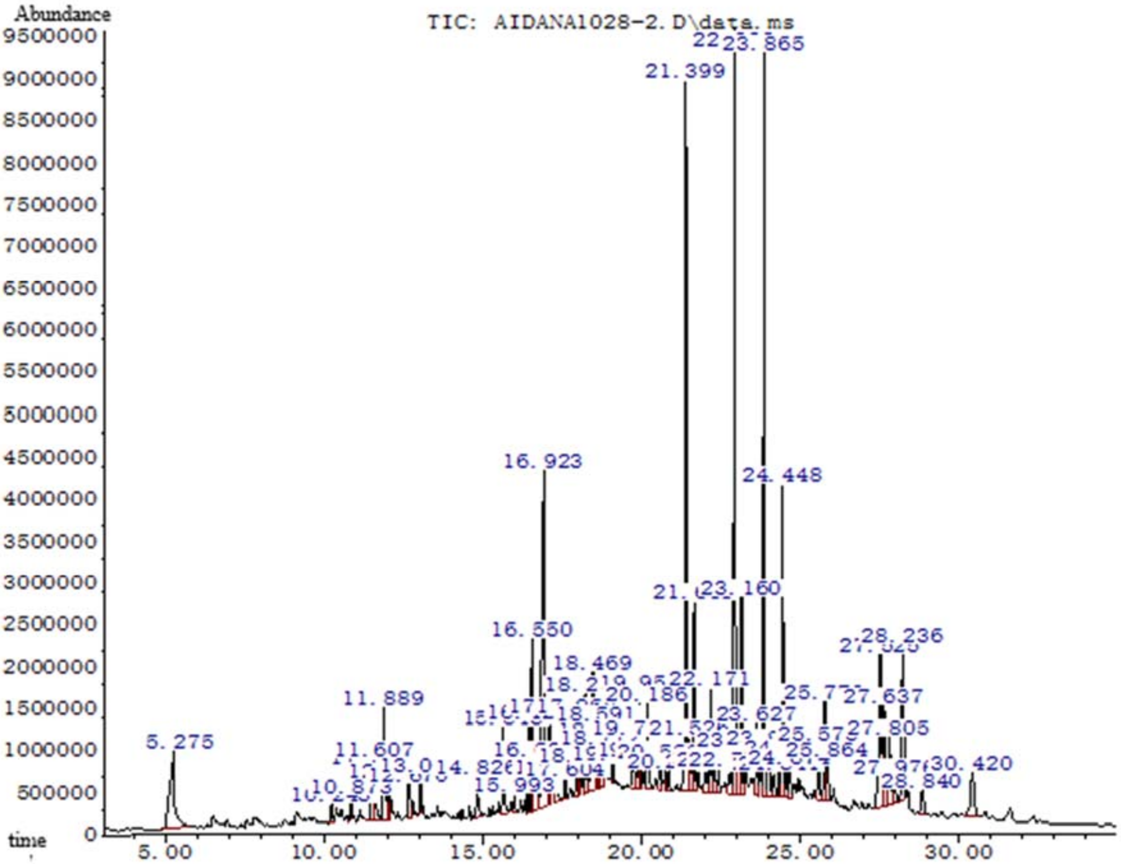

Figure 1 – Total ionization chromatogram of hexane part from *S. hypericifolia* L.

Table 1 shows the main content of liposoluble components from the hexane extract of the aerial part of *S. hypericifolia* L. The fat-soluble content from the hexane extract of the aboveground part of *S. hypericifolia* L. was determined, in which the main components are octacosanol (9.59%), docosene-1 (8.57%), squalene (8.12%), n-hexadecanoic acid (7.50%), linoleic acid (3.88%), gamma.- sitosterol (3.71%), hexanoic acid (3.45%), tridecan, 7-hexyl- (3.40%), lupeol (2.98%).

According to the results, the presence of octacosanol and other biologically active compounds justifies the use of hexane extract of the plant for the treatment of certain diseases. Octacosanol is used for herpetic infections, skin diseases, Parkinson's disease, amyotrophic lateral sclerosis (ALS, Lou Gehrig's disease), high cholesterol and “hardening of the arteries” (atherosclerosis), protects cells, relieves stress and restores sleep disturbed by stress [12-14]. Thus, octacosanol (polycosanol) can be used as a drug or dietary Supplement for the treatment of metabolic diseases without any side effects. Squalene weakens the development of cancer cells, strengthens the immune system, and can increase a person's life expectancy. Squalene, an isoprenoid from the group of polyphenyl compounds, is an intermediate metabolite in the synthesis of cholesterol, possessing antioxidant, immunostimulating, lipid-lowering, cholesterol-lowering, anti-carcinogenic and anti-inflammatory activity [15]; antimicrobial activity, especially against Mycobacterium tuberculosis [16]. In addition, squalene, the main component of the skin's surface polyunsaturated lipids, has a softening, cooling, and antioxidant effect on the skin, as well as antitumor activity [17]. n-hexadecanoic acid shows interesting biological activity against certain diseases and pathogens. For example, the anti-inflammatory, antioxidant, hypocholesterolemic [18], and antibacterial [19] activities described for n-hexadecanoic acid may offer a rationale for the traditional use of this type. These biological activities of the compounds present in *S. hypericifolia* L. extract support the medicinal use of the plant. Studies have identified the main biologically active compounds present in the two extracts. Identification of these compounds in the plant serves as the basis for determining the possible health benefits of the plant, which leads to further biological and pharmacological research.

Table 1 – The liposoluble components from the aerial part of *S. hypericifolia* L.

No.	**Name of the compound**	**Retention time, R_t min**	**MW**	**Peak Area %**
1	**2**	**3**	**4**	**5**
1	Hexanoic acid	5.279	116	3.45
2	trans-2,3-Epoxydecane	10.24	156	0.28
3	Cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene-, [S-(R*,S*)]-	10.877	204	0.26
4	3-Buten-2-one, 4-(2,2,6-trimethyl-7-oxabicyclo[4.1.0]hept-1-yl)-	11.506	208	0.81
5	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-	11.608	202	1.01
6	2(4H)-Benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-, (R)-	11.888	180	2.11
7	Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	12.041	204	0.69
8	Dodecanoic acid	12.67	200	0.75
9	Cedrol	13.043	222	0.45
10	Tetradecanoic acid	14.827	228	0.68
11	2-Pentadecanone, 6,10,14-trimethyl-	15.643	268	1.37
12	Z-8-Hexadecene	15.991	224	0.21
13	Hexadecanoic acid, methyl ester	16.424	270	0.97
14	Dibutyl phthalate	16.552	278	1.92
15	Hexadecenoic acid, Z-11-	16.637	254	1.28
16	n-Hexadecanoic acid	16.926	256	7.50

Continuation of the table

1	2	3	4	5
17	Hexadecanoic acid, ethyl ester	17.087	284	1.18
18	Octane, 1-bromo-	17.291	192	0.55
19	E,Z-2,13-Octadecadien-1-ol	17.605	266	0.27
20	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	17.971	294	1.36
21	9-Octadecenoic acid (Z)-, methyl ester	18.056	296	0.37
22	Sulfurous acid, pentadecyl pentyl ester	18.226	362	1.32
23	Linoelaidic acid	18.472	280	3.88
24	9,12-Octadecadienoic acid (Z,Z)-	18.591	280	1.00
25	6-Nitroundec-5-ene	18.667	199	0.69
26	Oleic Acid	18.71	282	0.71
27	Heptadecane	19.101	240	0.20
28	n-Tetracosanol-1	19.738	354	0.91
29	11-Octadecynoic acid, methyl ester	19.891	294	0.36
30	Tricosane	19.959	324	1.08
31	4,8,12,16-Tetramethylheptadecan-4-olide	20.188	324	1.33
32	2-Methyl-Z,Z-3,13-octadecadienol	20.562	280	0.53
33	Tridecane, 1-bromo-	20.774	262	0.29
34	E-2-Octadecadecen-1-ol	20.876	268	0.23
35	1-Docosene	21.403	308	8.57
36	cis-10-Nonadecenoic acid	21.522	296	1.16
37	Docosanoic acid, methyl ester	21.666	354	2.49
38	Acetate, 2-[(acetyloxy)methyl]-4,4-dimethoxybutyl ester	22.040	248	0.54
39	Undecanoic acid, ethyl ester	22.167	214	1.35
40	1-Acetoxynonadecane	22.295	326	0.55
41	1-Hexacosene	22.431	364	0.38
42	Oxirane, tridecyl-	22.796	226	0.50
43	Octacosanol	22.932	410	9.59
44	Carbonic acid, eicosyl prop-1-en-2-yl ester	23.051	382	0.77
45	Tetracosanoic acid, methyl ester	23.161	382	2.29
46	Hexadecanoic acid, ethyl ester	23.629	284	1.04
47	Squalene	23.866	410	8.12
48	Adenosine, 2-methyl-	23.985	281	0.90
49	2-[2-(Tert.butyl-dimethyl-siloxyl-methyl)-pyrrolidin-1-ylmethyl]-5-methyl-4-phenyl-thiazol	24.164	402	0.45
50	1-Hexacosene	24.342	364	0.36
51	Tridecane, 7-hexyl-	24.444	268	3.40
52	Hexacosanoic acid, methyl ester	24.546	410	0.54
53	Cyclopropanecarboxaldehyde, 2-methyl-2-(4-methyl-3-pentenyl)-, trans-(.+-.)-	24.673	166	0.58
54	Stigmastan-6,22-dien, 3,5-dedihydro-	25.574	394	0.89
55	Cyclohexane, (1-butylhexadecyl)-	25.769	364	1.80
56	6-Methoxy-2,7,8-trimethyl-2-(4,8,12-trimethyltridecyl)chroman	25.863	430	0.58
57	.gamma.-Sitosterol	27.528	414	3.71
58	Stigmastanol	27.638	416	2.14
59	1.alpha.,2.alpha.-Epoxy-1.beta.-methylcholesta-4,6-dien-3-one	27.808	410	1.65
60	30-Norlupan-28-oic acid, 3-hydroxy-21-methoxy-20-oxo-, methyl ester, (3.beta.)-	27.978	502	0.59
61	Lupeol	28.233	426	2.98
62	5.alpha.-Ergost-8(14)-ene	28.836	384	0.59
63	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene-	30.416	204	1.51

Conclusion. Liposoluble components were extracted with hexane from the aerial part of *S. hypericifolia* L., which were analyzed by GC-MS method. More than sixty-three compounds were isolated from hexane extract. Their relative contents were determined by normalizing the peak areas. For the first time, the active substances of hexane extract of a medicinal plant (*S. hypericifolia* L.) collected in the Almaty region of Kazakhstan were determined. Of the hexane extract, the dominant compounds are octacosanol (9.59%), docosene-1 (8.57%), squalene (8.12%), and n-hexadecanoic acid (7.50%). These compounds have high biological activites, namely anti-inflammatory, antimicrobial, antitumor, antibacterial [15-19]. This shows the need for further research of toxicological aspects for the development of safe herbal medicines.

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SPIRAEA HYPERICIFOLIA L. МАЙДА ЕРИТІН СЫҒЫНДЫНЫҢ ХИМИЯЛЫҚ КОМПОНЕНТТЕРІ

Аннотация. Дәрілік флораны игеру және фармакологиялық әсерінің кең спектрі бар биологиялық белсенді заттардың жаңа бастау көзін қарқынды іздеу фармацевтика өнеркәсібін дамытуда өзекті саналады. Өсімдік шикізатының перспективалы бастау көзінің қатарына *Spiraea* L. (*Rosaceae Juss.*) жатады.

Spiraea L., *spirea* түрі *Rosaceae Juss* жапырақты бұта тұқымдасына және *Spiraeoideae Focke* тұқымдасына жатады. *Rosaceae Juss* тегінің түрлері халық медицинасында қолданылатын және үлкен ресурстық әлеуеті бар өсімдіктер ретінде айтарлықтай қызығушылық тудырады. Солтүстік жарты шардағы қоңыржай және субтропикалық аймақта кең таралған 100-ден астам түрі бар. *Spiraea*-да биологиялық белсенділігі жоғары фенолды қосылыс ретінде флавонол, флавон, флаван, фенолкарбон қышқылы саналады. *Rosaceae Juss* тектес өсімдіктердің түрлі бөлігінде сапонин, эфир майы, стероидты гликозидтер анықталды. Қытай медицинасында анальгетикалық, ыстықты түсіретін және қабынуға қарсы қасиеті бар дәрілік өсімдік ретінде қолданылады. Қазіргі заманғы зерттеулерде фенолкарбон қышқылының антимикробтық, фитотоксикалық туындыларымен байланысты *Rosaceae Juss* тектес өсімдік түрлерінің биологиялық белсенділігі өте жақсы зерттелген. Флавандардың ісікке қарсы белсенділігі анықталды.

Spiraea hypericifolia L. еуразиялық аймақта кең таралған және генетиканың дамыған өкілінің бірі болып саналады. *S. hypericifolia* L. жапырағында п-гидроксибензойн, кофеин, ферула, хлороген қышқылдары, апигенин флавондары, лютеолин және флавонолдардың изокверцитрин мен авикулиннің 5-глюкозидтері анықталды. *Spiraea* тектес өсімдіктер түрлі сипаттағы бас ауруы, сондай-ақ буын, асқазан-ішек ауруы, гельминтоз және гинекологиялық аурулардағы ревматикалық ауруды кетіруге арналған құрал ретінде қолданылады. Күшті антибактериалды және антивирустық әсер ОРЗ, тұмау, герпес кезінде қолдануға себеп болады.

Аталған зерттеудің мақсаты – отандық фитопрепараттарды алу барысында негізгі компоненттердің әлеуетті көзі – Алматы облысы тобылғысының майда еритін компоненттерінің сандық құрамын зерттеу болып саналады.

Бұл зерттеуде алғаш рет *Spiraea hypericifolia* L. майда еритін сығындысының химиялық құрамы анықталды. *Spiraea hypericifolia* L. дәрілік өсімдігінің жерүсті бөлігіндегі майда еритін сығындысынан бөлінген компоненттер ГХ-МС әдісі арқылы талданды. Гексан бөлігінен барлығы алпыс үш қосылыс бөлінді және олардың салыстырмалы құрамы шың ауданын қалыпқа келтіру жолымен анықталды, негізгі компоненттер октакозанол (9,59%), докозен-1 (8,57%), сквален (8,12%) және н-гександекан қышқылы (7,50%) болып саналады. Бұл қосылыстар биологиялық белсенділігі жоғары болып келеді, атап айтқанда, қабынуға, микробқа, ісікке, бактерияға қарсы.

Түйін сөздер: *Spiraea hypericifolia* L., гексан сығындысы, майда еритін компоненттер, ГХ-МС.

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ХИМИЧЕСКИЕ КОМПОНЕНТЫ ЖИРОРАСТВОРИМОГО ЭКСТРАКТА *SPIRAEA HYPERICIFOLIA* L.

Аннотация. Освоение лекарственной флоры и интенсивный поиск новых источников биологически активных веществ с широким спектром фармакологического действия весьма актуальны для развития фармацевтической промышленности. К числу перспективных источников растительного сырья относятся представители рода *Spiraea* L. (*Rosaceae Juss*.).

Род *Spiraea* L., *spirea* представляет собой листопадные кустарники семейства *Rosaceae Juss*., подсемейство *Spiraeoideae Focke.* Виды рода *Rosaceae Juss* представляют значительный интерес как растения, используемые в народной медицине и имеющие большой ресурсный потенциал. Род широко распространен в умеренной и субтропической зоне северного полушария, насчитывая более 100 видов. В *Spiraea* обнаружены фенольные соединения с высокой биологической активностью: флавонолы, флавоны, флаваны, фенолкарбоновые кислоты. В различных частях видов растений рода *Rosaceae Juss* найдены сапонины, эфирное масло, стероидные гликозиды. В китайской медицине применяются как лекарственные растения с анальгетическими, жаропонижающими и противовоспалительными свойствами. В современных исследованиях достаточно хорошо изучена биологическая активность видов растений рода *Rosaceae Juss*, связанная с наличием производных фенолкарбоновых кислот - антимикробная, фитотоксическая. Обнаружена противоопухолевая активность флаванов.

S. hypericifolia L. имеет наиболее обширный Евразийский ареал и считается одним из наиболее эволюционно развитых представителей рода. В листьях *S. hypericifolia* L. обнаружены п-гидроксибензойная, кофейная, феруловая, хлорогеновая кислоты, флавоны апигенин, лютеолин и 5-глюкозиды флавонолов изокверцитрин и авикуларин. Растения рода Spiraea применяются как средство для снятия головных болей различного характера, а также ревматических болей в суставах, при желудочно-кишечных заболеваниях, гельминтозах, гинекологических заболеваниях. Мощное антибактериальное и антивирусное действие обуславливает применение при ОРЗ, гриппе, герпесе.

Целью данного исследования является изучение количественного содержания жирорастворимых компонентов таволги Алматинской области – потенциального источника ключевых компонентов для получения отечественных фитопрепаратов.

В этом исследовании впервые были определены химические составляющие жирорастворимого экстракта *Spiraea hypericifolia* L. Компоненты, выделенные из жирорастворимого экстракта надземной части лекарственного растения *S. hypericifolia* L ., были проанализированы методом ГХ-МС. Всего из гексановой части было выделено шестьдесят три соединения и их относительное содержание было определено путем нормализации площади пиков, в котором основными компонентами являются октакозанол (9,59%), докозен-1 (8,57%), сквален (8,12%) и н-гексадекановая кислота (7,50%) отдельно. Эти соединения обладают высокой биологической активностью, а именно противовоспалительной, противомикробной, противоопухолевой, антибактериальной.

Ключевые слова: *S. hypericifolia* L., гексановый экстракт, жирорастворимые компоненты, ГХ-МС.

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UNIQUE PROPERTIES OF GRAPHENE

Abstract. The article is devoted to the unique material graphene (carbon modification), discovered in 2004 by immigrants from Russia Andrei Geim (Andre K. Geim) and Konstantin Novoselov (Konstantin Novoselov), who won the Nobel Prize in physics for this discovery in 2010. Graphene a two-dimensional monoatomic thick carbon block allotrope building, has attracted enormous attention due to its remarkable physical properties and chemical functionalization capabilities. Graphene is a potential nanofiller that can significantly improve the performance of polymer-based composites at extremely low loading. The article is an excursion through the publications of foreign and domestic authors, revealing the unique properties and prospects of using graphene, in particular, in nanotechnology and nanocomposites. Also, this review presents various mechanical, thermal and electrical, as well as other important properties of graphene, which were also discussed along with their potential applications.

A graphene-based technical breakthrough is possible because this is the finest substance in the world and can simultaneously possess several very important and unique electronic, electrical properties. Firstly, this substance can be an excellent conductor, since it consists of chains of carbon hexagons, through which electric current is very easily transmitted. Secondly, with some modification, graphene can be an effective insulator. You can make a microcircuit, which consists of conductors, semiconductors and insulators. Each of these characteristics of a substance can be achieved based on graphene.

Key words: graphene, electronic properties, mechanical properties, thermal properties, chemical properties.

Introduction. Graphene is another manifestation of the unique chemical properties of carbon. Graphene is one of the most promising materials for the 21st century. Graphene, a single-layer form of graphite, is a planar sheet one atom thick of carbon atoms bound by sp^2, which are located in the hexagonal lattice [1]. Graphene can be described as a monatomic layer of graphite. This is the main structural element of other allotropes, including graphite, charcoal, carbon nanotubes, and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of a family of flat polycyclic aromatic hydrocarbons.

Research on graphene has expanded rapidly since the substance was first isolated in 2004. The studies were based on theoretical descriptions of the composition, structure, and properties of graphene, which were calculated decades earlier. High-quality graphene has also proven to be surprisingly easy to isolate, which makes further research possible.

Andre Geim and Konstantin Novoselov received the Nobel Prize in Physics in 2010 "for pioneering experiments with two-dimensional matter graphene" [2].

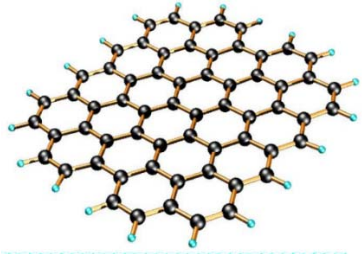
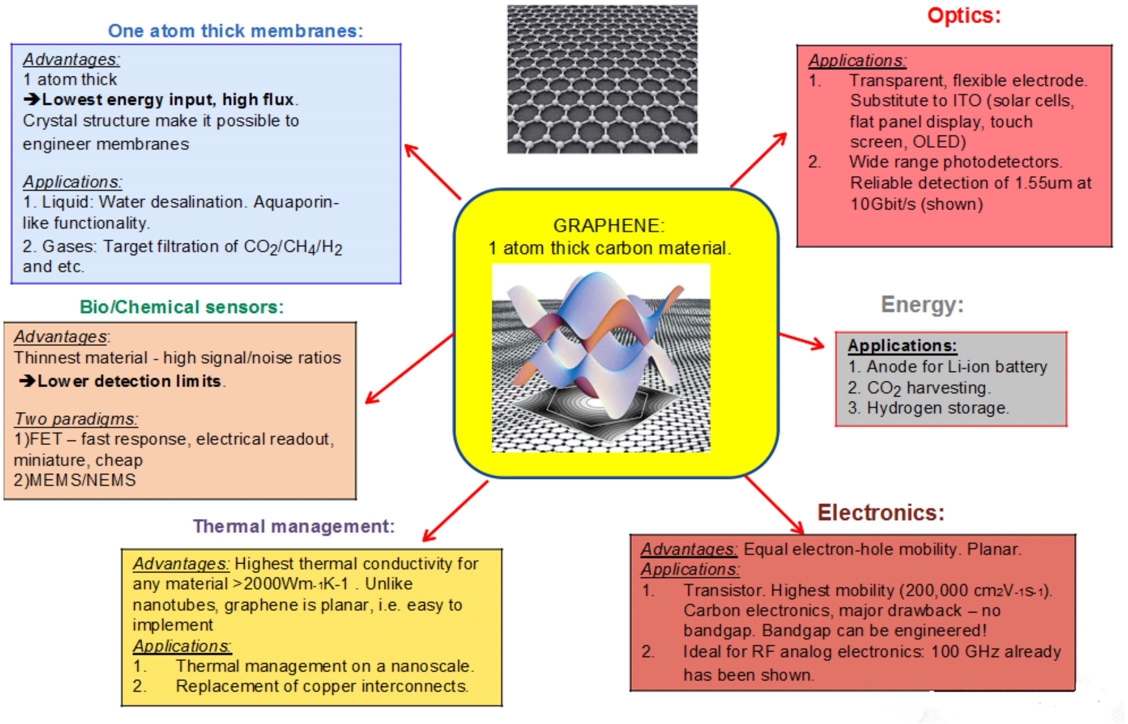


Figure 1- Idealized structure of a single graphene sheet

The remarkable properties of graphene are unique mechanical, thermal, electrical and optical properties. The conductivity, mechanical strength and chemical stability of graphene determine the prospects for its application in various fields (Fig. 2) [4]. That is, due to the aforementioned properties, graphene is widely used as conductive nanoelements for high frequency transistors, solar cells, sensors, supercapacitors, and various composite materials [3-5].

Among the remarkable properties of graphene are unique mechanical, thermal, electrical and optical properties. Most of these features are ideal, intact graphene sheets.



One atom thick membranes:

Advantages:
1 atom thick
➔**Lowest energy input, high flux**.
Crystal structure make it possible to engineer membranes

Applications:
1. Liquid: Water desalination. Aquaporin-like functionality.
2. Gases: Target filtration of $CO_2/CH_4/H_2$ and etc.

Bio/Chemical sensors:

Advantages:
Thinnest material - high signal/noise ratios
➔**Lower detection limits**.

Two paradigms:
1)FET – fast response, electrical readout, miniature, cheap
2)MEMS/NEMS

Thermal management:

Advantages: Highest thermal conductivity for any material $>2000 Wm^{-1}K^{-1}$. Unlike nanotubes, graphene is planar, i.e. easy to implement
Applications:
1. Thermal management on a nanoscale.
2. Replacement of copper interconnects.

GRAPHENE:
1 atom thick carbon material.

Optics:

Applications:
1. Transparent, flexible electrode. Substitute to ITO (solar cells, flat panel display, touch screen, OLED)
2. Wide range photodetectors. Reliable detection of 1.55um at 10Gbit/s (shown)

Energy:

Applications:
1. Anode for Li-ion battery
2. CO_2 harvesting.
3. Hydrogen storage.

Electronics:

Advantages: Equal electron-hole mobility. Planar.
Applications:
1. Transistor. Highest mobility (200,000 $cm^2V^{-1}s^{-1}$). Carbon electronics, major drawback – no bandgap. Bandgap can be engineered!
2. Ideal for RF analog electronics: 100 GHz already has been shown.

Figure 2 - Properties and applications of graphene

Optical Properties. The ability of graphene to absorb quite large 2.3% of white light is also a unique and interesting property (Fig.3), especially considering that its thickness is only 1 atom [6]. This is due to the aforementioned electronic properties; Electrons act as massless charge carriers with very high mobility. It was proved several years ago [7, 8] that the amount of absorbed white light is based on a constant fine structure, and does not depend on the characteristics of the material. Adding another layer of graphene increases the amount of white light absorbed by about the same amount (2.3%). The graphene opacity $\pi\alpha \approx 2.3\%$ corresponds to the universal value of the dynamic conductivity $G = e2 / 4\hbar$ (± 2-3%) in the visible frequency range. Because of these impressive characteristics, it was noted [9] that as soon as the optical intensity reaches a certain threshold (known as saturation fluence), saturable absorption takes place (very high-intensity light causes a decrease in absorption).

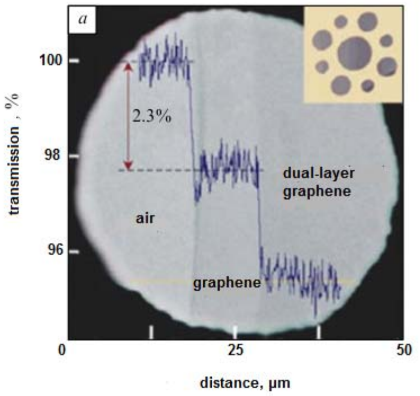


Figure 3 - Light transmission by mechanically exfoliated graphene

This is an important feature with regard to fiber laser mode locking. Due to the graphene properties of the wavelength-insensitive ultrafast saturable absorption, full-band mode locking is achieved using an erbium-doped dissipative soliton fiber laser capable of tuning a wavelength of up to 30 nm [10].

Electronics Properties. One of the most useful properties of graphene is that it is a semimetal with zero overlap (with holes and electrons as charge carriers) with a very high electrical conductivity [11–13]. In graphene, each atom is bonded to 3 other carbon atoms in a two-dimensional plane, leaving 1 electron freely available in the third dimension for electron conductivity. These very mobile electrons are called pi (π) electrons and are located above and below the graphene sheet. These pi-orbitals overlap and help increase carbon-carbon bonds in graphene [14]. Fundamentally, collaborative studies over the past 50 years have proved [15-19] that at the Dirac point in graphene, electrons and holes have zero effective mass. This is because the ratio of energy and motion (excitation spectrum) is linear for low energies near 6 separate angles of the Brillouin zone [20]. These electrons and holes are known as Dirac fermions or decanters, and the 6 angles of the Brillouin zone are known as Dirac points. Due to the zero density of states at the Dirac points, the electronic conductivity is actually quite low. However, the Fermi level can be changed by doping (with electrons or holes) to create a material that potentially conducts electricity better than, for example, copper at room temperature [21]. Graphene has a lower resistivity than any other known material at room temperature, including silver [22].

Tests have shown that the electronic mobility of graphene is very high, with previously reported results exceeding 15,000 cm^2 • V - 1 • s - 1, and theoretically potential limits of 200,000 cm^2 • V - 1 • s - 1 (acoustic photons limited by scattering of graphene) [23-25]. Graphene electrons are said to be very similar to photons in their mobility due to lack of mass. These charge carriers can travel distances less than a micrometer without scattering; a phenomenon known as ballistic transport. However, the quality of graphene and the substrate used will be a limiting factor [26]. For example, when using silicon dioxide as a substrate, mobility can be limited to 40,000 cm^2 • V -1 • s -1 [27]. Although all this makes graphene the fastest and most efficient conductor, it cannot be easily used for the manufacture of transistors, since it does not have a forbidden zone [28]. There are several ways to open the forbidden zone that exist, and some are under development [29-32].

Mechanical Properties

Graphene is one of the thinnest materials in the world - its thickness is only one carbon atom (about 0.34 nm). It is also recognized as the most durable two-dimensional material - much harder than steel or diamond with the same dimensions [33]. Graphene has a tensile strength (the maximum stress that a material can withstand when stretched or stretched to fracture or fracture) in excess of 1 TPa. There is only one material that can be stronger than graphene — carbine [34], which is a chain of carbon atoms, mainly a graphene ribbon, one atom wide. Carbin is very difficult to synthesize.

Since this is a single 2D sheet, it has the highest surface area of all materials. When left to their own devices, graphene sheets will fold and form graphite, which is the most stable three-dimensional carbon form under normal conditions [35]. Graphene sheets are flexible, and in fact graphene is the most extensible crystal — you can stretch it to 20% of its original size [36-39] without breaking it. Finally, ideal graphene is also very impenetrable, and even helium atoms cannot pass through it [40]. Because of the bond strength of 0.142 Nm carbon bonds, graphene is the most durable material ever discovered, with a tensile strength of 130,000,000,000 Pascals (or 130 gigapascals) compared to 400,000,000 for A36 structural steel or 375,700,000 for Aramida (Kevlar) [41-43]. Graphene is not only unusually strong, but also very light - 0.77 milligrams per square meter (for comparison, 1 square meter of paper is about 1000 times heavier). It is often said that one sheet of graphene (only 1 atom thick), sufficient in size and sufficient to cover the entire football field, will weigh less than 1 gram [44].

What makes this especially special is that graphene also has elastic properties that can retain their original size after deformation. In 2007, atomic force microscopes (AFM) were carried out on graphene sheets that were suspended above silicon dioxide cavities [45–49]. These tests showed that graphene sheets (with a thickness of 2 to 8 Nm) had constant springs in the region of 1-5 N / m and Young's modulus (different from three-dimensional graphite) of 0.5 TPa. Again [50], these excellent figures are based on theoretical perspectives using flawless graphene, which does not contain any flaws and is currently very expensive and difficult to reproduce artificially, although production methods are constantly being improved, ultimately reducing costs and complexity.

Thermal management

The stable operation of electronic devices is highly dependent on temperature. There is a constant search for materials capable of dissipating the heat released during the operation of instruments and devices. Graphene is an ideal heat conductor - it has a record thermal conductivity. Graphene conducts heat in all directions - it is an isotropic conductor [51-53]. When measuring the thermal conductivity of suspended graphene, the thermal conductivity at room temperature was 5000 W / m • K (obtained from the measurement of the Raman spectra), i.e. 2.5 times more than that of diamond, whose thermal conductivity was considered the largest of the materials known today. Such a value could solve the problem of heat removal in nanoelectronics [54].

It is believed that the high thermal conductivity of graphenes is due to the structural perfection of those small samples on which it was measured. Unfortunately, this value decreases with increasing size; Thus, the thermal conductivity of graphenes with a length of 1 to 5 μm decreases in the range from 5000 to 3000 W / m • K; Such a dependence is usually associated with the phonon mechanism of thermal conductivity. However, in other experiments, single-layer graphene is usually fixed on substrates, usually dielectric, which leads to scattering by the phonons of the substrate and impurities. So, the graphene layer on the SiO2 surface had a thermal conductivity of only 600 W / m • K [55], which, however, is still greater than that of copper; its thermal conductivity is 400 W / m • K at room temperature, but really thin films are used, whose thermal conductivity is lower (less than 250 W / m • K). For thermal conductivity in the direction perpendicular to the graphene plane, see [56].

Biosensors

It is known that graphene as a two-dimensional material has a unique set of electrophysical properties: high mobility of charge carriers in combination with their low concentration; the maximum possible ratio of area to volume; low noise [57]. The combination of these properties leads to the fact that the adsorption of a minimum amount of impurities on the surface of graphene can significantly change its overall conductivity. Thus, graphene is a very promising material for the manufacture of various types of sensors (figure 4).

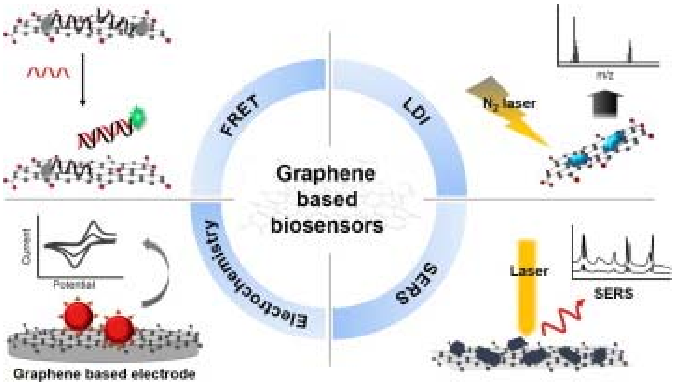


Figure 4 - Graphene based biosensors

In [58], it was shown that graphene is capable of sensing the adsorption of even one molecule. The attached gas molecules, depending on their charge and type of conductivity of the graphene film, behave as donors or acceptors, i.e., they change the concentration of mobile charge carriers. As a result, depending on the type of adsorbed molecule, a decrease or increase in the film resistance was observed [59–60]. It should be noted that one of the serious drawbacks of the graphene gas sensor is the lack of selectivity. Indeed, by a change in conductivity it cannot be said which molecule was adsorbed onto the surface of graphene. Moreover, some molecules contribute the opposite sign; thus, the total change in resistance can be close to zero. The problem of selectivity of the graphene-based sensor can be solved by using the antigen – antibody reaction. The components of this pair can only interact with each other and with no other proteins. t is known that at certain stages of many human diseases in the blood, antigen markers appear that are specific for one or for a group of diseases. These antigens can interact with specific antibodies previously applied to the surface of the graphene sensor. The reaction, as in the case of a gas sensor, leads to a change in the resistance of the graphene film. The use of an antigen – antibody pair allows one to solve the biosensor selectivity problem and opens up very wide possibilities for the use of graphene-based sensors in medicine and biology. This approach can lead to the creation of portable biosensors capable of detecting diagnostically significant disease markers in biological fluids that are currently detected only using a laborious and lengthy enzyme-linked immunosorbent assay [61].

Chemical Properties. Despite the fact that all graphene atoms are exposed to the environment, it is an inert material that does not react with other atoms. However, graphene can "absorb" various atoms and molecules. This can lead to changes in electronic properties, and can also be used for the manufacture of sensors or other applications [62].

Graphene can also be functionalized by various chemical groups [63-64], which can lead to various materials, such as graphene oxide (functionalized by oxygen and helium) [65, 66] or fluorinated graphene (functionalized by fluorine) [67]. Great interest in studying the functional properties of graphene, due to the fact that it is a promising material for many industries, has a high commercial potential [68].

Findings. In this review, we have described some of the distinguishing properties of graphene, such as mechanical, thermal, electrical, and optical properties. Because of these unique properties, graphene is widely used as conducting nanoelements for high-frequency transistors, solar cells, sensors, supercapacitors, and various composite materials. The electrical conductivity, mechanical strength, and chemical stability of graphene determine the prospects for its use in various fields.

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ГРАФЕННІҢ БІРЕГЕЙ ҚАСИЕТТЕРІ

Аннотация. Графен – графиттің бірқабатты күйі, алтыбұрышты торда орналасқан sp^2 байланысқан көміртек атомдарының қалыңдығы бір атомнан тұратын жазық парақ. Графен көміртек атомдарының байланысқан құрылымының ерекше комбинациясының, сондай-ақ сансыз және күрделі физикалық қасиеті болғандықтан материалтану, электроника және нанотехнология болашағына айтарлықтай әсер етуге қабілетті. Ерекше құрылымы мен минималды диаметріне байланысты оны сенсорлық құрылғы, жартылай өткізгіш немесе интегралды схема компоненттері ретінде пайдалануға болады. Мұндай көміртектің екіөлшемді формасының қасиеттері мен қолданысы болашақ құрылғы мен жүйеге жаңа мүмкіндіктер ашты.

Графеннің үздік қасиеттері оның релятивистік бөлшектер тәрізді әрекет ететін заряд тасымалдаушысы болғандықтан пайда болады.

Графеннің заряд тасымалдаушылық сипатына байланысты тағы бір эффект – спираль болғандықтан хиралды симметрия пайда болады. Бірқабатты және екіқабатты графендегі электронды күйдің хиралды табиғаты электронның потенциалды кедергі арқылы өтуі барысында маңызды рөл атқарады.

Графен өндірудің түрлі әдісі бар, мысалы, «тотығу - қабыршақтану - тотықсыздану» үдерісі кезінде графит графит оксидіне айналып, графиттің базалық жазықтығы ковалентті байланысқан оттекті функционалды тобымен жабылады. Бұл жағдайда тотыққан графит гидрофильді (ылғал сүйгіш) келеді және ультрадыбыс әсерінен сулы ерітіндіде оңай графен қабаттарына қабыршақтанады. Мұндай графен жақсы механикалық және оптикалық сипаттамаға ие, бірақ «скотч әдісі» арқылы алынған графенмен салыстырғанда электр өткізгіштігі нашар.

Фундаменталды зерттеулер үшін сапалы графен қабаттарын, сондай-ақ электронды микросхема құруға бағытталған графен өсірудің эпитаксиалды әдісі арқылы алуға мүмкіндік беретін скотч негізінде механикалық қабыршықтандырумен қатар, химиктер графенді ерітіндіден алу жолдарын қарастыруда. Бұл әдіс жоғары өнімді әрі арзан келетіндіктен, графен қабаттарын түрлі материалмен біріктіріп, нанокомпозит құруға және оларды түрлі наноқұрылымдарға енгізуге мүмкіндік береді.

Графеннің дисперсиялылығымен шектелетін ерекше қасиеттері бар, әсіресе гидрофобты табиғатына байланысты полярлық полимер матрицаларымен араласқан кезде ерекше қасиетке ие болады. Графен көптеген, мысалы, электроника және функционалды нанокомпозиттер сияқты көптеген басқа қосымшада үлкен потенциалмен қамтамасыз ете алады.

Графеннің жоғары электронды қозғалғыштығы, бір атомның минималды қалыңдығы, төмен меншікті кедергісі сияқты қасиеттері түрлі биологиялық және химиялық сенсорларды құрудың перспективаларын ашады, сонымен қатар күн энергиясын түрлендіруге арналған фотоэлектрлік құрылғыларда немесе сенсорлы экрандарда қолдануға болатын жұқа пленкаларға түрлі нұсқаларды ұсынады.

Графен негізінде жоғары сезімтал фотопленка жасалуы мүмкін. Графендегі плазмалық толқындар терагерц диапазон қабылдағышын құрудың перспективасын ашады. Графен спинінің ерекше әрекеті жаңа сфинтронды құрылғылар пайда болуы мүмкін, ал жылу өткізгіш қасиеті жоғары болғандықтан графен қазіргі заманғы интегралды схемаларда жылу қабылдағыш ретінде қызмет ете алады.

Графен қолданудың басқа бағыттары да перспективалы болып көрінеді. Сонымен, графен пластмассадан жасалған қоспада жоғары температураға төзімді композициялық өткізгіш материалдарды жасауға мүмкіндік береді деп болжанады. Графеннің беріктігі ультра жұқа, жеңіл және икемді жаңа механикалық тұрақты материалдарды жасауға мүмкіндік береді. Болашақта графен негізіндегі композициялық материалдардан автомобиль, ұшақ пен спутник жасауға болады. Энергияны сақтау құрылғыларында – аккумулятор және суперкапакатор, сондай-ақ оттегі мен сутектің араласуынан электр энергиясын өндіретін отын ұяшықтарында графенді қолдану жоспарлануда.

Егер графен зерттеу жұмыстары дәл осындай қарқынмен дамитын болса, онда біз осы ғасырдағы ғылыми-техникалық прогрестің жаңа кезеңіне куә боламыз, ал графенді практикалық қолдануға қызығушылық танытатын мемлекет жетекші техникалық күшке айналады.

Түйін сөздер: графен, электрондық қасиеттер, механикалық қасиеттер, жылу өткізгіш, химиялық қасиеттер.

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УНИКАЛЬНЫЕ СВОЙСТВА ГРАФЕНА

Аннотация. Графен, однослойная форма графита, представляет собой планарный лист толщиной в один атом из атомов углерода, связанных sp^2, которые расположены в гексагональной решетке [2]. Графен с уникальным сочетанием структур связанных атомов углерода с его бесчисленными и сложными физическими свойствами способен оказать значительное влияние на будущее материаловедения, электроники и нанотехнологий. Благодаря своей специализированной структуре и минимальному диаметру, его можно использовать в качестве сенсорного устройства, полупроводника или для компонентов интегральных схем. Сообщаемые свойства и применения этой двумерной формы углерода открыла новые возможности для будущих устройств и систем.

Все эти удивительные свойства графена возникают из-за уникальной природы его носителей заряда, которые ведут себя подобно релятивистским частицам.

Ещё один эффект, обусловленный характером носителей заряда в графене, связан с наличием спиральности, что приводит к существованию так называемой киральной симметрии. Киральная природа электронных состояний в однослойном и двухслойном графене играет важную роль в прохождении электрона через потенциальный барьер.

Существуют различные методики получения графена: например, преобразование графита в оксид графита, когда происходит процесс «оксидирование - расслоение -восстановление», в ходе которого базисные плоскости графита покрываются ковалентно связанными функциональными группами кислорода. При этом окисленный графит становится гидрофильным (влаголюбивым) и легко расслаивается на отдельные графеновые листы под действием ультразвука, находясь в водяном растворе. Такой графен обладает хорошими механическими и оптическими характеристиками, но худшей электрической проводимостью по сравнению с графеном, полученным с помощью «скотч-метода».

В дополнение к механическому отслоению с помощью скотча, позволяющему получить графеновые слои высокого качества для фундаментальных исследований, и эпитаксиальному способу выращивания графена, направленному на создание электронных микросхем, химики работают над получением графена из раствора. Помимо высокой производительности и низкой себестоимости, этот метод позволил бы интегрировать графеновые слои с различными материалами для создания нанокомпозитов и внедрять их в различные наноструктуры.

Графен обладает уникальными свойствами, которые могут быть ограничены его диспергируемостью, особенно в смеси с полярными полимерными матрицами, из-за его гидрофобности в природе. Графен может обеспечить большой потенциал во многих приложениях, таких как электроника и функциональные нанокомпозиты, среди многих других.

Такие свойства графена, как высокая подвижность электронов, минимальная толщина в один атом, низкое удельное сопротивление открывают перспективы для создания различных биологических и химических датчиков, а также различных вариантов тонких плёнок, которые могут найти применение в фотоэлектрических устройствах для преобразования солнечной энергии или в сенсорных экранах.

На основе графена могут быть созданы высокочувствительные фотоплёнки. Плазменные волны в графене открывают перспективы создания источников и приемников терагерцового диапазона. Особое поведение спина в графене может привести к созданию новых приборов спинтроники, а благодаря свойству высокой теплопроводимости графен может служить теплоотводом в современных интегральных схемах, в которых разогрев является серьёзной проблемой.

Многообещающими представляются и другие направления использования графена. Так, предполагается, что в смеси с пластмассами графен даст возможность создавать композитные проводящие материалы, устойчивые к действию высоких температур. Прочность графена позволяет конструировать новые механически устойчивые материалы, сверхтонкие, легкие и эластичные. В будущем из композитных материалов на основе графена возможно будет делать автомобили, самолеты и спутники. Уже сейчас предполагается использовать графен в устройствах для хранения энергии – аккумуляторах и суперконденсаторах, а также топливных элементах, вырабатывающих электроэнергию от соединения кислорода с водородом.

Если графеновая революция пойдет такими же стремительными темпами, то мы явимся свидетелями нового витка научно-технического прогресса уже в этом веке, а страна, которая проявит интерес к практическому применению графена, станет ведущей технической державой.

Ключевые слова: графен, электронные свойства, механические свойства, термические свойства, химические свойства.

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DETERMINATION OF THE GLASS TRANSITION TEMPERATURE OF METHACRYLATE COPOLYMERS

Abstract. We have obtained a new synthetic copolymers based on methyl methacrylate (MMA) and butyl methacrylate (BMA), with use of the dinitrile as an initiator of Azobisisobutyronitrile acid (AIBN). Hence, the obtained results show the important role of the structure of the polymer melt at a specific temperature or heat resistance intensive degradation of polymeric materials and other characteristics of the TGA. Heat resistance, as well as a certain temperature loss of the samples depends on the chemical structure of polymers, expressed in terms of the glass transition temperature, the compactness of the macromolecular coil in the copolymer, which is also determined by the structure of the coil. The role of the latter in determining the thermal resistance decreases as the glass transition temperature of the copolymer. It was found that the thermal degradation of butyl methacrylate copolymers studied by the mechanism of copolymerization and decomposition side butyl substituent.

Keywords: methyl methacrylate, butyl methacrylate, copolymers, differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA).

Introduction. Self-curing PMMA are materials formulated by the mixing of two-component, one solid (powder) based on PMMA spherical beads and another liquid includes monomer and an initiator to enable the polymerization reaction to occur at room temperature and a high level of heat being generated during the exothermic reaction. In self-curing, the polymerization reaction of methacrylate monomers is initiated by the activation reaction of BPO, with an amine accelerator at room temperature, which gives free radicals for addition to monomer molecules [3]. A high level of heat being generated during the exothermic reaction [1]. Authors [2] prepared copolymer latexes based on methyl methacrylate (MMA) and butyl methacrylate (BMA) using macroradical initiator technique. Different ratios of acrylic monomers were designed to investigate the effect of monomer compositions on physico-mechanical properties of acrylic films for paint application. The results showed that, physico-mechanical properties increased with increasing the ratio of MMA in the copolymer. The work was further extended to include the application of the obtained copolymer latexes to make acrylic syrups containing varying content of MMA-monomer to be self curing and modify physico-mechanical properties of paint solvent free.

Materials and apparatus. Methyl methacrylate, butyl methacrylate, Azobisisobutyronitrile acid production company «Aldrich Chemical Co.» USA was used without further purification and other chemicals as ethanol and acetone used in this experiment.

Synthesis and Characterization of Copolymer. The preparation of copolymer and the methods of analysis (FT-IR and SEM) have been previously described [3]. DSC was carried out using a Perkin Elmer Differential Scanning Calorimeter DSC. The samples were tested under N_2 atmosphere at a scanning rate ± 20^{o}C min^{-1}. The thermal gravimetric analysis (TGA) was conducted on a TGA/SDTA 851e under nitrogen flow.

Structure of Copolymers. The structure of the copolymer latexes based on methyl methacrylate (MMA) and butyl methacrylate (BMA) is shown in figure 1.

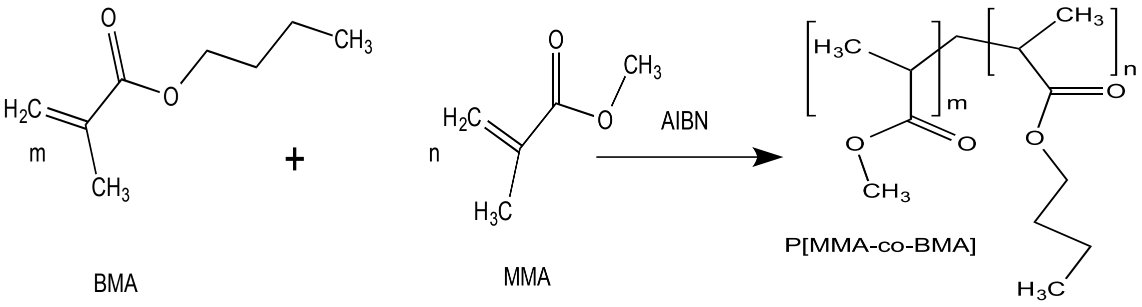

Figure 1 - General reaction for the synthesis of MMA/BMA copolymer [3]

The copolymer latexes were synthesized with different ratios (M1=10/90, M2=50/50 and M3=90/10 respectively) using azobisisobutyronitrile (AIBN) as free radical initiator. The properties of the prepared copolymer latexes have been previously reported by authors [3]. The results showed that physico-mechanical properties of the copolymer were increased by increasing the ratio of MMA in the copolymer latexes.

Differential scanning calorimetry (DSC). This assumption confirmed by the results of differential scanning calorimetry. DSC curves obtained are shown in figure 1 and in table 1.

Table 1 - Differential Scanning Calorimetry copolymer of MMA:BMA

[MMA-BMA] mol. %	Тш, °C (a)	Тш, °C (б)	Temperature range, °C (c)	Lost mass % (c)	Residual mass % (c)	PDTmax, °C (c)
10-90	43.30	34.15	25-280 280-500	1,7 98,3	98,3 0	435
50-50	63.10	57.12	24-277 277-500	1,4 93,5	93,5 0	426
90-10	98.40	94.34	25-274 274-500	10 90	90 0	420
Note – a – Values from DSC Analysis б – Values determined by the Fox equation c – Values derived from thermogravimetric analysis						

Figure 2 shows a differential scanning calorimetry (DSC) of the studied samples. Seen from the curves that the samples undergo transformations, there is no monotony and regularity of change DSK - signal with increasing temperature. Therefore, we can assume that the melting copolymers requires energy, which is reflected by a sharp decrease in the DSC signal. From the DSC data it follows that the curve of the copolymer of MMA:BMA has an endothermic peak at 98^0C, which corresponds to the glass transition temperature. Then, from 100 to 200^0C in all systems, probably no chemical reaction occurs, and DSC - signal changes due to the removal of volatile impurities. The results obtained are in good agreement with the known views on the mechanism of thermal transformations of methacrylates [4], DSC and TGA data are in good agreement. Based on TGA and DSC data expansion process systems investigated under the temperature can be divided into three areas:

I - 10 to 250^0C - an area resistant to aging;

II - from 325 to 425^0C - region of rapid aging of the destruction of the copolymer;

III - above 450^0C - the area of destruction.

Decomposition MMA:BMA is mainly on the mechanism of copolymerization, and accompanied by the destruction of lateral substituents of the methacrylate units in the copolymer can be expanded through the destruction of the lateral ester groups.

Destructive flow starts at 250^0C. In which the endothermic peak at 325^0C indicates the gap of methacrylate linkages and an exothermic peak area at 450^0C – resulted by oxidation. Thus, copolymers based on MMA: BMA possess high thermal stability and are more resistant to thermal degradation.

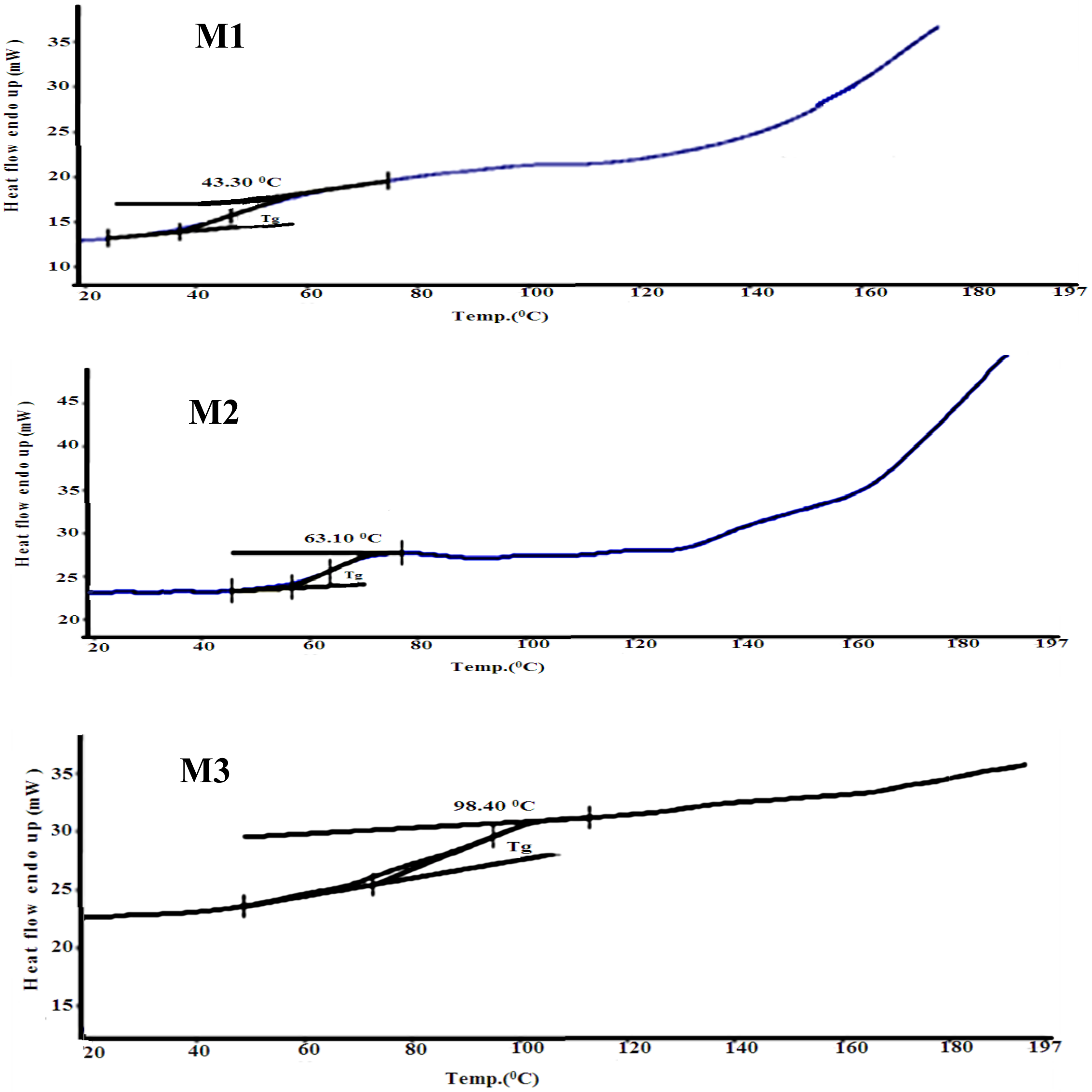

Figure 2 - DSC curves for polymers MMA: BMA 10:90 (1), 50:50 (2), 90:10 (3)

Thermo gravimetric analysis (TGA). To study the thermo physical properties of the synthesized copolymers and the starting reagents, studying these thermal properties by thermo gravimetric analysis (TGA) [8, 9]. TGA results are presented in table 1 and figure 3.

In a first step (20...280^0C) going destruction of oxygen-containing groups: the carbonyl and ether, which is accompanied by mass loss of the sample 12, 5...13, 6 % (table 1). Intensive thermal destruction corresponds to the interval 280–400^0C, the loss of mass is 67, 5...68, 4 %.

Figure 3 shows the TGA - curves copolymer MMA: BMA, weight loss of the copolymer observed at 250^0C, this is due to the loss and removal of volatile impurities. A loss of mass 10% observed at 225^0C. The rate of thermal-oxidative decomposition of the copolymer increases markedly with temperature 425^0C. The endothermic effect at 325^0C, in which 450^0C becomes exothermic peak showing the thermal oxidative degradation of the polymer [5, 6]. Over 450^0C mass is removed and the remaining 20% of solid residue (see figure 2). The total drop weight is 80%.

The glass transition temperature of copolymers obtained by radical copolymerization in the presence of a dinitrile, Azobisisobutyronitrile acid, is higher than for the homopolymers, which indicates the formation of block copolymers. To analyze the properties of the copolymers are selected in the two monomers, which were used in the copolymerization reactions of methyl methacrylate (MMA), butyl methacrylate (BMA).

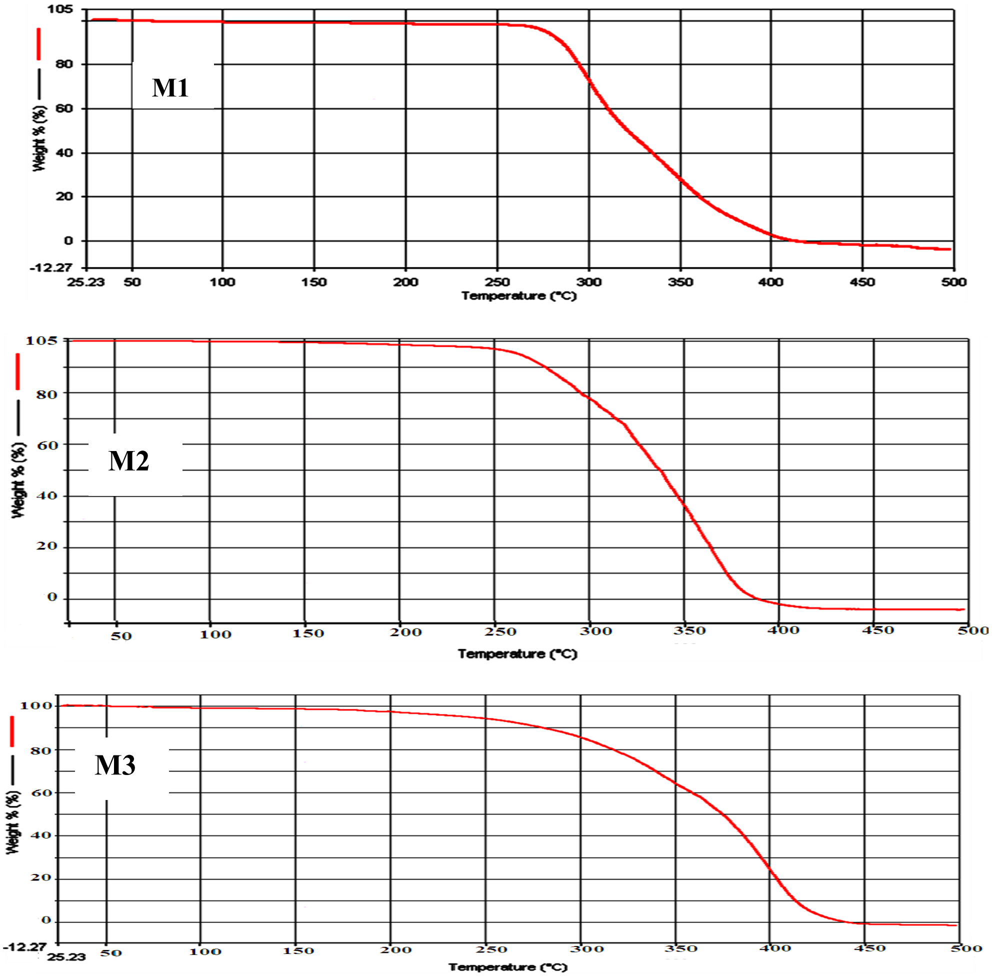

Figure 3 - The mass loss versus the temperature of copolymer.
Composition MMA: BMA 10:90 (1), 50:50 (2), 90:10 (3)

Copolymers based on these compounds are completely amorphous high molecular weight substances which are easily formed in the block and suitable for thermal characteristics of study [7, 8].

The glass transition temperature of copolymers T_C calculated by the following equations.

$$\frac{1}{T_g}=\frac{W_1}{T_{g1}}+\frac{W_2}{T_{g2}}+\frac{W_3}{T_{g3}}$$

where T_C – The glass transition temperature of the copolymer, Tg_1 and Tg_2 – two glass transition temperatures of homopolymers and W_1, и W_2 - weight of the two repeat units in the copolymer.

In general, there is good agreement between the calculated and experimental values of T_C. When using the experimental values of T_C for homo polymers and substituting them into the equation in most cases corresponds to the calculation experiment is somewhat improved. The calculated values of the characteristics defined for the ideal polymer system.

Conclusion. Polyampholytic properties of cross linked copolymers of MMA: BMA, partly due to the presence of unsaturated groups and carboxyl methacrylate structure characteristic for which presence confirmed also that by decreasing the content of the hydrophobic monomer MMA copolymers are obtained which are insoluble in water. Ionization of the carboxyl groups is a major contributor to the process of swelling and aspirations to the distribution of solvent throughout the volume of the polymer network.

MMA:BMA decomposition proceeds predominantly by the copolymerization mechanism, and is also accompanied by the destruction of side substituents; some of the methacrylic units in the copolymer decompose through the destruction of side ether groups.

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МЕТАКРИЛАТ СОПОЛИМЕРЛЕРІНІҢ ШЫНЫЛАНУ ТЕМПЕРАТУРАСЫН АНЫҚТАУ

Аннотация. Жұмыс мақсаты ретінде қанықпаған түрлі метакрил мономері негізінде жаңа сополимер синтезделіп алынды. Жаңа түрлі қатынастағы сополимерлер ММА-БМА синтезделді және физика-химиялық қасиеттері зерттелді.

Негізгі нәтижелер:

– алғаш рет ММА-БМА негізінде сополимерлер бастапқы қоспадағы мономердің түрлі қатынастағы массада бос радикалды сополимерлену әдісі арқылы синтезделді;

– алынған сополимер ТГТ және ДСК әдісі негізінде термиялық қасиеттер қарастырылды. Осы мәліметтер негізінде шынылану температурасы анықталды.

Шынылану температурасы ($T_ш$) – полимерлердің маңызды параметрінің бірі, полимерлердің жылу сыйымдылық өлшемі ретінде кеңірек қолданылады. Бұл әдіс үлгілерді белгілі жылдамдықпен қыздыру барысында бөлінген жылу ағынын өлшеуге негізделген. Осы жылу ағыны дифференциалды сканерлеуші колориметрлік қондырғыда жазылады. Сополимердің шынылану температурасы осы мономерлер негізінде алынған жекелеген гомополимер $T_ш$ мәнінің арасында болады және сополимер құрамында белгілі бір мономер буынының мөлшері көп болуына байланысты мәні жылжып отырады. Полиметилметакрилаттың (ПММА) шынылану температурасы 105-120^{0}С, ал полибутилметакрилаттың шынылану температурасы 20^{0}С көрсетеді. Зерттелген ММА-БМА сополимерінің шынылану температурасы бастапқы мономер құрамындағы ММА мөлшері 90% (М3) болғанда 98^{0}С, ал 50% (М2) көрсеткенде 63^{0}С және 10% (М1) болғанда 43^{0}С тең екені анықталды. Сополимер құрамында ММА мономерінің мөлшері көп болған сайын шынылану температурасы ПММА шынылану температурасына жақындай түсетіні байқалады. Фокс теңдеуі арқылы анықталған мәні тәжірибелік мәнмен ұқсастығын аңғаруға болады.

Бұл термогравиметриялық талдау (ТГТ) – дифференциалды сканерлеуші калориметриялық талдау сияқты кеңінен қолданылатын әдіс болып саналады. Осы әдіспен үлгі массасының не массалық үлесінің температураға немесе уақытқа тәуелді өзгерісін өлшейді. Бұл талдау тұрақты атмосфералық қысымда және 25-5000С температуралық диапазонында 1000 С / мин жылдамдықтағы газ тәріздес азотты қолдану арқылы жасалды. Жұмыста зерттелген сополимерлердің деструкцияға ұшырау жағдайы көрсетілген.

Полимердегі мономерлердің түрлі қатынасына байланысты шынылау температурасы ($T_ш$) үнемі өзгеріп отырады. Осы полимерлер қаттылығын $T_ш$ шынылау температурасымен анықтайды, оған Фокстың эмпирикалық теңдеуін қолдану арқылы төмендегідей есептеу жүргізілді.

Осындай термоқаттыланған полимерлер үшін есептелген шынылау температурасы ($T_ш$) үлдірдің соңғы $T_ш$ мәні емес, өйткені полимер тізбектері тігілген сайын оның $T_ш$ температурасы жоғарлайтынын ескеру қажет.

Синтезделген ММА-БМА сызықты сополимерінің термомеханикалық қасиеттері зерттелді және бастапқы реагенттің термиялық қасиеттерін ТГТ арқылы анықтау үшін мәліметтер қолданылды. ММА буыны 10% (М1) болғанда 25-280^{0}С аралығында сополимер бастапқы салмағының 1,7% жоғалтса, ал ММА буыны 90% (М3) болғанда 25-274^{0}С температура аралығында 10% массасын жоғалтады. Бастапқы сатыда үлгі құрамындағы дымқыл, су, еріткіш қоспаларының температурасын жоғарылатқанда, олар жылдам ыдырайды. Ал 280-500^{0}С температуралық аумақта екінші рет массасын жоғалтады. Алғашқы үлгілер жалпы массаның 98% массасынан айырылса, соңғы үлгі жалпы массаның 90% жоғалтады. Сополимердің максималды ыдырау температурасы да (PDT) 435^{0}С, 426^{0}С, 420^{0}С температураны көрсетіп, ММА буыны 10%-дан 90%-ға артқан сайын төмендейтінін аңғаруға болады. Максималдық ыдырау температурасы полимер құрылымына байланысты. Алынған нәтижелер жұмыста келтірілген метакрилаттың өзгерісінің жылу механизмдеріне сәйкес келеді.

Алынған мәліметтер негізінде ТГТ және ДСК бойынша ыдырау үдерісіндегі зерттелген жүйеге температура әсері 3 аймаққа келесідей бөлінетіні анықталды.

I – 10-нан 250^0 С дейін – тозуға кедергі аймағы; II – 325-тен 425^0 С дейін – сополимер деструкциясының тез тозу аймағы; III – 450^0 С жоғары – деструкция аймағы.

Түйін сөздер: метилметакрилат, бутилметакрилат, сополимерлер, дифференциалды сканерлеу калориметриясы (ДСК), термогравиметриялық талдау (ТГА).

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ОПРЕДЕЛЕНИЕ ТЕМПЕРАТУРЫ СТЕКЛОВАНИЯ МЕТАКРИЛАТНЫХ СОПОЛИМЕРОВ

Аннотация. Для этой цели был синтезирован новый сополимер на основе различных ненасыщенных метакриловых мономеров. Синтезированы новые сополимеры разных соотношений ММА-БМА и изучены их физико-химические свойства.

Основные результаты:

- Впервые на основе ММА-БМА сополимеры были синтезированы методом свободно радикальной сополимеризации мономера в исходной смеси в разных массах.
- Термические свойства полученного сополимера были изучены методом ТГТ и ДСК. На основании этих данных была определена температура стеклования.

Температура стеклования (Тс) является одним из важнейших параметров полимеров, которые широко используются в качестве критерия теплоемкости полимеров. Этот метод основан на измерении тепловых потоков, выделяемых при нагревании образцов с определенной скоростью. Этот тепловой поток регистрируется на дифференциальном сканере колориметра. Температура глазирования сополимера находится между значениями индивидуального гомополимера Tsh, полученного на основе этих мономеров, и эта величина варьируется из-за большого количества конкретных мономерных звеньев в сополимере.

Было обнаружено, что температуры стеклования исследуемого сополимера ММА-ВМА составляют 98^0C при 90% (М3), 63^0C при 50% (М2) и 43^0C при 10% (М1). Замечено, что чем выше содержание мономера ММА в сополимере, тем ближе температура стеклования к ПММА. Видно, что значения, определяемые уравнением Фокса, аналогичны экспериментальным значениям.

Этот термогравиметрический анализ (ТГТ) является широко используемым методом, таким как дифференциальный сканирующий калориметрический анализ. Этот метод измеряет изменение массы или массовой доли образца в зависимости от температуры или времени. Этот анализ был выполнен с использованием газообразного азота при постоянном атмосферном давлении и температурном интервале 25-500^0C со скоростью 100^0 C / мин. Работа показывает, что изученные сополимеры разрушены.

Температура стеклования (Тс) постоянно меняется из-за различных соотношений мономеров в полимере. Твердость этих полимеров определяется температурой стеклования Тс, до которой были выполнены следующие расчеты с использованием эмпирического уравнения Фокса.

Рассчитанная температура стеклования (Тс) для таких термических полимеров не является конечной величиной Тс пленки, так как следует учитывать, что при сшивании полимерных цепей ее температура Тс увеличивается.

Термомеханические свойства синтезированного линейного сополимера ММА-ВМА были изучены и данные были использованы для определения термических свойств исходного реагента с использованием ТГТ. Сополимер теряет 1,7% своей начальной массы в интервале 25-2800^0C в парах ММА при 10% (М1) и теряет 10% своей массы в интервале температур 25-2740^0C в парах ММА при 90% (М3). На начальной стадии, когда содержание влаги в образце, температура смесей воды и растворителя повышаются, они быстро разлагаются. А в температурном интервале 280-500^0C теряет вес во второй раз. В то время как первые образцы теряют 98% от общей массы, последние образцы теряют 90% от общей массы. Можно видеть, что максимальная температура разложения сополимера (PDT) также уменьшается с увеличением температуры от 10% до 90%, что указывает на температуру 435^0C, 426^0C, 420^0C. Максимальная температура разложения зависит от структуры полимера. Полученные результаты соответствуют тепловым механизмам изменения метакрилата, приведенным в работе.

На основании данных ТГА и ДСК процесс разложения исследуемых систем под действием температуры можно разделить на 3 области:

I – от 10 до 250^0 C – область, устойчивая к старению;

II – от 325 до 425^0 C – область быстрого старения с деструкцией сополимера;

III - выше 450^0 C – область деструкции.

Разложение ММА:БМА идет преимущественно по механизму сополимеризации, а также сопровождается разрушением боковых заместителей, часть метакриловых звеньев в сополимере разлагается через разрушение боковых эфирных групп.

Ключевые слова: метилметакрилат, бутилметакрилат, сополимеры, краска, пленка, прочность на растяжение, относительное удлинение при разрыве, твердость по Шору.

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CARBOXYLATION OF HYDROXYARENES WITH POTASSIUM ETHYL CARBONATE

Abstract. The influence of the conditions for carrying out the carboxylation reaction of phenol and its derivatives (petrochemical products) with alkaline salts of alkylcarbonic acids (potassium ethyl carbonate), easily synthesized from carbon dioxide, alcohols and alkaline metal hydroxides, was studied in order to develop new, effective methods for producing practically valuable p-hydroxybenzoic acid and other hydroxybenzoic acids (a class of compounds having a wide range of biologically active properties and other beneficial properties) is relevant and timely. A new simple and convenient method for the synthesis of p-hydroxybenzoic acid by the reaction of phenol carboxylation with potassium ethyl carbonate has been developed, which allows one to obtain the target product without impurity of o-hydroxybenzoic acid. For the first time, optimal conditions were found for the regioselective p-carboxylation of phenol (pressure of carbon dioxide, temperature and duration of the process) under which the yield of p-hydroxybenzoic acid is 71,0%, and the effect of various substituents in the aromatic ring on the yield of the target products of the carboxylation of phenol derivatives is determined sodium and potassium carbonates. The influence of the nature of the alkyl groups of potassium alkyl carbonates on the carboxylation activity of the latter in the phenol carboxylation reaction was determined. We have studied that temperature has a strong influence on the direction of phenol carboxylation. When carrying out the reaction below 200°C, carboxylation proceeds to the o- and p-positions with the formation of o-hydroxybenzoic and p- hydroxybenzoic acids; the o-isomer predominates (44,9-66,7%). When carrying out the reaction above 200°C, only p-hydroxybenzoic acid is formed without an impurity of o-hydroxybenzoic acid.

Key words: carboxylation, hydroxyarenes, hydroxybenzoic acid, carbon dioxide, potassium ethyl carbonate, p-hydroxybenzoic acid.

Introduction. Carbon dioxide in the future may become one of the most important sources of carbon raw materials for chemical synthesis [1,3]. Oil and coal reserves are gradually being depleted. After oil and coal natural gas reserves will also run out. Carbon dioxide reserves are almost inexhaustible. The most promising sources of CO_2, as carbon raw materials can be waste gases of chemical industry enterprises and power plants, as well as natural gas deposits, in some of the which the CO_2 content reaches 30%. Carbon dioxide recovery in chemical synthesis is also of great environmental significance, since it is one of the ways to reduce CO_2 emissions, the main component greenhouse gases into the atmosphere [2].

Use of carbon dioxide as a carbon source in organic synthesis is an urgent problem of modern organic chemistry. The huge interest in this problem is evidenced by the ever-accelerating growth of scientific publications on this subject. Analysis of the available data shows that carbon dioxide, contrary to popular beliefs, is able to enter into various reactions. At the same time, a small number of CO_2 based reactions have been implemented on an industrial scale, which is primarily due to the insufficient development of carbon dioxide chemistry at the moment [4-6].

In the Republic of Kazakhstan, the development of petrochemistry is very acute. All three oil refineries existing in the republic do not have the so-called petrochemical wing-petrochemical plants based on petroleum hydrocarbons and carbon oxides. The country also has an acute issue of developing industrial fine organic synthesis to meet the needs of the population and the national economy in such useful organic products as medicines, food preservatives, detergents, etc.

Oxybenzoic acids are widely used o-hydroxybenzoic acid (salicylic acid) and its derivatives exhibit biological activity and are used as pharmaceuticals (aspirin, p-aminosalicylic acid, etc.) [8,9]. o-Oxybenzoic acid is used to obtain polymeric materials and liquid crystal polyesters with high heat resistance [10,11].

The most common industrial method for the synthesis of hydroxybenzoic acids is carboxylation of phenol with carbon dioxide under pressure (Kolbe – Schmidt reaction) [7,12,13]. One of the big disadvantages of this method is the need for preliminary synthesis of dry sodium (potassium) phenolates, which is associated with great experimental difficulties: distillation of water in a vacuum and the extreme hygroscopicity of dry alkali metal phenolates [14-16]. In connection with the foregoing, it is of interest to synthesize oxybenzoic acids that exclude the use of alkali metal phenolates. One of these methods is the carboxylation of phenol with alkaline salts of alkyl carbonic acids.

It is known that in the Kolbe – Schmidt reaction, the use of potassium phenolate promotes the formation of p-hydroxybenzoic acid [17-18]. In order to verify the effect of the nature of the alkaline metal in the starting salts of carbonic esters on the direction of carboxylation, the phenol carboxylation reaction with potassium ethyl carbonate was studied [19-20].

Experimental part. The reagents used were dry sodium and potassium carbonates, reactive phenol by Sigma Aldrich. The experiments were carried out without the use of solvents in gaseous carbon dioxide. The individuality of the synthesized products was determined by physicochemical constants (mp), the study of mixed samples (absence of melting temperature depression) with pure reactive samples of the reaction products, as well as according to IR and PMR spectroscopy. IR spectra were recorded on a Nicolet 5700 single-beam infrared spectrometer of Thermo Electron Corporation (USA) in the region of 400–4000 cm $^{-1}$. NMR1H spectra were recorded on a Brucker DPX 400 instrument, operating frequency 300 MHz. Tetramethylsilane was used as the standard. The chemical used were dry potassium ethyl carbonate, synthesized by reacting carbon dioxide with potassium ethyl carbonate as described in [20], and phenol. The experiments were conducted in the solvent free mode in a medium of gaseous CO_2. The IR spectra were recorded on a Mattson SatelliteFTIR Fouriertransform IR spec trometer in the frequency range of 4000–400 cm–1 and the NMR spectra were recorded on a Bruker DPX 400 instrument operating at a frequency of 300 MHz.

Synthesis of salicylic acid. A glass reactor placed into a steel autoclave and equipped with a stirrer, electric heating, and carbon dioxide gas inlet (outlet) fittings, was loaded with 2,3 g (0,025 mol) of phenol and 3,46 g (0,027 mol) of potassium ethyl carbonate (reactants ratios was [phenol] : [potassium ethyl carbonate] = 1 : 1,1); the autoclave was pressurized; purged twice with CO_2 to remove air and filled with CO_2 to a pressure of 10 atm; after which stirring and heating were switched on. The reaction mixture was heated to 215°C over 6 h (at a heating rate of 40°C/h) and held at this temperature and a CO_2 pressure of 10 atm for 5 h. After that, stirring and heating were stopped and the autoclave was cooled down to room temperature. The reaction mixture was treated with water. The obtained aqueous solution was extracted with ether to separate unreacted phenol. Unreacted phenol was recovered from the ether phase. The product (p-hydroxybenzoic acid) was isolated by acidifying the aqueous phase with hydrochloric acid to afford 2,46 g (71,0%) of p-hydroxybenzoic acid; melting temperature 203-205^{0}C ; after recrystallization (water) at melting point 214-216^{0}C.

Synthesis of salicylic acid 7.05 g (0.075 mol) of phenol and 2.8 g (0.025 mol) of sodium ethyl carbonate are charged into a glass liner placed in a steel autoclave equipped with a stirrer, electric heating and the inlet (outlet) of carbon dioxide gas. The autoclave is sealed, flushed twice with carbon dioxide to remove air, and then filled with carbon dioxide to a pressure of 10 atm, include stirring and heating. The temperature of the reaction mixture is raised to 160 ° C over 4 hours, and at this temperature and a carbon dioxide pressure of 10 atm, it is held for 1 hour. After this, stirring and heating are stopped, the autoclave is cooled to room temperature. The reaction mixture is treated with water. The aqueous phase is extracted with toluene to separate unreacted phenol. The reaction product (salicylic acid) is isolated by acidification of the aqueous phase with hydrochloric acid. 3 g (86.0%) of salicylic acid are obtained; so pl. 154-155^{0}C.

It should be noted that at present the properties of alkaline salts of alkyl carbonic acids have been studied very little. They are difficult to clean white crystalline substances, extremely poorly soluble in many organic solvents (ether, ethanol, acetone, benzene, etc.); they do not have a clear melting point: when heated to 380-400^0 C, they slowly decompose without melting with the release of gaseous products.

We also use potassium ethyl carbonate (as a carboxylating agent), synthesized by bubbling carbon dioxide through a solution of potassium hydroxide in ethanol, for the fixation and storage / disposal of carbon dioxide from industrial waste gases. The method for the synthesis of potassium alkyl carbonates from potassium metal is quite convenient for their synthesis in laboratory conditions, it is not suitable for industrial production due to the explosiveness of the mixture of hydrogen released at the stage of production of alcoholates with air. In [21], a method was described for producing potassium ethylate by the interaction of potassium hydroxide with ethanol in simple equipment that almost completely transfers potassium hydroxide to potassium ethylate when using quicklime as a water-removing agent. Based on the improvement of the method for producing potassium ethylate described in [21], we developed a simple and convenient method for the synthesis of potassium and sodium ethylates from ethanol and the corresponding sodium and potassium hydroxides (reaction 2) [22]. This reaction proceeds with the release of water; therefore, quicklime was used as a dewatering agent to shift the equilibrium to the right.

$$MOH + C_2H_5OH \rightleftharpoons C_2H_5OM + H_2O \qquad (2)$$

$$M = Na, K$$

Potassium ethylate is synthesized in two vessels interconnected with two tubes (flasks A and B), and potassium ethylate is obtained from caustic potassium and ethanol in vessel A, and alcohol with quicklime is drained in vessel B (Fig. 1). Both vessels are heated to a boil of ethanol. Vapors of alcohol and water liberated during the reaction (azeotropic mixture) from vessel A flows into the refrigerator, condensate from which flows through the alcohol gate to the second vessel B, where the wet alcohol is dried with quicklime, after which the alcohol vapor flows through the other tube into vessel A, continuously bubbling through an alcoholic solution of potassium hydroxide and potassium ethylate. The process is carried out for 3-7 hours at a ratio of reagents [KOH]: [C_2H_5OH] = 1: 8.

The developed simple, industrially applicable method for the production of potassium and sodium ethylates was used by us for the synthesis of potassium ethyl carbonate and sodium ethyl carbonate. The latter are used as carboxylating reagents of hydroxyarenes for the synthesis of hydroxyaromatic acids.

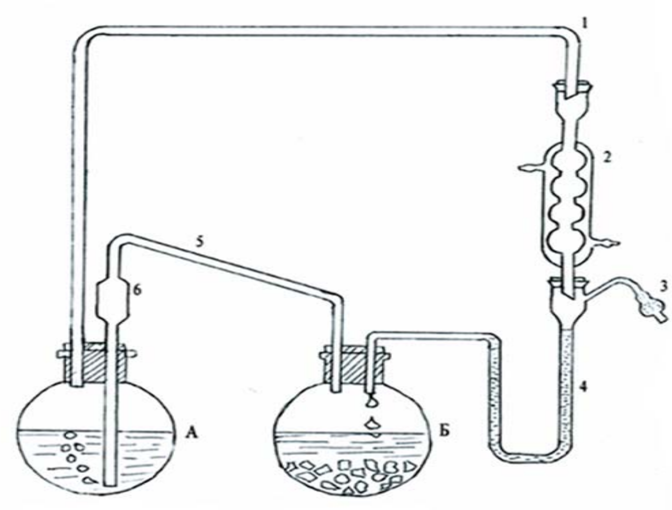
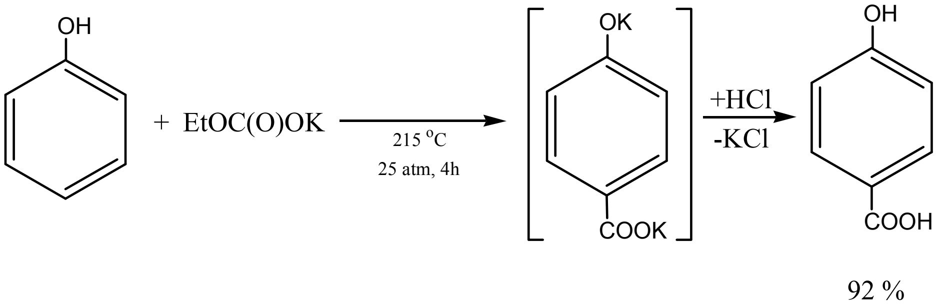


Figure 1 - Installation for the synthesis of sodium ethoxide

A and B - reaction vessels (flasks) 1 - tube for distillation of the azeotropic mixture, 2 - refrigerator, 3 - calcium chloride tube, 4 - alcohol shutter, 5 - tube for distillation of dried alcohol, 6 - anti-expansion

Results and discussion. The effect of phenol carboxylation with potassium ethyl carbonate on the course of the reaction and the yield of products was studied. The pressure of the gaseous medium (carbon dioxide) of the reaction (T = 215^0C, τ = 7 h (6 h rise to 215^0C + 1 h exposure at this temperature); [phenol]: [potassium ethyl carbonate] = 1: 1,1) has a significant effect the output of p-hydroxybenzoic acid; the optimal pressure of the gaseous medium is 25 atm. Under the same conditions, the influence of temperature (from 130 to 220^{0}C) on the course of the phenol carboxylation reaction with potassium ethyl carbonate at a CO_2 pressure of 25 atm was studied.



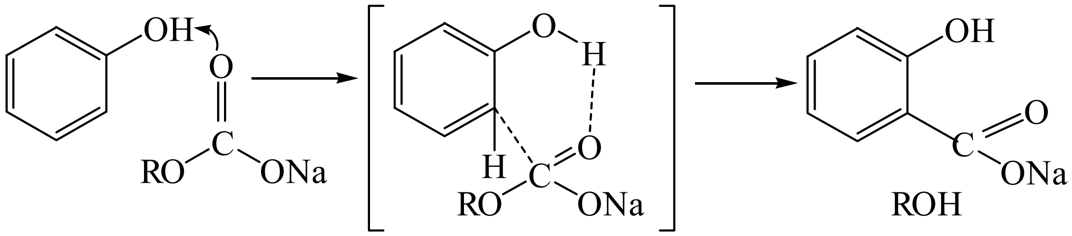
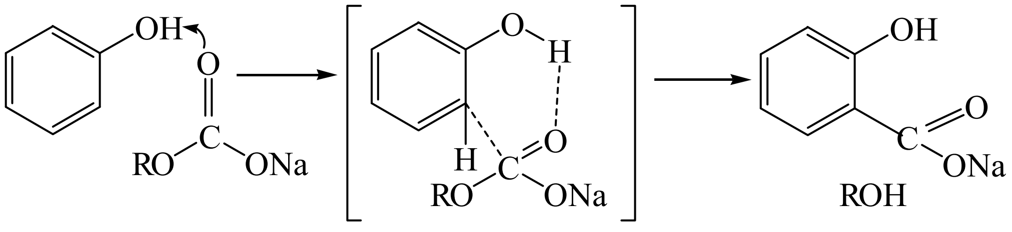


Figure 2 - The mechanism of the phenol carboxylation reaction with sodium and potassium ethylcarbonates

The following mechanism of the phenol carboxylation reaction with sodium and potassium ethyl carbonates can be suggested (Scheme 1). Apparently, the reaction proceeds through the initial association of metal alkyl carbonates through the oxygen of the carbonyl group with phenolic hydroxyl. Then, the metal-alkyl carbonate molecule activated in this way electrophilically attacks the o-position of the starting phenol with stabilization of the transition state by the formation of a six-membered ring. At lower temperatures (<200° C), carboxylation to the o-position takes place both in the case of sodium alkyl carbonate and potassium ethyl carbonate. At high temperatures (> 200° C) in the case of potassium ethyl carbonate, due to the larger volume of potassium ion, stabilization due to the formation of an intermediate six-membered state becomes impossible and carboxylation proceeds to a less spatially shielded p-position with the formation of p-hydroxybenzoic acid.



Scheme 1

Carboxylation at temperatures below 200^{0}C occurs with the formation of salicylic acid. The highest yield (78%) of salicylic acid is observed at 180^{0}C. With a further increase in temperature to 195^{0}C, the yield of salicylic acid decreases to 45%, while the yield of p-hydroxybenzoic acid gradually increases to 20%. A subsequent increase in temperature leads to the formation of only p-hydroxybenzoic acid, the maximum yield of which (92%) is observed at a temperature of 215^{0}C; a further increase in temperature decreases the yield of p-hydroxybenzoic acid, apparently due to a possible decarboxylation reaction.

Thus, a simple and convenient method for the synthesis of p-hydroxybenzoic acid by the reaction of phenol carboxylation with potassium ethyl carbonate has been developed, which allows one to obtain the target product without impurity of o-hydroxybenzoic acid. The optimal process conditions were found:

P_{CO_2} = 2.5 MPa, T = 210^{0}C, τ = 7 hours, at which the yield of p-hydroxybenzoic acid is 71.0%. It should be noted that all previously known methods for the synthesis of p-hydroxybenzoic acid are based on the reaction of carboxylation of potassium phenolate with carbon dioxide (Kolbe-Schmidt synthesis), in which a mixture of o- and p-isomers is always formed; in this case, as a rule, the main reaction product is o-hydroxybenzoic acid.

The possibility of using alkaline salts of alkyl carbonic acids as a carboxylating reagent in the carboxylation of hydroxyarenes became known after the appearance of I. Jones in 1958 about the carboxylation of sodium phenol and potassium ethyl carbonate [26]. After that, starting in 1969, a number of works by Japanese researchers [23–25] appeared on the use of alkaline salts of alkyl carbon acids for the carboxylation of phenol and its derivatives.

The observed temperature dependence of the yield of phenol carboxylation reaction products with potassium ethyl carbonate differs from that of phenol carboxylation reaction with sodium ethyl carbonate. We believe that such a strong difference can be caused not only by the previously described [27, 28] thermal rearrangement of the initially formed alkaline salt of salicylic acid to the salt of p-hydroxybenzoic acid at high temperature. Apparently, here a certain role is played by both the nature of the alkali metal (Na, K) in the initial salts of ethyl carbonic acid, and the mechanism of this reaction.

Conclusion. In summary, it has been shown that potassium ethyl carbonate can be used as a carboxylating agent in the carboxylation reaction of phenol. It has been found that the carboxylation of proceeds regioselectively with the formation of acid p-hydroxybenzoic acid. Optimum conditions for con ducting this reaction have been found. The developed simple and convenient methods for the synthesis of p-hydroxybenzoic acids can be used for their industrial manufacturing. Carboxylation of hydroxyarenes (phenols and its derivatives) with alkali salts of alkyl carbon acids (metal alkyl carbonates) is a convenient method for the synthesis of hydroxy aromatic acids. Since the appearance of the first report in this field in 1957 (I. Jones) to date, there have been relatively few publications on the carboxylation of organic compounds with metal alkyl carbonates. The analysis of the known published data on the use of alkali salts of alkylcarboxylic acids for carboxylation of hydroxyarenes shows the undoubted promise of the method for the synthesis of hydroxyaromatic acids, which are widely used, by the carboxylation of hydroxyarenes with metal alkyl carbonates.

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КАЛИЙ ЭТИЛКАРБОНАТЫМЕН ГИДРОКСИАРЕНДЕРДІ КАРБОКСИЛДЕУ

Аннотация. Көмірқышқыл газынан, спирттен және сілтілік металл гидроксидтерінен оңай синтезделген алкилкарбон қышқылының сілтілі тұзымен (калий этил карбонаты) фенол мен туындыларының карбоксилдену реакциясын жүргізу жағдайының әсері зерттелді. П-гидроксибензой қышқылын және басқа да гидроксибензой қышқылдарын (биологиялық белсенді қасиеті мен басқа да пайдалы қасиетінің кең спектріне ие қосылыс класы) өндірудің тиімді әдістері өзекті және маңызды болып саналады. Гидроксибензой қышқылын синтездеудің жетілдірілген әдісі көптеген параметрлерді (қысым, температура, реакция уақыты, реактивті заттар компоненттерінің қатынасы) оңтайландыруға мүмкіндік береді, тезірек, жеңіл және арзан және өнім шығымын көбейтеді. Фенолды калий этил карбонатымен карбоксилдеу реакциясымен п-гидроксилбензой қышқылын синтездеудің жаңа қарапайым және ыңғайлы әдісі жасалды, ол мақсатты өнімді о-гидроксилбензой қышқылын қоспасыз алуға мүмкіндік береді. Мақсатқа жету үшін және алға қойған міндеттерді шешу үшін келесі тапсырмалар орындалды: гидроксиарен мен оның туындыларын металл алкилді карбонаттармен карбоксилдену реакциясының оңтайлы параметрлерін табу; түрлі қысымда, температурада, реакция ұзақтығында және реактивтердің түрлі арақатынасында гидроксиарендердің сілтілі алкилді қышқыл тұзымен карбоксилдену реакциясының параметрлерін зерттеу. Технологиялық үдерістің оңтайлы параметрлеріне қол жеткізгенде мақсатты өнім, гидроксиароматикалық қышқылдардың шығымы артады деп болжанды.

Алғаш рет фенолдың региоселективті п-карбоксилденуінің оңтайлы жағдайы анықталдың (көмірқышқыл газының қысымы, температура және үдерістің ұзақтығы), бұл кезде п-гидроксибензой қышқылының шығымы 71,0% құрайды, сонымен қатар фенолды туындылардың карбоксилдену мақсатты өнімдері шығымында хошиісті сақинадағы түрлі алмастырғыш әсері натрий және калий карбонаттары негізінде анықталады. Фенол карбоксилдеу реакциясындағы калий алкилді карбонаттарының алкил топтары соңғысының карбоксилдену белсенділігіне әсері анықталды. Біз температура фенолдың карбоксилдену бағытына қатты әсер ететіндігін зерттедік. Реакцияны 200 °С-тан төмен жүргізгенде карбоксилдену о- және п-позицияларда о-гидроксибензой және п-гидроксибензой қышқылдарының түзілуі негізінде жүреді; о-изомер басым (44,9-66,7%). Реакцияны 200 °С-тан жоғары температурада жүргізгенде тек п-гидроксибензой қышқылы о-гидроксибензой қышқылын қоспасыз түзеді.

Калийэтилкарбонат және натрийэтилкарбонат гидроксиарендердің (фенолдар мен оның туындылары) тиімді карбоксилдеуші реагенттері екендігі анықталды. Гидроксибензой және гидроксинафтой қышқылдарын синтездеудің негізгі өнеркәсіптік тәсілі бірқатар кемшілігі бар көміртегі диоксиді қысымымен (Кольбе-Шмидт реакциясы) сілтілі металдардың тиісті феноляттары мен нафтоляттарын карбоксилдеу болып саналады.

Гидроксиарендердің карбоксилдеу реакциясымен гидроксиароматикалық қышқылдарды және оның туындыларының алкил көмір қышқылының сілтілік тұзы арқылы алудың зертханалық регламенті әзірленді, ол «Мұнайхимиялық синтездер» курсы аясында зертханалық және тәжірибелік жұмыстарды жүзеге асыруда, сондай-ақ әл-Фараби атындағы ҚазҰУ химия факультетінің «Органикалық заттардың химиялық технологиясы» және «Мұнайхимия» мамандығы бойынша дипломдық және магистрлік жобаларды орындау кезінде оқу бағдарламасында қолдануға болады.

Түйін сөздер: карбоксилдеу, гидроксиарендер, гидроксибензой қышқылы, көмірқышқыл газы, калий этил карбонаты, п-гидроксибензой қышқылы.

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КАРБОКСИЛИРОВАНИЕ ГИДРОКСИАРЕНОВ ЭТИЛКАРБОНАТОМ КАЛИЯ

Аннотация. Изучено влияние условий проведения реакции карбоксилирования фенола и его производных (продуктов нефтехимии) щелочными солями алкилкарбоновых кислот (калий этилкарбонат), легко синтезируемых из диоксида углерода, спиртов и гидроксидов щелочных металлов. Эффективные способы получения практически ценной п-гидроксибензойной кислоты и других гидроксибензойных кислот (класс соединений, обладающих широким спектром биологически активных свойств и других полезных свойств) актуальны. Разработанный способ синтеза гидроксибензойных кислот позволяет значительно быстрее, проще и дешевле оптимизировать большинство параметров (давление, температура, продолжительность реакции, соотношение компонентов реагирующих веществ) и максимально увеличить выход продуктов. Разработан новый простой и удобный метод синтеза п-гидроксибензойной кислоты по реакции карбоксилирования фенола с этилкарбонатом калия, который позволяет получить целевой продукт без примеси о-гидроксибензойной кислоты. Для максимального достижения цели и раскрытия проблем были выполнены следующие задачи: нахождение оптимальных параметров проведения реакции карбоксилирования гидроксиаренов и их производных металлалкилкарбонатами. Исследование параметров проведения реакции карбоксилирования гидроксиаренов щелочными солями алкилугольных кислот при различных давлении, температуры, продолжительности реакции и при разных соотношениях реагентов. При достижении оптимальных параметров процесса ожидается повышение выхода целевых продуктов – гидроксиароматических кислот.

Впервые были найдены оптимальные условия для региоселективного п-карбоксилирования фенола (давление диоксида углерода, температура и продолжительность процесса), при котором выход п-гидроксибензойной кислоты составляет 71,0%, а также влияние различных заместителей в ароматическом кольце по выходу целевых продуктов карбоксилирования фенольных производных определяется карбонаты натрия и калия. Установлено влияние природы алкильных групп алкилкарбонатов калия на карбоксилирующую активность последних в реакции карбоксилирования фенола. Мы изучили, что температура сильно влияет на направление карбоксилирования фенола. При проведении реакции ниже 200 °С карбоксилирование протекает в о- и р-положениях с образованием о-гидроксибензойной и п-гидроксибензойной кислот; преобладает о-изомер (44,9-66,7%). При проведении реакции при температуре выше 200 °С образуется только п-гидроксибензойная кислота без примеси о-гидроксибензойной кислоты.

Установлено, что калийэтилкарбонат и натрийэтилкарбонат являются эффективными карбоксилирующими реагентами гидроксиаренов (фенолов и их производных). Основным промышленным способом синтеза гидроксибензойных и гидроксинафтойных кислот является карбоксилирование соответствующих фенолятов и нафтолятов щелочных металлов под давлением диоксида углерода (реакция Кольбе-Шмидта), имеющий ряд серьезных недостатков.

Разработали лабораторный регламент получения гидроксиароматических кислот реакцией карбоксилирования гидроксиаренов и их производных щелочными солями алкилугольных кислот, который может использоваться в учебной программе при реализации лабораторных и практических работ в рамках курса «Нефтехимические синтезы», а также при выполнении дипломных и магистерских проектов по специальности «Химическая технология органических веществ» и «Нефтехимия» химического факультета КазНУ им. аль-Фараби.

Ключевые слова: карбоксилирование, гидроксиарены, гидроксибензойная кислота, диоксид углерода, этилкарбонат калия, п-гидроксибензойная кислота.

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EFFECTIVE CATALYSTS FOR THE SELECTIVE RESTORATION OF AROMATIC MONO- AND DINITRO COMPOUNDS

Abstract. This article discusses the issues of catalytic reduction of aromatic nitro compounds to obtain valuable intermediate and final products-aromatic amines. The most important method for producing amines from nitro compounds is catalytic reduction with hydrogen on catalysts. The article describes in detail the choice of catalysts for hydrogenation of nitro compounds at atmospheric and high hydrogen pressure. Studies of hydrogenation reactions of aromatic nitro compounds on nickel, copper and iron catalysts are discussed. Hydrogenation of aromatic nitro compounds on catalysts based on palladium, platinum, and rhodium deposited on various carriers, including nanodiamonds, is considered. Catalysts based on supported palladium catalysts with copper additives showed high selectivity in the hydrogenation of nitro groups in nitro compounds with functional groups; and with the addition of platinum and rhodium, during the reduction of both nitro groups and the aromatic ring in nitrobenzene. In the works on the use of nanodiamonds, it was found that catalysts based on platinum and palladium nanoparticles of 4-5 nm in size, fixed on nanodiamonds, were highly active in liquid-phase hydrogenation reactions of nitro compounds under mild conditions. The data described by the authors on theoretical issues and practical problems of catalytic hydrogenation of aromatic nitro compounds are very relevant. The article is based on the analysis of domestic and foreign literature and may be useful to specialists in the field of catalysis.

Keywords: aromatic nitro compounds, catalytic reduction, aromatic amines, selective catalysis, liquid-phase hydrogenation.

Introduction. Nitro compounds are derivatives of hydrocarbons of the general formula R-NO_2 having in their composition a nitro group directly linked to an aliphatic or aromatic radical. Depending on the nature of the hydrocarbon radical “R”, nitro compounds are divided into aliphatic and aromatic. The simplest representative of nitro compounds of the aliphatic series is nitromethane, chemical compound with the formula CH_3-NO_2. Aliphatic nitro compounds are divided into primary, secondary and tertiary. Compounds containing several nitro groups, when heated or detonation decompose with an explosion, therefore many of them found application as explosives. Nitro groups (especially in symmetric trinitro compounds) greatly increase the ability of a carbon atom located in the ortho position to nitro groups to oxidize. The most important property of the nitro group is its ability to be reduced to an amino group. Amines find wide application in the production of various dyes, drugs, corrosion inhibitors, stabilizers, polyurethanes, antiknock additives for gasolines and motor fuels and others [1-4]. Amines are organic compounds that are derivatives of ammonia, in the molecule of which one, two or three hydrogen atoms are replaced by hydrocarbon radicals. A typical representative of a number of aromatic amines is aniline.

In the last 30-40 years, the processes of catalytic reduction of aromatic nitro compounds by hydrogen to amines have practically superseded all other methods for the production of aromatic amines in large-tonnage plants.

Catalysts for nitro compounds hydrogenation. One of the topical areas is the development and investigation of highly efficient and selective catalysts for the hydrogenation of aromatic nitro compounds to the corresponding amines, since amines find wide application in the production of various dyes, drugs, corrosion inhibitors, stabilizers, polyurethanes, antiknock additives for gasolines and motor fuels and others. The reduction of nitro compounds can be carried out in the presence of both homogeneous and heterogeneous catalysts. Solid phase heterogeneous catalysts are widely used in industry. This is due to the difficulty in isolating and regenerating a homogeneous catalyst. Heterogeneous hydrogenation catalysts for aromatic nitro compounds [5] can be divided into the following groups: 1) catalysts containing nickel, copper and noble metals, including blacks; 2) heterogeneous catalysts on a fiberglass woven matrix; 3) heterogeneous catalysts on a metal-polymeric matrix. An important role as a part of the catalyst is played by the carrier. Carriers for catalysts use various carbon carriers: activated carbon, carbon fiber, nanodiamond, fullerene black, as well as various oxides such as Al_2O_3, SiO_2, $CaCO_3$; polymeric, fiberglass and other matrices. Recently, carbon nanomaterials have been used as a catalyst carrier: fullerenes and fullerene black, carbon nanotubes and nanofibres, nanodiamonds and graphene materials. Particular interest is given to nanodiamonds (ND) and graphene-like materials. ND have unique properties: high strength, high specific surface with different functional groups located on it, which can be easily modified.

The hydrogenation of nitrobenzene is one of the model reactions for studying the activity of samples of potential catalysts. Most studies of the reduction of nitro compounds, as shown by the analysis of patents and literature data, are carried out using nickel catalysts [6]. The most common catalyst for the reduction of various objects, including nitro compounds, is currently Raney nickel. Skeletal nickel catalyst was developed by M. Raney in 1924-1925. Raney Nickel, obtained from alloys of Ni with Mg or Zn, has a much lower catalytic activity in most reactions. The skeletal nickel catalyst has a structure of metallic nickel with crystal sizes of 4-8 nm. It varies little with prolonged storage under a 1% solution of NaOH. The magnitude of nickel crystals depends on the leaching temperature, increasing with the growth of the latter. This is very important, since for each hydrogenated compound there is an optimal crystal size, which, for example, for the reduction of NB is 5.9 nm, for phenol hydrogenation - 3.0 nm. The reactivity of nickel is heavily influenced by leaching conditions, in particular temperature, which determine both the activity of the surface and the strength of hydrogen retention.

The supported catalysts are widely used in processes with both a mobile and a stationary catalyst bed. A very important role in their performance (running time, longevity, activity, mechanical strength, etc.) is played by the nature of the carrier. The most common among the latter are silicon and aluminum oxides. As in the production of Raney nickel, the production of supported nickel catalysts is determined by the conditions of metal deposition, the reduction temperature of the catalyst, and the degree of saturation with hydrogen. In the work [7], bimetallic $Fe\text{-}Cu/SiO_2$ systems were proposed for the process of liquid-phase hydrogenation of p-dinitrobenzene to p-phenylenediamine.

Palladium is of particular interest for theoretical chemistry due to its position in the periodic table: it is the only element with the electronic configuration $d^{10}s^0p^0$, which can vary depending on the type of chemical binding and determines the specific behavior of this metal. It was shown that catalysts based on deposited palladium catalysts with copper additives have shown high selectivity in hydrogenation of nitrogroups in nitro compounds with functional groups. Thus a catalyst with composition Pd-Cu(9:1)/sibunit, Pd-Cu(8:2)/sibunit was active in a case of selective obtaining 4,4’-diaminostilbene-2,2’-disulfonic acid (DAS) by hydrogenation of 4,4’-dinitrostilbene-2,2’-disulfonic acid (trans-DNS) in water. DAS can be used to produce phosphorescent whiteners for fibers and paper. Catalysts based on supported palladium catalysts with the addition of platinum and rhodium showed high selectivity during hydrogenation during the reduction of both nitro groups and the aromatic ring in nitrobenzene using iso-propanol and ethanol as solvents [2, 3, 8]. The role of palladium in catalytic reactions is largely determined by the different structure of active sites on its surface. As is known, the first stage of catalytic hydrogenation is the adsorption of hydrogen and substrates on the surface of the catalyst [9-12]. Regarding the forms and methods of activating hydrogen on the active centers of hydrogenation catalysts in the literature there are different viewpoints. The relative inertness of hydrogen is due to the high dissociation energy of its molecule (432.9 $kJ\times mol^{-1}$). The bond between the H_2 atoms can be weakened by donor-acceptor coordination with a metal in which hydrogen can act as both a donor and an electron acceptor to form charged particles of $H_2^{\delta+}$ and $H_2^{\delta-}$, whose dissociation energies (259.6 and 77.9 $kJ\times mol^{-1}$, respectively) is much lower than the dissociation energy of the H_2 molecule. On the metal surface there are at least four hydrogen forms having different reactivity in liquid-phase hydrogenation processes: weakly bound molecular $H_2^{\delta+}$, as well as tightly atomic hydrogen: ionized $H_2^{\delta+}$, $H_2^{\delta-}$ and unionized H between which is set the adsorption equilibrium [13].

The values of adsorption, charges, binding energies and the ratio of different forms of hydrogen depend both on the nature and dispersity of the catalyst, and on the nature of the solvent. In addition to these forms, dissolved hydrogen is present in the volume of the metal, which penetrates into the crystal lattice of palladium through sites adsorbing weakly bound molecular forms (adsorption heat of 7 $kJ\times g\text{-}atom^{-1}$). Calculation of the thermal effects of all stages of hydrogen sorption based on the results of the microbalance experiment showed that the dissolution of hydrogen in palladium is energetically more favorable (activation energy 15 $kJ\times g\text{-}atom^{-1}$) than its migration along the surface to centers with a higher heat of adsorption (activation energy 55 $kJ\times g\text{-}atom^{-1}$). During dissolution, a multicenter bonding of hydrogen to palladium can take place, in particular, in the case of the Pd/Al_2O_3 catalyst, up to 5 hydrogen atoms can be adsorbed on one Pd atom.

The behavior of palladium in catalytic processes is associated with different geometric structures of the active centers of its surface. According to D.V. Sokolsky [5, 6, 13], hydrogen on the surface of metals exists in a “predissociative form”, in which the H-metal bond is stronger than the H-H bond. The results of quantum chemical calculations, which were carried out later, are consistent with this statement. The choice of the optimum catalysis in the case of catalytic hydrogenation can be solved with its preliminary electrochemical characteristics. The measurement of the potential of the catalyst immediately gives an answer to the question of the type of reaction. Thanks to the application of electrochemical methods, developed by the catalytic school of D.V. Sokolsky, it became possible to determine the concentrations of reactants on the surface of catalysts during the reaction, of particular importance in the practice of catalytic hydrogenation has been the application of these methods to powder catalysts. The method of liquid hydrogenation is now one of the most developed methods in the theoretical and practical relation. In contrast, the gas-phase reduction of aromatic nitro compounds requires the use of high temperatures to ensure the evaporation of the nitro compounds. Solvent can influence both for the rate, and the reaction mechanism. Rate of diffusion depends on viscosity of solvent. Rates of the chemical reactions can sufficiently change depending on the solvent nature. A high degree of chemo-, regio-, stereoselectivity of catalysts in the reactions of hydrogenation is very important. Catalysts based on metals of the platinum group: metal black and supported catalysts have found wide application for the production of amines. Catalytic systems based on platinum group metals deposited on various sorbents reveal higher activity and stability than nickel catalysts. In the earliest works (50-70 years of XX century) the catalyst, regardless of its composition, was used in amounts equal to or exceeding several times the amount of hydrogenated nitro compound. It should be noted that the black metal due to their properties, did not find practical application in the production of amines. At the same time, platinum metals deposited on various carriers, even at low contents, show high activity and selectivity of action during the reduction of aromatic nitro compounds.

Despite the high cost, the catalysts based on platinum group metals are widely used in the hydrogenation of organic compounds, in particular, for the production of aromatic amines from the corresponding nitro compounds. A special role in this is played by the catalysts of the platinum group deposited on various carriers [8, 14]. The reduction of 3,4-dichloronitrobenzene in the presence of iridium and platinum catalysts was studied and it was established that the limiting stage of the process is the step of converting the corresponding arylhydroxylamine into an amino compound. The orders of the reaction along the substrate and hydrogen are calculated, and the optimum process conditions are determined.

Platinum and palladium catalysts deposited on coal showed high activity and stability in the reduction of nitrobenzene, nitroanilines, p- and o-nitrophenols and other nitro compounds with various substituents. Palladium-containing catalysts differ significantly in properties from catalytic systems based on other metals of the platinum group, as well as Ni or Cu. Pd-based catalysts are one of the most effective catalytic systems for the hydrogenation of double (also conjugated) and triple bonds. In cases where it is necessary to hydrogenate only nitro groups in aromatic nitro compounds, without affecting the double bonds of the aromatic ring, it is necessary to use Pd-systems.

To improve the processes of organic and inorganic synthesis, catalysts based on rare-earth elements are increasingly being used. Rare-earth elements are used as an active phase, promoting additives, and their oxides are used as a carrier. In some works [14, 15] it is pointed out that one of the directions of use of rare and platinum metals is associated with the development of catalysts for various purposes. For example, deep oil processing involves a variety of catalytic processes using Re, Pt, Pd-containing catalysts. Hydrogenation in the liquid phase of nitrobenzene, o-nitroanisole, p-nitrotoluene, p-nitrophenol, chloronitrobenzene, 1,3,5-trinitrobenzene in Pd and Pt catalysts with rare earth metal oxide additives was studied. The highest process speed was detected using catalysts with additives Gd_2O_3, Tb_2O_3, Dy_2O_3. It was found that the activity of 1% Pt/Gd_2O_3 catalyst exceeds the activity of the catalyst 1% Pt/Al_2O_3 by 3.5 times, and the activity of 1% Pt/Sm_2O_3 catalyst is higher than the activity of 1% Pt/Al_2O_3 by 3.2 times. Authors found that the activity of platinum-based catalysts containing Eu_2O_3 and Sm_2O_3 in the hydrogenation of nitrobenzene by a potentiometric method was studied. Analysis of the products of the hydrogenation reaction of nitrobenzene on 1% Pt catalysts containing oxides of Eu_2O_3, Sm_2O_3 and Al_2O_3 as carriers by gas-liquid chromatography showed the presence of only one product, aniline, which indicates a high selectivity of hydrogenation. Metal-containing graphene materials proved to be catalytically active, stable and selective in hydrogenation reactions. It is of interest to obtain Pd-containing catalysts based on nanodiamonds and amine-functionalized graphite oxide and to study their catalytic properties in model hydrogenation reactions of compounds with different chemical bonds (nitro group, > C = C <and > C = N- bonds) and also to compare the obtained characteristics with the catalyst on activated carbon prepared by a similar procedure. The $Pt/TiO_2/RGO$ catalyst in the hydrogenation of nitrobenzene without a solvent showed high selectivity and activity (TOF = 59,000 h^{-1}) as compared to Pt/TiO_2 and Pt/RGO in 2.6 and 1.7 times, respectively. In addition, the catalyst can be reused for six times without loss of activity. The authors conclude that the catalyst structure is stable. In comparison, Pt/TiO_2 catalytic activity decreases by about 40% already in the second cycle, but Pt/RGO retains good catalytic activity after three cycles of use in hydrogenation. A study of the catalytic properties of Pt/NB and Pd/ND (ND-nanodiamonds) in the hydrogenation of NB showed that the catalysts have high activity and stability, as well as selectivity: aniline is the only reaction product (no by-products formed, which was confirmed analysis of reaction mixtures by gas chromatography) [16-19] (fig.1). Physicochemical analyzes of carriers (ND, activated carbon of M200 grade) and catalysts based on them (1 wt% Pd/Nd, 1 wt% Pd/C) by SEM, energy dispersive X-ray spectroscopy (EDX) were carried out, as well as the XPS. The structure of the used carriers was used by the SEM method: M20 activated carbon (fig.2a) and ND (fig.2b). In fig. 2b it is visible that the structure of ND represents fractal system with various size of separate grains whereas the structure of activated carbon (fig.2a) consists of separate graphite flakes of various forms and the sizes.

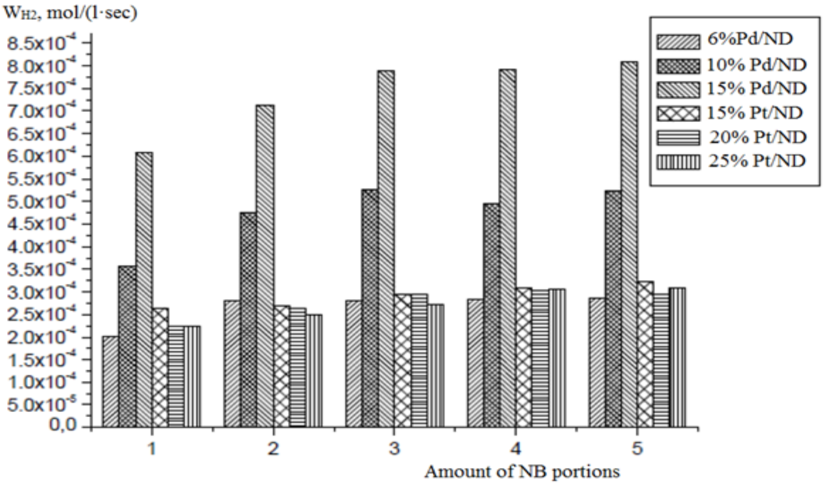
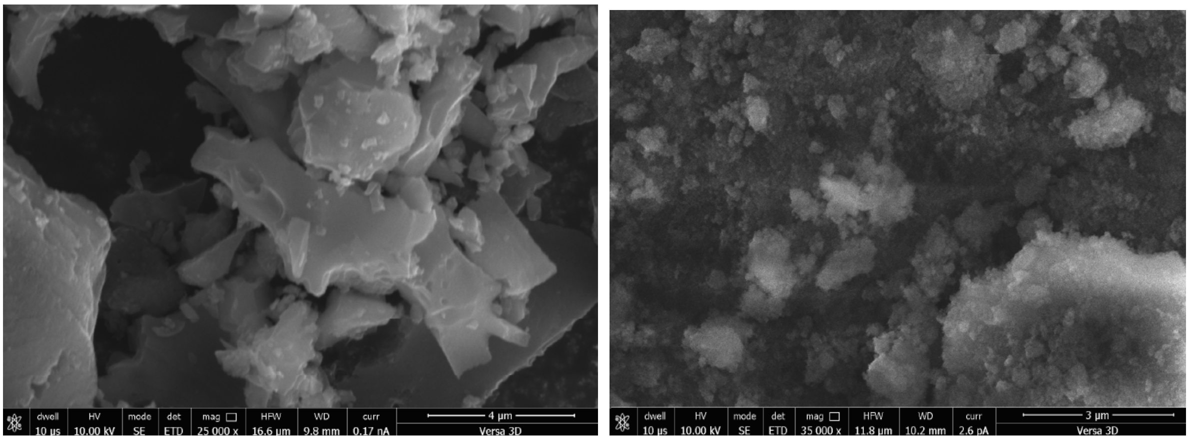


Figure 1 - Velocity of hydrogenation reaction of nitrobenzene

Comparing the results of the analysis of catalysts, it can be stated that palladium fixed to ND does not wash off during the reaction from the carrier, whereas, in the case of Pd/C, metal losses amounted to almost 50% of the initial content. This may be the result of the participation of nitrogen-containing groups of ND (amino or amide) in the process of palladium fixation. Indeed, in the XPS spectra before and after the reaction in the presence of Pd/ND the presence of nitrogen is fixed, while the Pd/C is not. In Pd/C part of the metal (7-9%) is in places inaccessible to the reductant and therefore remains inactive. After the reaction in both catalysts, the main peaks shift both $Pd_3d_{5/2}$ and $Pd_3d_{3/2}$ towards higher binding energies, apparently due to partial oxidation of the metal centers by formation of surface complexes with charge transfer from palladium to nitrobenzene. In addition, the nature of the carrier affects the binding energy of the palladium electrons. In the case of ND, this value at $Pd_3d_{5/2}$ level is 335.0 eV, whereas for coal it is 335.3 eV.



a b

Figure 2 - SEM image of activated carbon M200 (a) and ND (b)

Properties of 1 wt. % Pd/ND and 1 wt. % Pd/C were studied in the hydrogenation reactions of nitrobenzene and its para-substituted analogues (p-nitroaniline, p-nitrophenol, p-nitrobenzoic acid), as well as cyclohexene, hexene-1, allyl alcohol, acrylic, methacrylic, crotonic and cinnamic acids (fig.3). The proposed substrates differ in the nature and location of the groups being reduced, which makes it possible under comparable conditions to trace the influence of the nature of the catalyst on the kinetic parameters of hydrogenation, and also to study the effect of the substituent in nitroarenes on the rate of reduction of the NO_2 group. In the hydrogenation of nitrobenzene and its para-substituted analogs (p-nitroaniline, p-nitrophenol, p-nitrobenzoic acid), 1 wt. % Pd/ND is more active than 1 wt. % Pd/C. Apparently, the NO_2-group is sterically more accessible for contact centers of the catalyst of 1 wt. % Pd/ND and worse for catalyst 1 wt. % Pd/C, which can be explained by the strictly ordered nanoscale structure of ND in comparison with activated carbon, in the structure of which there are pores of various diameters [20], where, apparently, a part of palladium is fixed, thereby becoming inaccessible to the substrate molecules. However, judging by the XPS data, the proportion of palladium that is not reduced does not exceed 7-9%. The hydrogenation of nitrobenzene is most easily carried out for each of the catalysts.

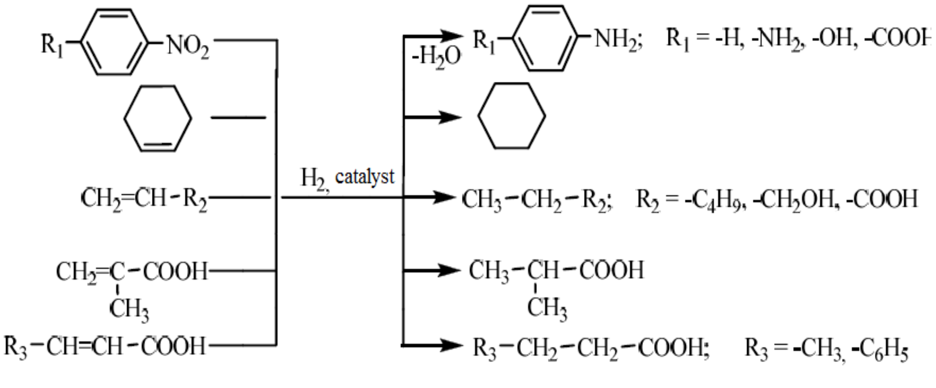


Figure 3 - Scheme of substrate transformation in model hydrogenation reactions

Conclusion. This article provides a brief overview of the studies of the catalytic reduction of aromatic nitro compounds to the corresponding amines. Increasing attention of chemists is attracted by the possibility of using nitro derivatives for the needs of industry and agriculture, both directly and as a relatively cheap chemical material in the synthesis of various products with high applied value. A special place among the chemical transformations of nitro compounds is occupied by the reduction reaction. There is no need to dwell on the enormous industrial significance of this reaction in the aromatic series. Studies of hydrogenation reactions of aromatic nitro compounds on nickel, copper and iron catalysts are described. Hydrogenation of aromatic nitro compounds on catalysts based on palladium, platinum, and rhodium deposited on various carriers, including nanodiamonds, is considered. Data interpretation was carried out using materials published in domestic and foreign sources.

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АРОМАТТЫ МОНО ЖӘНЕ ДИНИТРОҚОСЫЛЫСТАРДЫ СЕЛЕКТИВТІ ТОТЫҚСЫЗДАНДЫРУДЫҢ ТИІМДІ КАТАЛИЗАТОРЛАРЫ

Аннотация. Мақалада ароматты нитро қосылыстарды катализдік тотықсыздандыру арқылы маңызды аралық және соңғы өнім – арамотатты аминдерді алу қарастырылған. Әртүрлі алуан синтетикалық бояғыш (сурет, бояу өнеркәсібі, табиғи және синтетикалық талшықтарды бояуда), фотохимикат, отын тұрақтандырғыш пен қоспа, жағармай, өсімдікті химиялық қорғау құралы, синтетикалық талшық, сорбент, дәрілік заттарды және т.б. алу өндірісінде жоғары реакциялық қабілетіне сәйкес ароматты моно-, ди - және полиаминдер кеңінен қолданылады. Аминді алудың маңызды жолының бірі – нитроқосылыстарды сутекпен катализатор қатысында тотықсыздандыру. Нитроқосылыстарды катализдік тотықсыздандыруда КСРО, ТМД елдері, Ресей және Қазақстан ғалымдары үлкен үлес қосты. Қазіргі уақытта кейбір елдерде ТМД-ны қоса алғанда, нитроқосылыстарды еріткіш қатысында тотықсыздандыру арқылы амин алу – негізгі әдістердің бірі. Еріткіштерді қолдану нәтижесінде үдеріс бу әдісімен гидрлеуге қарағанда жеңіл жағдайда жүреді. Нитроқосылыстарды сұйық фазада катализдік тотықсыздандырғанда процесс төмен температурада жүретіндіктен энергия жұмсалуы мен жүйенің қопарылғыштық қауіпсіздігі төмендейді. Аминді осы әдіспен синтездеу мақсатты өнімнің экологиялық таза және шығымы жоғары болады. Мақалада сутектің атмосфералық және жоғары қысымда нитроқосылыстарды гидрлеу үшін катализаторды таңдаудың барлық мәселелері толық жазылған. Әртүрлі тасымалдағыштарға (оның ішінде наноалмазда бар) қондырылған палладий, платина, родий негізіндегі катализаторда ароматты нитроқосылыстарды гидрлеу мәселесі қарастырылған. Мыс қосылған қондырылған палладий катализаторы негізіндегі катализаторлар функционалды топ – нитротопты гидрлегенде, ал платина және родий қосындылары – нитробензолдағы нитротопты және ароматты сақинаны тотықсыздандыруда жоғары селективтілік көрсетті. Жұмыста наноалмазға қондырылған өлшемі 4-5 нм платина және палладий нанобөлшектері негізіндегі катализаторлар жұмсақ жағдайда нитроқосылыстарды сұйық фазада гидрлеу реакциясында жоғары белсенділік көрсеткені анықталды. Мақала тақырыбы ғылыми және қолданбалы тұрғыдан өте қызықты. Теориялық сұрақ бойынша адсорбция, молекуланың реакциялық қабілетін кванттық-химиялық тұрғыдан сипаттау, тотықсыздану механизмі, металдардың электрондық күйі, ароматты нитроқосылыстардың өзгеру процесінің химизмі және ароматты нитроқосылыстарды катализдік гидрлеудің практикалық мәселелері туралы авторлардың жазған мәліметтері өте өзекті. Мақала отандық және шетелдік әдебиеттерді талдау негізінде жазылған, сонымен бірге химиялық және химиялық-технологиялық мамандығында оқитын студенттерге, магистранттарға, докторанттарға, катализ саласындағы мамандарға пайдалы болуы мүмкін.

Түйін сөздер: ароматты нитроқосылыстар, катализдік тотықсыздандыру, ароматты аминдер, селективті катализ, сұйық фазада гидрлеу.

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ЭФФЕКТИВНЫЕ КАТАЛИЗАТОРЫ ДЛЯ СЕЛЕКТИВНОГО ВОССТАНОВЛЕНИЯ АРОМАТИЧЕСКИХ МОНО- И ДИНИТРОСОЕДИНЕНИЙ

Аннотация. В данной статье рассматриваются вопросы каталитического восстановления ароматических нитросоединений для получения ценных промежуточных и конечных продуктов – ароматических аминов. Ароматические моно-, ди- и полиамины, благодаря их высокой реакционной способности, широко используются в производстве различных соединений: синтетических красителей различных оттенков (для фотографий, в лакокрасочной промыш-ленности, для окрашивания натуральных и синтетических волокон), фотохимикатов, стабили-заторов топлива и получения присадок, смазочных масел, химических средств защиты растений, синтетических волокон, сорбентов, лекарственных средств и т.д. Наиболее важным способом получения аминов из нитросоединений является каталитическое восстановление водородом на катализаторах. Большой вклад в изучение каталитического восстановления нитросоединений внесли ученые из СССР, стран СНГ, России и Казахстана. В настоящее время в некоторых странах, включая СНГ, метод восстановления нитросоединений в растворителях является одним из основных способов получения аминов. Благодаря применению растворителей, процесс проводится в более мягких условиях, чем при паровом методе гидрирования. Использование жидкофазного каталитического восстановления нитросоединений позволяет проводить процесс при достаточно низких температурах, что приводит к значительному снижению энергозатрат и взрывоопасности системы. Этот способ синтеза аминов является более экологически чистым, целевые продукты реакции, амины образуются с достаточно высокими выходами. В статье подробно описаны вопросы выбора катализаторов для гидрирования нитросоединений при атмосферном и повышенном давлении водорода. Описываются исследования реакций гидрирования ароматических нитросоединений на никелевых, медных и железных катализаторах. Рассмотрено гидрирование ароматических нитросоединений на катализаторах на основе палладия, платины, родия, нанесенных на различные носители, включая наноалмазы. Катализаторы на основе нанесенных палладиевых катализаторов с добавками меди показали высокую селективность при гидрировании нитрогрупп в нитросоединениях с функциональными группами, а с добавками платины и родия – при восстановлении и нитрогрупп, и ароматического кольца в нитробензоле. В работах по применению наноалмазов было установлено, что катализаторы на основе наночастиц платины и палладия размером 4-5 нм, закрепленные на наноалмазах, имели высокую активность в реакциях жидкофазного гидрирования нитросоединений в мягких условиях. Тема статьи интересна и с научной, и прикладной точек зрения. Описанные авторами данные по теоретическим вопросам (адсорбция, квантово-химическое описание реакционной способности молекул, механизмы восстановления, электронное состояние металлов, химия процессов превращения ароматических нитросоединений) и практическим проблемам каталитического гидрирования ароматических нитросоединений являются весьма актуальными. Статья составлена на основе анализа отечественной и зарубежной литературы и может быть полезна специалистам в области катализа и студентам, докторантам, обучающимся по специальностям химического и химико-технологического профиля.

Ключевые слова: ароматические нитросоединения, каталитическое восстановление, ароматические амины, селективный катализ, жидкофазное гидрирование.

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BIMETALLIC Co-Pd CATALYSTS FOR DRY AND BIREFORMING OF METHANE

Abstract. Carbon dioxide reforming of methane represents a promising method to effectively convert both greenhouse gases – CH_4 and CO_2 into valuable energy resources *via* syngas. Adding steam to a feed allow to adjust syngas composition that is important for its following application. This work considers the bimetallic Co-based catalyst modified with additive of noble metal – Pd and supported on alumina tested in the dry (DRM) and combined steam-dry (CSDR) reforming so-called bireforming of methane (BRM) to produce synthesis gas with a controllable ratio of H_2/CO. The addition of small amount of noble metal (2-5% from total metal mass) to the Co-based catalyst caused an increase in efficiency of the catalyst in the both processes. The bimetallic 5%Co-Pd/Al_2O_3 catalyst revealed the high stable activity and selectivity during its long-term continuous testing. Thus, in BRM the extent of conversion of CH_4 and CO_2 are 93 and 84% respectively at t = 700°C, CH_4:CO_2:H_2O = 1:1:0.5 under atmospheric pressure. No losses of activity and selectivity of the 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst were observed during for 100 hours of its continuous operation. The catalysts were characterized by BET, SEM, TEM, and TPR methods. The catalysts studied can be considered as a prospective base to develop the effective catalysts for methane conversion into valuable syngas with controllable ratio.

Key words: Dry Reforming of Methane, Bireforming of Methane, Syngas, Bimetallic Co-Pd supported catalysts.

1. **Introduction.** It is known that the reserves of dominantly used fossil fuel (crude oil) are depleting. On the other hand, natural gas, which is primarily composed of methane, is expected to last longer than oil reserves. Current industrial processes utilize methane as a main feedstock for converting it to the valuable synthesis gas (syngas, a mixture of CO and H_2) which is further used in diverse downstream processes, such as production of oxygenated compounds, methanol synthesis, Fischer-Tropsch (FT) synthesis for production of liquid hydrocarbons and numerous other carbonylation and hydrogenation or reduction processes [1-2].

The most common methane reforming processes for hydrogen production are known as: “steam reforming (SRM)”, “partial oxidation (POM)”, “dry reforming (DRM)” or combination of the exothermic POM process with endothermic ones – SRM or DRM “autothermal reforming (ATR)” and are still developed [2-9]. All processes represent itself oxidative reactions that collectively named in the literature as oxyforming processes [10].

In various reforming processes, biogas can be used as a methane source, which directly depends on its composition. In general, syngas and H_2 from syngas can be produced by methane or biogas reforming in a wide temperature range of 600-1000°C (endothermic and reversible reactions), involving predominantly catalytic processes that are often combined. Both reforming processes can be performed under low pressure (in most cases under atmospheric pressure) in tubular fixed-bed or fluidized reactors [11-13].

In DRM and SRM, methane, the most abundant hydrocarbon, is reformed through the reactions (1)-(4) to H_2, CO and CO_2. These reactions take place catalytically at temperatures as high as 800 °C for satisfactory methane conversion [1, 14-15].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \; \Delta H^\circ_{298} = 247.3 \text{ kJ mol}^{-1} \quad \text{(Eq. 1)}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \; \Delta H^\circ_{298} = 206.1 \text{ kJ/mol} \quad \text{(Eq. 2)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \; \Delta H^\circ_{298} = -41.17 \text{ kJ/mol} \quad \text{(Eq. 3)}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \; \Delta H^\circ_{298} = 165.0 \text{ kJ/mol} \quad \text{(Eq. 4)}$$

Although SRM producing CO and H_2 (Eq. 2) has great energy expenditure, this is the most widespread industrial route to obtain H_2. The H_2/CO ratio produced in SRM is equal to three, therefore this way is the most appropriate one from the H_2 generation point of view [11]. The Water-Gas Shift Reaction, commonly known as “Shift Reaction” (Eq. 3), occurring in DRM and SRM processes enables to produce an additional amount of H_2. Equation 4 shows the reaction of methane SR associated with the Shift Reaction [2, 11, 16-17].

Currently, a combination of SR with DR of methane has attracted much attention. The H_2/CO product ratio can be controlled by changing the H_2O/CO_2 ratio in the reaction feed [18-19], thus it is feasible to produce synthesis gas with the H_2/CO ratio of about 2, which is suitable for the methanol and Fisher–Tropsch syntheses [1-2]. Addition of steam to the feed has some practical benefits over CH_4 reforming with CO_2 alone: (i) the carbon formation is reduced because of the oxidation of carbonaceous species, and (ii) syngas with a broader range of H_2/CO ratios can be produced by alteration of the relative concentrations of steam and CO_2 in feed stream based on the final FT products [1-2, 18-19].

Transition metals such as Ni, Pt, Rh or Pd possess the catalytic activity in SRM, among them the Ni catalysts have the advantage of having lower costs. On the other hand, Ni has greater deactivation susceptibility by the coke formation due to the high temperatures used, which makes the Pt and Pd catalysts interesting with regards to stability. The most active catalysts for DRM, reported in literature, are those that use the transition metals of the group 8 of the Periodic Table, particularly Pt, Rh, and Ru. These metals have been used as catalysts for the DRM because of their excellent catalytic reactivity and anti-coking property [7-8]. However, these metals are expensive and less abundant and are therefore not suitable for commercial applications. More affordable transition metals such as Ni and Co have been studied as alternative catalysts for the DRM because of their low cost and good catalytic performance [20-21]. Addition of noble metals in small amount can be used to enhance the catalyst stability.

Earlier we have studied the 5%Co-Pd system supported on alumina demonstrated activity in dry conversion of methane with producing syngas and oxygenates under elevated pressure and relatively low temperature [22]. Interaction in a bimetallic Co-Pd system supported on a solid support material can play an important role in determining the catalytic performance to achieve high effective catalysts for syngas production either by dry or combined dry-steam reforming of methane. In this paper we report the experimental results on testing the bimetallic Co-based alumina supported catalyst modified with a low amount of noble metal – Pd (2-5% from total metal content) in DRM and BRM.

2. **Experimental.** The bimetallic 5%Co-Pd/Al_2O_3 catalysts were synthesized by co-impregnation method and tested in dry and combined dry-steam reforming of methane. The total content of Co and Pd metals was equal to 5% of the catalyst mass. Ratio of Co:Pd is varied from 98:2 to 95:5 that corresponds to 4.75÷4.9/0.1÷0.25 mas.%. The processes were carried out in a tubing quartz reactor equipped with a heating furnace, a syringe pump, and mass flow controllers. Prior to the reaction, the catalyst sample in the amount of 6 ml was loaded into the reactor and pretreated by H_2 at 300°C for 1 h.

Testing the catalysts in DRM, CSDRM and SRM have been carried out using a feed – $CH_4:CO_2:H_2O=1/0\div1/0.5\div1$, varying temperature within 300-800°C, P_{atm} and gas hourly space velocity (GHSV) varying within 1000-2000 h^{-1}. “Pure” feed without diluting by inert gas have been used. The duration of each test under the certain conditions (temperature, feed ratio, and GHSV) was 10-12 hours. With an aim to determine the catalyst stability, the continuous long-term test of the catalyst 100 hours was carried out in bireforming of methane, because of it has high level conversion of methane.

Initial and final gas products were analyzed using on-line the GCs with a TCD (Chromatek-Krystall-5000 and Chromatek-Gazochrom-2000 using columns: Hayesep N, NaX, CaX and activated carbon;

carrier gases are Ar and air). The CH_4 and CO_2 conversion and H_2/CO ratio were calculated using the following formulas (1-3):

$$X(CH_4) = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100 \tag{1}$$

$$X(CO_2) = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100 \tag{2}$$

$$H_2/_{CO} = \frac{[H_2]_{out}}{[CO]_{out}} \tag{3}$$

where $X(CH_4)$ is conversion of methane (%), $X(CO_2)$ is conversion of carbon dioxide (%).

The conversion of water was not calculated because of the difficulties in differentiating unreacted water and water formed by the secondary reaction. The yields of the reaction products, hydrogen ($Y(H_2)$) and carbon oxide ($Y(CO)$), expressed in micromoles formed by 1 gram of the catalyst per second (µmol/g/s) were calculated, and thus selectivity and productivity of the catalyst were assessed and compared.

To understand the effects of the reaction feed and process conditions on the catalyst characteristics, the physico-chemical properties of the catalysts were characterized by BET, SEM, TEM, and TPR methods before and after reaction.

3. Results and discussion

3.1 Catalyst characterization

XRD analysis of fresh and spent samples of 5%Co-Pd/Al_2O_3 catalysts did not reveal phases except γ-alumina characterized by reflexes of 1.39, 1.98 and 2.42 (ASTM 10-425). This can be caused by a high dispersion of the metal phase and/or their X-Ray amorphous state. The TEM analysis confirmed the high dispersion of metallic particles: their sizes were less than 3 nm. No sintering of the particles was observed after the catalyst operation.

The BET surface area of the 5%Co-Pd(4.9:1)/Al_2O_3 catalyst was markedly decreased from 159.1 to 89.3 m^2/g after its long-term operation in both DRM and BRM processes. One of the possible reasons for this may be the presence of the residual reaction products adsorbed on the catalyst surface, which was not treated after testing and prior BET study.

The addition of a noble metal, Pd, has a significant effect on the reducibility of cobalt oxides. This has been demonstrated by means of TPR-study. Figure 1 shows the effect of Pd additive on Co reduction. There is a two-step reduction *via* $Co_3O_4 \rightarrow CoO \rightarrow Co°$ as it was proposed earlier for a similar Co-based catalyst [23]. It is clear from Figure 1 that the reduction temperatures of the Co oxides are significantly shifted to lower values. The shift is enhanced with increase in Pd amount. Thus, the first and second peaks corresponding to the reduction of Co_3O_4 and CoO respectively are shifted in the following sequence of 230 → 210 → 190°C and 410 → 380 → 328°C, respectively, while the Pd content is increased from 0.25 to 1.5 mas.% (figure 1).

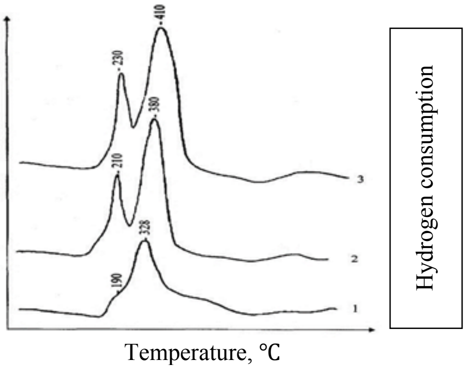

Figure 1 – H_2-TPR profiles of the 5%Co-Pd/$A1_2O_3$ catalysts with varying content of Pd:
1– Co-Pd(3.5:1.5); 2 – Co-Pd (4.5:0.5); 3 – Co-Pd(4.75:0.25)

3.2 Catalyst test

The Co-containing alumina supported bimetallic catalysts – 5%Co-Pd/Al_2O_3 were examined in dry (DRM) and bireforming (BRM) of methane. Due to the highly endothermic nature of reforming reactions (Eqs.1-2), the temperature has the most significant effect on methane reforming. Conversion CH_4 and CO_2 as well as yields of H_2 and CO in DRM and BRM as a function of temperature are exhibited in figures 2 and 3, respectively. In DRM, the yields of hydrogen and carbon oxide are grown with increase in temperature and are almost the same over the entire temperature range studied. Their values reach 15.03 and 15.3 µmol/g·s respectively at 700℃ (figure 2). Whereas in BRM under the same conditions: t=700℃ and ratio C/O=1 in a feed the yield of hydrogen is slightly higher – 15.5 and Y(CO) decreases to 11.1 µmol/g·s (figure 3). These results may be explained by lower content of C and higher H in a feed: CH_4:CO_2=1:1 (DRM) and CH_4:CO_2:H_2O=1:0.5:0.5 (BRM). Accordingly, the ratio of H_2/CO is higher in BRM – 1.4 in contrast to DRM – 1.0. Extents of methane and carbon dioxide conversion are 82.7 and 85.6% and 91.1 and 78.3% in DRM and BRM, respectively. Enhanced conversion of CO_2 is caused by its twice lower content in the BRM feed.

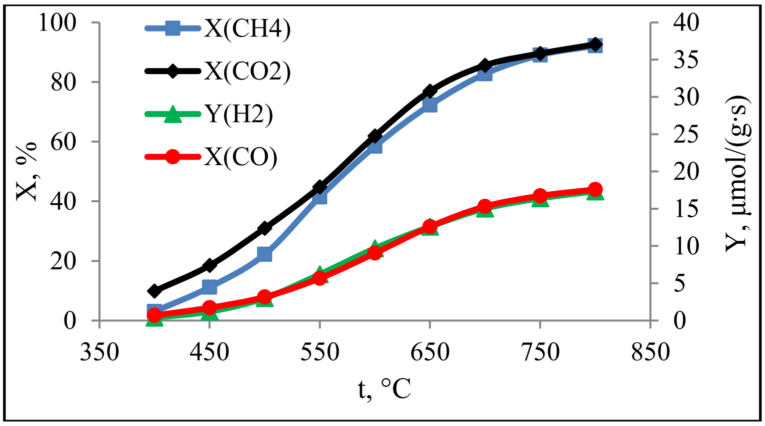

Figure 2 – Effect of the temperature on the DRM over 5%Co-Pd(4.9:0.1)/Al_2O_3 under P=1 atm, CH_4:CO_2=1:1, GHSV=1000 h^{-1}

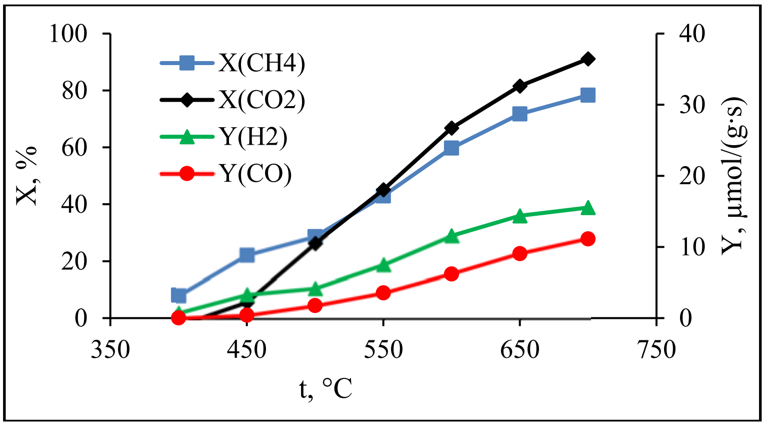

Figure 3 – Effect of the temperature on the BRM over 5%Co-Pd(4.9:0.1)/Al_2O_3 under P=1 atm, CH_4:CO_2:H_2O=1:0.5:0.5, GHSV=1000 h^{-1}

The 5%Co-Pd(4.9:0.1)/Al_2O_3 has been long-term tested in BRM in order to determine the catalyst stability. During 100 hours of testing, the catalyst retained its activity: X(CH_4)≈93 and X(CO_2) ≈84% on average and produced syngas with the same yield and consequently selectivity: Y(H_2) ≈18.5 and Y(CO)≈15.4 µmol/g*s under the following conditions: CH_4:CO_2:H_2O=1:1:0.5, P=0.1 MPa, T=700°C, GHSV=1250 h^{-1} (Fig.4). The ratio of H_2/CO=1.2.

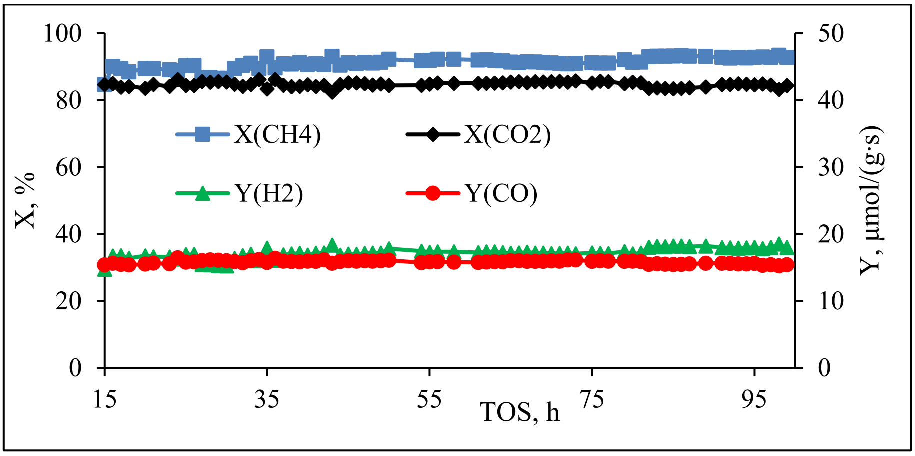

Figure 4 – Effect of time on stream on BRM over the 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst under P=1 atm, CH_4:CO_2:H_2O=1:1:0.5, GHSV=1250 h^{-1}, t=700°C

In table 1, the comparison of DRM and BRM is presented at varying ratios of reagents (CH_4, CO_2, H_2O) in a feed. In terms of high methane conversion and hydrogen yield, the content of both O and H in a reagent mix should be higher. Both CO_2 and H_2O facilitate carbon removal from the catalyst surface.

Table 1 – Effect of feed composition on methane conversion and yield of products over 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst under P=1 atm and t=700°C

Process	Feed: ratio, vol.				Conversion, %		Yield, μmol/g*s		Ratio of H_2/CO
	reagents	C/O/H	O/C	H/C	CH_4	CO_2	H_2	CO	
DRM	CH_4:CO_2=1:1	2/2/4	1	2	82.7	85.6	15.03	15.3	~ 1
BRM	CH_4:CO_2:H_2O=1:0.5:0.5	1.5/1.5/5	1	3.3	78.3	91.1	15.5	11.1	1.4
BRM	CH_4:CO_2:H_2O=1:1:0.5	2/2.5/5	1.25	2.5	93	84	18.5	15.4	1.2

The synthesized Co-Pd/Al_2O_3 catalysts have showed the high activity and stability in methane reforming. The high activity of the bimetallic catalysts is the result of the Co-Pd interaction demonstrated by H_2-TPR. Addition of Pd facilitates Co reproducibility. As well as metal-metal and metal-support interaction can prevent the sintering of small metal species into big particles and the coke formation. No visible coke formation was observed after long-term testing of the catalyst. No coke and metal sintering were revealed by TEM-study too.

Conclusions. The bimetallic 5%Co-Pd/Al_2O_3 catalysts with small amount of Pd – 0.1-0.25 mas.% have performed the high stable activity and selectivity in reforming of methane under atmospheric pressure and elevated temperatures producing syngas with H_2/CO ratio varied depending on the feed composition. Conversion of CH_4 and CO_2 is varied within 78-93% at 700°C. No loss of activity and selectivity of the 5%Co-Pd(4.9:0.1)/Al_2O_3 catalyst was observed during for 100 hours of its continuous operation.

The addition of Pd to the Co-based catalyst is accompanied with formation of the high dispersed state of metals as well as increasing in Co reducibility due to the Co-Pd interaction. In summary, the Co-Pd systems studied can be considered as a prospective base to develop the effective catalysts for methane conversion into valuable syngas with controllable ratio by regulating steam content in an initial feed CH_4:CO_2:H_2O.

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МЕТАННЫҢ СУСЫЗ ЖӘНЕ БИРЕФОРМИНГІНЕ АРНАЛҒАН БИМЕТАЛДЫ Co-Pd КАТАЛИЗАТОРЛАР

Аннотация. Метанның көмірқышқылды конверленуі қоспарникті газды (CH_4 және CO_2) синтез-газ арқылы бағалы энергия ресурстарына айналдыратын болашағы зор тиімді әдіс болып саналады. Шикізатқа су буының қосылуы синтез-газды алдағы уақытта қолдануда маңызды құрамының реттелуіне мүмкіндік береді, сонымен қатар кокс түзілісін төмендетеді. Бұл жұмыс Pd асыл металл үлесі негізінде модифицирленген Co құрамды биметалды катализаторды метанның көмірқышқылды (сусыз риформингі) және H_2/CO қатынасының реттелуі негізінде синтез-газ алуға мүмкіндік тудыратын булы көмірқышқылды (метан бириформингі) конверленуінде зерттеуге негізделген. Катализатор қасиеттері БЭТ, СЕМ, ЖЭМ және ТБТ әдістері арқылы сипатталды.

5%Co-Pd/Al_2O_3 биметалды катализаторлары біріккен сіңіру әдісі негізінде синтезделді және метанның көмірқышқылды және булы көмірқышқылды риформингінде сыналды. Co және Pd металының жалпы мөлшері катализатор массасының 5%-ын құрайды. Co:Pd қатынасы 98:2-ден 95:5-ке дейін ауытқиды, яғни 4,75÷4,9/0,1÷0,25 (%) массалық құрамына сәйкес келеді. Үдеріс қыздыру пеші, шприц сорғысы және газ шығынын бақылағыштармен жабдықталған құбырлы кварц реакторында жүргізілді.

5%Co-Pd/Al_2O_3 катализаторларының бастапқы қолданылған сынамаларының РФА талдамасы 1,39, 1,98 және 2,42 (ASTM 10-425) рефлекстері арқылы сипатталған γ-алюминий тотығынан басқа фазаларды көрсетпеді. Бұл металл фазасының жоғары дисперстілігіне немесе олардың ренгенді аморфтық күйіне байланысты болуы мүмкін. ЖЭМ талдамасы металдық ұсақ бөлшектердің жоғары дисперсті күйде екенін дәлелдейді: өлшемі 3 нм-ден кіші болып көрінді. Катализатор жұмысынан кейін ұсақ бөлшектердің бірігу үдерісі байқалмады. Co құрамды катализаторға аз мөлшерде Pd (металл массасының 2-5%-ы) қосылғандықтан, металдар жоғары дисперсті күйге келді, сонымен қатар Co-Pd өзара қатынас нәтижесінде Co тотықсыздануының артуы ЖБТ зерттеуі негізінде расталды.

Co құрамды катализаторға аз мөлшердегі асыл металдың қосылуы екі үдеріс кезінде катализатор әсерін ұлғайтты. 5%Co-Pd/Al_2O_3 катализаторлары метанның көмірқышқылды және булы көмірқышқылды конверленуінде сыналды. Конверлеу реакцияларының жоғарғы эндотермиялық сипатына байланысты температураның метан конверленуіне айтарлықтай өте жоғары әсері бар. Реагенттердің конверлену дәрежесі және өнімдердің шығымы 400-ден 800°С-ге дейін температураның жоғарылау бойымен артады. Сутегі мен көміртек монототығының шығымы МКҚК-де зерттелген температураның барлық аумағында біркелкі болып келеді және сәйкесінше 800°С-де 15,03 мкмоль/г·с-ке тең. МБКҚК-де сутегінің шығымы 15,5-ке дейін артады, ал CO шығымы 11,1 мкмоль/г·с-ке дейін төмендеді (CH_4:CO_2:H_2O=1:0,5:0,5). Сәйкесінше, H_2/CO қатынасы МБКҚК үдерісінде МКҚК-іне – 1,0 қарағанда жоғары – 1,4-ке тең. Метанның және көміртек қос тотығының конверлену дәрежесі МКҚК жағдайында 82,7 және 85,6%-ды құрады, сәйкесінше, МБКҚК жағдайында 91,1 және 78,3%-ға тең.

5%Co-Pd/Al_2O_3 биметалды катализатор ұзақмерзімді үздіксіз сынау кезінде жоғары тұрақты белсенділікті және талғамдылды көрсетті. 5%Co-Pd(4,9:0,1)/Al_2O_3 катализатордың белсенділігі мен талғамының төмендеуі 100 сағат тұрақты жұмыс атқарғанда байқалмады. Орта есеппен X(CH_4)≈92 және X(CO_2)≈84% тең, ал келесі үдеріс (CH_4:CO_2:H_2O=1:1:0,5, P=0,1 МПа, T=700°С, GHSV=1250 $ч^{-1}$) жағдайында синтез-газ біркелкі талғаммен Y(H_2) ≈18,5 және Y(CO)≈15,4 мкмоль/г·с алынады. H_2/CO қатынасы 1,2-ге тең. Ұзақмерзімді сынақтан кейін көрінетін кокс түзілусі байқалмады.

Сондықтан 5%Co-Pd/Al_2O_3 биметалды катализатор атмосфералық қысым кезінде және жоғары температурада шикізат құрамына байланысты өзгеріп отыратын H_2/CO қатынасы тән синтез-газ түзілісімен жүретін метанның конверлену үдерісінде жоғары және тұрақты белсенділікті көрсетті. Зеттелген катализаторларда МКҚК және МБКҚК үдерісінің салыстырылу жағдайы метанның конверлену температурасының төмендеуі тұрғысында қарағанда МБКҚК тиімді екендігі көрінді. Co-Pd қарастырылған жүйелерін метанды бақыланатын қатынасқа ие (берілетін шикізатқа су буының берілуін реттеу арқылы) синтез-газға конверлеуге арналған тиімді катализаторлар жасау үшін келешегі бар негіз ретінде қарастыруға болады.

Түйін сөздер: метанның сусыз риформингі, метан бириформингі, синтез-газ, Co-Pd биметалды орнатылған катализаторлар.

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БИМЕТАЛЛИЧЕСКИЕ Co-Pd КАТАЛИЗАТОРЫ ДЛЯ СУХОГО РИФОРМИНГА И БИРИФОРМИНГА МЕТАНА

Аннотация. Углекислотная конверсия метана является многообещающим способом эффективного преобразования обоих парниковых газов – CH_4 и CO_2 в ценные энергетические ресурсы через синтез-газ. Добавление паров воды в исходную смесь позволяет регулировать состав синтез-газа, что важно для его дальнейшего использования, а также снизить коксообразование. Данная работа посвящена исследованию биметаллического кобальтсодержащего катализатора модифицированного добавлением благородного металла – Pd, нанесённого на оксид алюминия, в процессах углекислотной (УКМ) и пароуглекислотной (ПУКМ) конверсии метана для получения синтез-газа с контролируемым соотношением H_2/CO. Свойства катализатора были охарактеризованы методами БЭТ, СЭМ, ПЭМ и ТПВ.

Биметаллические 5%Co-Pd/Al_2O_3 катализаторы были синтезированы методом совместной пропитки и протестированы в процессах углекислотной и пароуглекислотной конверсии метана. Общее содержание металлов Co и Pd равнялось 5% от массы катализатора. Соотношение Co:Pd варьировалось от 98:2 до 95:5, что соответствует их массовому содержанию 4.75÷4.9/0.1÷0.25 (%). Процессы проводились в проточном кварцевом реакторе, оснащённом нагревателем, шприцевым насосом и регуляторами массовых потоков.

РФА анализ исходного и использованного образцов катализаторов 5%Co-Pd/Al_2O_3 не выявил наличия каких-либо фаз, кроме γ-оксида алюминия, характеризующегося набором рефлексов: 1,39, 1,98 and 2,42 (ASTM 10-425). Это может быть связано с высокой дисперсностью металлической фазы и/или её рентгеноаморфным состоянием. Исследование методом ПЭМ подтвердило высокую дисперсность металлических частиц: их размер составил менее 3 нм. Спекания частиц после проведения процессов не наблюдалось. Добавление небольших количеств Pd (2-5% от общей массы металлов) к кобальтсодержащему катализатору сопровождалось образованием высокодисперсного состояния металлов, а также увеличением восстанавливаемости Co в результате взаимодействия Co-Pd, что подтверждается данными ТПВ-исследования.

Добавление небольших количеств благородного металла в кобальтсодержащем катализаторе привело к увеличению его эффективности в обоих процессах. Катализаторы – 5%Co-Pd/Al_2O_3 были испытаны в процессах углекислотной и пароуглекислотной конверсии метана. В связи с высоко эндотермическим характером реакций конверсии температура имеет наиболее значительное влияние на конверсию метана. Степени конверсии реагентов и выходы продуктов растут с ростом температуры от 400 до 800°C. Выходы водорода и монооксида углерода практически одинаковы в процессе УКМ (CH_4:CO_2=1:1) во всём исследованном температурном интервале и равны 15.3 мкмоль/г·с при 700℃. В процессе ПУКМ при таких же температуре и соотношении C/O=1 в исходной смеси (CH_4:CO_2:H_2O=1:0,5:0.5) выход водорода несколько выше – 15.5, тогда как Y(CO) понижается 11.1 мкмоль/г·с. Соответственно соотношение H_2/CO выше в процессе ПУКМ – 1,4 по сравнению с УКМ – 1.0. Степени конверсии метана и диоксида углерода составили 82.7 и 85.6% в случае УКМ и 78.3 и 91.1% в случае ПУКМ, соответственно.

Биметаллический катализатор 5%Co-Pd/Al_2O_3 проявил высокую стабильную активность и селективность в течение продолжительных непрерывных испытаний. Снижения активности и селективности катализатора 5%Co-Pd(4.9:0.1)/Al_2O_3 не наблюдалось в течение 100 часов его постоянной работы. X(CH_4)≈92 и X(CO_2) ≈84% в среднем, синтез-газ образуется с одинаковым выходом: Y(H_2) ≈18.5 и Y(CO)≈15.4 мкмоль/г·с при следующих условиях: CH_4:CO_2:H_2O=1:1:0.5, P=0.1 MPa, T=700°C, GHSV=1250 h^{-1}. Соотношение H_2/CO=1,2. Видимого образования кокса после длительных испытаний не наблюдалось.

Таким образом, биметаллический катализатор 5%Co-Pd/Al_2O_3 проявляет высокую и стабильную активность в процессах конверсии метана при атмосферном давлении и повышенных температурах с образованием синтез-газа с соотношением H_2/CO, меняющимся в зависимости от состава сырья. Сравнение процессов УКМ и ПУКМ на исследованных катализаторах показывает, что ПУКМ более эффективен с точки зрения снижения температуры конверсии метана. Приведенные системы Co-Pd можно рассматривать как перспективную основу для разработки эффективных катализаторов для конверсии метана в синтез-газ с контролируемым соотношением посредством регулирования содержания паров воды в подаваемом сырье – CH_4:CO_2:H_2O.

Ключевые слова: сухой риформинг метана, бириформинг метана, синтез-газ, биметаллические Co-Pd нанесенные катализаторы.

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INTERACTION OF THE Fe/γ-Al_2O_3 CATALYTIC SYSTEM WITH PROBE MOLECULES
IV. STUDY OF THE INTERACTION OF HYDROGEN WITH γ-Al_2O_3 OXIDE AND THE Fe/γ-Al_2O_3 SYSTEM

Abstract. The work is devoted to the study of the interaction of heterogeneous catalytic systems with adsorbed molecules. The results of the interaction with a hydrogen of γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system using IR spectroscopy, methods of temperature programmed desorption and temperature programmed reduction by hydrogen are presented. An ability of the system to adsorb and activate the initial H_2 probe molecule was defined and an assessment of the active (adsorption) centers was made.

Various adsorption centers were detected during their interaction with hydrogen in the temperature range 293-773K on the surface of both γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system using IR spectroscopy. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with hydrogen.

The adsorbed hydrogen is desorbed in the form of two peaks on the temperature scale from the γ-Al_2O_3 surface and in the form of three peaks from the surface of the Fe/γ-Al_2O_3 system. The appearance of additional desorption peaks for the Fe/γ-Al_2O_3 system is associated with iron deposited on alumina. It was concluded that on the surface of γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system, there are adsorption centers that differ in energy characteristics (binding energy). Moreover, these characteristics may also depend on the percentage of the iron-containing component on the surface of aluminum oxide.

Two adsorption peaks are observed on the temperature scale for γ-Al_2O_3 oxide and in the case of the Fe/γ-Al_2O_3 system, in addition to two adsorption peaks, a desorption peak is also observed using the TPR method of hydrogen. γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system contain different states of metal oxide forms, since several maxima are clearly distinguishable on the TPR curves of hydrogen which indicates the reduction of particles of various compositions.

Key words: heterogeneous catalysis, physicochemical research methods, adsorbed molecules.

Introduction. One of the most common and highly effective methods for studying adsorption centers on the surface of supports and heterogeneous catalysts are infrared spectroscopy [1-5], temperature programmed desorption (TPD) and temperature programmed reduction (TPR) [6-10]. The use of IR spectroscopy to study the donor-acceptor surface properties is based on the spectral probe method. The properties of adsorption centers are judged by the absorption spectra of the adsorbed molecules, as well as by the change in the position of the absorption bands observed during adsorption.

The strength of active sites is judged by the position of the peaks on the temperature scale in the TPR and TPD methods and the activation energy of the probe molecule, and its area can serve as a measure of the quantity of centers of various types.

This work is a continuation of studies on the interaction of a heterogeneous catalytic system with adsorbed molecules [11-13].

Experimental. Fe/γ-Al_2O_3 system with an iron content of 3; 13 wt.% was prepared by impregnating [10-13] the initial γ-Al_2O_3 oxide with an aqueous solution of iron acetate, followed by drying and calcination in air.

IR spectroscopy

Sample preparation and obtaining IR spectra took place in several stages. At the first stage, the sample (a tablet with KBr filler) was placed in a sealed quartz cell and heated to 523K with simultaneous evacuation for 2 hours. Then, the temperature dropped to 293K. Then, the temperature decreased to 293K. Next, hydrogen purging began at the required temperature (from a given temperature range of 293-773K) for 150 minutes. After that, a temperature of 293K was established then the cell was purged with an inert gas for 30 minutes and after that the IR spectrum was taken.

Equipment - Nicolet iS5 IR spectrometer, Thermo Scientific, USA. Operation mode: resolution 1 cm^{-1}, number of scans - 200.

Temperature programmed desorption (TPD-H_2)

A chromatographic version of temperature programmed desorption was used. The sample with the molecules of the probe substance preliminarily adsorbed on it was subjected to heating at a certain constant speed in the flow of the carrier gas. During desorption, the substance in the gas phase passed through the cell of the thermal conductivity detector (TCD), and the resulting signal was recorded.

Conditions for preparing samples for hydrogen adsorption:

- vacuum treatment 30 minutes;
- sample dehydration in a stream of dry argon (3-5 ml/min) at a temperature of 623K for 120 minutes.

Hydrogen adsorption:

- hydrogen feed rate 5 ml/min;
- adsorption duration one hour; temperature range 293-773K.

Programmed desorption of hydrogen:

- temperature variation range from 293 to 773K;
- speed - 12K/min;
- carrier gas velocity (argon) - 75 ml/min;
- detector sensitivity 1:8.

Desorbed ammonia was detected by chromatograph's TCD and was recorded as a TPD spectrum. At certain temperatures, the TPD spectrum had maxima that characterized the adsorption sites of the sample. The amount of hydrogen desorbed in the corresponding temperature range was determined by peak areas, having previously established how much hydrogen corresponds to the area unit.

Equipment - ″CETARAM″ thermo analyzer, France.

Hydrogen temperature programmed reduction (H_2-TPR)

Conditions for preparing samples for hydrogen reduction:

- vacuum treatment 30 minutes;
- sample dehydration in a stream of dry argon (5 ml/min) at a temperature of 623K for 120 minutes.

Hydrogen reduction:

- temperature variation range from 293 to 773K;
- speed - 12K/min;
- carrier gas velocity (argon) - 75 ml/min;
- hydrogen concentration 5%;
- detector sensitivity 1:8.

Equipment - ″CETARAM″ thermo analyzer, France.

Results and discussion. *Investigation of the Fe/γ-Al_2O_3 system using FTIR spectroscopy during hydrogen adsorption.*

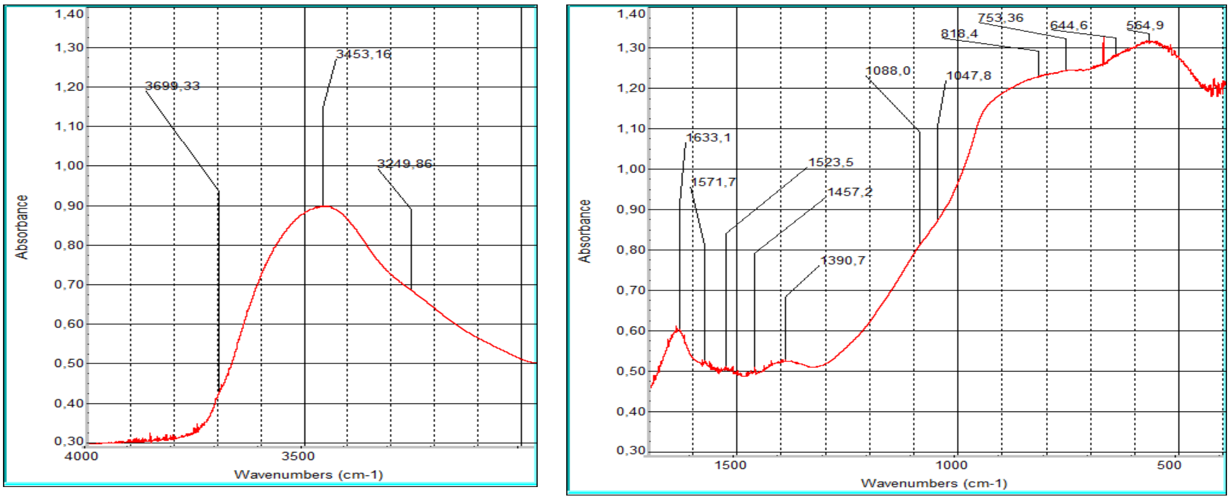
The interaction of γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system with H_2 was studied in the ″In Situ″ mode in the temperature range 293-773K. The data obtained for γ-Al_2O_3 are necessary as reference points for comparison when studying the Fe/γ-Al_2O_3 system.

Figures 1-14 show the IR spectra of γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system when interacting with hydrogen at different temperatures and table 3 shows the results of their interpretation.

In the initial γ-Al_2O_3 oxide (Figs. 1-7, Table 1), as well as in its interaction with hydrogen, the IR spectra contain absorption bands corresponding to -OH groups bound on the surface by hydrogen bonds, absorption bands from Al-O bonds, and also vibrations of CH bonds in the -CH, -CH_2, -CH_3 groups (in trace amounts). A small amount of hydrocarbons, apparently, remained in the γ-Al_2O_3 oxide after synthesis.

There is also an absorption band related to -OH bridging groups bound to aluminum ions in octahedral and (or) tetrahedral coordination. However, upon interaction with hydrogen, this absorption band disappears.

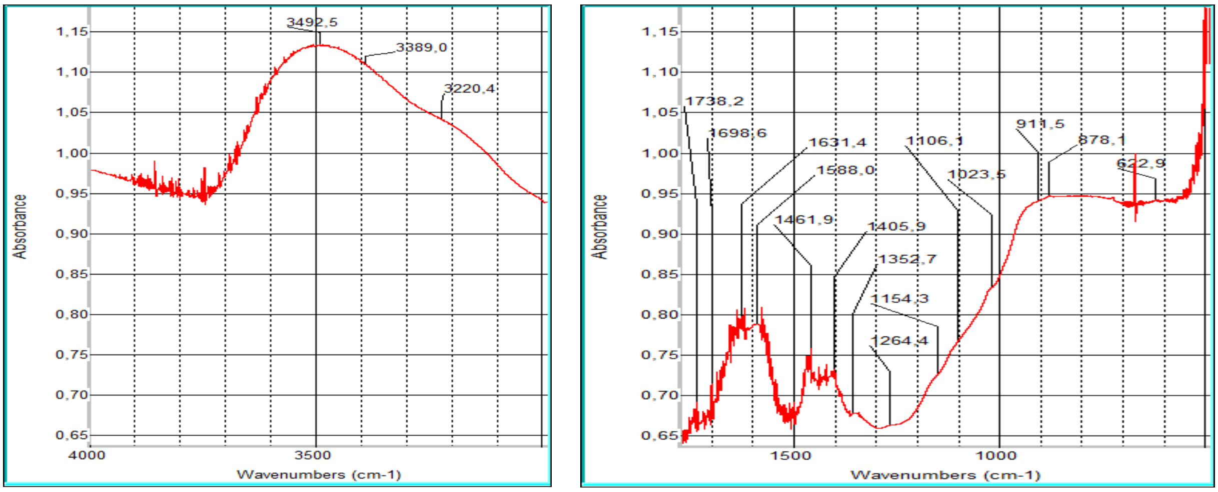
Absorption bands appear associated with the Lewis acid sites upon interaction with hydrogen. As temperature increases the relative intensity of the absorption bands corresponding to the Lewis centers decreases noticeably and the band shifts to the long-wavelength region (figures 2-7, table 1).



a b

a - 4000-3000 cm^{-1} range; b - 1700 - 400 cm^{-1} range

Figure 1 - IR spectrum of the initial γ-Al_2O_3 oxide



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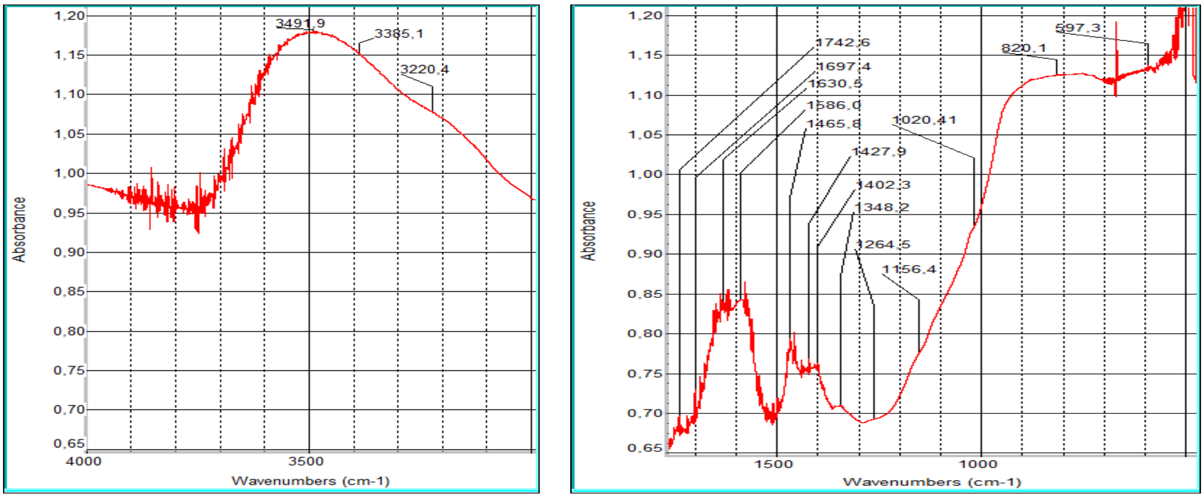
a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

Figure 2 - IR spectrum of γ-Al_2O_3 oxide after hydrogen adsorption at 293K



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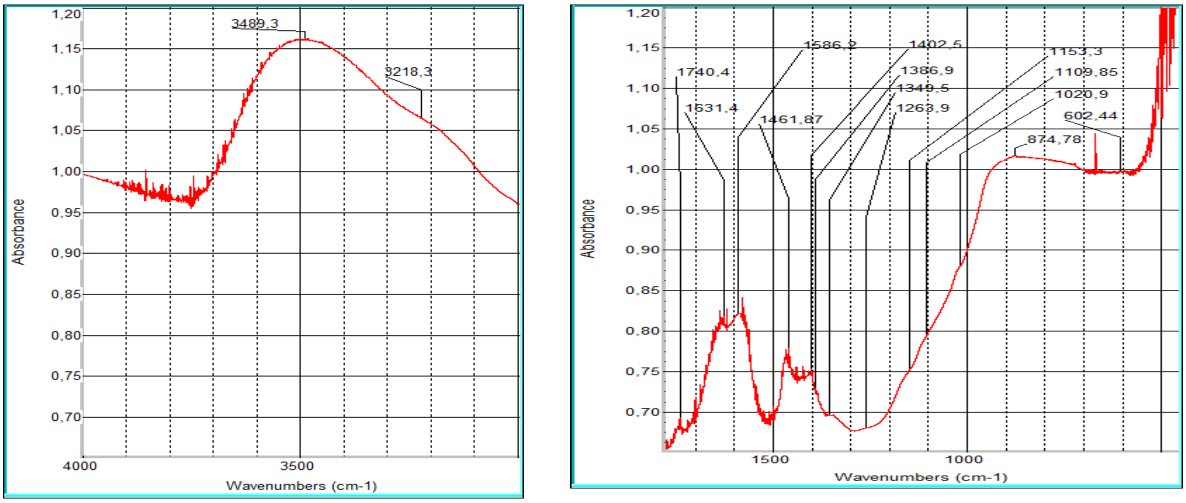
a – 4000-3000 cm^{-1} range; b –1750-400 cm^{-1} range

Figure 3 - IR spectrum of γ-Al_2O_3 oxide after hydrogen adsorption at 373K



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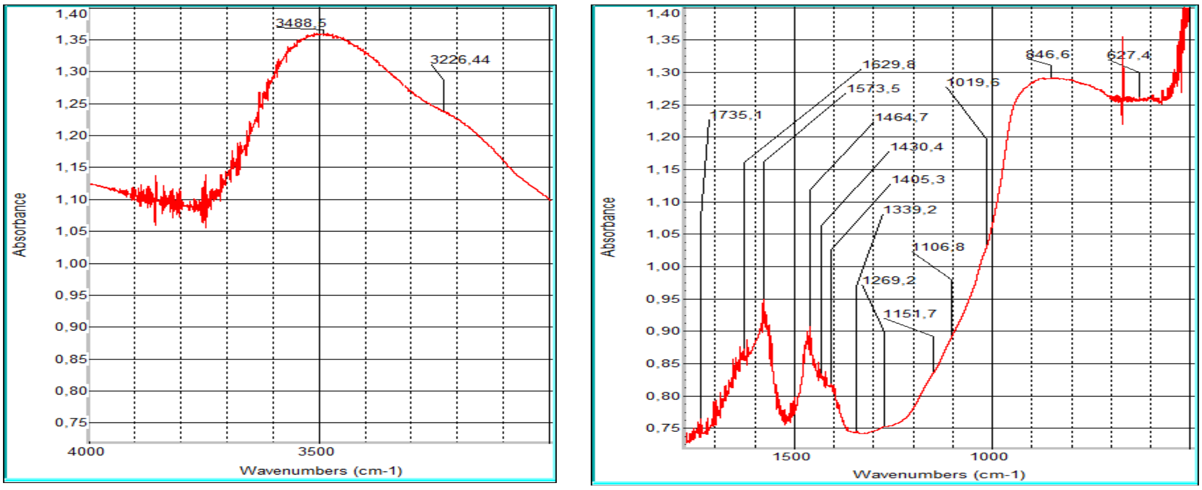
a – 4000-3000 cm^{-1} range; b – 1750-400 cm^{-1} range

Figure 4 - IR spectrum of γ-Al_2O_3 oxide after hydrogen adsorption at 473K



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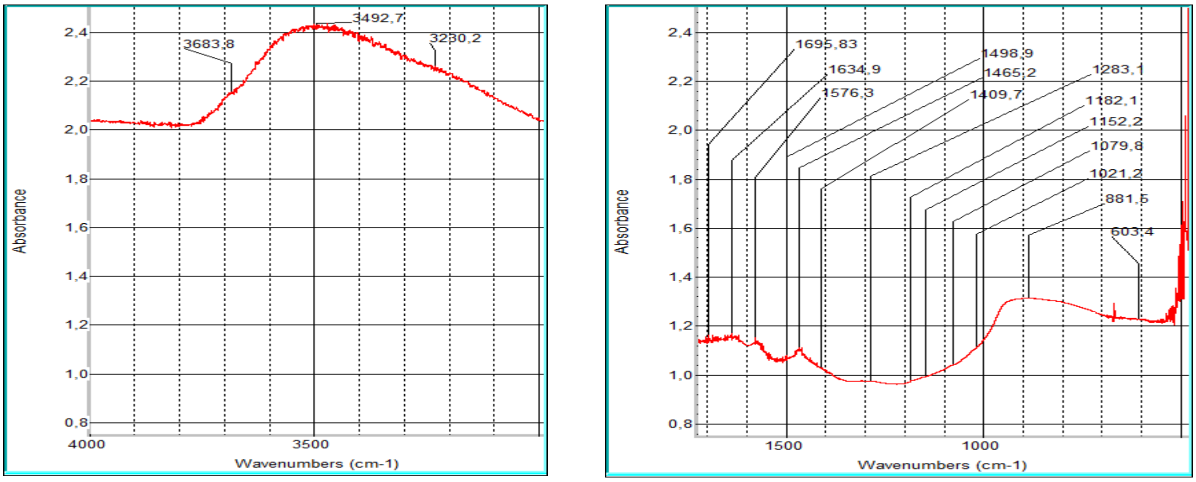
a – 4000-3000 cm^{-1} range; b – 1750-400 cm^{-1} range

Figure 5 - IR spectrum of γ-Al_2O_3 oxide after hydrogen adsorption at 573K



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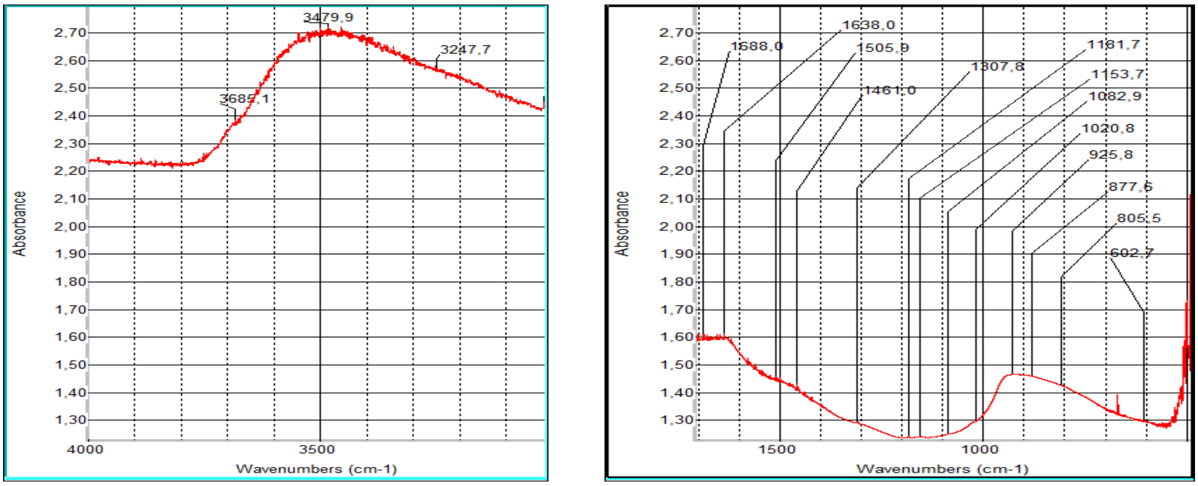
a – 4000-3000 cm^{-1} range; b – 1750-400 cm^{-1} range

Figure 6 - IR spectrum of γ-Al_2O_3 oxide after hydrogen adsorption at 673K



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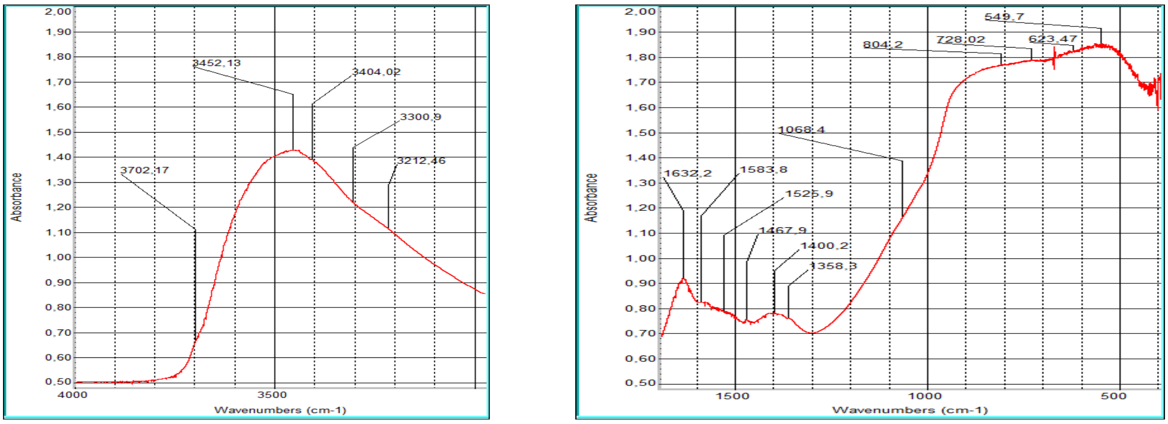
a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

Figure 7 - IR spectrum of γ-Al_2O_3 oxide after hydrogen adsorption at 773K



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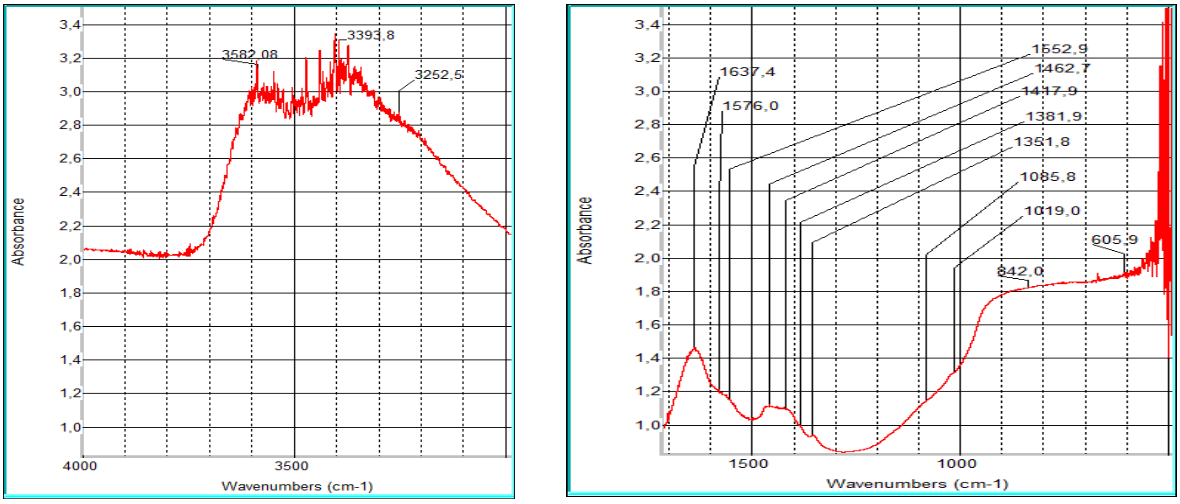
a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

Figure 8 - IR spectrum of the initial 13%Fe/γ-Al_2O_3 system



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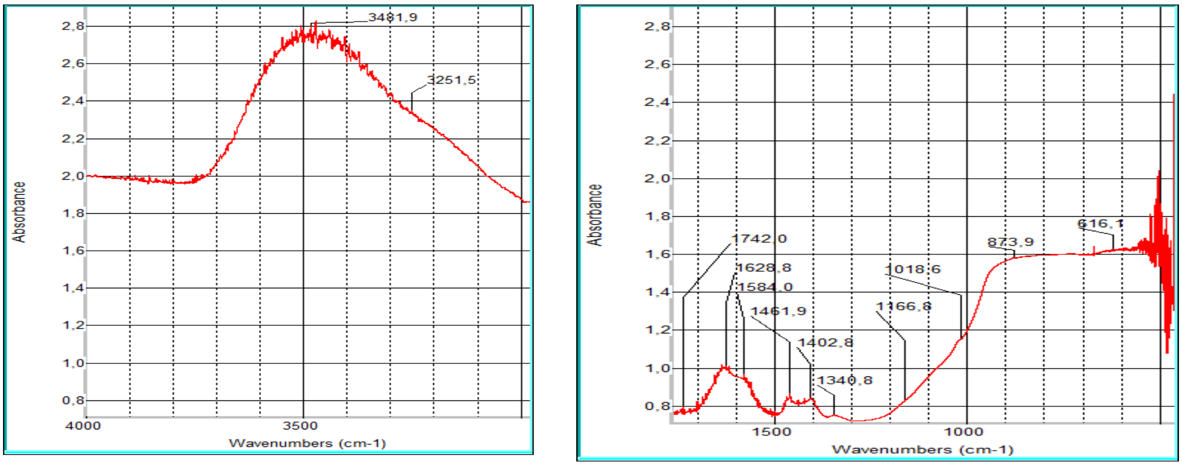
a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

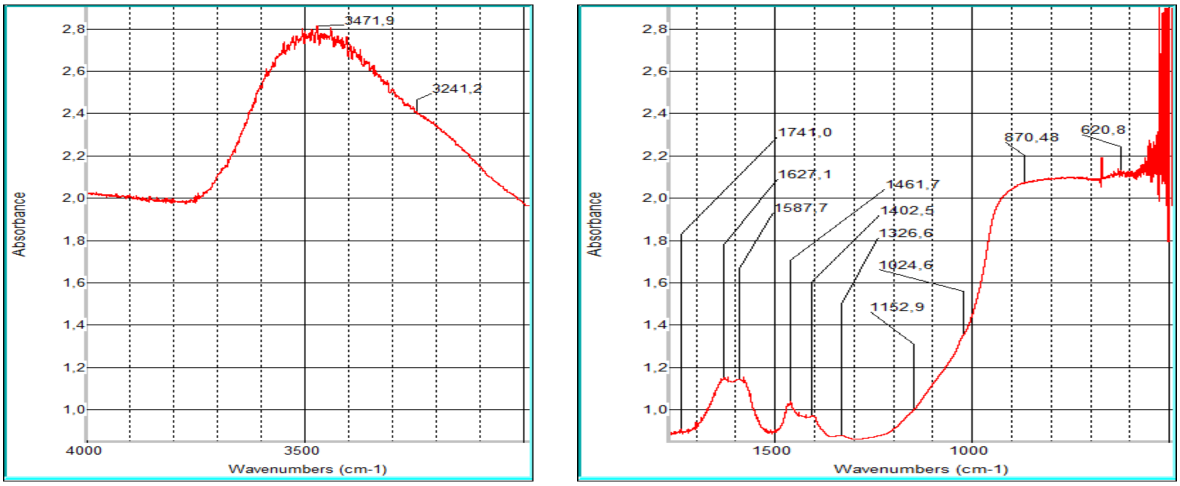
Figure 9 - IR spectrum of the 13%Fe/γ-Al_2O_3 system after hydrogen adsorption at 293K



a b

a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

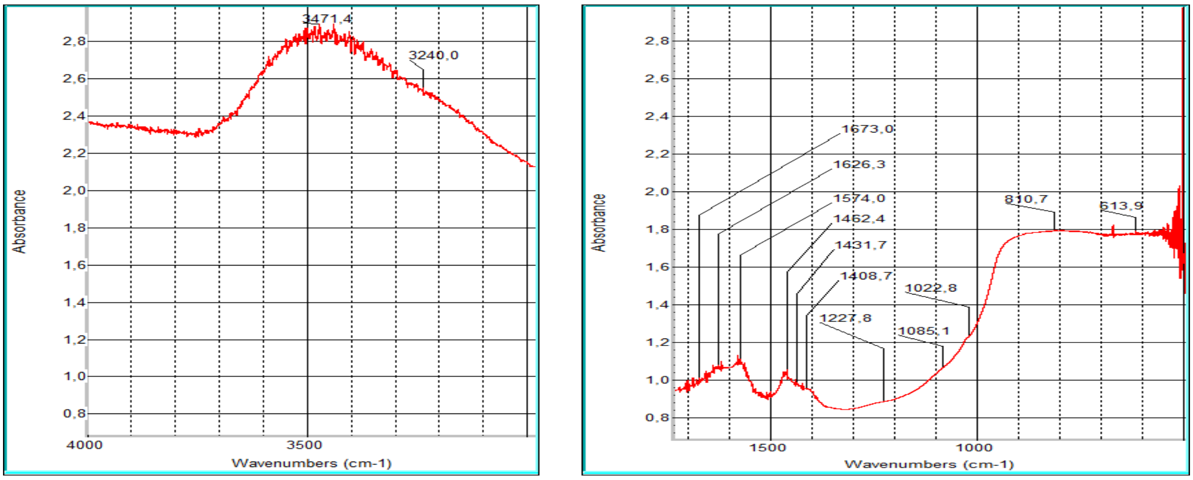
Figure 10 - IR spectrum of the 13%Fe/γ-Al_2O_3 system after hydrogen adsorption at 373K



a b

a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

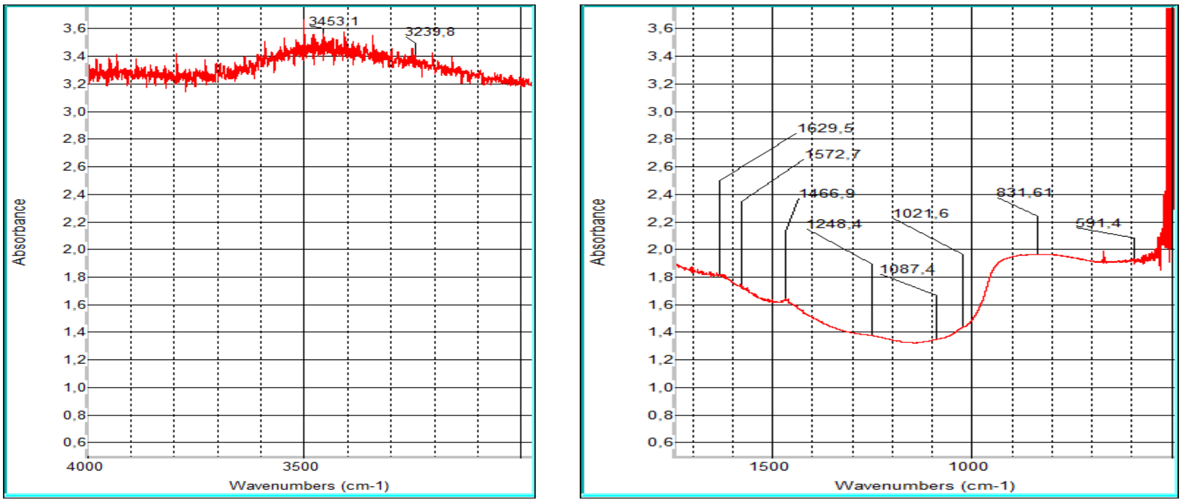
Figure 11 - IR spectrum of the 13%Fe/γ-Al_2O_3 system after hydrogen adsorption at 473K



a b

a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

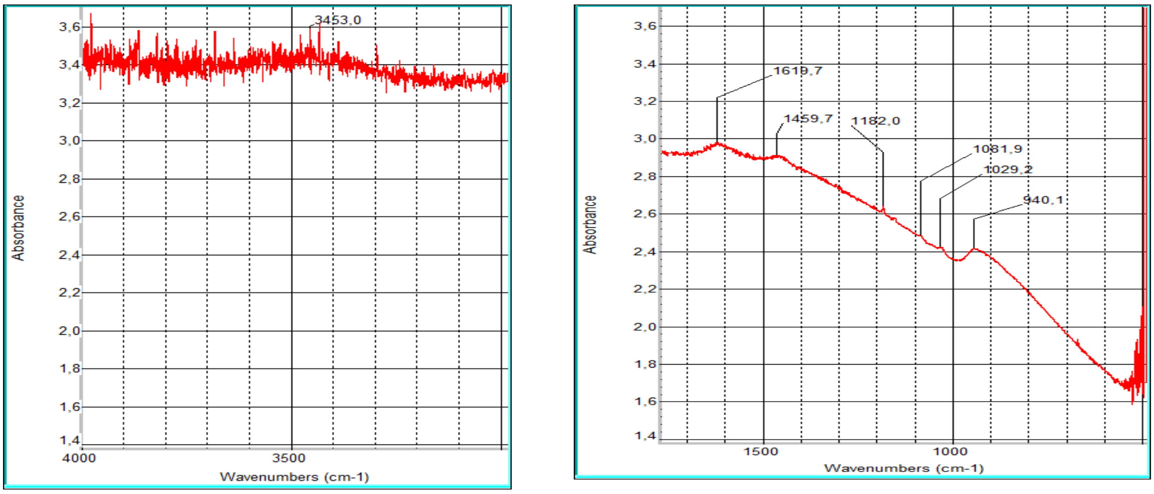
Figure 12 - IR spectrum of the 13%Fe/γ-Al_2O_3 system after hydrogen adsorption at 573K



a b

a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

Figure 13 - IR spectrum of the 13%Fe/γ-Al_2O_3 system after hydrogen adsorption at 673K



a b

a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

Figure 14 - IR spectrum of the 13%Fe/γ-Al_2O_3 system after hydrogen adsorption upon interaction with H_2 in the range 773K

Table 1 - Interpretation of the data of the IR spectra of γ-Al_2O_3 and γ-Al_2O_3 upon interaction with H_2 in the range 293-773K

T, K	Absorption bands, cm^{-1}		Assignment of absorption bands
	Sample		
	γ-Al_2O_3	Fe/γ-Al_2O_3	
1	2	3	4
Initial states			
293	3699	3702	Stretching vibrations of bridging -OH groups bound to aluminum ions in octahedral and (or) tetrahedral coordination
	3453, 3250	3452, 3212	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
		3404, 3301,	Stretching vibrations of -OH groups bound on the surface of alumina by hydrogen bonds
	1633, 1571, 1524, 645	1632, 1584, 1526, 623	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1457, 1391	1468, 1400, 1358	Bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups (traces)
	1088, 1048	1068	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination
	818, 753	804, 728	Bending vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination, as well as, possibly, in Al-O-Fe groups in the Fe/γ-Al_2O_3 system
	565	550	Stretching vibrations of M-O bonds (M = Al; Fe)
Interaction with hydrogen			
293	3493, 3220	3582, 3253	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds, including those on the surface of hydroxides (3582 cm-1)
	3389	3394,	Stretching vibrations of -OH groups formed upon dissociative adsorption of hydrogen on the surface
	1631, 1588, 623	1637, 1576, 606	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1462, 1406, 1353	1463, 1420, 1382, 1352	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1264, 1154, 912		Bending vibrations related to -OH groups of different coordination
	1738, 1699		Stretching vibrations related to $-AlH^-$ groups (Lewis acid sites)
	1106, 1024, 878	1086, 1019	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination
	820-700 region	842	The wide unresolved absorption band (820-700 cm^{-1}) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the $-AlH^-$ groups (Lewis acid sites) can also be located. The band at 842 cm^{-1} (for the Fe/γ-Al_2O_3 system), possibly, refers to bonds in the Al-O-Fe groups.
373	3492, 3220	3483, 3252	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	3385		Stretching vibrations of -OH groups formed upon dissociative adsorption of hydrogen on the surface
	1631, 1586, 597	1629, 1584, 616	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1466, 1428, 1402, 1348	1462, 1403, 1341	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1265, 1156	1167	Bending vibrations related to -OH groups of different coordination
	1743, 1697	1742	Stretching vibrations related to $-AlH^-$ groups (Lewis acid sites)
	1020	1019	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination
	820-700 region	874	The wide unresolved absorption band (820-700 cm^{-1}) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the $-AlH^-$ groups (Lewis acid sites) can also be located. The band at 874 cm^{-1} (for the Fe/γ-Al_2O_3 system), possibly, refers to bonds in the Al-O-Fe groups.
473	3489, 3218	3472, 3241	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1631, 1586, 602	1628, 1588, 621	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds

Continuation of table 1

1	2	3	4
	1462, 1403, 1387, 1350	1462, 1403, 1327	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1264, 1153	1153	Bending vibrations related to -OH groups of different coordination
	1740	1741	Stretching vibrations related to $-AlH^-$ groups (Lewis acid sites)
	1110, 1021, 875	1125	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
573	3489, 3226	3471, 3240	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1630, 1574, 627	1626, 1574, 614	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1465,1430,1405, 1339	1462, 1432, 1409	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1269, 1152	1228	Bending vibrations related to -OH groups of different coordination
	1735	1673	Stretching vibrations related to the groups $-AlH^-$ and $-FeH^-$ (Lewis acid sites)
	1107, 1020, 847	1085, 1023	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
	820-700 region	811	The wide unresolved absorption band (820-700 cm^{-1}) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the $-AlH^-$ groups (Lewis acid sites) can also be located. The band at 811 cm^{-1} (for the Fe/γ-Al_2O_3 system), possibly, refers to bonds in the Al-O-Fe groups.
673	3684		Stretching vibrations of terminal -OH groups bonded with aluminum ions
	3493, 3230	3453, 3240	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1635, 1576, 603	1630, 1573, 591	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1499, 1465, 1410	1467	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1283, 1182, 1152	1248	Bending vibrations related to -OH groups of different coordination
	1696		Stretching vibrations related to $-AlH^-$ groups (Lewis acid sites)
	1080, 1021, 882	1087, 1022	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
	820-700 region	832	The wide unresolved absorption band (820-700 cm^{-1}) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the $-AlH^-$ groups (Lewis acid sites) can also be located. The band at 832 cm^{-1} (for the Fe/γ-Al_2O_3 system), possibly, refers to bonds in the Al-O-Fe groups.
773	3685		Stretching vibrations of terminal -OH groups bonded with aluminum ions
	3480, 3248	3453	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1638, 1506, 603	1620	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1461, 1308	1460	Bending vibrations of -OH groups (against the background of bending vibrations of CH bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1162, 1154, 925	1182	Bending vibrations related to -OH groups of different coordination
	1688		Stretching vibrations related to $-AlH^-$ groups (Lewis acid sites)
	1083, 1021, 878	1082, 1029, 940	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
	806 (in 820-700 region)		The wide unresolved absorption band (820-700 cm^{-1}) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the $-AlH^-$ groups (Lewis acid sites) can also be located.

In the initial Fe/γ-Al_2O_3 system (figure 8, table 1), as well as in the initial γ-Al_2O_3 oxide there are absorption bands related to -OH bridging groups associated with aluminum ions in the octahedral and (or) tetrahedral coordination, absorption bands related to -OH groups bound on the surface by hydrogen bonds, absorption bands related to Al-O bonds. In addition, an absorption band related to Fe-O bonds is observed in the initial Fe/γ-Al_2O_3 system. This absorption band disappears while interacting with hydrogen. The absorption band associated with the -OH bridging groups also disappears while interacting with hydrogen, similar to what happened in the case of γ-Al_2O_3 oxide.

It should be noted that in the Fe/γ-Al_2O_3 system (initial state) there are absorption bands belonging to the -OH groups on the surface of aluminum hydroxides. This is in good agreement with the data presented in our works [11, 12]. There were noted that during the synthesis of the Fe/γ-Al_2O_3 system by impregnation partial hydrolysis of aluminum oxide can occur resulting in the formation of a certain amount of aluminum hydroxide.

Upon interaction with the hydrogen of the Fe/γ-Al_2O_3 system, as in the case of alumina, absorption bands appear associated with the Lewis acid sites. The relative intensity of the absorption bands corresponding to Lewis centers also decreases as temperature increases similarly to what was observed for γ-Al_2O_3 oxide.

At the same time there are noticeable differences (figures 8-14, table 1), in particular, the absorption bands in the 1283-912 cm^{-1} region corresponding to the bending vibrations of the -OH groups appear only starting from 373K and this is only one band. The decrease in the number of absorption bands is possibly associated with a partial coating of the hydroxyl surface of the support with an iron-containing component. In addition, in the long-wavelength region of the IR spectra there are absorption bands that can be attributed to bonds in the Al-O-Fe groups.

Absorption bands related to stretching vibrations associated with Lewis centers are present only in a limited 373-573K temperature range. In addition, at 573 K, a significant (more substantial than in the case of γ-Al_2O_3) band shift to the long-wavelength region occurs. Perhaps this is due to the fact that at 573K Lewis centers can be associated with iron. It should be noted that the absorption bands corresponding to the Lewis centers are not recorded at temperatures above 573K, which is in good agreement with the onset of iron reduction in the Fe/γ-Al_2O_3 system [29]. It follows that the -Fe-H^- fragments are unstable at higher temperatures. Therefore, we can conclude that the reduction of Fe^{3+} to the Fe^{2+} state occurs upon dissociative adsorption of hydrogen (by a peculiar hydride mechanism) with the formation of hydride states of iron and their subsequent decomposition with the release of hydroxyl groups (water vapor).

3 Study of the Fe/γ-Al_2O_3 system using temperature programmed desorption during hydrogen adsorption in 293-773K temperature range

The surface properties of γ-Al_2O_3 oxide (as a reference point) and the Fe/γ-Al_2O_3 system with different iron contents (3% Fe/γ-Al_2O_3; 13%Fe/γ-Al_2O_3) were studied. The results of TPD-H_2 for γ-Al_2O_3 oxide are shown in Figure 15 (1) and Table 2.

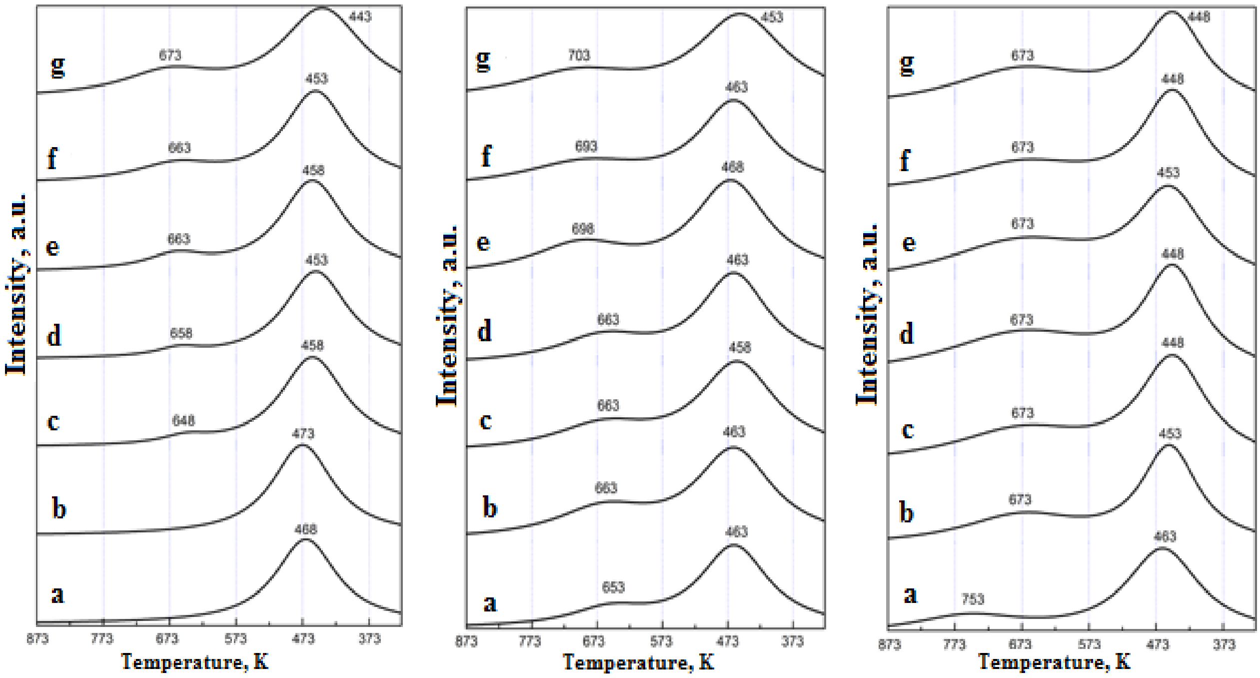
Adsorbed hydrogen is desorbed from the γ-Al_2O_3 surface on a temperature scale in the form of two peaks (table 2). Over the entire temperature range of adsorption the low-temperature desorption peak A is in 463-443K range. The amount of desorbed gas for peak A is extreme with a maximum position at an adsorption temperature of 373K.

The high-temperature peak B in quantitative terms is much inferior to the lower-temperature peak A. As the adsorption temperature goes up its intensity increases slightly, and the position shifts to the high-temperature region, moreover, peak B appears only at adsorption temperatures above 373K.

It should be noted that the dependence of the total amount of desorbed gas on the adsorption temperature passes through a maximum at 373K.

As follows from Figure 15 (2, 3) and Table 3, in the case of the 3% Fe/γ-Al_2O_3 system at adsorption temperatures above 473K, the third desorption peak C′ appears, and the amount of desorbed gas corresponding to this peak slightly increases with increasing temperature. For the 13%Fe/γ-Al_2O_3 system, the third desorption peak C″ exists only at an adsorption temperature of 293K. At the same time, the temperature ranges for the existence of peaks A, A′, and A″ for γ-Al_2O_3 oxide and Fe/γ-Al_2O_3 systems are almost identical.

As for the amount of desorbed gas corresponding to these peaks, here the picture is not so clear. As noted above, for γ-Al_2O_3 oxide, the amount of desorbed gas for peak A passes through a maximum at an adsorption temperature of 373K. The amount of desorbed gas for the A′ peak (3%Fe/γ-Al_2O_3 system) passes through a minimum at an adsorption temperature in the range 473-573K. A similar picture is observed for the A″ peak (13%Fe/γ-Al_2O_3 system).



1 2 3

H_2 adsorption temperature: a - 293K; b - 373K; c - 423K; d - 473K;
e - 573K; f - 673K; g - 773K

1 - γ-Al_2O_3; 2 - 3%Fe/γ-Al_2O_3; 3 - 13% Fe/γ-Al_2O_3

Figure 15 - TPD-H_2 profiles of γ-Al_2O_3 oxide, 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems

Table 2 - TPD-H_2 study results for γ-Al_2O_3 oxide

Adsorbent	Adsorption temperature H_2, K	The maxima temperature of adsorption peaks, K		The amount of desorbed gas, 10^{-4} mol/g		The total amount of desorbed gas, 10^{-4} mol/g
		A	B	A	B	
γ-Al_2O_3	293	458	-	1.96	-	1.96
	373	463	-	3.66	-	3.66
	423	458	648	2.63	0.27	2.90
	473	453	658	2.43	0.43	2.86
	573	458	663	2.35	0.55	2.90
	673	453	663	2.13	0.55	2.68
	773	443	673	1.94	0.55	2.50

The results of TPD-H_2 for the Fe/γ-Al_2O_3 system are shown in figure 15 (2, 3) and are shown in table 3.

The amount of desorbed gas corresponding to the B″ peak (13%Fe/γ-Al_2O_3 system) increases slightly with adsorption temperature, as was observed for γ-Al_2O_3 oxide (B peak). In the case of the 3%Fe/γ-Al_2O_3 system (B′ peak), the amount of desorbed gas passes through a maximum at 373K with an increase in the adsorption temperature.

The dependence of the total amount of desorbed gas for 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems on the adsorption temperature, unlike γ-Al_2O_3 oxide, passes through a minimum (table 3).

Table 3 - Results of TPD-H_2 studies for Fe/γ-Al_2O_3 system

Adsorbent	Adsorption temperature H_2, K	The maxima temperature of adsorption peaks, K			The amount of desorbed gas, 10^{-4} mol/g			The total amount of desorbed gas, 10^{-4} mol/g
		A′	B′	C′	A′	B′	C′	
3%Fe/γ-Al_2O_3	293	463	653	-	2.98	0.90	-	3.88
	373	463	663	-	3.03	1.03	-	4.06
	423	458	663	-	3.14	0.97	-	4.11
	473	463	663	-	1.84	0.68	-	2.52
	573	468	-	698	1.87	-	0.66	2.53
	673	463	-	693	2.62	-	0.73	3.35
	773	453	-	703	2.61	-	0.76	3.37
13%Fe/γ-Al_2O_3		A″	B″	C″	A″	B″	C″	
	293	463	-	753	3.07		0.81	3.88
	373	453	673	-	2.46	0.66	-	3.12
	423	448	673	-	2.38	0.70	-	3.08
	473	448	673	-	2.17	0.82	-	2.99
	573	453	673	-	2.24	0.84	-	3.08
	673	448	673	-	2.52	0.83	-	3.35
	773	448	673	-	2.50	0.86	-	3.36

The appearance of the third additional desorption peak of C′, C″ for the 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 systems, respectively, in comparison with γ-Al_2O_3 oxide is associated with the presence of an iron-containing component on the surface of aluminum oxide. The differences between the 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems (temperature ranges for the existence of the B′, B″ and C′, C″ peaks) can be explained by the fact that for the 13%Fe/γ-Al_2O_3 system coating the surface of alumina with an iron-containing component is multilayer [11, 12].

Summarizing this section, we can conclude that on the surface of γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system there are adsorption centers that differ in energy characteristics (binding energies). Moreover, these characteristics may also depend on the percentage of the iron-containing component on the surface of aluminum oxide.

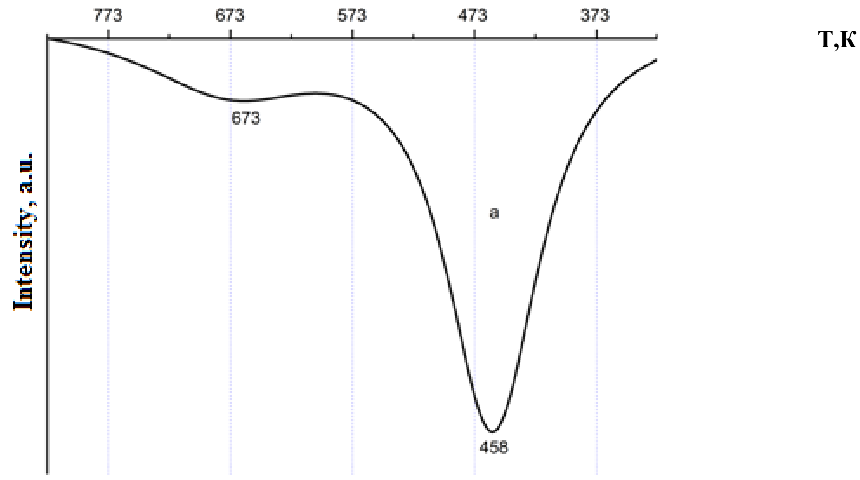
4 Study of the Fe/γ-Al_2O_3 system using temperature programmed hydrogen reduction in 293 - 773K temperature range

The surface properties of γ-Al_2O_3 oxide (as a reference point) and the Fe/γ-Al_2O_3 system with different iron contents (3%Fe/γ-Al_2O_3; 13%Fe/γ-Al_2O_3) were studied.

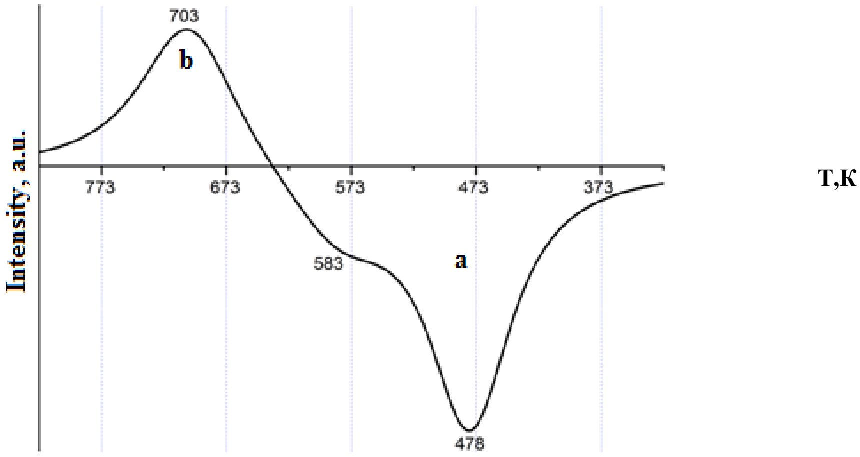
Figure 16 shows the TPR-H_2 curves for γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system. The results are shown in table 4.

The TPR-H_2 profiles for γ-Al_2O_3 oxide (figure 16 (1), table 4) in the adsorption region (a) contain two peaks at temperatures of 458 and 673K, and the second peak is noticeably lower in intensity. In a given temperature range no desorption peaks are observed, which probably indicates the strength of hydrogen bonding with the surface of γ-Al_2O_3 oxide.

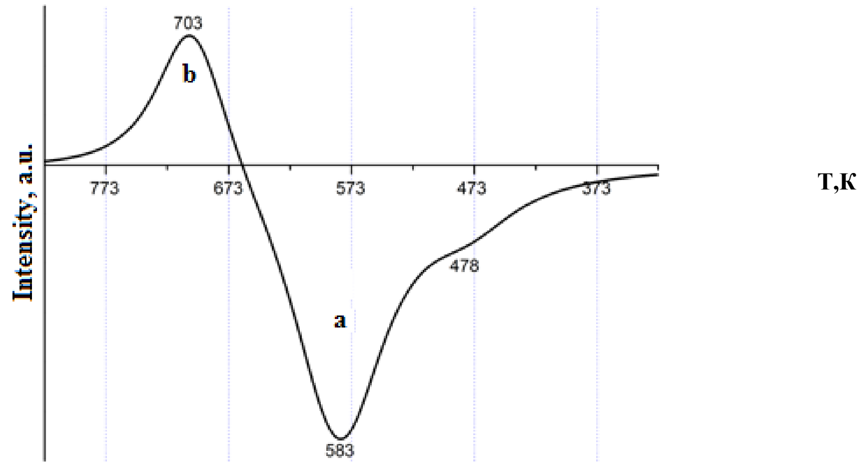
The TPR-H_2 profiles for the 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems in the adsorption region (a) also contain two peaks, but at 478 and 583 K (figure 16 (2), (3), table 4). A higher temperature peak is also noticeably lower in intensity.



(1)



(2)



(3)

a – adsorption region; b – desorption region (1) - γ-Al_2O_3; (2) - 3%Fe/γ-Al_2O_3; (3) - 13%Fe/γ-Al_2O_3

Figure 16 - TPR-H_2 profiles for γ-Al_2O_3 oxide
and the Fe/γ-Al_2O_3 system in the temperature range 293-773K

Table 4 - The results of the study using TPR-H_2 for γ-Al_2O_3 oxide
and the 3%Fe/γ-Al_2O_3 system in 293-773K temperature range

Adsorbent	The maxima temperature of adsorption peaks, K		The maxima temperature of adsorption peaks, K	W_{ADS}, 10^{-4} mol/g		ΣW_{ADS}, 10^{-4} mol/g	W_{DES}, 10^{-4} mol/g
	A	B	C	A	B	A + B	C
γ-Al_2O_3	458	673	-	0.94	0.22	1.16	-
3%Fe/γ-Al_2O_3	478	583	703	0.92	0.33	1.25	0.84
13% Fe/γ-Al_2O_3	478	583	703	0.35	0.90	1.25	0.70

W_{ADS} - amount of adsorbed substance; ΣW_{ADS} - total amount of adsorbed substance; W_{DES} - amount of desorbed substance.

Noteworthy is the temperature shift of the adsorption peaks for the Fe/γ-Al_2O_3 system, regardless of the iron content, in comparison with γ-Al_2O_3 oxide. This may be due to the fact that in the case of the Fe/γ-Al_2O_3 system with 3 and 13% of iron content and is almost completely coated with an iron-containing component, as was shown using scanning electron microscopy in [11, 12] and therefore, adsorption should take place on it.

In addition, (figure 16, table 4), on the TPR-H_2 profile for the Fe/γ-Al_2O_3 system, regardless of the iron content, there is a desorption region (b) with a peak maximum at 703K. It should be noted that the desorption (from 56 to 67%) of the reagent adsorbed at lower temperatures occurs in the range of ~630-773K. This interval is well superimposed [29] on the temperature interval of the reduction of Fe^{3+} states to Fe^{2+} states.

Since several adsorption peaks are clearly distinguishable on the TPR-H_2 profiles, it can be assumed that γ-Al_2O_3 oxide and 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 systems contain different states of metal oxide forms. The presence of a desorption region in the range of 630-773K for 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 systems is apparently associated with the reduction of the Fe^{3+} state to Fe^{2+} upon dissociative hydrogen adsorption, for example, by the mechanism:

$$Fe_2O_3 + H^- + H^+ \rightarrow FeO + OH^- + H^- \rightarrow FeO + H_2O\uparrow$$

Conclusion. Studies of the Fe/γ-Al_2O_3 system in the temperature range 273-773K showed that its surface is heterogeneous and represents a set of adsorption centers with different energy characteristics.

Lewis acid centers were detected using IR spectroscopy on the surface of both γ-Al_2O_3 oxide (support) and the Fe/γ-Al_2O_3 system, during their interaction with hydrogen in the temperature range 293-773K. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with hydrogen and decreases with its growth both for γ-Al_2O_3 and for the Fe/γ-Al_2O_3 system.

For the Fe/γ-Al_2O_3 system the –OH groups' absorption bands in the region of 1283-912 cm^{-1} appear only starting from 373 K and this is only one band. The decrease in the number of absorption bands is apparently associated with a partial coating of the hydroxyl surface of the support with an iron-containing component. In addition, in the long-wavelength region of the IR spectra there are absorption bands that can be attributed to bonds in the Al-O-Fe groups.

It was shown that on the surface of γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system, there are adsorption centers that differ in their energy characteristics (binding energies) by TPD-H_2 method. Moreover, these characteristics may also depend on the percentage of the iron-containing component on the surface of aluminum oxide.

Using the TPR-H_2 method, it was found that γ-Al_2O_3 oxide and 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 systems contain different states of metal oxide forms, since several extrema are clearly distinguishable on the TPR-H_2 profiles.

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Fe/γ-Al_2O_3 КАТАЛИТИКАЛЫҚ ЖҮЙЕНІҢ ЗОНДТЫ МОЛЕКУЛАЛАРМЕН ӨЗАРА ӘРЕКЕТІ

IV. γ-Al_2O_3 ОКСИДІ ЖӘНЕ Fe/γ-Al_2O_3 ЖҮЙЕСІНІҢ СУТЕГІМЕН ӨЗАРА ӘРЕКЕТІН ЗЕРТТЕУ

Аннотация. Жұмыс гетерогенді каталитикалық жүйелердің адсорбталған молекулалармен өзара әрекетін зерттеуге арналған. Мұнда бастапқы γ-Al_2O_3 оксид сутегісімен және ИК-спектроскопия, термобағдарламаланған десорбция, сутегімен термобағдарламаланған түрдегі тотықсыздандыру әдістері арқылы алынған темірдің түрлі құрамды Fe/γ-Al_2O_3 жүйелерінің өзара әрекеттесу нәтижелері келтірілген.

Алюминий оксиді γ-Al_2O_3 және Fe/γ-Al_2O_3 жүйесіне қатысты жүргізілген зерттеулер темір құрамына қарамастан 273 - 773К температуралық интервалында беті біркелкі емес және өз алдына түрлі энергетикалық сипаттамасы бар адсорбциялық орталықтар жиынтығы екендігін көрсетті.

ИК-спектроскопия арқылы γ-Al_2O_3 оксиді (тасымалдаушы) секілді Fe/γ-Al_2O_3 жүйесінде де олардың сутегімен өзара әрекеттесуі кезінде 293-773К температуралық интервалда Льюистің қышқылды орталықтары анықталды. Осы орталықтарға жауап беретін жұтылу жолақтарының салыстырмалы қарқыны сутегімен өзара әрекеттесу температурасына байланысты және ол жоғарылағанда γ-Al_2O_3 сияқты Fe/γ-Al_2O_3 жүйелері үшін де төмендейді.

Fe/γ-Al_2O_3 жүйесі үшін жұтылу жолақтары 1283 – 912 см$^{-1}$ аймағында, ОН-топтар үшін тек қана 373К бастап пайда болады және бұл тек бір ғана жолақ. Жұтылу жолақтары санының азаюы темірқұрамдас компоненттер тасымалдаушысының гидроксильді бетінің жартылай жабылуына байланысты болуы мүмкін. Бұдан басқа ИК-спектрлердің ұзын толқынды аймағында Al-O-Fe топтарындағы байланысқа жатқызуға болатын жұтылу жолақтары бар.

Fe/γ-Al_2O_3 жүйесінде бастапқы күйде Fe-O байланысына жататын жұтылу жолағы байқалады, алайда сутегімен өзара әрекеттескен кезде бұл жұтылу жолағы жоғалады. Fe/γ-Al_2O_3 жүйесінің сутегімен өзара әрекеттесуі кезінде ОН-көпірлік топтарымен байланысты жұтылу жолағы да жоғалады, γ-Al_2O_3 оксиді жағдайында да солай болады.

ТПД-H_2 әдісі көрсеткендей, γ-Al_2O_3 оксидтің бетінде және Fe/γ-Al_2O_3 жүйелерінде өзінің энергетикалық сипаттамалары бойынша (байланыс энергиясы) ерекшеленетін адсорбциялық орталықтар бар. Бұл сипаттамалар алюминий оксидінің бетінде темір құрамды компоненттердің пайыздық мөлшеріне байланысты болуы мүмкін.

ТПВ-H_2 әдісі арқылы γ-Al_2O_3 оксиді және 3% Fe/γ-Al_2O_3, 13% Fe/γ-Al_2O_3 жүйелері металл оксиді қалыптарының түрлі күйі пайда болады, өйткені ТПВ-H_2 қисығында бірнеше экстремумдар анық ажыратылады.

Құрамында темір болғандығына қарамастан 3% Fe/γ-Al_2O_3, 13% Fe/γ-Al_2O_3 жүйесі үшін 630-773К температуралық интервалда 703К кезінде максимум жағдайы бар десорбция аймағы байқалады. 3% Fe/γ-Al_2O_3, 13% Fe/γ-Al_2O_3 жүйесі үшін десорбция аймағының болуы темірқұрамдас компоненттердің, нақтырақ айтқанда, сутегі диссоциативті адсорбциясы кезінде жай-күйінің Fe^{3+}-тен Fe^{2+} дейін қалпына келуіне байланысты, мысалы, механизм бойынша:

$$Fe_2O_3 + H^- + H^+ \rightarrow FeO + OH^- + H^- \rightarrow FeO + H_2O\uparrow$$

Түйін сөздер: гетерогенді катализ, физика-химиялық зерттеу әдістері, адсорбцияланған молекулалар.

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ВЗАИМОДЕЙСТВИЕ КАТАЛИТИЧЕСКОЙ СИСТЕМЫ Fe/γ-Al_2O_3 С МОЛЕКУЛАМИ-ЗОНДАМИ. IV. ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ ВОДОРОДА С ОКСИДОМ γ-Al_2O_3 И СИСТЕМОЙ Fe/γ-Al_2O_3

Аннотация. Работа посвящена исследованию взаимодействия гетерогенных каталитических систем с адсорбированными молекулами. В ней представлены результаты по взаимодействию с водородом исходного оксида γ-Al_2O_3 и систем Fe/γ-Al_2O_3, с различным содержанием железа, полученные с помощью ИК-спектроскопии, методов термопрограммированной десорбции и термопрограммированного восстановления водородом.

Проведённые исследования оксида алюминия γ-Al_2O_3 и систем Fe/γ-Al_2O_3, независимо от содержания железа, в температурном интервале 273 - 773К показали, что их поверхность неоднородна и представляет собой набор адсорбционных центров с различными энергетическими характеристиками.

С помощью ИК-спектроскопии на поверхности как оксида γ-Al_2O_3 (носитель), так и систем Fe/γ-Al_2O_3 при их взаимодействии с водородом в температурном интервале 293 – 773К были обнаружены кислотные центры Льюиса. Относительная интенсивность полос поглощения, отвечающих этим центрам, зависит от температуры взаимодействия с водородом и с её ростом падает как для γ-Al_2O_3, так и для систем Fe/γ-Al_2O_3.

Для систем Fe/γ-Al_2O_3 полосы поглощения в области 1283 – 912 $см^{-1}$, групп – ОН появляются только начиная с 373К, и это только одна полоса. Уменьшение количества полос поглощения, видимо, связано с частичным покрытием гидроксильной поверхности носителя железосодержащей компонентой. Кроме того, в длинноволновой области ИК-спектров присутствуют полосы поглощения, которые можно отнести к связям в группах Al-O-Fe.

В системе Fe/γ-Al_2O_3 в исходном состоянии наблюдается полоса поглощения, относящаяся к связям Fe-O, однако при взаимодействии с водородом эта полоса поглощения пропадает. При взаимодействии с водородом системы Fe/γ-Al_2O_3 исчезает и полоса поглощения, связанная с мостиковыми группами -ОН, то же самое происходит и в случае оксида γ-Al_2O_3.

Методом ТПД-H_2 показано, что на поверхности оксида γ-Al_2O_3 и систем Fe/γ-Al_2O_3 присутствуют адсорбционные центры, различающиеся по своим энергетическим характеристикам (энергии связи). Причём, эти характеристики могут зависеть и от процентного содержания железосодержащей компоненты на поверхности оксида алюминия.

Методом ТПВ-H_2 установлено, что оксид γ-Al_2O_3 и системы 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 содержат различные состояния оксидных форм металла, поскольку на кривых ТПВ-H_2 четко различимы несколько экстремумов.

В температурном интервале 630 –773К для систем 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 независимо от содержания железа, наблюдается область десорбции с положением максимума при 703К. Наличие области десорбции для систем 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3, видимо, связано с восстановлением железосодержащей компоненты, а именно состояния Fe^{3+} до Fe^{2+} при диссоциативной адсорбции водорода, например, по механизму:

$$Fe_2O_3 + H^- + H^+ \rightarrow FeO + OH^- + H^- \rightarrow FeO + H_2O\uparrow$$

Ключевые слова: гетерогенный катализ, физико-химические методы исследования, адсорбированные молекулы.

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Памяти
Емельяновой Валентины Степановны

31 мая 2020 года на 76 году жизни после болезни скончалась известный ученый, ветеран труда СССР Емельянова Валентина Степановна.

Валентина Степановна прожила полных 75 лет. Из них 60 лет приходилось на осознанную работу над своим становлением как Человека и Личности. Успешно получив базовое образование, Валентина Степановна всю жизнь посвятила семье и работе. Семейные заботы понятны всем. Но вырастить достойными людьми четверых детей и одновременно серьёзно заниматься научным трудом – таких примеров немного. Мало кто женщин отважится на такое. Но это личная жизнь.

Другая сторона жизни любого человека – это трудовая деятельность на благо государства, общества и семьи. В этом отношении Валентина Степановна – настоящий труженик и творческая личность.

Она увлеклась химией будучи ещё ученицей средней школы №35 г. Алма-Аты, получила отличное образование в Днепропетровском химико-технологическом институте и продолжала совершенствовать свои профессиональные познания в Институте органического катализа и электрохимии Академии наук Казахской ССР, плодотворно проработав в Институте более 20 лет. Здесь первыми её учителями и наставниками были академик Дмитрий Владимирович Сокольский, заведующий лабораторией гомогенного катализа Яков Абрамович Дорфман, а помогла с трудоустройством и опекала первое время Алма Гасиевна Сармурзина, дружба с которой продолжалась всю их жизнь. Успешно защитила кандидатскую диссертацию в 1974 г.

Большую роль в жизни Валентины Степановны сыграл академик НАН РК Жубанов Каир Ахметович, который в 1992 г. на базе Казахского государственного университета создал Научно-исследовательский институт новых химических технологий и материалов. Емельянова В.С. посвятила этому Институту 20 лет, проработав в нём в должности зам - директора, занимаясь планированием, организацией и обеспечением научных исследований, содействием кафедрам химического факультета в подготовке высококвалифицированных научных кадров, проектированием, разработкой и внедрением результатов исследований и опытно-конструкторских работ в соответствующие отрасли производства и учебный процесс химического факультета, направленных на подъем и стабилизацию экономики РК.

Трудовая деятельность Емельяновой В.С. включала также ответственную работу – учёного секретаря Отделения химико-технологических наук Национальной академии наук Республики Казахстан и заместителя декана по науке на химическом факультете Казахского государственного университета.

Подытоживая, надо отметить, что вся жизнь Валентины Степановны до последнего дня была посвящена химической науке, на этом поприще она достигла немалых успехов. Надо отметить, что не карьера была её целью. Главный интерес для Валентины Степановны проявлялся в самом творческом процессе научных исследований.

Ею разработаны и испытаны в промышленных условиях металлокомплексные и иммобилизованные на полимерную матрицу катализаторы, которые сочетают лучшие свойства гомогенных и гетерогенных катализаторов. Катализаторы изучены в процессах низкотемпературного: окисления SO_2, восстановления SO_2 оксидом углерода, сульфоокисления алкенов и аренов, окислительного дехлорирования n-дихлорбензола, анаэробного мезофильного превращения углеводов. В последнее время Емельяновой В.С. были вовлечены в сферу деятельности алюмосиликатные микросферы золы уноса, являющиеся техногенными отходами ТЭС. Ею разрабатывались техника и технология фракционного разделения микросфер с выделением ферромагнетиков, научные основы приготовления и использования магнитных композиций в различных процессах с магнитным полем и без него.

Под её руководством защищено 9 кандидатских диссертаций. В процессе научной деятельности получила 25 авторских свидетельств СССР и 5 патентов РК, было подано 5 заявок на предпатенты РК. В соавторстве издано 10 монографий на русском и английском языках, опубликовано более 400 трудов в журналах Республики Казахстан и за рубежом, в том числе в журналах, индексируемых базами данных Web of Science или Scopus. Валентина Степановна входила в состав экспертов Государственной экспертизы РК и Фонда науки РК. Была руководителем 8 проектов и программ: «Разработка технологии получения биогаза методом каталитической мезофильной переработки сельскохозяйственных отходов с целью его использования для отопления и получения электроэнергии» и «Разработка технологий адсорбционной каталитически-хемоадсорбционной очистки газовых выбросов от сернистых соединений с одновременным отделением сульфокислот и сульфоксидов в качестве продуктов реакций»; соруководителем программ «Разработка технологии глубокой переработки органического и минерального сырья и получения наноструктурированной композиционной продукции различного назначения», «Теория и практика утилизации гуминовых веществ – возобновляемых источников химического сырья», «Разработать научные основы переработки горючих ископаемых и получения новых материалов», «Получение фундаментальных знаний в процессах получения и использования новых наноразмерных магнитных композитов», проекта «Разработка технологии получения и использования магнитоактивных наноразмерных композиционных материалов на базе углеводородного и техногенного сырья казахстана», «Разработка технологии получения новых полифункциональных пористых магнитоуправляемых наноразмерных материалов на основе ценосфер зол уноса для иммобилизации, отверждения и нейтрализации радиационных отходов».

Имела государственную награду – «Ветеран труда СССР», ей было присвоено воинское звание «лейтенант войск химической защиты».

Все эти достижения являются следствием очень важной черты характера Валентины Степановны – чувства долга и ответственности в любом деле.

Важно отметить и то, что в отношениях с окружающими её по жизни людьми она была честным, добрым и отзывчивым ЧЕЛОВЕКОМ!

Коллектив АО «Институт топлива, катализа и электрохимии им. Д.В.Сокольского»
выражает глубокое соболезнование родным и близким.

Памяти
Голодова Валентина Александровича


30-11-20

12 июня 2020 года на 84 году жизни после продолжительной болезни скончался известный ученый в области катализа и физической химии доктор химических наук, профессор, мастер парашютного спорта СССР **Валентин Александрович Голодов**.

В.А..Голодов родился 15 ноября 1935 года (Алма-Ата). Окончил химический факультет Казахского государственного университета им. С. М. Кирова (1960) по специальности «катализ».

Работал там же: 1960–1969 – инженер, младший, старший научный сотрудник проблемной лаборатории. В 1968–1978 – учёный секретарь, с 1978 зав. лабораторией координационного катализа, с 1987 – замдиректора Института органического катализа и электрохимии Академии наук КазССР.

Научные исследования посвящены разработке гомогенных катализаторов для процессов с участием оксида углерода и диоксида серы, явлениям синергизма в катализе, некоторые разработки внедрены в производство.

Им опубликовано более 200 научных статей в журналах Казахстана, СССР и за рубежом, получено 35 авторских свидетельств СССР (ныне патентов) на изобретения.

Читал на химическом факультете КазГУ курсы лекций по катализу, выступал с научными докладами на республиканских, всесоюзных и международных конференциях и конгрессах, в том числе в университетах и исследовательских институтах Германии, США, Японии, Италии и Индии.

В.А. Голодов награждён медалями ВДНХ СССР, лауреат конкурса фонда Сороса, под его руководством защищено 10 кандидатских диссертаций, в течение ряда лет был членом экспертного совета ВАК Казахстана по присуждению ученых степеней и присвоению научных званий.

Прошёл 10-месячную научную стажировку в Высшей технической школе в лаборатории лауреата Нобелевской премии Э. О. Фишера (г. Мюнхен, ФРГ, 1986), результатом которой была совместная публикация в советском журнале, авторское свидетельство СССР (патент) и перевод на русский язык монографии «Пи-комплексы металлов» (М.: Мир, 1975. – 40 п.л.).

Мастер парашютного спорта СССР (525 прыжков), автор 4 мировых и союзных рекордов в групповых прыжках (днём и ночью) на точность приземления, участник республиканских и всесоюзных соревнований.

Коллектив АО «Институт топлива, катализа и электрохимии им. Д.В.Сокольского»
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Памяти
Мухамеджановой Сабиры Гафуровны

19 марта 2020 года на 64 году жизни после болезни скончалась ученый-химик, кандидат химических наук **Сабира Гафуровна Мухамеджанова.**

С.Г. Мухамеджанова родилась в 1956 году в Кызылординской области. Окончила в 1978 году химический факультет Казахского государственного университета им. С.М.Кирова.

С 1983 года работала в Институте топлива, катализа и электрохимии им. Д.В Сокольского. В 1995 году ею была защищена кандидатская диссертация на тему «Синтез и каталитические свойства полимерметаллических комплексов на основе металлов платиновой группы с поливинилпиридинами».

Мухамеджанова С.Г. являлась квалифицированным специалистом в области катализа металлополимерными комплексами. Ею разработаны новые нанодисперсные катализаторы с полимерными лигандами, работающими по принципу ферментов в мягких условиях, для синтеза промышленно важных органических веществ. Ее труды опубликованы в зарубежных высокорейтинговых изданиях. Результаты ее исследований докладывались на международных научных конференциях и симпозиумах.

На работе Сабиру Гафуровну ценили за ум и внимательность. Нам будет не хватать ее доброты, тонкого юмора и ослепительной улыбки. Она навсегда остается в наших сердцах верным другом и мудрым советчиком, всегда готовым оказать помощь в любой сложившейся ситуации.

Коллектив АО «Институт топлива, катализа и электрохимии им. Д.В.Сокольского»
выражает глубокое соболезнование родным и близким.

МАЗМҰНЫ

Ғалымды еске алу

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Уважаемые авторы научных журналов НАН РК!

Президиумом НАН РК принято решение, в целях повышения международного рейтинга академических изданий, объединить следующие 3 журнала, начиная с № 5 (сентябрь-октябрь), 2020 г., с высокорейтинговыми журналами НАН РК, входящими в международные базы Scopus, WoS и др.:

1. **«Известия НАН РК. Серия биологических и медицинских наук»** объединить с журналом «Доклады НАН РК»;

2. **«Известия НАН РК. Серия аграрных наук»** – «Доклады НАН РК»;

3. **«Известия НАН РК. Серия общественных и гуманитарных наук»** – с журналом «Вестник НАН РК».

Статьи, которые публиковались в журналах «Известия НАН РК. Серия биологических и медицинских наук» и «Известия НАН РК. Серия аграрных наук», впредь будут публиковаться в журнале **«Доклады НАН РК»**, а статьи, публикуемые в журнале «Известия НАН РК. Серия общественных и гуманитарных наук», – в журнале **«Вестник НАН РК»**.

При подаче статей просим указывать название журнала и отрасль науки, согласно представленного перечня (см. ниже) в данном журнале:

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2. Естественные (астрономия, физика, химия, биология, география и технические науки). Примеры технических наук: космонавтика, кораблестроение, машиностроение, системотехника, электротехника, электросвязь, радиоэлектроника, ядерная энергетика и т.д.

Адрес сайта «**Вестник НАН РК**» – http://www.bulletin-science.kz/index.php/en/arhive

II. Научный журнал **«Доклады НАН РК»** посвящен исследованиям в области получения наноматериалов, биотехнологии и экологии.

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1. Получение наноматериалов в области естественных наук, медицины и сельского хозяйства.
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3. Общая биология и биотехнология в медицине.
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Кроме того, в журналах «Известия НАН РК. Серия физико-математическая», «Известия НАН РК. Серия химии и технологий» и «Известия НАН РК. Серия геологии и технических наук» также указаны отрасли науки, по которым будут приниматься научные статьи для экспертизы и дальнейшего опубликования:

III. Научный журнал **«Известия НАН РК. Серия физико-математическая»** посвящен исследованиям в области математики, физики и информационной технологии.

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1. Математика.
2. Информатика.
3. Интеллектуальный анализ данных и распознавание образов.
4. Математическое моделирование социальных и экономических процессов.
5. Механика.
6. Механика машин и роботов.
7. Теория управления и космические исследования.
8. Физика.
9. Ядерная физика.
10. Теоретическая физика.
11. Астрономия.
12. Ионосфера.

Адрес сайта «**Известия НАН РК. Серия физико-математическая**» – http://physics-mathematics.kz/index.php/en/archive

IV. Научный журнал **«Известия НАН РК. Серия химии и технологий»** посвящен исследованиям в области химии и технологий новых материалов.

Редакционная коллегия принимает статьи по следующим отраслям науки:

1. Органическая химия.
2. Неорганическая химия.
3. Высокомолекулярные соединения.
4. Физическая химия (катализ, электрохимия).
5. Технология новых материалов.
6. Технология органических веществ.
7. Технология неорганических веществ.
8. Технология химических удобрений.
9. Технология полимерных и строительных материалов и силикаты.
10. Технология пищевых продуктов.
11. Фармацевтическая химия.

Адрес сайта **«Известия НАН РК. Серия химии и технологии»** –

http://chemistry-technology.kz/index.php/en/arhiv

V. Научный журнал «**Известия НАН РК. Серия геологии и технических наук**» посвящен исследованиям в области геологии и технических наук:

Редакционная коллегия принимает статьи по следующим отраслям науки:

1. Геология.
2. Региональная геология.
3. Петрология.
4. Геология нефти и газа.
5. Геология и генезис рудных месторождений.
6. Гидрогеология.
7. Горное дело и геомеханика.
8. Фундаментальные проблемы обогащения минерального сырья.
9. Инженерная геология.
10. Геофизика и сейсмология.
11. География.

Адрес сайта **«Известия НАН РК. Серия геологии и технических наук»** – http://www.geolog-technical.kz/index.php/en/archive