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АО «ИНСТИТУТ ТОПЛИВА, КАТАЛИЗА И
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СЕРИЯ ХИМИИ И ТЕХНОЛОГИИ

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АЛМАТЫ, ҚР ҰҒА АЛМАТЫ, НАН РК ALMATY, NAS RK

NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

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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INTERACTION OF THE Fe/γ-Al_2O_3 CATALYTIC SYSTEM WITH PROBE MOLECULES I. RESEARCH OF THE γ-Al_2O_3 AND THE Fe/γ-Al_2O_3 INITIAL SYSTEM

Abstract. The work is the first part of the studies devoted to the interaction of a heterogeneous catalytic system with adsorbed molecules. It presents the results for the initial oxide γ-Al_2O_3 and Fe/γ-Al_2O_3 system with an iron content of 0.5; 3; 13% by weight, obtained with a wide range of physicochemical methods. The Fe/γ-Al_2O_3 system was chosen as the object of the study, since it exhibits catalytic activity in many chemical processes and can later be used as a model.

The performed work showed that during the preparation of the Fe/γ-Al_2O_3 system by impregnation, the structure of the support can be modified. The nature of the filling of the support surface with the iron-containing phase depends substantially on its percentage and can be multilayered.

It is established that the Fe/γ-Al_2O_3 system contains iron in the form of Fe^{3+}. Depending on the iron content, iron-containing aggregates of various sizes may be present in it, both in the paramagnetic and in the magnetically ordered states.

Key words: heterogeneous catalysis, physicochemical methods of investigation.

Introduction

This work is the beginning of a series of studies devoted to the interaction of a heterogeneous catalytic system with adsorbed molecules. This formulation of the problem is topical, since, in heterogeneous catalysis, the most important stage is the adsorption stage [1, 2].

The iron-containing Fe/γ-Al_2O_3 (γ-Al_2O_3-support) system was chosen as the object of research because it exhibits catalytic activity in many chemical processes, such as the production of ammonia [3-5] and carbon nanotubes [6, 7], in CO hydrogenation reactions (Fischer-Tropsch synthesis) [8, 9], in the oxidation of hydrogen sulphide to elemental sulfur [1], deep processing of solid fossil and renewable organic raw materials [10], in gasoline reforming reactions [11], and many other reactions [12]]. Thus, the catalytic system Fe/γ-Al_2O_3 being practically multifunctional, in the future, can be used as a model system.

Experimental

The Fe/γ-Al_2O_3 system with an iron content of 0.5; 3; 13 wt.% was prepared by impregnation [1, 13, 14] of the initial γ-Al_2O_3 oxide with an aqueous solution of iron acetate, followed by drying and calcination in air.

A wide range of physicochemical methods during the research was used.

X-ray diffractometry. The X-ray diffractometer Dron-4-07 with cobalt anode tube was used.

Mode:

- speed 2 deg/min;
- working parameters of the tube: 30 kV, 20 mA.

Transmission electron microscopy. Equipment - EM-125K, accelerating voltage of 75 kV.

Scanning electron microscopy. JSM 6610 LV, JEOL, Japan is a scanning low-vacuum electron microscope. Accelerating voltage 20 kV.

BET method (low-temperature nitrogen adsorption). Equipment -AccuSorb, Micromeritics, USA. The standard procedure. Calcination of the sample at 230-250° C for 3 hours with evacuation. The relative error in determining the specific surface area is ± 5%.

Mossbauer spectroscopy. Equipment - MS 1104Em, Russia. The source was cobalt 57 in a chromium matrix with an activity of 100 μCi. The spectra were processed on a PC by the "least squares" method. The isomeric shifts are given in terms of α-Fe. The temperature of the spectra is 23°C. The shooting mode is "on the skylight". The error in determining the isomer shift (IS) is ΔIS = ± 0.03 mm/s; quadrupole splitting (QS) ΔQS = ± 0.03 mm/s; relative content (S) ΔS = ± 2%.

Results and Discussion

The study of γ-Al_2O_3 oxide and Fe/γ-Al_2O_3 system was carried out.

X-ray diffractometry.

X-ray diffraction patterns (Fig. 1) of γ-Al_2O_3 oxide and Fe/γ-Al_2O_3 system with various iron contents were obtained.

Following results were obtained:

- Initial γ-Al_2O_3:

Reflexes at 4.5641; 2.7959; 2.3981; 2.2883; 1.9767; 1.5258; 1.3950 Å - γ-Al_2O_3 phase (ASTM 10-424);

- 0.5% Fe/γ-Al_2O_3 system:

Reflexes at 4.5641; 2.8032; 2.3815; 2.2891; 1.9781; 1.5210; 1.3994 Å - γ-Al_2O_3 phase (ASTM 10-424);

Reflexes at 4.8524; 4.3735; 4.3158; 3.3285; 2.4580; 2.3815; 1.8017; 1.7475 Å - gibbsite phase of $Al(OH)_3$ (ASTM 33-18);

Reflexes at 4.1784; 2.6891; 2.4580 Å - α-FeO(OH) (goethite) phase (ASTM 29 - 713);

- 3% Fe/γ-Al_2O_3 system:

Reflexes at 4.5562; 2.8003; 2.3898; 2.2807; 1.9829; 1.5214; 1.3976 Å - phase γ-Al_2O_3 (ASTM 10-424);

Reflexes at 4.8579; 4.3698; 4.3230; 3.3264; 2.4580; 2.3898; 1.7978; 1.7501 Å - gibbsite phase of $Al(OH)_3$ (ASTM 33-18);

Reflexes at 4.1784; 2.6904; 2.4580 Å - α-FeO(OH) (goethite) phase (ASTM 29 - 713)

- 13% Fe/γ-Al_2O_3 system:

Reflexes at 4.5681; 2.7974; 2.3908; 2.2853; 1.9733; 1.5217; 1.3994 Å - γ-Al_2O_3 phase (ASTM 10-424);

Reflexes at 4.8434; 4.3771; 4.3158; 3.3161; 2.4481; 2.3908 Å - gibbsite phase of $Al(OH)_3$ (ASTM 33-18);

Reflexes at 4.1817; 2.6837; 2.4481Å - α-FeO(OH) (goethite) phase (ASTM 29-713).

The data obtained indicate that the original alumina is indeed γ-Al_2O_3. Partial hydrolysis of aluminum oxide occurs during the synthesis of the Fe/γ-Al_2O_3 system, resulting in the formation of aluminum hydroxide in the form of gibbsite. It should be noted that the highest degree of hydrolysis is observed for the Fe/γ-Al_2O_3 system with the lowest iron content and it decreases monotonically with its growth (Fig. 1). This is probably due to the fact that as the concentration of iron acetate increases, in the solution there is an ever-decreasing amount of free water capable of causing hydrolysis of aluminum oxide [15].

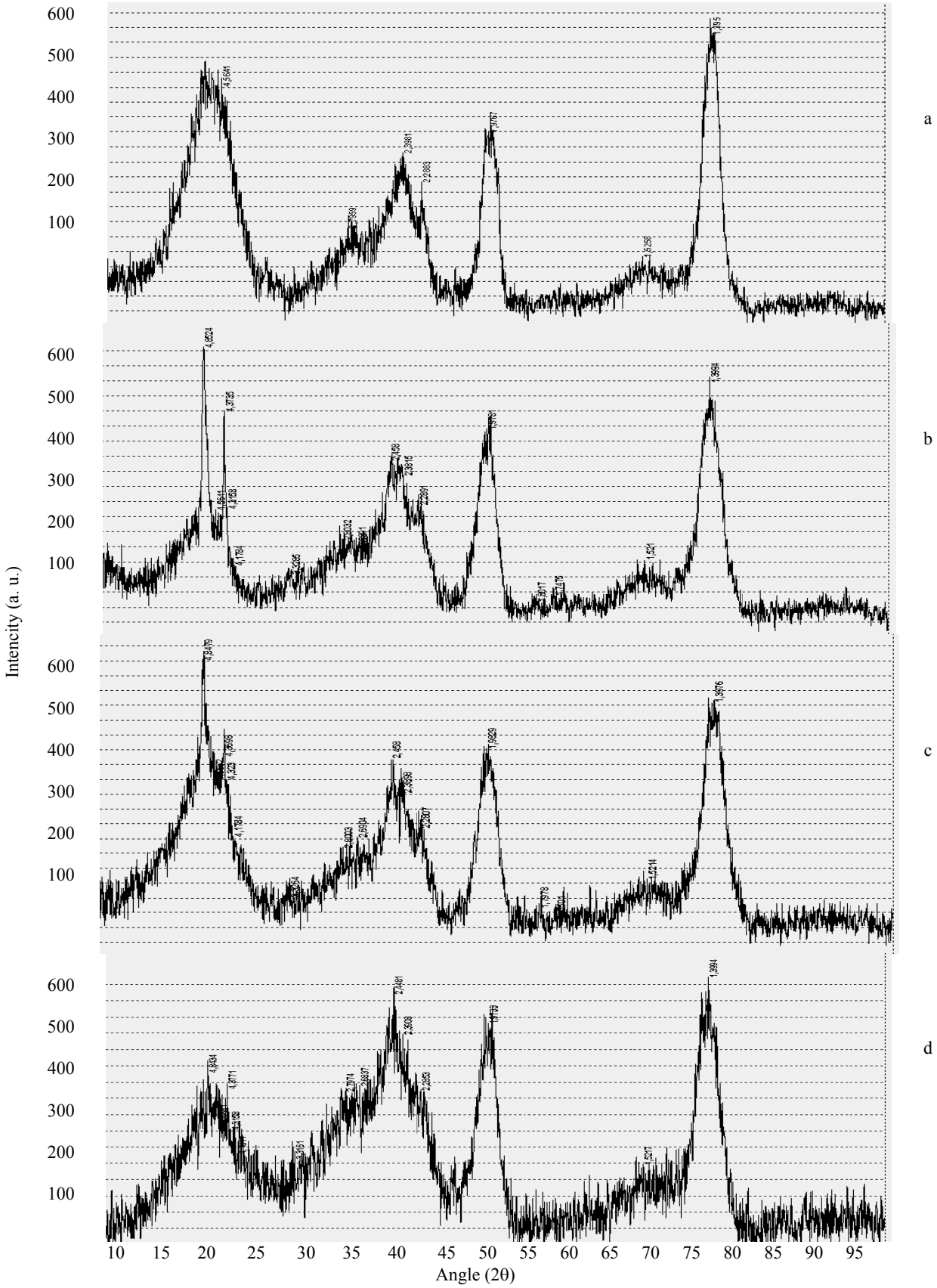

Figure 1 – Diffraction patterns of γ-Al_2O_3 oxide and Fe/γ-Al_2O_3 system
a - γ-Al_2O_3; b - 0.5% Fe/ γ-Al_2O_3; c - 3% Fe/ γ-Al_2O_3; d - 13% Fe/γ-Al_2O_3

Transmission electron microscopy.

Microphotographs of the initial aluminum oxide γ-Al_2O_3 and the Fe/γ-Al_2O_3 system with different iron contents are shown in Fig. 2.

There are two kinds of particles in γ-Al_2O_3 sample. The first type is characterized by aggregates of large, semitransparent, plate-like particles with a hexagonal facets (the (111) plane of α-Al_2O_3 crystallites) reaching almost micron sizes (400-800 nm) (Fig. 2a).

The second type of particles is small transparent plates of elongated rectangular shape (planes (001), (111) of γ-Al_2O_3 crystallites) which in the width are 5-10nm (Fig. 2b). Microdiffraction was taken from various parts of the sample. The pictures show reflexes that are located on the rings. They correspond to γ-Al_2O_3 (JCPDS, 10-425). A trace amount of δ-Al_2O_3 (JCPDS, 16-394), $Al(OH)_3$ gibbsite (JCPDS, 7-324) and θ-Al_2O_3 (JCPDS, 11-517) also were observed.

Micrograph of the 0.5%Fe/γ-Al_2O_3 system is shown in Fig. 2c. It has large particles with signs of faceting ranging in size from 200 to 1000 nm. Microdiffraction produces symmetrical and individual reflexes, which correspond to γ-Al_2O_3 (JCPDS, 10-425). A large 200nm in size particle of a pointed shape and small aggregates made up of particles of 10-40 nm in size are shown in Fig. 2d. Microdiffraction gives a large number of symmetrical and individual reflexes, which can be attributed to a mixture of phases: gibbsite (JCPDS, 7-324), β-AlO(OH) Diaspore (JCPDS, 5-355), γ-AlOOH Boehmite (JCPDS, 21-1301), with a significant predominance of the former.

Only phases of aluminum oxides and hydroxides in the sample were found. The low iron content in the system did not allow the detection of iron-containing phases because of a small amount they did not reach the field of view of the microscope.

The microphotographs of the 3% Fe/γ-Al_2O_3 system have many dense aggregates; also large particles of lamellar type of medium transparency are present in the sample, which is shown in Fig. 2e. A conglomerate of transparent particles of lamellar type of micron size, surrounded by small aggregates of small dense particles 5-10 nm in size is shown in Fig. 2e. Microdiffraction gives a large set of reflexes that are located along a distorted hexagonal view, and individual reflexes, which can be attributed to a mixture of the phases γ-FeO(OH) - goethite (JCPDS, 29-713), FeOOH (JCPDS, 26-792), $Al(OH)_3$ - gibbsite (JCPDS, 29-41), γ-Al_2O_3 (JCPDS, 10-425).

There is an aggregate of transparent particles of lamellar type ~ 0.5 micron in size for a 13%Fe/γ-Al_2O_3 system in Fig. 2g. Microdiffraction gives reflexes located on a distorted hexagonal view, which can be referred to δ-FeOOH (JCPDS, 13-87). In addition, this micrograph has round-shaped particles with dimensions of 10-30nm. Microdiffraction gives reflexes (rings) related to FeOOH (JCPDS, 26-792). In Fig. 2h, the particles are larger, for them microdiffraction shows a large set of reflections of the following phases: Fe_2O_3 (JCPDS, 32-469) and γ-Al_2O_3 (JCPDS, 10-425).

Scanning electron microscopy

Microphotographs of the initial aluminum oxide γ-Al_2O_3 and the Fe/γ-Al_2O_3 system with different iron content are shown in Fig. 3.

From microphotographs it follows that aggregates of various sizes (Fig. 3a, b, c) are present on the surface of the support γ-Al_2O_3, from tens to micrometers. Porous structure of the support surface is clearly visible when the magnification is large (Fig. 3c).

The relief of the support is "smoothed" when the acetate of iron is deposited on γ-Al_2O_3 (Figure 3), and the effect is most pronounced at 13% iron content. It can be assumed that an iron-containing film (crust) is formed on the surface of the support, and this, in fact, leads to a visible "smoothing" effect of the relief. In the case of the Fe/γ-Al_2O_3 system with 0.5% iron content (Fig. 3d, e, f), the complete surface coverage of the γ-Al_2O_3 support by the iron-containing component is not noticeable, apparently due to its small amount. On the contrary, it can be assumed that for a system with 13% iron content (Fig. 3 j, k, l), the coating is multilayer.

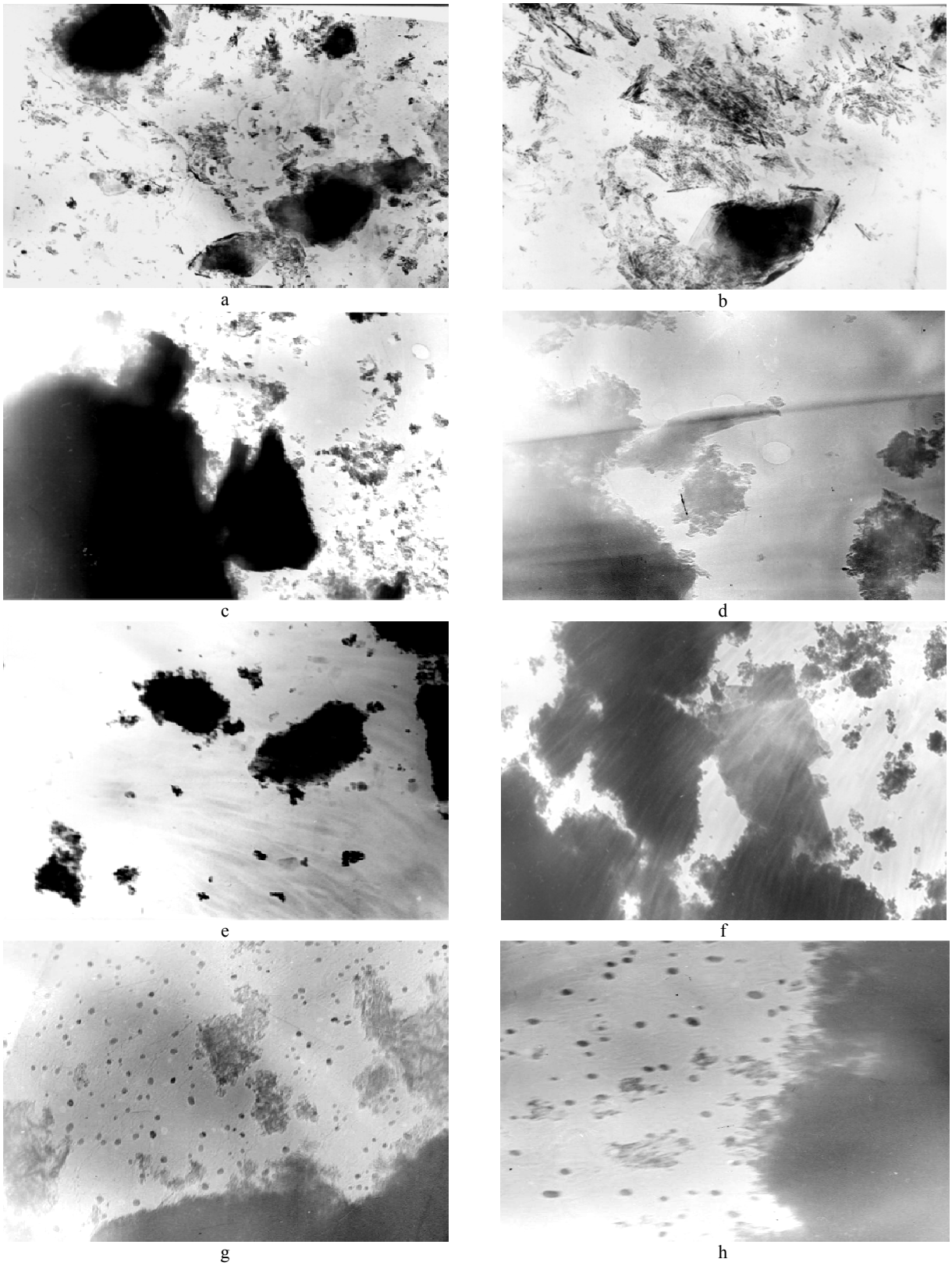

Figure 2 - Micrographs of the initial aluminum oxide γ-Al_2O_3 and the Fe/γ-Al_2O_3 system with an iron content of 0.5; 3 and 13%
a, b - initial γ-Al_2O_3 oxide; c, d – 0.5%Fe/γ-Al_2O_3 system; e, f - 3%Fe/γ-Al_2O_3 system; g, h 13%Fe/γ-Al_2O_3 system.
Magnification: a, c, e, f – 24000 times; b, d, g, h – 50000 times

BET method

Specific surface area and its texture (porosity) for γ-Al_2O_3 oxide and Fe/γ-Al_2O_3 system with different iron content are determined. The results are shown in Table 1 and are shown in Fig. 4. The data for γ-Al_2O_3 in agreement with the results of [16].

Table 1 – The specific surface area of the γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system

Sample	Parameter		
	SW, m^2/g	$V_{ADSmax.}$, mL/g	V_{true}, mL/g
γ-Al_2O_3	214	180	0,28
0.5%Fe/γ-Al_2O_3	211	196	0,31
3%Fe/γ-Al_2O_3	190	115	0,18
13%Fe/γ-Al_2O_3	173	101	0,16
Note: SW - specific surface area, m^2/g; V_{ADSmax} - total pore volume with gas filling, mL/g; V_{true} - total true pore volume, mL/g			

From Table 1 it follows that when the iron is precipitated to the support, as the content thereof increases, the value of the specific surface tends to decrease, indicating the filling of the surface.

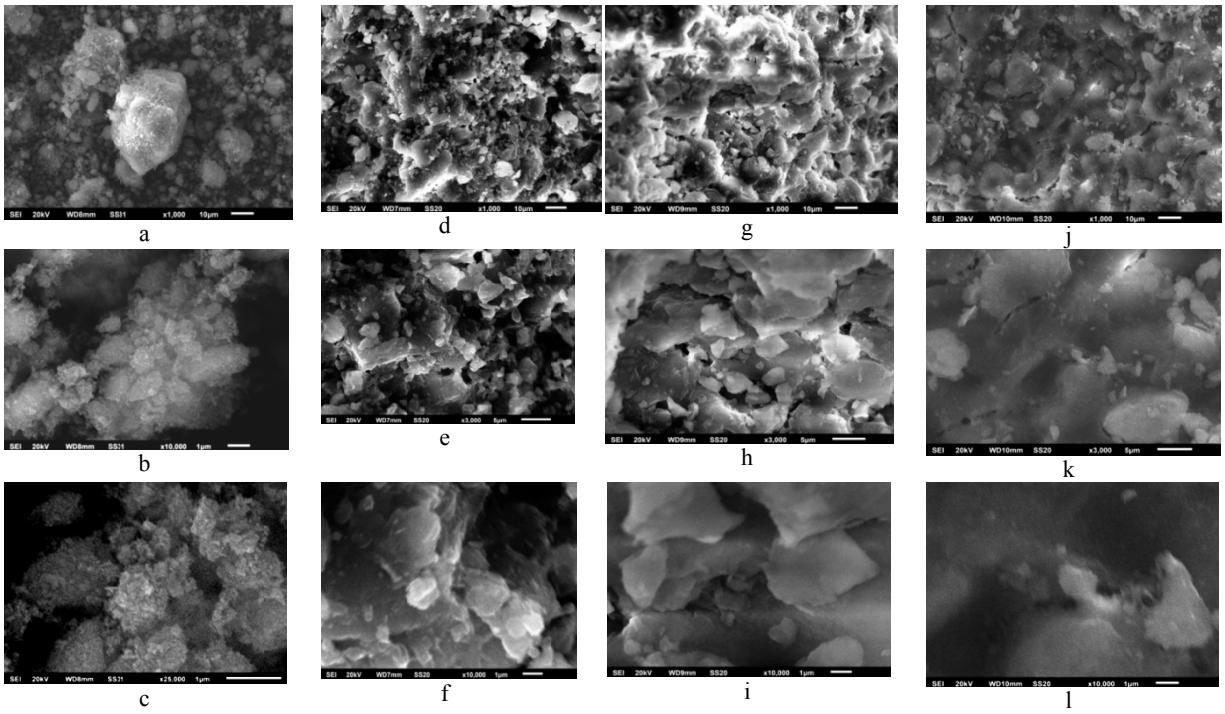

Figure 3 - Microphotographs of aluminum γ-Al_2O_3 and Fe/γ-Al_2O_3 systems with different iron content
γ-Al_2O_3 - (a, b, c); 0.5%Fe/γ-Al_2O_3 (d, e, f); 3%Fe/γ-Al_2O_3 (g, h, i); 13%Fe/γ-Al_2O_3 (j, k, l).
Magnification: (a, d, g, j) – 1000 times; (e, h, k) – 3000 times; (b, f, i, l) – 10000 times; (c) – 25000 times

At the same time, the pore volume has a maximum at the point for the system of 0.5%Fe/γ-Al_2O_3. The presence of an extremum can probably be explained by the hydrolysis of γ-Al_2O_3 and the transition of a part of aluminum oxide to the hydroxide, which was discussed above. In aluminum hydroxide, the total pore volume is noticeably higher than that of γ-Al_2O_3 [17]. Since the iron-containing component does not completely cover the support surface in the 0.5%Fe/γ-Al_2O_3 system (Fig. 3d, e, f), therefore, at least some of the pores of the hydroxide are accessible.

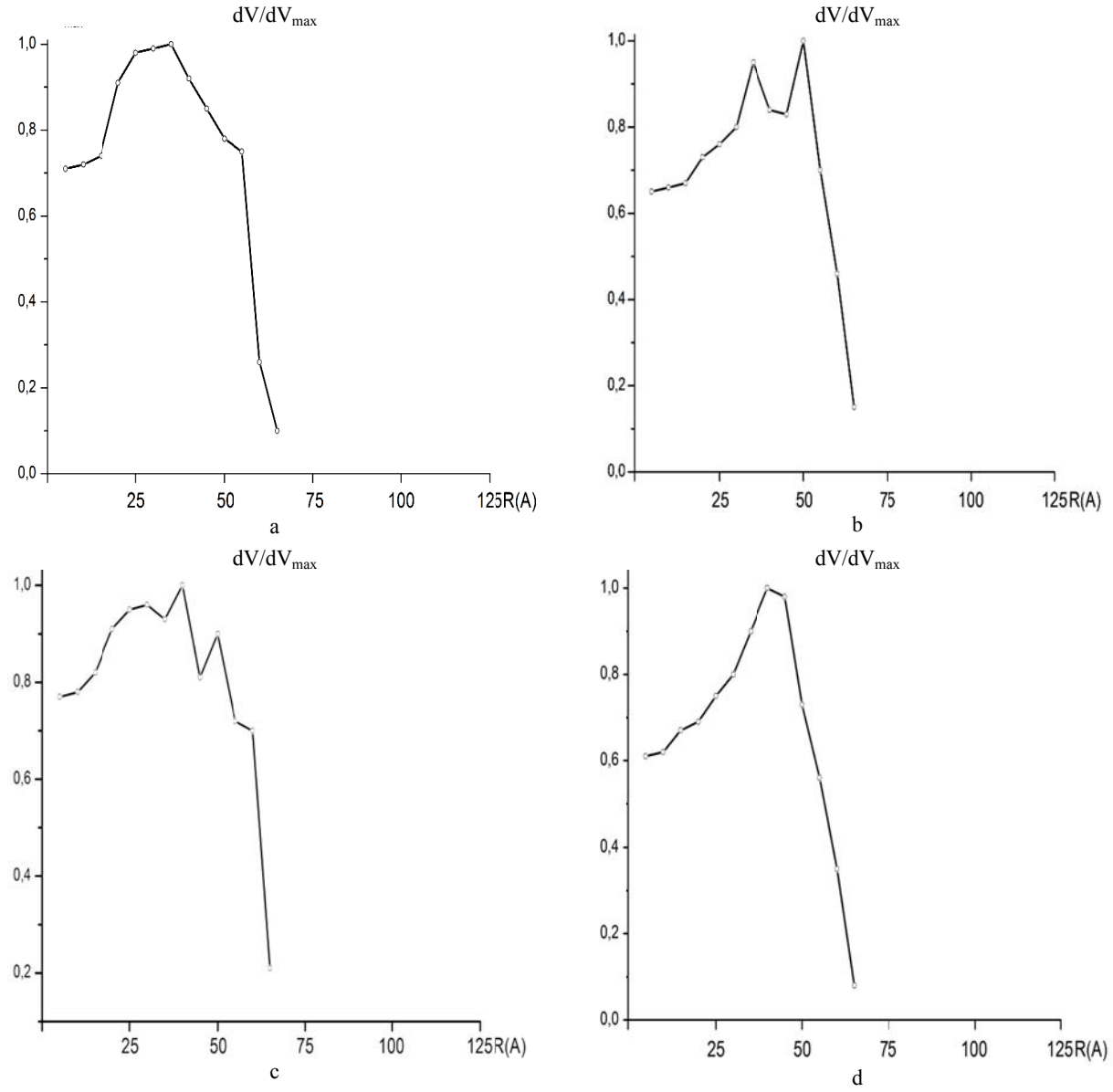

Figure 4 - Pore size distribution in γ-Al_2O_3 and in the Fe/γ-Al_2O_3 system with different iron content
a - γ-Al_2O3; b - 0.5%Fe/γ-Al_2O_3; c - 3% Fe/γ-Al_2O_3; d - 13%Fe/γ-Al_2O_3
R(A) is the pore radius in angstroms (Å); dV/dVmax the ratio
of the pore volume of a given radius to the maximum volume

The combination of these factors may lead to an increase in the total pore volume for the 0.5%Fe/γ-Al_2O_3 system.

With an increase in the iron content the total pore volume decreases which on one side may indicate their possible filling, and on the other hand, the difficulty of accessing the probe gas (nitrogen). The latter can be indicated by scanning electron microscopy data (Figure 3), from which it follows that with a high content of iron in the system, the support surface is almost completely closed.

In Fig. 4 - pore size distribution for γ-Al_2O_3 and Fe/γ-Al_2O_3. The pore size for γ-Al_2O_3 and the Fe/γ-Al_2O_3 system fits within a narrow range of values and their radius does not exceed 65-70Å (Fig. 4). When the iron-containing component is applied to alumina, the pore size distribution in comparison with γ-Al_2O_3 (Fig. 4a) varies, for 0.5%Fe/γ-Al_2O_3, a "dip" is observed in the 40-45Å region (Fig. 4b), it follows that in the first place pores of this size are filled. For the 3%Fe/γ-Al_2O_3 system, this "gap" is retained, although the shape of the distribution varies (Fig. 4c), which is apparently related to the filling of the surface with

an iron-containing component. For a system of 13%Fe/γ-Al_2O_3, due to the filling of the surface, the access of the probe gas to the pores of small size is essentially limited and the pore size distribution shows the presence of basically larger pores (Fig. 4d). All this occurs against the background of a decrease in the total volume of pores (Table 1).

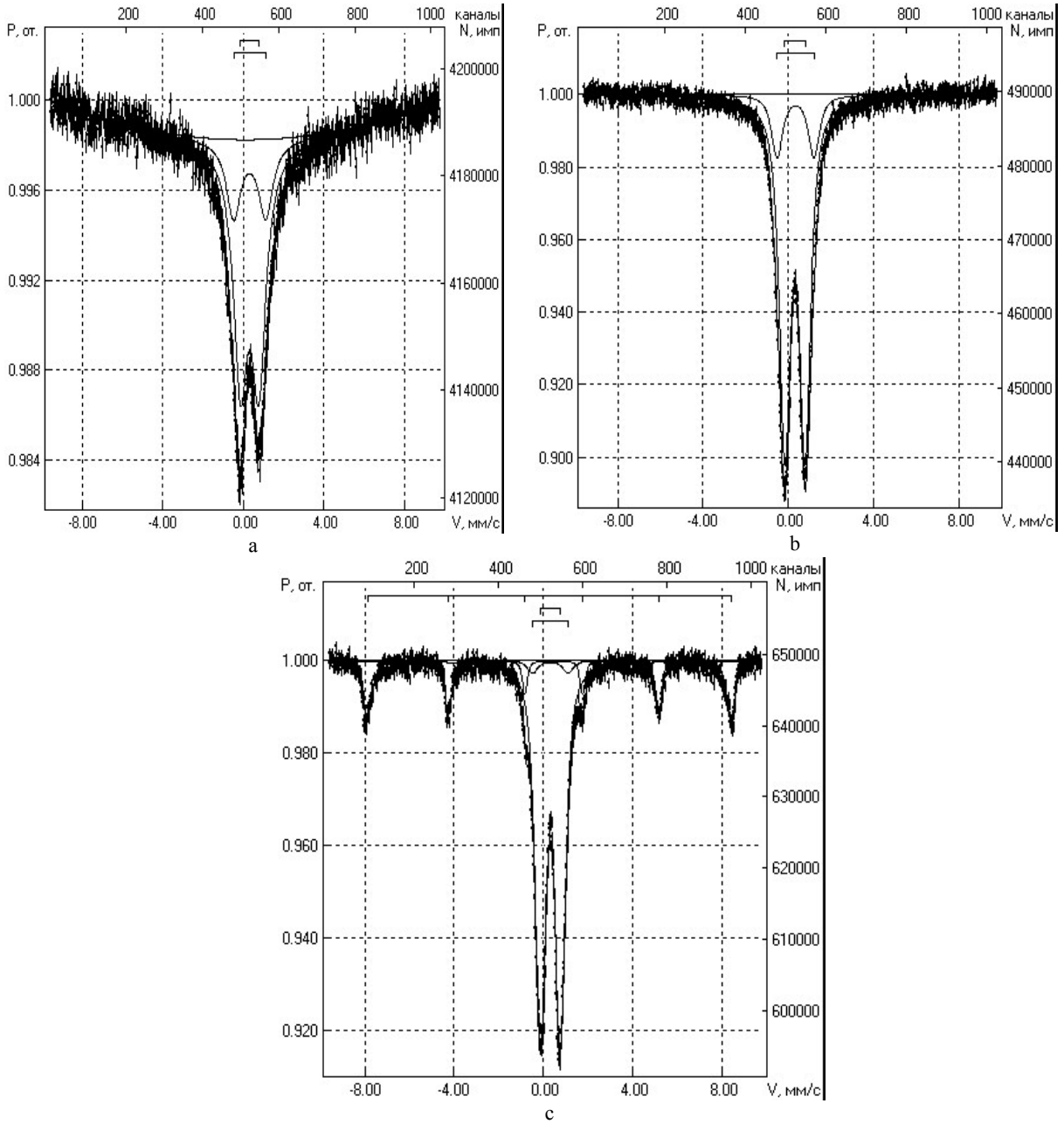

Figure 5 - Mossbauer spectra of the Fe/γ-Al_2O_3 system with different iron content
a – 0,5%Fe/γ-Al_2O_3; b – 3%Fe/γ-Al_2O_3; c – 13%Fe/γ-Al_2O_3

Mossbauer spectroscopy

Mössbauer spectra of the Fe/γ-Al_2O_3 system with different iron contents are shown in Figure 5. The spectra showed that the system, based on the values of isomeric shifts, contains various forms of Fe^{3+} both in the paramagnetic state and in the magnetically ordered one.

The following iron forms are present in the system:

0.5%Fe/γ-Al_2O_3

Fe_1^{3+} form - IS = 0.32 mm•s^{-1}; QS = 0.95 mm•s^{-1}; S = 62%

Fe_2^{3+} form - IS = 0.32 mm•s^{-1}; QS = 1.59 mm•s^{-1}; S = 38%
3%Fe/γ-Al_2O_3
Fe_1^{3+} form - IS = 0.31 mm•s^{-1}; QS = 0.98 mm•s^{-1}; S = 70%
Fe_2^{3+} form - IS = 0.32 mm•s^{-1}; QS = 1.62 mm•s^{-1}; S = 30%
13%Fe/γ-Al_2O_3
Fe_1^{3+} form - IS = 0.32 mm•s^{-1}; QS = 0.93 mm•s^{-1}; S = 77%
Fe_2^{3+} form- IS = 0.31 mm•s^{-1}; QS = 1.59 mm•s^{-1}; S = 3%
α-Fe_2O_3 - IS = 0.37 mm•s^{-1}; QS = - 0.21 mm•s^{-1}; H_{eff} = 506 kOe; S = 20%
(H_{eff} is the Zeeman hyperfine magnetic splitting)

The forms of Fe_1^{3+} and Fe_2^{3+}, irrespective of the iron content in the Fe/γ-Al_2O_3 system, have similar parameters and are paramagnetic. At the same time, having almost identical IS, they differ significantly in QS. The shape of Fe_2^{3+} with a large value of QS can be attributed to iron on the surface of the support, and the form of Fe_1^{3+} with smaller QS - to a more deeply located [18, 19].

It should be noted that with an increase in the iron content in the system, a gradual increase in the relative content of the more deeply located form of Fe_1^{3+} takes place, which agrees with the BET data.

There is also a magnetically ordered phase that corresponds to α-Fe_2O_3 in the 13% Fe/γ-Al_2O_3 system, in addition to the Fe_1^{3+} and Fe_2^{3+} forms [20]. A somewhat smaller value of H_{eff} (should be 515-517 kOe) indicates that the particles giving in the Mössbauer spectrum of the Zeeman hyperfine magnetic splitting are of the order of 8-12 nm [21]. At such particle sizes, H_{eff} has a smaller value than for bulk samples.

Conclusion

The performed work has shown that during the preparation of the Fe/γ-Al_2O_3 system by impregnation, the structure of the support can be modified. The nature of the filling of the support surface with the iron-containing phase depends substantially on its percentage and can be multilayered.

It has been established that the Fe/γ-Al_2O_3 system contains iron in the form of Fe^{3+}. Depending on the iron content, iron-containing aggregates of various sizes can be present in the system, both in the paramagnetic and magnetically ordered states.

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МОЛЕКУЛА ЗОНДЫ БАР Fe/γ-Al_2O_3 КАТАЛИЗДІК ЖҮЙЕНІҢ ӨЗАРА ӘРЕКЕТТЕСТІГІ
I. γ-Al_2O_3 ЖӘНЕ Fe/γ-Al_2O_3 БАСТАПҚЫ ЖҮЙЕНІҢ ЗЕРТТЕЛУІ

Бұл жұмыс адсорбцияланған молекулаға ие гетерогенді катализдік жүйенің өзара әрекеттестігіне арналған зерттеудің бірінші бөлігі болып табылады. Оған бастапқы γ-Al_2O_3 тотығы және 0,5; 3; 13 вес.% темір мөлшері бар Fe/γ-Al_2O_3 жүйесі бойынша кең ауқымды физика-химиялық әдістер жиынтығы көмегімен алынған нәтижелер ұсынылған. Көптеген химиялық процестерде катализдік белсенділік көрсетіп, келешекте модельдік ретінде қолдану мүмкіндігі болғандықтан Fe/γ-Al_2O_3 жүйесі зерттеу нысаны болып таңдалған болатын.

Жүргізілген жұмыс сіңіру әдісімен Fe/γ-Al_2O_3 жүйесін дайындау процесінде тасығыш құрылымының модификациясы мүмкін екендігін көрсетті. Теміркұрамды фазамен тасығыш бетінің толтырылу сипаты айтарлықтай оның пайыздық мөлшеріне тәуелді және көп қабатты болуы мүмкін.

Fe/γ-Al_2O_3 жүйесі Fe^{3+} формалы темір құрайтындығы анықталды. Темірдің мөлшеріне байланысты оған әртүрлі пішіндегі, яғни парамагнитті және магнит тәртіпті күйдегі теміркұрамды агрегаттар қатысуы мүмкін.

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ВЗАИМОДЕЙСТВИЕ КАТАЛИТИЧЕСКОЙ СИСТЕМЫ Fe/γ-Al_2O_3
С МОЛЕКУЛАМИ-ЗОНДАМИ
I. ИССЛЕДОВАНИЕ γ-Al_2O_3 И ИСХОДНОЙ СИСТЕМЫ Fe/γ-Al_2O_3

Аннотация. Работа является первой частью исследований, посвящённых взаимодействию гетерогенной каталитической системы с адсорбированными молекулами. В ней представлены результаты по исходному

оксиду γ-Al_2O_3 и системе Fe/γ-Al_2O_3 с содержанием железа 0,5; 3; 13 вес.%, полученные с помощью широкого набора физико-химических методов. Система Fe/γ-Al_2O_3 была выбрана объектом исследования, поскольку она проявляет каталитическую активность во многих химических процессах и в дальнейшем может быть использована как модельная.

Проведённая работа показала, что в процессе приготовления системы Fe/γ-Al_2O_3 методом пропитки возможна модификация структуры носителя. Характер заполнения поверхности носителя железосодержащей фазой существенно зависит от её процентного содержания и может быть многослойным.

Установлено, что система Fe/γ-Al_2O_3 содержит железо в форме Fe^{3+}. В зависимости от содержания железа, в ней могут присутствовать железосодержащие агрегаты различного размера, как в парамагнитном, так и в магнитоупорядоченном состояниях.

Ключевые слова: гетерогенный катализ, физико-химические методы исследования.

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