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Д.В. Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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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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IINVESTIGATION OF THE CATALYTIC AND ISOMERIZATION ACTIVITY OF MULTI-COMPONENT SKELETAL NICKEL CATALYSTS IN THE HYDROGENATION OF HEXENE-1

Abstract. In this work, the effect of the amount of catalyst, modifying additives, and the phase composition of the alloys on the catalytic and isomerizing activity of skeletal in the hydrogenation reaction of hexane-1 is investigated.

It has been shown that for all studied catalysts, the yield of products in the processes of migration and isomerization depends very strongly on the weighed portion of the catalyst introduced into the reaction medium. So, for example, the yield of hexane-2 with an increase in the catalyst weight increases linearly to 0.5g of nickel, while at the initial stage of the reaction the yield of hexane-2 reaches 62%. With a further increase in the catalyst weight (up to 1 g of Ni), the yield of hexane-2 decreases.

The results of chromatographic analysis indicate a high activity of modified skeletal nickel catalysts in the reaction of migration of -C = C- bonds during hydrogenation of hexene-1. Modification of Fe, Pd, Sn and Ag increases the migration coefficient (Kmigr) from 0.66 to 0.70-0.77, while additions of Ti, Mo, Ti-Mo and Zr practically do not change it.

The activity of the catalyst increases with the introduction of the metals Cu, Zn, Pb, Ti-Mo, Mo, Bi, Ag, and Mo-Cu (W=120-290 cm^3/min·g Ni) into the initial alloy, while the addition of Fe, Pd and Mn (W=56-80 cm^3/min·g Ni), while the influence of the components Ti, Zr and Sn is insignificant (W=115-117 cm^3/min·g Ni).

Keywords: catalyst, hydrogenation, hexene-1, skeletal nickel, activity, selectivity, migration, alloy.

Introduction. The ability of metals of group VIII of the Periodic Table to catalyze the reaction of a double-bond migration over the carbon chain and *cis-trans* conversion in the hydrogenation of olefinic hydrocarbons is outlined in a series of papers [1-24]. It was found that group VIII metals have various effects on the nature of these side reactions. This is explained by the different content and state of hydrogen sorted by these metals [4], and the phase composition and modifying agents of the initial alloys [2,6]. However, the data available in various papers differ markedly. The authors of [6] attribute these differences to differences of the catalyst preparation methods.

Multi-component skeletal nickel catalysts successfully used in various hydrogenation processes have been found to be very effective from an industrial point of view. This is caused by high activity and selectivity, simplicity of preparation and regeneration, work stability, resistance to intoxication. In recent years, intensive studies have demonstrated that modification of skeletal nickel by different metals allows regulating catalyst performance over a wide range [3].

In accordance with the data of the studies [3,4], dissolved hydrogen is mostly involved in isomerization of hexene-1 over skeletal nickel, and a surface adsorbed hydrogen is involved in the reaction of hydrogenation. In this context, it can be expected that the amount of catalyst introduced into the reaction medium should have a considerable impact on the hydrogenation process, migration and isomerization, since the amount of adsorbed as well as dissolved hydrogen entering the reaction at the initial stage changes.

In the present paper the effect of the amount of catalyst, modifying agents and phase composition of initial alloys on catalytic and isomerization activity of skeletal nickel in hexene-1 hydrogenation reaction has been studied.

Experiment.

Table 1 presents the physical and chemical properties of hexene-1.

Table 1 - Main physical and chemical properties of hexane-1

Name, synoname	Formula	Molecular mass	Boiling point °C	Density d_4^{20}	Refractive index n_D^{20}	Solubility in:		
						water	ethanole	hexane
Hexane-1 Byhylethylene	CH_3-CH_2-CH_2-CH_2-CH=CH_2	84.16	63.5	0.6732	1.3821	insoluble	∞	∞

The catalyst was prepared as follows: a sample weight (0.4-0.8 g) of crushed, powdered alloy, fraction 0.06-0.20 mm (the alloy composition is given in Table 1) was processed with 20% KOH solution at 96 ˚C, in a boiling water bath for 2 hours. Water washing from alkali was carried out with distilled water by decantation 4-5 times, up to negative reaction to OH- ions in washing water. Then, the catalyst was washed with solvent in which hydrogenation was carried out (ethanol).

Hydration was performed in a thermostatic "catalytic duck" [1,2] at atmospheric pressure and temperature of 20 ˚C. The rate of reaction (amount of absorbed hydrogen per unit time, cm^3/min) and catalyst potential (mV) relative to the calomel reference electrode were recorded simultaneously by method [1,2]. Before the reaction, the catalyst was saturated with hydrogen in the solvent (volume 25 cm^3) until the reversible hydrogen potential was determined. Hydration was performed in a kinetic regime (700-800 swings/min).

The selectivity coefficient of hydrogenation of hexene-1 was determined by formula 1, the migration coefficient -C=C bond for hydrogenation of hexene-1 was determined by formula 2, the isomerization coefficient was determined by formula 3; stereospecificity was determined by formula 4.

$$\text{К}_S = \text{yield hexene-1, \%/yield(hexene-1+hexane), \%} \quad (1)$$

$$\text{К}_{migr} = \frac{yield(sic-hexene-1+tranc-hexene-1)}{yield(hexene-1+sic-hexene-1+trans-hexene-1)} \quad (2)$$

$$\text{К}_{isom} = \frac{yield\ trans-hexene-1,\%}{yield(sis-hexene-1+trans-hexene-1),\%} \quad (3)$$

$$S_t = \text{sic-hexene-1/trans-hexene-1} \quad (4)$$

Chromatographic analysis was performed using a Chromos GH-1000 (Chromos, Russia) with flame ionization detector in isothermal mode using BP21 (FFAP) capillary column with polar phase (PEG modified with nitroterephthalate) 50 m long and 0.32 mm inner diameter. The column maintained the temperature of 90 ^{0}C, the temperature in the vaporization chamber was 200 ^{0}C, the carrier gas was helium, the volume of injection volume was 0.2 μl. Samples of liquid reaction mixture were taken 2-3 times during the experiment.

Table 2 presents the composition of products of the hydrogenation reaction of hexene-1 over skeletal nickel from Ni-Al (I:I) alloy depending on the amount of catalyst.

The data in table 2 show that the yield of products in the migration and isomerization processes for all investigated catalysts is highly dependent on the catalyst weighed amount introduced into the reaction medium.

For instance, the yield of hexene-2 with an increase in the catalyst weight increases linearly up to 0.5 g of nickel, at that the yield of hexene-2 reaches 62 % in the initial stage of reaction. The yield of hexene-2 decreases with a further increase in the catalyst weight (up to 1 g Ni).

The data analysis in table 2 shows that the catalyst suspension during the hydrogenation of 1-hexene also affects the ratio of hydrogenation and migration of C=C bond. The values of the migration coefficients (F_{migr}) and Bond selectivity (F_{sel}) [7], characterizing these processes highly depends on the amount of catalyst in the reaction medium. At the initial stage, for instance, the value of F_{migr} (the ratio of the yield of hexene-2 to the total of hexenes) increases from 0.05 to 1 g when the catalyst weight increases from 0.12 to 0.95, and the value of F_{sel} (the ratio of the yield of hexene-2 to hexane) - from 0.51 to 4.78. Recent data indicate that in the case of a small catalyst weight, the migration process runs at a rate that is half that of hydrogenation of hexene-1, while in the case of large catalyst weight (1 g Ni) the reaction with regard to hexene-2 formation is 5 times faster than the reaction of hexene-1 hydrogenation.

At hydrogenation of hexene-1 over skeletal nickel right from the beginning of the reaction trans-isomer is obtained in a considerably larger amount than cis-isomer. The value of F_{isom} - isomerization coefficient (the ratio of the yield of trans isomer to the sum of hexene-2 yield) is 0.71-0.80. This value almost remains unchanged to the point of disappearance of hexene-1 from the reaction and does not depend on the phase composition of the initial alloys and the weighed amount of catalyst. At the end of the reaction after the disappearance of hexene-1 the value of F_{isom} slightly increases as a result of the difference in the rate of hydrogenation of trans and cis-isomers to hexane.

As the table 2 shows, the value of migration and selectivity coefficients for the same weight of catalyst significantly changes in the process of hexene-1 hydrogenation. Thus, F_{migr} increases from 0.1 to 0.97 in the course of the reaction. The F_{sel} value in this case decreases by an order of magnitude. Thus, these coefficients also change significantly depending on the amount of hydrogen absorbed. But when the catalyst weighed amount in the reaction medium is large (0.5-1 g), the values of such migration coefficients are highly distorted owing to the fact that by this time hexene-1 is absent in the reaction medium and only the hydrogenation of hexene-2 is in the process. Thus, if hydrogenation of hexene-1 is performed over a weighed amount of a nickel catalyst of 0.3-0.5 g, the values of the F_{migr} coefficient will range from 0.75 to 0.95 (at the time of absorption of 0.3 mol of hydrogen). In paper [6], the data relating to the migration coefficient fluctuate within the same limits. In paper [6], the data relating to the migration coefficient fluctuate within the same limits. On the basis of the data obtained, it can be considered that skeletal nickel belongs to the number of catalysts with high isomerization ability second only to palladium. [5].

Table 2 - Composition of catalysis obtained by hydrogenation of hexene-1 over skeletal nickel from Ni:Al (1:1) alloy

Catalyst weight, g	The amount of absorbed hydrogen, mole	Reaction product,%				F_{migr}	F_{sel}	F_{isom}
		Hexane	Hexene-1	Hexene-2				
				Trans	*Cis*			
0.05	0.14	13.8	75.8	7.4	3.0	0.12	0.75	0.71
	0.28	28.0	58.9	9.6	3.5	0.18	0.47	0.69
	0.45	44.9	39.4	11.3	4.5	0.28	0.35	0.71
	0.60	60.3	22.2	12.5	5.0	0.44	0.29	0.71
	0.76	75.9	6.3	12.6	5.2	0.74	0.23	0.71
0.15	0.15	14.9	67.6	13.0	4.5	0.20	1.17	0.74
	0.31	30.9	49.4	14.0	5.7	0.29	0.64	0.71
	0.51	51.0	29.9	13.9	5.2	0.39	0.57	0.73
	0.78	77.6	6.8	11.6	4.0	0.67	0.20	0.74
0.25	0.16	15.8	42.6	32.3	9.3	0.49	2.63	0.78
	0.30	29.5	23.4	35.4	11.7	0.67	1.60	0.75
	0.46	46.4	7.2	33.8	12.6	0.87	1.00	0.73
	0.67	67.0	2.5	22.4	6.5	0.92	0.42	0.78
0.50	0.23	23.4	14.3	43.3	19.0	0.81	2.66	0.73
	0.34	34.3	4.4	44.1	17.2	0.93	1.78	0.72
	0.54	54.4	2.6	33.3	9.7	0.94	0.79	0.77
	0.72	71.6	-	23.3	5.2	-	0.40	0.82
0.75	0.19	18.8	8.1	52.7	20.4	0.90	3.89	0.72
	0.37	36.7	-	43.9	19.4	-	1.97	0.69
	0.51	51.0	-	35.1	13.6	-	0.95	0.72
	0.67	65.0	-	27.6	5.9	-	0.50	0.82
1.00	0.17	16.6	4.0	57.2	22.2	0.95	4.78	0.72
	0.39	38.6	1.6	47.2	11.9	0.97	1.53	0.80
	0.55	53.5	-	37.4	7.9	-	0.85	0.83
	0.71	70.3	-	24.1	4.4	-	0.41	0.85

If, however, the migration coefficient of skeletal nickel with a weighed amount of the catalyst is calculated as 0.05 g (i.e. over the same weighed amount of the catalyst that is used for hydrogenation over Pd, Rh, Pt and other catalysts), the F_{migr} values will be equal to 0.12. Therefore, skeletal nickel by its isomerization ability belongs to a number of metals that weakly catalyze C=C bond migration, such as Pd, Rh, Pt [5,8,10] and others.

Table 3 - Hydrogenation of hexene-1 over multi-component skeletal nickel catalysts

Alloy composition	Content of Ni-Al-Me mass.%	$W_{C\equiv C}$	$\Delta E_{init.}$	K_s	S_t
Ni-Al	50-50	110	200	0.66	0.75
Ni-Al-Cu	40-55-5	140	140	0.52	0.74
Ni-Al-Cu	30-60-10	290	120	0.43	0.74
Ni-Al-Ag	48-50-2	125	175	0.70	0.75
Ni-Al-Zn	43-44-13	246	130	0.58	0.74
Ni-Al-Zn	28-36-36	270	250	0.52	0.74
Ni-Al-Ti	47-50-3	117	280	0.65	0.75
Ni-Al-Zr	45-50-5	115	200	0.62	0.78
Ni-Al-Sn	45-50-5	117	220	0.74	0.74
Ni-Al-Pb	40-50-10	194	150	0.59	0.75
Ni-Al-Ta	45-50-5	200	180	0.60	0.75
Ni-Al-Bi	45-50-5	122	200	0.69	0.77
Ni-Al-Cr	47-50-3	100	170	0.54	0.76
Ni-Al-Mo	45-50-5	125	280	0.66	0.74
Ni-Al-Mn	40-50-10	56	150	0.53	0.78
Ni-Al-Fe	45-50-5	80	180	0.77	0.79
Ni-Al-Pd	48-50-2	65	250	0.74	0.78
Ni-Al-Ti-Mo	44-50-3-3	150	200	0.62	0.80
Ni-Al-Ti-Cr	44-50-3-3	90	220	0.51	0.75
Ni-Al-Mo-Cu	42-50-3-5	120	80	0.62	0.75
Ni-Al-Cr-Cu	42-50-3-5	105	160	0.46	0.76

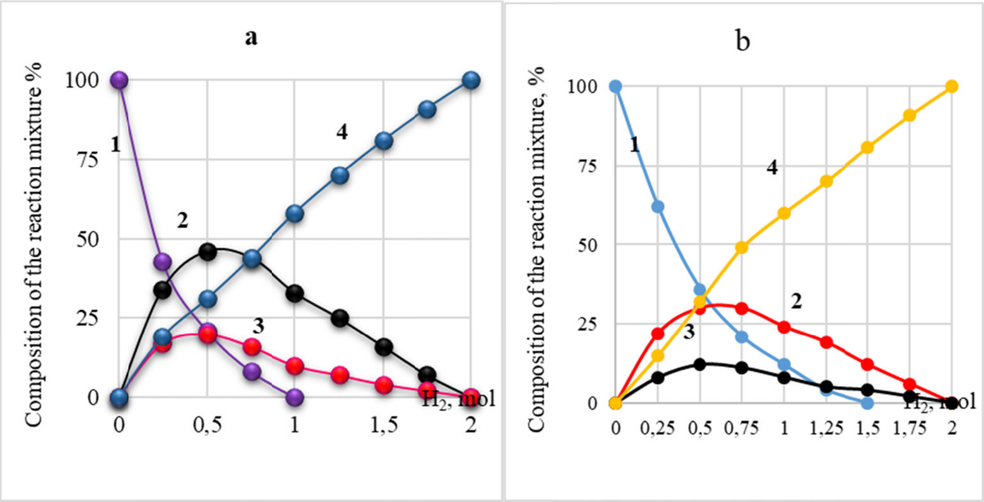
W- is the specific activity of the catalyst, cm^3 H_2/min·g Ni;
$\Delta E_{init.}$ – initial displacement of the catalyst potential, мV;
S_t - stereospecificity (cis-hexene-2 / trans hexene-2);
K_s – is the selectivity coefficient.

Modification of skeletal nickel with different metals (table 3) has a profound effect on the catalytic activity and isomerization ability of the skeletal nickel catalyst in the process of hexene-1 hydrogenation (table 3), which may be related to changes in the energy characteristics of adsorbed hydrogen on the catalyst surface.

The results of chromatographic analysis (table 3, figure 1) suggest high activity of modified skeletal nickel catalysts in the -C=C bond migration reaction during hexene-1 hydrogenation.

Modifying Fe,Pd, Sn and Ag increases the migration coefficient (C_{migr}) from 0.66 to 0.70-0.77, while Ti, Mo, Ti-Mo and Zr additives almost do not change it. The introduction of Cu, Cr-Cu, Ti-Cu, Zn, Mo-Cr and Mn reduces the ability of the catalyst to transfer -C=C bond (C_{migr}=0.43-0.53). Modifying additives almost do not change the ratio of cis/trans isomers of hexene-1 (C_{isom}=0.74-0.80).

Catalyst activity increases when Cu, Zn, Pb, Ti-Mo, Mo, Bi, Ag and Mo-Cu metals are introduced into the initial alloy (W=120-290 cm^3/min-g Ni), and Fe, Pd and Mn additives decrease it (W=56-80 cm^3/min-g Ni), while the influence of Ti, Zr and Sn components is insignificant (W=115-117 cm^3/min-g Ni). The strongest adsorption of hexene-1 is observed over catalysts containing Mo, Pd, Zn, Ti, Bi, Mo-Cr, Sn and Zr (ΔE=200-280 mV). The doping of Cu, Cr, Pb, Mn, Mo-Cu and Cr-Cu alloy leads to its reduction (ΔE=80-170 mV).



1- hexene-1, 2- trans-hexene-2, 3- cis-hexene-2, 4-hexane.
Figure 1 - Change in the composition of the reaction mixture in the process of hydrogenation of hexene-1 over skeletal nickel from Ni-Al-Pd and Ni-Al-Cr-Cu alloys
Conditions: a sample weight of the catalyst 0.12, temperature 20 ^{0}C, H_2 pressure 0.1 MPa, solvent ethyl alcohol 25 ml, initial amount of 1-hexene 2.23 m/mol

Conclusion

1. The effect of the amount of catalyst, modifying additives and phase composition of initial Ni-Al alloys on the process of isomerization of hexene-1 over skeletal nickel has been examined. It was established that the reaction of transfer of the double bond does not depend on the phase composition of the initial alloys, it is influenced only by the chemical nature of metal (Ni).

2. It is demonstrated that for all examined catalysts the yield of products in the processes of migration and isomerization is very strongly dependent on the catalyst weight introduced into the reaction medium. For instance, the yield of hexene-2 increases linearly up to 0.5 g of nickel with the increase of the catalyst weight, while at the initial stage of the reaction the yield of hexene-2 reaches 62 %. With a further increase in the weight of catalyst (up to 1 g of Ni) the yield of 2-hexene decreases.

3. The results of chromatographic analysis suggest a high activity of modified skeletal nickel catalysts in the -C=C bond migration reaction in the process of hydrogenation of hexene-1. Modifying Fe, Pd, Sn and Ag increases the migration coefficient (C_{migr}) from 0.66 to 0.70-0.77, and Ti, Mo, Ti-Mo and Zr additives almost do not change it. The introduction of Cu, Cr-Cu, Ti-Cu, Zn, Mo-Cr and Mn reduces the ability of the catalyst to transfer -C=C bond (C_{migr}=0.43-0.53).

4. Catalyst activity increases when Cu, Zn, Pb, Ti-Mo, Mo, Bi, Ag and Mo-Cu metals are introduced into the initial alloy (W=120-290 cm^{3}/min-yield), and Fe, Pd and Mn additives decrease it (W=56-80 cm^{3}/min- g Ni), while the effect of Ti, Zr and Sn components is insignificant (W=115-117 cm^{3}/ min · g Ni).

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ГЕКСЕН-1 ГИДРЛЕУ РЕАКЦИЯСЫНДАҒЫ КӨПКОМПОНЕНТТІ ҚАҢҚАЛЫ НИКЕЛЬ КАТАЛИЗАТОРЛАРЫНЫҢ КАТАЛИТИКАЛЫҚ ЖӘНЕ ИЗОМЕРЛЕУШІ БЕЛСЕНДІЛІГІН ЗЕРТТЕУ

Аннотация. Бұл жұмыста катализатор мөлшерінің, модификациялы қоспалар мен бастапқы құймалардың фазалық құрамының гексен-1 гидрлеу реакциясында қаңқалы никелдің каталитикалық және изомерлеу белсенділігінің әсері зерттелді.

Барлық зерттелген катализаторлар үшін миграциялау мен изомерлеу процестеріндегі өнімдердің шығымы реакция ортасына енгізілген катализатордың мөлшеріне тәуелді екендігі көрсетілген. Сонымен, катализатор салмағының өсуімен гексен-2 шығымы сызықты түрде 0,5 г никельге дейін арттады, ал реакцияның бастапқы сатысында гексен-2 шығымы 62%-ға жетеді. Катализатор салмағының одан әрі артуымен (1 г Ni-ге дейін) гексен-2 шығымы төмендейді.

Хроматографиялық талдаудың нәтижелері гексен-1 гидрлеу кезінде -С = С- байланыстарының миграциялау реакциясында модификацияланған қаңқалы никель катализаторларының жоғары активтілігін көрсетеді. Fe, Pd, Sn және Ag модификациясы миграциялау коэффициентін (Кмигр) 0,66-дан 0,70-0,77-ге дейін арттырады, ал Ti, Mo, Ti-Mo және Zr қоспалары оны іс жүзінде өзгертпейді.

Катализатордың белсенділігі бастапқы құймаға Cu, Zn, Pb, Ti-Mo, Mo, Bi, Ag, Mo-Cu (W = 120-290 см^3/ мин г Ni) металдарын енгізген кезде жоғарылайды, ал Fe, Pd және Mn (W = 56-80 см^3/мин · g Ni), ал Ti, Zr және Sn компоненттерінің әсері шамалы (W = 115-117 см^3/мин·g Ni).

Түйін сөздер: катализатор, гидрлеу, гексен-1, қаңқалы никелі, белседілік, селективтілік, миграциялау, құйма.

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ИССЛЕДОВАНИЕ КАТАЛИТИЧЕСКОЙ И ИЗОМЕРИЗУЮЩЕЙ АКТИВНОСТИ МНОГОКОМПОНЕНТНЫХ СКЕЛЕТНЫХ НИКЕЛЕВЫХ КАТАЛИЗАТОРОВ В РЕАКЦИИ ГИДРИРОВАНИЯ ГЕКСЕНА-1

Аннотация. В настоящей работе исследовано влияние количество катализатора, модифицирующих добавок и фазового состава исходных сплавов на каталитическую и изомеризующую активность скелетного никеля в реакции гидрогенизация гексена-1.

Показано, что для всех исследованных катализаторов выход продуктов в процессах миграции и изомеризации очень сильно зависит от навески катализатора, вносимой в реакционную среду. Так, например, выход гексена-2 с увеличением навески катализатора линейно возрастает до 0,5 г никеля, при этом в начальной стадии реакции выход гексена-2 достигает 62 %. При дальнейшем увеличении навески катализатора (до 1 г Ni) выхода гексена-2 уменьшается.

Результаты хроматографического анализа свидетельствуют о высокой активности модифицированных скелетных никелевых катализаторов в реакции миграции -С=С- связи при гидрировании гексена-1. Модифицирование Fe, Pd, Sn и Ag увеличивает коэффициент миграции ($К_{мигр}$) от 0,66 до 0,70-0,77, а добавки Ti, Mo, Ti-Mo и Zr практически не изменяют его.

Активность катализатора возрастает при введении в исходный сплав металлов Cu, Zn, Pb, Ti-Mo, Mo, Bi, Ag и Mo-Cu (W=120-290 см^3/мин·г Ni), а добавки Fe, Pd и Mn уменьшают ее (W=56-80 см^3/мин·г Ni), в то время как влияние компонентов Ti, Zr и Sn незначительно (W=115-117 см^3/мин·г Ni).

Ключевые слова: катализатор, гидрирования, гексен-1, скелетный никель, активность, селективность, миграция, сплав.

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