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PHASE COMPOSITION, MAGNETIC AND CATALYTIC PROPERTIES OF NANOSTRUCTURED NICKEL-CONTAINING NAX ZEOLITE IN THE REACTION OF OXIDATIVE CONVERSION OF PROPANOL-1

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Nickel-containing (1-10 wt.%) Catalysts based on NaX zeolite in the reaction of 1-propanol oxidative conversion have been investigated. The phase composition and magnetic properties of these systems before and after the reaction have been characterized by the methods of X-ray phase analysis (XPA) and electronic magnetic resonance (EMR). The dependence of the catalytic properties on the nickel content in the catalysts and the reaction temperature has been established. It was shown that the main gas-phase products of this reaction are propylene C_3H_6, propenal (acrolein) C_3H_4O, propanal C_3H_6O, and carbon dioxide CO_2. At reaction temperatures up to 623K, propylene is formed from the target products, and at temperatures above 623K, propanal and propenal are formed. It is assumed that the latter are formed as a result of the oxidation and oxidative dehydrogenation of propylene formed at the initial stage of the conversion of propanol-1. It was shown that among the studied catalysts, the highest propanal yield was observed for samples containing 5 wt% nickel, and the highest propenal yield was observed for a 10 wt% Ni / NaX sample. With the conversion of propanol-1 on NiNaX catalysts, propene can be obtained with a yield of 22.3% with an alcohol conversion of 65.4% at a temperature of 623K. At the same time, at temperatures above 623K, propanol-1 is dehydrogenated into propanal, and propenal is also formed. It was found that the zeolite matrix provides the formation of highly dispersed nickel oxide during the decomposition of deposited nickel nitrate. The average size of the resulting NiO particles does not exceed 30 nm, which is noticeably smaller than that of NiO particles formed during the decomposition of individual nickel nitrate. The EMR spectroscopy data show that the nickel oxide stabilized in the zeolite structure is superpara/ferromagnetic. It is assumed that the active phase in the obtained systems are nanostructured NiO particles with active oxygen. The mechanism of the reaction with the participation of NiO particles and the possibilities of X-ray diffractometry and EMR spectroscopy as methods for controlling the size-dependent catalytic properties of nickel-containing zeolite systems are discussed.

Keywords: *oxidative conversion, propanol, nickel-containing zeolite NaX, phase composition, magnetic properties.*

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Introduction

Currently developed methods for modifying zeolites, including ion exchange, changing the composition of the crystal lattice give the ample opportunities for the directed regulation of their acid-base and redox properties. Along with this, methods are also being developed for obtaining effective catalysts, which are based on the introduction of guest particles of various natures into the structure of zeolites. Within the framework of this approach, the creation of zeolite-oxide systems containing active components in a highly dispersed state is studied. The structure of zeolites makes it possible to arrange the oxide particles introduced into zeolite, control their properties in dependence on their size. The possibilities of the directed introduction of particles of oxides of various elements, ranging from alkali metals to platinum group metals, into the zeolite structure, opens up new possibilities for creating active centers with unusual properties. The data accumulated over the past two decades on the features of the course of catalytic reactions in systems containing nanosized particles formed the basis for the formation of a new promising direction - catalysis by nanosized particles [1, 2]. The successful formation and development of this direction is associated with the development of nanostructured catalysts of various composition, structure, morphology, as well as methods for controlling changes in the most important characteristics of the catalyst, in particular, the size of particles and the state of their surface [3, 4].

This work presents the results of a study of the dependence of the phase composition, magnetic and catalytic properties of nickel-containing zeolite NaX in the reaction of oxidative conversion of propanol-1 on the nickel content in the samples, the formation of nanosized Ni NiO structures and their participation in this reaction.

Experimental part

The catalysts of composition NiNaX were obtained by impregnation of NaX zeolite with an aqueous solution of nickel(II) nitrate, followed by drying at 378 K and calcining at 523-573 K until the complete decomposition of nickel(II) nitrate. Further, the samples were calcined in air at 823K for 10 hours [5, 6]. Thus were obtained samples of the catalyst composition NiNaX containing 1; 2.5; 5.0; 7.5 and 10% wt. % nickel. The samples obtained were tested as catalysts for the oxidative dehydrogenation of propanol. The oxidative dehydrogenation of propanol was carried out using a flow-through catalytic unit. The composition of the gas-phase reaction products was determined using an LXM-80 chromatograph, Russia. Propylene CH_3-$CH=CH_2$, acrolein $H_2C=CH$-CHO, propionic aldehyde CH_3CH_2CHO, and carbon dioxide CO_2 were identified as reaction products. The content of nickel and impurity iron in the samples was determined by atomic absorption spectroscopy using İC-3000 spectrometer from Thermo Scientific, USA. X-ray diffractometer XRD D2 Phaser and radio spectrometer EMXmicro, Bruker, Germany were used to determine the phase composition and magnetic properties of catalysts, respectively, subjected to redox treatments, exposure to the reaction medium, before and after the catalytic cycle.

Results and discussion

Table 1 shows the results of catalytic studies of propanol conversion on Ni / NaX catalyst samples.

Table1. The results of studies of the conversion of propanol on catalyst samples of composition Ni/NaX (reaction conditions: volume of catalyst - 5 ml, space velocity of the reaction mixture supply - 2400 h^{-1}, ratio of alcohol:air = 1:10).

Catalyst	Reaction Temperature, K	Yield of reaction products, %				Conversion of propanol-1, %
		CO_2	C_3H_6	C_3H_4O	C_3H_6O	
1 wt.% Ni/NaX	423	0.0	0.0	0.0	0.0	0.0
	473	0.0	0.0	0.0	0.0	0.0
	523	21.6	8.7	0.0	0.0	30.3
	573	31.7	20.9	0.0	0.0	50.6

	623	38.6	15.4	0.0	2.6	56.6
	673	41.6	12.3	0.0	3.9	57.8
	723	43.6	8.2	0.0	6.5	58.3
2.5 wt.% Ni/NaX	423	0.0	0.0	0.0	0.0	0.0
	473	0.0	0.0	0.0	0.0	0.0
	523	25.6	11.3	0.0	1.3	38.2
	573	35.0	17.9	0.0	2.6	55.5
	623	40.3	20.1	0.0	6.5	66.9
	673	41.6	18.9	0.0	3.9	67.4
	723	42.9	9.2	0.0	2.6	68.0
5 wt.% Ni/NaX	423	0.0	0.0	0.0	0.0	0.0
	473	0.0	0.0	0.0	0.0	0.0
	523	26.9	14.8	0.0	1.3	43.0
	573	35.0	19.9	0.0	2.6	57.5
	623	37.9	22.3	0.0	5.2	65.4
	673	38.4	20.6	0.0	7.8	67.0
	723	39.7	16.9	0.0	13.0	70.0
10 wt.% Ni/NaX	423	0.0	0.0	0.0	0.0	0.0
	473	0.0	0.0	0.0	0.0	0.0
	523	11.4	3.8	1.8	2.6	19.6
	573	23.7	6.7	3.6	5.2	39.2
	623	36.5	7.2	2.4	1.3	47.4
	673	42.9	4.1	0.0	0.0	48.0
	723	47.4	1.5	0.0	0.0	48.9

Fig.1 shows the curves of the accumulation of reaction products versus: a) the nickel content in the samples and b) the reaction temperature.

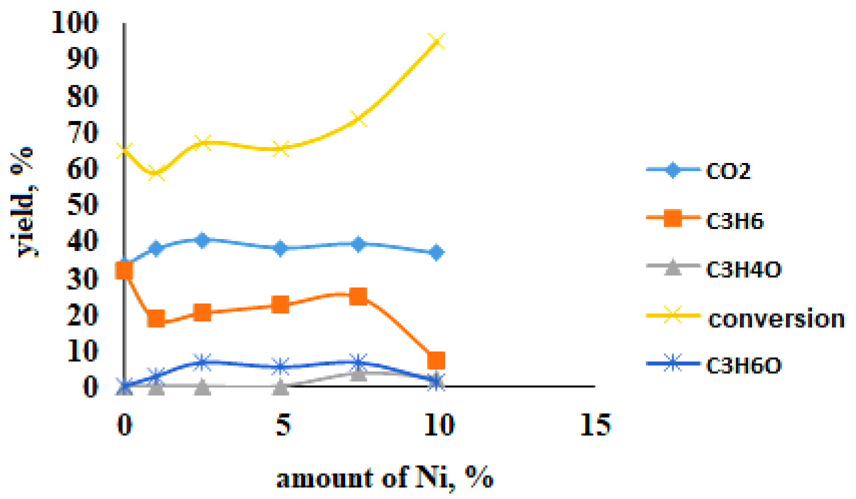


Fig. 1, a. Dependence of the yields of the propylene oxidation reaction products on the nickel content in the catalyst composition.

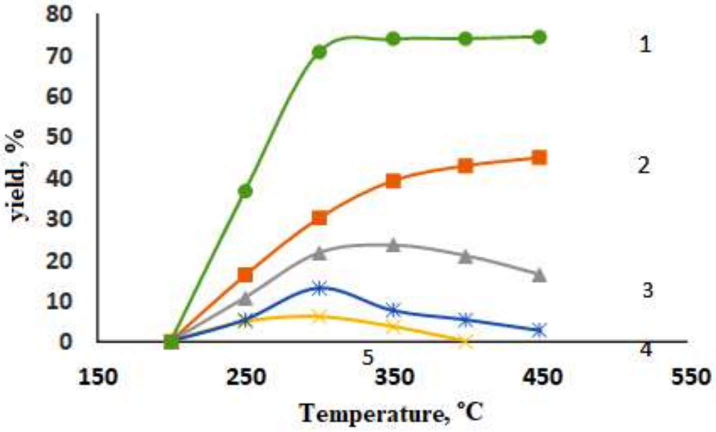


Fig. 1, b. Effect of temperature on the yield of propylene oxidation reaction products on a catalyst with 7.5 wt% supported nickel on zeolite.
1 - Conversion, 2 -CO_2, 3 -C_3H_6, 4 -C_3H_6O, 5 -C_3H_4O

Fig. 2 shows X-ray diffraction patterns and Table 2 shows the values of their parameters observed for samples of NaX zeolite containing: a) 1, b) 2.5, c) 7.5 and d) 10 wt% nickel before and after work in within 6 hours.

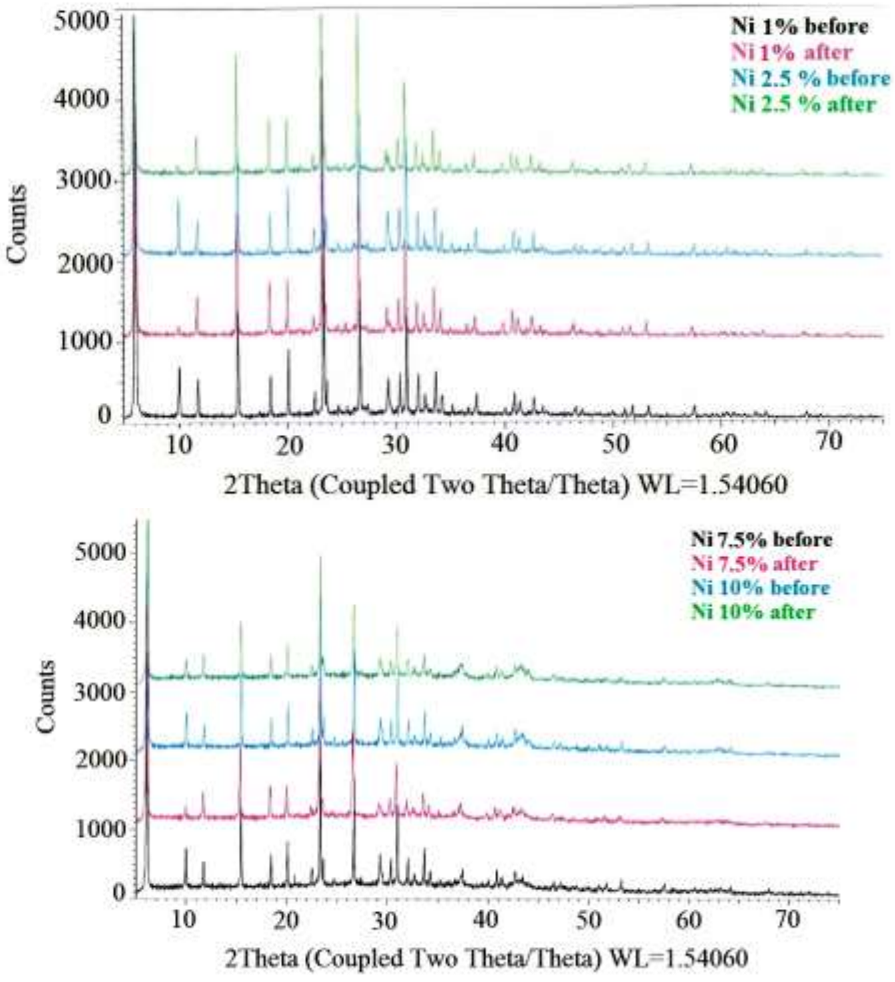


Fig. 2. X-ray diffraction patterns of samples of NaX zeolite containing 1; 2.5; 7.5 and 10 wt% nickel before and after work in within 6 hours.

For a sample of the initial zeolite, reflections are observed at 2θ = 6.116; 10.002; 23.347; 26.669; 32.037°, characteristic of the NaX zeolite [7, 8]. The obtained diffractogram practically coincides with the diffractogram presented by the International Zeolite Association (ICA) for the NaX zeolite [9].

Table 2. Values of diffractogram parameters* observed for the NaX zeolite containing 2.5 wt% nickel sample before working for 6 hours.

2θ	d	I	2θ	d	I	2θ	d	I
6.116	14.43900	100	30.362	2.94156	13.3	46.618	1.94672	2.1
10.002	8.83607	15.8	30.994	2.88303	35.8	49.971	1.82367	1.3
11.737	7.53392	9.2	32.037	2.79147	12.4	51.142	1.78464	1.3
15,459	5.727726	32.0	33.653	2.66100	13.9	51.755	1.76494	3.6
18,443	4.80672	13.8	34.231	2.617740	5.6	53.270	1.71826	4.0
20,105	4.41314	22.6	35.230	2.54547	1.8	57.528	1.60078	3.2
22,506	3.94744	7.3	36.720	2.44552	3.2	60.668	1.52523	0.9
23,347	3.80709	68.0	37.386	2.40345	4.7	63.222	1.46961	1.6
23,608	3.76553	9.3	40.870	2.20626	7.4	64.180	1.44997	1.6
24,692	3.60260	2.7	41.403	2.17908	5.0	67.959	1.37826	1.5
26,699	3.33620	45.6	42.670	2.11727	6.2			
29,299	3.04582	12.7	43.478	2.07974	3.1			

* Angle 2θ values in degrees, interplanar distances *d* in angstroms, relative intensity *I* in%.

Three dominant diffraction reflections at 2θ = 37.386 (111); 43.478 (200) and 63.222 (220) rather clearly indicate the formation of NiO particles in the zeolite structure [10]. The sharpness and intensity of the reflections indicate a well-crystallized state of NiO nanoparticles. These results confirm that the nickel (II) nitrate supported on the zeolite completely decomposes to NiO after oxidative treatment with an air flow of the NaX zeolite sample impregnated with an aqueous solution of nickel (II) nitrate at 550 ° C. An average crystal size (D) of NiO particles was estimated in line with a formula $D = k\lambda / \beta\cos\theta$, where λ = 0.154056 nm is the X-ray wavelength, β = FWHM (full width at half maximum of the peak), θ is the diffraction angle obtained of 2θ the value corresponding to the most intense reflection in the diffractogram (200), and k is a constant equal to 0.9 [11]. An average crystal size of individual NiO and NiO formed in the structure of NaX is shown in Tab. 3.

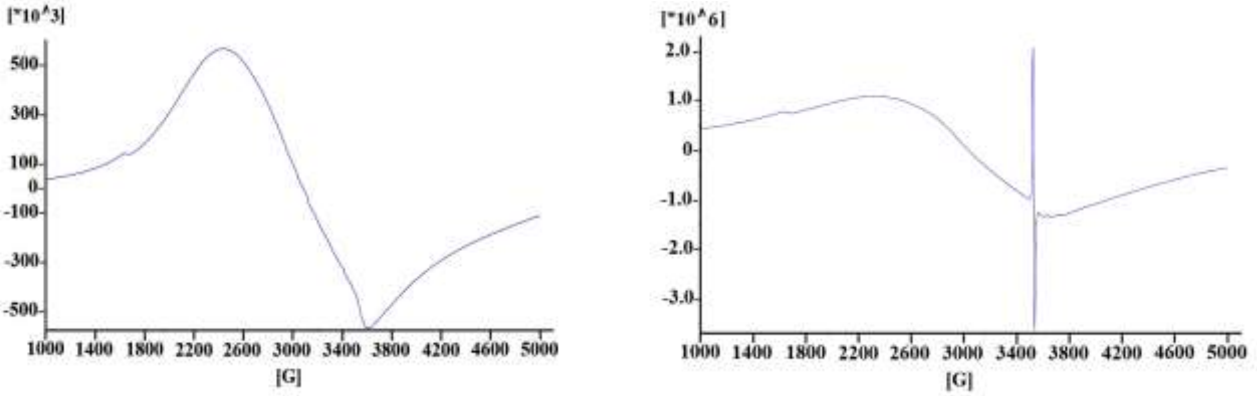
Table 3 clearly shows that the NiO nanoparticles formed in the NaX structure have a smaller crystal size than individual NiO nanoparticles. Thus, it can be concluded that the structure of the zeolite forms a nucleation point and prevents agglomeration of nanoparticles.

Table 3. Crystallite size and values of magnetic resonance parameters of pure and formed in the structure of the zeolite NaX nickel oxide NiO

Nanoparticles	Individual crystalline NiO	NiO/NaX
Size (nm), data of XRD	32.65	28,31

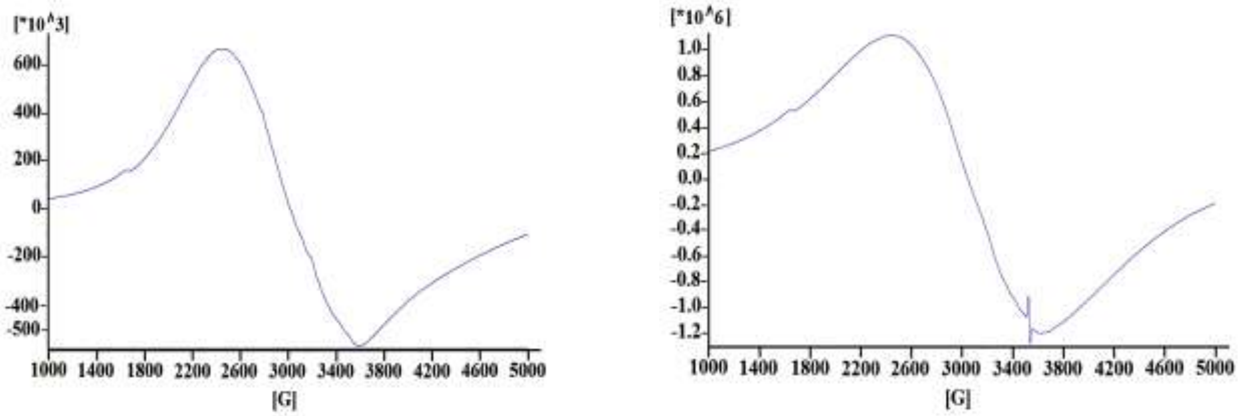
Value of g -factor	1.92	2.1
Line width, ΔH_{pp} (mT)	72,5	66,9

Figure 3 shows the EPR spectra of samples of the initial NaX zeolite and NaX zeolite containing: a, b) 1 and c, d) 7.5 wt% nickel before and after working for 6 hours.



a) 1%Ni/NaX, before reaction

b) 1%Ni/NaX, after reaction



c) 7.5%Ni/NaX, before reaction

d) 7.5%Ni/NaX, after reaction

Fig. 3. EPR spectra of samples of NaX zeolite containing: a, b) 1 and c, d) 7.5 wt% nickel before and after working for 6 hours.

For a sample of the initial NaX zeolite containing less than 0.1 wt% iron and manganese in the form of impurities, an EPR spectrum is observed from a superposition of three signals. The first two signals are weak. The first of them, characterized by a g-factor of ~ 4.3 and a width of ΔH = 12 mT, is most likely due to lattice tetrahedral Fe(III) ions with low symmetry associated with terminal OH groups of the zeolite framework [12], the second , a six-component signal due to the interaction of an unpaired electron with the ^{55}Mn manganese isotope (nuclear spin I = 5/2, natural content 100%) with a g-factor equal to 2.00 and a hyperfine splitting constant A(Mn) = 8.9 mT, belongs to Mn^{2+} ions isolated in the zeolite structure (electron configuration $3d^5$, electron spin S = 5/2). The third signal is broad, almost isotropic, intense, characterized by a g-factor equal to ~ 2.3 and belongs to iron oxide nanoclusters in the bulk of the zeolite framework. All three signals are well known in the literature and have been recorded in many zeolite matrices [13-15]. Studies show that the introduction of even a small amount of nickel (~ 1 wt%) into the starting NaX leads to a noticeable change in its EPR spectrum. Against the background of a broad signal from the side of high magnetic fields, there is a signal in the form of a hump with a g-factor of ~ 2.1 and a width of ΔH = 19-20 mT, which most likely belongs to nanosized NiO particles [16, 17]. With an increase in the amount of nickel introduced into the initial zeolite to 10 wt%, the EPR spectra become more complex and consist of the superposition of a sufficiently large number of signals, for example, for a 5 wt% NiNaX sample - of at least six signals. Exposure to the reaction mixture for 6 hours significantly changes the EPR spectrum. In all cases, the EPR spectra indicate the formation of a noticeable amount of coke on the surface of the spent catalyst. Narrow signals with g-factor equal to 2.0026 and line width ΔH = 0.9 mT, clearly manifested against the background of broad signals, belong to paramagnetic coke deposits [18, 19]. The formation of coke is accompanied by the reduction of oxide structures of nickel to metallic nickel (for example). Note that the coked sample calcined in air at 773 K shows an EPR spectrum almost identical to the EPR spectrum of the original sample. It is quite possible that nanosized particles of nickel oxide NiO are catalytically active centers of this reaction, and the stages of alternating reduction - oxidation, respectively, of NiO and Ni particles are key in the catalytic cycle. The transformation of propanol-1 can proceed in the following directions:

intramolecular dehydration:

$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH = C_3H_6 + H_2O \qquad \Delta H^o_{298} = +36{,}11$ kJ/mole

intermolecular dehydration:

$2CH_3\text{-}CH_2\text{-}CH_2\text{-}OH = CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2O \qquad \Delta H^o_{298} = -20{,}17$ kJ/mole

dehydration:

$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH = CH_3\text{-}CH_2\text{-}CHO + H_2 \qquad \Delta H^o_{298} = +71{,}93$ kJ/mole

5 wt% NiNaX catalysts dehydrate propanol-1 to propene with a yield of 22.3% at an alcohol conversion of 65.4% and a temperature of 623K, which indicates a high content of Bronsted acid sites on their surface. At the same time, the absence of the formation of ether, which is thermodynamically more favorable (see equations 3-6), is most likely due to the kinetic difficulties of this process. On the contrary, the conversion of propanol-1 on these catalysts at temperatures above 623 K is accompanied by a decrease in propene and an increase in the content of propanal and propenal in the reaction products. This circumstance may be due to the oxidation of propene to propanal and oxidative dehydrogenation to propenal.

Conclusion

Nickel-containing catalysts based on NaX zeolite in the reaction of 1-propanol oxidative conversion were studied. The phase composition and magnetic properties of these systems before and after the reaction have been characterized by XRD and EPR spectroscopy. The dependence of the catalytic properties on the nickel content in the catalysts has been established. It was shown that among the studied catalysts, samples containing less than 5 wt% nickel exhibit the highest activity in the dehydrogenation reaction. It has been established that the decomposition of nickel nitrate in zeolites provides the formation of highly dispersed nickel oxide in the zeolite structure. The average size of the formed NiO particles does not exceed 30 nm, which is noticeably smaller than during the decomposition of individual nickel nitrate. It is important to note that less than 50% NiO is detected by XRD, and in X-ray diffraction patterns of NiNaX samples, the intensity of reflections of the NiO phase in most cases is less than 40% of the theoretical value. It is shown that the conditions of redox treatments make it possible to optimize the concentration, phase composition and size of the active component and thereby regulate the yield of the target reaction products. The EMR spectroscopy data show that the NiO phase recorded in the diffractograms is most likely superpara/ferromagnetic and it can be a catalytically active component of nickel-containing zeolite samples in the dehydrogenation of propanol-1: $NiO + CH_3\text{-}(CH_2)_2\text{-}OH = Ni + CH_3\text{-}CH_2\text{-}CHO + H_2O$; $Ni + O_2 = 2NiO$. In this case, the methods of X-ray diffractometry and EMR spectroscopy can be very successfully used as methods for monitoring the structural-dimensional characteristics of the NiO / NaX system.

For the conversion of propanol-1 on the catalysts under study, as in the conversion of C_1-C_2 alcohols, the nature of the conversions is determined not only by thermodynamic factors, but also by the features of the metal-oxide / zeolite system. At the same time, noticeable differences are observed in the activity of catalysts in the conversion of propanol-1 depending on the nickel content in the zeolite structure and the reaction temperature. The products obtained in these processes (olefin, aldehydes) are of undoubted practical interest, and the identification of ways to control the selectivity of obtaining these products of the conversion of light alcohols is currently attracting the attention of researchers. The reactions of dehydration and dehydrogenation of alcohols usually proceed according to the mechanisms of elimination of E1, E2, and E1cB [20]. In the case of oxides and zeolites, the ratio of these reactions is determined by the presence of both acid-base and redox centers on the catalyst surface. The possibility of varying the structural and dimensional characteristics of nickel oxide particles in the zeolite structure makes it possible to regulate their catalytic properties.

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ФАЗОВЫЙ СОСТАВ, МАГНИТНЫЕ И КАТАЛИТИЧЕСКИЕ СВОЙСТВА НАНОСТРУКТУРИРОВАНОГО НИКЕЛЬ-СОДЕРЖАЩЕГО ЦЕОЛИТА NAX В РЕАКЦИИ ОКИСЛИТЕЛЬНОЙ КОНВЕРСИИ ПРОПАНОЛА-1

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Исследованы никельсодержащие (1-10 мас.%) катализаторы на основе цеолита NaX в реакции окислительной конверсии пропанола-1. Методами рентгенофазового анализа (РФА) и электронного магнитного резонанса (ЭМР) охарактеризованы фазовый состав и магнитные свойства этих систем до и после реакции. Установлена зависимость каталитических свойств от содержания никеля в катализаторах и температуры проведения реакции. Показано, что основными газофазными продуктами этой реакции являются пропилен C_3H_6, пропеналь (акролеин) C_3H_4O, пропаналь C_3H_6O и диоксид углерода CO_2. При температуре реакции до 623К из целевых продуктов образуется пропилен, а при температурах выше 623К – пропаналь и пропеналь. Предполагается, что последние образуются в результате окисления и окислительного дегидрирования пропилена, образующегося на начальной стадии конверсии пропанола-1. Показано, что среди изученных катализаторов, наибольший выход пропаналя наблюдается для образцов, содержащих 5 мас.% никеля, а наибольший выход пропеналя - для образца с 10 мас% Ni/NaX. При конверсии пропанола-1 на катализаторах NiNaX удается получить пропен с выходом 22.3% при конверсии спирта 65.4% при температуре 623К. В то же время при температурах выше 623 К пропанол-1 дегидрируется в пропаналь, а также образуется пропеналь. Установлено, что цеолитовая матрица обеспечивает формирование высокодисперсного оксида никеля при разложении нанесенного на нее нитрата никеля. Средний размер образующихся частиц NiO не превышает 30 нм, что заметно меньше, чем частиц NiO, образующихся при разложении индивидуального нитрата никеля. Данные ЭМР спектроскопии показывают, что оксид никеля, стабилизированный в структуре цеолита, является суперпара/ферромагнитным. Предполагается, что активной фазой в полученных системах являются наноструктурированные NiO-частицы с активным кислородом. Обсуждаются механизм реакции с участием частиц NiO и возможности методов рентгеновской дифрактометрии и ЭМР спектроскопии в качестве методов контроля размерно-зависимых каталитических свойств никель-содержащих цеолитовых систем.

Ключевые слова: окислительное дегидрирование, пропанол, никель-содержаший цеолит NaX, фазовый состав, магнитные свойства.

PROPANOL-1- in OKSİDLƏŞDİRİCİ ÇEVRİLMƏ REAKSİYASINDA TƏRKİBİNDƏ NANOQURULUŞLU NİKEL OLAN NaX SEOLİTİNİN FAZA TƏRKİBİ, MAQNİT VƏ KATALİTİK XASSƏLƏRİ

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Propanol-1-in oksidləşdirici çevrilmə reaksiyasında təərkibində nikel olan (1-10 çəki %-i ilə) NaX seolit əsaslı katalizatorlar tədqiq edilmişdir. Bu sistemlərin reaksiyadan əvvəlki və sonrakı faza tərkibi və maqnit xassələri, rentgen faza analizi (RFA) və elektron maqnit rezonansı (EMR) üsulları ilə xarakterizə edilmiş, onların katalitik xüsusiyyətləri katalizatorlarda olan nikelin miqdarından və reaksiya temperaturundan asılılığı müəyyən edilmişdir. Göstərilmişdir ki, bu reaksiyanın qaz fazasının əsas məhsulları propilen C_3H_6, propenal (akrolein) C_3H_4O, propanal C_3H_6O və karbon dioksid CO_2-dir. 623K-yə qədər reaksiya temperaturunda hədəf məhsullardan propilen, 623K-dan yuxarı temperaturlarda propanal və propenal əmələ gəlir. Sonuncuların uyğun olaraq propanol-1-in konversiyasının ilkin mərhələsində əmələ gələn propilenin oksidləşməsi və oksidləşdirici dehidrogenləşməsi nəticəsində əmələ gəldiyi güman edilir. Göstərilmişdir ki, tədqiq olunan katalizatorlar arasında propanala görə ən yüksək çıxım tərkibində % 5 nikel olan katalizator nümunələri və propenala görə ən yüksək çıxım isə tərkibində 10 nikel olan NiNaX nümunələri üçün müşahidə edilmişdir. Propanol-1-in NiNaX katalizatorlaru üzərində 623K temperaturda alkoholun 65.4 % çevrilməsi zamanı 22.3% çıxımla propen alınır. Eyni zamanda, 623K-dən yüksək temperaturda propanol-1 propanala dehidrogenləşdirilir və bununla yanaşı propenal da əmələ gəlir. Seolit matrisinin onun üzərinə çökdürülən nikel nitratın parçalanması zamanı yüksək dispersli nikel oksidinin əmələ gəlməsini təmin etdiyi aşkar edilmişdir. Yaranan NiO hissəciklərinin orta ölçüsü 30 nm-dən çox deyil, bu da fərdi nikel nitratının parçalanması zamanı əmələ gələn NiO hissəciklərinin ölçüsündən xeyli kiçikdir. EMR spektroskopiyasının tətbiqinin nəticələri göstərir ki, seolitin tərkibində sabitləşmiş nikel oksidi superpara/ferro- maqnitdir. Hesab edilir ki, bu sistemlərdə aktiv oksigeni olan nanoquruluşlu NiO hissəcikləri aktiv faza kimi iştirak edir. NiO hissəciklərinin iştirakı ilə gedən reaksiya mexanizmi və tərkibində nikel olan seolit əsaslı sistemlərdə ölçülərdən asılı katalitik xüsusiyyətlərin monitorinqinin aparılmasında rentgen diffraktometriyası və EMR spektroskopiyası metodlarının imkanları müzakirə olunur.

Açar sözlər: oksidləşdirici konversiya, propanol, nikel tərkibli zeolit NaX, faza tərkibi, maqnit xassələri.