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Hydrogenation of polyaromatic compounds over NiCo/chrysotile catalyst

The activity and selectivity of the bimetallic NiCo/chrysotile catalyst during the hydrogenation of model objects (anthracene and phenanthrene) for 1 hour at an initial hydrogen pressure of 3 MPa and a temperature of 400 °C were studied. The chrysotile mineral used as a substrate for active centers of nickel and cobalt is a waste product of asbestos production at Kostanay Minerals JSC (the Republic of Kazakhstan). The catalyst was characterized by a complex of methods of physical and chemical analysis. The chrysotile mineral consists of nanotubes with an inner diameter of about 10 nm and an outer diameter of about 60 nm. The amount of hydrogenation products is 61.91 %, destruction — 15.08 % and isomerization — 8.37 % during the hydrogenation of anthracene. The amount of hydrogenation products is 26.09 %, and that of destruction is 2.51 % during the hydrogenation of phenanthrene. It was found that the catalyst selectively accelerates the hydrogenation reaction and allows increasing the yields of hydrogenation products. The schemes of the hydrogenation reaction of model objects were drawn up according to the results of gas chromatography-mass spectrometric analysis of hydrogenates.

Keywords: polyaromatic hydrocarbons, anthracene, phenanthrene, nanocatalyst, hydrogenation, chrysotile, nickel, cobalt.

Introduction

Research on the processing of heavy and solid hydrocarbon raw materials has been a topical theme in recent years. Increasing the depth of processing of heavy oil residues, primary coal tar and improving the quality of the obtained low-boiling low-molecular compounds are one of the key areas of coal and oil refining [1, 2]. Heavy oil residue and primary coal tar usually contain a large amount of undesirable aromatic compounds and are much more difficult to convert into a pure transport fuel. In this regard, the hydrotreating process is introduced into the structure of coal and oil refining, which makes it possible to obtain a wide range of products of high demand [3, 4].

Therefore it is highly desirable to improve the efficiency of aromatic hydrogenation. This can be achieved by optimizing the process and improving the catalysts, which in turn requires a deeper understanding of the aromatic hydrogenation process.

Comparison with previous studies has shown that the nature of the catalyst strongly affects the relative reactivity of aromatic compounds [5]. Currently there is a wide range of catalysts for the hydroconversion of heavy hydrocarbon feedstock, which are due to their various purposes. As is known, metals of the VIII group of the periodic system (nickel, cobalt, iron) are usually used as the hydrogenating component [6, 7], as well as oxides and sulfides of the metals of the VIII group [6, 8]. It is known from literary sources [8, 9] that a combination of nickel and tungsten has a greater hydrogenating activity.

Model combinations, such as anthracene, phenanthrene, pyrene, naphthalene, etc., are often used to determine the mechanisms of activity and selectivity of the selected catalysts in the hydrogenation process, which make it possible to establish a more detailed mechanism for heavy hydrocarbons concentration and scientifically based methods for predicting their control [10].

Sahle-Demessie et al. [11] and Liu et al. [12] show the results of catalytic hydrogenation, where anthracene is hydrogenated to di-, tetra- and octa-hydroanthracene, depending on the conditions. Phenanthrene, in comparison with the linear isomer — anthracene, undergoes hydrogenation more difficultly [13, 14]. A completely hydrogenated molecular form — perhydrophenanthrene was obtained along with di-, tetra- and octa-hydroderivatives under more severe conditions and in a larger amount of catalyst [15].

The aim of this work is to evaluate the activity and selectivity of the NiCo/chrysotile catalyst during the hydrogenation of polyaromatic model objects, such as anthracene and phenanthrene.

Experimental

Obtaining and physicochemical studies of the catalyst

Preliminary leaching with a 20 % hydrochloric acid solution was carried out to remove magnesium and calcium salts in the original chrysotile. The preparation of a binary catalyst was carried out by first dissolving nickel nitrate (20 %) in water with heating, followed by the addition of leached chrysotile to the resulting solution. The resulting mixture was stirred and dried at room temperature, and then dried in an oven at 105 °C until constant weight. Then, cobalt nitrate was dissolved in water and the process was repeated with the already obtained dry mass of chrysotile with a nickel salt. Further, the heat treatment of nickel and cobalt salts deposited on chrysotile was carried out in a muffle furnace at 500 °C for 2 hours. The mass fraction of nickel and cobalt in the total mass of the obtained NiCo/chrysotile catalyst is 5 % each.

A Dron-4-07 X-ray diffractometer was used (a tube with a cobalt anode, tube parameters: 30 kV, 20 mA) to determine the phase composition of the catalyst obtained.

The surface morphology of the leached chrysotile and the NiCo/chrysotile catalyst were obtained using a MIRA3 TESCAN scanning electron microscope and a Jeol JEM-1400Plus transmission electron microscope.

Using a NanoS90 laser particle sizer and Zetasizer Nano (DTS) software, the particle size and distribution of the catalyst were determined, and water was used as the dispersant.

Process of catalytic hydrogenation of model objects

Hydrogenation of polyaromatic hydrocarbons (anthracene (Interchem, Russia) and phenanthrene (Merck, Russia)) was carried out in an autoclave (manufactured in the People’s Republic of China) with an internal stirrer with a capacity of 0.05 L. Hydrogenation of anthracene and phenanthrene lasts 60 minutes at an initial hydrogen pressure of 3.0 MPa, a temperature of 400 °C. The working pressure was ~6.0 MPa. The mass of the polyaromatic hydrocarbon of 1 g and the mass of the catalyst of 0.01 g were premixed. Then the prepared mass was loaded into the autoclave. The reactor was purged with hydrogen, and required gas pressure was supplied. The reactor was held for a specified time after reaching the temperature required. The reaction mixture was dissolved in benzene when it was cooled to room temperature.

The gas chromatography-mass spectrometry analysis of anthracene and phenanthrene hydrogenation products was performed on an Agilent Technologies 7890A gas chromatograph with a 5975C mass-spectrometric detector. The column temperature was gradually varied from 60 to 300 °C with time; a flow rate of helium was 8 mL/s. The test sample with a volume of 1 μL was introduced into the column using a 7683B autosampler. The test sample entered the ionization chamber of the mass spectrometer after separation in the column. The incoming molecules underwent fragmentation by electron impact with energy of 70 eV at a temperature of 250 °C in the chamber. After extracting from the ionization chamber by an electrostatic field the fragments arrived at a quadrupole capacitor. The mass spectra of test sample components were obtained with the use of the quadrupole capacitor. The chromatograms and mass spectra were processed using the MSD ChemStation E02.00.493 software. The NIST-8 database of mass spectra was used to identify compounds.

Results and Discussion

Parameters of NiCo/chrysotile catalyst

The chrysotile mineral used as a substrate for active centers of nickel and cobalt is a waste product of asbestos production at Kostanay Minerals JSC (the Republic of Kazakhstan), which is a serpentine raw material $3MgO\cdot 2SiO_2\cdot H_2O$. Man-made waste contains a significant amount of magnesium oxide, on average 38–42 % by weight, and derivatives of silicon dioxide as main accompanying components [16]. Chrysotile fibers consist of 12–20 twisted planes. It was found that the twist of the fibers decreases after leaching of chrysotile using a hydrochloric acid solution due to the removal of magnesium oxide. Thus, the acidity of chrysotile increases due to an increase in the concentration of SiO_2.

The natural mineral chrysotile is of great interest because its macroscopic matrix consists of nanotubes, the inner diameter of which is about 10 nm, and the outer diameter is about 60 nm. These nanotubes can be about 1 cm long, and they are arranged in a close-to-hexagonal packing. Chrysotile has been successfully used for the formation of semiconductor, ferroelectric, and metal nanowires [17]. When a catalyst is prepared by wet mixing, chrysotile nanotubes can be filled with nickel and cobalt ions from the corresponding salts solutions. Figure 1 shows the diffraction pattern of the catalyst obtained.

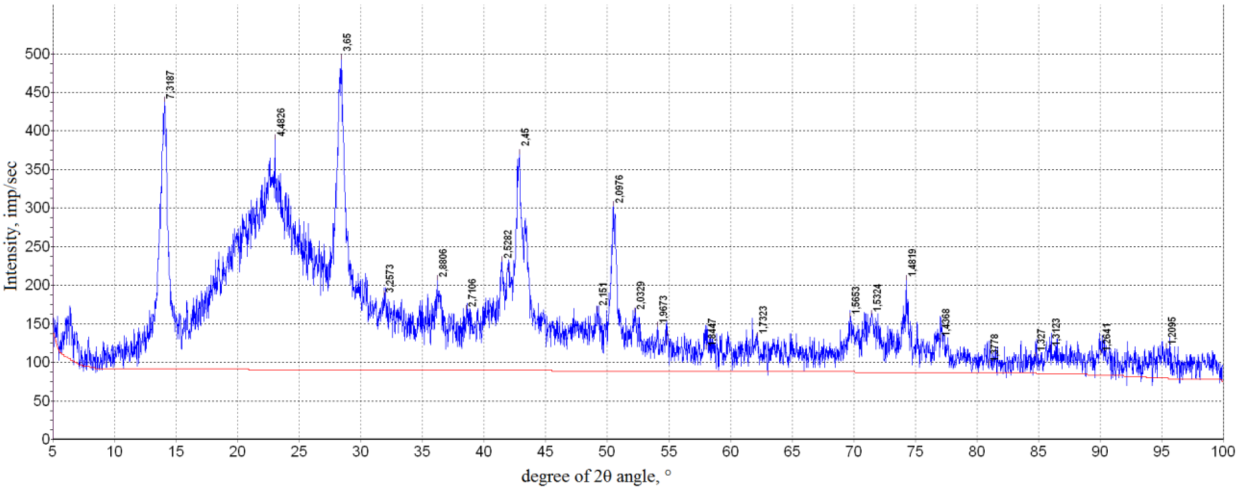

Figure 1. X-ray diffractograms of NiCo/chrysotile

According to the diffraction pattern, the reflections are 7.31; 4.48; 3.65; 2.52; 2.09; 1.53 Å correspond to the crystal structures of chrysotile $Mg_3[OH]_4\{Si_2O_5\}$, reflections 2.88; 2.45; 2.03; 1.56; 1.43 Å — cobalt oxide $CoCo_2O_4$, reflections 2.42; 2.09; 1.48; 1.26; 1.20 Å — nickel oxide NiO.

Figure 2 shows photomicrographs of leached chrysotile and catalyst NiCo/chrysotile.

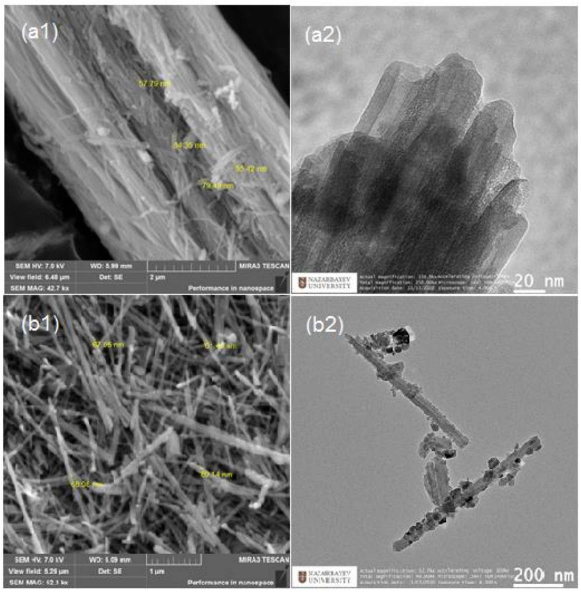

Figure 2. SEM (1) and TEM (2) micrographs of chrysotile (a) and NiCo/chrysotile (b)

The micrographs (a1 and a2) show that the chrysotile tubes are tightly packed in the short order. However, in the long range order, chrysotile can be described as “amorphously” packed. The mineral consists of nanotubes with an inner diameter of about 10 nm and an outer diameter of about 60 nm. Oxides of nickel and cobalt with a diameter of ~50 nm deposited on the surface of chrysotile tubes are visible (micrographs b1 and b2).

The particle size and distribution of the catalytic additive particles, determined using a laser particle sizing device, are shown in Figure 3.

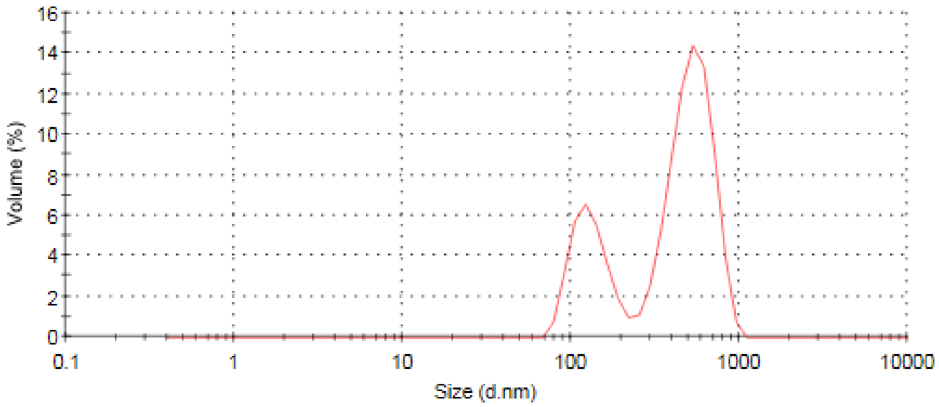

Figure 3. Size and distribution of particles in an aqueous suspension of NiCo/chrysotile

According to the laser determiner, the average particle size of the catalyst is 546.5 nm.

Influence of the catalyst on hydrogenation of model objects

Table 1 shows the results of the hydrogenation of anthracene and phenanthrene in the presence of NiCo/chrysotile catalyst.

Table 1

The yield of products of anthracene and phenanthrene hydrogenation process in the presence of NiCo/chrysotile

No.	Individual chemical composition	The yield of products, %	
		Anthracene	Phenanthrene
1	1-Methyl-2-(phenylmethyl)-benzene	3.51	0.20
2	2-Ethyl-naphthalene	1.38	1.10
3	2-Butyl-naphthalene	2.20	0.25
4	Biphenyl	–	0.40
5	2-Methyl-1,1'-biphenyl	1.04	–
6	2-Ethyl-1,1'-biphenyl	6.95	0.37
7	Fluorene	–	2.75
8	9-Methyl-9H-fluorene	–	0.90
9	9,10-Dihydro-anthracene	24.83	2.82
10	1,2,3,4-Tetrahydro-anthracene	34.92	1.68
11	1,2,3,4,5,6,7,8-Octahydro-anthracene	2.16	–
12	9,10-Dihydro-phenanthrene	–	13.45
13	1,2,3,4-Tetrahydro-phenanthrene	–	4.09
14	Anthracene	14.65	–
15	Phenanthrene	8.37	74.70
16	Undetermined	–	0.57
	Conversion	76.99	28.60

It was noted that phenanthrene is hydrogenated less selective than anthracene, although the order of the shortened bond in it is greater than in anthracene. Obviously, the number of shortened bonds should also be taken into account: in phenanthrene, one with an order of 1.775, in anthracene — four, although with an order of 1.738. Thus, an important tendency determining the rate of hydrogenation of aromatic hydrocarbons is its dependence on the presence of shortened bonds and their number if the process is not complicated by the peculiarities of the catalysts effect [18].

Diagrams have been presented in Figures 4 and 5 according to the results of the hydrogenation of anthracene and phenanthrene in the presence of NiCo/chrysotile catalyst at an initial hydrogen pressure of 3 MPa and a temperature of 400 °C.

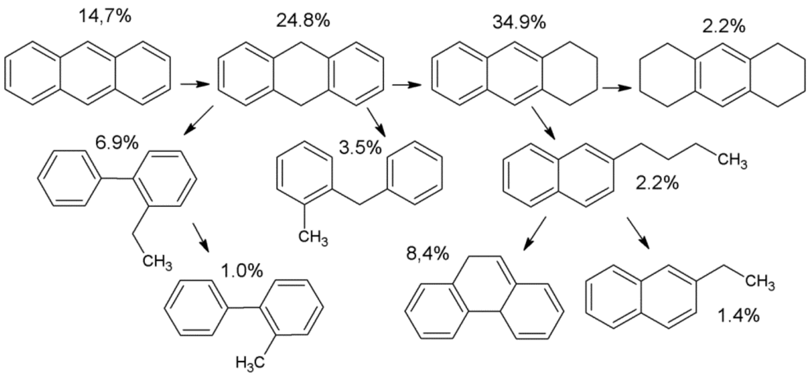

Figure 4. Scheme of anthracene hydrogenation reactions according to hydrogenated product composition

During the hydrogenation of anthracene the amount of hydrogenation products is 61.91 %, destruction — 15.08 % and isomerization — 8.37 %. It is known that the first reaction in anthracene hydrocracking is stepwise hydrogenation to di-, tetra- and octahydro-anthracenes, alternately [11, 12]. The cyclohexane ring of the tetrahydroanthracene is then cracked to naphthalenes. The conversion of anthracene to 1-methyl-2-(phenylmethyl)-benzene occurs stepwise through the formation of dihydro-anthracene.

A general pattern of naphthenic rings opening along with α-bonds has been observed according to the results of model objects hydrogenation. The preferential cleavage of this bond under conditions simulating coal liquefaction, i.e., under the hydrogen pressure is explained by the ipso-attack of atomic hydrogen, formed by the interaction of molecular hydrogen with radicals [18]. The formation of 1-methyl-2-(phenylmethyl)-benzene from dihydroanthracene (1) and 2-butyl-naphthalene from tetrahydroanthracene (2) occurs by cleavage of α-bonds initiated by ipso-attack H• (Fig. 5).

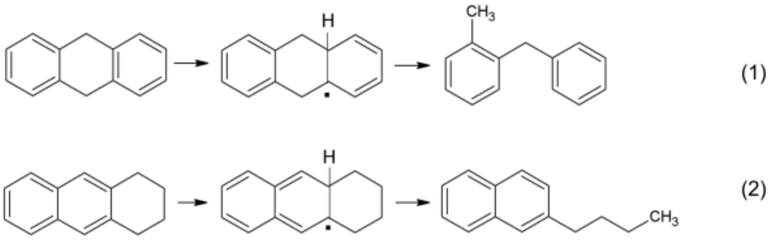

Figure 5. Scheme of 1-methyl-2-(phenylmethyl)-benzene formation from dihydroanthracene (1) and 2-butyl-naphthalene from tetrahydroanthracene (2)

The amount of hydrogenation products is 26.09 %, and that of destruction is 2.51 % during the phenanthrene hydrogenation.

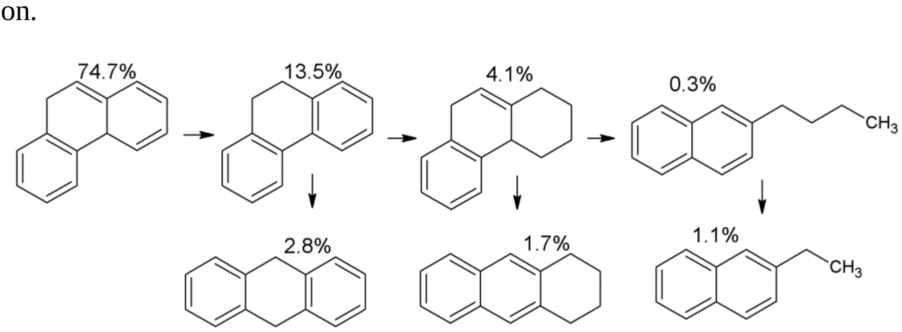

Figure 6. Scheme of phenanthrene hydrogenation reactions according to hydrogenated product composition

Successive hydrogenation and cracking reactions prevail in the process of phenanthrene hydrogenation. Apparently, 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene formed as a result of phenanthrene hydrogenation are isomerized to 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene, respectively [19]. The formation of 2-butyl-naphthalene from tetrahydrophenanthrene also occurs by cleavage of the α-bond initiated by ipsoattack H• (Fig. 7).

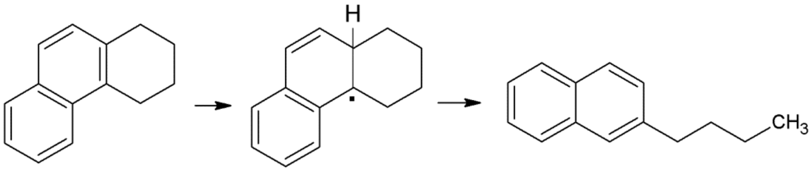

Figure 7. Scheme of 2-butyl-naphthalene formation from tetrahydrophenanthrene

9-methyl-9H-fluorene formed during the hydrogenation of phenanthrene is a Fluorene product present in the starting phenanthrene (3.7 %). Also, most likely, 1-methyl-2-(phenylmethyl)-benzene, 2-ethyl-1,1'-biphenyl, biphenyl are the degradation products of dibenzothiophene present in the starting phenanthrene (2.1 %).

Earlier, we found that during the hydrogenation of a mixture of anthracene and phenanthrene with a ratio of 1:1 in the presence of a catalytic additive CoO/microsphere, at an initial hydrogen pressure of 3 MPa and a temperature of 420 °C, the conversion of the mixture is 92.5 %, where the amounts of unreacted anthracene and phenanthrene accounted for 1.3 % and 6.2 %, respectively [20]. The high conversion of the mixture can be explained by the fact that the products of anthracene hydrogenation (di-, tetrahydroanthracene) act as a hydrogen donor. 9,10-Dihydroanthracene and 1,2,3,4-tetrahydroanthracene formed during the phenanthrene hydrogenation in the presence of a NiCo/chrysotile catalyst can also be hydrogen donors.

Conclusions

Thus, when studying the effect of the NiCo/chrysotile catalyst on the hydrogenation of anthracene and phenanthrene for 1 hour at an initial hydrogen pressure of 3 MPa and a temperature of 400 °C, it was found that the catalyst selectively accelerates the hydrogenation reaction and allows increasing the yields of hydrogenation products and is ~62 % and ~26 %, respectively. The yields of the degradation products of anthracene and phenanthrene are ~15 % and ~2.5 %, respectively. Anthracene conversion is ~77 % and phenanthrene conversion is ~29 %.

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Е.А. Аубакиров, А.Р. Бродский, Фен Юн Ма, Д.К. Макенов

Полиароматты қосылыстардың NiCo/хризотил катализаторында гидрогенизациялау

Модельдік объектілерді (антрацен мен фенантрен) 1 сағат бойы сутегінің бастапқы қысымы 3 МПа және 400 °С температурада гидрогенизациялаған кезде биметалдық NiCo/хризотилді катализатордың белсенділігі мен селективтілігі зерттелді. Никель мен кобальттың белсенді орталықтары үшін субстрат ретінде пайдаланылған хризотил минералы «Қостанай минералдары» АҚ (Қазақстан Республикасы) асбест өндірісінің қалдығы болып табылады. Катализатор физика-химиялық талдау әдістерінің кешенімен сипатталды. Хризотил минералы ішкі диаметрі шамамен 10 нм және сыртқы диаметрі шамамен 60 нм болатын нанотүтіктерден тұрады. Антраценді гидрогенизациялау кезінде гидрлеу өнімдерінің мөлшері 61,91 %, деструкция өнімдері 15,08 % және изомеризация өнімдері 8,37 % құрады. Фенантренді гидрогенизациялау кезінде гидрлеу өнімдерінің мөлшері 26,09 %, ал деструкция өнімдері 2,51 % болды. Катализатор гидрлеу реакциясын селективті түрде жылдамдататыны және гидрлеу өнімдерінің шығымын арттыруға мүмкіндік беретіні анықталды. Гидрогенизаттарды хромато-масс-спектрометрлік талдау нәтижелері бойынша модельдік объектілерді гидрогенизациялау реакциясының схемалары жасалды.

Кілт сөздер: полиароматты көмірсутектер, антрацен, фенантрен, нанокатализатор, гидрогенизация, хризотил, никель, кобальт.

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Гидрогенизация полиароматических соединений на катализаторе NiCo/хризотил

Исследованы активность и селективность биметаллического катализатора NiCo/хризотил при гидрогенизации модельных объектов (антрацена и фенантрена) в течение 1 ч при исходном давлении водорода 3 МПа и температуре 400 °С. Минерал хризотил, использованный в качестве подложки для активных центров никеля и кобальта, является отходом асбестового производства АО «Костанайские минералы» (Республика Казахстан). Катализатор охарактеризован комплексом методов физико-химического анализа. Минерал хризотил состоит из нанотрубок с внутренним диаметром около 10 нм и внешним диаметром около 60 нм. При гидрогенизации антрацена количество продуктов гидрирования составляет 61,91 %, деструкции — 15,08 % и изомеризации — 8,37 %. При гидрогенизации фенантрена количество продуктов гидрирования составляет 26,09 %, а деструкции — 2,51 %. Установлено, что катализатор селективно ускоряет реакцию гидрирования и позволяет увеличить выход продуктов гидрирования. По результатам хромато-масс-спектрометрического анализа гидрогенизатов были составлены схемы реакции гидрогенизации модельных объектов.

Ключевые слова: полиароматические углеводороды, антрацен, фенантрен, нанокатализатор, гидрогенизация, хризотил, никель, кобальт.

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