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Influence of nanocatalytic systems on the hydrogenation of model object — anthracene

The influence of nanocatalysts β -FeOOH, Fe(OA)₃, Fe₃O₄ and spherical catalysts NiO/SiO₂, Fe₂O₃/SiO₂ on the hydrogenation process of model object is evaluated. These catalysts are established to be new developed catalytic additives promoted deeper chemical modification and destruction of hydrocarbons, as a result they can increase the yield of light products. It is shown that spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ can be used for hydrogenation of multiplet systems, such as coal, coal tar or its fractions.

Key words: hydrogenation of model object, anthracene, nanocatalytic systems, multiring hydrocarbon, destruction, spherical catalysts, donor of hydrogen.

Nowadays the search of new catalysts and technologies of solid hydrocarbonaceous materials and oil residues is one of the most important directions in the development of the petrochemical industry. A significant issue in the hydrogenation of heavy hydrocarbon feedstocks is improving the efficiency of heterogeneous catalytic reactions. Therefore, great attention is paid for the development of scientific approaches in creating new catalytic systems possessing the activity and selectivity. Many alternatives of catalysts, in particular nanocatalysts for hydrogenation process are prepared [1].

Selection of effective catalysts and their use in the destructive hydrogenation of heavy hydrocarbon feedstock make possible to carry out the process in milder conditions and increase the conversion of the organic mass and the quality of distillate products. Model compounds, such as anthracene, phenanthrene, pyrene, naphthalene, etc. often are used to determine the activity and selectivity of selected catalysts in the hydrogenation process. It is allowed to reveal the mechanisms for processing of heavy coal and elaborate the science-based methods for predicting their behavior [2]. Although much experimental work has been done on the hydrogenation of polyaromatic hydrocarbons, there is still a demand by the industry for an economical and efficient commercial process. Therefore, in the present work the catalytic hydrogenation process of model object was investigated in the presence of nanocatalytic systems.

Experimental Part

To study the influence of nanocatalysts and spherical catalysts on the product yield of model objects in the hydrogenation process several experiments were carried out. The conditions are given in the Table 1. Premixed input components were placed in a pressure reactor (autoclave). The moment of reaching operating temperature by autoclave is considered at the beginning of reaction. The heating rate of the autoclave was 10 °C per min. The products of hydrogenation were washed by benzene.

Table 1

**Conditions for hydrogenation of anthracene in the presence of nanocatalysts
 β -FeOOH, Fe(OA)₃, Fe₃O₄ and spherical catalysts NiO/SiO₂, Fe₂O₃/SiO₂**

№	Anthracene, g	Nanocatalytic systems					T, °C	P, MPa	τ , min
		β -FeOOH	Fe(OA) ₃	Fe ₃ O ₄	NiO/SiO ₂	Fe ₂ O ₃ /SiO ₂			
1	1	0,01	–	–	–	–	400	3	60
2		–	0,01	–	–	–			
3		–	–	0,01	–	–			
4		–	–	–	0,01	–			
5		–	–	–	–	0,01			
6		–	–	–	0,01	–	300		
7		–	–	–	–	0,01			

Nanocatalysts β -FeOOH, $\text{Fe}(\text{OA})_3$ and Fe_3O_4 were prepared according to the procedure [3–5]. Spherical catalysts NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ were prepared by an impregnation method. Ash from thermal power station was used as the substrate, the content of which has been investigated by X-ray method: $\text{SiO}_2=55,391\%$, $\text{Al}_2\text{O}_3=2,014\%$, $\text{Fe}_2\text{O}_3=7,715\%$, $\text{TiO}_2=1,745\%$, $\text{CaO}=2,606\%$, $\text{K}_2\text{O}=2,354\%$, $\text{MgO}=1,531\%$, $\text{Na}_2\text{O}=2,734\%$, other unidentified compounds=1%. The substrate was impregnated by 10% solutions of the salts of nickel and iron (NiCO_3 and $\text{FeSO}_4 \cdot 9\text{H}_2\text{O}$) followed by drying and kilning. The surface topography of spherical catalysts was observed by probe microscope GSPM-5400. The parameters of the porous structure of the samples were studied by gas adsorption instrument ASAP Micromeritics (USA). The fractional composition of the hydrocarbon part of model object was detected by high performance liquid chromatography Agilent Technologies 5975 and identification of compounds was quantified by mass spectral database NIST 98.

Discussion of Results

It is shown from Figures 1–3 that the synthesized catalysts have retained a spherical structure which is similar to conformation of substrate. It can be assumed from these data that the nature of the substrate played a key role in getting the nanoscale particles and highly refined structure. It is showed that more efficient catalysts in processing of hydrocarbon raw materials are superfine particles distributed uniformly throughout the volume of raw materials [6–9]. Appropriateness of application of nanoparticles in catalysis is connected with the chemical activity which is proportional to the specific surface of the catalyst. Many properties of nanoparticles depend on their size, so it is possible to manage activity and selectivity of nanocatalysts by changing its ones [10].

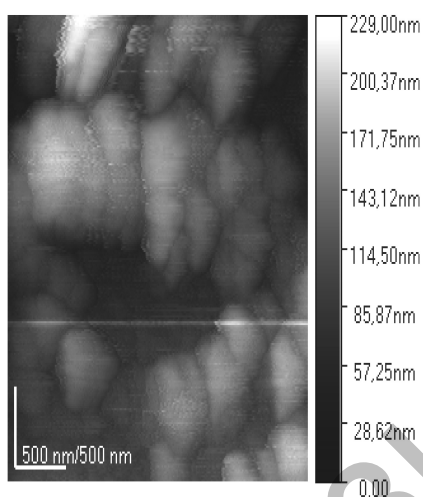


Figure 1. The surface topography of substrate SiO_2

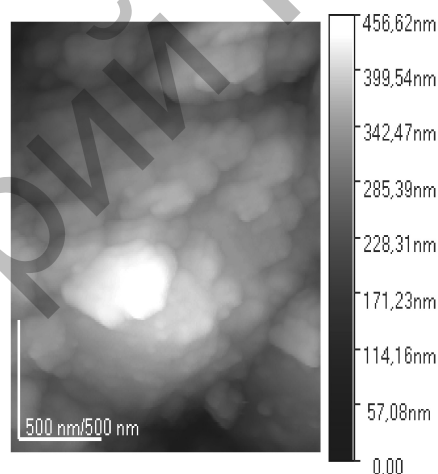


Figure 2. The surface topography of spherical catalyst NiO/SiO_2

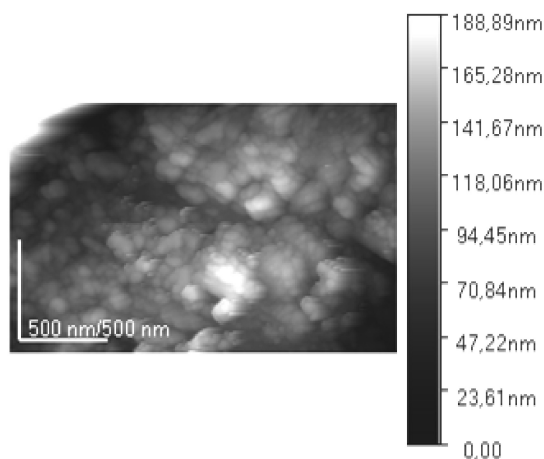


Figure 3. The surface topography of spherical catalyst $\text{Fe}_2\text{O}_3/\text{SiO}_2$

The analysis of the adsorption isotherms of nitrogen on the synthesized catalysts showed the different pore sizes (Fig. 4). The isotherms (curves 1, 3) can be attributed to type 4, which has hysteresis loop. Shape of the hysteresis loops varies considerably for different porous materials. It should be pointed out that the adsorption for this type of isotherm is summarized by micropores and mesopores with the capillary condensation. The adsorption isotherm (curve 2) is characteristic for microporous adsorbents and such isotherms are considered to determine only volume of micropores.

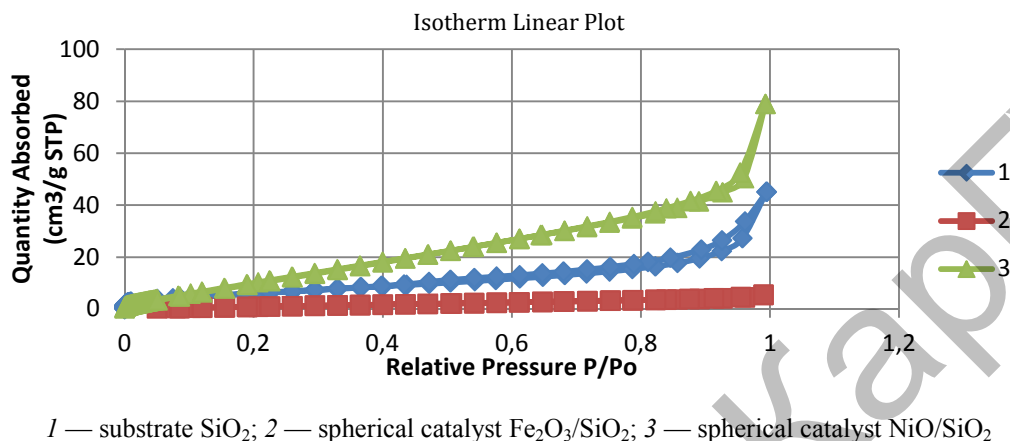


Figure 4. The adsorption isotherms of nitrogen on the spherical catalysts

Pore size distribution analysis of spherical catalysts by the method DFT indicates that the spherical catalyst Fe₂O₃/SiO₂ has micro-mesoporous structure and spherical catalyst NiO/SiO₂ is characterized by presence of only mesopores (Fig. 5, 6).

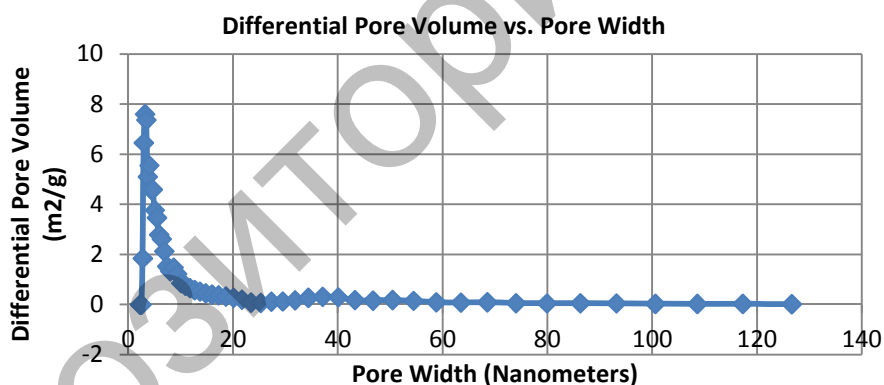


Figure 5. Pore size distribution of spherical catalyst Fe₂O₃/SiO₂ by the method DFT

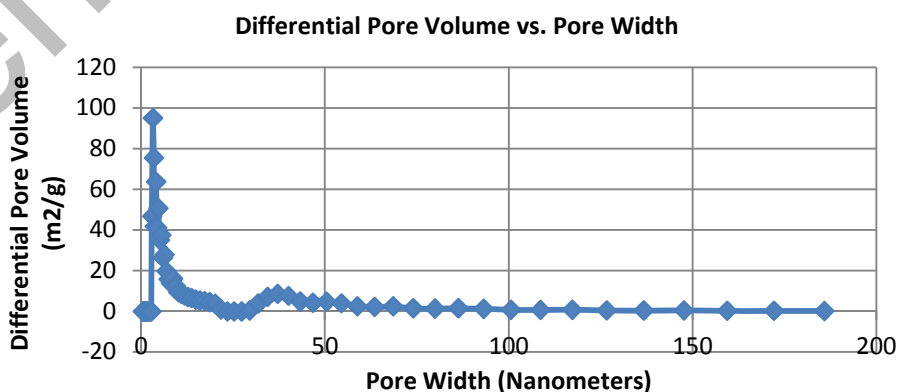


Figure 6. Pore size distribution of synthesized catalyst NiO/SiO₂ by the method DFT

The product yield of hydrogenation process of anthracene in the presence of nanocatalysts β -FeOOH, $\text{Fe}(\text{OA})_3$ and Fe_3O_4 is shown in the Table 2.

Table 2

The product yield of hydrogenation process of anthracene

Name	Nanocatalysts		
	β -FeOOH	$\text{Fe}(\text{OA})_3$	Fe_3O_4
Naphtalene	2.15	2.43	2.7
1-Butylnaphtalene	20.93	11.04	5.5
2-Ethyldiphenyl	1.03	0.85	2
1,2,3,4-Tetraanthracene	59.4	55.55	7.3
9,10-Dihydroanthracene	15.98	23.54	77.12
Anthracene	0.51	6.21	5.4

It follows from this data that in the hydrogenation of anthracene using nanocatalyst β -FeOOH the hydrogenation product yield is 75.38 % and degradation product yield is 24.11 % and unreacted material yield is 0.51 %. In the case using the nanocatalyst $\text{Fe}(\text{OA})_3$, the hydrogenation product yield is 79.09 % and degradation product yield is 14.32 %, an unreacted material yield is 6.21 %. By adding 1 % Fe_3O_4 hydrogenation product and degradation product yields are 84.65 % and 9.87 %, respectively, unreacted material yield is 5.4 %. Comparison of these results showed a significant change in the ratio of hydrogenation and hydrogenolysis products and the ratio of conversion. At the point of hydrogenolysis product yield and unreacted materials, the most efficient nanocatalyst is β -FeOOH; at the point of the hydrogenation products yield, the most effective nanocatalyst is Fe_3O_4 (Fig. 7). On the contrary, authors [11] noted that the destruction of the hydrocarbons did not happen at the hydrogenation of anthracene and naphthalene in tetralin due to less activity of the catalyst.

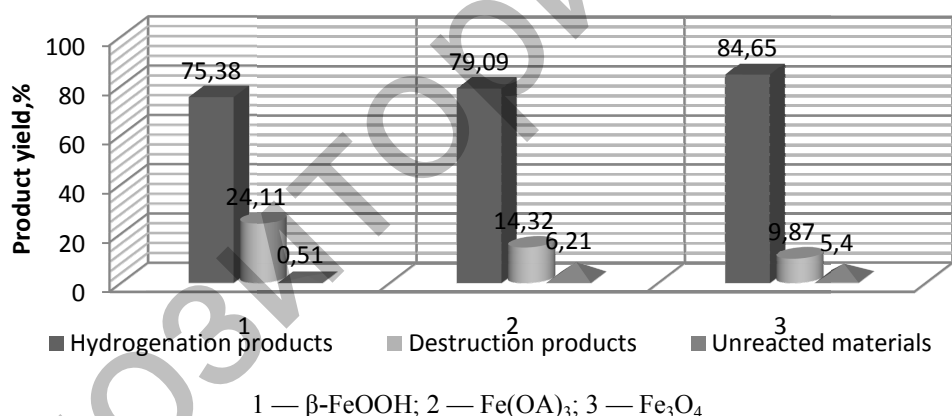


Figure 7. The ratio of hydrogenation and hydrogenolysis products in the presence of nanocatalysts

The product yield of hydrogenation process of anthracene in the presence of spherical catalysts NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ at 300 °C and 400 °C is shown in the Table 3.

Table 3

The product yield of hydrogenation process of anthracene

Name	Spherical catalysts			
	NiO/SiO_2		$\text{Fe}_2\text{O}_3/\text{SiO}_2$	
	300 °C	400 °C	300 °C	400 °C
1-Methylnaphtalene	1.68	0.71	–	8.22
1,6-Dimethylnaphtalene	0.11	24.78	–	4.34
1,2,3,4-Tetraanthracene	65.48	0.18	88.72	86.474
9,10-Dihydroanthracene	32.73	69.48	10.26	–
Anthracene	–	0.74	1.02	0.1

In the hydrogenation of anthracene at 300 °C the hydrogenation products yield is 98.2 % in the presence of spherical catalyst NiO/SiO₂. At 400 °C the hydrogenation product and degradation product yields are 69,66 % and 25,49 %, respectively. There is negligible quantity in the content of unreacted materials. In the presence of spherical catalyst Fe₂O₃/SiO₂ hydrogenation product yield is 98.98 % at 300 °C. At 400 °C the hydrogenation product is 86.47 %, degradation product yield is 11,56 %. Based on these data, the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ are the most efficient ones at the point of hydrogenation product yield and are not inferior to nanocatalysts β-FeOOH, Fe(OA)₃ and Fe₃O₄, furthermore these catalysts have a number of advantages, such as the availability and low cost.

Authors [12] describes the hydrocracking of polycyclic hydrocarbons by multistep mechanism including hydrogenation, hydroisomerization, cracking and repeated hydrogenation. Similarly, anthracene is hydrogenated to di- and tetraanthracene at the first stage of step-wise transformation. Then cyclohexane rings of tetraanthracene are subjected to cracking and isomerization to naphthalene. It is known that hydrogenated polycyclic aromatic hydrocarbons are more active hydrogen donors, so they can cause of a deep conversion of a feedstock. Therefore, the high hydrogenation product yield can be explained by catalytic action which relates to the hydrogenation of aromatic polycyclic hydrocarbons.

Thus, the influence of nanocatalysts β-FeOOH, Fe(OA)₃, Fe₃O₄ and spherical catalysts NiO/SiO₂, Fe₂O₃/SiO₂ on the hydrogenation process of model object is evaluated. It is established that the nanocatalysts and spherical catalysts increase the formation rate of hydro-derivatives of anthracene, in particular 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene. The most optimum amount of the catalyst systems at ratio of 1 % allows to increase of hydrogen donor which prevents condensation reactions and decreases the stability of the associates. It is demonstrated that spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ can be used for hydrogenation of multiplet systems, such as coal, coal tar or its fractions. These catalysts are established to be new developed catalytic additives promoted deeper chemical modification and destruction of hydrocarbons, as a result spherical catalysts can increase the yield of light products.

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Нанокаталитикалық жүйелердің модельдік объекті — антраценнің гидрогенизация үрдісіне әсері

Модельді объект — антраценнің гидрогенизациясын жүргізудегі β -FeOOH, Fe(OA)₃, Fe₃O₄ нанокатализаторларының және NiO/SiO₂, Fe₂O₃/SiO₂ сфералық катализаторларының әсері бағаланған. Синтезделген каталитикалық жүйелер көмірсутектік шикізаттың деструкциясы мен терең химиялық модификациясына әсер ететіні анықталған. Көмір, таскөмір шайыры немесе оның фракциялары тәрізді мультиплеттік жүйелердің гидрогенизациясында синтезделген катализаторлар қолданыла алатыны көрсетілген.

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Влияние нанокаталитических систем на гидрогенизацию модельного объекта — антрацена

Проведена оценка влияния нанокатализаторов β -FeOOH, Fe(OA)₃, Fe₃O₄ и сферических катализаторов NiO/SiO₂, Fe₂O₃/SiO₂ на процесс гидрогенизации модельного объекта — антрацена. Установлено, что синтезированные каталитические системы способствуют более глубокой химической модификации и деструкции углеводородного сырья. Показано, что синтезированные нанокатализаторы могут быть использованы для гидрогенизации мультиплетных систем, таких как уголь, каменноугольная смола или их фракции.

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