

Influence of catalytic systems on process of model object hydrogenation

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Abstract On the basis of β -FeOOH, $\text{Fe}(\text{OA})_3$, Fe_3O_4 iron and spherical catalysts NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ derived from slag waste coals of heating electrical stations, the hydrogenation of model polycyclic hydrocarbon at presence of nanodimensioned catalysts anthracene was studied. On the example of conversion of anthracene, it was shown that upon release of hydrogenation of the product yield and degradation of polycyclic hydrocarbons in the hydrogenation, the mentioned catalyst systems appeared to be in the following order: nanoparticles β -FeOOH, $\text{Fe}(\text{OA})_3$ and Fe_3O_4 > spherical catalysts NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ > commercial cobalt-molybdenum catalyst. The results showed that the catalysts studied are promising catalysts for the hydrogenation of polycyclic hydrocarbons and may be used for direct coal liquefaction.

Keywords Anthracene · Multi-ring hydrocarbons · Nanocatalysts · Spherical catalysts · Hydrogenation

1 Introduction

Currently the search on new catalysts and development of new technologies of solid hydrocarbon raw material and oil leftovers refinement are important directions in oil chemistry industry. One of the main tasks at hydrogenation of heavy hydrocarbon raw material is increasing the effectiveness of heterogenic catalytic reactions. Selection of effective catalysts and their application in process of destructive hydrogenation of heavy hydrocarbon raw material allows carrying out the process in more soft conditions, increasing organic masses conversion, output and quality of distilled products. As follows, large attention is paid to the development of scientific approaches at creation of new generation of catalytic systems that require increased activeness and selectiveness. Lots of variants of preparing of hydrogenation catalysts are under consideration, particularly nano-catalysts and natural materials that

can be used as catalysts available for hydrocarbon processing (Ma et al. 2012).

To define activity and selectivity mechanisms of chosen catalysts in hydrogenation process model combinations are often used such as anthracene, phenanthrene, pyrene, naphthalene, and others, which allow establishing more detailed mechanism of heavy hydrocarbon refinement and scientifically developing vindicated methods for forecasting their management. That is why the aim of the present work is to study the anthracene model object catalytic hydrogenation process at the presence of nano-catalyst additives β -FeOOH, $\text{Fe}(\text{OA})_3$, Fe_3O_4 and spherical catalysts NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$.

2 Experimental

Experiments were carried out to study the influence of nano-catalysts β -FeOOH, $\text{Fe}(\text{OA})_3$, Fe_3O_4 and spherical catalysts NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ on model objects output products in process of hydrogenation. Initial components were mixed beforehand and placed into the reactor of high pressure with volume of 0.2 L at temperature of 300 and 400 °C during 60 min in excess of hydrogen with pressure

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of 3 MPa. The moment when autoclave reaches working temperature was considered as the start of reaction. Speed of autoclave heating was 10 °C per minute. Created product was washed by benzene.

Study of hydrogenation process products of model objects were defined by chromatography-mass spectrometry on HP 5890/5972 MSD device of “Agilent” enterprise (USA).

Nanocatalytic systems on the basis of β -FeOOH, $\text{Fe}(\text{OA})_3$ and Fe_3O_4 iron were synthesized and their physical–chemical characteristics, morphological types, activity and selectivity were tested by authors (Park et al. 2004; Piao et al. 2008). It is known that advantages of catalytic systems on the base of iron are their accessibility and possibility of regeneration by simple ways that is why they are of current interest. Therefore, there is a need to study the influence of nanocatalysts on product yield during process of hydrogenation of anthracene.

Spherical catalysts NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ are the oxides of nickel and iron, evenly distributed over the outer surface of the silicon-containing microsphere carrier. Microspheres siliceous carrier is one of the components of slag waste coal of coal-fired plants, resulting from the combustion of coal-fired power plants as a result of melt granulation of the mineral coal and blow of crushed droplets by internal gases. As a result of this process, hollow silicate microspheres with almost perfect spherical shape are obtained. The content of silicon-containing microsphere carrier was studied by roentgen spectral method: $\text{SiO}_2 = 55.391\%$, $\text{Al}_2\text{O}_3 = 2.014\%$, $\text{Fe}_2\text{O}_3 = 7.715\%$, $\text{TiO}_2 = 1.745\%$, $\text{CaO} = 2.606\%$, $\text{K}_2\text{O} = 2.354\%$, $\text{MgO} = 1.531\%$, $\text{Na}_2\text{O} = 2.734\%$, and 1 % of other non-defined substances.

Microsphere siliceous carrier was separated from the ash waste in laboratory conditions by immersion of the liquid to the waste mentioned above. Due to the density difference, the heavy ash fraction settled to the bottom and hollow light silicon-containing microspheres emerged to the liquid surface. After that, they were collected from the surface of the liquid and dried. After that 10 % solutions of nickel and iron (NiCO_3 and $\text{FeSO}_4 \cdot 9\text{H}_2\text{O}$) were prepared, and applied on a silicon carrier microspheres with subsequent drying and calcination at 600 °C for 60 min and injected in an amount of 1 %.

Morphology of spherical catalysts surfaces is shown as in Figs. 1 and 2, obtained on probe microscope GSPM-5400. Parameters of porous structure of spherical catalysts were studied on ASAP Micrometrics (USA) device.

3 Results and discussion

It is shown from Figs. 1, 2 and 3 that NiO/SiO_2 , $\text{Fe}_2\text{O}_3/\text{SiO}_2$ synthesized spherical catalysts had taken the structure

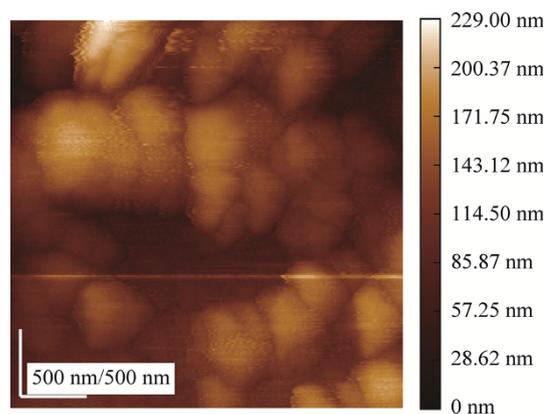


Fig. 1 Surface topography of SiO_2 carrier

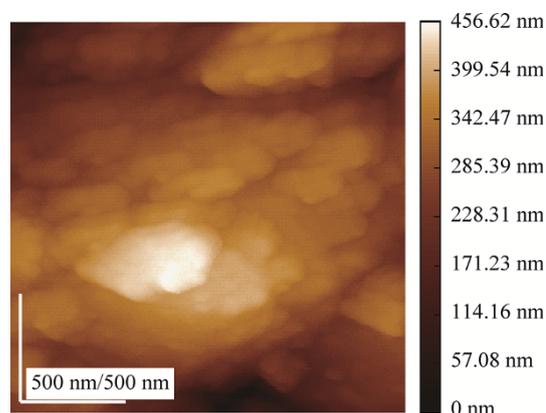


Fig. 2 Surface topography of NiO/SiO_2 spherical catalyst

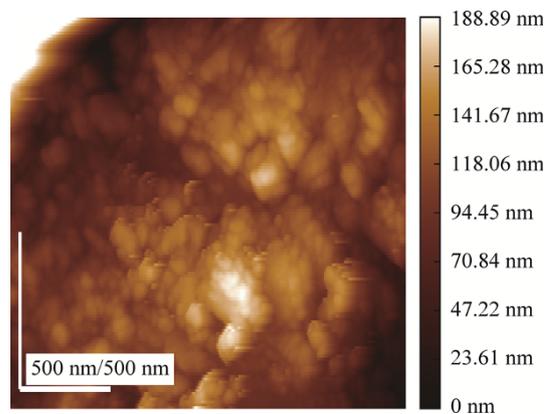


Fig. 3 Surface topography of $\text{Fe}_2\text{O}_3/\text{SiO}_2$ spherical catalyst

of the carrier. Applied iron and nickel salts were evenly distributed on outer surface of microspheres siliceous carrier. Upon those data, it might be assumed that nature of the carrier had played key role in receiving of nanodimensional

and high disperse particles. In the literature (Zekel et al. 2007), it was shown that during processes of refinement of hydrocarbon raw material those catalysts are more effective than were inserted into process as high disperse particles evenly distributed in the whole volume of raw material. Rationality of applying nano particles in catalysis is connected, at first, with chemical activity, which is proportional to unit surface of catalyst. It should be noted that to increase the catalyst activity it is required not only to increase the internal surface but also to create specific porous structure of the catalyst grains that provides a sufficient speed for supplying reactants to the outermost periphery of the grain surface portions and the inner discharge of them from the reaction products. For each of the catalytic process, depending on the conditions of its implementation, kinetic dependences and specific catalytic activity of the catalyst optimal porous structure may be set which provides the highest speed of the reaction (Volkova et al. 2014).

Lots of characteristics of nano particles depend on their size that is why it is possible to control the activeness and selectiveness of nano-catalysts by changing their sizes (Eremin 2009).

Analysis of isotherms of nitrogen adsorption on spherical catalysts showed that there were pores of different sizes in them (Fig. 4). Obtained isotherms (curves 1, 2) might be referred to IV type to which the presence of hysteresis curve is specific. The forms of hysteresis curves are different for various porous materials. Adsorption for

isotherms of such types constructs from adsorption in micro pores and capillary condensation in mesopores. Adsorption isotherm (curve 3) is specific for microporous adsorbents; it is thought that from this kind of isotherms only volumes of micropores might be defined.

The isotherms data of nitrogen adsorption parameters of porous structure of spherical catalysts $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and NiO/SiO_2 are represented on the Table 1.

According to Table 1, the spherical catalysts $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and NiO/SiO_2 can be referred to mesoporous with a small content of the micropores (1.09 % and 7.4 %, respectively). Thus for spherical catalysts the main volume of mesopore is in pores with a diameter of 18–27 nm ($\text{Fe}_2\text{O}_3/\text{SiO}_2$) and 18–19 nm (NiO/SiO_2) (Fig. 5).

Hydrogenation of a model object anthracene at the presence of nanocatalysts $\beta\text{-FeOOH}$, $\text{Fe}(\text{OA})_3$ and Fe_3O_4 . During anthracene hydrogenation process at the presence of $\beta\text{-Fe}_3\text{O}_4$ nano-catalyst, hydrogenation products yield appeared to be the highest and was 84.65 %. In case of hydrogenation with the use of $\beta\text{-FeOOH}$ and $\text{Fe}(\text{OA})_3$ nano-catalyst, hydrogenation products yields were 75.38 % and 79.09 %, respectively. The yields of the destruction products in the hydrogenation of anthracene at the presence of nanocatalysts $\beta\text{-FeOOH}$, $\text{Fe}(\text{OA})_3$ and Fe_3O_4 totalled with 24.11 %, 14.32 % and 9.87 % respectively (Table 2).

Comparison of results of this hydrogenation has shown the significant change in correspondence of hydrogenation products and hydrogenolyses, and indicator of conversion level. Reviewing from viewpoint of hydrogenolyses yield

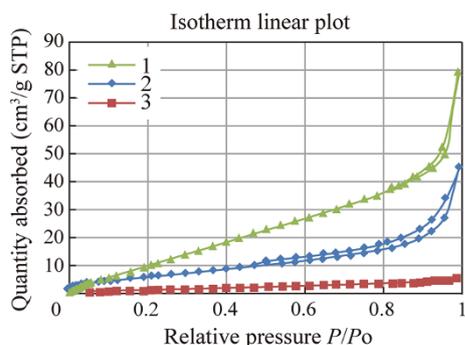


Fig. 4 The isotherm of nitrogen adsorption on the spherical catalysts. (1- $\text{Fe}_2\text{O}_3/\text{SiO}_2$, 2- NiO/SiO_2 , 3- SiO_2 carrier)

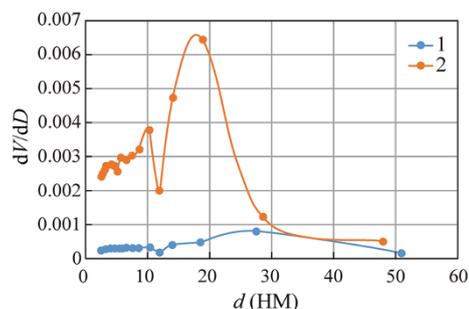


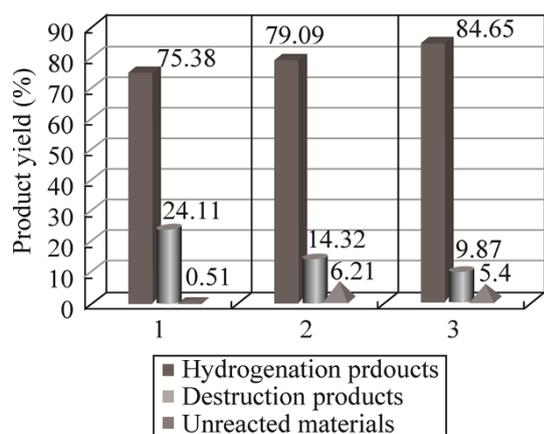
Fig. 5 Mesopores volume distribution by sizes of spherical catalysts. (1- $\text{Fe}_2\text{O}_3/\text{SiO}_2$, 2- NiO/SiO_2)

Table 1 Main characteristics of porous structure of spherical catalysts $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and NiO/SiO_2

Spherical catalysts	S_{sp} (m^2/g)	Total volume of pores (sm^3/g)	R (nm)	Correspondent content of pores (%)	
				Micropores <2	Mesopores 2–50 nm
NiO/SiO_2	42.8043	0.11878	0.85–27.9	7.4	92.6
$\text{Fe}_2\text{O}_3/\text{SiO}_2$	22.5666	0.06111	0.87–25.6	1.09	98.91

Table 2 The yield products of anthracene hydrogenation process

Name	Nanocatalysts		
	β -FeOOH	Fe(OA) ₃	Fe ₃ O ₄
Naphtalene	2.15	2.43	2.7
1-butylNaphtalene	20.93	11.04	5.5
2-ethylidiphenyl	1.03	0.85	2
1,2,3,4-tetraantracene	59.4	55.55	7.3
9-10-dihydroantracene	15.98	23.54	77.12
Antracene	0.51	6.21	5.4

**Fig. 6** The yield of hydrogenation, hydrogenolysis and non-reacted substances. (1-FeOOH, 2-Fe(OA)₃ and 3-Fe₃O₄) nanocatalysts

product and amount of non-reacted substances, β -FeOOH was the most effective one from all the used nano-catalysts; from position of hydrogenation products yield, the most effective was Fe₃O₄ nano-catalyst (Fig. 6).

According to Li et al. (2011), it was found that Jiangjunmiao coal had a higher oil yield and conversion with the synthesized iron-based catalysts than that with the commercial Fe₂O₃ catalyst. Possible reason is that the long-chain organic molecules existed in synthesized catalysts. Highly catalytic activity of the oil-soluble catalysts is the result from their high dispersity and smaller particle size of particles. High specific surface and vast active sizes of synthesized nano- β -FeOOH, Fe(OA)₃ and Fe₃O₄ are beneficial to break down the structure of coal and transfer of hydrogen to coal fragment radicals. Compared with commercial iron powders, the synthesized iron-based catalysts are more effective for the hydrogenation of anthracene.

Hydrogenation of a model object anthracene at the presence of spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂. The yield of anthracene hydrogenation at the presence of NiO/SiO₂ and Fe₂O₃/SiO₂ spherical catalysts at temperature of 300 and 400 °C are given in Table 3.

Table 3 The yield products of anthracene hydrogenation process

Name	Spherical catalysts			
	NiO/SiO ₂		Fe ₂ O ₃ /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-tetraantracene	65.48	0.18	88.72	86.474
9-10-dihydroantracene	32.73	69.48	10.26	
Antracene		0.74	1.02	0.1

During hydrogenation of anthracene and the model object at a temperature of 300 °C, the yield of hydrogenation products was approximately 98.2 % at presence of NiO/SiO₂ and Fe₂O₃/SiO₂ spherical catalysts. It should be noted that the spherical catalysts NiO/SiO₂, Fe₂O₃/SiO₂ contribute to the selective hydrogenation of anthracene to 9,10-dihydroanthracene and 1,2,3, 4-tetrahydroanthracene at temperature of 300 °C. During hydrogenation of anthracene model object at temperature of 400 °C yields of destruction products at presence of NiO/SiO₂ and Fe₂O₃/SiO₂ totalled with 25.49 % and 11.56 % respectively. Based on these data it can be concluded that the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ allow controlling the outputs of hydrogenation products or destruction depending on the temperature.

For comparison, it should be noted that, during hydrogenation of anthracene at the presence of commercial cobalt- molybdenum catalyst of Ryazan plant at 430 °C, hydrocarbon destruction processes were merely present because of the lesser extent of the catalyst activity (Sharipov et al. 1990). Hydrogenating product composition was as follows: dihydroanthracene–27.2 %, tetrahydroanthracene–65.7 %, oktahydroanthracene–7.1 %. High product yield in anthracene hydrogenation process in the presence of spherical catalysts might be assumed by catalytic action, which is associated with the flow of step-by-step hydrogenation of di-anthracene and tetrahydroanthracene; cyclogexane rings of tetrahydroanthracene are then hydroisomerized and cracked to naphthalene. Activity of spherical catalysts is determined by the specific surface area and mesoporous structures. Mesopores are prevalent in all catalysts, the resulting spherical mesoporous catalysts in their textural characteristics are analogues of zeolites. Acid function is defined by a silicon carrier and hydrogenation function is determined by the salt deposited on a nickel and iron catalysts. As is known from the literature sources (Kairbekov et al. 2008), the mechanism of the reaction involves a heterolytic dissociation of hydrogen into a metal cation, followed by sequential addition of the

hydride ion and the proton on the double bond of hydrogenated compound.

4 Conclusions

Thus, spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ were obtained by simple and environmentally friendly method for the model polycyclic hydrocarbons hydrogenation process. From the nitrogen adsorption isotherm data and surface morphology of spherical catalysts it was seen that spherical catalysts Fe₂O₃/SiO₂ and NiO/SiO₂ have a nearly ideal spherical shape and may be referred to mesoporous materials, while the bulk of the mesopores in pores is of a diameter of 18–27 nm (Fe₂O₃/SiO₂) and 18–19 nm (NiO/SiO₂). The feasibility of using the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ in the process of hydrogenation of polycyclic hydrocarbons model is connected with the chemical activity, which is proportional to the specific surface area and high-dispersing, and the porous structure of these catalytic systems. It should be noted that along with nanocatalysts β-FeOOH, Fe(OA)₃, Fe₃O₄, the spherical catalysts NiO/SiO₂, Fe₂O₃/SiO₂ contribute to the selective hydrogenation of anthracene to 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene and are more active compared with a commercial cobalt-molybdenum catalyst seen from the hydrogenation product yield and destruction during the anthracene hydrogenation. From the experimental data, it can be concluded that nanosized and spherical catalysts are newly developed catalyst systems; they can contribute to a deeper chemical modification of

the organic mass of hydrocarbons leading to significantly higher yield of light products.

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