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Effect of catalytic systems on the hydrogenation of phenanthrene

This paper shows the effectiveness of the synthesized catalytic additives in the process of hydrogenation of phenanthrene in the presence of ethanol as a hydrogen donor. Ferrosphere, NiO/SiO_2 covered the surface of ferrosphere and Fe_2O_3/SiO_2 covered the surface of ferrosphere were used as catalytic additives. Ferrosphere was extracted from energy ashes of Karaganda thermal power plant. NiO/SiO_2 and Fe_2O_3/SiO_2 covered the ferrosphere were prepared by the method of «wet mixing». The phase composition, surface morphology, average size and distribution of particles of ferrospheres and nanocatalytic additives NiO/SiO_2 and Fe_2O_3/SiO_2 covered the ferrospheres were determined. The composition of the reaction products was determined by the method of chromato-mass spectrometry on the gas chromatograph of Agilent Technologies 7890A with mass spectrometric detector 5975C. Identification of the substances was carried out using the NIST 98 mass-spectral database. A synergistic effect of nanocatalytic additives NiO/SiO_2 and Fe_2O_3/SiO_2 covered the ferrospheres was established. The high degree of phenanthrene conversion is observed on the hydrogenation in the presence nickel and iron catalytic additives on the ferrosphere. According to the results of hydrogenation of phenanthrene efficiency range of the catalytic additives was built: NiO/SiO_2 on the ferrosphere > > Fe_2O_3/SiO_2 on the ferrosphere > NiO/SiO_2 > Fe_2O_3/SiO_2 > ferrosphere.

Keywords: polyaromatic hydrocarbons, phenanthrene, hydrogenation, catalytic systems, ferrosphere, sol-gel method, «wet mixing» method, coal.

Introduction

Currently due to the shortage of the «light oil» resource most of the researches related to the processing of heavy oil and solid hydrocarbon raw materials is being considered. As it is known synthetic liquid fuel get 7–8 times more from coal than from oil. Despite the high losses scientific works on improvement of hydrogenation of coal, coal tar and liquefaction of products are continued in most countries.

According to modern concepts the main part of the organic mass of coal is a three-dimensional polymer of irregular structure, the rigidity of the framework of which is enhanced by internal donor-acceptor interactions. Studies show that the products of destruction of the organic mass of coal are complex combination of hydrocarbons in which compounds with the number of aromatic rings up to three predominate, but hydrocarbon derivatives with four or more rings form a certain part [1].

The decomposition of the organic mass of coal is carried out to obtain liquid products. Liquefaction of the initial product and saturation with hydrogen are carried out during hydrogenation. Depending on the process conditions and the depth of conversion of the organic mass of coal, hydrogenation allows to turn solid fuel into high-quality motor fuel (gasoline, diesel fuel) or raw materials for organic synthesis (hydrocarbons, phenols, nitrogenous compounds). The composition of the hydrogenation products depends on the amount of hydrogen entering into the reaction, the quality of the catalysts and the parameters of the process itself (pressure, temperature, contact time) [2].

The study of destructive hydrogenation of polyaromatic compounds was carried out to improve the process of coal liquefaction mentioned above. One of the polycyclic aromatic compounds in solid fuels is phenanthrene, which was first obtained from coal tar.

The purpose of this work is to investigate the process of catalytic hydrogenation of phenanthrene as a model object, which constitutes the organic mass of coal.

Experimental

For experiments phenanthrene was used as model object; ferrosphere, synthesized nanocatalytic additives NiO/SiO_2 and Fe_2O_3/SiO_2 separately covered the ferrosphere were used as catalytic additives. Ferrosphere was extracted from the energy ashes which were obtained by burning coal at Karaganda thermal power plant.

Ferrosphere was used as a carrier of catalytic additives NiO/SiO_2 and Fe_2O_3/SiO_2. Catalytic additives added to the ferrosphere were prepared by the «wet mixing» method.

The catalytic additive Fe_2O_3/SiO_2 was covered the ferrosphere by mixing the ferrosphere with 20 % solutions of ferric chloride and sodium silicate, followed by heating the mixture to a temperature of 70–80 ºC for 2 hours. Then the resulting suspension of the initial compounds was dried at a temperature of 100–105 ºC. The dry mass was calcined at a temperature of 500–550 ºC for 60 minutes and then molded into a tablet. The second catalytic additive NiO/SiO_2 covered the ferrosphere was prepared similarly. Ferrosphere was mixed with 20 % solutions of nickel sulfate and sodium silicate.

The activity of the prepared catalytic additives in the hydrogenation of phenanthrene was determined under autoclave conditions: T — 380 ºC, P — 3 MPa, t — 120 min, the amount of catalytic additive 1.0 mass %, 5 ml of ethanol as a hydrogen donor. The use of alcohols allows to obtain significant yields of liquid products in the absence of catalysts and molecular hydrogen. The ability to interact with active radical centers, preventing their recombination, determines the stabilizing role of aliphatic alcohols [3].

The mixture of phenanthrene and catalytic additives was pre-mixed, and then the prepared mass and ethanol were loaded into the autoclave. The reactor was purged with molecular hydrogen and pressurized with it. Then the reactor was heated to the required temperature (380 ºC) and kept for a given time. The heating rate of the autoclave was 10 ºC/min. After the experiment, it was cooled to room temperature; the reaction mixture was dissolved by chloroform. The composition of the reaction products was determined by the method of chromato-mass spectrometry on the gas chromatograph of *Agilent Technologies 7890A* with mass spectrometric detector *5975C*. Identification of the substances was carried out using the *NIST 98* mass-spectral database.

Results and Discussion

The phase composition of catalytic additives was studied on a X-ray diffractometer *MiniFlex 400/300*. The diffractograms of the synthesized samples of NiO/SiO_2 on the ferrosphere (sample 1) and Fe_2O_3/SiO_2 on the ferrosphere (sample 2) are presented (Fig. 1).

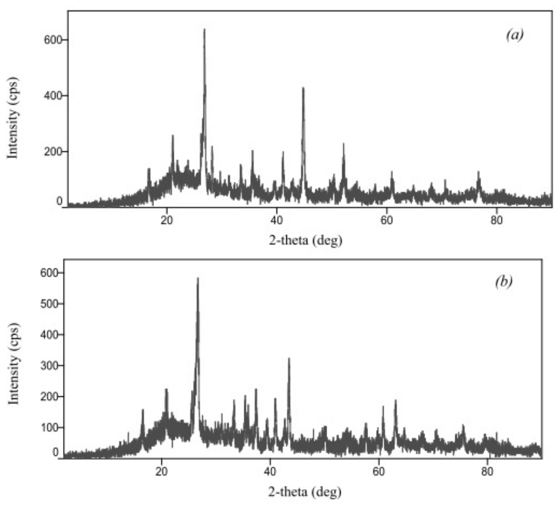

Figure 1. X-ray diffractograms of NiO/SiO_2 catalytic additives covered the ferrosphere (*a*); Fe_2O_3/SiO_2 catalytic additives covered the ferrosphere (*b*)

The diffractograms of samples 1 and 2 show the presence of phases respectively NiO/SiO_2 and Fe_2O_3/SiO_2.

Electronic micrographs of initial ferrosphere and the samples 1 and 2 are shown in Figure 2.

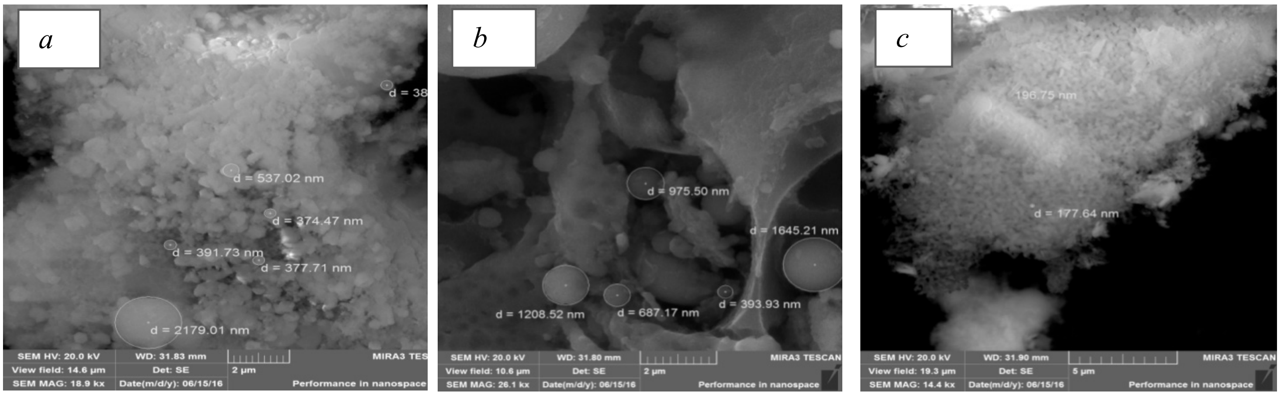

Figure 2. Electronic micrographs of NiO/SiO_2 on the ferrosphere (*a*), Fe_2O_3/SiO_2 on the ferrosphere (*b*), initial ferrosphere (*c*)

The study showed that spherical formations of ferrospheres have a particle size of 975.5 nm. The nickel-silicon composition (sample 1, *b*) is spherical formations with the diameter of 374 nm. These formations tend to coalesce, forming conglomerates with fouling of small spheres of nickel oxides and iron oxides.

The average particle size of the prepared nickel and iron samples was determined by using nanosizer *NanoS90* (Fig. 3).

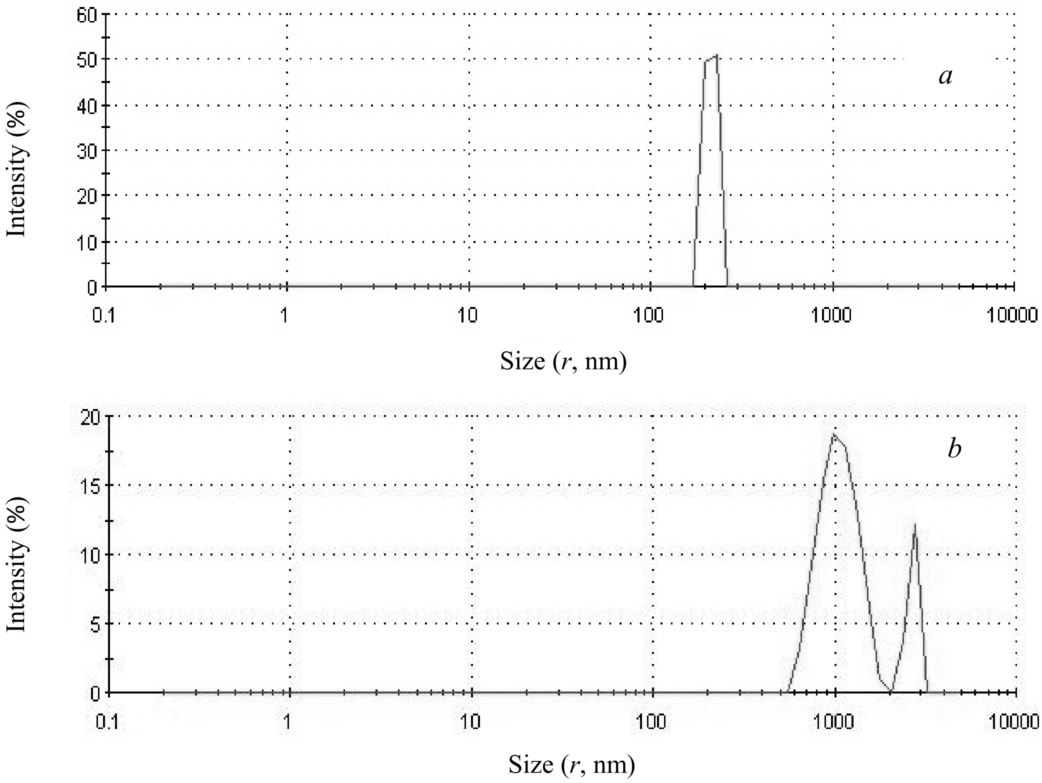

Figure 3. Average particle size of NiO/SiO_2 on the ferrosphere (*a*), Fe_2O_3/SiO_2 on the ferrosphere (*b*)

The average particle size was 213.9 nm for sample 1 and 1064 nm for sample 2.

The results of phenanthrene hydrogenation are presented in Table. The main products of hydrogenation of phenanthrene in the presence of the catalytic additives are the products of the hydrogenolysis and hydriding.

Table

The yield of the products of phenanthrene hydrogenation without catalyst and in the presence of the catalytic additives

Individual chemical composition	Yield of the products, %					
	Without catalyst	Ferrosphere	NiO/SiO_2 [4]	Fe_2O_3/SiO_2 [4]	NiO/SiO_2 on the ferrosphere	Fe_2O_3/SiO_2 on the ferrosphere
	1	2	3	4	5	6
Naphthalene	–	–	0.14	0.08	–	–
1-Methylnaphthalene	–	–	0.11	–	3.6	–
2-Ethylnaphthalene	–	–	–	0.05	–	–
2-Butylnaphthalene	–	0.9	–	–	–	4.2
Fluorene	–	–	0.98	0.97	–	–
9-Methylfluorene	–	–	0.42	0.18	–	–
9,10-Dihydroanthracene	–	0.7	0.41	0.44	–	7.5
9,10-Dihydrophenanthrene	–	–	4.5	4.3	34.3	16.4
1,2,3,4-Tetrahydrophenanthrene	–	3.2	–	–	13.2	3.5
1,2-Dihydrophenanthrene	4.2	–	–	–	–	–
1,1-Biphenyl	–	–	1.54	0.03	11.2	–
Benzene	–	–	–	–	2.2	–
2-Methyl-1,1-biphenyl	–	–	–	–	–	5.7
Anthracene	–	–	8.8	9.3	–	–
Phenanthrene	95.8	95.2	83.1	84.65	35.5	62.7
Conversion	4.2	4.8	16.9	15.35	64.5	40.0

There are isomerization reactions along with the hydrogenation reactions as a result of the polyaromatic hydrocarbon processing in the presence of ferrosphere and Fe_2O_3/SiO_2 on the ferrosphere as catalytic additives: 9,10-dihydrophenanthrene isomerized into linear 9,10-dihydroanthracene. Angular-linear isomerization of 9,10-dihydrophenanthrene into 9,10-dihydroanthracene and further dehydrogenation of 9,10-dihydroanthracene with the formation of anthracene were shown in the work [5].

Experimental results of hydriding and hydrogenolysis reactions of polyaromatic hydrocarbon hydrogenation process are presented in Figure 4.

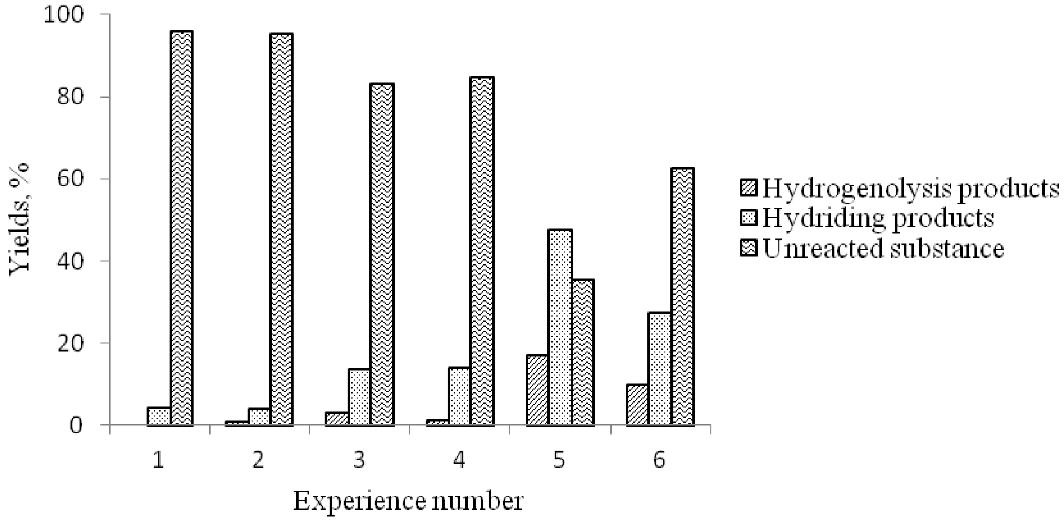

Figure 4. The yield of the hydrogenolysis and hydriding products of phenanthrene hydrogenation (experience numbers taken from Table)

It has been established that the yield of hydrogenation products of phenanthrene is 64.5 % in the presence of NiO/SiO_2 covered the ferrosphere, in contrast to the using the ferrosphere as catalytic additive, where the yield of hydrogenation products is 4.8 %. This fact may indicate a synergistic effect.

Conclusions

So the synergistic effect of binary nanocatalysts in the process of phenanthrene hydrogenation was revealed. The results indicated high activity of the catalytic additive NiO/SiO_2 covered the ferrosphere. The high degree of phenanthrene conversion is observed on the hydrogenation in the presence nickel and iron catalytic additives on the ferrosphere. An efficiency range of the studied catalytic additives was obtained on the basis of products yield data: NiO/SiO_2 on the ferrosphere > Fe_2O_3/SiO_2 on the ferrosphere > NiO/SiO_2 > > Fe_2O_3/SiO_2 > ferrosphere.

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Каталитикалық жүйелердің фенантрен гидрогенизациясына әсері

Мақалада сутегі доноры ретінде этанолдың қатысуымен фенантренді гидрогенизациялау үрдісінде синтезделген каталитикалық қоспалардың тиімділігі көрсетілген. Каталитикалық қоспалар ретінде ферросфера, ферросфера бетіне қондырылған NiO/SiO_2 және ферросфера бетіне қондырылған Fe_2O_3/SiO_2 қолданылды. Ферросфера Қарағанды ЖЭО-ның энергетикалық күлдерінен алынған. Ферросфера бетіне қондырылған NiO/SiO_2 және Fe_2O_3/SiO_2 каталитикалық қоспалары «дымқыл араластыру» әдісімен алынды. Ферросфераның және ферросфера бетіндегі NiO/SiO_2 және Fe_2O_3/SiO_2 нанокаталитикалық қоспаларының фазалық құрамы, бетінің морфологиясы, орташа өлшемі және таралуы анықталған. Реакция өнімдерінің құрамы *5975C* масс-спектрометриялық детекторы бар *Agilent Technologies 7890A* газды хроматографында хромато-масс-спектрометрия әдісімен зерттелді. *NIST 98* масс-спектрлік деректер базасын қолдану арқылы заттарға сәйкестендірілу жүргізілді. Ферросфераға қондырылған NiO/SiO_2 және Fe_2O_3/SiO_2 нанокаталитикалық қоспалардың синергетикалық әсері анықталды. Фенантрен конверсиясының жоғары дәрежесі ферросферадағы никель мен темірдің каталитикалық қоспаларының қатысуымен гидрогенизациясы кезінде байқалады. Фенантрен гидрогенизациясы нәтижесі бойынша каталитикалық қоспалардың тиімділік қатары анықталды: ферросферадағы NiO/SiO_2 > ферросферадағы Fe_2O_3/SiO_2 > NiO/SiO_2 > Fe_2O_3/SiO_2 > ферросфера.

Кілт сөздер: полиароматты көмірсутектер, фенантрен, гидрогенизация, каталитикалық жүйелер, ферросфера, золь-гель әдісі, «дымқыл араластыру» әдісі, көмір.

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Влияние каталитических систем на гидрогенизацию фенантрена

В статье показана эффективность синтезированных каталитических добавок в процессе гидрогенизации фенантрена в присутствии этанола в качестве донора водорода. В роли каталитических добавок выступали ферросфера, NiO/SiO_2 на поверхности ферросферы и Fe_2O_3/SiO_2 на поверхности ферросферы. Ферросферу извлекли из энергетической золы Карагандинской ТЭЦ. NiO/SiO_2 и Fe_2O_3/SiO_2 на ферросферах получили методом «мокрого смешения». Определены фазовый состав, морфология поверхности, средний размер и распределение частиц ферросфер и нанокаталитических добавок NiO/SiO_2 и Fe_2O_3/SiO_2 на ферросфере. Состав продуктов реакции выявили методом хромато-масс-спектрометрии на газовом хроматографе *Agilent Technologies 7890A* с масс-спектрометрическим детектором *5975C*. Идентификацию веществ проводили с использованием масс-спектральной базы данных *NIST 98*. Было установлено синергетическое действие нанокаталитических добавок NiO/SiO_2 и Fe_2O_3/SiO_2 на ферросфере. Высокая степень конверсии фенантрена наблюдалась при гидрогенизации в присутствии каталитических добавок никеля и железа на ферросфере. По результатам гидрогенизации фенантрена построен ряд эффективности каталитических добавок: NiO/SiO_2 на ферросфере > Fe_2O_3/SiO_2 на ферросфере > NiO/SiO_2 > Fe_2O_3/SiO_2 > ферросфера.

Ключевые слова: полиароматические углеводороды, фенантрен, гидрогенизация, каталитические системы, ферросфера, золь-гель метод, метод «мокрого смешения», уголь.

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