Проаналізовано поведінку цеолітвмісного каталізатора для каталітичного крекінгу вакуумного газойлю по технології аерозольного нанокаталізу. Обґрунтовано доцільність впровадження процесу. Вивчено вплив механохімічної активації на активний стан цеолітвмісного каталізатора тип Y. Розглянуті основні параметри каталітичного крекінгу за традиційної технології та технології аерозольного нанокаталізу. Показана доцільність розробки дослідно-промислової установки за технологією аерозольного нанокаталізу

Ключові слова: каталітичний крекінг, вакуумний газойль, аерозольний нанокаталіз, віброзрідження, бензинова і дизельна фракція

Проанализировано поведение цеолитсодержащего катализатора для каталитического крекинга вакуумного газойля по технологии аэрозольного нанокатализа. Обоснована целесообразность внедрения процесса. Изучено влияние механохимической активации на активное состояние цеолитсодержащего катализатора тип Y. Рассмотрены основные параметры протекания каталитического крекинга по традиционной технологии и технологии аэрозольного нанокатализа. Показана целесообразность разработки опытно-промышленной установки по технологии аэрозольного нанокатализа

Ключевые слова: каталитический крекинг, вакуумный газойль, аэрозольный нанокатализ, виброожижение, бензиновая и дизельная фракция

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STUDY OF KINETIC PARAMETERS FOR THE CATALYTIC CRACKING PROCESS IN Y TYPE AEROSOL CATALYST

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1. Introduction

The catalytic cracking of vacuum gas oil is the most common process of secondary processing of oil. Its task is to obtain high-quality gasoline with an octane number of 90–92 by the research method. It is known that the basic products of catalytic cracking is the diesel fraction and a gas fraction, this is mostly butane-butylene fraction. The existing plants for catalytic cracking are the suppliers of raw material for the chemical industry. Light gas oils of catalytic cracking are the material for the carbon black raw material and naphthalene; heavy gas oil can serve as raw material for the production of high-quality coke. Industrial catalytic cracking has been successfully developed with the use of aluminosilicate and zeolite catalysts. Most studies into catalytic cracking led to conclusions that the synthetic zeolites of types X and Y could become optimal for the process. They are the analogs of natural alumosilicates – faujasite. Synthetic zeolites have a specific ratio SiO_2:Al_2O_3 and a pore size within the limits of 0.8–1.3 nm. In this case, volume of the inner pores of catalysts exceeds 50 % of the total volume of particles [1].

Enterprises are oriented to purchasing foreign catalytic processes of petroleum processing. The implementation of petroleum processing using the natural catalysts might contribute to better competitiveness of domestic refineries in the world market. We shall consider this task by employing a technology of aerosol nanocatalysis.

2. Literature review and problem statement

It is widely known that zeolite is an additive in the composition of the aluminosilicate catalyst of cracking. It allows increasing activity, selectivity, adsorptivity and thermostability of structure. However, the stability of these catalysts at thermal and thermo steaming treatment changes in line with the stability of zeolite [2].

The Omsk refinery (Russia) operates catalytic cracking plants, which employ a series of catalysts – microspherical zeolite catalyst. The studies that started in 2004 have demonstrated the effectiveness of catalysts based on the ultra-stable zeolite of a series "Lux". These catalysts are prepared separately and they have complex composition. The following components are included into its composition: stabilized zeolite of the type Y in form HREE (REE are the rare-earth elements), amorphous dispersed alumosilicate and the aluminum-containing component, which consists of reprecipitated aluminum hydroxide and suspension of bentonitic clay (montmorillonite) [3].

Scientists at the Institute of Problems of Hydrocarbons Processing of the Siberian branch of the Russian Academy of Sciences (IPHP SB RAS) have developed a nomenclature of the bizeolite catalysts of cracking, which make it possible to increase the yield of olefins C_2–C_4. Activity of bizeolite catalysts depends on many constituents. In particular, the propertis of zeolites Y and ZSM-5 in the structure of a catalyst; semisynthetic matrix that employs natural bentonitic clay; the ratio of proton and proton-free acidic centers [4].

In the industrial installations, the catalytic cracking of vacuum gas oil is carried out at a temperature of 450–550 °C when only the zeolite-containing aluminosilicate catalysts with rare-earth metals are used [1].

The beginning of the XXIth century – the century of nanotechnologies – saw a rise in nanocatalysts with granules or crystallites the size within the range of nanometers [5, 6]. This trend has also captured petroleum processing. When examining the properties of nanoparticles, their advantage over microparticles and particles the size of a millimeter becomes obvious [7].

It is a well-known fact that the catalysts containing zeolite need to be regenerated. Because of their high activity, a zeolite filler is clogged with coke first of all, followed by the aluminosilicate matrix [8, 9].

An alternative to the industrial catalysts of catalytic cracking is, possibly, the aerosol catalysts, used in the new promising technology of aerosol nanocatalysis (AnC) [10, 11]. We shall verify this on the zeolite-containing catalyst of type Y. Activity of a catalyst is the basic factor when studying the kinetics of cracking process in the heterogeneous catalysis. It also depends on the quantity of active particles in the used catalyst.

3 The aim and tasks of research

The aim of present research is to study kinetics of the process and the behavior of active nanoparticles in the implementation of catalytic cracking of vacuum gas oil on the zeolite-containing catalyst of type Y.

To accomplish the set aim, the following tasks are to be solved:

– to examine chemical transformations in the process of cracking on the zeolite-containing catalyst of type Y under conditions of AnC technology;

– to study kinetics of the process considering the activity of particles of the zeolite-containing catalyst of type Y.

4. Materials and methods for examining the process of cracking

Schematic diagram of the laboratory installation for catalytic cracking under conditions of AnC is rather simple and is described in detail in [12].

Vacuum gas oil is a source material. This is a product of the preliminary distillation of oil, which is obtained when distilling off fuel oil under vacuum and is used either for the production of oils or for the processes of cracking.

The laboratory installation consists of three major parts: a feed unit of vacuum gas oil, reactor block and a unit for separating the products of cracking. The feed unit is an injector. Vacuum gas oil enters the reactor directly. Reactor is a cylindrical apparatus, which contains a catalytic system. It consists of the dispersive material and particles of the catalyst, and is in constant motion. The products of cracking from the reactor enter the separation block, which consists of a refrigerator-condenser, a tank for liquid products of reaction and a gas fraction capacitance. A gas fraction is analyzed using a chromatograph; and the condensed liquid one is subjected to fractionation.

5. Results of examining the process of cracking

Results of experimental studies on the zeolite-containing catalyst of type Y (a sample of this catalyst is provided by specialists from the Institute of Bio-organic Chemistry and Petroleum Chemistry of the Ukrainian Academy of Sciences) were obtained in the range of temperatures 450–550 °C and oscillation frequency 4–7.5 Hz [12]. Composition of the received reaction products is shown in Fig. 1–3.

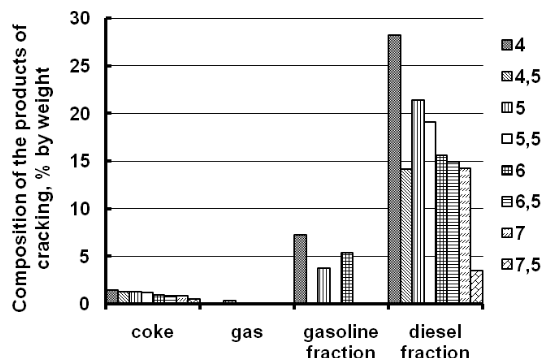

Fig. 1. Composition of products of the catalytic cracking reaction in the aerosol catalyst of type Y at temperature 450 °C and different reaction oscillation frequency

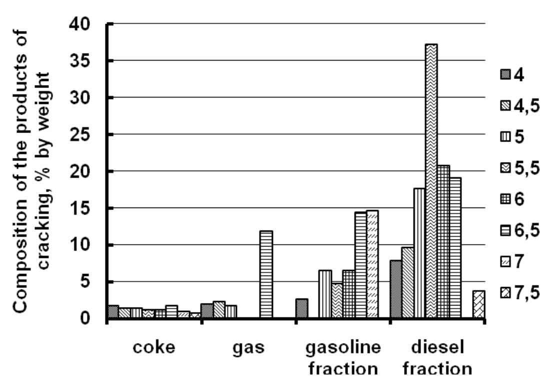

Fig. 2. Composition of products of the catalytic cracking reaction in the aerosol catalyst of type Y at temperature 500 °C and different reaction oscillation frequency

Under industrial conditions, the catalytic cracking of vacuum gas oil is carried out in the installation G-43-107M/1 at temperature 525 °C on the catalyst Nexus-345p. In this case, the reaction products, given in Table 1, are obtained [13, 14]:

Table 1 shows that the gasoline fraction predominates in the reaction products; however, the catalyst is rapidly clogged with coke and it needs to be regenerated. In the industry, there is an unprocessed residue – coke – from 5 to 5.5 % by weight, and a low speed of cracking relative to the weight of the catalyst.

Table 1

Products of cracking in the industrial installation G-43-107M/1 at temperature 525 °C

Composition of the products of cracking, % by weight				Conversion, % by weight	Selectivity, % by weight	Yield, % by weight	Cracking rate ($r_{industr}$)	
coke	gases	gasoline fraction	diesel fraction				kg/(m^3·h)	kg/(kg_{cat}·h)
5–5.5	17.8	50.2	15.5	86	74.9	65.7	205.3	0.444

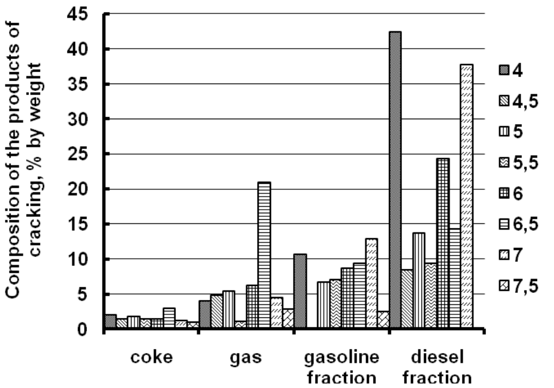

Fig. 3. Composition of products of the catalytic cracking reaction in the aerosol catalyst of type Y at temperature 550 °C and different reaction oscillation frequency

6. Discussion of results of catalytic cracking in the aerosol catalyst

As a result of the experiment, it was noted that the temperature of ignition of the catalyst of type Y under conditions of AnC technology with a vibrating bed reached 450 °C.

By analyzing experimental data [12], we shall examine an influence of control parameters of the process on the selectivity and rate of cracking.

Fig. 4 shows a dependence of selectivity on the bright petroleum products on the temperature at different oscillation frequencies. It is noted that it is possible to assume the temperature of 500 °C being optimal. In this case, the oscillation frequency is desirable to maintain at 5 and 5.5 Hz, which corresponds to high selectivity.

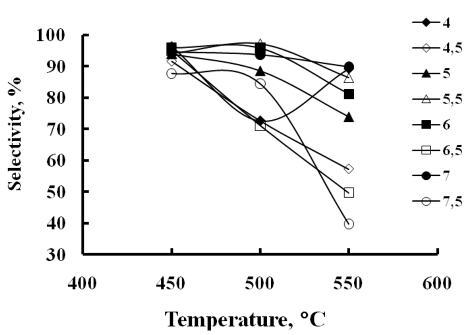

Fig. 4. Effect of temperature on the selectivity by the light petroleum products of the catalytic cracking process in the aerosol catalyst of type Y at oscillation frequency of the reactor from 4 to 7,5 Hz

Fig. 5 shows a dependence of the cracking process rate relative to the mass of the catalyst on the temperature at different oscillation frequencies. It folows hence that the optimal temperature is assumed to be 500 °C for the frequency of oscillations at 5.5 Hz, and 550 °C for the oscillation frequency at 4 and 7 Hz. This spread in the oscillation frequencies testifies to its oscillatory nature.

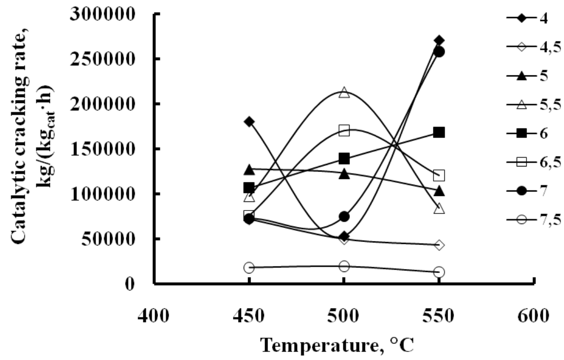

Fig. 5. Effect of temperature on the catalytic cracking rate by the mass of aerosol catalyst of type Y at oscillation frequency of the reactor from 4 to 7,5 Hz

However, high selectivity was observed at 500 °C and 5.5 Hz, therefore, these parameters can be assumed to be optimal for the zeolite-containing catalyst of type Y that operates by the aerosol nanocatalysis technology.

By applying the theory of particle collision, we shall calculate the number of active impacts that occur in the process of catalytic cracking of vacuum gas oil on the zeolite-containing catalyst of type Y. Effect of temperature of the process on the number of active impacts at different oscillation frequencies of the system are shown in Fig. 6, 7.

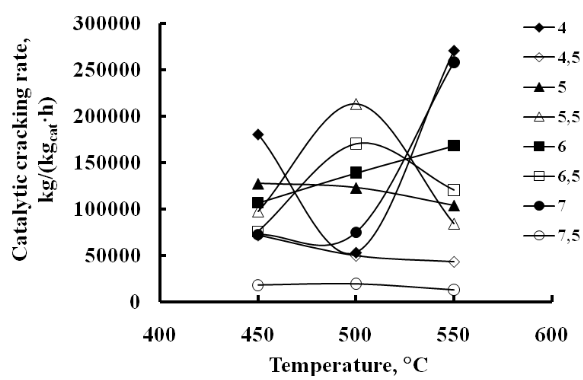

Fig. 6. Effect of temperature on the number of active impacts of particles of the catalyst of type Y at oscillation frequency of the reactor from 4 to 5.5 Hz

Upon considering the dependences in Fig. 6, 7, it is obvious that a maximum quantity of active impacts occurs at 550 °C at oscillation frequency 4 and 6.5 Hz. Let us note that the frequency of 4 Hz and 550 °C demonstrated the optimum regime both by the reaction rate and by the number of active impacts. Therefore, this regime can be duly considered as optimum. We shall remind that at 550 °C, the maximum reaction rate was observed also at 7 Hz, but the number of active impacts proved to be close to 6 Hz. However, the selectivity by the obtained light products (mainly, diesel fraction) of the frequency of 7 Hz appeared to be sufficient to exceed the frequency of 6 Hz. This proves a direct influence of the oscillation frequency on the activity of particles of the catalyst.

The oscillation frequency of 6.5 Hz and 550 °C contributed to the creation of a large number of active impacts of particles, which in turn led to the formation of the gas fraction of hydrocarbons and low selectivity by the light petroleum products.

By the indicator of octane number, experimental data [12] are at the level of 90 points according to the research method. This testifies to the fact that quality of the gasoline fraction [15, 16], obtained under conditions of AnC technology with a vibrating bed matches the standards of gasoline fraction of the catalytic cracking.

Next, we shall compare the existing catalysts of cracking with the catalyst of type Y on the aerosol nanocatalysis technology. Data are given in Table 2.

The zeolite-containing catalyst of type Y under the conditions of aerosol catalysis with vibrating bed is promising for the catalytic cracking of vacuum gas oil.

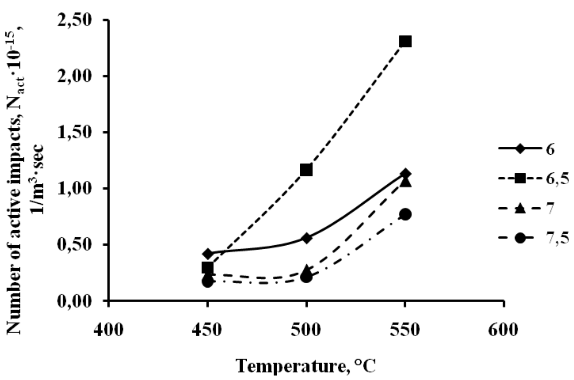

Fig. 7. Effect of temperature on the number of active impacts of particles of the catalyst of type Y at oscillation frequency of the reactor from 6 to 7.5 Hz

2. We demonstrated the possibility to control the process using the parameters of chemical transformation, in particular temperature and the oscillation frequency. It is noted that selectivity of the cracking process by the light petroleum products is larger than the industrial indicators by 22.3 % by weight. The optimum regime of cracking process by the AnC technology with vibrating bed is the temperature of 550 °C and the oscillation frequency of 4 Hz.

Table 2

Comparison of indicators of zeolite-aluminosilicate catalysts of the cracking process

Indicators	Catalyst, % by weight			
	traditional cracking [4]	HY/ZSM-5= =10/15 [4]	trade mark Lux-2 [3]	type Y in AnC
cracking temperature, °C	527	527	520–525	500–550
regenerator temperature, °C	N/A	N/A	670–690	not required
conversion, %	81.8	78.5	60	43
circulation frequency	N/A	N/A	6.5–7.0	continuously in situ
Catalyst loading, kg/$t_{raw\ mat}$	N/A	N/A	0.33	0.15
cracking products:				
Propane-Propylene Fraction	9.3	17.3	N/A	0–20
Butane-Butylene Fraction	16.5	21.2	N/A	
olefins C_2–C_4	13.7	31.0	4	
gasoline (boiling point – 216 °C)	46.6	30.7	50	15
light gas oil	12.7	14.5	13.7	37–43
heavy gas oil	5.5	7.0	10.5	
coke	6.4	6.0	5.6	0–3

We carried out an effectiveness analysis of the cracking process by the aerosol nanocatalysis technology, which:

– will make it possible to decrease the consumption of materials at the stage of separating the products based on the obtained selectivity;

– will increase the conversion in one run on the zeolite-containing catalyst of type Y, using a technological scheme with the recycle of raw material;

– will make it possible to control selectivity of the process with the help of temperature and oscillation frequency;

– could be proposed for the implementation either in parallel to the acting installations or as the independently acting unit for small-scale refineries.

7. Conclusions

1. We considered the process of catalytic cracking by the AnC technology. We used as a catalyst the zeolite-containing material of type Y in the vibrating state. It is established that the amount of catalyst can be reduced practically by 10^6 times compared with the industrial process.

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