The Oligomerization of C4-Hydrocarbons in the Microwave Field

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Abstract. The paper shows the possibility of oligomerization of olefinic hydrocarbons fraction C4 on the zeolite catalyst BAK-70 under the exposure of microwave radiation. The change of physical and chemical properties of the catalyst under the influence of microwave radiation is shown. The catalyst is slightly sintered, which affects the yield of reaction products. There is a decrease in the output of oligomerizate, but decreases the content of aromatic hydrocarbons of 68% and increases the selectivity of the process of 5.5%. In order to achieve better process parameters for microwave assisted oligomerization, it is necessary to improve the structure and physical properties of the catalyst, so that an efficient, industrially applicable process.

1. Introduction

At present in connection with expansion of production volume of non-aromatic high-octane components of gasoline, a great interest in the catalytic oligomerization of C4-hydrocarbons mixture is taken.

As the raw material for oligomerization are used light olefins obtained as a result of pyrolysis and crude oil cracking as well in the processing of natural gas using Fisher-Tropsh processing technology in which they are the main product [1].

The polymerization of olefins is an equilibrium reaction, opposite to their cracking:

\[ 2C_nH_{2n} \rightarrow C_{2n}H_{4n} \quad \Delta H^{\circ}_{298} = 63-105 \text{ kJ/mole} \]

During the oligomerization of olefins proceed also some side reactions, especially when the temperature is raising: upon that the paraffins, naphthenes (cyclanes), aromatic hydrocarbons, resinous condensation products are formed. Therefore olefin polymerization is to be carried out at the possible lowest temperature, at which, nevertheless, sufficient speed of the main process can be achieved [2].

To obtain low [molecular weight] polymers (oligomers), the elevated temperatures and acidic type catalysts are usually used. Among them, a heterogeneous contact developed by Ipatyev is of practical importance. It is prepared of kieselguhr (diatomaceous soil), asbestos or other materials impregnating them with phosphoric acid [3-7].

In recent years, the world new oligomerization technologies are introduced using, for example, a high-silica zeolite in Maxey refinery, Lithuania (the recycling of propane-propylene and butane-butylene fractions with obtaining of high-octane component of gasoline); in the Moscow oil refinery are built two installations for the processing of butane-butylene fraction; in the JSC "Synthes-
Kauchuk" Sterlitamak (Russia) is installed a plant for fraction C₄ oligomerization [8, 9]. All these processes are performed using the hydroficated Russian catalysts of the pentasils family. The use of heating by electromagnetic radiation of microwave range for the intensification of chemical reactions engages the attention of many scientists in recent decades. To date, in particular, the intensive research experience in the implementation of petrochemical processes in the microwave field [10-15] is gained, which allows not only the intensifying the process, but also the reducing of energy consumption, the improving of product yields and the process selectivity.

It should be noted that the oligomerization processes under the action of microwave radiation also attracted the attention of researchers. For example, in the study [16], the oligomerization of methane using nickel catalysts on alumina (aluminium oxide) under the exposure of microwave field was studied. The authors note the increase in the selectivity of the process which directly depends on the radiation frequency.

Currently in the industrial processes for olefins' oligomerization, the new generation catalysts based on zeolites of the pentasil family are applied [17-20]. The studying of the possibility of carrying out the process in the microwave field using industrial catalysts based on zeolites is of great scientific interest. The aim of this work is to study the catalytic oligomerization process of hydrocarbon fractions C₄ in the microwave field, in the presence of a catalyst based on zeolites of the pentasil family.

2. Methods
It was studied the catalyst BAK-70, modified by zinc and used in the process of oligomerization of C₄-hydrocarbons at JSC "Synthes-Kauchuk". The zeolite catalyst BAK-70 belongs to the family of pentasils which differ from other types of zeolites through their structure and frame composition with the predominance of silicon. The catalyst BAK-70 modified by zinc is characterized through the presence of two types of Brønsted acidic sites and three types of Lewis acidic sites.

The specific surface area of the catalyst was determined by the method based on measuring the pressure difference in the system before and after adsorption of air by the sample at liquid nitrogen temperature. The mechanical strength of the catalyst was determined by crushing.

The process was carried out in a flow reactor. The fused silica reactor was heated by microwave radiation at a frequency of 2.45 GHz, being placed in the resonator chamber of a household microwave oven. The contact gas sampled was analyzed chromatographically. Upon completion of the process, the catalyst was withdrawn and analyzed using the procedures specified above.

The characteristics of the initial heating, tried and tested in the manufacturing environment for 10.100 hours, in the laboratory conditions for 50 hours and in the microwave field for 50 hours is presented in the Table 1.

The oligomerization of olefins is carried out in a flow reactor. The heating of the quartz reactor is carried out under microwave radiation of microwave band of 2.45 GHz. The selected contact gas is analyzed by chromatographic method. At the end of the process, the catalyst is extracted and analyzed using the following methods.

The specific surface area of the catalyst is measured by the method based on measuring of pressure differences in the system before and after the adsorption of the air by the specimen at the temperature of liquid nitrogen.

The mechanical strength of the catalyst is measured by the crushing method.

3. Discussing the Results
As seen from the Table 1, the effect of microwave radiation does not cause a significant change in the chemical composition of the catalyst BAK-70. However, in the process of application of the catalyst in the microwave field, the increase in its mechanical strength (by 2.4 times) along with the decrease in specific surface area of the catalyst (by 20%) and increase in bulk density (by 20%) are observed. Such a change in the last two indicators indicates a slight sintering of the catalyst, which in turn affects the product yield (Table 2).
Table 1. Basic physical and chemical properties of the catalyst BAK-70 in the conventional environment and upon using the microwave radiation (2.45 GHz).

| Name of indicator | Virgin material | Used material | After 50 hours testing in the laboratory equipment | After 50 hours of testing in the microwave field |
|-------------------|----------------|---------------|--------------------------------|----------------------------------|
| 1. Mass fraction in the catalyst: | | | | |
| – silicon oxide | 68.38 | 65.32 | 68.02 | 68.74 |
| – zinc | 3.05 | 4.20 | 3.51 | 3.18 |
| – sodium oxide | 1.02 | 1.50 | 1.13 | 1.25 |
| – aluminium oxide | 21.50 | 20.07 | 21.20 | 21.36 |
| 2. Mass fraction of loss at roasting, 550 °С, % | | | | |
| | 4.53 | 1.61 | 8.03 | - |
| 3. Mass fraction of dust and crumbs, % | | | | |
| | 0.1 | 0.5 | 1.4 | 1.0 |
| 4. Bulk density, g/cm³ | | | | |
| | 0.74 | 0.673 | 0.733 | 0.844 |
| 5. Mechanical strength at crushing, kg/granule | | | | |
| | 7.07 | 8.89 | 4.88 | 11.43 |
| 6. Specific surface area, m²/g | | | | |
| | 262.79 | 265.4 | 77.25 | 61.89 |

Table 2. Oligomerization of olefins on the catalyst BAK-70 under various conditions.

| Composition | In the production environment T=280-400 °С P=1.2-1.3 MPa W=3,0±0.5 h⁻¹ | In the laboratory, at atm. pressure T=360 °С at W=500 h⁻¹ | In the microwave field, at atm. pressure T=360 °С W=500 h⁻¹ |
|-------------|--------------------------------|--------------------------------|--------------------------------|
| ΣС₅normal | 1.27 | 9.29 | 12.8 |
| ΣC₅ | 29.7 | 7.72 | 20.23 |
| ΣC₆ | 17.93 | 11.27 | 10.6 |
| ΣC₇ | 17.5 | 9.64 | 10.9 |
| Aromatics | 4.0 | 33.52 | 10.7 |
| ΣC₈ | 29.6 | 28.56 | 35.4 |
| Σ light hydrocarbons | | 11.97 | 3.3 |
| ΣC₄ | | 42.27 | 78.62 |
| The output to C₄-hydrocarbons passed through the reactor | 79.06 | 45.74 | 18.73 |
| The output to C₅H₁₀-hydrocarbons passed through the reactor | 77.5 | 58.65 | 23.14 |
| The output to decomposed C₄-hydrocarbons | 70.9 | 79.27 | 83.86 |

It should be also noted that in the electromagnetic field reduces the formation of coke on the catalyst BAK-70 by 12% compared with the conventional way of process implementation.

According to the results of compositional analysis of the obtained products 1) in the production reactor, 2) in the electrically heated laboratory reactor at atmospheric pressure, 3) in the microwave field (Table 2) it was observed that the yield of the target product – oligomerize – is lower upon the using the microwave radiation compared to conventional method, due to the changes in some key parameters of the catalyst. Nevertheless the advantages of the microwave method of oligomerization
can be attributed to the increase in selectivity of the catalyst (5.5%) by reducing the speed of the reactions of disproportionation of hydrocarbons and in low content of aromatic hydrocarbons (aromatics) in the reaction products (68%).

4. Conclusions
The data in Table 2 show that the use of microwave radiation in the oligomerization of the C4 hydrocarbon fractions has a positive effect. However, the industrial implementation of the process is constrained by the limited possibilities of using zeolites as a catalyst because of the negative impact of high energy field on their structure, which causes the sintering of particles on the pore surface and, consequently, a decrease in catalytic activity.

The use of thermally stable catalysts in the hydrocarbon oligomerization processes will make it possible to maintain the catalyst properties, such as specific surface area, porosity, phase composition, and amount of active sites available for the conversion, required for efficient performance of the process. Suppression of the thermally induced catalyst transformations that do not occur to so a large extent during conventional heating, will allow more accurate identification of the effects of microwave radiation on the process.

Thus, in order to achieve better process parameters for microwave assisted oligomerization, it is necessary to improve the structure and physical properties of the catalyst in terms of thermal stability and optimization of the microwave treatment time and intensity, so that an efficient, industrially applicable process for converting olefin components of refinery and natural gas into valuable chemical intermediates can be developed.

5. References
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