THE CHARACTERISTICS OF CATALYSTS IN THE CATALYTIC AROMATIZATION REACTION OF PROPANE- BUTANE FRACTIONS

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Abstract. To examine the catalytic aromatization reaction of propane-butane fraction (MoO₃)·(ZnO)ₓ·(ZrO₂)ₓ in the mesoporous catalyst, this experiment was conducted under the following optimal conditions: when 1.0 mass% Zr nanopowders were added to the mesoporous catalyst (MoO₃)·(ZnO)ₓ·(ZrO₂)ₓ containing the flow differential reactor, V_{kat} = 1.0 cm³, the size of catalyst granules 0.5-1.0 mm, the temperature 450-650°C, P = 0.1 MPa, volumetric rate of propane 600 h⁻¹. It was determined that both types of acid centers’ concentrations and strengths were increased.

Introduction. The most efficient way of recycling propane-butane fractions is recycled them chemically and obtain aromatic hydrocarbons. It is known that aromatic hydrocarbons are primary products in the main organic synthesis industry. At present, the aromatic hydrocarbons are processed from recycling liquid products of oil, catalytic reforming and pyrolysis processes. Changing in the petrochemical complex raw material base are leading to a shortage of these hydrocarbons Therefore, searching for alternative energy sources to replace petroleum products for obtaining aromatic hydrocarbons remains an important task. Nowadays the main alternative sources are natural gas and petroleum gases are aromatic compounds.
A number of scientists have been conducting research on the catalytic synthesis of aromatic hydrocarbons [1-5]. In those reactions, high-silicon zeolites containing Zn, Zr and Pt have shown high catalytic activity [2,5,6]. The disadvantage of the catalytic interaction of these systems is that the formation of a certain amount of methane and high molecular weight aromatic hydrocarbons (naphthalene, alkyl naphthalene) are produced as a result of reaction. In this situation the stable shelf life of catalysts is reduced. Majority of researches of obtaining aromatic hydrocarbons from natural gas and petroleum gases take place in one step.

Zeolite catalysts, especially those modified with metals and metal oxides, are widely used in petroleum refining and petro chemistry [7-11]. The traditional method of obtaining such catalytic systems is to absorb the metal salts into the carrier and gradually decompose the introduced precursor [12-19]. However, in this method, the modifiers are not equally distributed over the entire volume of the carrier, but modifiers are localized on the surface of the zeolite crystals. Thus the performance of the catalyst deteriorates.

Also the acidity centers of the catalyst play an important role in the catalytic activity of the catalytic system. Hydrothermal synthesis is important in ensuring the isomorphic exchange of aluminum or silicon in the zeolite crystal lattice for modifiers. The acidity and textural characteristics of the catalyst are improved due to isomorphic exchange in hydrothermal synthesis. This article presents the results of the study of the kinetic laws of the catalytic aromatization reaction of propane on the catalyst (MoO$_3$)$_x$∙(ZnO)$_y$∙(ZrO$_2$)$_z$. High silicon zeolite from kaolin was used as a carrier, which was taken from Pakhtachi district (the Republic of Uzbekistan).

The purpose of this research work is to obtain a catalytic catalyst containing (MoO$_3$)∙(ZnO)$_y$∙(ZrO$_2$)$_z$ and to study its physicochemical and catalytic properties in the aromatization reaction of propane.

**Experimental.** The catalytic aromatization reaction of propane was studied in a flow differential reactor under the following optimal conditions. $V_{\text{kat}}=1.0$ cm$^3$ the size of the catalyst granules is 0.5-1.0 mm. Temperature 450-650ºC, $P = 0.1$ MPa, volumetric rate of propane 600 hour$^{-1}$.

The reaction products were analyzed GC (Svet 100M, Russia).

Zinc and zirconium were introduced into carrier during the hydrothermal synthesis phase. Hexamethylene diamine and citric acid were used as structural agents. Aqueous solutions of zirconyl nitrate ZrO(NO$_3$)$_2$ and Zn(NO$_3$)$_2$ were used as a source of zirconium and zinc oxides respectively. The synthesis of the catalyst (MoO$_3$)∙(ZnO)$_y$∙(ZrO$_2$)$_z$ was carried out in a steel autoclave and the temperature was 200-230 ºC. High resolution transmission electron microscopy images were obtained on JEM-2010 and JEM-2200FS electron microscopes (JEOL Ltd.) with a lattice resolution of 0.14 and 0.1 nm, respectively.

Energy dispersive X-ray (EDX) spectra and elemental analysis were obtained in a scanning mode on a JEM-2200FS dark-field instrument (HAADF-STEM) using a JED-2300T spectrometer. The XPS spectra were recorded on an ES300 photoelectron spectrometer (Kratos Analytic) in the mode of constant transmission energy of the photoelectron energy analyzer. High silicon zeolite (HSZ) derived from activated and enriched bentonite was used in this research work. It was synthesized as follows: mixing 30 g of bentonite in 300 ml of bidistilled water. The suspension was prepared and mixed slowly, at that time the particles of the minerals contained in the bentonite were separated into fractions.

The chemical composition of the sample was analyzed by an energy-dispersion spectrometer and radiographic method with a scanning electron microscope.
Results and discussion. It is known from the scientific literature that the catalytic properties of modified catalysts are directly related to their acidic properties. The acidity centers of zeolite catalysts are an important factor in determining their catalytic activity, the centers are divided into 2 types: weak acidic and strong acidic centers. Studies have shown that the acidity of the catalyst decreases as soon as the amount of zirconium in the catalyst increases which leads to a decrease in its catalytic activity. The results of the study of the acidic properties of the obtained catalysts are given in Table 1.

### Table 1

| Catalyst                      | $T_{\text{MAK}}$, °C | Concentration of acidic centers (mkmol/g) | $C_1$ | $C_2$ | $C_3$ |
|------------------------------|----------------------|------------------------------------------|-------|-------|-------|
| 5.0% Mo/HSZ                  |                      |                                          |       |       |       |
| 1,0% Zr-5.0% Mo/HSZ         |                      |                                          |       |       |       |
| 1.5% Zr-5.0% Mo/HSZ         |                      |                                          |       |       |       |
| 2.0% Zr-5.0% Mo/HSZ         |                      |                                          |       |       |       |
| $T_1$                        | 188                  | 330                                      | 198   | 528   |
| $T_2$                        | 390                  | 240                                      | 617   |       |
| 1,0% Zr-6.0% Mo/HSZ         |                      |                                          |       |       |       |
| 1.5% Zr-6.0% Mo/HSZ         |                      |                                          |       |       |       |
| 2.0% Zr-6.0% Mo/HSZ         |                      |                                          |       |       |       |
| $T_1$                        | 195                  | 377                                      | 210   | 565   |
| $T_2$                        | 398                  | 240                                      | 617   |       |
| 1.0% Zr-6.0% Mo/HSZ         |                      |                                          |       |       |       |
| 1.5% Zr-6.0% Mo/HSZ         |                      |                                          |       |       |       |
| 2.0% Zr-6.0% Mo/HSZ         |                      |                                          |       |       |       |
| $T_1$                        | 205                  | 355                                      | 210   | 565   |
| $T_2$                        | 410                  | 240                                      | 617   |       |
| All samples tested have 2 different types of acidity centers. When 1.0 mass% Zr nanopowders was added to 6.0 mass% Mo / HSZ catalysts, the reaction was indicated that both types of acid centers' concentrations and strength increased. For the sample of 1.0% Zr · 6.0% Mo / HSZ, the concentrations of weak acid centers are 377 mkmol/g and the concentrations of strong acid centers are 240 mkmol/g, the properties of the catalyst without Zr were corresponding 42 and 48 mkmol/g higher than the properties of the catalyst with Zr. As soon as the amount of zirconium in the catalyst increases, the concentrations of the acid centers of both types decrease. For example, when the content of zirconium in the Mo/HSZ catalyst increases by 2.0%, the concentrations of acid centers decrease by 120 mkmol/g. Thus, the results of the study of the acidic properties of Zr-modified catalysts to 6.0% Mo / HSZ show that with the addition of Zr to the 6.0% Mo / HSZ catalyst leads to a redistribution of the concentration and strength of the acid centers. As a result, the ratios of the acid centers change, which leads to a change in the acidic properties of the zeolite.

### Table 2

Composition of products of catalytic conversion of propane-butane fraction in zinc-molybdenum catalyst treated with zirconium nano powders

| $W, \, \text{c}^{-1}$ | $T_{\text{reaction}}, \, ^\circ\text{C}$ | $X, \%$ | $S_1, \%$ | $S_2, \%$ | $S_3, \%$ | $S_4, \%$ | $Y_{\text{Ap}}, \%$ |
|----------------------|------------------------------------------|---------|------------|------------|------------|------------|-------------------|
|                      | (MoO$_3$)$_2$·(ZnO)$_y$/HSZ               |         |            |            |            |            |                   |
| 800                  | 550                                      | 57      | 6.1        | 61.0       | 2.5        | 30.4       | 17.3              |
| 800                  | 600                                      | 57      | 6.1        | 61.0       | 2.5        | 30.4       | 17.3              |
| 800                  | 650                                      | 98      | 7.2        | 46.4       | 1.0        | 45.4       | 43.6              |
| 900                  | 650                                      | 97      | 7.7        | 40.1       | 1.6        | 50.6       | 49.0              |
| 1000                 | 650                                      | 95      | 8.0        | 33.0       | 2.3        | 56.7       | 53.9              |
| 1200                 | 650                                      | 93      | 2.5        | 28.2       | 3.2        | 60.1       | 55.9              |
|                      | (ZrO$_3$)$_2$·(MoO$_3$)$_y$·(ZnO)$_y$/HSZ|         |            |            |            |            |                   |
| 800                  | 550                                      | 73      | 6.6        | 47.4       | 1.7        | 44.3       | 32.3              |
| 800                  | 600                                      | 73      | 6.6        | 47.4       | 1.7        | 44.3       | 32.3              |
| 800                  | 650                                      | 98      | 8.3        | 26.3       | 0.9        | 64.5       | 63.2              |
| 900                  | 650                                      | 98      | 8.8        | 22.7       | 1.2        | 67.4       | 65.8              |
| 1000                 | 650                                      | 97      | 9.0        | 20.8       | 2.5        | 67.5       | 65.5              |
| 1200                 | 650                                      | 92      | 9.2        | 16.2       | 2.8        | 71.8       | 66.1              |
It is obvious from Table 2, the introduction of zinc into a zinc-molybdenum catalyst leads to an increase in the overall activity of the catalyst. The maximum amount of aromatic hydrocarbons is formed in the presence of a catalyst containing 1.0% Zr. The maximum yield and selectivity of formation of aromatic hydrocarbons in the presence of a catalyst containing 1.0% Zr was observed when the volumetric rate of the starting materials was 500 h⁻¹ and the temperature was 650°C and were 65.1% and 71.8%, respectively.

Figure 1 below shows the effect of temperature on propane conversion, yield and selectivity of aromatic hydrocarbons in the catalytic aromatization reaction of propane.

Fig. 1. Influence of temperature on propane conversion, yield and selectivity of aromatic hydrocarbons

As can be seen from Figure 1, the conversion of propane begins at 500 ºC to 600 ºC and above to form target products - aromatic hydrocarbons. With the increase in the temperature process, there is an increase in the degree of conversion of propane and the selectivity for the formation of aromatic hydrocarbons, when the reaction temperature is 600 ºC, it reaches 94% and 37% respectively. Similar temperature dependence of propane aromatization indicators are observed for other Zr containing zeolites carrier.

Conclusion. Thus, the catalytic aromatization reaction of the propane-butane fraction \((\text{MoO}_3)\cdot(\text{ZnO})_y(\text{ZrO}_2)_z\) was selected as a result of the process under the following optimal conditions: When 1.0 mass% Zr nanopowders are added to a mesocellular catalyst containing flow differential reactor, \(V_{\text{kat}} = 1.0 \text{ cm}^3\), size of catalyst granules 0.5-1.0 mm, temperature 450-650°C, \(P = 0.1 \text{ MPa}\), volumetric rate of propane 600 h⁻¹. It has been conformed to increase the concentrations and strength of both types of acid centers.

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