Non-oxidative methane conversion over Mo/ZSM-5 catalysts with mesoporous structure

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Abstract. Physicochemical and catalytic properties of 4.0% Mo/ZSM-5 catalysts manufactured on the basis of zeolites with a hierarchical pore system are investigated. The effect of the conditions of synthesis of zeolites with an additional mesoporous structure on their textural and acidic characteristics is studied. The structure and morphology of crystals of synthesized zeolites and catalysts produced from them are determined by the methods of X-ray diffraction analysis and high-resolution scanning transmission electron microscopy. It is shown that 4.0% Mo/ZSM-5 catalysts produced from zeolites with a mesoporous structure exhibit higher activity and stability in the course of methane dehydroaromatization.

1. Introduction
Rational use of natural and associated petroleum gases, the main component of which is methane, is of great importance for the production of valuable petrochemical products, as well as for solving environmental problems. It is known that Mo-containing ZSM-5 zeolites exhibit the highest activity and selectivity in the course of methane dehydroaromatization [1-3]. One of the disadvantages of these catalysts is the rapid loss of activity as a result of the carbonization of their active sites. The presence of a mesoporous structure in the zeolitic matrix improves the egress of aromatic compounds from the volume of the zeolite to the catalyst surface, which leads to an increase in its activity and stable operation in the course of methane dehydroaromatization [4].

The purpose of this work was to obtain Mo/ZSM-5 catalysts based on zeolites with a mesoporous structure and to study their physicochemical and catalytic properties in the reaction of methane dehydroaromatization.

2. Materials and methods
Zeolites with a mesoporous structure were manufactured by the method of hydrothermal synthesis from alkaline alumina silica gels with a molar ratio 15Na₂O:5.4R:Al₂O₃:40SiO₂:2200H₂O, where R is hexamethylenediamine. At the stage of synthesis, P354 grade carbon black powder (produced by the Center for New Chemical Technologies of the Federal Research Center Boreskov Institute for Catalysis, Omsk), whose content varied from 0.5 up to 5.0 wt% was added to the reaction mixture. Carbon black has the following characteristics: the specific surface area is 110 m²/g, the pore volume is 0.034 cm³/g; elemental composition: C – 96.4%, O – 2.5%, S – 0.5%, N and H per 0.3%. The carbon particles, being compositionally homogeneous, have a 30-60 nm globular shape.
The resulted suspension was stirred for 0.5 h, placed into an autoclave, and synthezised at 170-175 °C for 4 days. The solid phase obtained was filtered using a Buchner funnel, washed with distilled water to pH = 6-7, and dried at 100 °C in a drying cabinet for 4 hours. To remove the template and carbon black, the synthesized zeolite was calcined in air at 550 °C for 6 hours. To convert the zeolite from the sodium to the ammonium form, decationization with a 25% aqueous solution of NH₄Cl at a temperature of 90 °C for 2 hours was carried out. The samples prepared were referenced as follows: K1 was the initial zeolite obtained without carbon; K2, K3, K4, K5, and K6 were zeolites obtained by adding carbon black in the amount of 0.5; 1.0; 2.0; 3.5 and 5.0 wt%, respectively.

The quality of the synthesized zeolites was monitored using IR spectroscopy and X-ray diffraction. The IR spectra of the samples were recorded using a Nicolet 5700 IR Fourier spectrometer within the range 2000-400 cm⁻¹. The degree of crystallinity of zeolites was determined by IR spectroscopy according to the method described in [5]. X-ray diffraction analysis was performed using a Bruker DISCOVERD8 diffractometer in the angle range 2θ = 10-70 degrees. The parameters of the porous structure and the determination of the specific surface of the samples were evaluated using a TriStar 3020 automated gas-adsorption analyzer (Micromeritics, USA). The specific surface was calculated from the isotherm of low-temperature sorption of nitrogen vapors (BET method). Electron-microscopic studies of the morphology of zeolite crystals were performed using an LEO-1420 electron scanning microscope. The acidic properties of the samples were investigated by the method of temperature-programmed desorption of ammonia, which allowed to determine the strength and concentration of acid sites. The 4.0% Mo/ZSM-5 catalysts were prepared by dry mechanical mixing of zeolites in the NH₄ form, synthesized with various amounts of technical carbon, and nano-sized Mo powder obtained by the method of electrical explosion of a conductor in argon. The average size of Mo particles was 70-110 nm. The resulted mixtures were calcined in a muffle furnace at 550 °C for 4 hours.

The process of non-oxidative methane conversion (purity level of 99.99% by volume) was carried out in a flow fixed bed reactor at a temperature of 750 °C, atmospheric pressure and a volumetric flow rate of methane 1000 h⁻¹. The volume of the catalyst loaded into the quartz reactor was 1.0 cm³ and the size of its granules was 0.5-1.0 mm. The reaction products were analyzed by GLC using a Chromatoc-Crystal 5000.2 chromatograph every 40 min of catalyst operation. To assess the catalytic activity of the samples, the degree of methane conversion and the yield in the resulted reaction products were determined.

3. Results and discussion

Figure 1 shows the IR spectra and X-ray diffraction patterns of zeolites synthesized with the addition of carbon black in the amount of 1.0 and 3.5% and without it. It is evident from the presented data that the use of carbon black during the synthesis of zeolite has no effect on its structural characteristics. All the zeolites obtained belong to the ZSM-5 structural type, and their crystallinity is 100%.

Figure 2 shows electron microscopic images of zeolite synthesized without the use of carbon black (Figure 2a) and with carbon black additives (Figure 2b and 2c). The particles of the initial zeolite K1 are quite homogeneous in their composition. They have the appearance of polycrystalline spheroids with sizes from 6 to 8 microns. A looser compound (junction) of crystals in polycrystalline spheroids is observed on the micrograph of zeolite synthesized with the addition of 1.0% carbon, after calcination at 550 °C, while their sizes vary over a wider range from 4 to 8 μm (Figure 2b). As the amount of carbon increases to 3.5% during the synthesis of zeolite and the subsequent calcination, the zeolite crystals become even more heterogeneous (Figure 2c). The size of polycrystalline spheroids varies from 4 to 9 microns. In addition, the formation of larger particles sized up to 12 microns, whose morphology differs from the structure of particles of the initial K1 zeolite.
Figure 1. IR-spectra (a) and XRD patterns (b) of zeolites synthesized without the use of carbon black and with the use of various amounts of carbon: 1 – 0%, 2 – 1.0%, 3 – 3.5%.

Figure 2. Electron micrographs of zeolites synthesized without the use of carbon black (a) and with the use of carbon black amounts of 1.0% (b) and 3.5% (c).

Values of specific surface area, area and volume of micropores, as well as the total pore volume of samples obtained on the basis of zeolites synthesized with different contents of carbon black, are presented in Table 1. The largest specific surface area 398 \( m^2/g \) is observed for the initial zeolite K1. With an increase in the concentration of carbon black used in the synthesis of zeolite from 0.5 to 5.0%, a decrease in the specific surface area and an increase in the volume of mesopores from 0.02 to 0.08 \( cm^3/g \) are observed. At the same time, the volume of micropores slightly varies from 0.15 to 0.18 \( cm^3/g \).

Table 1. Surface properties of zeolites.

| Sample | \( S_{BET} (m^2/g) \) | \( S_{micro} (m^2/g) \) | \( V_{total} (cm^3/g) \) | \( V_{micro} (cm^3/g) \) | \( V_{meso} (cm^3/g) \) |
|--------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| K1     | 398                   | 322                    | 0.20                   | 0.18                   | 0.02                   |
| K3     | 379                   | 301                    | 0.21                   | 0.15                   | 0.06                   |
| K4     | 378                   | 299                    | 0.22                   | 0.16                   | 0.06                   |
| K5     | 375                   | 290                    | 0.24                   | 0.17                   | 0.07                   |
| K6     | 373                   | 279                    | 0.26                   | 0.18                   | 0.08                   |

Figure 3 shows the dependences of the pore distribution on the size in ZSM-5 zeolites with micro- and mesoporous structures.
Figure 3. Pore size distribution in ZSM-5 zeolites with micro and mesoporous structure.

It can be seen that the zeolite ZSM-5 with a microporous structure has practically no peak in the range of 3–4 nm, only a small shoulder is observed. When carbon black is added at the stage of zeolite synthesis, mesopores are formed with an average size 3–4 nm, as evidenced by the appearance of a characteristic peak in this region.

The study of the acidic properties of the initial zeolite K1 and zeolites with a mesoporous structure showed the presence of two peaks with clearly pronounced temperature maxima on the thermal desorption curves. This indicating suggests the presence of two types of acid sites. It is evident from the data in Table 2, that the strength and concentration of the acid sites of the initial zeolite K1 and the mesoporous zeolite K3 synthesized with the addition of 1.0% carbon black are close.

Table 2. Acidic characteristics of zeolites.

| Sample | Temperature, °C | Concentration, µmol/g |
|--------|-----------------|-----------------------|
|        | T_L | T_H | C_L | C_H | C_X |
| K1     | 235 | 480 | 753 | 388 | 1141 |
| K3     | 235 | 475 | 767 | 389 | 1156 |
| K4     | 230 | 470 | 617 | 364 | 981  |
| K5     | 235 | 470 | 643 | 368 | 1011 |
| K6     | 245 | 475 | 874 | 372 | 1246 |

Note. T_L, T_H – temperatures of maximum low- and high-temperature peaks on thermodesorption curves; C_L, C_H and C_X – concentrations of weak and strong acid sites and their sum, respectively.

An increase in carbon content in the reaction gel from 2.0 to 3.5% results in the formation of mesoporous zeolites K4 and K5 with a lower concentration of weak and strong acid sites. For the sample K6, obtained using 5.0% carbon, a significant increase in the number of low-temperature acid sites (up to 874 µmol/g) and their strength is observed, while the concentration of strong acid centers varies slightly and the total content of acid centers reaches 1246 µmol/g. Thus, the acidic properties of zeolites and their textural and structural characteristics depend on the amount of carbon black used in the synthesis of zeolites.

The test results of 4.0% Mo/ZSM-5 catalysts manufactured on the basis of zeolites synthesized with the addition of different amounts of carbon in the course of non-oxidative conversion of methane to aromatic hydrocarbons are shown in Figure 4a. It can be seen that in all cases the use of carbon in the synthesis of zeolites results in an increase in the activity of the catalysts in comparison with the zeolite K1 obtained without using carbon. The catalytic properties of zeolite catalysts depend on the
amount of carbon used in the synthesis of zeolites. Hence, the mesoporous Mo/K3 catalyst exhibits the highest activity and stability.

![Graphs showing methane conversion, ethane and ethylene yield, benzene and naphthalene yield over time for Mo/K1 to Mo/K6 catalysts.](image)

**Figure 4.** Time dependence of methane conversion (a), total yield of ethane and ethylene (b), and yield of benzene (c) and naphthalene (d) formed due to the use of Mo/K1, Mo/K2, Mo/K3, Mo/K4, Mo/K5; and Mo/K6 catalysts.

An increase in the concentration of carbon black in the reaction alumina silica gel used to synthesize the zeolite up to 3.5% reduces the activity of the Mo-containing zeolite catalyst, but its activity is higher than that of the Mo/K1 catalyst during the first 180 min of reaction. Then the methane conversion approaches to the conversion rates for the Mo/K1 catalyst and remains the same. The increase in the concentration of carbon added in the course of zeolite synthesis to 5.0% results in a noticeable decrease in the activity of the zeolite catalyst.

Analysis of the gaseous products formed in the course of methane conversion shows that they consist mainly of ethane and ethylene, whose yields increase as the process runs, reaching maximum values in the reaction time interval 220-300 minutes (Figure 4b). Then the formation of ethane and ethylene is reduced as a result of the carbonization of the active sites of Mo-containing zeolite catalysts. It is obvious that a higher formation of gaseous products is characteristic of mesoporous catalysts, which, apparently, is due to their higher cracking activity in this process. The highest amount of gaseous products is formed on the catalyst Mo/K6, obtained on the basis of a zeolite synthesized with the highest addition of carbon black and containing the maximum number of acid sites. The liquid products of methane conversion contain aromatic hydrocarbons, mainly benzene and naphthalene (Figure 4c and 4d). The highest amount of benzene is formed in the first 20 minutes of the reaction over all the catalysts under study, after which its yield gradually decreases. The increase in
the concentration of carbon black used during the synthesis of zeolites results in an increase in the formation of benzene over the catalysts obtained on their basis. The yield in naphthalene reaches its maximum value in 20-60 min of the reaction, then its formation decreases (Figure 4d). The sharpest decrease in naphthalene yield is observed for the Mo/K6 catalyst.

4. Conclusion
Thus, high silica ZSM-5 zeolites with a hierarchical pore system have been synthesized using carbon black. Investigation of their physicochemical properties has shown that the resulted catalysts differ significantly in textural, structural, and acidic characteristics, which leads to differences in their catalytic properties. The highest activity and stability in the course of non-oxidative conversion of methane into aromatic hydrocarbons have been exhibited by a mesoporous catalyst obtained on the basis of a zeolite, synthesized with carbon used in an amount of 1.0%.

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