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Preparation of Mo/ZSM-5 Catalysts for Non-Oxidative Methane Conversion over Zeolites with Micro- and Mesoporous Structure and Investigation of Their Properties

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Abstract

The effect of the nature of the carbon template used in the synthesis of zeolites with a mesoporous pore system on their physicochemical properties is studied. It was revealed with the help of IR spectroscopy and X-ray phase analysis that the nature of the carbon material used in the synthesis of zeolites does not affect their crystallinity, which is 100 % for all zeolites. Investigation of the textural characteristics of the samples showed that the addition of carbon material to the reaction mixture during the synthesis of zeolite results in a decrease in the specific surface area and an increase in the volume of mesopores. The volume of micropores changes only slightly. The addition of carbon at the stage of zeolite synthesis leads to the formation of mesopores, the sizes of which are 3.5–20.0 nm in the case of the use of carbon black, and 3.3–8.6 nm in the case of nanoglobular carbon. The catalytic properties of Mo/ZSM-5 catalysts prepared on the basis of synthesised zeolites are studied, and the dependence of their activity and stability during the non-oxidative conversion of methane on the physicochemical properties of the zeolites used is shown. The formation of a mesoporous structure in the zeolite promotes a more uniform and dense distribution of Mo clusters with sizes not exceeding 1 nm in zeolite channels. It is shown that 4.0 % Mo/ZSM-5 catalysts based on zeolites with a mesoporous structure exhibit higher activity and stability in the non-oxidative conversion of methane to aromatic hydrocarbons than the catalysts based on zeolites with a microporous structure. The highest methane conversion is achieved over a 4.0 % Mo/ZSM-5 catalyst based on zeolite synthesised with carbon black.

Keywords: ZSM-5 zeolite, molybdenum nanopowder, carbon, mesopores, acidity, activity, methane dehydroaromatization

INTRODUCTION

At present, the problem of the reasonable use of gaseous hydrocarbons for obtaining valuable products of petroleum chemistry and organic synthesis is urgent for solving the problems connected with ecology and environmental protection. An efficient method of processing natural gas and associated petroleum gas, with methane as the major component, is their transformation into aromatic hydrocarbons in the presence of bifunctional zeolite catalysts. The highest activity and stability in non-oxidative methane conversion into aromatic hydrocarbons is exhibited by the catalytic system Mo/ZSM-5 [1–3]. However, the narrow channels of zeolites hinder mass transfer processes, which results in rapid coke formation and a sharp decrease in catalyst activity. One of the ways to enhance the stability of Mo/ZSM-5 catalysts is the creation of a secondary mesoporous structure in the zeolite [4]. The presence of mesopores 2–50 nm in diameter promotes a uniform distribution of molybdenum over zeolite volume and simplifies the diffusion of the formed aromatic compounds to catalyst surface area thus increasing its activity and stability.

In the present work, we present the results of the investigation into the effect of the nature of carbon template using for zeolite synthesis on the physicochemical and catalytic properties of the synthesized Mo/ZSM-5 system in non-oxidative methane conversion into aromatic hydrocarbons.

EXPERIMENTAL

Zeolites with micro- and mesoporous structure were obtained by means of hydrothermal synthesis from the alkaline aluminosilicic gels with the composition $15Na_2O \cdot 5.4R \cdot Al_2O_3 \cdot 40SiO_2 \cdot 2209H_2O \cdot 1C$, where R is hexamethylenediamine. Liquid glass (19.0 % SiO_2, 7.2 % Na_2O) was used as a source of silicon for zeolite synthesis, while technical-grade carbon (C_t) and nano-globular carbon (C_n) were used as carbon templates. Technical carbon of P354 grade was manufactured at the Centre for New Chemical Technologies of the Federal Research Centre Institute of Catalysis SB RAS (Omsk). This material possesses the following characteristics: specific surface area 110 m^2/g, pore volume 0.034 cm^3/g; elemental composition, %: C 96.4, O 2.5 , S 0.5, N 0.3, H 0.3. Coal particles are uniform in their composition and have a globular shape, 30–60 nm in size. Technical carbon was activated preliminarily for 1 h by mixing in a 1 M NaOH solution at room temperature, and then dried at 550 °C. Nanoglobular carbon was obtained at M. A. Lavrentyev Institute of Hydrodynamics SB RAS (Novosibirsk) by means of pulsed gas detonation synthesis; its specific surface area is not less than 250 m^2/g, carbon particles are uniform in their composition and are 20–36 nm in size. Carbon templates were added into the reaction mixture in the amount of 1.0 mass %. The resulting suspension was mixed for 0.5 h and placed into the autoclave. The synthesis was carried out at a temperature of 170–175 °C for 4 days. Then the solid phase was separated by filtering with a Buchner funnel, washed with distilled water to pH 6–7, and dried at a temperature of 110 °C in the drying chamber for 4 h. To remove templates, the synthesized zeolites were annealed in the air at a temperature of 550 °C for 6 h. To transfer zeolite from sodium into ammonium form, decationation was carried out with a 25 % aqueous solution of NH_4Cl at a temperature of 90 °C for 2 h.

The quality of the synthesized zeolites was controlled with the help of IR spectroscopy and X-ray phase analysis (XRD). IR spectra were recorded using an Fourier transform IR spectrometer Nikolet 5700 (Thermo Electron Corporation, USA) within the range of 400–2000 cm^{-1}. X-ray phase analysis of zeolites was carried out with a D8 DISCOVER diffractometer (Bruker, Germany) within the angle range $2\theta = 10–70°$. The degree of crystallinity of the samples was determined according to the procedure described in [5].

The 4.0 % Mo/ZSM-5 catalysts were prepared by means of solid-phase mixing of zeolites in NH_4-form, synthesized in the presence of C_t or C_n, with nano-sized Mo powder obtained by means of electric explosion of the conductor in argon medium [6]. The average size of Mo particles was 70 nm. The resulting mixtures were annealed in a muffle furnace at a temperature of 550 °C for 4 h.

The parameters of the porous structure were evaluated and the specific surface area (S) of the samples was determined with an automatic gas adsorption analyzer TriStar 3020 (Micromeritics, USA). The specific surface area of zeolites was calculated from the isotherms of low-temperature sorption of nitrogen vapour (BET procedure).

The acid properties of the samples were investigated by means of temperature-programmable desorption of ammonia, which allows determination of the strength and concentration of acidic centres.

The morphology of zeolite crystals was studied with a scanning electron microscope LEO-1420 (Carl Zeiss, Germany).

The structure of catalysts was examined by means of high-resolution transmission electron microscopy (HRTEM) using an atomic-resolution electron microscope JEM-2200FS (JEOL, Japan).

Non-oxidative methane conversion (purity 99.99 vol. %) was carried out in a flow-type set-up with the static catalyst bed at a temperature of 750 °C, atmospheric pressure and the volume flow rate of raw material supply equal to 1000 h^{-1}. The volume of the catalyst loaded into the quartz reactor was 1.0 cm^3, the size of its granules was 0.5–1.0 mm. Reaction products were analyzed by means of gas chromatography every 40 min of catalyst operation. To evaluate the catalytic activity of the samples, the degree of methane transformation and the yield of the formed reaction products were determined.

RESULTS AND DISCUSSION

Investigations of the obtained zeolites by means of IR spectroscopy and XRD showed that the nature of carbon material used for synthesis has no effect on the structure and degree of crystallinity of the zeolites. All the samples relate to zeolite of structural type ZSM-5, and their crystallinity is 100 %.

The acidity characteristics of zeolites synthesized with different carbon materials and Mo-containing catalysts obtained on their basis are presented in Table 1. One can see that the temperature maxima of ammonia desorption from the mesoporous zeolite synthesized using C_n are higher (250 and 470 °C) than the parameters for the mesoporous zeolite synthesized with the addition of C_t (245 and 465 °C), which points to stronger acid centres of the former zeolite. The concentrations of the strong acid centres for zeolites synthesized with different carbon sources differ from each other insignificantly and are equal to 380 and 387 μmol/g for ZSM-5 + C_t and ZSM-5 + C_n catalysts, respectively. The addition of Mo to mesoporous zeolites causes a decrease of both the strength and concentration of strong acid centres due to molybdenum migration into zeolite channels and the interaction with Bronsted acid centres [7]. The most substantial decrease in the concentration of string acid centres is observed for the Mo/ZSM-5 catalyst synthesized using C_n.

Investigation of the texture characteristics of the catalysts are depicted in Table 2. The largest specific surface area is observed for initial zeolite ZSM-5 and is equal to 323 m^2/g. The addition of carbon materials into reaction mixture during zeolite synthesis causes a decrease of specific surface area in both cases, but at the same time the volume of mesopores increases in comparison with initial ZSM-5 from 0.02 to 0.07 cm^3/g for C_n and from 0.02 to 0.08 cm^3/g for C_t, respectively. The volume of micropores decreases slightly.

TABLE 1

Acid characteristics of zeolites and catalysts based on them

Sample	Temperature, °C		Concentration, μmol/g		
	T_I	T_{II}	C_I	C_{II}	C_Σ
ZSM-5	235	480	753	388	1141
ZSM-5 + C_t	245	465	777	380	1157
ZSM-5 + C_n	250	470	834	387	1221
4.0 % Mo/ZSM-5 + C_t	225	460	810	315	1125
4.0 % Mo/ZSM-5 + C_n	232	465	843	256	1099

Note. T_I and T_{II} are temperatures of the maxima of low- and high-temperature peaks of ammonia desorption, respectively; C_I and C_{II} are concentrations of weak and strong acid centres, respectively; C_Σ is total concentration of acid centres.

TABLE 2

Texture characteristics of zeolites

Sample	S_{BET}, m^2/g	S_{meso}, m^2/g	V_{total}, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g
ZSM-5	323	66	0.20	0.18	0.02
ZSM-5 + C_t	287	94	0.23	0.15	0.08
ZSM-5 + C_n	297	92	0.24	0.17	0.07

Note. S_{BET} is specific surface area determined by means of BET procedure; S_{meso} is specific surface area of mesopores; V_{total} is the total volume of pores; V_{micro}, V_{meso} is the volume of micro- and mesopores, respectively.

The data on the distribution of mesopores in the synthesized zeolites are presented in Fig. 1. The addition of carbon material at the stage of zeolite synthesis causes the formation of mesopores with a size of 3.5–20.0 nm (in the case of C_t) and 3.3–8.6 nm (in the case of C_n).

Figure 2 shows the HRTEM images of Mo/ZSM-5 catalysts obtained on the basis of zeolites with micro- and mesoporous structure after the operation in methane dehydroaromatization for 380 min. The images exhibit differences in the distribution of active phases in the catalysts. For the catalyst based on microporous zeolite, small clusters of Mo particles ~1 nm in size inside zeolite channels and particles up to 10 nm on zeolite surface are observed (see Fig. 2, *a*). The catalyst with mesoporous structure contains the clusters of Mo particles ~1 nm in size with very dense positions inside zeolite channels and the particles with a size up to 10 nm on the surface (see Fig. 2, *b*), which is evidence of more uniform distribution of molybdenum within the sample volume.

Figure 3 illustrates the effect of the nature of the carbon template, which is used to form the mesoporous structure in zeolites, on the catalytic properties of Mo/ZSM-5 systems prepared on this basis in methane dehydroaromatization. One can see that the highest activity was exhibited by the catalyst obtained on the basis of zeolite that was synthesized using C_t (see Fig. 3, *a*). The highest methane conversion (12.3 %) is observed during the initial 20 min of reaction in the presence of the Mo/ZSM-5 + C_t sample. The activity of the Mo/ZSM-5 + C_n sample is insignificantly higher than the activity of initial catalyst Mo/ZSM-5 and is equal to 11.3 %. For all samples, the degree of methane transformation decreases in the

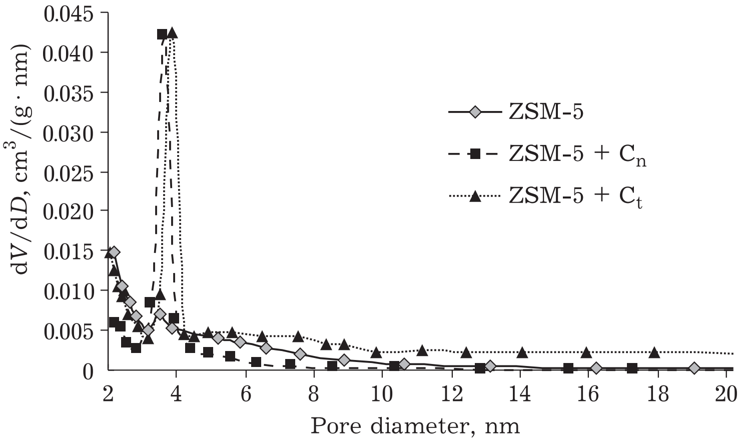

Fig. 1. Distribution of mesopores in zeolites synthesized with different carbon templates. C_n and C_t template content: 1 mass %.

course of methane dehydroaromatization. At the same time, the activity of the catalyst obtained on the basis of zeolite that was synthesized using technical carbon is higher during the whole time of tests in comparison with other catalysts.

The higher activity of the Mo/ZSM-5 + C_t catalyst in comparison with the Mo/ZSM-5 + C_n catalyst may be explained by the differences in pore size distribution. The zeolite synthesized using C_t is characterized by the presence of mesopores 3.5–20 nm in size, while the zeolite obtained using C_n contain mesopores 3.3–8.6 nm in size.

Analysis of the gaseous products formed in methane transformation at Mo/ZSM-5 catalysts with micro- and mesoporous structure showed that the products contain ethane and ethylene; their summarized yield does not exceed 1.1 % (see Fig. 3, *b*). The highest yield of gaseous products is observed with the Mo/ZSM-5 + C_n catalyst: it reaches 1.08 % during reaction for 260 min.

Mainly benzene and naphthalene are present among the liquid products of methane transformation, and the yield of benzene is much higher than the yield of naphthalene. The largest amount of benzene and naphthalene is formed with the Mo/ZSM-5 + C_t catalyst: after reaction for 20 min the yield is 6.4 and 3.5 %, respectively.

CONCLUSION

The 4.0 % Mo/ZSM-5 catalysts of non-oxidative methane conversion were obtained on the basis of zeolites with micro- and mesoporous system. The effect of the nature of the carbon template, which

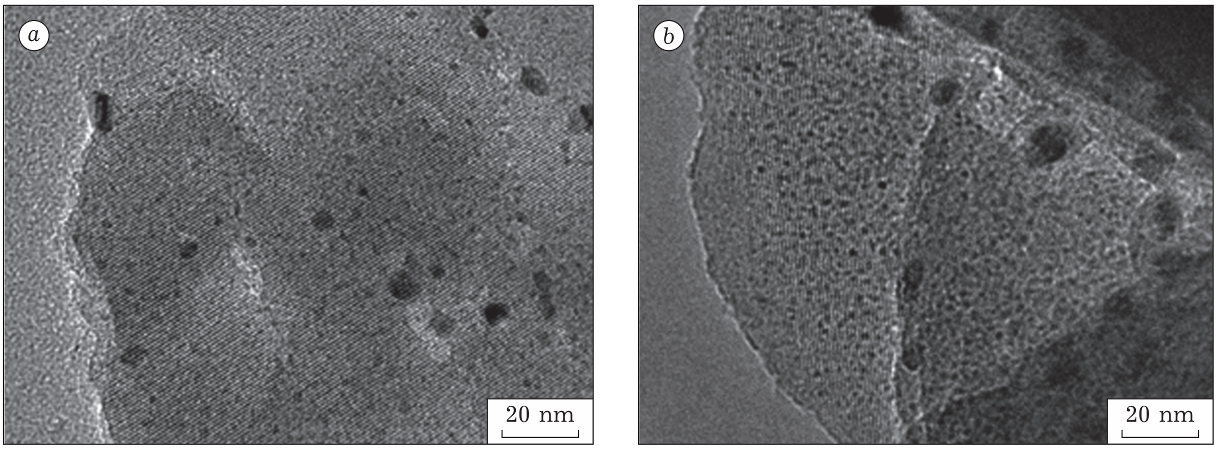

Fig. 2. HRTEM images of 4.0 % Mo/ZSM-5 catalysts obtained on the basis of zeolites with micro- (*a*) and mesoporous (*b*) structure after methane dehydroaromatization.

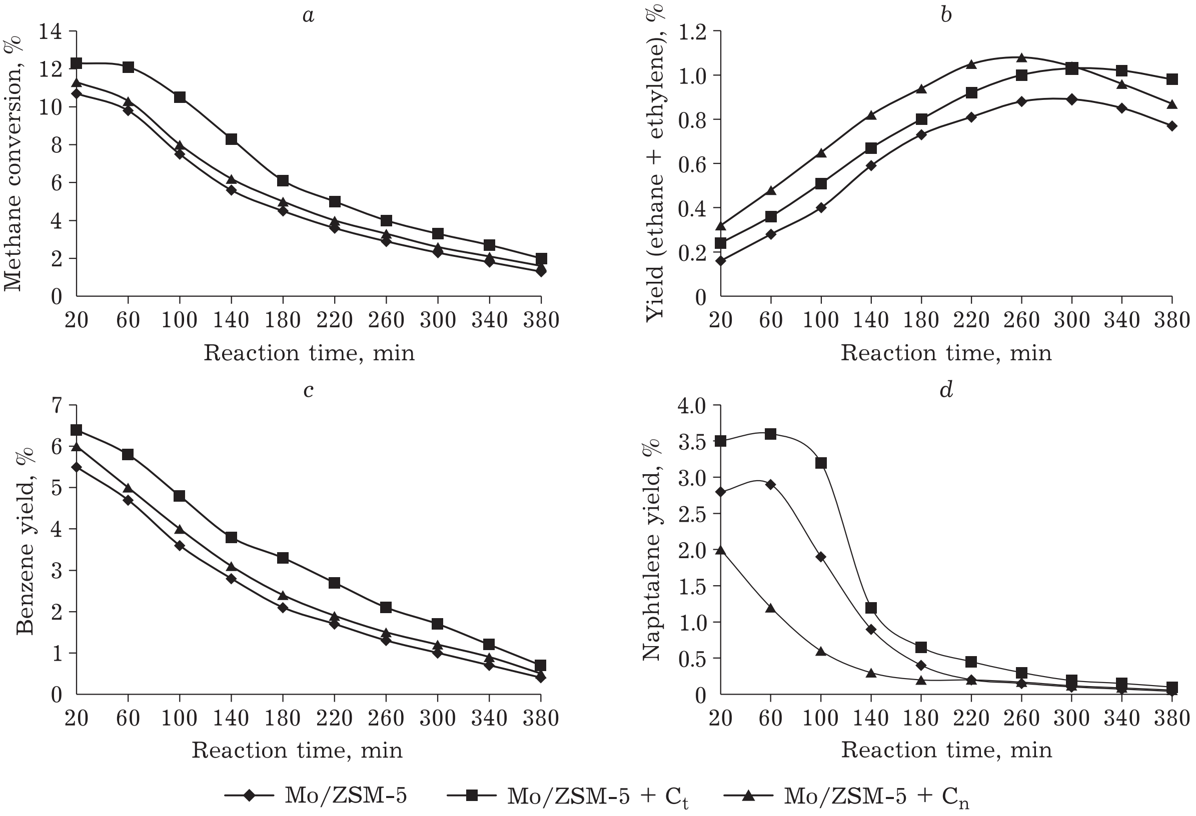

Fig. 3. Changes in methane conversion (*a*), total yield of ethane and ethylene (*b*), the yields of benzene (*c*) and naphthalene (*d*) with the time of operation of the 4.0 % Mo/ZSM-5 catalyst obtained on the basis of zeolites synthesized with different carbon templates. The content of C_n and C_t templates: 1 mass %.

is used for zeolite synthesis, on the texture and acid characteristics of the zeolites is demonstrated. The addition of the carbon template does not affect the degree of crystallinity of the resulting zeolites. It is established that the addition of the carbon template into the reaction mixture for zeolite synthesis leads to an increase in total pore volume as a consequence of an increase of mesopore volume from 0.02 to 0.08 cm^3/g and from 0.02 to 0.07 cm^3/g for zeolites prepared using technical and nanoglobular carbon, respectively. The differences in the distribution of the active molybdenum phase in Mo/ZSM-5 catalysts obtained on the basis of micro- and mesoporous zeolites are shown. For Mo/ZSM-5 catalyst based on mesoporous zeolite, clusters ~1 nm in size are observed, with the very dense arrangement in zeolite channels. Due to the creation of mesoporous structure in the synthesized zeolites, the uniformity of the distribution of active component is successfully achieved; the activity and stability of Mo/ZSM-5 catalysts obtained on their basis are improved.

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