


Catalytic performance of the modified H-ZSM-5 zeolite in methanol transformation to hydrocarbons

Antonina A. Stepacheva¹  · Valentin Yu. Doluda¹ · Natalia V. Lakina¹ · Vladimir P. Molchanov¹ · Alexander I. Sidorov¹ · Valentina G. Matveeva^{1,2} · Mikhail G. Sulman^{1,3} · Esther M. Sulman¹

Received: 5 October 2017 / Accepted: 28 January 2018 / Published online: 31 January 2018
© Akadémiai Kiadó, Budapest, Hungary 2018

Abstract In the current work, we present the study of the catalytic performance and characterization of the modified H-ZSM-5 zeolite for methanol to hydrocarbons process. The modification of zeolite was performed by both alkali and acid treatment. The changes in the zeolite structure were studied using low-temperature nitrogen physisorption, NH₃ chemisorption, and X-Ray photoelectron spectroscopy. It was found that the zeolite modification with oxalic acid (0.01 M) resulted in the lower catalytic activity loss (48%) after 120 h on stream as compared to both initial and alkali treated H-ZSM-5. Further, the chosen zeolite sample was modified with Co, Fe, and Ni by wet impregnation with the corresponding metal nitrates. The Ni-containing catalyst showed the highest catalytic performance in time on stream. The decrease in the methanol transformation rate for the Ni-containing zeolite was found to be only 27%. The metal-containing catalysts showed the minimal coke formation as well as the minimal decrease in acidity and surface area as compared to the initial zeolite and the samples treated with both alkali and oxalic acid.

Keywords Methanol-to-hydrocarbons process · H-ZSM-5 · Desilication · Dealumination · C₅₊ hydrocarbons

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11144-018-1359-3>) contains supplementary material, which is available to authorized users.

✉ Antonina A. Stepacheva
a.a.stepacheva@mail.ru

¹ Tver State Technical University, A. Nikitin str. 22, 170026 Tver, Russia

² Tver State University, Zhelyabova str. 33, 170100 Tver, Russia

³ A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova str. 28, 119991 Moscow, Russia

Abbreviations

MTO	Methanol to olefins
MTH	Methanol to hydrocarbons
MTS	Methanol to syn-fuel
DME	Dimethyl ether
XPS	X-ray photoelectron spectroscopy
TEM	Transmission electron microscopy

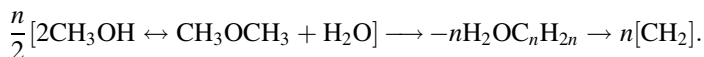
Introduction

The modern tendencies in chemical engineering consisting of the development of new, cost-effective, clean and sustainable technologies for energy production from natural resources are caused by the needs of the growing global population, the diminishing of fossil fuel sources and climate change mitigation. Since oil, coal and natural gas remain the major energy sources and renewable energy sources are not yet technologically or economically feasible to satisfy current and near-term energy demands, the conversion of C_1 compounds such as CO, CO_2 , CH_4 and CH_3OH into valuable chemicals and fuels is a great attention [1, 2]. Among C_1 chemistry several catalytic processes are of particular interest, i.e., MTO (methanol to olefins), MTG (methanol to gasoline) and MTS (methanol to syn-fuel) [3].

The formation of various types of hydrocarbons from methanol has been studied since the end of 19th century. The earliest report on hydrocarbon formation from methanol is that of LeBel and Greene, who described the decomposition of methanol in molten $ZnCl_2$ [4] in 1880. Hexamethylbenzene and light gases were identified as the main products. In 1914 Sernagiotto [5] reported the decomposition of methanol with P_2O_5 . The reaction yielded a mixture of hydrocarbons including propene, butane, hexene, and hexane. A patent was later granted to Grosse and Snyder [6] for the conversion of methanol and dimethyl ether (DME) to hydrocarbons over $ZnCl_2$, at 375–675 °C and high pressure. Topchiev and Ballod [7] compared the activity of silica gel, alumina and silica-alumina (Al_2O_3 30%, SiO_2 70%) in methanol conversion to DME. The aluminosilicate catalyst resulted in the formation of CO, C_2H_4 , CO_2 , and C_2H_6 in addition to DME at 400 °C. Gorin [8] studied the conversion of a mixture of DME and isobutane over amorphous silica-alumina at 370 °C, 150 psig, and 6.8 h^{-1} GHSV. The conversion of DME to hydrocarbons was 94%, while no change in isobutane occurred. In the absence of isobutane, at a higher temperature, lower pressure, and higher space velocity, considerable amount of methane, CO, and carbon was produced, while the yield of C_5 hydrocarbons was less than 15%.

A new age of methanol to hydrocarbons synthesis began with the application of various zeolites. The first MTH process, in the modern sense of the term, was proposed in the late 1970s [9–12] and then commercialized by Mobil in 1986 [13]. Hydrocarbon formation from methanol is catalyzed by Brønsted acids. The MTH process is commonly conducted via two-step technology involving primary

methanol dehydration to DME and the following DME conversion to the mixture of olefins, paraffin, and aromatic compounds. The general reaction which takes place on zeolite surface can be represented as follows [9, 14]:



Here $[\text{CH}_2]$ is an average formula for the paraffin-aromatic mixture.

Among the zeolites used in MTH process ZSM-5, SAPO-34 and MCM-22 are the most studied. As it was shown in [15, 16] SAPO-34 zeolite exhibits high selectivity towards DME and olefins formation. At the same time, this catalyst shows high deactivation rate due to the coke formation mainly on the external surface of the zeolite. MCM-22 is also characterized by the rapid deactivation as it was described in [17, 18]. In order to exclude fast deactivation, numerous studies devoted to the modification of zeolite surface were done. Wang et al. [18, 19] reported the enhancing of MCM-22 zeolite stability by the treatment with oxalic acid. Chen et al. [20] studied the influence of MCM-22 zeolite treatment with boronic acid. In that case, the increase in the catalyst stability was also observed. The studies showed that the treatment of MCM zeolite resulted in the increase of the selectivity towards the light olefins. Numerous studies show that ZSM-5 zeolite is the most suitable catalyst for methanol transformation to gasoline-range hydrocarbons [21–24]. This is due to its higher surface area as compared to the other zeolites, higher resistance to coke formation and the acid nature of the active sites. At the same time, ZSM-5 shows higher activity in the term of overall transformation process as well as high selectivity to C_{5+} hydrocarbons.

The formation of the aromatic compounds is another factor determined the effectivity of the catalyst. The high amount of aromatics negatively affects the resulted fuel properties as well leads to the fast deactivation of the catalyst due to the formation of polycyclic aromatic hydrocarbons on the catalyst surface [25–32]. Thus, the deactivation remains the main problem of the use of ZSM-5 zeolite in MTH process. Numerous studies are devoted to the modification of H-ZSM-5 zeolite structure in order to enhance the catalytic stability and decrease the selectivity towards the aromatics formation. The change in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is one of the ways used for the catalyst activity increase. In [33–39] it was shown that the decrease in Si/Al ratio increases the number of the accessible acid sites on both external and internal surface. However, at the same time, an increase in the coke formation rate is observed. The increase in Si/Al ratio increases the selectivity both towards the aromatic and C_{5+} formation, meanwhile the formation of gaseous hydrocarbons decreases. The treatment of the ZSM-5 zeolite with NaOH solution leads to the increase of gasoline-range hydrocarbons yield by 40% as it was demonstrated in [34]. At the same time, the decrease in the formation of aromatics was observed, thus, the catalyst resulted in the higher stability.

The other way to modify the ZSM-5 is the incorporation of different metals and their oxides in zeolite structure. The addition of Zn to the H-ZSM-5 [40, 41] led to the increase in the catalyst crystallinity, meanwhile, the decrease in the total surface area and the decrease in the sum of the acid sites were observed. Thus, Zn-H-ZSM-5 catalyst showed higher selectivity towards the liquid hydrocarbons reaching the

yield up to 62.5% and lower deactivation rate. It is noteworthy that no changes in zeolite morphology were observed. Zaidi and Pant [22] modified ZSM-5 with copper and zinc oxides. It was shown that the addition of the metal-containing modifiers led to the increase in the formation of the aromatics. Sadeghi et al. [42] also reported that the modification of zeolite with CuO and ZnO led to the increase in the yield of aromatics and octanes and to the decrease in the coke formation. The addition of Pd to the H-ZSM-5 zeolite [43, 44] resulted in the increase of gasoline-range hydrocarbon yield as well as the increase in the rate of alkanes isomerization. Thus, the modification of the commercial ZSM-5 zeolite with the metals and their oxides results in the increase in the gasoline yield as well as the decrease in the deactivation rate due to the increase in the Lewis acid sites amount on the catalyst surface.

In this work, we studied the influence of H-ZSM-5 zeolite modification on its catalytic performance in MTH process. Three different methods of zeolite modification were used: (i) treatment with NaOH solution; (ii) treatment with oxalic acid solutions; and (iii) the incorporation of Ni, Fe and Co into the H-ZSM-5 zeolite treated with oxalic acid.

Experimental

Materials

For the catalysts synthesis zeolite H-ZSM-5 (CBV 5524G, ZeolystInt., USA), NaOH (reagent grade, KhimMedServis, Russia), oxalic acid ($C_2H_2O_4$, reagent grade, KhimMedServis, Russia), ammonium nitrate (NH_4NO_3 , reagent grade, KhimMedServis, Russia), nickel nitrate ($Ni(NO_3)_2$, reagent grade, KhimMedServis, Russia), cobalt nitrate ($Co(NO_3)_2$, reagent grade, KhimMedServis, Russia) and ferric nitrate ($Fe(NO_3)_3$, reagent grade, KhimMedServis, Russia) were used as received. Methanol (CH_3OH , MeOH, reagent grade, Sigma-Aldrich, USA) was used without any treatment as a reactant.

H-ZSM-5 treatment with NaOH and oxalic acid solutions

The sample of commercial zeolite H-ZSM-5 with the mass of 3 g was calcined at 600 °C for 12 h. After the cooling in the air, the sample was mixed with 500 mL of the solution of NaOH for desilication or oxalic acid for dealumination process. The concentration of both base and acid solutions was varied from 0.01 to 0.2 M for 5 h. Afterwards, the sample was filtrated, washed with water for neutral pH and dried under air for 24 h. Then the catalyst sample was stirred with 500 mL of 1 M NH_4NO_3 solution for 5 h. The following catalysts filtration, washing, drying, and calcination were also provided.

Modification of H-ZSM-5 with iron group metal

After the testing of the catalytic performance, the most active zeolite samples treated with a 0.01 M solution of oxalic acid were modified by the impregnation method with the solutions of Ni, Fe and Co nitrates during 12 h. Then the catalysts were washed for the absence of nitrate ion and calcined at 450 °C for 12 h.

Catalysts characterization

The specific surface area of the modified zeolites was estimated by low-temperature nitrogen physisorption using surface area analyzer Beckman CoulterSA3100 (Coulter Corporation, USA). The analysis was performed at -196 °C and p_s/p_0 adsorption 0.9814. In the analysis, t -plot and BET model were used. To process the adsorption data, the Harkins and Jura equation was applied.

To estimate the number of the acid sites on the zeolite sample surface ammonia chemisorption was performed using Micromeritics AutoChem 2910 (Micromeritics, USA) analyzer. The catalyst sample pretreated with helium (He flow rate 10 mL/min) at 300 °C in the quartz cuvette was cooled down to 25 °C and then the mixture of 10 vol% of ammonia in helium was injected onto the catalyst after 5 min interval until the acid sites were saturated. The quantity of the chemisorbed ammonia was calculated using calibration method.

X-Ray photoelectron spectroscopy (XPS) was used in order to estimate the Si/Al ratio. The spectra were obtained using Mg K_{α} ($h\nu = 1253.6$ eV) radiation with an ES-2403 spectrometer modified with analyzer PHOIBOS 100 (SPECS, Germany). All the data were acquired at an X-ray power of 200 W and an energy step of 0.1 eV. The data analysis was performed by CasaXPS. Mathematical modeling of Si and Al peaks was performed according to the 2p sublevels.

The analysis of carbon deposits formed on the surface of the catalyst was performed by gravimetric analysis. The catalysts samples were weighted after the calcination at 600 °C in the air.

Catalyst testing

The evaluation of the catalytic performance of the synthesized catalyst was carried out in a continuous two-step mode. The scheme of the laboratory set-up is presented in Fig. 1. The laboratory set-up includes two reactors: (i) for methanol to DME conversion and (ii) for DME to hydrocarbons transformation. In typical experiments, 7.5 g of zeolite-based catalyst was sieved and the fraction with the diameter of 0.125 mm was taken for the reactors filling. Before the experiment the system was purged with nitrogen for 40 min, nitrogen feed rate was maintained at 10 mL/min. Then the reactors were heated to the required temperature (370 °C). After the stabilization of the reaction temperature methanol was fed at constant feed rate 1 mL/min. The overall pressure was maintained at 1 bar.

The estimation of the methanol transformation rate was performed by gaseous chromatography using the state-of-the-art analytic complex including gas chromatograph (Crystall 2000 M, MetaChrom, Russia) equipped with the flame

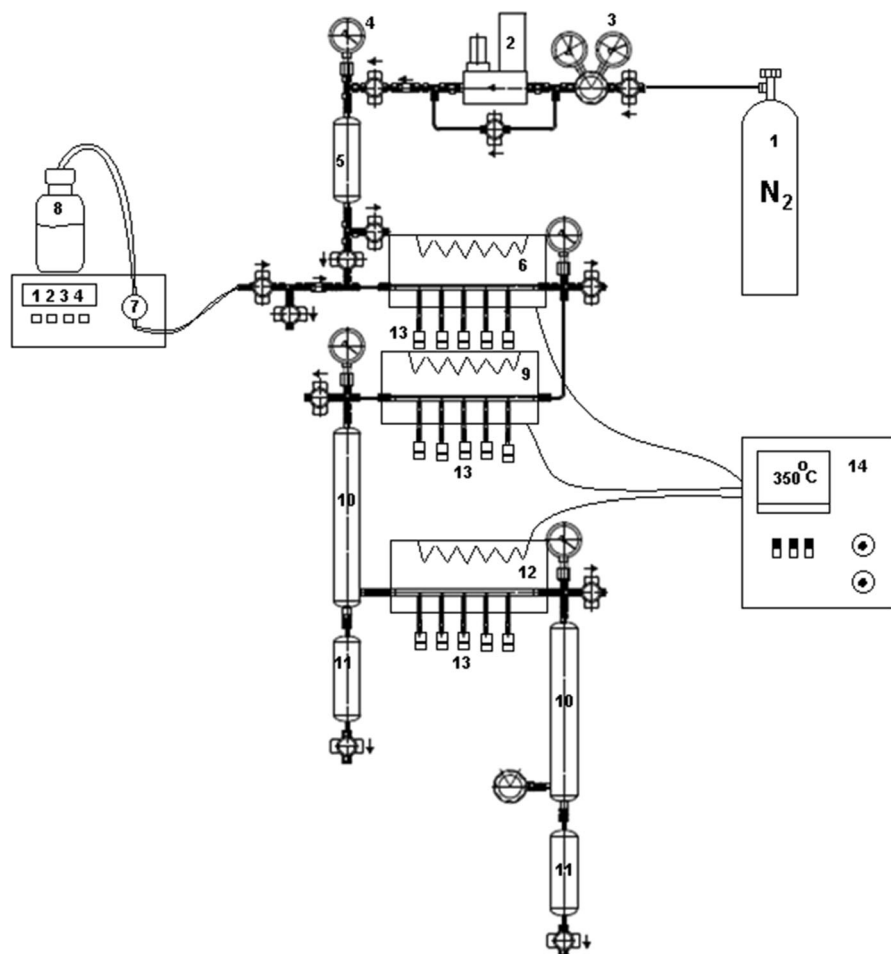


Fig. 1 The scheme of the laboratory set-up of methanol to hydrocarbons synthesis process: 1—nitrogen tanks, 2—nitrogen flow controller, 3—pressure regulator, 4—manometer, 5—gas tank, 6—gas mixer, 7—high pressure pump for methanol, 8—methanol flask, 9—reactor for methanol to DME synthesis, 10—reflux, 11—water and methanol collector, 12—reactor for hydrocarbons from methanol synthesis, 13—thermocouple, 14—thermocontroller

ionization detector and thermo conductivity detector. The reaction mixture was directly injected into the chromatograph using automatic sampling valve with the volume of 0.25 mL. The chromatographic analysis was provided under the following conditions: evaporator temperature was 270 °C; the consumption of gas-carrier (helium) 30 mL/min; gas-carrier pressure 3.5 atm; duration of the analysis was 30 min; packed column 2.5 m × 3 mm filled with Haesep Q adsorbent with the fraction of 80/100 mesh; initial column temperature 40 °C was held for 4 min; then the column was heated to 250 °C with the rate 15 °C/min and maintained at this temperature for 12 min, temperature of the detectors was 260 °C. To determine the composition of the mixture the method of absolute concentrations

was used. DME, aliphatic hydrocarbons (both C₂–C₁₂ paraffin and olefins) and aromatic hydrocarbons (benzene and toluene) were the main products of the process.

Results and discussion

Characterization of initial catalyst samples

The changes in the textural properties of zeolite samples after the desilication and dealumination treatment were studied by nitrogen physisorption. The analysis of the adsorption isotherms (Fig. S1) showed that the initial H-ZSM-5 sample was of type I typical for microporous materials. After the treatment of the initial zeolite with alkali and oxalic acid, the resulting samples show the adsorption isotherms of type IV characterizing the mesoporous materials. The uptake of nitrogen at intermediate pressures of $p_s/p_0 > 0.4$ indicates the formation of a hierarchical porous structure combining micropores and mesopores. The hysteresis loop of H4 type is observed for all treated samples indicating the formation of an irregular structure with a broad size distribution and the presence of narrow slit-like pores in the zeolite. The hysteresis loop for the sample H-ZSM-5-0.2-NaOH is of an H2 type indicating the ink-bottle type pores. Moreover, the absence of hysteresis loop at the $p_s/p_0 > 0.95$ for all treated samples indicates that none aggregated mesopores was formed during the treatment of the zeolite. It is noteworthy that the deposition of iron group metals on the surface of H-ZSM-5 treated with 0.01 M oxalic acid does not change the pore structure of the sample.

The pore size distribution of the H-ZSM-5 zeolite samples is shown in Figs. 2, 3, 4 and 5. All the samples have the pores centered in the range of 2–20 nm. It is clearly seen that the initial zeolite sample has micropores with the mean diameter of 2 nm. The treatment of the H-ZSM-5 with NaOH leads to the shift in the maximum pore size distribution to 4.5 nm. At the same time, a number of the pores in the range of 5–15 nm also increases (Fig. 3). But for the sample H-ZSM-5-0.2-NaOH, the narrow pore size distribution in the range of 4–7 nm is observed. This may be due to the slower diffusion of the alkali into zeolite pores at higher desilicating agent concentration. The treatment of the initial zeolite with oxalic acid, in turn, leads to the occurrence of pores with a wide distribution in the range of 3–17 nm (Fig. 4). The most noticeable peaks are seen in the range of 3–7 nm. The increase in the oxalic acid concentration leads to the smooth in the pore size distribution curve. This can be explained by the slower diffusion of the dealuminating agent into zeolite pores at higher concentration. In the case of the 0.2 M oxalic acid, the resulting zeolite has narrow pore size distribution at 3 nm. The introduction of the metal into the samples of H-ZSM-5 treated with 0.01 M oxalic acid slightly changes its porosity (Fig. 5). The shift in pore size distribution to 4 nm for Co- and Fe-containing samples can be seen. Ni-containing zeolite, in turn, has maximum pore size distribution at 5.7 nm. At the same time, the number of pores at 5.0, 5.6 and 9.0 nm decreases for metal-containing catalysts as compared to H-ZSM-5-0.01-

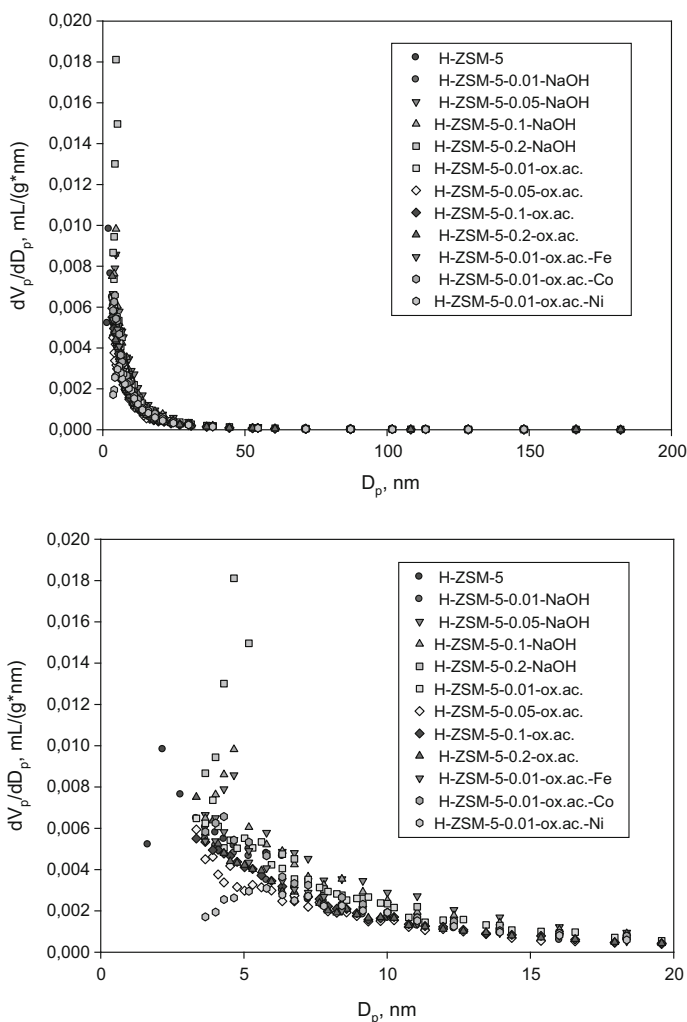


Fig. 2 Pore size distribution for the initial zeolite and the samples treated with NaOH, oxalic acid solutions and modified with transition metals (nitrogen low-temperature adsorption measurements were performed at $-196\text{ }^{\circ}\text{C}$ and p_s/p_0 adsorption 0.9814)

ox.ac. sample. This effect can be explained by the deposition of the active metals in the pores of the zeolite.

Table 1 represents the physic-chemical properties of the obtained zeolite samples before the reaction. It is clearly seen that the treatment of the initial zeolite with alkali decreases the Si/Al ratio with the increase in NaOH concentration (Table 1, lines 2–5). At the same time, the acidity of the alkali treated zeolite slightly decreases, that can be connected with the leaching of Si species from the zeolite surface. As it was expected, the total surface area of the treated H-ZSM-5 increases reaching the maximum for H-ZSM-5-0.05-NaOH sample due to the changes in the

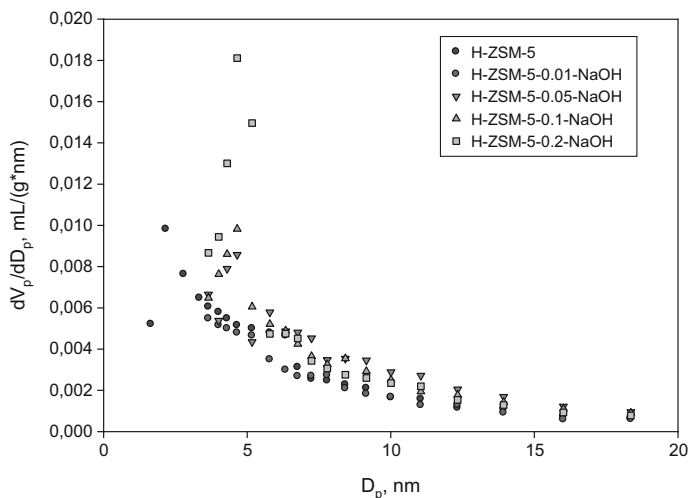


Fig. 3 Pore size distribution for zeolite samples treated with NaOH (nitrogen low-temperature adsorption measurements were performed at $-196\text{ }^{\circ}\text{C}$ and p_s/p_0 adsorption 0.9814)

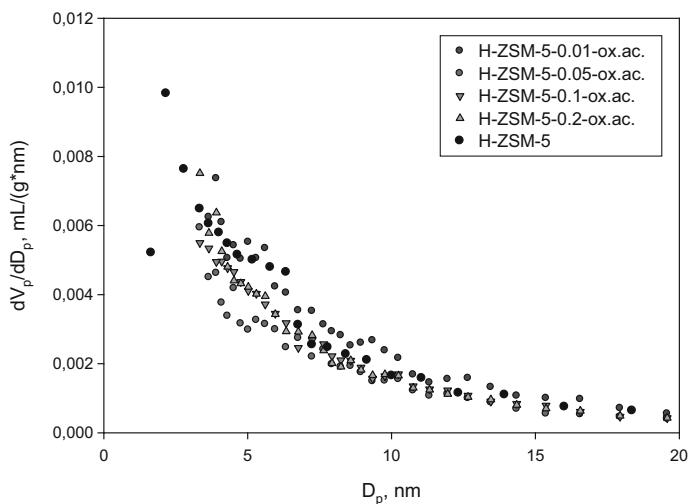


Fig. 4 Pore size distribution for zeolite samples treated with oxalic acid (nitrogen low-temperature adsorption measurements were performed at $-196\text{ }^{\circ}\text{C}$ and p_s/p_0 adsorption 0.9814)

pore structure during the treatment. The further decrease in the surface area can be attributed to the formation of pores with narrow size distribution.

The zeolite treatment with oxalic acid (Table 1, lines 6–9) leads to the increase in the acidity and Si/Al ratio. It is noteworthy that the increase in the oxalic acid concentration above 0.1 M does not lead to the further increase in the catalyst acidity; however, the Si/Al ratio keeps increasing. It can be explained by the reaching the maximum acidity for H-ZSM-5-0.1-ox.ac. sample. Thus, the further

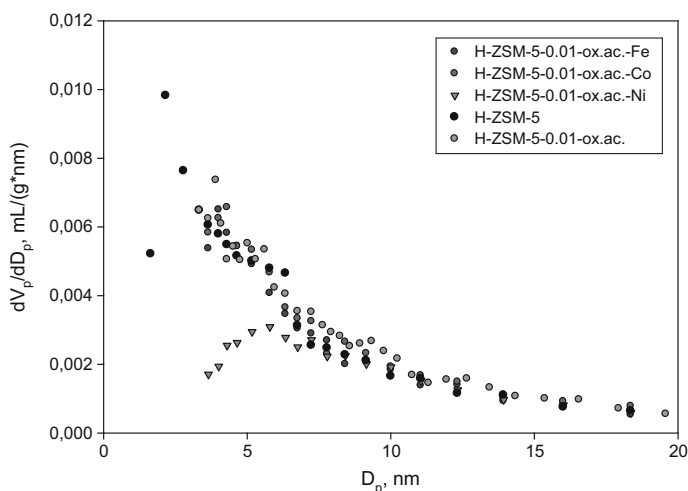


Fig. 5 Pore size distribution for zeolite samples modified with oxalic acid and transition metals (nitrogen low-temperature adsorption measurements were performed at $-196\text{ }^{\circ}\text{C}$ and p_s/p_0 adsorption 0.9814)

Table 1 The characterization of ZSM zeolite samples before MTH process

Sample	Si/Al ^a	Acidity (mmol/g) ^b	$S_{t\text{-plot}}$, (m ² /g) ^c	C (Me) (wt%) ^d
H-ZSM-5	57	0.41	324	—
H-ZSM-5-0.01-NaOH	42	0.40	372	—
H-ZSM-5-0.05-NaOH	36	0.39	411	—
H-ZSM-5-0.1-NaOH	24	0.38	402	—
H-ZSM-5-0.2-NaOH	15	0.37	401	—
H-ZSM-5-0.01-ox. ac.	64	0.40	334	—
H-ZSM-5-0.05-ox. ac.	75	0.43	347	—
H-ZSM-5-0.1-ox. ac.	89	0.45	350	—
H-ZSM-5-0.2-ox. ac.	115	0.45	354	—
H-ZSM-5-0.01-ox. ac.-Ni	64	0.37	316	0.31
H-ZSM-5-0.01-ox. ac.-Fe	64	0.34	318	0.29
H-ZSM-5-0.01-ox. ac.-Co	64	0.36	327	0.38

^aCalculated by XPS data

^bCalculated by NH₃ chemisorption

^cAccording to the t-plot model of nitrogen physisorption

^dCalculated by XFA data

decrease in Al content does not impact the overall acidity. The increase in the specific surface area is also observed for the acid treated zeolite samples but to a smaller extent. However, in this case, no maximum of the surface area occurs, that can be explained by the more significant changes in the zeolite structure in comparison with the initial H-ZSM-5. The deposition of metals on the surface of the

zeolite treated with 0.01 M oxalic acid (Table 1, lines 10–12) does not change the Si/Al ratio but slightly decreases the catalyst acidity due to the blockage of the acid sites with metal particles. The surface area of the metal-containing zeolites decreases in comparison with H-ZSM-5-0.01-ox.ac. sample and even with H-ZSM-5 sample. It can be explained by the formation of the metal particles in the zeolite pores. It is noteworthy that the highest surface area is observed for Co-containing catalyst in spite of the highest metal loading.

Catalysts testing

The catalytic performance of the zeolite samples was studied in the methanol transformation process in order to obtain hydrocarbons. The results of the methanol transformation rate study for the used catalysts are shown in Fig. 6 and Table 2. All the catalysts showed the high initial methanol transformation rate, which was slightly less only for the H-ZSM-5-0.2-ox.ac. sample. It can be explained by the lower accessibility of the acid sites due to the high Si/Al ratio.

The study of the catalytic performance in time on stream showed, that the highest decrease in the methanol transformation rate was observed for H-ZSM-5 and H-ZSM-5-0.2-ox.ac. catalysts. The treatment of the zeolite with NaOH leads to the decrease in the methanol transformation rate by the factor of 1.8–3.3. It should be noted that the increase in the NaOH concentration increases the time-on-stream catalytic performance of the zeolite. The increase in the concentration of oxalic acid, in contrast, decreases the time-on-stream catalytic performance of the zeolite. This can be explained by the increase in the coke formation rate on the catalyst surface. Among the treated zeolites, H-ZSM-5-0.01-ox.ac. showed the higher

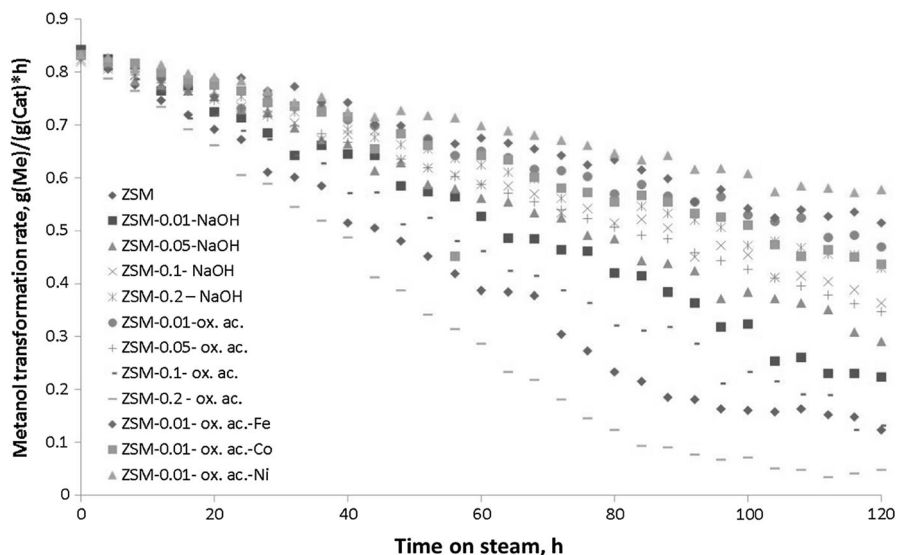


Fig. 6 Comparison of methanol transformation rate on time on stream for studied ZSM-5 samples (catalyst mass 7.5 g, temperature 370 °C, methanol feed rate 1 mL/min, overall pressure 1 bar)

Table 2 Methanol transformation rate for ZSM-5 samples (catalyst mass 7.5 g, temperature 370 °C, methanol feed rate 1 mL/min, overall pressure 1 bar)

Sample	Methanol transformation rate, $\text{g}_{\text{MeOH}}/(\text{g}_{\text{cat}} \text{ h})$		
	Initial	After 20 h	After 120 h
H-ZSM-5	0.83	0.70	0.14
H-ZSM-5-0.01-NaOH	0.85	0.73	0.25
H-ZSM-5-0.05-NaOH	0.85	0.75	0.30
H-ZSM-5-0.1-NaOH	0.85	0.75	0.38
H-ZSM-5-0.2-NaOH	0.82	0.75	0.46
H-ZSM-5-0.01-ox. ac.	0.85	0.80	0.48
H-ZSM-5-0.05-ox. ac.	0.85	0.75	0.37
H-ZSM-5-0.1-ox. ac.	0.85	0.73	0.147
H-ZSM-5-0.2-ox. ac.	0.82	0.67	0.05
H-ZSM-5-0.01-ox. ac.-Ni	0.85	0.80	0.60
H-ZSM-5-0.01-ox. ac.-Fe	0.85	0.78	0.55
H-ZSM-5-0.01-ox. ac.-Co	0.83	0.80	0.46

performance in time on stream. Thus, it can be concluded that the Si/Al ratio equal to 64 is the most appropriate for MTH process leading the higher methanol transformation rate and the higher catalyst stability.

Metal-containing zeolites showed both high initial and time on stream catalytic performance in MTH process. H-ZSM-5-0.01-ox.ac.-Ni was found to be the most stable catalyst showing only 25% loss in the activity after 120 h on stream. This can be explained by the higher acidity in comparison with the other metal-containing zeolites as well as the wider pore size distribution. The last one allows decreasing the pore blockage during the coke formation on the catalyst surface.

Table 3 represents the data on the selectivity for all used samples of ZSM-5. It is well seen that the treatment of the initial zeolite with both NaOH and oxalic acid leads to the decrease in the formation of aromatic hydrocarbons as well as to the increase in the selectivity towards the formation of gasoline-range hydrocarbons. It is noteworthy that the increase in the NaOH and oxalic acid concentration results in the slight decrease in the selectivity for aromatics. However, for a high concentration of the treating agent the percentage of the formed aromatic compounds increases. Moreover, it should be noted that the zeolite treatment practically does not affect the formation of $\text{C}_9\text{--C}_{12}$ hydrocarbons. It can be due to the changes in the zeolite structure. The minimal selectivity towards the formation of aromatics was observed for the H-ZSM-5-0.01-ox.ac. zeolite. These results well correlate with the data on the methanol transformation rate and the activity loss for the studied samples. The incorporation of the iron subgroup metals into the zeolite pores leads to the decrease in both aromatic and olefins percentage. This can be explained by the high activity of the chosen metals in the hydrogenation reactions. The saturation of the formed olefins can take place due to the hydrogen formation in

Table 3 Selectivity data for ZSM-5 samples after 120 h in stream (catalyst mass 7.5 g, temperature 370 °C, methanol feed rate 1 mL/min, overall pressure 1 bar)

Catalyst	C ₁ –C ₅	C ₆ –C ₈	C ₉ –C ₁₂	Olefins	Aromatics
H-ZSM-5	65.2	25.3	9.5	38.7	47.2
H-ZSM-5-0.01-NaOH	52.4	38.3	9.3	43.9	39.4
H-ZSM-5-0.05-NaOH	48.3	42.1	9.6	51.4	29.2
H-ZSM-5-0.1-NaOH	43.8	46.5	9.7	46.6	32.6
H-ZSM-5-0.2-NaOH	36.9	52.8	10.3	31.1	52.8
H-ZSM-5-0.01-ox. ac.	26.9	64.7	8.4	59.3	17.5
H-ZSM-5-0.05-ox. ac.	26.6	65.2	8.2	59.6	16.3
H-ZSM-5-0.1-ox. ac.	25.8	65.9	8.3	60.7	15.8
H-ZSM-5-0.2-ox. ac.	22.9	67.3	9.8	32.4	50.9
H-ZSM-5-0.01-ox. ac.-Ni	26.2	65.7	8.1	12.1	12.3
H-ZSM-5-0.01-ox. ac.-Fe	21.7	53.2	25.1	33.6	14.9
H-ZSM-5-0.01-ox. ac.-Co	25.8	65.9	8.3	19.5	13.7

water–gas shift reaction on the metal surface. The deposition of Ni and Co on the surface of the treated zeolite does not lead to the change in product distribution in terms of carbon number, though, the addition of Fe to the zeolite results in the formation of higher hydrocarbons that correlates with the high selectivity of iron towards the higher olefins. Thus, H-ZSM-5-0.01-ox.ac.-Ni was found to be the most effective catalyst for MTH reaction.

Characterization of catalyst samples after MTH process

The results of the characterization of zeolite samples after 120 h on stream in MTH process are shown in Table 4. It can be noted that for all treated zeolites the increase in the Si/Al ratio is observed. It can be explained by the leaching of Al by the water formed during the MTH process. The acidity of the catalysts also decreases after the process that can be connected by the catalyst surface carbonization and thus the decrease in the acid sites accessibility. The higher decrease in the acidity was observed for the initial H-ZSM-5 sample and H-ZSM-5 treated with 0.1 and 0.2 M oxalic acid. Moreover, for these catalysts, the highest carbon deposition was observed. The data obtained well correlate with the decrease in the catalytic performance of the samples in time on stream. The same results are observed for the specific surface area of the treated zeolite samples.

In the case of the metal-containing zeolites, no changes in the Si/Al ratio were observed, that indicates the prevention of Al leaching by the water. Moreover, for these catalysts, the lower decrease in both the acidity and surface area was observed. The higher loss in the activity of Fe- and Co-containing catalysts can be explained by the leaching of the active metal from the catalyst surface, while for Ni-containing catalyst the decrease in the catalytic performance can be attributed only to the coke

Table 4 The characterization of ZSM zeolite samples after 120 h of MTH process

Sample	Si/ Al ^a	Acidity (mmol/ g) ^b	S _{t-plot} , (m ² / g) ^c	C (Me) (wt%) ^d	Carbon deposits (wt%) ^e
H-ZSM-5	59	0.06	72	–	5.2
H-ZSM-5-0.01-NaOH	49	0.11	105	–	4.5
H-ZSM-5-0.05-NaOH	42	0.13	144	–	3.9
H-ZSM-5-0.1-NaOH	32	0.17	178	–	3.4
H-ZSM-5-0.2-NaOH	24	0.19	224	–	2.9
H-ZSM-5-0.01-ox. ac.	87	0.23	175	–	2.7
H-ZSM-5-0.05-ox. ac.	82	0.18	152	–	3.5
H-ZSM-5-0.1-ox. ac.	81	0.07	64	–	5.1
H-ZSM-5-0.2-ox. ac.	134	0.03	21	–	5.8
H-ZSM-5-0.01-ox. ac.-Ni	64	0.23	214	0.31	1.3
H-ZSM-5-0.01-ox. ac.-Fe	65	0.28	182	0.24	1.9
H-ZSM-5-0.01-ox. ac.-Co	64	0.25	227	0.31	1.8

^aCalculated by XPS data^bCalculated by NH₃ chemisorption^cAccording to the t-plot model of nitrogen physisorption^dCalculated by XFA data^eAccording to gravimetric analysis

formation. It is noteworthy that the metal-containing catalysts showed minimal coke formation.

Conclusions

A series of the modified H-ZSM-5 catalysts were synthesized and studied in MTH process. The physical–chemical analysis showed that while using NaOH solutions for H-ZSM-5 treatment the shift in the pore size distribution from 2 to 4–7 nm was observed. In the case of the treatment of H-ZSM-5 with oxalic acid, the wide pore size distribution in the range of 3–15 nm was obtained. The alkali treatment of the initial zeolite sample leads to the decrease in the total acidity due to the decrease in Si/Al ratio, while for the zeolite treatment with acid the total acidity, in contrast, increases. All the catalysts showed the high initial methanol transformation rate. The study of the catalytic performance in time on stream showed that Ni-containing H-ZSM-5 treated with 0.01 M oxalic acid was found to be the most stable catalyst showing only 25% loss in the activity after 120 h on stream. Besides, this catalyst results in 65% yield of aliphatic gasoline-range hydrocarbons. The analysis of the zeolite samples after the process showed the decrease in the acidity and surface area for all catalyst samples. Moreover, the increase in the Si/Al ratio was observed due

to the leaching of Al by the water. In contrast, the metal-containing zeolites showed the minimal decrease in the acidity and surface area after MTH process as well as the minimal carbonization of the surface. Thus, the deposition of the iron subgroup metals allows decreasing the surface carbonization and prevention the dealumination of the zeolite-based catalysts during MTH process.

Acknowledgements This work was supported by the Ministry of Science and Education of the Russian Federation.

References

1. Lee E, Cheng Z, Lo CS (2015) *Catalysis* 27:187–208
2. Sousa-Aguiar EF, Appel LG (2011) *Catalysis* 23:284–315
3. Dinjus E, Arnold U, Dahmen N, Hofer R, Wach W (2009) In: Hofer R (ed) RSC green chemistry no. 4, sustainable solutions for modern economies. The Royal Society of Chemistry, London
4. Le Bel JA, Greene WH (1880) *Am Chem J* 2:19–20
5. Sernagiotto E (1914) *Gazz Chim Ital* 44(1):51–56
6. Grosse AV, Snyder JC (1950) US Patent 2493038A
7. Topchiev KV, Ballod AV (1951) *Russ Chem Rev* 20(2):161–175
8. Gorin E, Gorin MH (1948) US Patent 2456584 A
9. Chang CD, Silvestri AJ (1977) *J Catal* 47:249–259
10. Chen NY, Reagan WJ (1979) *J Catal* 59:123–129
11. Chang CD, Lang WH, Smith RL (1979) *J Catal* 56:169–173
12. Harney BM, Mills GA (1980) *Hydrocarb Process* 64:67–71
13. Diebold J, Scahill J (1988) In: Soltes J, Milne TA (eds) *Pyrolysis oils from biomass*. American Chemical Society, Washington, DC
14. Chang CD (1999) In: Song C, Garces JM, Sugi Y (eds) *Shape-selective catalysis: chemicals synthesis and hydrocarbon processing*. American Chemical Society, Washington, DC
15. Baek S-C, Lee Y-J, Jun K-W, Hong SB (2009) *Energy Fuels* 23:593–598
16. Chen D, Moljord K, Holmen A (2012) *Microporous Mesoporous Mater* 164:239–250
17. Min H-K, Park MB, Hong SB (2010) *J Catal* 271:186–194
18. Wang P, Huang L, Li J, Dong M, Wang J, Tatsumi T, Fan W (2015) *RSC Adv* 5:28794–28802
19. Huang L, Wang P, Li J, Wang J, Fan W (2016) *Microporous Mesoporous Mater* 223:230–240
20. Chen J, Liang T, Li J, Wang S, Qin Z, Wang P, Huang L, Fan W, Wang J (2016) *ACS Catal* 6:2299–2313
21. Mei C, Wen P, Liu Z, Liu H, Wang Y, Yang W (2008) *J Catal* 25:8243–8249
22. Zaidi HA, Pant KK (2004) *Catal Today* 96:155–160
23. Qi L, Wei Y, Xu L, Liu ZM (2015) *ACS Catal* 5(7):3973–3982
24. Pérez-Uriarte P, Gamero M, Ateka A, Díaz M, Aguayo AT, Bilbao J (2016) *Ind Eng Chem Res* 55(6):1513–1521
25. Beeckman JW, Froment GF (1979) *Ind Eng Chem Fundam* 18(3):245–256
26. Beeckman JW, Froment GF (1982) *Ind Eng Chem Fundam* 27:243–250
27. Benito PL, Gayubo AG, Aguayo AT, Olazar M, Bilbao J (1996) *Ind Eng Chem Res* 35:3991–3998
28. Schulz H (2010) *Catal Today* 154:183–194
29. Bleken FL, Barbera K, Bonino F, Olsbye U, Lillerud KP, Bordiga S, Beato P, Janssens TVW, Svella S (2013) *J Catal* 307:62–73
30. Brogaard RY, Weckhuysen BM, Nørskov JK (2013) *J Catal* 300:235–241
31. Ramasamy KK, Gerber MA, Flake M, Zhang H, Wang Y (2014) *Green Chem* 16(2):748–760
32. Palumbo L, Bonino F, Beato P, Bjørgen M, Zecchina A, Bordiga S (2008) *J Phys Chem C* 112:9710–9716
33. Li M, Zhou Y, Ju C, Fang Y (2016) *Appl Catal A* 512:1–8
34. Wan W, Fu T, Qi R, Shao J, Li Z (2016) *Ind Eng Chem Res* 55(51):13040–13049
35. Wan Z, Wu W, Li GK, Wang C, Yang H, Zhang D (2016) *Appl Catal A* 523(5):312–320
36. Meng F, Wang Y, Wang S (2016) *RSC Adv* 6:58586–58593

37. Bjørgen M, Joensen F, Holm MS, Olsbye U, Lillerud K-P, Svelle S (2008) *Appl Catal A* 345:43–50
38. Ahmadpour J, Taghizadeh M (2015) *C R Chim* 18(8):834–847
39. He Y, Liu M, Dai C, Xu S, Wei Y, Liu Z, Guo X (2013) *Chin J Catal* 34:1148–1158
40. Wang X, Gao X, Dong M, Zhao H, Huang W (2015) *J Energy Chem* 21(4):490–496
41. Fattahi M, Behbahani RM, Hamoule T (2016) *Fuel* 181:248–258
42. Sadeghi S, Haghighi M, Estifae P (2015) *J Na. Gas Sci Eng* 24:302–310
43. Dagle RA, Lizarazo-Adarme JA, Lebarbier Dagle V, Gray MJ, White JF, King DL, Palo D (2014) *Fuel Process Technol* 123:65–74
44. Wang C, Zhang D, Fang C, Ge Q, Xu H (2014) *Fuel* 134:11–16