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Promoted Mo/H-ZSM-5 Catalysts for Methane Dehydroaromatization: from Powder to Extruded Material

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Abstract

To bridge the gap between research and technical catalysts for methane dehydroaromatization (MDA), a procedure for producing extruded promoted Mo/ZSM-5 catalysts was developed. The influence of the type (M = Fe, Co, Ni) and content (0.1–1 wt.%) of the promoter on the textural, structural, electronic and redox characteristics and catalytic properties of 2Mo/ZSM-5 sample in MDA was studied and optimal composition of promoted M–2Mo/ZSM-5 catalyst was selected. The optimized 0.5Co–2Mo/ZSM-5 catalyst was formed into cylindrical extrudates with a diameter of 4.8 mm and a length of 5.5 mm. The mechanical crushing strength, physicochemical and catalytic properties of the extrudates were regulated by changing the chemical composition (Ca-montmorillonite, SiO₂ sol) and content (10–30 wt.%) of the binder, as well as the order of introduction of the metal active component (before or after extrusion). The characteristics of the as-synthesized and spent extruded 0.5Co–2Mo/ZSM-5 catalysts were studied using low-temperature nitrogen adsorption, powder X-ray diffraction, electron microscopy, ultraviolet-visible diffuse reflectance spectroscopy, IR spectroscopy of adsorbed CO, temperature-programmed reduction and thermal analysis. The optimal formula for the extruded material and the method for producing it were found. The composite containing 80 wt.% 0.5Co–2Mo/ZSM-5 catalyst and 20 wt.% Ca-montmorillonite binder is characterized by high mechanical crushing strength and suitable catalytic properties in the MDA reaction.

1. Introduction

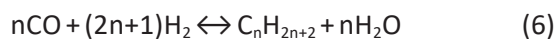
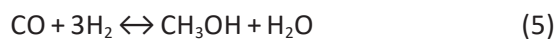
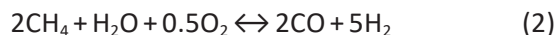
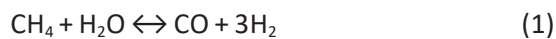
Responsible consumption of coal, oil, and natural gas helps preserve their reserves for future generations and reduce their negative environmental impact. However, the fossil fuel sector currently accounts for almost a third of anthropogenic methane emissions, which in 2024 amounted to 120 million tons (Mt) [1]. In addition, comparable methane losses occur during gas flaring: around 110 Mt of associated gas was flared at upstream oil and gas facilities

and LNG liquefaction plants in 2024 [2]. Therefore, addressing methane emissions and flaring by developing technologies for gas capture and its utilization is an urgent problem [3,4].

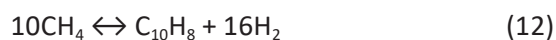
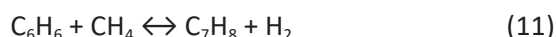
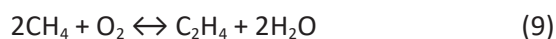
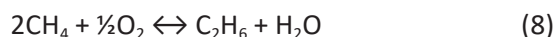
Chemical processing of methane into high-value-added chemical products is a promising way of using methane [5]. Syngas (a mixture of H₂+CO with a molar ratio H₂/CO = 0.5–4.5) is the main product of methane conversion via steam (reaction 1) or autothermal (reaction 2) reforming. It is used as feedstock for the production of hydrogen (reactions 1–3), methanol (reactions 4, 5), and higher hydrocarbons (reactions 6, 7).

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Along with traditional multi-stage processes, methods are being developed for the direct catalytic conversion of methane into valuable products such as C_2 hydrocarbons by oxidative coupling of methane (reactions 8, 9), aromatic hydrocarbons and hydrogen by dehydroaromatization of methane (reactions 10–12), and nanostructured carbon materials (nanotubes, nanofibers) by decomposition of methane (reaction 13) [6–9].



Methane dehydroaromatization (MDA) is endothermic and equilibrium-limited process with a quite high reaction temperature $700\div 800^\circ\text{C}$. The yield of aromatic products is low, amounting to 8–12%. Benzene predominates among the aromatic hydrocarbons formed; toluene and naphthalene are also produced. Lowering the methane aromatization temperature to $550\text{--}650^\circ\text{C}$ is possible by converting methane in the presence of additional reagents, such as light alkanes [10–12]. The catalysts for this

process are zeolites (H-ZSM-5, H-ZSM-11, BEA) modified with metals (Zn, Ga, Mo, Cu) [10]. In this case, the main pathway of methane incorporation into aromatics involves the alkylation of aromatic molecules, produced from C_{3+} hydrocarbons, by methane [12]. It should be noted that a number of processes for the aromatization of light C_{3+} hydrocarbons have been implemented in the industry. In particular, the Cyclar Process allows the conversion of propane, butane, or liquefied petroleum gas (LPG) into aromatic hydrocarbons and hydrogen. Unlike MDA, the aromatization of light C_{3+} hydrocarbons proceeds under relatively mild conditions ($450\text{--}550^\circ\text{C}$, $0.3\text{--}0.7\text{ MPa}$) and is characterized by a high yield of aromatic hydrocarbons (benzene, toluene, xylene) of ~ 65 wt.% [13]. As a rule, Ga-, Zn-, and Pt-modified MFI-type zeolites are used as catalysts [14–16]. Controlled multi-element modification of H-ZSM-5 was shown to be an effective strategy for tuning the catalyst properties and its efficiency in aromatization of light alkanes [17].

As in the case of the aromatization of light C_{3+} hydrocarbons, zeolites modified with transition metals are the most efficient catalytic systems for MDA process, with the Mo/ZSM-5 system being the unrivaled leader. The generally accepted bifunctional mechanism is that on the Mo active site, C–H bond activation and C–C coupling occur with the formation of C_2 hydrocarbons, which is further propagated to aromatic products over the Brønsted acid sites of H-ZSM-5. Alternatively, the hydrocarbon pool mechanism is proposed, in which benzene is derived from secondary reactions of confined in zeolite channels polyaromatic carbon species with the initial products of methane activation [18]. In both cases (Fig. 1), Mo-containing species (Mo(oxy)carbide or atomically dispersed Mo centers anchored to the zeolite framework) localized in the zeolite channels are methane activation centers [19–21].

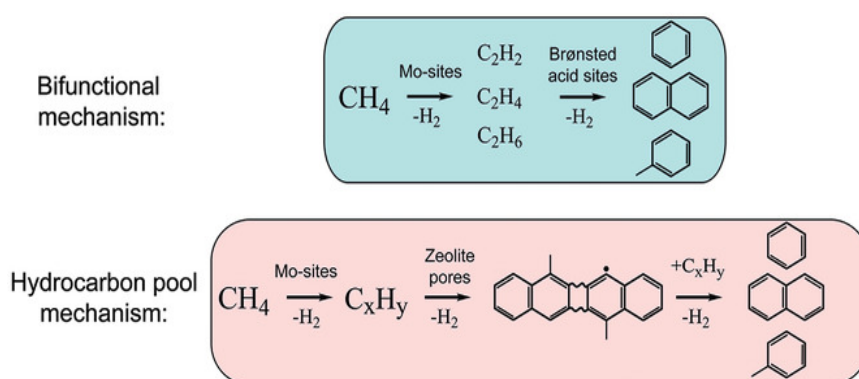


Fig. 1. Two proposed reaction mechanisms for the MDA reaction [18].

A serious problem in MDA is the low degree of methane conversion in one pass and the high rate of formation of carbon deposits, which leads to rapid catalyst deactivation. In this regard, various approaches are being developed to overcome these drawbacks: silanization or dealumination of the outer surface of the zeolite, promotion, optimization of the porous structure, as well as the synthesis method and composition of the samples [22–28]. It is also inevitable that the process should be carried out in a reactive-regenerative mode [23, 29–31].

A separate important task is to develop a method for producing the technical catalyst for MDA, having a shape (granules, extrudates or monoliths) that will be suitable for use at the pilot and industrial levels [32]. Typically, the composition of technical catalysts includes a binder (clays, alumina sol and/or silica sol), the introduction of which allows for the production of a extrusion mass with the required rheological properties, and then for the formation and shaping of the catalyst, achieving its required characteristics for large-scale application [33, 34]. The content and composition of the binder, as well as the molding methods, affect the catalytic properties of materials and their resistance to coking [35–39]. It was shown that the extruded Mo catalyst (extrudates of cylindrical shape with a diameter of 1.6 mm and a length of 4–6 mm) containing 30 wt.% binder (peptised pseudoboehmite) provides lower methane conversion (6.3 vs. 14.1% at 750 °C and reaction time of 20 min) and benzene yield (3.4 vs. 6.7%) compared to the granulated catalyst without a binder [35]. In addition of dilute effect of the binder addition, the sample with a binder is characterized by lower acidity. Furthermore, the molybdenum deposition by impregnation of the shaped with binder H-ZSM-5 leads to its stabilization also on the binder surface, which reduces the concentration of active Mo species. In another study [36], the binder additive (20 wt.% SiO_2 + 40 wt.% clay) to Mo/ZSM-5 sample functioned mainly to enhance the polyaromatization of formed aromatics to coke on their external surfaces and consequently lower the benzene formation activity and selectivity of the catalyst. According to [37], using SiO_2 sol as a binder may result in a more active extruded Mo/ZSM-5 catalyst (cylindrical pieces with dimensions of 1 mm × 2 mm) than using Al_2O_3 -precursor as a binder, since the latter creates additional strong Brønsted acid sites, which promoted coke formation, and meanwhile decreased the aromatic yield. It was reported that the optimal manufacturing procedure of extruded NiO-Mo/ZSM-5 catalyst (extrudates of cylindrical shape with a diameter of

2 mm and a length of 4 mm) included silylation of H-ZSM-5, Mo loading by a rotary ball milling method, modification by adding bulk NiO through physical mixture, and molding using an inorganic binder (acid peptized pseudoboehmite sol, silica sol, and kaolin contents at 15, 10, and 10 wt.%, respectively) [38]. To prevent the migration of MoO_3 from its primary support H-ZSM-5 onto the binder, the carburization of Mo/ZSM-5 prior to its mixture with any of the binders was proposed, that improved the activity of the final catalysts [39].

Since the catalyst composition, binder properties, and extrusion conditions collectively determine the material's final functional properties, a systematic approach integrating formulation development and molding remains highly desirable. So, our work is devoted to the development of the optimal composition and method for manufacturing a technical form of a promoted Mo/ZSM-5 catalyst and elucidation of composition–properties–activity correlation by studying sample activity in MDA reaction and their characteristics using low-temperature nitrogen adsorption, powder X-ray diffraction, electron microscopy, ultraviolet-visible diffuse reflectance spectroscopy, IR spectroscopy of adsorbed CO, X-ray photoelectron spectroscopy, temperature-programmed reduction and thermal analysis. This work on the development of effective nanostructured metal-zeolite catalysts is a continuation of the scientific work initiated by Z.R. Ismagilov, K.D. Dosumov and Z.A. Mansurov [27, 40–43], and carried out with the aim of creating a technology for converting natural and associated petroleum gas into valuable chemical products. This technology is in demand both in Russia and Kazakhstan. The main novelty of this study lies in the comprehensive optimization of the extruded Mo/ZSM-5 catalyst, simultaneously balancing promotion, binder selection, and the extrusion procedure to achieve enhanced performance. Furthermore, the fabrication process utilizes readily available domestic raw materials, making the developed methodology highly feasible for scale-up and potential commercial application.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of powder catalysts M–2Mo/ZSM-5 (M = Fe, Co, Ni)

Powder catalysts M–2Mo/ZSM-5 (M = Fe, Ni, Co) were prepared by sequential wetness impregnation method using powder zeolite H-ZSM-5 (molar ratio

Si/Al = 17) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ as initial reagents. The Mo content was constant and equal to 2 wt.% while M content was varied and equal to 0.1, 0.5 and 1 wt.%. The H-ZSM-5 was previously calcined at 500 °C for 4 hours. The thermal treatment of the catalysts included drying at 90 °C for 4 h and subsequent calcination at 500 °C for 4 h after each impregnation.

2.1.2. Preparation of extruded samples

The extruded samples in the form of cylinders with a diameter of 4.8 mm and a length of 5.5 mm were prepared by mixing powder catalyst 0.5Co–2Mo/ZSM-5 (mode 1) or powder zeolite H-ZSM-5 (mode 2) with a binder (suspension of the calcium form of montmorillonite $\text{Ca}_{0.2}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}$ (CaM) or colloidal silicasol (SiO_2)), and then the mixture was extruded, dried at 100 °C for 4 h and calcinated at 500 °C for 4 hours. The content of the binder was varied from 10 to 30 wt.%.

In case of mode 2 the loading of Mo and Co was carried out by sequential wetness impregnation of the obtained extruded zeolite H-ZSM-5 with an aqueous solution of the corresponding salts, similar to the procedure described for the powder zeolite H-ZSM-5.

Unless otherwise specified, extrudates were manufactured using mode 1.

2.2. Catalyst characterization

Samples were studied using a set of methods: low-temperature nitrogen adsorption on Micromeritics ASAP 2400 instrument (Micromeritics, Norcross, GA, USA), X-ray phase analysis (XRD) on the diffractometer (Freiberger Präzisionsmechanik, Freiberg, Germany) with $\text{CoK}\alpha$ radiation ($\lambda = 1.79021 \text{ \AA}$), transmission electron microscopy (TEM) using a JEM-2010 (JEOL Ltd., Tokyo, Japan), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DR) on a Shimadzu UV-2501 PC spectrophotometer with an ISR-240 A diffuse reflectance attachment, IR spectra on a BOMEM MB 102 FTIR spectrometer (Quebec, Canada), temperature-programmed hydrogen reduction (H_2 -TPR) on a setup equipped with a flow reactor and a thermal conductivity detector and simultaneous thermal analysis (thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTGA), differential thermal analysis (DTA)) using a Q-1500 D (Hungary). A more detailed description of the equipment and analysis conditions is provided in our previous publications [40, 41, 44, 45].

2.3. Catalyst testing

The catalyst testing was carried out in a flow quartz reactor (internal diameter 9 mm) at atmospheric pressure, at 700 °C, flow rate 810 ml(STP)/(cm³·h) (for powder catalysts) and 570 ml(STP)/(cm³·h) (for extruded catalysts) of 90 vol.% CH_4 and 10 vol.% Ar unless otherwise stated (STP: 1 atm and 25 °C). For the catalytic activity testing, a 600 mg sample with a grain size of 250–500 μm was used. To achieve this, the powder catalysts were pressed into tablets and then crushed to isolate a fraction with a grain size of 250–500 μm . Extruded catalysts were crushed to isolate the target 250–500 μm fraction, thereby eliminating diffusion limitations. Initially, the catalyst was treated in situ at 700 °C for 1 h in Ar flow. The composition of the reaction mixture was analyzed by gas chromatography on a Kristall 2000M chromatograph with a flame ionization detector and a thermal conductivity detector [46].

3. Results and discussion

3.1. Physicochemical and catalytic properties of powder catalysts M–2Mo/ZSM-5 (M = Fe, Co, Ni)

As noted above, modifying the composition of the Mo/ZSM-5 catalyst by introducing additives is one of the most effective approaches to improving the methane dehydroaromatization process [24, 28, 47]. The metals Fe, Ni, and Co, which exhibit activity in the conversion of methane and light hydrocarbons, were selected as promoters for Mo/ZSM-5 catalysts with Mo content of 2 wt.% and molar ratio Si/Al of 17. According to our previous detailed research [41, 42, 46, 48], compared with Mo/ZSM-5 catalysts with Mo content of 1, 5 or 10 wt.%, the 2Mo/ZSM-5 sample exhibits higher activity, stability, and ability to operate in the reaction-regeneration mode. At higher Mo content, the proportion of Mo species stabilized on the zeolite surface increases, and during the oxidative regeneration of the spent catalyst, undesirable formation of aluminum molybdate is observed, which leads to irreversible deactivation of the catalyst. Increasing the Si/Al molar ratio (17 $\rightarrow$ 45) results in a decrease in the process efficiency due to a lower concentration of Brønsted acid sites [42, 46, 48].

According to low-temperature nitrogen adsorption data, the prepared M–2Mo/ZSM-5 catalysts are characterized by a specific surface area (S_{BET}) of 315–340 m²/g, which is close to S_{BET} of unmodified 2Mo/ZSM-5 (333 m²/g), initial H-ZSM-5 (336 m²/g) and literature data for such materials [47]. There is

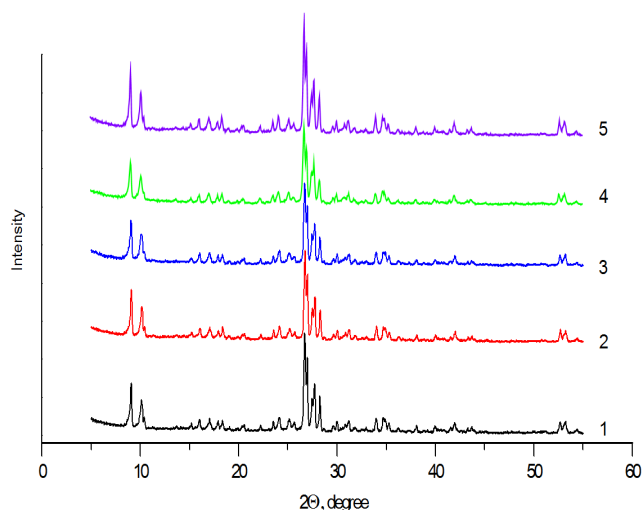


Fig. 2. XRD patterns for H-ZSM-5 (1), 2Mo/ZSM-5 (2), 1Fe-2Mo/ZSM-5 (3), 1Co-2Mo/ZSM-5 (4) and 1Ni-2Mo/ZSM-5 (5) samples before MDA reaction.

a tendency for S_{BET} ($333 \rightarrow 315 \text{ m}^2/\text{g}$) and total pore volume ($0.19 \rightarrow 0.14 \text{ cm}^3/\text{g}$) to decrease with increasing M content ($0.1 \rightarrow 1.0 \text{ wt.}\%$), which is due to the blocking of zeolite pores by particles of deposited metal oxides. Type of M promoter has no effect on textural characteristics.

The X-ray diffraction patterns of the M-2Mo/ZSM-5 samples before reaction are identical to each other (Fig. 2) and correspond to the structure of zeolite H-ZSM-5 (triplet at $2\theta = 26.7^\circ, 27.7^\circ, 28.3^\circ$) given in [49]. The preservation of the zeolite structure after Mo and M loading is confirmed by the same crystallinity degree of H-ZSM-5 and the M-2Mo/ZSM-5 catalysts. The size of the coherent scattering region for zeolite crystallites is the same for the studied samples and is $750 \text{ \AA}$. The absence of reflections in the X-ray diffraction patterns corresponding to metal-containing phases indicates their highly dispersed state. This is quite expected, since usually traces of oxide phases of transition metals in a support matrix with a specific surface area of more than $70 \text{ m}^2/\text{g}$ are detected at a metal content of about 5–10 wt.% [50].

Figure 3 shows the UV-vis DR spectra of M-2Mo/ZSM-5 samples before the MDA reaction. Based on the bands observed in the spectra [51–54], it can be concluded that molybdenum and iron cations are stabilized predominantly in the form of oxide particles MoO_3 and Fe_2O_3 , respectively. After the Ni loading into the 2Mo/ZSM-5 sample, an absorption band appears with a maximum at 13700 cm^{-1} and two shoulders at 12400 and 15200 cm^{-1} , which are due to d-d transitions of Ni^{2+} cations in the octahedral oxygen coordination. These Ni^{2+}OH cations

most likely stabilized in the ion-exchange positions of the H-ZSM-5 zeolite, which was also previously observed for the Y-type zeolite modified with Ni^{2+} cations [55]. However, the location of $\text{Ni}^{2+}_{\text{OH}}$ cations in the MoO_3 particles is also possible [56]. Co-modified 2Mo/ZSM-5 sample shows triplet of absorption bands at $17400, 18900, 19700 \text{ cm}^{-1}$ and shoulder at 13500 cm^{-1} . Their energy corresponds to d-d transitions of Co^{2+} cations in the octahedral and tetrahedral oxygen coordination [52–54]. The $\text{Co}^{2+}_{\text{OH}}$ cations are most likely located in the ion-exchange positions of the H-ZSM-5 zeolite [53, 57], although their presence in CoMoO_4 is also possible [58].

In the FTIR spectra of adsorbed CO at -196°C for H-ZSM-5 zeolite, bands are observed in the region of $2129\text{--}2142, 2167,$ and 2174 cm^{-1} , which are caused by vibrations of capillary-condensed CO and CO interacted with OH-groups of AlOHSi sites, respectively [59]. In addition, bands are present at 2191 and 2208 cm^{-1} , corresponding to vibrations of CO adsorbed on Lewis acid sites (LAS) Al^{3+} and indicating the presence of extraframework aluminum. Figure 4 shows the IR spectra of CO adsorbed on the surface of the 1Co-2Mo/ZSM-5 catalyst recorded at temperatures of $25, -100, -170,$ and -196°C . It can be seen that the bands that were observed in the spectrum for the unmodified zeolite are retained ($2166, 2173, 2186$ and 2209 cm^{-1}), and an additional band appears, corresponding to the vibrations of CO adsorbed on the LAS Co^{2+} (2196 cm^{-1}) [60, 61]. Thus, the catalysts contain two types of hydroxyl groups, as well as strong LAS, characterized by CO vibration frequencies above 2200 cm^{-1} , and intermediate-strength LAS, characterized by CO vibration frequencies at 2186 and 2196 cm^{-1} .

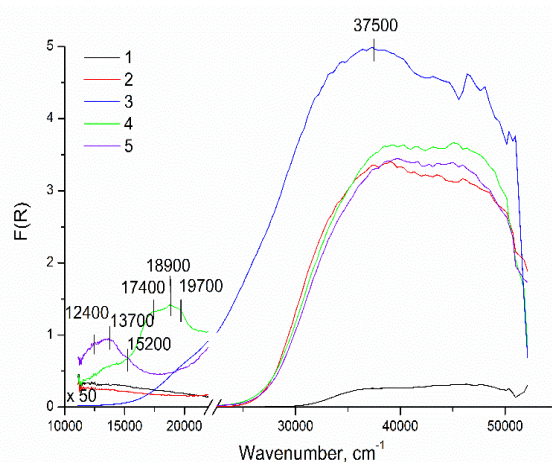


Fig. 3. UV-Vis DR spectra for H-ZSM-5 (1), 2Mo/ZSM-5 (2), 1Fe-2Mo/ZSM-5 (3), 1Co-2Mo/ZSM-5 (4) and 1Ni-2Mo/ZSM-5 (5) samples before MDA reaction.

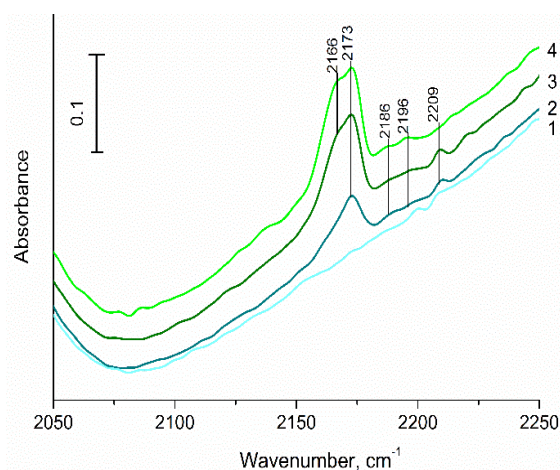


Fig. 4. FTIR spectra of adsorbed CO (2.5 Torr) on the surface of 1Co-2Mo/ZSM-5 catalyst before MDA reaction. Temperatures: 1 – 25 °C; 2 – -100 °C; 3 – -170 °C; 4 – -196 °C.

Crucial characteristics of the MDA catalyst include the concentration and strength of its acid sites; these sites promote the target oligomerization of C_2 hydrocarbons to form aromatic compounds, yet they can also act as centers for carbon deposition [19]. The introduction of modifying additives into H-ZSM-5 partially neutralizes excess Brønsted acid sites (BAS), converting them into milder LAS, which ultimately enhances the stability of the catalytic system. It has been shown that the concentration of acid sites in Mo/ZSM-5 decreases with increasing Mo content because during the preparation and calcination process, molybdenum can diffuse into the channels of the H-ZSM-5 crystal lattice and replace Brønsted protons [62]. Ammonia temperature

programmed desorption (NH_3 -TPD) is a well-established and powerful technique for quantifying both the concentration (total amount) and the strength of acid sites in zeolite-based catalysts [17, 28, 62, 63]. As a rule, the NH_3 -TPD profiles of the H-ZSM-5 samples exhibit two distinct desorption peaks: a low-temperature peak (150–250 °C) attributed to weak acid sites (or physisorbed NH_3 , and a high-temperature peak (350–500 °C) corresponding to the desorption from strong Brønsted and Lewis acid sites. The introduction of Fe, Co and Ni, as well as the binder, will change the acidic characteristics of the 2Mo/ZSM-5 catalyst, which will be the subject of our subsequent research.

According to H_2 -TPR data for M-2Mo/ZSM-5 catalysts, hydrogen consumption occurs over a wide temperature range of 300–900 °C (Fig. 5).

As a rule, the reduction of the bulk MoO_3 phase to the MoO_2 phase occurs in the temperature range of 450–650 °C through the formation of Mo_4O_{11} or other stoichiometrically intermediate phases [64]. The reduction of bulk MoO_2 to Mo by pure hydrogen starts at temperatures above ~600 °C [65]. The reduction to Mo^0 can start before all the MoO_3/Mo_4O_{11} is converted to MoO_2 and the parallel existence of all four phases is possible [66]. The reduction of supported MoO_3 phase is tuned by interaction with the support, and the temperature range of hydrogen consumption depends on both the dispersion and localization of Mo species. In [67], at least five different phases of Mo species were identified, which differ in the form of stabilization and, consequently, in the ability to be reduced. In particular, reducing at 350–570 °C was associated with well-dispersed Mo

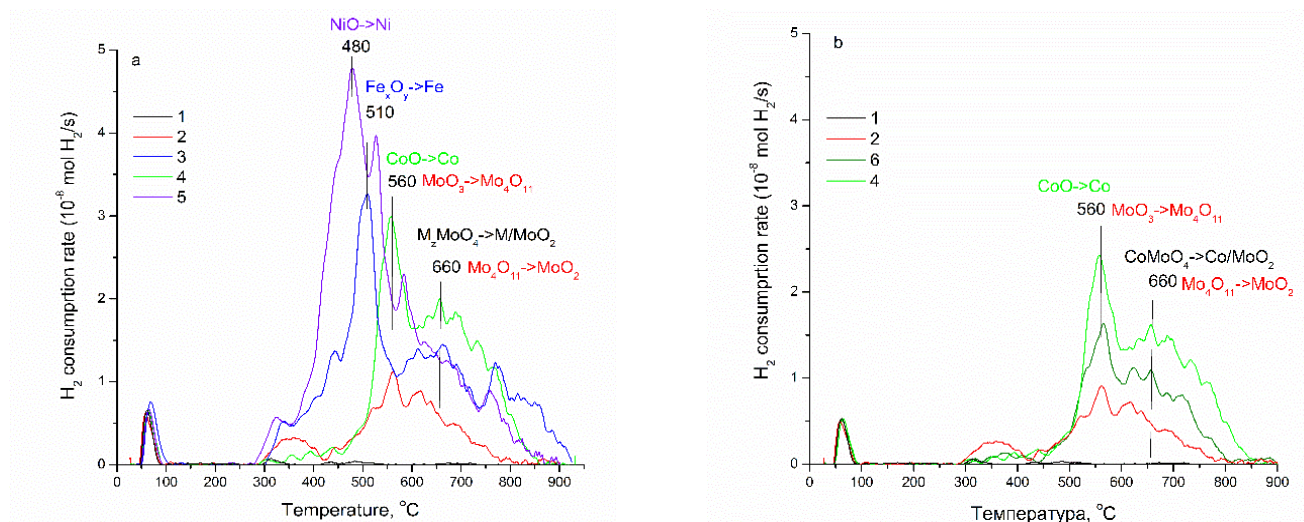


Fig. 5. H_2 -TPR profiles of H-ZSM-5 (1), 2Mo/ZSM-5 (2), 1Fe-2Mo/ZSM-5 (3), 1Co-2Mo/ZSM-5 (4), 1Ni-2Mo/ZSM-5 (5) and 0.5Co-2Mo/ZSM-5 (6) samples before MDA reaction: effect of type (a) and content (b) of M.

monomers located on the external surface of the zeolite; at 570–680 °C – with Mo dimers/polymers located on the external surface of zeolite; at 680–800 °C – with Mo dimers/polymers located in the inner micropores of the ZSM-5; at 800–915 °C – bulk-like phase of MoO_3 located on the external surface of zeolite and at temperatures above 915 °C – well-dispersed Mo monomers located in the inner channels of the zeolite. According to [68], for Mo/ZSM-5 there are a low-temperature region (in the range of 273–380 °C) of hydrogen consumption, associated with the partial reduction of amorphous polymeric molybdate particles; a second region (380–600 °C), attributed to the reduction of MoO_3 to MoO_2 ; a third region (600–900 °C), attributed to the reduction of MoO_2 to Mo^0 ; and a high-temperature region ($T > 900$ °C), associated with the reducibility of $[\text{Mo}_2\text{O}_3]^{2+}$ particles confined within zeolite channels, which are more difficult to reduce. Thus, taking into account the literature data [64–68] and the results of X-ray diffraction (Fig. 2), it can be assumed that in our case the observed hydrogen consumption in a wide temperature range of 300–900 °C for the 2Mo/ZSM-5 catalyst (Fig. 5) may be due to the multi-stage reduction of highly dispersed molybdenum oxide structures localized both on the outer surface of the zeolite crystallites and inside the zeolite channels.

The introduction of M changes the temperature profile of hydrogen consumption (Fig. 5). The behavior of the changes depends on the type and content of M. In the case of Ni, significant hydrogen consumption appears in the low-temperature range (350–550 °C) with a maximum at 480 °C. A similar picture is observed with the introduction of Fe. However, in this case, the peak maximum shifts

to 510 °C. For both metals, a similar hydrogen consumption mode is observed in the high-temperature region of 600–900 °C: compared to the unmodified sample, the intensity of hydrogen consumption is slightly higher. In the case of Co, other changes in the temperature profile of hydrogen consumption are detected (Fig. 5a). Hydrogen consumption is not observed in the region $T < 500$ °C, but in the temperature range of 500–800 °C its consumption increases proportionally to the increase in the Co content (Fig. 5b). Taking into account the literature data [69–71], it can be assumed that changes in the hydrogen consumption profile upon the introduction of M into the composition of 2Mo/ZSM-5 in the temperature range of 400–600 °C are determined by the reduction of M^{n+} cations in the different individual M^{n+} -species, while in the temperature range of 600–900 °C is largely associated with the reduction of the phases of interaction of M^{n+} with MoO_x (for example, M molybdates). The H_2 -TPR results are consistent with UV-Vis DR spectroscopy data.

Figures 6 and 7 present the results of screening promoted catalysts in the MDA reaction. For the studied samples, the methane conversion decreases from 25–30 to 9–13% during the reaction (Fig. 6a). Benzene yield initially increases and reaches a plateau at 5–7% after 75 min of reaction (Fig. 6b). These are typical values and time dependence of MDA process parameters on Mo/ZSM-5 [22, 25]. The type and content of M influence the conversion of methane and the yield of aromatic products (benzene, toluene, naphthalene) (Fig. 7). For each type of additive, the optimal content was found: 1Fe, 0.5Co and 0.1Ni. The highest yields of aromatic products (8.5%) were achieved in MDA over the 0.5Co–2Mo/ZSM-5

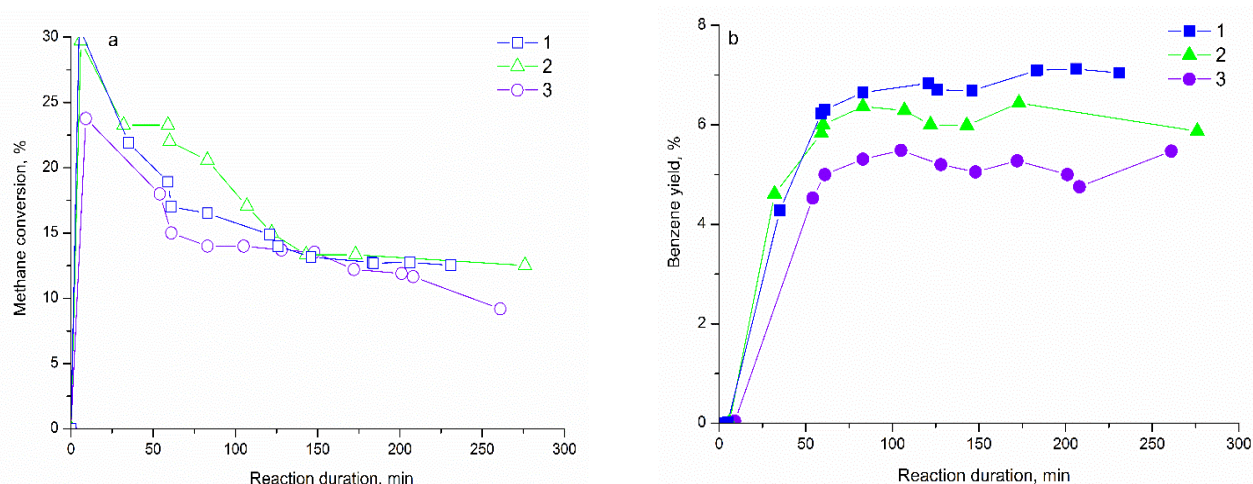


Fig. 6. Methane conversion (a) and benzene yield (b) during MDA over 1Fe–2Mo/ZSM-5 (1), 1Co–2Mo/ZSM-5 (2), 1Ni–2Mo/ZSM-5 (3) catalysts.

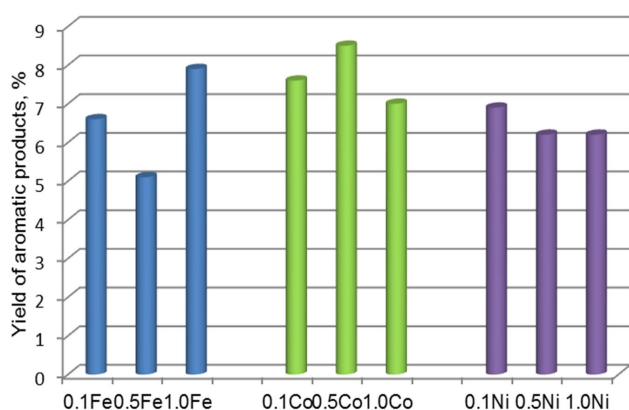


Fig. 7. Yield of aromatic products (benzene, toluene, naphthalene) in MDA over M-2Mo/ZSM-5 catalysts: effect of type (M = Fe, Co, Ni) and content (0.1, 0.5 and 1.0 wt.%) of M.

catalyst. Therefore, this composition was chosen for further development of the recipe for obtaining an extruded form of the catalyst.

The mechanism of Mo/ZSM-5 catalyst promotion by Fe, Co, and Ni depends on the type and metal content, the M/Mo molar ratio, and the Si/Al molar ratio of the H-ZSM-5 zeolite. It has been shown [28, 47, 63–72] that these promoters interact with BAS, decreasing their concentration and thus tuning the impact of the H-ZSM-5 zeolite on C_2 oligomerization into target products, as well as on catalyst coking. In addition, the introduction of a promoter alters the density of anchoring sites required for Mo species stabilization, consequently influencing Mo localization and the concentration of active sites for CH_4 activation. Another key effect is the interaction of promoters with Mo species, leading even to the formation of mixed phases, which further affects the composition and localization of the active centers. Furthermore, all introduced metals are capable of forming MMo (M = Fe, Co, Ni) alloy nanoparticles that catalyze methane cracking to hydrogen and carbon nanotubes or nanofibers. The generated hydrogen can subsequently facilitate the removal of amorphous carbon deposits from the zeolite surface via hydrogenation, thereby preventing pore blockage and enhancing the long-term operational stability of these bimetallic systems. As a consequence, the optimal promoter loading varies due to their diverse and multifunctional modes of action. According to UV-Vis DR spectroscopy data (Fig. 3), in our M-Mo/ZSM-5 catalysts Ni^{2+} cations are predominantly stabilized at the ion-exchange sites of the H-ZSM-5 zeolite, whereas Fe^{3+} cations are primarily localized within oxide particles on the zeolite surface. Cobalt

cations are detected both at the ion-exchange sites and within the surface oxide phases. In addition to different localization, promoters influence the reducing behavior of molybdenum cations (Fig. 5) and, consequently, their ability to form active carbide or oxycarbide species under reaction conditions. Detailed characterization of the promoted samples by NH_3 -TPD and TEM-EDX and X-ray photoelectron spectroscopy (XPS) will help to better understand the mechanism of action of promoters, which will be the subject of our further research.

3.2. Development and optimization of the granulation method

The development of the granulation method included optimizing the binder type (a suspension of calcium form montmorillonite $Ca_{0.2}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot 4H_2O$ (CaM), or colloidal silicasol (SiO_2)) and content (10–30 wt.%), as well as the impregnation mode of the active metal component (before (mode 1) and after (mode 2) extrusion).

In the case of the CaM binder, the strength of the extruded H-ZSM-5 increased (28/85 → 58/150 kg/cm²) with an increase in the binder content from 10 to 30 wt.% (Table 1). At the same time, their moisture capacity decreased (0.67 → 0.42 cm³/g). When using a colloidal SiO_2 solution as a binder, a satisfactory extrusion mixture was obtained only at a binder content of 20 wt.%. At a lower SiO_2 content (10 wt.%), a dry, non-moldable powder was formed, while at a higher content (30 wt.%), the mixture tended to flow. It should be noted that prolonged aging of these extrusion mixtures (24 h vs. 1–3 h) significantly improved the mechanical crushing strength of the extrudates (5/10 → 9/48 kg/cm²). In general, the mechanical crushing strength of extruded H-ZSM-5 zeolite obtained using CaM as a binder was substantially higher than that of extrudates formed using SiO_2 (58/150 vs. 9/48 kg/cm²). It can be concluded that the required content of the binder is 20–30 wt.% in the case of CaM and 20 wt.% in the case of SiO_2 .

The molding of 2Mo/ZSM-5 and 0.5Co-2Mo/ZSM-5 catalysts allows one to obtain extrudates with mechanical crushing strength and moisture capacity close to those of extrudates H-ZSM-5 (Table 1). The higher mechanical crushing strength of extrudates molded using CaM compared to samples granulated using SiO_2 makes the use of CaM as a binder preferable. The impregnation mode has virtually no effect on the mechanical crushing strength and moisture capacity of the extrudates 0.5Co-2Mo/ZSM-5.

Table 1. Physicochemical characteristics of the extruded samples H-ZSM-5, 2Mo/ZSM-5, 0.5Co–2Mo/ZSM-5 before MDA reaction.

Composition of sample, wt. %	Mode of introducing the active component	Mechanical crushing strength, kg/cm ² *	Moisture capacity, cm ³ /g	S _{BET} , m ² /g	V _Σ , cm ³ /g	S _μ , m ² /g	V _μ , cm ³ /g	Phase composition
Extruded H-ZSM-5								
H-ZSM-5**	without active component	–	–	366	0.21	346	0.16	H-ZSM-5
[90(H-ZSM-5) + 10CaM]	without active component	10/20	0.67	–	–	–	–	–
[80(H-ZSM-5) + 20CaM]	without active component	28/85	0.57	308	0.19	281	0.13	H-ZSM-5, CaM
[70(H-ZSM-5) + 30CaM]	without active component	58/150	0.42	272	0.18	243	0.11	H-ZSM-5, CaM
[90(H-ZSM-5) + 10SiO ₂]***	without active component	–	–	–	–	–	–	–
[80(H-ZSM-5) + 20SiO ₂]***	without active component	5/10	0.56	343	0.25	247	0.09	H-ZSM-5
[80(H-ZSM-5) + 20SiO ₂]	without active component	9/48	0.65	–	–	–	–	–
[70(H-ZSM-5) + 30SiO ₂]***	without active component	–	–	–	–	–	–	–
Extruded 2Mo/ZSM-5								
2Mo/ZSM-5**	1	–	–	333	0.19	321	0.15	H-ZSM-5
[80(2Mo/ZSM-5) + 20CaM]	1	24/98	0.65	275	0.19	249	0.12	H-ZSM-5, CaM
[70(2Mo/ZSM-5) + 30CaM]	1	28/72	0.60	249	0.21	214	0.10	H-ZSM-5, CaM
[80(2Mo/ZSM-5) + 20SiO ₂]	1	4/13	0.72	275	0.18	249	0.12	H-ZSM-5
Extruded 0.5Co–2Mo/ZSM-5								
0.5Co–2Mo/ZSM-5**	1	–	–	325	0.20	299	0.14	H-ZSM-5
[80(0.5Co–2Mo/ZSM-5) + 20CaM]	1	24/59	0.64	264	0.17	236	0.11	H-ZSM-5, CaM
[70(0.5Co–2Mo/ZSM-5) + 30CaM]	1	57/189	0.56	232	0.12	232	0.10	H-ZSM-5, CaM
[80(0.5Co–2Mo/ZSM-5) + 20SiO ₂]	1	9/31	0.57	296	0.14	167	0.08	H-ZSM-5
[80(0.5Co–2Mo/ZSM-5) + 20CaM]	2	21/100	0.64	258	0.17	238	0.11	H-ZSM-5, CaM
[70(0.5Co–2Mo/ZSM-5) + 30CaM]	2	21/141	0.56	222	0.12	201	0.10	H-ZSM-5, CaM
[80(0.5Co–2Mo/ZSM-5) + 20SiO ₂]	2	12/52	0.57	315	0.14	188	0.08	H-ZSM-5

* – the mechanical crushing strength on the lateral side and end-on (axial) side, respectively, ** – powder sample for comparison, *** – without prolonged aging of the extrusion mass (24 hours).

However, impregnation by mode 2 leads to some cracking of the extrudates. Thus, it is better to mold pre-synthesized powder catalyst 0.5Co–2Mo/ZSM-5.

According to low-temperature nitrogen adsorption data, the extruded catalysts are characterized by a specific surface area of 220–315 m²/g and pore volume of 0.12–0.18 cm³/g, which is lower than that of powdered materials and depends on the type and content of the binder (Table 1). The degree of deterioration of textural characteristics increases with increasing content of the CaM binder and does not practically depend on the impregnation mode. With the same binder content, the use of SiO₂ for extrusion, compared to CaM, leads to a more significant decrease in the surface area of crystallites (S_{μ}) and volume of micropores.

X-ray diffraction data show that the ZSM-5 zeolite remains the major phase in the extruded samples (Table 1). When using CaM as a binder, the latter, unlike SiO₂, forms a crystalline phase, while SiO₂ forms an X-ray amorphous phase. Increasing the CaM content in the extrudates from 20 to 30 wt.% leads to an increase in the intensity of the corresponding signals. The impregnation mode does not have a noticeable effect on the diffraction curves, i.e. the phase composition of the H-ZSM-5 zeolite and the CaM and SiO₂ binders remains virtually unchanged.

Figure 8 shows the UV-Vis DR spectra for extrudates (before MDA reaction) differing by composition, binder type and impregnation mode. In the spectra of extrudates molded using CaM absorption bands are observed at 20600 and 39300/39700 cm⁻¹, which also appear in the UV-Vis DR spectra of bulk CaM and can be associated with the presence of Fe³⁺ cations in the composition of this binder. In

contrast to the powder Co–Mo/ZSM-5 catalyst, for extrudates, the intense absorption in the visible region by the CaM binder does not allow identification of the forms of stabilization of cobalt cations. The use of SiO₂ binder does not affect the forms of stabilization of the Co cations (Fig. 3, Fig. 8b).

The FTIR spectra of adsorbed CO at -196 °C for 0.5Co–2Mo/ZSM-5 extrudates molded using CaM and SiO₂ as binder show bands at 2175, 2190/2185, 2198/2196 and 2204/2208 cm⁻¹ (Fig. 9), the positions of which are close to those observed for the powder catalyst (Fig. 4). Thus, when a binder is added, the Bronsted acid sites (2175 cm⁻¹) as well as the strong LAS and intermediate-strength LAS are preserved.

Figure 10 shows the H₂-TPR data for powder and extruded materials of different compositions. In the case of H-ZSM-5 (Fig. 10a), the addition of CaM, unlike SiO₂, changes the profile of the hydrogen consumption curve: a peak appears with a maximum at 560 °C. As the CaM content increases, H₂ consumption increases. Since CaM contains iron oxides as an impurity (Fe content is 1.4 wt.%), this H₂ consumption is attributed to their reduction. For the extruded 2Mo/ZSM-5 catalyst obtained using CaM or SiO₂ binders, an increase in H₂ consumption is observed (Fig. 10b). This effect is more pronounced for the sample with CaM binder. Since the SiO₂ binder does not contain iron oxides, we cannot attribute the increase H₂ consumption to its presence in the extruded sample. In the powder sample, the H₂/Mo molar ratio is around 0.5, while for the extruded sample it is approximately 1, which is close to the theoretical value of 1 (MoO₃ + H₂ → MoO₂ + H₂O). It can be argued that the introduction of a binder improves the reducibility of molybdenum cations.

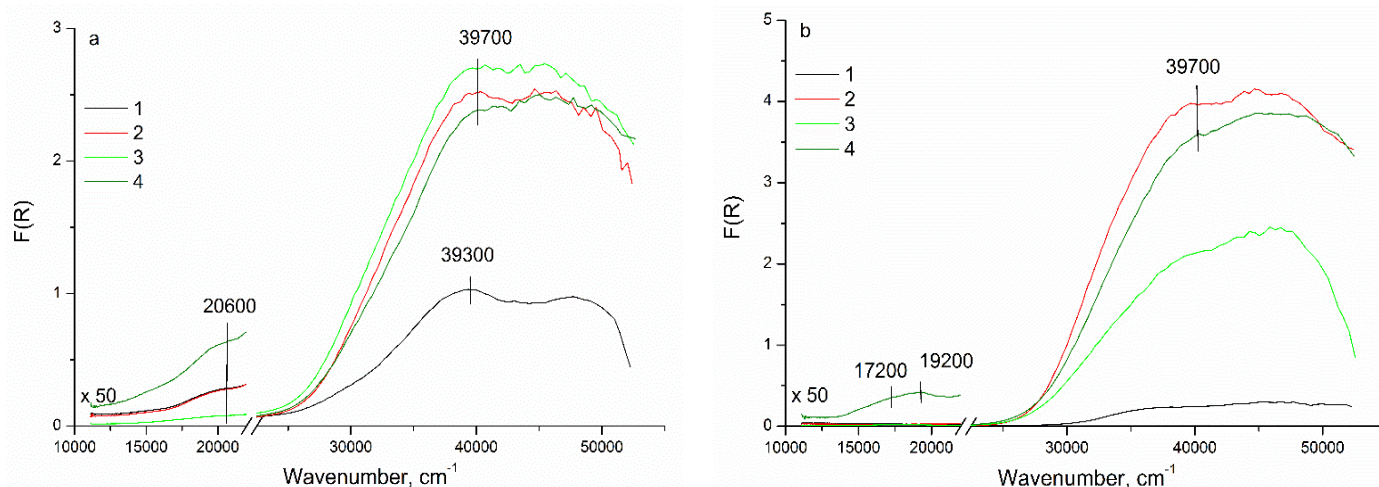


Fig. 8. Spectra of UV-Vis DR for extrudates before MDA reaction: H-ZSM-5 (1), 2Mo/ZSM-5 (2), 0.5Co–2Mo/ZSM-5, impregnation mode 1 (3) and 0.5Co–2Mo/ZSM-5, impregnation mode 2 (4) molded using CaM (a) and SiO₂ (b) as binder. Binder content is 20 wt.%.

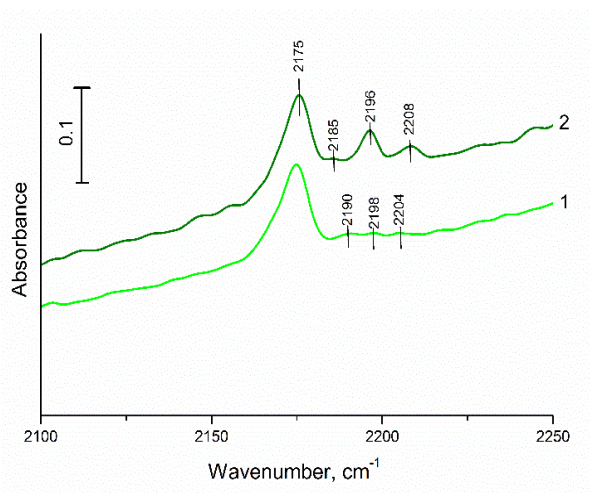


Fig. 9. FTIR spectra of adsorbed CO (2.5 Torr) at -196 °C on the surface of extrudates 0.5Co-2Mo/ZSM-5 (before MDA reaction) molded using CaM (1) and SiO₂ (2) as binder.

It can be assumed that contact with a wet binder and the subsequent calcination procedure contribute to a change in the Mo species and its localization, including the appearance of Mo species on the surface of the binder. Similar changes occur in the case of the extruded 0.5Co-2Mo/ZSM-5 catalyst (Fig. 10c). It should be noted that H₂ consumption increases with increasing binder content in the extrudates. The most significant differences from the powder sample are observed when the active component is loaded after extrusion (Fig. 10c, curves 1 and 4). In this case, it is guaranteed that part of the metal active component will be localized on the surface of the binder. Accordingly, the introduction of the binder alters the metal species, decreasing its concentration on the zeolite and increasing the proportion of species that are reduced by hydrogen during the TPR experiment.

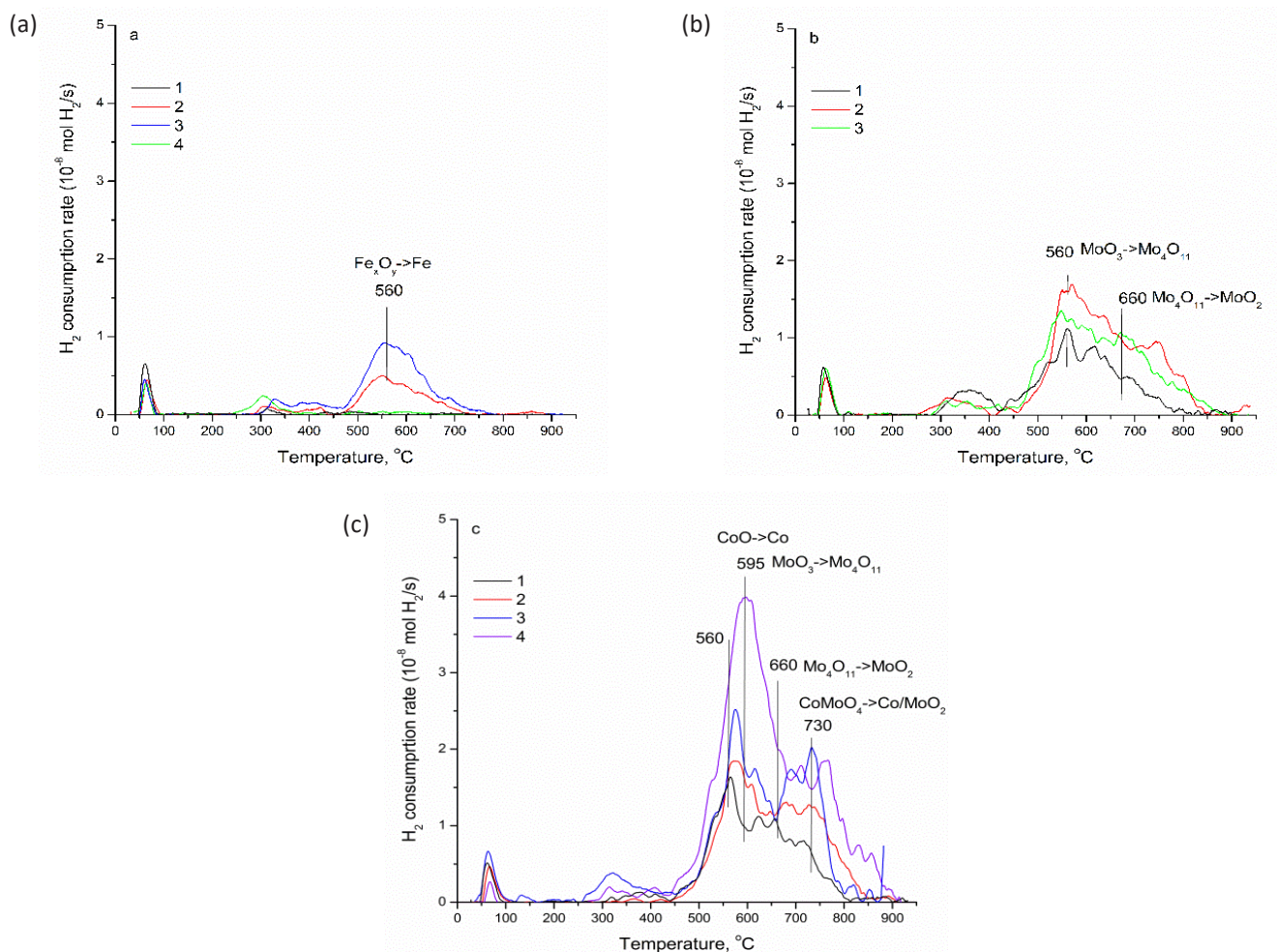


Fig. 10. H₂-TPR profiles of powder and extruded H-ZSM-5 (a), 2Mo/ZSM-5 (b) and 0.5Co-2Mo/ZSM-5 (c) before MDA reaction. Material form and composition: (a) – powder H-ZSM-5 (1), extrudates [80(H-ZSM-5) + 20CaM] (2), extrudates [70(H-ZSM-5) + 30CaM] (3), extrudates [80(H-ZSM-5) + 20SiO₂] (4); (b) – powder 2Mo/ZSM-5 (1), extrudates [80(2Mo/ZSM-5) + 20CaM] (2), extrudates [80(2Mo/ZSM-5) + 20SiO₂] (3); (c) – powder 0.5Co-2Mo/ZSM-5 (1), extrudates [80(0.5Co-2Mo/ZSM-5) + 20CaM] (2), extrudates [70(0.5Co-2Mo/ZSM-5) + 30CaM], impregnation mode 1 (3); extrudates [70(0.5Co-2Mo/ZSM-5) + 30CaM], impregnation mode 2 (4).

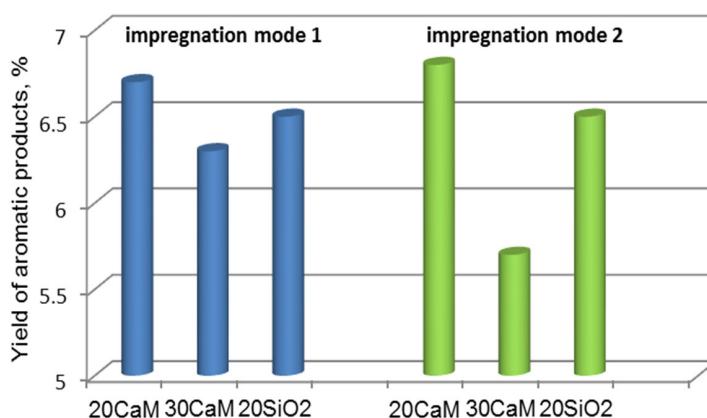


Fig. 11. Yield of aromatic products (benzene, toluene, naphthalene) in MDA over extruded catalysts 0.5Co–2Mo/ZSM-5: effect of type (CaM, SiO₂) and content (20 and 30 wt.%) of binder; impregnation mode.

The study of extruded catalysts in the MDA reaction showed that the time dependences of the process parameters were similar to those observed for powder samples. The extruded 0.5Co–2Mo/ZSM-5 catalysts provide methane conversion at the level of 12–16% and aromatic compound yield in the range of 6–7% (Fig. 11).

Regardless of the method of loading the metal active component, the activity of the samples is improved in the next series of binders: 30CaM < 20SiO₂ < 20CaM. This behavior can be caused by various factors, including pore blocking, diffusion limitations, changes in acidity, metal migration, and interactions between the active phase and the binder. A comparison of the catalytic activity data (Fig. 11) and textural properties (Table 1) of the extruded catalysts reveals that the observed trend is not determined by the specific surface area or pore volume of the samples. Although sample [70(0.5Co–2Mo/ZSM-5) + 30CaM] exhibits lower values of S_{BET} and V_{Σ} , they differ from those of the best-performing catalyst, [80(0.5Co–2Mo/ZSM-5) + 20CaM], by no more than 15%, which is insignificant. The dilution effect is more substantial: the sample with 30 wt.% binder contains a lower proportion of the 0.5Co–2Mo/ZSM-5 catalyst and, consequently, fewer active sites for the MDA reaction. In the case of impregnation mode 2, the situation is exacerbated by the fact that during granule impregnation, the active component is fixed onto both the zeolite and the CaM binder. As a result, the proportion of active sites decreases more sharply, leading to a more pronounced decline in activity (Fig. 11). The difference in activity between samples with identical binder content (20 wt.%) but varying chemical compositions (CaM, SiO₂) is likely due to the different distribution of the active com-

ponent through oxide matrix (H-ZSM-5, binder CaM or SiO₂). Owing to these compositional variations, the migration and anchoring pattern of the Mo-Co active component during molding/impregnation and subsequent calcination and pretreatment differs. This, in turn, determines the proportion of metal located within the zeolite channels and its dispersion on the surface of the oxide matrix, thereby dictating the functional properties of the catalyst. Additional characterization via XPS, TEM, and EDX mapping can elucidate the nanostructure of these extruded catalysts, which will be the focus of our future research.

It can be concluded that the optimal formula of the extruded catalyst is [80(0.5Co–2Mo/ZSM-5) + 20CaM], and the procedure for loading the metal active component is impregnation mode 1. In this case, it is possible to obtain extrudates with sufficient catalytic properties and mechanical crushing strength, avoid their cracking, maintain satisfactory textural characteristics, and reduce the proportion of the metal species on the binder.

3.3. Catalytic properties of extruded catalyst 0.5Co–2Mo/ZSM-5 and its characteristics after the MDA reaction

The optimum [80(0.5Co–2Mo/ZSM-5) + 20CaM] extrudates were tested in the MDA reaction at different reaction times as well as in a reaction-regeneration mode and then characterized using a number of methods. Both methane conversion and benzene yield decreased monotonically with time on stream (Fig. 12). The benzene yield decreased by 50% after 11 h of reaction and was 1.7% after 16 hours. Conversion at the end of the experiment was 4.2%.

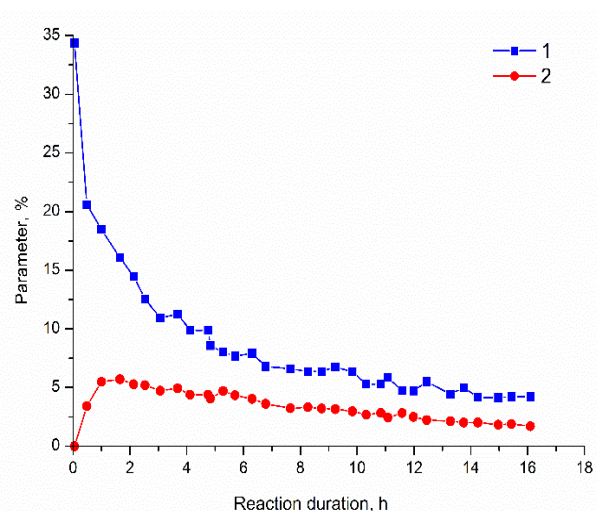


Fig. 12. Methane conversion (1) and benzene yield (2) during MDA over extruded catalyst 0.5Co–2Mo/ZSM-5. Binder type – CaM, binder content – 20 wt.%, impregnation mode 1.

The observed catalyst deactivation is caused by the formation and accumulation of carbonaceous deposits during the MDA reaction [41, 46, 73, 74]. Indeed, thermal analysis data show that the amount of carbon deposits after 4 and 16 h of MDA reaction is 5.5 and 7.7 wt.% respectively (Table 2). According to our previous studies on powder Mo/ZSM-5 catalysts, two types of carbonaceous deposits can be distinguished: those formed as graphite layers with a thickness of 2–3 nm on the surface of Mo₂C nanoparticles that were >2 nm in size, and friable carbonaceous deposits with a thickness of up to 3 nm with a disordered structure on the external surface of the zeolite [46]. Because carbonization of the Mo₂C particle surface occurs within the first minutes of the reaction, the methane activation is catalyzed by 1-nm molybdenum-containing clusters located inside the ZSM-5 channels [74]. The accumulation of friable carbonaceous deposits on the zeolite sur-

face and the degree of their condensation (atomic ratio C/H) increase with time-on-stream. This blocks the zeolite pores and restricts reactant access to the active sites, thereby leading to progressive catalyst deactivation.

Due to the formation of carbon deposits and the resulting deterioration of MDA reaction performance, the process was carried out in reaction-regeneration mode. Regeneration was performed at 610 °C for 3 h in an oxygen flow. The completion of the regeneration process was monitored chromatographically (by the disappearance of CO₂ in the reaction products). Figure 13 shows that the catalytic activity remains practically unchanged during multi-cycle regeneration. After 2 h of reaction, the methane conversion was 12, 14 and 13%, the yield of aromatic compounds was 7, 6 and 6%, respectively, in the first, second and third reaction cycles.

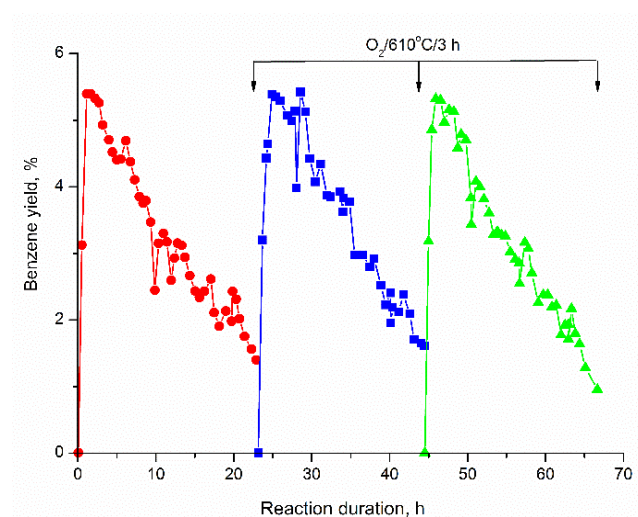


Fig. 13. Benzene yield during MDA at reaction-regeneration mode over extruded catalyst 0.5Co–2Mo/ZSM-5. Binder type – CaM, binder content – 20 wt.%, impregnation mode 1.

Table 2. Physicochemical characteristics of the extruded sample 0.5Co–2Mo/ZSM-5 after various treatments.

Sample	Treatment	S_{BET} , m ² /g	V_{Σ} , cm ³ /g	S_{μ} , m ² /g	V_{μ} , cm ³ /g	Phase composition	Content of carbon deposits, wt.%
Before reaction	500 °C/air/4 h	264	0.17	236	0.11	H-ZSM-5, CaM	–
After pretreatment	700 °C/Ar/1 h	253	0.17	174	0.08	H-ZSM-5	–
After 4 h of reaction	700 °C/MDA/4 h	169	0.12	126	0.06	H-ZSM-5	5.5
After 16 h of reaction	700 °C/MDA/16 h	137	0.11	104	0.05	H-ZSM-5	7.7
After 3 cycles of reaction/regeneration	700 °C/MDA/22 h 610 °C/O ₂ /3 h	263	0.18	179	0.08	H-ZSM-5	–

Table 2 shows physicochemical characteristics of the extruded sample 0.5Co–2Mo/ZSM-5 after various treatments. Pre-treatment of the catalyst in an inert environment at elevated temperatures leads to a decrease in textural characteristics, primarily the volume ($0.11 \rightarrow 0.08 \text{ cm}^3/\text{g}$) and surface area ($236 \rightarrow 174 \text{ m}^2/\text{g}$) of micropores. As a result of the MDA reaction, further deterioration of the textural characteristics of the catalyst occurs, which increases with increasing reaction time. After 16 h of MDA reaction, the specific surface area decreases from 253 to $137 \text{ m}^2/\text{g}$, and the total pore volume from 0.17 to $0.11 \text{ cm}^3/\text{g}$. It should be noted that oxidative treatment during the regeneration process restores the textural characteristics to the values that were obtained after pretreatment (Table 2).

The X-ray phase analysis data shows that the structure of the zeolite H-ZSM-5 is preserved after various treatments, but there are no reflections associated with the CaM phase in the diffraction pattern of the catalyst after pretreatment, reaction, and regeneration. Apparently, pretreatment in an Ar at 700°C leads to the loss of structural water and dehydroxylation of clay [75], which causes partial destruction of the crystal lattice and amorphization of CaM. According to the TEM data, the loaded metallic active component is present in a highly dispersed form both on the surface of the zeolite and on the binder in the fresh and pretreated in Ar catalyst. This is evidenced by the absence of any particles

of phases of Mo and Co compounds in the images and the presence of signals from Mo and Co in the EDX spectra from the zeolite and CaM regions (Fig. 14). Samples after 4 and 16 h of MDA reaction are almost identical in morphology and phase structure. The deposited metals lose their dispersion and form particles. On the surface of the H-ZSM-5 zeolite, molybdenum carbide (Mo_2C) particles with dimensions of about 20 nm are observed, which are surrounded by graphite-like layers with a thickness of up to 20 nm (Fig. 15). Mo clusters localized inside the zeolite channels are also observed. As we demonstrated previously [46], molybdenum carbide particles localized on the outer surface of the zeolite become coated with carbon during the first hours of the reaction and become deactivated. Long-term activity is ensured by molybdenum-containing clusters localized within the zeolite channels.

Inside the layered structure of the CaM binder, particles of CoFe alloy with a size of 5–8 nm are observed (Fig. 15a). Apparently, this localization became possible due to the expansion of layers or their partial destruction. According to EDX data, the composition of the CoFe alloy particles varies – larger particles contain more cobalt than iron. It can be assumed that such metal particles are also formed on the outer surface of CaM, but they are carried away from the surface of CaM by growing carbon nanotubes and nanofibers. The length of fibers and tubes can reach several tens of microns, and the thickness

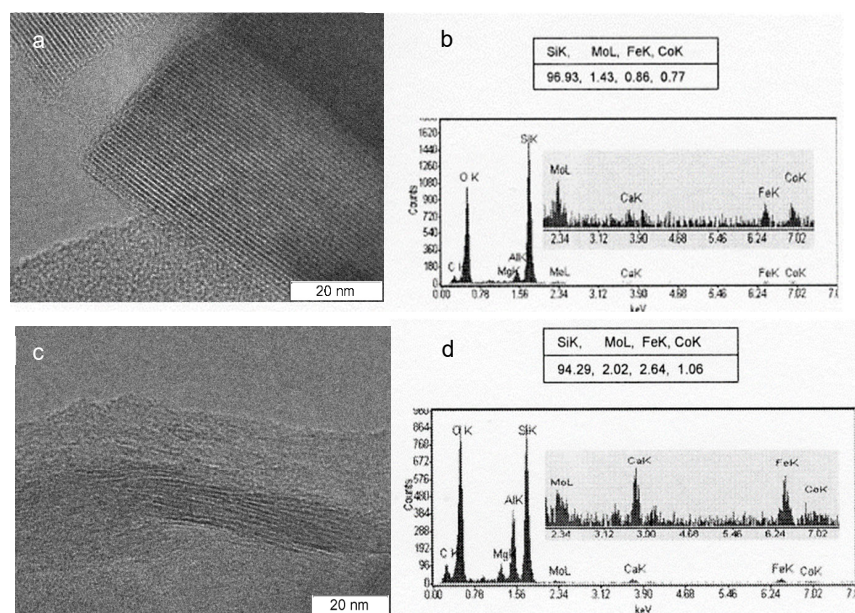


Fig. 14. TEM-EDX data for the extruded sample 0.5Co–2Mo/ZSM-5 after pretreatments in Ar. a – channel structure of ZSM-5 zeolite; b – EDX spectrum of the zeolite; c – CaM stacked layered structure; d – EDX spectrum of the CaM. Inserts show an enlarged portion of the spectrum. The composition of the indicated elements, in atomic %, is shown above.

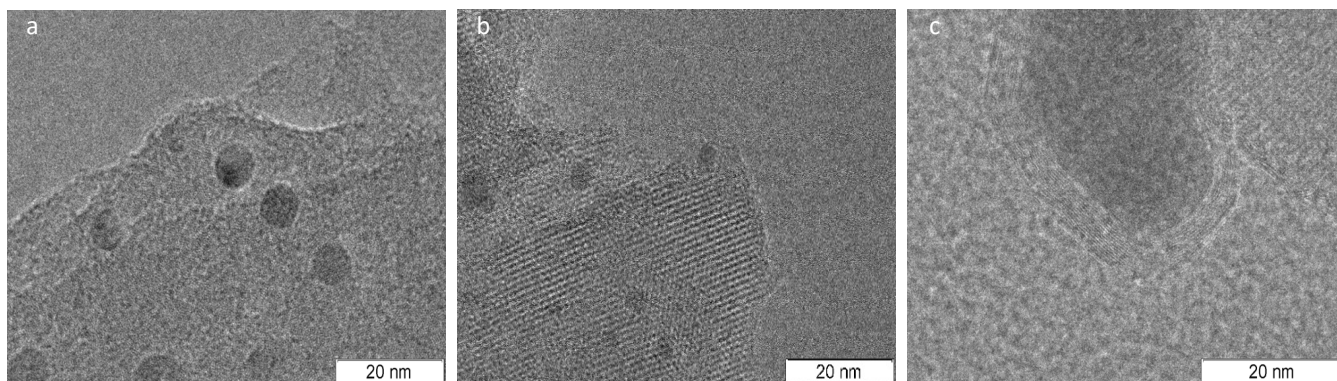


Fig. 15. TEM-EDX data for the extruded sample 0.5Co-2Mo/ZSM-5 after 4 h (a, b) and 16 h (c) in MDA reaction. a – CoFe alloy particles within the layered structure of CaM; b – large Mo_2C particles on the outer surface of the zeolite and Mo clusters localized inside the zeolite channels; c – graphite-like layers on the surface of Mo_2C .

varies from 20 to 100 nm (Fig. 16). According to EDX data, the particles on which carbon nanotubes grow have a composition with a significant predominance of Co, while in the particles on which the nanofibers grow, Fe predominates. Metal particles located at the ends of fibers or tubes have a surface open to reaction with methane, which stabilizes their activity in a side reaction of methane decomposition into carbon and hydrogen. This process increases coking rate but does not interfere with the target reaction [48], which occurs within the zeolite channels (Fig. 1). In addition, the formation of the second useful product of the MDA – hydrogen – occurs.

Carbon formation was more pronounced for the sample with a longer MDA reaction time of 16 hours. Indeed, according to thermal analysis data, with an increase in the duration of the MDA reaction from 4 to 16 h, the amount (5.5 → 7.7 wt.%) and burnout temperature (538 → 556 °C) of carbon deposits increase, which indicates an increase in the degree of their condensation (atomic ratio C/H) [76].

Regeneration of the catalyst resulted in the complete removal of all forms of carbon. The structure of

the ZSM-5 zeolite did not undergo significant changes compared to the state of the original sample, while the layered structure of CaM became defective. Large particles (20–40 nm) with a polycrystalline, defective structure are observed on the ZSM-5 surface. The particles have the shape of a spreading droplet (Fig. 17), indicating strong topochemical interaction between the deposited particle and the support surface. The EDX spectrum indicates their composition with an atomic ratio of Co:Mo≈50:50, which may indicate the formation of an oxide phase of cobalt molybdate CoMoO_4 . The sizes of the particles localized on CaM are 10–15 nm, which exceeds the sizes of Co-Fe particles in the samples immediately after the reaction and indicates their sintering during regeneration. Small cavities and voids (≈10 nm) are observed in the structure of the layered CaM plates of this sample. Their origin can be attributed to the corrosion of the CaM structural packages due to deep interaction with Co-Fe particles. According to EDX data, Co, Fe and Mo are found in the composition of these particles, which indicates the formation of a mixed oxide of these elements.

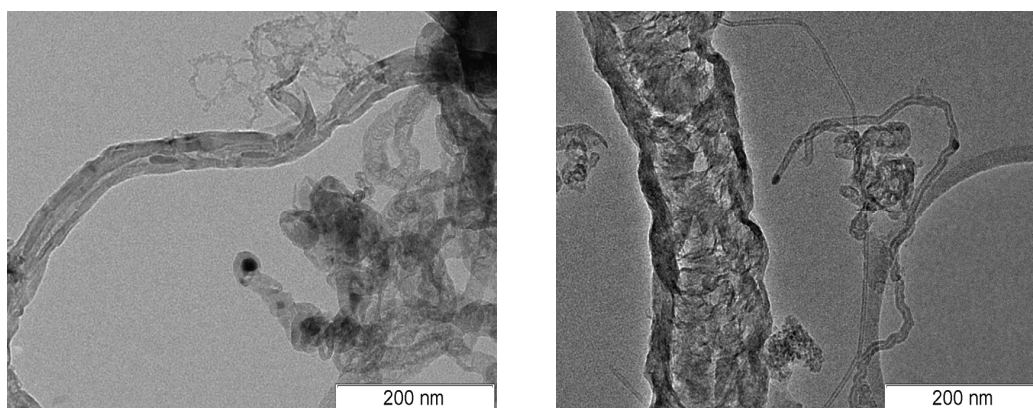


Fig. 16. Different forms of carbon in the extruded sample 0.5Co-2Mo/ZSM-5 after 16 h in MDA reaction.

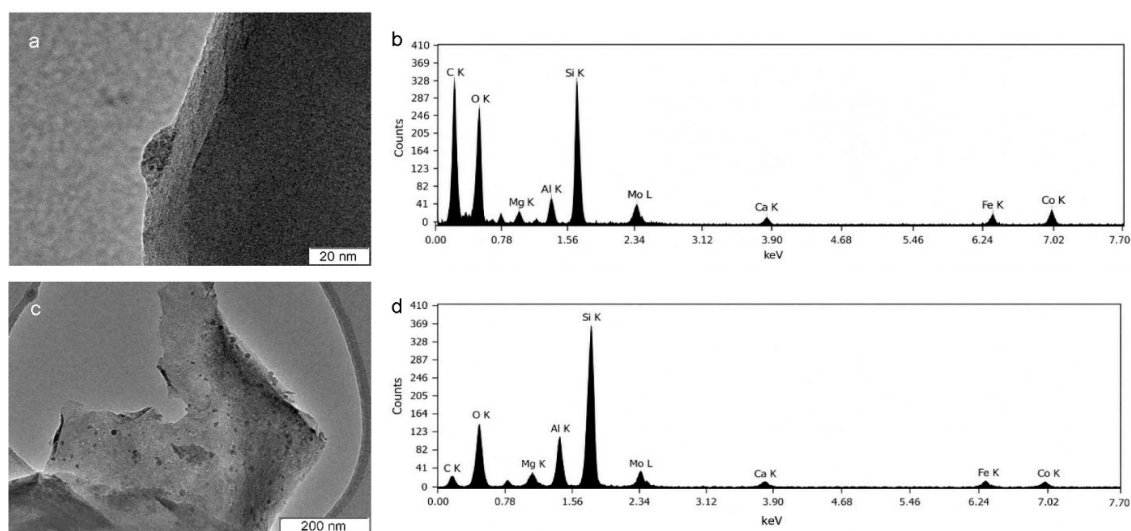


Fig. 17. TEM-EDX data for the extruded sample 0.5Co-2Mo/ZSM-5 after 3 cycles of reaction/regeneration in MDA reaction. a – spreading form of a Mo-Co particle on the outer surface of the zeolite; b – EDX spectrum of the particle in image "a"; c – particles of mixed oxide Co,Fe,Mo-O on the surface of defective CaM; d – EDX spectrum of Co,Fe,Mo-O particles localized on CaM.

Thus, based on the characterization of the fresh, spent, and regenerated extruded catalyst 0.5Co-2Mo/ZSM-5 (Table 2, Figs. 14–17) using a combination of techniques (thermal analysis, N_2 adsorption, XRD, TEM-EDX, etc.), the following model of catalyst evolution during its life cycle can be proposed. Calcination and pretreatment in Ar of the extruded catalyst 0.5Co-2Mo/ZSM-5 lead to undesirable redistribution of metal components and their stabilization as highly dispersed species also on the binder. However, this does not prevent the sample from providing the satisfactory activity during MDA reaction in the reaction-regeneration mode. Under MDA conditions, phase transformations of the supported metal oxides occur: the surface Mo oxide species on the catalyst surface convert into Mo_2C particles covered by graphite-like layers, while Co and Fe (originating from the binder) form a CoFe alloy that catalyzes methane decomposition to yield carbon nanotubes or nanofibers. Mo(Co) clusters localized within the zeolite channels near the Brønsted acid sites of H-ZSM-5 provide the yield of target products. The accumulation of carbon deposits blocks the zeolite micropores and restricts access to the active sites, causing progressive catalyst deactivation with time-on-stream. Regeneration allows the removal of carbon deposits while preserving the structure of the H-ZSM-5 zeolite, but does not return all metal components to a highly dispersed state. In particular, the particle size of mixed oxides localized on the external surface of the zeolite H-ZSM-5 increases from 20 to 40 nm, while on CaM, it increases from

5–8 to 10–15 nm. It should be noted that these metal-containing particles do not directly participate in the formation of target products, but rather act as centers for the formation of carbon deposits and hydrogen. Assuming that the main role in the target reaction is played by Mo clusters localized in the zeolite channels, it can be proposed that their number and state remain practically unchanged in the reaction-regeneration cycles, which ensures the stability of the MDA reaction parameters.

Table 3 presents comparative data on the properties of the formed catalysts for the MDA reaction. It can be seen that the catalyst provides comparable activity values with samples from the literature data.

4. Conclusions

A method for producing extruded catalyst 0.5Co-2Mo/ZSM-5 for the process of direct conversion of methane into aromatic hydrocarbons has been developed. Through a systematic and comprehensive approach, the following conclusions were reached:

1. The type and content of the promoter ($M = Fe, Co, Ni$) influence the conversion of methane and the yield of aromatic products (benzene, toluene, naphthalene) in MDA. For each type of additive, the optimal content was found: 1Fe, 0.5Co and 0.1Ni. The highest yields of aromatic products (8.5%) were achieved in MDA over the 0.5Co-2Mo/ZSM-5 catalyst.

2. Among the binder types and compositions studied, compared to SiO_2 , Ca montmorillonite (20 wt.%) provided the highest micropore volume and

Table 3. Properties of the binder-added catalysts for the MDA reaction.

Catalyst composition	Binder composition	Impregnation mode	Geometric dimensions*, mm	Mechanical crushing strength, N/mm ²	S _{BET} , m ² /g	V _S , cm ³ /g	S _μ , m ² /g	V _μ , cm ³ /g	Phase composition	Carbon accumulation rate, gC/(g _{cat} ·h)	Methane conversion, %	Benzene yield, %	Aromatics products yield, %	Ref.
0.5Co–2Mo/ZSM-5	Ca montmorillonite, 20 wt.%	Impregnation mode 1	4.8x5.5	5.9	264	0.17	236	0.11	H-ZSM-5 CaM	0.0048	13.8	5.7	6.7	This work
4Mo/ZSM-5	Pseudoboehmite, 30 wt.%	Impregnation mode 2	1.6x4-6	n.d.**	313	0.58	n.d.	0.07	H-ZSM-5	n.d.	6.3	3.4	4.8	[35]
NiO–6Mo/ZSM-5	Pseudoboehmite, 15 wt.% + SiO ₂ 10 wt.% + kaolin 10 wt.%	Impregnation mode 1	2x4	2	261	0.16	247	n.d.	n.d.	0.0033	n.d	n.d.	4.1	[38]
6Mo/ZSM-5	SiO ₂ 40 wt.%	Impregnation mode 2	1x2	n.d.	239	n.d.	123	0.06	n.d.	n.d.	7.7	n.d.	2.7	[37]

* – diameter x length of extrudates, ** – no data

mechanical properties, resulting in excellent catalytic performance of the extruded catalyst [80(0.5Co–2Mo/ZSM-5) + 20CaM]. The procedure for loading the metal active component is impregnation mode 1.

3. In the MDA process in the reaction-regeneration mode, the extruded catalyst 0.5Co–2Mo/ZSM-5 provides stable performance from cycle to cycle. The changes occurring in the catalyst under pretreatment, MDA reaction and regeneration conditions were traced using the methods of low-temperature nitrogen adsorption, powder X-ray diffraction, electron microscopy and thermal analysis. It was found that after 16 h of the reaction, the textural characteristics of the catalyst moderately decrease and the size of the Mo-containing phase increases.

4. It was revealed that during the reaction, carbon deposits of graphene layers, nanotubes and nanofibers are formed with a carbon accumulation rate of 4.8 mgC/(g_{cat}·h). The observed changes in the textural and structural properties of the catalyst are not critical, since they do not affect the efficiency of the process, which remained stable (aromatics products yield of 6–7 %) over 3 reaction cycles of 22 h each.

The conducted research indicates the potential of methane conversion technology using the MDA method for preserving this valuable fossil resource and producing aromatic hydrocarbons.

Abbreviation

BAS – Brønsted acid sites
 DTA – differential thermal analysis
 DTGA – differential thermogravimetric analysis
 EDX – energy-dispersive X-ray spectroscopy
 IR spectra – infrared spectra
 H₂-TPR – temperature-programed hydrogen reduction
 LAS – lewis acid sites
 LNG – liquefied natural gas
 LPG – liquefied petroleum gas
 MDA – methane dehydroaromatization
 Mt – million tons
 NH₃-TPD – ammonia temperature programmed desorption
 STP – standard temperature and pressure
 Syngas – synthesis gas (a mixture of H₂+CO)
 TEM – transmission electron microscopy
 TGA – thermogravimetric analysis
 XRD – X-ray phase analysis
 XPS – X-ray photoelectron spectroscopy
 UV-Vis DR – ultraviolet-visible diffuse reflectance spectroscopy

CRedit authorship contribution statement

Zinfer Ismagilov, **Zulkhair Mansurov**, **Kusman Dosumov**: conceptualization. **Ekaterina Matus**, **Ilyas Ismagilov**, **Mikhail Kerzhentsev**: methodology. **Ekaterina Matus**: synthesis. **Mikhail Kerzhentsev**, **Olga Sukhova**, **Tatiana Surovtsova**: formal analysis. **Olga Sukhova**, **Ilyas Ismagilov**, **Svetlana Yashnik**: investigation. **Svetlana Yashnik**, **Ilyas Ismagilov**: data curation. **Ekaterina Matus**: writing – original draft preparation. **Ekaterina Matus**, **Mikhail Kerzhentsev**: writing – review and editing. **Sergey Khairulin**, **Denis Nurmukhametov**: supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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