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Metal/zeolite catalysts of methane dehydroaromatization

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Abstract. Results of studying methane dehydroaromatization over metal/zeolite catalysts have been reviewed. Special attention has focused on molybdenum catalysts based on HZSM-5 zeolites. The effect of catalyst synthesis and reaction conditions on the catalytic properties of the systems has been scrutinized. Information on the mechanism of the process and the nature of active sites has been reported. The bibliography includes 137 references.

I. Introduction

Methane — the major component of natural gas — is currently suggested as an alternative source for producing valuable chemicals.[1–3] The forecasted increase in the use of natural gas as a feedstock for chemical industry is mainly based on the evidence of the higher growth rate of oil prices as compared with that of natural gas prices.[4–6]

Nowadays, methane is mainly used as a fuel. The chemical industry consumes only 2.5% – 5% of produced gas.[4,7] A wider use of methane in the chemical industry is prevented by its high chemical and thermal stability.

Natural gas is converted into organic compounds mainly by means of steam and carbon dioxide reforming[8,9] and oxidative conversion[10] of methane to synthesis gas (a mixture of CO and H_2) with subsequent synthesis of a mixture of alkanes, alkenes, and alcohols by the Fischer – Tropsch method;[1,11] methanol or dimethyl ether.[1,12]

Among one-step methane conversion reactions, noteworthy are the direct insertion of methane into C_3-C_4 hydrocarbons to give mono- and polyaromatic hydrocarbons,[13] oxidative coupling of methane to ethylene or ethane,[14,15] methane pyrolysis and oxypyrolysis[16] and selective oxidation of methane to methanol.[17,18] In the presence of oxygen, the resulting hydrocarbons are readily oxidized to carbon dioxide and water, which considerably reduces the reaction selectivity at high methane conversions. This accounts for the higher prime cost of hydrocarbon feedstock produced from methane as compared with analogues of petroleum origin. In general, processes of one-step conversion of methane are at the level of laboratory research, and exploring new ways of efficient utilization of natural gas is an urgent task.

A promising approach in this context is dehydroaromatization of methane — a method of selective methane conversion directly to aromatic hydrocarbons without oxygen. In the 1990s, Chinese researchers proposed for this process an efficient molybdenum-containing HZSM-5 zeolite catalyst.[19] Non-oxidizing conditions of this reaction ensure the high selectivity for the formation of aromatic hydrocarbons. According to thermodynamic calculations,[20] the equilibrium conversion of methane at 700 °C is 12%, with benzene and naphthalene forming in approximately equimolar amounts.

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Dehydroaromatization of methane to benzene ($6\,CH_4 \rightarrow C_6H_6 + 9\,H_2$) can occur under both oxidative[21] and non-oxidative conditions.[7,19,22–26] However, in the presence of oxygen, the major products are CO and CO_2, and the selectivity of benzene formation on zeolite-supported catalysts is only 3% at 600 °C.[21] The possibility of methane dehydroaromatization under non-oxidative conditions was demonstrated for the first time in the 1980 – 1990s.[7,27] The process was carried out in a pulse mode at 740 °C over Cr/-, Ga/-, Zn/- or Pt – Cr/ZSM-5 catalysts. Thermodynamically, non-oxidative dehydroaromatization of methane to benzene is unfavourable. However, notwithstanding the fact that ΔG for this reaction is zero only at 1075 °C,[28] noticeable amounts of benzene can form even at 700 – 900 °C.[7] Calculation of thermodynamic equilibrium for the reactions presented in Scheme 1 and equilibrium concentrations of the corresponding products in the temperature range 527 – 927 °C (Table 1) has shown that the methane dehydroaromatization reaction in this temperature range is thermodynamically more favourable than the conversion of methane to ethane or ethylene.[7] In particular, the equilibrium conversion of methane to benzene at 727 °C is 13.8%.

Scheme 1

$$6\,CH_4 \longrightarrow C_6H_6 + 9\,H_2$$

$$2\,CH_4 \longrightarrow C_2H_6 + H_2$$

$$2\,CH_4 \longrightarrow C_2H_4 + 2\,H_2$$

The possibility of formation of aromatic products directly from methane with high selectivity suggests the dehydroaromatization of methane as an alternative method of rational utilization of natural gas. At present, the best catalysts for methane dehydroaromatization are molybdenum-containing zeolites Mo/ZSM-5.[23,25] In addition, as follows from Scheme 1, the reaction yields a large amount of hydrogen: 9 mol H_2 per mol of C_6H_6.[29,30]

Nowadays, these processes are mainly studied at the laboratory level. Pilot plants for the production of benzene from methane were built in 2000 – 2006 on the basis of natural gas feedstock to the design of NEDO Consortium and on the basis of biogas feedstock to the design of NLCE Renewable Energy in Bekkai (Hokkaido, Japan). Methane dehydroaromatization has not been commercially implemented.

Table 1. Equilibrium composition of the products of methane conversion to benzene, ethane and ethylene.[7]

T/°C	CH_4 conversion (%)	Equilibrium mixture composition (mass %)				
		C_6H_6	C_2H_6	C_2H_4	H_2	CH_4
		$6\,CH_4 \rightarrow C_6H_6 + 9\,H_2$				
527	2.5	2.0			0.5	97.5
727	13.8	11.2			2.6	86.2
927	40	32.6			7.4	60.0
		$2\,CH_4 \rightarrow C_2H_6 + H_2$				
527	1.0		0.9		0.1	99.0
727	3.0		2.8		0.2	97.0
927	5.0		4.7		0.3	95.0
		$2\,CH_4 \rightarrow C_2H_4 + 2\,H_2$				
527	1.0			0.9	0.1	99.0
727	5.0			4.3	0.6	95.0
927	20.0			17.5	2.5	80.0

Development of the scientific basis for the direct conversion of natural gas to aromatic hydrocarbons is an important task, since it opens the possibility to create new catalysts of dehydroaromatization. These catalysts can be used in compact modular units for the utilization of natural gas and associated petroleum gas intended for use directly in the fields. The use of such systems will enable the conversion of natural gas and associated petroleum gas to valuable chemicals without significant additional costs for the production of synthesis gas.

II. Catalytic systems suitable for methane dehydroaromatization

1. Supports for dehydroaromatization catalysts

Among possible catalysts of methane dehydroaromatization, metal/zeolite systems attract much attention since their structure ensures the stabilization of transition metal ions. In addition, in metal/zeolite catalysts, the acid sites of crystalline aluminosilicates are located near the transition metal ions, which is responsible for the appearance of unique catalytic properties of bifunctional systems.

The zeolite structure has a huge impact on the efficiency of the catalyst. Therefore, for studying the activity of the catalyst, it is necessary to know the structural features of various zeolites. High selectivity to benzene is observed on catalysts that have a two-dimensional pore system with a pore diameter close to the dynamic diameter of a benzene molecule. It has been demonstrated that catalysts characterized by low activity lack either pores of ~ 6 Å in diameter or a two-dimensional pore system.[31]

In this section, we consider zeolites used as a support for catalysts of methane dehydroaromatization.

The MCM-22 zeolite has a high thermal stability and large specific surface area. For methane dehydroaromatization, the Mo/MCM-22 catalyst is used since the pure MCM-22 is inactive in this reaction and promotes coke formation. With an increase in the molybdenum content from 0 mass % to 6 mass %, the methane conversion increases and passes through a maximum at 6 mass % and then sharply decreases as the molybdenum concentration increases to 10 mass %.[32] The highest conversion (9.9%) on the 6% Mo/MCM-22 catalyst is observed at 700 °C.[33] The maximum yield of benzene over this catalyst is > 7%, while the selectivity to benzene is 80%, and the yield of naphthalene is no more than 0.6% after 3-h reaction. After 24 h of operation, the catalytic performance decreases, and the total operation time exceeds 48 h.

The uniqueness of the Mo/MCM-22 catalyst is in the structure of the zeolite *per se* and in specific features of the molybdenum distribution over the zeolite surface. Methane is first activated at Mo metallic sites, but the aromatization of intermediates, such as ethylene and ethane, occurs at acid sites. It has been demonstrated that the high catalytic performance is observed only when there is an optimal ratio between these sites and their specific arrangement. In the course of impregnation and annealing, molybdenum readily reacts with aluminium atoms of the zeolite framework, while the Brønsted acid sites (BASs) act as a trap for molybdenum migrating into internal channels. As a result,

molybdenum is fixed on Brønsted acid sites to form Mo – O – Al groups, which leads to its optimal distribution.

A modification of the HZSM-5 zeolite with a high silicate modulus (the Si : Al ratio) containing phosphoric and rare earth (RE) oxides (ZRP-1 zeolite) has been used as the support for molybdenum catalysts of methane dehydroaromatization. The chemical composition of this modification can be represented by the formula $x\,RE_2O_3 \cdot y\,Na_2O \cdot Al_2O_3 \cdot z\,SiO_2$, where $x = 0.01 - 0.03$, $y = 0.4 - 1.0$ and $z = 20 - 60$. It is assumed that the role of phosphoric and rare earth oxides is in the blocking of the acid sites on the external surface of the zeolite and in acidity regulation. At the same time, it has been found that the preparation of catalysts is accompanied by a slight decrease in channel size, the loss of aluminium from the zeolite and formation of different P- and Al-containing compounds inside the pores.[34]

It has been experimentally demonstrated that the Mo/HZRP-1 catalyst is more active in methane dehydroaromatization at high Mo loadings. The benzene formation rate over Mo/HZRP-1 rapidly increases with an increase in Mo content from 0 mass % to 6 mass % and slowly increases with a further increase in Mo content from 6 mass % to 20 mass %. The reaction over 6% Mo/HZRP-1 yields a larger amount of naphthalene as compared with 20% Mo/HZRP-1. Catalysts based on HZRP-1 with high Mo loadings are distinguished by a smaller volume of internal pores accessible for bulky molecules like naphthalene, so that the reaction yields a larger amount of mononuclear aromatic hydrocarbons. However, high molybdenum loadings promote coke formation; therefore, the 20% Mo/HZRP-1 catalyst is more prone to coking than 6% Mo/HZRP-1.

The conversion of methane over 20% Mo/HZRP-1 is higher than that over 6% Mo/HZRP-1, but it decreases more rapidly with time so that the conversion on both catalysts is nearly the same after 6 h of operation. The maximum conversion is observed over 20% Mo/HZRP-1, being ~11% at 700 °C 30 min after the beginning of reaction; however, within 6 h, the conversion is reduced to ~5%.

The HSAPO-34 zeolite has been used as the support for a molybdenum catalyst of methane dehydroaromatization. This zeolite is a crystalline narrow-pore silicoaluminophosphate with a pore diameter of ~4.3 Å. The MoO_3/HSAPO-34 catalyst at 650 °C afforded a methane conversion of 0.6%; the selectivity to benzene was 72.9%. The MoO_3/HSAPO-34 system has low stability: the methane conversion and selectivity to benzene rapidly deteriorate with increasing contact time, and the catalyst becomes almost inactive after 3 h of operation.[31]

Special attention is attracted by systems based on ZSM-type zeolites: ZSM-5, ZSM-8 and ZSM-11.

The ZSM-8 zeolite has an orthorhombic crystal lattice and a two-dimensional system of channels with an average diameter of ~5 Å.

Over the MoO_3/HZSM-8 catalyst, a maximum conversion of methane of ~4% at the 87% selectivity to benzene has been achieved. With an increase in reaction duration, the MoO_3/HZSM-8 activity sharply decreases, and after 40 min, the reaction yields a large amount of CO.[31]

The ZSM-11 zeolite has a tetragonal crystal lattice and a two-dimensional porous structure consisting of straight perpendicularly intersecting channels 5.1×5.5 Å in size formed by 10-membered rings.

The MoO_3/HZSM-11 catalyst shows a rather high and stable selectivity to benzene during the entire process. A maximum methane conversion over MoO_3/HZSM-11 of 8.0% with selectivity higher than 90% has been achieved at 700 °C.

A team of Chinese researchers from Jilin University have reported the use of new zeolite systems TNU-9 (Ref. 35) and IM-5 (Ref. 36) for dehydroaromatization. TNU-9 has a very complicated structure: its monoclinic unit cell is twice as large as that of ZSM-5. It contains silicon atoms of 24 types with different crystallographic and topological characteristics. The three-dimensional zeolite structure composed of 10-membered rings contains large 12-membered cavities accessible only through the 10-membered channels. These channels are 0.52×0.6, 0.51×0.55 and 0.54×0.55 nm in size. The zeolite has high thermal and hydrothermal stability. Compared with the analogous 6% Mo/ZSM-5 catalyst, the 6% Mo/TNU-9 catalyst showed a higher conversion of methane, higher selectivity to benzene and a higher yield of aromatic compounds, as well as better performance stability (Table 2).[35] The best conditions for methane aromatization on this catalyst are as follows: Si : Al = 50 and 700 °C.

The orthorhombic unit cell of the IM-5 zeolite is three times larger than that of ZSM-5 and, like TNU-9, contains silicon atoms of 24 types. The zeolite has two intricate two-dimensional systems of 10-membered-ring channels intersecting to form cavities ~2.5 nm in size. The 6% Mo/IM-5 catalyst noticeably outperformed the analogous 6% Mo/ZSM-5 catalyst in terms of methane conversion (6.3 and 5.8%, respectively) and showed somewhat higher selectivity to benzene and lower selectivity to naphthalene.[36]

The ZSM-5 zeolite is often used as the support for catalysts of methane dehydroaromatization.[37] It has a two-dimensional pore system and an orthorhombic or monoclinic crystal lattice. The pores are formed by 10-membered rings. The pore system consists of straight elliptic channels 5.4×5.6 Å in size and sinusoidal channels 5.1×5.5 Å in

Table 2. Comparison of the test results for the 6% Mo/TNU-9 and 6% Mo/ZSM-5 catalysts in the methane dehydroaromatization reaction.[35]

Catalyst	Operation time /min	CH_4 conversion (%)	Selectivity (%)			Yield of aromatics (%)
			benzene	toluene	naphthalene	
Mo/TNU-9	60	11.3	81.2	2.2	16.6	6.2
	300	9.8	89.2	1.1	9.7	5.4
Mo/ZSM-5	60	9.5	67.4	2.4	30.2	5.6
	300	6.9	78.3	1.5	20.2	4.1

size, arranged perpendicularly to each other. The uniqueness of the structure is in that the channel diameter is roughly equal to the kinetic diameter of benzene molecule, and the aromatization of intermediate C_2 products proceeds more rapidly.[38]

The activity of Mo/zeolite catalysts in the methane dehydroaromatization reaction decreases in the series:

MoO_3/HZSM-5 > MoO_3/HZSM-11 > MoO_3/HZSM-8 > MoO_3/H-β > MoO_3/HMCM-41 > MoO_3/HSAPO-34 > MoO_3/HMOR ≈ MoO_3/HX ≈ MoO_3/HY > MoO_3/HSAPO-5 ≈ MoO_3/HSAPO-11.[31]

Among available supports, ZSM-5 zeolite is most widely used since it leads to the highest methane conversion and high selectivity of benzene formation. Metals (M) active in dehydroaromatization are considered in the next section for M/ZSM-5 systems.

2. Active components of methane dehydroaromatization catalysts

Molybdenum, tungsten, iron, vanadium, chromium, manganese, cobalt and gallium are used as active metals for M/ZSM-5 systems. Key factors determining the efficacy of a catalyst are the structure of channels, zeolite acidity, active metal valence and distribution, metal loading and annealing temperature.

The activity and stability of a W-based catalyst on the HZSM-5 support have been reported.[37, 39–41] Tungsten-containing catalysts on the ZSM-5 zeolite have been prepared by two methods: impregnation with a neutral solution or with a solution in H_2SO_4 at pH = 2–4. Both catalysts showed good performance in aromatization. The activity and selectivity of the W – H_2SO_4/HZSM-5 catalyst exceed those of W/HZSM-5.

The pH of the initial tungstate solution is one of the crucial factors responsible for the preparation of a highly active catalyst for methane dehydroaromatization. In particular, W/HZSM-5 prepared by dissolving ammonium tungstate in deionized water at pH 7–9 or by mixing tungstic acid with an aqueous ammonia solution has shown a low activity in the methane aromatization reaction at 700–750 °C. At the same time, the W – H_2SO_4/HZSM-5 catalyst obtained from an aqueous solution of ammonium tungstate acidified with H_2SO_4 to pH 2–3 has led to high methane conversions and selectivities to benzene. It is suggested that the introduction of a small amount of H_2SO_4 not only increases the solubility of ammonium tungstate in water but also promotes the formation of polytungstate in the initial solution.[40]

The conversion of methane over W – H_2SO_4/HZSM-5 strongly depends on the Si : Al ratio. The highest conversion is achieved at Si : Al = 30, and an increase in the Si : Al ratio causes a decrease in methane conversion.

The conversion of methane and selectivity to aromatic hydrocarbons depend on the gas flow rate: With an increase in flow rate, both parameters considerably decrease. With increasing operation time, the catalytic activity of 3% W – H_2SO_4/HZSM-5 is deteriorated at different Si : Al ratios, and high gas flow rates lead to a decrease in methane conversion and in the yield of aromatic hydrocarbons. The highest conversion, 9.6%, is achieved at 700 °C. The maximum selectivity for formation of aromatic hydrocarbons is as high as 97%.

The methane dehydroaromatization reaction over Mn/HZSM-5 has been studied.[42] The catalyst has been prepared by the impregnation of the support with a manganese acetate tetrahydrate solution followed by annealing. At 750 °C, the methane conversion of 4.4% and the yield of aromatic compounds of 4.0% were achieved over the 4% Mn/HZSM-5 catalyst.

Catalysts based on HZSM-5 containing cobalt with addition of gallium as the active metal were studied. The cobalt content varied from 0.5 mass % to 3 mass % at a Ga content of 2 mass %.[43] The catalysts were prepared by the impregnation of the zeolite with aqueous solutions of cobalt and gallium nitrates. An increase in Co loading led to a sharp increase in the yield of benzene and in the selectivity of its formation. A maximum yield of aromatics was achieved over 2% Co – 2% Ga/HZSM-5, being 9.9 mass % at a methane conversion of 12.8%. The highest selectivity to benzene was 66.5%. This increase in the selectivity to benzene was accompanied by considerable suppression of carbon deposition. The selectivity to naphthalene remained roughly constant.[43]

Most attention has been given to catalysts containing molybdenum as the active component (Mo/HZSM-5). The Mo/HZSM-5 catalysts have been studied in a wide range of molybdenum loadings. The methane conversion exceeds 11% at 700 °C and 16% at 750 °C and is more than 6% even after 30 h of operation; a maximum conversion is as high as 25%.[44] The selectivity to benzene is on average 55% and that to naphthalene, 10%.[45] The average yield of benzene is 6 mass % – 7 mass %.

Thus, the best catalysts for methane dehydroaromatization are Mo/ZSM-5, which are addressed in next sections.

III. Mo/ZSM-5 catalysts for methane dehydroaromatization

1. Effect of the method of synthesis of Mo/ZSM-5 catalysts on their activity

Two main approaches are used for preparing Mo/HZSM-5 catalysts of dehydroaromatization.

1. A zeolite support is impregnated with aqueous solutions of molybdenum compounds [usually, ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$].

2. A zeolite and molybdenum compounds (usually MoO_3) are mechanically mixed, and the active phase forms as a result of a solid-phase reaction.

The impregnation method is most commonly used for producing Mo/zeolite catalysts of methane dehydroaromatization.[19, 20, 22–26, 46–48] To this end, the hydrogen form of zeolite is most frequently used. As a rule, incipient wetness impregnation or wet impregnation is employed. The ammonium heptamolybdate concentration varies within wide limits so that the annealed samples contain from 1 mass % to 20 mass % Mo.[22, 24, 26, 47] The pH of an impregnation solution is usually not specified, although the change in the pH of an ammonium heptamolybdate solution has an effect on the properties of the resulting catalyst.[49] The introduction of sulfuric acid into the impregnation solution increases the initial activity of a catalyst, but sharply deteriorates its stability. Increasing pH by adding ammonium hydroxide enables the synthesis of an active and stable catalyst. The

impregnation of a zeolite is carried out at either room[22–26,46] or elevated (*e.g.*, 85 °C) temperature.[20] The impregnation time is from 30 min[21] to 24 h.[46] Further treatment of catalysts is also different. As a rule, the zeolite impregnated with a solution of molybdenum compounds is dried at 90 – 120 °C (Ref. 25) for 4,[20,26] 6 (Ref. 24) or 10 h.[22–26] Then, the samples are annealed 3 h in air at temperatures from 500 to 720 °C.[22,46] The annealing time can be 4,[50] 6 (Ref. 46) or even 30 h.[50]

With an increase in the annealing temperature of Mo/ZSM-5 catalysts (from 500 to 700 °C), the methane conversion and selectivity of formation of aromatic hydrocarbons decrease.[25,26,47] Conversely, the selectivity of formation of C_2 hydrocarbons increases. This effect is enhanced with increasing the Mo loading of a catalyst. It is suggested that the high-temperature annealing leads to molybdenum aggregation into large agglomerates plugging zeolite channels.[26] In addition, high-temperature treatment results in degradation of the zeolite crystal lattice and formation of aluminium molybdate $Al_2(MoO_4)_3$, which can be a cause of deterioration of catalytic properties.[24]

An increase in the calcination time of the 6% Mo/ZSM-5 catalyst at 500 °C from 3 to 18 h improves its catalytic activity.[50] In addition, the catalyst operatioal stability becomes better. A further increase in the heat treatment time to 30 h has no effect on the catalytic properties. It has been demonstrated that the long-term calcination (18 h) favours the migration of molybdenum into zeolite channels and its interaction with Brønsted acid sites, which affords an increase in the catalytic performance of the sample.[50]

The process of preparation of the Mo/HZSM-5 catalyst by impregnation of the NH_4ZSM-5 zeolite with a solution of ammonium heptamolybdate has been scrutinized.[26] It has been demonstrated that heptamolybdate decomposes in two steps at 241 and 346 °C. According to IR spectroscopy data, the number of NH_4^+ cations in the samples annealed at 300 °C sharply decreases, and after annealing at 500 °C, the ammonium form completely converts to the hydrogen form. Annealing the samples in an oxygen-containing atmosphere at 700 °C leads to the appearance of new IR absorption bands attributed by the authors to the interaction of molybdenum oxide with the oxygen of the zeolite framework which results in the formation of inactive MoO_4^{2-} ions and in the reduction of methane conversion and selectivity to benzene. An increase in the annealing temperature from 300 to 500 °C is accompanied by the disappearance of the characteristic MoO_3 bands from the spectrum of 10% Mo/ZSM-5, which is explained by the higher dispersion and migration of a fraction of molybdenum oxide species into zeolite pores. Thus, the annealing at 500 °C results in complete decomposition of ammonium ions and formation of highly dispersed molybdenum species even at rather high Mo loadings (10 mass %).

Although there is a large diversity of preparation conditions for Mo/ZSM-5 catalysts, some features characteristic of the catalytic performance in the methane dehydroaromatization reaction can be identified. In particular, it has been shown that within the first 35 – 45 min CH_4 interacts with the Mo/ZSM-5 catalyst to form H_2O, CO, CO_2 and H_2.[20,23,25,46] This time interval is referred to as induction period, and it is believed that catalyst active sites form during this period of time. Then, C_2 hydrocarbons (ethane, ethylene) and aromatics (benzene, toluene) appear among the reaction products. Within the initial period of the reaction, the total methane conversion at 700 °C is 6% – 15%; then, it decreases with an increase in the reaction duration. The yield of benzene increases within the first 60 – 120 min of the reaction and then decreases. The selectivity of benzene formation first increases and then is stabilized at the level 60% – 85%. The concentration of C_2 hydrocarbons and the selectivity of their formation increase in the course of reaction. Hydrogen is also among the major products. The $H_2 : C_6H_6$ ratio is as high as 9 – 18 mol H_2 per mol of C_6H_6.[29]

To reduce the induction period, it has been suggested to preliminarily treat the Mo/ZSM-5 catalyst with ethylene or hydrogen,[46] as well as with a $CH_4 – H_2$ (1 : 4) mixture.[20,23,51] The preliminary treatment with oxygen also shortens the induction period.[52]

With an increase in the reaction temperature from 600 to 840 °C, both the total methane conversion and the selectivity of benzene formation increase.[26] However, taking into account available data,[47] we can state that this is the case only for the first 100 min of the reaction and that, on the whole, the higher reaction temperature leads to the faster deactivation of the Mo/ZSM-5 catalyst.[53] It has been shown that the total methane conversion and selectivity to aromatics decrease with an increase in the flow rate of the reaction mixture.[3,54]

An alternative method of fabrication of molybdenum/zeolite catalysts is mechanical mixing of molybdenum compounds and a zeolite with the subsequent solid-phase reaction. The absence of the impregnation stage in this method facilitates studying the influence of the support on the catalyst properties. For example, in studying the properties of molybdenum catalysts supported of zeolites, a required amount of molybdenum oxide MoO_3 was ground with the corresponding zeolite, and the mixture was calcined in air at 500 °C for 4 h.[31] Over the 3% MoO_3/HZSM-5 catalyst, a methane conversion of 6.9% and a selectivity to benzene of 90.8% (ignoring the formation of heavier products) have been achieved. Properties of M/HZSM-5 catalysts (M = Mo, Fe, V, W and Cr)[25] are summarized in Table 3).

Table 3. Results of tests of 2% M/ZSM-5 catalysts synthesized by two methods in the methane aromatization reaction.[25]

Metal	Preparation method[a]	CH_4 conversion (%)	Maximum selectivity (%)		
			benzene	naphthalene	aliphatic hydrocarbons
Mo	SS	2.6	71.5	0	31.7
	I	7.6	78.4	8.6	13.1
Fe	SS	0.8	0	0	17.7
	I	4.1	61.8	3.7	19.4
V	SS	0.6	35.4	0	20.1
	I	0.6	63.1	0	19.8
Cr	SS	0.2	0	0	20.1
	I	0.3	19.4	0	58.6
W	SS	0.3	0	0	12.7
	I	0.7	0	0	16.9

[a] SS is solid-phase synthesis, I is impregnation.

All metal/zeolite catalysts prepared by the solid-phase reaction showed lower activity as compared with analogous catalysts obtained by the impregnation method. Preliminary reduction in a CO atmosphere increased the catalyst activity and mitigated the difference between the catalysts prepared by impregnation and solid-phase reaction. A somewhat different method of synthesis of a catalyst for methane dehydroaromatization has been suggested.[55] The hydrogen form of HZSM-5 was mixed with molybdenum oxide MoO_3, calcined in an O_2-He (20% O_2) flow at 677 °C and used in the methane dehydrogenation reaction. It is believed that the method makes it possible to avoid processes associated with the release of the ammonium heptamolybdate decomposition products (N_2, NH_3, H_2O), which have an effect on the properties of the zeolite support. Characteristics of the catalyst prepared by mechanical mixing turned out to be close to the characteristics of catalyst prepared by impregnation. Later, the solid-phase synthesis of Mo/zeolite catalysts has been rather widely used.[35, 56 – 63]

However, the choice of a method of fabrication of the most efficient catalysts for methane dehydroaromatization is still a matter of debate. The 16% Mo/HZSM-5 catalyst prepared from a mechanical mixture of MoO_3 and HZSM-5 showed better catalytic performance that the 6% Mo/HZSM-5 sample prepared by impregnation with a solution of ammonium heptamplybdate.[59] An increase in the Mo loading of the samples obtained by impregnation deteriorated the catalytic performance. These results have been explained by a weaker interaction of molybdenum with zeolite in 'solid-phase' samples since in the latter the amount of molybdenum bound to the framework aluminium atoms is four times as low as in the 'impregnation' samples. As a result, in the course of catalyst activation, the aggregation of molybdenum carbide clusters is facilitated and some of acid sites previously occupied by molybdenum are vacated. These sites are involved in formation of an extra amount of aromatic compounds. The activity and selectivity of 6% Mo/HZSM-5 samples prepared by impregnation and mechanical mixing were close, but for the 'solid-phase' catalyst, these characteristics deteriorated faster during operation.[61] Preliminary reduction in hydrogen at 350 °C improved the catalytic performance of the catalyst prepared by impregnation, but led to a strong deactivation of the catalyst produced from a mechanical mixture of MoO_3 and HZSM-5. Catalysts containing 0.5 mass %, 2 mass % and 4 mass % of molybdenum prepared by mechanical mixing of molybdenum oxide with HZSM-5 by Vosmerikov *et al.*[64] have shown higher methane conversions at the reaction temperature 750 °C than the samples prepared by impregnation. However, with an increase in the Mo loading to 6 mass %, the catalyst activity has deteriorated, especially sharply for 'solid-phase' samples. The methane conversion on the sample prepared by impregnation has decreased to a lower extent and has turned out to be almost twice as high as that on the 'solid-phase' sample. Unfortunately, the yields of aromatic products and reaction selectivity for these catalysts have not been reported.

One of the problems of the mechanical mixing method is the difficulty to prepare a homogeneous blend of a molybdenum compounds with a zeolite. The volume of a molybdenum oxide powder is much smaller than the required zeolite volume, so that uniform blending presents a difficulty. As a rule, powders are ground in a mortar for 0.5 h [56, 61] or even for 0.1 h.[55] Vibratory ball milling for 4 h has also been used for obtaining a mixture.[64] To avoid inhomogeneity of a mixture, a weighed sample of molybdenum oxide has been dispersed under sonication in a small amount of distilled water.[60].

The resulting molybdenum oxide – zeolite mixture is calcined in air at 500 °C for 3 – 4 h [35, 45, 57, 62]) or at 700 °C for 0.5 h.[60] Calcination in an O_2-He (20% O_2) flow at 700 °C for 0.5 h [56, 58] and in a dry nitrogen flow at 500 °C for 2 h [63] is also used.

On heating, a part of molybdenum species remain on the external zeolite surface, while the other species migrate into zeolite pores and interact with acid sites. According to Ding *et al.*[58], molybdenum compounds formed after annealing ($Mo_2O_5^{2+}$ dimers) are catalytically inactive in the methane aromatization reaction. They are activated in contact with methane where molybdenum oxo species are reduced and carburized to form small (0.6 – 1 nm) MoC_x clusters with the concurrent regeneration of bridging OH groups that were initially replaced by molybdenum oxo dimers.

Study of the effect of the pretreatment of the Mo/ZSM-5 catalyst with a mixture of methane with one of the gases (H_2, C_2H_4, H_2O or CO_2) on the induction period duration and the initial catalyst activity has revealed that the presence of ethylene in a mixture with methane ($C_2H_4 : CH_4 = 0.005$) shortens the induction period but has no effect on the benzene formation rate.[65] An increase in the ethylene content ($C_2H_4 : CH_4 = 0.1$) leads to further shortening of the induction period; however, the catalyst activity is deteriorated. The pretreatment of the catalyst with a hydrogen – methane mixture ($H_2 : CH_4 = 0.1$) has almost no effect on the induction period duration, whereas the presence of H_2O or CO_2 considerably increases the induction period.

Although the properties of the catalysts prepared by different methods can vary considerably, major features of methane dehydroaromatization over Mo/ZSM-5 catalysts remain common to them.

Another approach to the synthesis of Mo/zeolite catalysts implies deposition of molybdenum carbide (Mo_2C) onto the HZSM-5 zeolite. To this end, the previously prepared molybdenum carbide is mixed with the zeolite suspended in water. Then, water is evaporated under vigorous stirring.[23] However, such a catalyst shows low activity as compared with the catalyst obtained by impregnation: the major reaction products are hydrogen and carbon rather than aromatic hydrocarbons. The low activity of these catalysts is suggested to be due to the low dispersion of molybdenum carbide species in the zeolite matrix.[23]

In addition, Mo_2C/ZSM-5 catalysts are synthesized by the treatment of calcined Mo/ZSM-5 samples, obtained by the impregnation method, with different gas mixtures, for example, with a methane – hydrogen mixture ($CH_4 : H_2 = 1 : 4$) at 700 °C for 2 h.[20, 23] In the first 30 – 40 min of the reaction, these catalysts are more active than the samples prepared by impregnation.

The composition of the gas mixture used for the pretreatment of Mo/ZSM-5 has an effect not only on the induction period duration,[61, 66] but also on the phase composition and activity of catalysts.[61, 66, 67] In particular, it has been demonstrated that oxygen pretreatment (as

compared with helium) leads to an increase in the methane conversion.[67]

After the pretreatment with a hydrogen – butane mixture, the Mo/ZSM-5 catalyst shows higher activity and resistance to coking than after the pretreatment with a hydrogen – methane mixture.[66] In the former case, the catalyst after the pretreatment contains the α-MoC_{1-x} phase with a cubic face-centered (fcc) lattice; in the latter case, the catalyst contains the β-Mo_2C phase with a hexagonal close packed (hcp) structure. It is believed that it is precisely the type of molybdenum carbide phase that is responsible for the differences in the performance of the catalysts.[66] This is supported by the results of other studies: the pretreatment of 6% Mo/ZSM-5, obtained by the impregnation method, in hydrogen at 350 °C enhances the activity and stability of the catalyst.[61] It is suggested that calcination in a hydrogen atmosphere leads to the formation of the fcc rather than hcp MoC_xO_y phase, which is harder to reduce to the C_x phase less active in methane dehydroaromatization. After such treatment, the 6% Mo/ZSM-5 catalyst prepared by the solid-phase method is catalytically inactive in this reaction. It is likely that pretreatment in hydrogen in this case inhibits the molybdenum migration into zeolite channels.

Attempts have been made to synthesize Mo/zeolite catalyst containing molybdenum in the zero oxidation state. To do this, molybdenum hexacarbonyl was sublimed onto dehydroxylated ZSM-5 with subsequent treatment of $Mo(CO)_6$/ZSM-5 with hydrogen. However, the resulting Mo^0/ZSM-5 samples turned out to be inactive in methane aromatization.[23]

Thus, a variety of methods are used for introducing molybdenum into the zeolite matrix to produce Mo/ZSM-5 catalysts. This is responsible for different activities of the resulting systems in methane dehydroaromatization. The most widely used methods are impregnation and solid-phase synthesis.

2. Effect of molybdenum loading on the activity of Mo/ZSM-5 catalysts

The molybdenum content in Mo/ZSM-5 catalysts varies in a wide range from 1 mass % to 20 mass %.[22, 24, 26, 47, 59]

It has been demonstrated that the catalytic activity of Mo/ZSM-5 samples prepared by the impregnation method increases with an increase in molybdenum loading to 2 mass % – 3 mass %,[22, 26, 52, 68], 4 mass %,[25] 6 mass %[48, 59, 69] or 10 mass %.[70] For Mo/ZSM-5 catalysts prepared by the solid-phase method, the activity increases with increasing the molybdenum content to 16%.[59] A further increase in molybdenum loading leads to a decrease in both the total methane conversion and the selectivity of benzene formation. It is suggested that such a behaviour is mainly associated with the formation of large molybdenum oxide particles, which block zeolite channels.[22, 26, 59] Another explanation of the observed dependence of catalytic activity on molybdenum loading has been given on the basis of studying Mo/ZSM-5 samples containing 1 mass % – 15 mass % Mo by X-ray photoelectron spectroscopy (XPS).[52] According to these data, the most active 3% Mo/ZSM-5 catalyst has the ratio $Mo_2C : MoO_3 \approx 0.4$. An increase in molybdenum content entails the increase in the fraction of molybdenum carbide. It is believed that the coexistence of molybdenum oxide and carbide in the catalyst is essential for methane activation. The sample containing 3 mass % Mo has an optimal ratio between these molybdenum compounds.

The difference in activity between the catalysts containing 2 mass % – 10 mass % Mo becomes more pronounced with an increase in calcination temperature from 500 to 700 °C.[47] The sharp deterioration of activity at a molybdenum content > 2 mass % is presumably caused by stronger interaction of molybdenum with the zeolite lattice and formation of aluminium molybdate.[24]

It has been also revealed that an increase in molybdenum content shortens the induction period.[25] It has been suggested that this is due to an increase in the fraction of readily reducible polymolybdate compounds on the external zeolite surface.

Thus, molybdenum loading is among key factors determining the activity of Mo/ZSM-5 catalysts, the optimal content depending on synthesis conditions.

3. Effect of physicochemical properties of zeolite on the activity of Mo/Zeolite catalysts

Study of the influence of zeolite type on the catalytic properties of 3% Mo/zeolite systems (Si : Al = 25) has demonstrated that the best catalysts are supported on ZSM-5, ZSM-8 or ZSM-11 zeolites.[31, 71] Their activity is significantly higher (by a factor of 5 – 10) than the activity of analogous catalysts based on MCM-41 and SAPO-34 zeolites. Over catalysts based on mordenite and zeolite X or Y, less than1% of methane converts to give only C_2 hydrocarbons and CO. For mordenite, ultrastable zeolite Y and FSM-16 zeolite, the high selectivity of coke formation (> 80%) is observed.[29] It is accepted that it is precisely the ZSM-5 structure with a system of intersecting channels of two types (see Section II.1) without large cavities that promotes the synthesis of small aromatic molecules and prevents the formation and accumulation of polyaromatics.[29, 31]

The kinetic diameter of a benzene molecule is ~6 Å and that of phenanthrene, ~8 Å.[72, 73] Therefore, the presence of narrower pores, as in SAPO-34 (the pore diameter (d_{pore}) is 4.3 Å), impedes the diffusion of aromatic compounds.[31] Zeolites with wider pores, such as X or Y (d_{pore} = 7.4 Å), with a system of large cavities up to 12 Å in size[74] enable the formation and accumulation of high-molecular-mass aromatic products, precursors of carbonaceous deposits.[75] However, the presence of large cavities in the zeolite structure not always deteriorates the catalyst performance in the methane dehydroaromatization reaction. In particular, it has been demonstrated that the presence of large cavities (7.1 × 18.2 Å) with narrow windows (4.0 × 5.4 Å) in Mo/MCM-22 catalysts ensures high selectivity of benzene formation and high resistance to deactivation.[32, 76, 77]

Comparison of data on the catalytic activity of Mo/ZSM-5 catalysts prepared by impregnation of the H-form[74] and NH_4-form[26, 47] of ZSM-5 indicates the absence of essential differences in the catalytic performance in methane dehydroaromatization. At the same time, the catalysts prepared by impregnation of Na-ZSM-5 zeolite are inactive in the methane dehydroaromatization reaction.[25, 26] This is supposed to be due to that Mo/Na-ZSM-5 catalysts lack Brønsted acid sites necessary for the oligomerization of carbon-containing moieties in the course of reaction.[25] It has been stated that an increase in the $H^+ : Na^+$ ratio in the initial zeolite leads to an increase in

Table 4. Effect of steam dealumination on the properties of 4% Mo/ZSM-5 catalyst.[80]

Catalyst	CH_4 conversion (%)	Selectivity (%)						Yield of aromatics (%)
		benzene	toluene	naphthalene	C_2H_4	C_2H_6	coke	
Initial	11.9	46.1	2.7	6.3	4.7	1.1	37.9	6.6
Steam-dealuminated	10.9	63.5	3.1	8.3	4.9	1.4	18.9	8.7

Note. The initial catalyst 4% Mo/ZSM-5; reaction conditions: 750 °C, pressure 1 atm, flow rate 600 h^{-1}; operation time 420 min.

the number of acid sites and, thereby, in the activity of Mo/ZSM-5 catalysts.

The Si : Al ratio in a zeolite varied within wide limits (Si : Al = 10–950) can also have an effect on the activity of Mo/ZSM-5 catalysts in methane dehydroaromatization, the highest activity being observed at Si/Al ≈ 20.[29] According to other data,[78] the formation rate of aromatic hydrocarbons increases with an increase in the Si : Al ratio from 14 to 28 and decreases at Si : Al = 54. In some studies (see, *e.g.*,[76]), only a decrease in activity with a decrease in Si : Al from 130 to 15 has been reported, without mentioning any optimal value.

One of the known methods of increasing the Si : Al ratio in zeolite catalysts is the preliminary dealumination of the initial zeolite under different conditions [treatment of the zeolite with hydrochloric acid,[79] in a steam flow at 500–550 °C for 6 h (Table 4),[80] in a dry N_2 flow at 600 °C for 6 h[81] or in oxalic acid at 70 °C[82]]. Both deterioration[82] and enhancement[79–82] of the activity of Mo/ZSM-5 catalysts prepared from dealuminated zeolites with roughly the same degree of dealumination have been observed.

It is known that varying the Si : Al ratio is accompanied by a change in the number and strength of Brønsted acid sites. This accounts for the effect of the silicate modulus on the activity of Mo/ZSM-5 catalysts. In particular, the optimal ratio Si : Al ≈ 20 correlates with a maximum concentration of BASs.[29] The authors of this work believe that an increase in the number of BASs favours the oligomerization of CH_x to benzene. The same catalysts are characterized by low coke formation (35%).[29] Another assumption implies that the increase in activity of Mo/ZSM-5 catalysts with a decrease in the Si : Al ratio is caused by an increase in dispersion of molybdenum in the zeolite matrix.[76] The molybdenum stabilization sites are suggested to be BASs, and the increase in their number with a decrease in the Si : Al ratio is favourable for the formation of smaller Mo-containing species. The increase in the silicate modulus for the Mo/ZSM-5 catalyst achieved by dealumination of the initial zeolite is accompanied by a decrease in the concentration of BASs and an increase in the content of Lewis acid sites (LASs).[81] This results in an increase in both the total methane conversion and the conversion to benzene. Zeolite dealumination makes it possible to achieve the optimal number of BASs.[58]

Steam delumination of a zeolite (Y,[83] BEA[84]) can generate a secondary porosity (mesoporosity) of the zeolite matrix, which will facilitate the diffusion of aromatic molecules.[85] This allows one to explain the increase in activity and stability of the 6% Mo/ZSM-5 catalyst by the fact that the pretreatment of HZSM-5 in a NaOH solution at 80 °C results in formation of a mesoporous structure.[86]

Preliminary hydrothermal treatment of the HZSM-5 zeolite (Si : Al = 28.6) in a 0.5 M aluminium nitrate solution[87] or in a 0.04 M NaOH solution[88] leads to an increase in activity of 6% Mo/ZSM-5 and in catalyst performance stability. This treatment reduces the amount of extraframework aluminium, which is accompanied by a decrease in the number of strong BASs and an increase in the number of medium BASs. In addition, the zeolite microporosity is somewhat increased.[87,88] Conversely, hydrothermal treatment of the zeolite in an aqueous medium leads to a decrease in crystallinity of ZSM-5 and to an increase in the volume of mesopores. The Mo/ZSM-5 catalyst based on this zeolite shows lower activity.

The size of zeolite crystallites also has a strong effect on Mo/ZSM-5 activity.[89] In particular, the total methane conversion over the catalyst based on a zeolite with a crystal size of 1000 nm is 1.5 times higher than that over the catalyst based on a zeolite with a crystal size of 70 nm. The selectivity of benzene formation is also higher for the sample with larger crystals.[89] The increase in the zeolite crystal size leads to migration of a fraction of molybdenum into zeolite channels. In the fine crystalline sample, molybdenum is mainly located on the external surface of the zeolite. This is assumed to be due to an increase in the fraction of the external surface with a decrease in the size of zeolite crystals.

Thus, physicochemical characteristics of initial zeolite (structure, atomic ratio Si : Al *etc.*) have a significant effect on the activity of Mo/zeolite catalysts in the methane dehydroaromatization reaction. The existence in zeolites of a porous channel structure with window size close to the diameter of a benzene molecule is responsible for high methane conversions and high selectivity of benzene formation.

4. Effect of temperature of the methane dehydroaromatization reaction on the activity of Mo/zeolite catalysts

The vast majority of studies of methane dehydroaromatization have dealt with a temperature range of 700–800 °C. Increasing temperature is thermodynamically favourable for methane aromatization. With an increase in temperature from 700 to 800 °C, the equilibrium methane conversion increases nearly twofold. The following trends in the effect of temperature on methane dehydroaromatization have been formulated:[38]

— Conversion at higher temperatures (800 and 850 °C) leads to a momentary increase in the yield of aromatics, but after 100 min of operation, there occurs a sharp decline, and the catalyst rapidly loses activity; at 850 °C, the catalyst becomes completely inactive after 250 min of operation.

— At 700 °C, the yield is somewhat lower without a noticeable increase in performance stability.

— The optimal temperature for methane aromatization is 725 °C.

IV. Physical and chemical properties of Mo/ZSM-5 catalysts

Mo/ZSM-5 catalysts are exposed to high temperatures required for the pretreatment methane dehydroaromatization reaction. This should lead to the change in the state of both molybdenum and the zeolite matrix. In this section, we consider physical and chemical properties of Mo/ZSM-5 catalysts prepared by impregnation and solid-phase synthesis at each step of preparation, pretreatment and operation under the reaction conditions.

1. Molybdenum state in Mo/ZSM-5 catalysts

A large number of studies have addressed the state of molybdenum in the zeolite matrix. There is no consensus on the location of molybdenum in Mo/ZSM-5 catalysts obtained by impregnation. This is due to that the location of molybdenum depends on many factors: molybdenum loading,[22, 26] temperature,[20, 26] reaction duration and gas phase composition in the course of calcination.[20, 50] Various analytical methods have provided evidence that, during calcination of Mo/ZSM-5 catalysts in air at 500 °C, molybdenum migrates into zeolite channels.[50, 69] Diffusion of some molybdenum species into zeolite channels is observed in calcination at 700 °C and becomes more pronounced upon calcination in humid air.[20]

Study of the induction period of the methane dehydroaromatization reaction has shown that molybdenum oxide is reduced by methane in two steps (Scheme 2).[51]

Scheme 2

$$4\,MoO_3 + CH_4 \longrightarrow 4\,MoO_2 + CO_2 + 2\,H_2O$$

$$4\,MoO_2 + 4\,CH_4 \longrightarrow 2\,Mo_2C + CO_2 + 5\,H_2O + CO + 3\,H_2$$

At higher Mo loadings, the molybdenum oxide reduction occurs at higher temperatures, which is attributed to the increase in the size of Mo-containing species, so that more stringent conditions are required for their reduction.

An *in situ* XPS study has shown that Mo_2C and MoO_3 species coexist on the surface of the working catalyst.[52]

It is believed that, after the completion of reaction, Mo/ZSM-5 catalysts contain two types of molybdenum compounds: those located on the external surface of the zeolite and those located inside its channels.[61, 69] It has also been demonstrated that molybdenum carbides form on the catalyst surface after the reaction.[20, 23, 29, 58, 66] The molybdenum carbide formation is an endothermic process and is accompanied by weight loss. However, according to some data,[20, 22, 61, 69] a part of molybdenum remains in a higher oxidation state (Mo^{5+}) even after the long-term contact with methane. It has been suggested that this part of molybdenum is located inside the zeolite channels.[20, 69]

Study of Mo/ZSM-5 samples with a molybdenum content of 2 mass % – 8 mass % obtained by solid-phase synthesis has shown that a part of molybdenum is located on the external surface of the zeolite in the form of molybdenum oxide particles no more than 3 nm in size and the other part, inside the zeolite channels in the form of $[Mo_5O_{12}]^{6+}$ species.[63] It has been assumed that the fraction of Mo located inside the zeolite channels increases with an increase in the total content of molybdenum.

It has been found that, during the treatment of a MoO_3/HZSM-5 (Mo : Al < 0.4) mixture in O_2 – He (1 : 4) at 700 °C, molybdenum migrates into zeolite channels and is fixed as $Mo_2O_5^{2+}$ dimers at cation exchange sites of the zeolite, thereby substituting for two protons of zeolite BASs.[90]

Under the reaction conditions, oxide species convert to MoC_x clusters (contain ~10 Mo atoms) located inside the zeolite channels.[56, 58, 90] This is also accompanied by partial regeneration of the BASs involved in the methane aromatization reaction. Molybdenum carbide clusters are resistant to agglomeration over a long reaction time (10 h at 680 °C).[58]

Under the reaction conditions, molybdenum oxide compounds located on the external zeolite surface convert to molybdenum carbide and those located in zeolite channels, to MoO_xC_y.[63] The samples obtained by solid-phase synthesis contain the metastable cubic phase α-Mo_2C, in addition to the stable hexagonal phase β-Mo_2C; at the same time, only the latter phase has been identified by X-ray diffraction in the catalysts prepared by impregnation.[59]

Thus, the state of molybdenum and its localization in zeolite strongly depend on Mo/ZSM-5 synthesis conditions. It is generally accepted that molybdenum oxides are transformed into carbides in the course of methane dehydroaromatization. The presence of molybdenum in a higher oxidation state in the working catalyst has been reported (see, *e.g.*,[61, 63]). As a rule, suggestions that molybdenum is stabilized inside the zeolite channels are based on the data on the decrease in the number of BASs in the zeolite. At the same time, numerous experimental results indicate that molybdenum is also located on the external zeolite surface.

2. State of the zeolite matrix in Mo/ZSM-5 catalysts

The introduction of molybdenum into HZSM-5 followed by calcination leads to a decrease in the specific surface area and pore volume of the zeolite. This effect becomes more pronounced at higher Mo loadings[22, 26, 59] or at higher calcination temperatures.[26] At high Mo loadings, large molybdenum crystallites are formed, which block zeolite channels.[26]

An increase in the Mo/ZSM-5 calcination temperature from 500 to 700 °C leads to a decrease in the degree of crystallinity of the HZSM-5 zeolite.[22, 26] This is accompanied by dealumination of the zeolite matrix, formation of aluminium molybdate and an increase in the Si : Al ratio in the zeolite.[24]

The acid properties of a zeolite change depending on the gas atmosphere, temperature and catalyst calcination duration.[20, 22, 50] In particular, the pretreatment of 2% Mo/ZSM-5 in a He or dry oxygen flow at 700 °C leads to a decrease in the concentration of OH groups of all types.[20] The use of air brings about analogous changes in the acid properties of the zeolite, but at considerably lower temperature (500 °C),[20, 48] which is caused by the influence of catalyst treatment conditions on the molybdenum diffusion process.

An increase in the calcination duration leads to a decrease in the BAS concentration in Mo/ZSM-5 catalysts.[50]

Studying the changes in physical and chemical properties of the zeolite matrix after the completion of reaction has revealed degradation of the zeolite texture. This is likely associated with coke formation in the course of reaction. The same reason is behind the decrease in the number of BASs in the course of reaction.[22, 29]

Thus, the introduction of molybdenum brings about considerable changes in the texture and acid properties of the zeolite matrix. The character of changes in physical and chemical properties of zeolite depends on the molybdenum content and location in the zeolite matrix, which are determined by Mo/ZSM-5 synthesis conditions. During the methane dehydroaromatization reaction, the zeolite experiences further changes in physical and chemical properties, which is due to formation of carbonaceous deposits under the reaction conditions.

V. Mechanism of methane dehydroaromatization over Mo/ZSM-5 catalysts and the nature of active sites

A bifunctional mechanism of methane dehydroaromatization over Mo/ZSM-5 catalysts, involving Mo-containing sites and Brønsed acid sites, is generally accepted.[20, 23, 25, 29, 58] According to this mechanism, methane is activated at Mo-containing sites to release hydrogen into the gas phase and to form surface CH_x species. Then, the products of their dimerization (C_2H_y) oligomerize at zeolite BASs to form benzene and naphthalene.[29]

In some cases, in the early step of catalyst operation (induction period), the catalyst is activated (the active phase is formed). At this step, the MoO_3 oxide formed upon catalyst calcination in an oxidative atmosphere is reduced to yield molybdenum carbide (Scheme 3).[91, 92]

Scheme 3

$$2\,MoO_3 + 2\,CH_4 \longrightarrow Mo_2C + CO_2 + 4\,H_2O$$

It has also been demonstrated that the presence of molybdenum oxides is not a necessary condition for methane activation.[93]

Ethylene is usually considered to be an intermediate of the reaction.[3, 20, 23] In particular, the results of temperature-programmed reduction of Mo/ZSM-5 with hydrogen (TPR H_2) after the temperature-programmed reaction with CH_4 enabled the conclusion that not only CH_4 activation yielding surface [CH_3] species but also their dehydrogenation to [CH_2] and subsequent condensation into C_2H_4 occur at the Mo-containing sites [Mo_2C and(or) $Mo_2C_xO_y$].[94]

Intermediates CH_x dimerize to form ethane, ethylene and acetylene. It is conventionally believed that ethylene is the intermediate for benzene formation (Scheme 4).

Scheme 4

$$CH_4 \longrightarrow CH_x^* \longrightarrow C_2H_4 \longrightarrow C_6H_6$$

It is assumed that further ethylene oligomerization occurs at BASs.[95] The hydrogen form of HZSM-5, which contains such sites on its surface, catalyzes the formation of benzene from ethylene; almost the same reaction occurs over the Mo_2C/HZSM-5 catalyst. However, as distinct from neat silica where ethylene aromatization does not occur, benzene forms over the Mo_2C/SiO_2 catalyst even in the absence of BASs. Thus, the presence of molybdenum in the catalyst can have impact not only on the methane dimerization reaction but also on the subsequent reactions.

Acetylene has been revealed among the products formed over the Mo/HZSM-5 catalyst at 750 °C.[76] The authors point to acetylene as a possible intermediate in the formation of benzene. The transformation of acetylene into benzene on HZSM-5 zeolites is well known; over these zeolites, the conversion of acetylene to benzene is 8 times faster than that of ethylene. The acetylene intermediate $CH_2{=}CH^*$ is more active that the ethylene intermediate $CH_3-CH_2^*$. Thus, benzene can also form through the stage of acetylene formation.

It has been noted that methane activation sites are Mo_2C species,[20, 23, 77, 96] and their partial oxidation deteriorates the activity of Mo/ZSM-5 catalysts.[77] By contrast, other researchers believe that the active sites are MoC_xO_y oxycarbides.[61, 63]

The presence of molybdenum in zeolite channels is assumed to be the cause of stable catalyst performance.[29, 58, 63, 75, 97, 98] Because of small amounts of supported molybdenum, sensitivity of the experimental methods is still insufficient for determining the structure of the molybdenum sites. In addition, molybdenum is located both within the micropores of zeolite and on its outer surface. Therefore, quantum chemical calculations are now increasingly being used to study the geometric and electronic structure of the active sites.

A methane molecule is a regular tetrahedron. The average bond energy for the four C–H bonds is 414 kJ mol^{-1}, and the dissociation energy for the first C–H bond is 435 kJ mol^{-1}. The methane molecule has a low-lying HOMO and a high-lying LUMO, which hinders electron transfer between methane and frontier orbitals of other molecules and makes methane one of the most stable molecules. In processes involving methane, such as dehydroaromatization, the most difficult stage is the activation of the first C–H bond of methane; the other three bonds are much easier to activate. Therefore, theoretical studies of aromatization mainly focus on the stage of cleavage of the first C–H bond.

It is known that, in the course of catalyst preparation, Mo migrates into zeolite channels and interacts with Brønsted acid sites to form precursors of sites active in dehydrocyclization.[76] Different models describing the structure of active sites have been suggested. Mo_2C species have been identified by X-ray spectroscopy on the catalyst surface after the reaction, which enables the conclusion that Mo_2C can be involved in methane activation.[99] It has been demonstrated later that Mo in the form of MoO_2 with a defect crystal structure rather than Mo_2C can play a decisive role in methane activation. Mössbauer spectroscopy has been used for studying spent Mo/HZSM-5 catalysts. These studies have demonstrated that carbon atoms are directly bonded to Mo atoms and MoC_x clusters form at the initial period of reaction.[58, 100, 101] It has been suggested that the MoC_x active sites have an Mo–Mo bond. Each Mo atom in such a site is linked with three carbon atoms at Mo–C distances of 0.20 – 0.21 nm, and the Mo–Mo distance is close to 0.280 – 0.282 nm. According to experimental data, MoO_x can be partially reduced to MoC_xH_y in the initial period of time.[61] It is assumed that methane reacts with molybdenum carbide to form ethylene

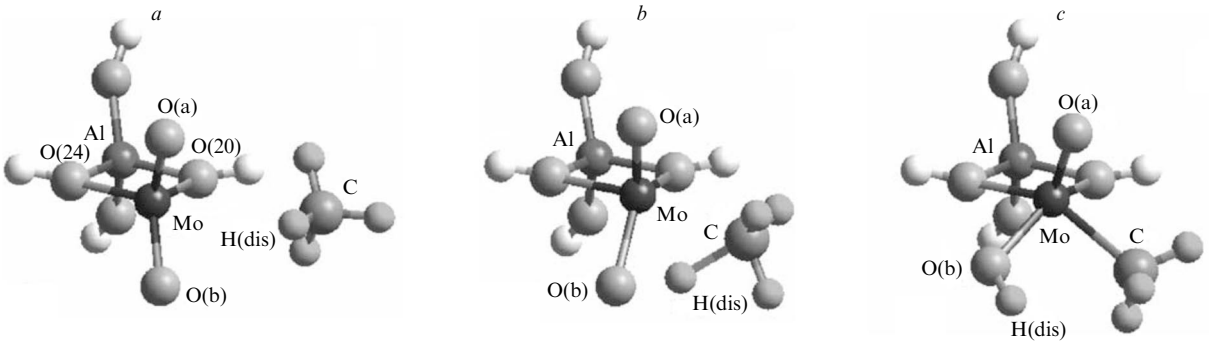


Figure 1. Structures of cluster models: adsorption complex (*a*), transition state (*b*) and methane addition product (*c*).[102]

and hydrogen, and then ethylene oligomerizes to yield benzene.

The mechanism of methane dissociation on the MoO_2/HZSM-5 catalyst has been studied by the density functional theory (DFT) method.[102] According to the calculations, the interaction of methane with an active site first leads to the formation of an adsorption complex (Fig. 1 *a*), which then dissociates into a methyl moiety and hydrogen. In the adsorption complex, the geometry of the methane molecule remains nearly the same, but the C – H bonds are polarized. In the transition state (Fig. 1 *b*), a hydrogen atom of the methane molecule [H(dis)] is located between the carbon atom and the oxygen atom bonded to molybdenum. This structure is characterized by one imaginary frequency 1406 cm^{-1}, corresponding to H – CH_3 and O – H stretching vibrations. Upon dissociation, the hydrogen interacts with oxygen to form an OH group, and the methyl group forms a bond to the Mo atom. The OH and CH_3 groups form covalent bonds to the Mo atom, thus stabilizing the methane addition product (Fig. 1 *c*).

The formation of the adsorption complex leads to a decrease in energy by 15 kJ mol^{-1}. The local and nonlocal density functional activation barriers for the C – H bond cleavage in the adsorption complex are 91 and 158 kJ mol^{-1}, respectively. The activation barrier for methane dissociation in the adsorption complex is considerably lower than that for the direct C – H bond cleavage on the HZSM-5 catalyst (343 kJ mol^{-1}). On the basis of the above data, the following mechanism of methane dissociation on catalytic active sites of Mo/HZSM-5 has been proposed. Upon the interaction of the molybdenum cation with the methane carbon atom, electron density is transferred from the methane molecule to the metal atom. This leads to a weakening of the C – H bond in methane and facilitates the dissociation of the hydrogen atom. Strong electrostatic attraction appears between the oxygen atom bonded to molybdenum and the dissociated hydrogen atom, so that they form a hydroxyl group covalently bound to molybdenum. Thus, the MoO_2 species is able to activate the C – H bond.

In studying the geometric and electronic structure of mononuclear $(MoO_2)^{2+}$ and binuclear $(Mo_2O_5)^{2+}$ sites in the HZSM-5 zeolite, cluster models of the zeolite containing aluminium atoms in the T3 – T3, T3 – T12, T6 – T6, T6 – T9 and T7 – T12 positions (Fig. 2) have been considered.[103, 104] The stability of the binuclear molybdenum clusters containing Al atoms in the T3 – T3, T6 – T6, T6 – T9 and T3 – T12

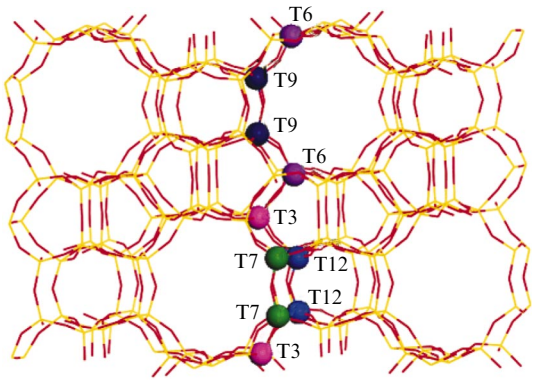
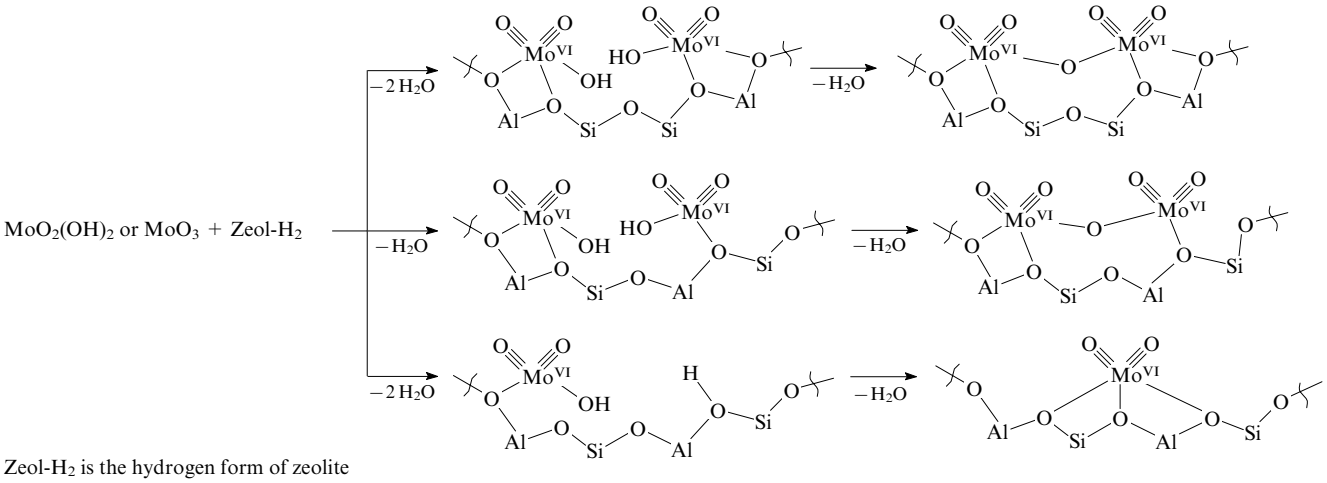


Figure 2. Structure of ZSM-5 zeolite along the [100] direction; neighbouring T positions are shown.[103]

positions is roughly the same. In the binuclear structures, each Mo atom is bonded to two bridging oxygen atoms O – Al – O. The terminal double Mo – O bond lengths are 1.7 Å, which is consistent with the experimentally determined Mo=O bond length, 1.73 Å. The Mo – O bond length in Mo – O – Mo is 1.91 Å (the experimental value is 1.84 Å), and the average distance between the Mo atoms and the framework oxygen atoms is 2.17 Å. At the same time, natural bond orbital (NBO) population analysis suggests that the terminal Mo – O bonds can be treated as triple bonds. The calculated vibration frequencies 995 and 1055 cm^{-1} correspond to O≡Mo≡O stretching vibrations. On the basis of the computational data, a scheme of formation of monomeric and dimeric structures (Scheme 5) has been suggested.[103]

The NBO population analysis for the binuclear complex demonstrates that the major contribution to the HOMO is made by the p orbital of the framework oxygen atom, and the largest contribution to the LUMO is made by the antibonding π*-orbital of the terminal Mo – O bond, and the binuclear structure is an electron-deficient active site. When methane reacts with the binuclear site, electron density is transferred from the HOMO of methane to the LUMO of the molybdenum complex. The transition state corresponding to the dissociation of C – H bond in methane has an imaginary frequency 1230 cm^{-1}. The activation energy is 63.5 kcal mol^{-1}.

Scheme 5



Zeol-H_2 is the hydrogen form of zeolite

Data on the geometric and electronic structure of molybdenum carbide on HZSM-5 have been reported.[105] Four cluster models of active sites have been considered: $Mo(CH_2)_2$/ZSM-5, $Mo(CH_2)_2CH_3$/ZSM-5, $Mo_2(CH_2)_4$/ZSM-5 and $Mo_2(CH_2)_5$/ZSM-5. The mononuclear and binuclear structures were constructed with the use of cluster models of the 5T and 12T zeolite, respectively. The first mononuclear model $Mo(CH_2)_2$/ZSM-5 has a symmetric structure (Fig. 3 *a*). The Mo atom is in the O–Al–O plane at the same distance from framework oxygen atoms. The Mo atom is linked with two methylene groups so that the C–Mo–C plane is perpendicular to the O–Al–O plane. In the second model, the Mo atom is bonded to two methylene groups and one methyl group (Fig. 3 *b*). The methylene groups are symmetrically bonded to the Mo atom, but the C–Mo–C plane is slightly tilted to the O–Al–O plane.

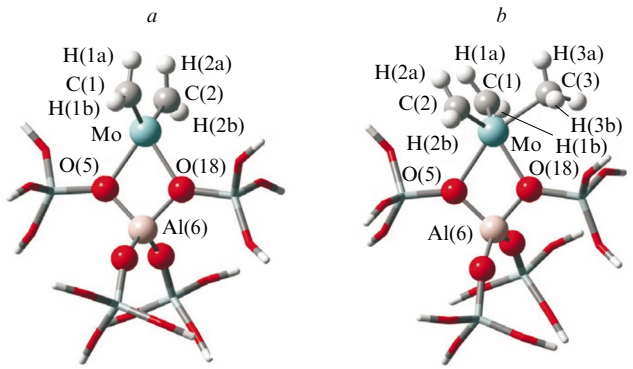


Figure 3. Optimized structures of monomeric active sites $Mo(CH_2)_2$/ZSM-5 (*a*) and $Mo(CH_2)_2CH_3$/ZSM-5 (*b*).[105]

In both models, the Mo atom is linked with the CH_2 group by a double bond similar to the bond in the Mo=CH_2 metallocarbene. NBO population analysis shows that the C=Mo=C system is characterized by π-orbital conjugation involving the zeolite framework oxygen atoms. The structure is stabilized due to σ-donation from the bonding orbital of the Al–O bond to the antibonding π-orbital of the Mo=C bond.

The binuclear structures contain the Mo–Mo bond, and each Mo atom is bonded to three carbon atoms. In the structure of $Mo_2(CH_2)_5$/ZSM-5 (Fig. 4 *a*), each molybdenum atom is bonded to two methylene groups, and the Mo atoms are linked with each other through the CH_2 group. The Mo–C bond lengths for the terminal CH_2 groups are different, being 0.1870 and 0.1915 nm. The distances

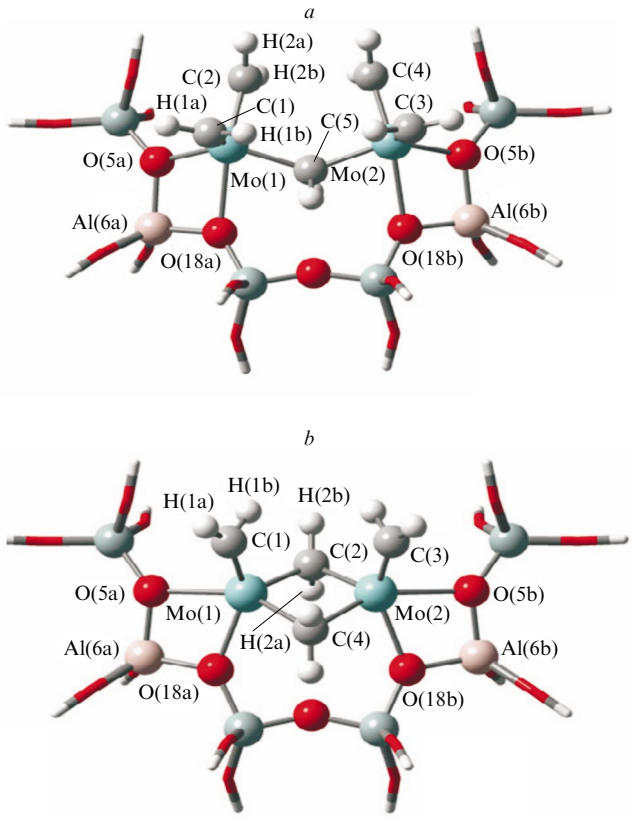


Figure 4. Optimized structures of binuclear active sites $Mo_2(CH_2)_5$/ZSM-5 (*a*) and $Mo_2(CH_2)_4$/ZSM-5 (*b*).[105]

between the Mo atom and the framework oxygen atoms are 0.2132 and 0.2421 nm, and the distance to the Al atoms is 0.3135 nm. The Mo – Mo distance is 0.3856 nm, which is close to the experimental data for the Mo_2O_5 structure and is consistent with the assumption that molybdenum oxide species are precursors of molybdenum carbide. In the second binuclear structure $Mo_2(CH_2)_4$/ZSM-5, each molybdenum atom is bonded to the terminal CH_2 group, and two Mo atoms are linked by two bridging CH_2 groups (Fig. 4 *b*). The distance between the Mo atom and the C atom of the terminal CH_2 group is 0.1833 nm, and that for the bridging CH_2 group is 0.2093 nm. The Mo – O bond lengths are 0.2309 and 0.2156 nm, and the distance between the Mo and Al atoms is 0.3113 nm. Like the mononuclear structure, the binuclear structures have π-orbital conjugation.

The mechanism of methane activation on such active sites implies heterolytic dissociation of the C – H bond to form H^+ and H_3C^- species, which then bind to the C and Mo atoms to form a stable intermediate compound. Among the described four structures, the binuclear cluster $Mo_2(CH_2)_5$/ZSM-5 has the lowest activation energy (106 kJ mol^{-1}); therefore, it is considered the most probable model of the active site at which methane C – H bond dissociation occurs.

Results of studying the methane dehydrogenation with subsequent aromatization on the model active sites H^+, $(HMO_2)^+$ (M = Mo or W) and $Mo(CH_3)_3$(AlOSi) have been reported.[106] The strength of acid sites changes in the following order: $H^+ > (HMO_2)^+ > Mo(CH_3)_3$(AlOSi). In all three cases, the modelled catalysts have vacant s or d orbitals. Methane is activated due to electron density transfer from the methane molecule to the vacant orbitals.

On the basis of calculation results, the following mechanism of methane activation has been suggested (Scheme 6).

Scheme 6

$$CH_4 + MC_x/HZSM\text{-}5 \longrightarrow H_2C^+ - MC_x/HZSM\text{-}5 + H_2$$

$$CH_4 + H_2C^+ - MC_x/HZSM\text{-}5 \longrightarrow$$

$$\longrightarrow H_2C^+ - H_2C - MC_x/HZSM\text{-}5 + H_2$$

$$H_2C^+ - H_2C - MC_x/HZSM\text{-}5 \longrightarrow C_2H_4 + M^+C_x/HZSM\text{-}5$$

Then, the resulting ethylene converts to benzene in ZSM-5 zeolite pores (Scheme 7).

Scheme 7

$$3\,C_2H_4 \longrightarrow C_6H_6 + 3\,H_2$$

An alternative route of aromatization is possible. It involves the oligomerization of the $H_2C^+ - H_2C - MC_x$/HZSM-5 intermediate and methane resulting in a long-chain complex (Scheme 8).

Scheme 8

$$CH_4 + H_2C^+ - (H_2C)_n - MC_x/HZSM\text{-}5 \longrightarrow$$

$$\longrightarrow H_2C^+ - (H_2C)_{n+1} - MC_x/HZSM\text{-}5 + H_2$$

Then, the resulting long-chain complex can undergo aromatization in zeolite pores (Scheme 9).

Scheme 9

$$H_2C^+ - (H_2C)_5 - MC_x/HZSM\text{-}5 \longrightarrow$$

$$\longrightarrow C_6H_6 + MC_x/HZSM\text{-}5 + 3H_2$$

The high acidity of catalysts facilitates the CH_x adsorption and formation of long-chain hydrocarbons, but decreases the selectivity to aromatics.

Methane activation with subsequent formation of the C – C bond on the (001) β-Mo_2C surface has been studied by the DFT method.[107] Among the four models considered for the adsorption of a methane molecule on the Mo_2C surface, two are stable and have identical structures with the adsorption energy −289 kJ mol^{-1}. In this case, methane is dissociatively adsorbed to form CH_3 and H species.

If two methane molecules are adsorbed, each of them dissociates into CH_3 and H independently of each other (Scheme 10).

Scheme 10

$$2\,CH_4 \longrightarrow 2\,CH_{3\,ads} + 2\,H_{ads}$$

When two methyl moieties come closer together, they form a C – C bond and surface H_{ads} and $C_2H_{5\,ads}$ species (Scheme 11).

Scheme 11

$$2\,CH_{3\,ads} + 2\,H_{ads} \longrightarrow C_2H_{5\,ads} + 3\,H_{ads}$$

Elimination of one of the hydrogen atoms from the-$C_2H_{5\,ads}$ species produces C_2H_4 linked with Mo_2C through two bonds (Scheme 12).

Scheme 12

$$C_2H_{5\,ads} + 3\,H_{ads} \longrightarrow C_2H_{4\,ads} + 4\,H_{ads}$$

The adsorption energy for two methane molecules is 554 kJ mol^{-1}, and the activation energy of formation of C_2H_5 from two adsorbed methyl groups is 741.3 kJ mol^{-1}. The reaction shown in Scheme 11 involves several processes: formation of the C – C bond in C_2H_5 from two CH_3 species, elimination of hydrogen atom and migration of the CH_3 species. The potential energy of the transition state for this reaction is only 187.3 kJ mol^{-1} higher that the energy of the initial species. Then, two variants are possible: formation of ethylene on the Mo_2C surface and four adsorbed hydrogen atoms (Scheme 12) and formation of ethane and hydrogen molecule. In the latter case, the total energy of the system increases by 575.9 kJ mol^{-1}, and the activation energy of the reaction in Scheme 12 is only 4.2 kJ mol^{-1}. Desorption of the ethylene molecule and two hydrogen molecules from the molybdenum carbide surface lead to an increase in the system energy by 795.4 kJ mol^{-1}. In hydrogen excess, desorption of the C_2H_5 species from the surface is possible (Scheme 13).

Scheme 13

$$C_2H_{5\,ads} + 3\,H_{ads} + 2\,H_2 \longrightarrow C_2H_5 + H_2 + 5\,H_{ads}$$

It cannot be ruled out that carbonaceous deposits are also involved in formation of active sites of a catalyst.[20, 46, 96] The necessity of modification of molybdenum carbide with carbonaceous deposits is believed to be caused by the high activity of 'unmodified' Mo_2C in methane decomposition to hydrogen and carbon.

Further oligomerization with chain elongation occurs on Brønsted acid sites of the catalyst. It has been shown that the decrease in the number of such sites has no effect on the reaction rate; *i.e.*, a relatively small number of active acid

sites are required for oligomerization to occur.[55] At the same time, it has been demonstrated that the catalyst supported on the zeolite completely converted to the Na form is inactive in methane dehydroaromatization.[26]

Thus, the bifunctional character of methane dehydroaromatization catalysts is generally accepted, but comprehensive data on the reaction mechanism are not yet available.

VI. Causes of deactivation of Mo/ZSM-5 catalysts and methods of their regeneration

A major cause of Mo/ZSM-5 catalyst deactivation is coking.[108, 109] The amount of carbonaceous deposits increases with an increase in reaction duration[108, 109] and temperature.[22] In the course of reaction, carbonaceous deposits are concentrated on the external surface of the zeolite.[108]

Temperature-programmed oxidation (TPO) data for the Mo/ZSM-5 catalyst after reaction suggest that a major reason of its deactivation is formation of carbonaceous deposits associated with the BASs of the zeolite and blocking its channels.[110]

1. Nature of carbonaceous deposits

The chemical composition of carbonaceous deposits formed under the reaction conditions on the catalyst surface is determined by their formation mechanism.[110] Two major mechanisms can be distinguished: consecutive and carbide-cycle mechanisms. The first mechanism implies that carbonaceous deposits form as a result of consecutive reactions of hydrocarbon condensation and polymerization, dehydrocyclization and binding of cyclic structures. This is accompanied by their gradual depletion in hydrogen up to the formation of a pseudographite structure due to release of light hydrocarbons and hydrogen. Upon coke formation by the consecutive mechanism, the H : C ratio in the carbonization products depend on the type of catalyst, hydrocarbon nature, temperature and reaction duration.[111] With increasing reaction time, the hydrogen content in carbonaceous deposits decreases.

Coke formation by the carbide-cycle mechanism is typical of catalysts containing metals that form unstable carbides (Fe, Ni).[110] In this case, the composition of carbonaceous deposits is more homogeneous. Differences pertain to the degree of graphitization, size and shape of aggregates.

Formation of carbonaceous deposits upon interaction of Mo/zeolite catalysts with methane has been observed in many studies.[22, 25, 46, 69] The selectivity of their formation is 20% – 40% (Ref. 20) and decreases with an increase in the reaction time.[29] The amount of carbonaceous deposits increases with increasing reaction temperature.[22]

It has been shown that the coke formation rate increases linearly with an increase in the content of Mo in the zeolite matrix from 0 mass % to 2 mass % and remains almost unaltered as the molybdenum concentration increases from 2 mass % to 10 mass % over the reaction time of 3 h.[69]

Three types of carbonaceous deposits are distinguished: carbide-like carbon in Mo_2C, carbon in carbonaceous deposits of pre-graphite type and graphite-like carbon.[108] Carbonaceous deposits of the pre-graphite type are concentrated on the external surface of the zeolite, and graphite-like carbon is localized inside the zeolite channels. In the course of reaction, mainly the amount of deposits of pre-graphite type increases.[108]

It has been found that a part of carbonaceous deposits is associated with the Brønsted acid sites of the zeolite, and the other part is carbon associated either with molybdenum carbide or with other molybdenum compounds in which molybdenum is partially reduced.[46] The TPO method also revealed two types of carbonaceous deposits characterized by the low (503,[94] ~470 °C[50, 51]) and high (592,[94] 543,[50] 557 °C[51]) oxidation temperature. It is suggested that carbonaceous deposits with the lower burnout temperature are concentrated on the molybdenum carbide surface, and those with the higher burnout temperature are associated with the BASs of the zeolite.[50, 109]

The presence of three peaks (459, 511 and 558 °C) in the TPO profile for the spent 6% Mo/ZSM-5 catalyst points to the existence of three types of carbonaceous deposits: (1) associated with Mo-containing sites located on the external surface of the zeolite, (2) associated with Mo-containing sites located in zeolite channels and (3) associated with Brønsted acid sites.[61] For the catalyst pretreated in a hydrogen atmosphere, the content of carbonaceous deposits localized at BASs is considerably lower, while the concentration of carbonaceous deposits associated with Mo-containing sites located on the external surface is higher.

According to the results of TPR H_2 and temperature-programmed reaction with CO_2 (TP CO_2), the treatment of the coked catalyst with carbon dioxide leads to a decrease in the content of carbonaceous deposits with both the low and high oxidation temperature; while the treatment with hydrogen decreases only the content of deposits with the high oxidation temperature.[94] Successive TPR H_2 and TP CO_2 experiments are unable to completely remove carbonaceous deposits.

Thus, in methane dehydroaromatization over Mo/ZSM-5 catalysts, carbonaceous deposits of different nature and localization are formed. A diversity of data on the character of carbonaceous deposits points to the possibility to control the rate and selectivity of their formation by varying the synthesis and test conditions of Mo/ZSM-5 catalysts.

2. Methods of regeneration of Mo/ZSM-5 catalysts

To regenerate the catalytic activity of coked Mo/ZSM-5 catalysts, they can be subjected to oxidative treatment. Generally, oxidative regeneration of coked catalysts is a set of chemical reactions between oxygen and carbonaceous deposits resulting in carbon oxides and water.[111] The oxidation of carbonaceous deposits occurs though formation and decomposition of oxygen – carbon complexes.[112, 113] In addition to the difference in the nature of carbonaceous deposits, the coke removal rate depends on both the regeneration conditions and the composition of the regenerated catalyst. For example, the presence of transition metals promoted the oxidation of carbonaceous deposits due to the increase in the oxygen – carbon complex formation rate.[111] Alkali metal carbonates also considerably promote carbon oxidation owing to formation of intermediate alkali metal peroxides or highest oxides in the course of regeneration.[113]

Several methods of regeneration of deactivated Mo/ZSM-5 catalysts have been proposed,[90, 114, 115] in particular, regeneration by means of treatment of the catalyst in an NO – air [1 : 50 by volume)] mixture at 450 °C.[114] The small addition of nitrogen oxide decreases the temperature

required for the complete coke removal by 100 °C as compared with regeneration in pure air. On the basis of TPO experiments, a mechanism of regeneration of the coked catalyst has been proposed (Scheme 14).

Scheme 14

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

$$NO_2 + [\text{carbonaceous deposits}] \longrightarrow$$

$$\longrightarrow NO + N_2O + N_2 + CO_x + H_2O$$

Lower regeneration temperature suppresses the sublimation and migration of MoO_x species and thus retains the initial molybdenum distribution in the zeolite matrix, which results in more stable catalyst performance in the reaction – regeneration cycles.[114]

After the treatment of coked catalysts with an H_2-He (1 : 5 by volume) mixture at 680 °C, the rate and selectivity of benzene formation is completely recovered, and the induction period vanishes.[90, 115] However, this method turned out to be inefficient for treatment of a severely deactivated catalyst. After the treatment of the Mo/ZSM-5 catalyst under TPO conditions (130 – 680 °C, 5 K min^{-1}) the induction period reappears, but the reaction rate in the steady state is typical of a freshly prepared sample.[90] The above procedures[90, 115] have not been tested in high-cycle regeneration.

The use of the periodic CH_4-H_2 switching operation mode increases the yield of aromatic hydrocarbons and reduces catalyst coking.[116] However, for stable catalyst performance in such a mode, the cycle duration should be only 5 – 10 min.

It is likely that the most suitable method of regeneration of spent Mo/ZSM-5 catalysts implies the use of TP CO_2 followed by TPR H_2, which leads to removal of carbonaceous deposits of all types.[94] It has been demonstrated that the use of only TPR H_2 leads to removal of up to 90% of carbonaceous deposits associated with Brønsted acid sites and up to 60% of coke associated with Mo-containing species.[109]

Thus, carbonization of Mo/ZSM-5 catalysts is an inevitable side process of the methane dehydroaromatization reaction, responsible for gradual deactivation of catalysts. Treatment of Mo/ZSM-5 catalysts after reaction with an oxygen-, CO_2- or hydrogen-containing mixture completely or partially restores the initial catalyst performance characteristics.

VII. Ways of improvement of methane dehydroaromatization

1. Promotion of Mo/zeolite catalysts

It has been shown that the presence of a second metal, in addition to molybdenum, in the zeolite matrix can have a significant effect on the activity and selectivity, as well as on the coking resistance of Mo/ZSM-5 catalysts.[22, 30, 54, 57, 67, 117]

The introduction of copper by ion exchange into the initial HZSM-5 catalyst followed by solid-phase synthesis of Mo/CuZSM-5 (CuZSM-5 + MoO_3) yields a more active and stable catalyst.[57] The presence of copper favours the increase in the concentration of Mo^{5+} ion, which are believed to be active site of catalyst. In addition, the introduction of copper suppresses zeolite dealumination and coking, thus increasing the catalyst service time. The character of carbonaceous deposits also changes: the oxidation temperature decreases, and the number of CH_x species increases.

The introduction of W, Zr[67] or Ru[54, 118] into Mo/ZSM-5 catalysts improves their activity and selectivity to aromatic hydrocarbons. It is assumed that this improvement in the characteristics of Mo – Ru/ZSM-5 catalysts is associated with the decrease in the number of strong Brønsted acid sites and the increase in the number of medium Brønsted acid sites, as well as with easier reduction of the initially formed molybdenum oxide.[54] The use of platinum as a modifying additive enhances the stability of the Mo/ZSM-5 catalyst due to the decrease in the amount of carbonaceous deposits formed in the course of reaction.[117] The introduction of Zn or La also suppresses the coking rate of Mo/zeolite samples.[40] It has been shown that the presence of Group VIII metals in 3% Mo – 3% M/ZSM-5 catalysts (M = Fe, Ni, Co) promotes the decomposition of methane into hydrogen and carbon, which deteriorates the selectivity to aromatics and their yield.[119] The highest selectivity to carbon is shown by the Mo – Ni catalyst, and the lowest, by the Mo – Fe catalyst. The introduction of a Ni nanopowder into the 4% Mo/ZSM-5 catalyst is demonstrated to be beneficial only at the nickel content of 0.1%.[120] At higher concentrations, nickel promotes the formation of carbon filaments that block catalyst pores and form massive coke deposits, which leads to the loss in stability. Doping the 3% MoO_3/HZSM-5 catalyst with Co^{2+} ions produces only a short-term increase in the methane conversion and hydrogen yield, whereas the introduction of iron ions enhances the catalyst activity at longer times but also enhances coke formation.[121] Doping with Al increases the yield of benzene, although this effect is unstable, and the addition of Ga enhances the catalyst activity and suppresses coke formation. It is notable that different acidities of dopant solutions can also have an effect on catalyst properties.

Gallium is often used for promoting methane dehydroaromatization catalysts. The addition of a small amount of gallium to Mo/HZSM-5 increases the conversion from 12.4% to 20.5% and slightly suppresses carbon formation. These effects are explained by the fact that Ga promotes the reduction of MoO_3 on the surface and in the pores of the zeolite.[122] Another explanation of the promoting effect of 0.1% – 0.6% Ga is that the addition of gallium enhances the adsorption of CO_x species and the formation of alkenes.[123]

The addition of lithium, phosphorus[22, 121] or vanadium[67] to the Mo/ZSM-5 catalyst decreases the catalyst activity. This effect is attributed to decrease in the number of BASs involved in methane aromatization.[22]

2. Other methods of modification of Mo/zeolite catalysts

Dealumination of the initial zeolite is an alternative method for suppression of coke formation in the course of reaction.[81, 124] This effect is explained by the extraction of a fraction of aluminium from the tetrahedral positions in the zeolite framework, which decreases the number and strength of Brønsted acid sites.[124] This is supported by TPO data demonstrating that dealumination suppresses the formation of coke deposits with high oxidation temperature associated with Brønsted acid sites.[81, 124] It has been shown that for a dealuminated Mo/ZSM-5 catalyst, the selectivity of coke formation decreases to 18.2% (from

37.9%) and the yield of aromatic hydrocarbons increases by 32%, while the methane conversion is retained at the same level (9.5%).[124]

It is known that silanation of the external surface of zeolites also suppresses coking of zeolite-supported catalysts.[125] The effect of silanation of the initial HZSM-5 zeolite on the activity of Mo/ZSM-5 catalysts in methane dehydroaromatization has been studied.[56,126] To keep intact the acid OH groups residing in zeolite channels, (3-aminopropyl)triethoxysilane has been used as a silicon source. Because of steric constraints, this compound reacts only with surface OH groups of the zeolite. It has been shown that silanation leads to the removal of 24% of OH groups. The optimum additive content is 0.5% (as SiO_2).[126] In the $Mo-SiO_2$/ZSM-5 catalyst, molybdenum is believed to react mainly with acid groups located inside the zeolite channels. In this case, methane dehydroaromatization occurs within the channels, *i.e.*, under steric constraints, which leads to an increase in selectivity to benzene and a decrease in selectivity to C_{12+} products in the presence of silanated Mo/ZSM-5. An analogous effect is achieved by modifying the zeolite external surface with the organotin compound $SnBu_4^n$.[127]

Yet another method to improve properties of methane dehydroaromatization catalysts is the introduction of structure-forming additives at the stage of zeolite synthesis. The introduction of triethoxyphenylsilane into the initial sol of the synthesis system increases the ZSM-5 crystal size and leads to formation of a secondary mesoporous structure.[62] The catalysts prepared from zeolite modified with an optimal amount of triethoxyphenylsilane showed higher catalyst performance stability. The selectivity to benzene on these catalysts is higher and that to naphthalene is lower than on the conventional catalyst. Secondary mesoporous system can be generated by introducing structure-forming matrices. As such, CMK-3 and C-MCM-41B carbon matrices have been used.[128] They were added to the initial gel in the course of ZSM-5 synthesis. Catalysts containing 6 mass % Mo supported on these zeolites showed higher yields of aromatics and were less prone to coking as compared with the molybdenum catalyst based on conventional ZSM-5.

3. Introduction of gas additives into the initial mixture

The composition of a gas mixture has a strong effect on methane dehydroaromatization. The major source of methane is natural gas. In addition to methane, natural gas contains C_2-C_4 hydrocarbons, with ethane being a major part of them. Natural gas produced in Russia contains, on average, ~4.7% of ethane, ~1.7% of propane and ~0.8% of butane.[14]

Ethane is also one of the products of the methane dehydroaromatization. It accounts for usually no more than 0.2%. The 6% Mo/ZSM-5 activity increases linearly with increasing ethane content from 2.6 vol.% to 16.8 vol.% in a mixture containing CH_4 and Ar.[129] The benzene formation rate in the reaction mixture containing two hydrocarbons ($CH_4 + C_2H_6 + Ar$) is two times higher than the sum of the benzene formation rates achieved in a flow containing one hydrocarbon ($CH_4 + Ar$; $C_2H_6 + Ar$). However, the increase in activity is accompanied by faster deactivation of the catalyst.

The introduction of ethane into the reaction mixture $N_2:CH_4:CO_2 = 25:25:1$ ($N_2:CH_4:C_2H_6:CO_2 = 25:25:2.8:1$) leads, in addition to the increase in the aromatics formation rate, to negative methane conversion due to its formation in the reaction. The ethane conversion at the early reaction period is 100% and decreases to 50% after 25 h on stream. TPO data for spent Mo/ZSM-5 catalysts reveal that, in the presence of ethane, the coke accumulation rate increases twofold.[130]

Mo/ZSM-5 catalyst are highly active in the conversion of ethane to aromatics.[45,131,132] In particular, in a C_2H_6 (1.1%)$-N_2$ mixture, the benzene yield can be as high as 30%.[45] When pure ethane is used, the yield of aromatic hydrocarbons is as high as 65%,[132] and the selectivity of methane formation is as high as 40%.

To improve the performance stability of Mo/ZSM-5 catalysts, small amounts of CO,[30,45] CO_2,[30,130] O_2,[133] H_2[134]) or H_2O[135] are added to methane. It has been shown that if methane contains 1.6% – 12% CO, the benzene formation rate is two times higher than in the absence of CO.[30] The content of CO_2 added to methane should not exceed 1.6%. The increase in CO_2 content to 12% leads to complete deactivation of the 3% Mo/ZSM-5 catalyst.[30,45] Being added to methane, CO_2 converts to CO (Scheme 15).[136] Therefore, the effect of CO_2 is analogous to the effect of CO.

Scheme 15

$$CO_2 + CH_4 \longrightarrow 2CO + 2H_2$$

$$CO_2 + [C] \longrightarrow 2CO$$

When 3% H_2 is added to methane, both the total methane conversion and methane conversion to benzene decrease,[134] which is caused by thermodynamics of the process. According to the stoichiometry of reaction (the first reaction in Scheme 1), increasing hydrogen pressure promotes the reverse hydrogenation reaction. However, as revealed,[137] the addition of 3.6% – 6% of hydrogen to the gas mixture enhances the catalyst resistance to coking, which partially compensates for the slight decrease in the initial activity. The benzene formation rate during catalyst operation decreases more slowly and the coke accumulation rate is lower than in the absence of hydrogen. In addition, during TPO of the spent catalyst, coke is removed at lower temperatures, which facilitates the regeneration of the catalyst.

Under non-oxidative conditions, molybdenum oxide in contact with methane converts first to oxycarbide (MoO_xC_y) and then to less active molybdenum carbide (Mo_2C). This carbide is responsible for the decrease in the activity of Mo/ZSM-5 catalysts in the course of reaction.[133] It has been assumed that the presence of small amounts of oxygen in the reaction mixture not only suppresses coke formation but also ensures the existence of molybdenum as (MoO_xC_y) oxycarbide over a long reaction period.[133] The critical oxygen concentration in the mixture, above which deep oxidation of methane prevails, increases with increasing reaction temperature.

Small water additions (1.7% – 2.2%) to methane feed increase the activity and performance stability of the 6% Mo/ZSM-5 catalyst.[135] The beneficial effect of water is due to the occurrence of the reaction $H_2O + C \rightarrow CO + H_2$, where C is carbon of carbonaceous deposit. In addition, water suppresses coke formation and leads to a decrease in coke oxidation temperature. However, the introduction of water in concentrations exceeding the optimal value results

in a sudden drop of catalytic activity, which is presumably caused by zeolite dealumination.[135]

VIII. Conclusions

Consideration of available data enables the conclusion that methane dehydroaromatization over Mo/ZSM-5 catalysts is a promising alternative strategy of rational utilization of natural gas. Methane dehydroaromatization on these catalysts occurs with high selectivity to benzene (up to 80% – 90%) and the methane conversion of 7% – 9%.

The most widely used method of preparation of Mo/ZSM-5 catalysts is impregnation with an ammonium heptamolybdate solution. Information is available that the introduction of other metals by impregnation of zeolite (Zn, La) or by ion exchange (Cu) somewhat improves the characteristics of the process.

The choice of initial zeolite is of importance, since its acidity has an effect on the activity and selectivity of Mo/ZSM-5 catalysts. It has been demonstrated that the catalyst activity increases with an increase in the number of Brønsted acid sites. At the same time, dealumination of the zeolite matrix decreases the BAS concentration and, thus, improves some characteristics of the methane dehydroaromatization process. Most likely, this is due to that BASs are involved in both the oligomerization of intermediate C_2 products to benzene and the formation of carbonaceous deposits.

The question about the state of molybdenum and its location in the structure of the zeolite is still debatable. The existence of several types of active sites and the possible reaction mechanism are discussed. Most researchers agree that methane activation begins with formation of CH_3 and CH_2 species on the catalyst surface, which then convert to ethane or ethylene and that molybdenum carbide plays an important role in methane activation. Nevertheless, the role of Mo^{5+} ions identified in the catalyst after the reaction along with molybdenum carbide remains unclear.

Recent studies have focused on understanding the nature of carbonaceous deposits formed on Mo/ZSM-5 catalysts. It is recognized that catalyst coking is the major cause of deactivation.

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