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Acidic and Catalytic Properties of Mo-Containing Zeolite Catalysts for Non-Oxidative Methane Conversion

A.V. Vosmerikov[1]*, G.V. Echevsky[2], L.L. Korobitsyna[1], N.V. Arbuzova[1],
L.M. Velichkina[1], S.P. Zhuravkov[3], Ya.Ye. Barbashin[1] and Ye.G. Kodenev[2]

[1]Institute of Petroleum Chemistry, Akademichesky Ave. 3, Tomsk 634021, Russia
[2]Boreskov Institute of Catalysis, Ak. Lavrentieva Ave. 5, Novosibirsk 630090, Russia
[3]Institute of Strength Physics and Material Science, Akademichesky Ave. 2/1, Tomsk 634021, Russia

Abstract

The conversion of methane into benzene, toluene and naphthalene at the reaction temperature of 750°C and gas hourly space velocity (GHSV) of 500-1500 h^{-1} over zeolites modified via impregnation with ammonium heptamolybdate and mechanical mixing with Mo oxide and nanopowder is studied under non-oxidative conditions. It has been established that the highest methane conversion per one run and maximal yield of aromatic hydrocarbons are reached for the sample containing 4.0 mass.% the Mo nanopowder. The stability of Mo-containing zeolite catalysts in the process of methane dehydroaromatization at different GHSV has been studied and a characteristic presence of the induction period caused by the formation of active Mo forms both on the external surface and into the zeolite channels has been established. Both the duration of induction period and stable catalyst operation are decreasing with increasing of GHSV. It was demonstrated that acidic properties of a Mo-containing zeolite catalyst depend on the Mo concentration and method of its introduction.

Introduction

The non-oxidative methane conversion over Mo/ZSM-5 catalysts has attracted considerable attention in recent years [1-5]. The study of this process is of a great interest both to develop an efficient method for natural gas conversion into valuable petrochemical feedstock and to solve a complex catalysis problem connected to methane activation, whose molecule is the most stable and symmetric. Researchers' efforts in this field aim at the development of the efficient catalytic systems, optimisation of the process conditions, establishment of the active phases present in the catalyst and reaction mechanism, as well as at the study of the coke nature and its role in this process. However, despite of increased and explicable interest of researchers to the reaction of non-oxidative methane dehydrocondensation into aromatic hydrocarbons, there are no definitive answers to many important questions. Thus, for example, the nature and preferential localisation of active Mo forms in a zeolite and their role in methane molecule activation have not been revealed. The dependence of the duration of the catalyst induction period on the catalyst preparation method and reaction conditions has not been established. The pattern of carbon deposits formation on the external surface and in zeolite channels as well as on active molybdenum-containing phases is not clear. The kinetics of the process have not been studied yet in detail etc. The answers to above and other questions may be given only by comprehensive study in this field using a complex of up-to-date physicochemical methods of analysis.

The purpose of the present investigation is to examine the influence of the Mo concentration and the method for Mo introduction into the zeolite matrix on acidic properties, catalytic activity and stability of Mo/ZSM-5 catalysts in the process of non-oxidative methane conversion.

Experimental

To prepare the catalysts, a high-silica zeolite with the silicate modulus (M) 40 synthesised at the Insti-

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*corresponding author. E-mail: pika@ipc.tsc.ru

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tute of Catalysis, SB RAS has been used. X-ray study has shown that its structure is similar to that of the ZSM-5 zeolite and its crystallinity degree is near 100%. Mo/ZSM-5 samples were prepared by two methods: impregnation and mechanical mixing. A zeolite was impregnated with aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AHM)) followed by drying at 100°C and calcination at 540°C for 6 hours. Mechanical mixing of the zeolite and oxide (MoO_3) was carried out in the KM-1 ball vibrating mill for 4 h. Then the mixtures produced were calcined at 540°C for 6 hours on air. The Mo nanopowder was produced by electroexplosion of the molybdenum wire in argon [6].

Conversion of methane (grade of 99.9%) was carried out at atmospheric pressure under flow conditions in a quartz reactor (12 mm internal diameter) at 750°C and GHSV of 500-1500 h^{-1}. The volume of catalyst loaded in the reactor was 1 cm^3 and the particles size was 0.5-1.0 mm. Before the reaction, the catalyst was heated in He flow to 750°C and then kept for 20 min at this temperature. To prevent the condensation or strong adsorption of higher hydrocarbons, a pipe at the outlet of the reactor and gas-sampling valve had the temperatures above 200°C. The reaction products were analysed using gas chromatography.

Acidic properties of Mo/ZSM-5 catalysts were studied using the method of programmed ammonia thermodesorption (TPD) allowing to determine the distribution of acidic sites by strength and their quantity. The procedure of thermodesorption experiments is described in [7].

The method of thermal analysis was used to study the coke formation process and the nature of coke deposits formed on Mo-modified zeolite catalysts during methane dehydrodearomatization. The study of coked samples was performed using "C" DTA-DTG instrument (MOM, Hungary) within 20-800°C. The sample (400-500 mg) was heated in a platinum crucible on air at the rate of 10 deg/min, the sensitivity was as following: TG = 100 mg, DTA = 1/5, DTG = 1/5.

Results and Discussion

The preliminary investigation has demonstrated that methane conversion over an unmodified zeolite under the above reaction conditions is very low and does not exceed 2%.

The data on the influence of the method for Mo introduction into a zeolite matrix on methane conversion are given on Fig. 1. As is seen from the Fig. 1, methane conversion increases with the Mo concentration in a zeolite and reaches maximal values over the catalysts containing 4.0% Mo (calculated as metal). A catalyst obtained by mechanical mixing of a zeolite with Mo NP possesses the highest activity, a relatively high methane conversion degree being reached already at a low Mo content (0.5%) and held at the level of 12% and higher in the samples containing from 0.5 to 4.0% of molybdenum. When the Mo concentration in zeolite catalysts surpasses 4%, a decrease in the methane conversion degree is observed, especially over the samples prepared by mechanical mixing. The most significant activity reduction is observed over a catalyst with Mo NP addition.

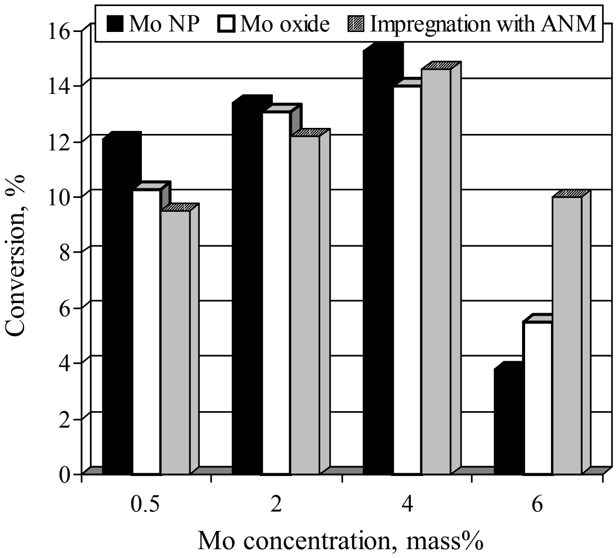

Fig. 1. Methane conversion *vs.* concentration of molybdenum introduced into a zeolite via different methods (T = 750°C, GHSV = 1000 h^{-1}).

Figure 2 shows the results of the study into the stability of the operation of 4.0% Mo/ZSM-5 catalysts prepared by different methods in the process of methane conversion. It is clear from the data listed that the catalyst prepared by mechanical mixing of a zeolite with the Mo nanopowder possesses the highest operation stability and the attained conversion degree over this catalyst is quite high (>10%) for 240 min of operation. The sample prepared via mechanical mixing of zeolite with the Mo oxide exhibits the highest methane conversion for the first 120 min of operation. However, the catalyst activity is drastically lost with the increase in reaction time. As a result, at 420 min of its operation the conversion degree reduces to 0.9%. The operation of a catalyst prepared via impregnation is characterised by a monotonous reduction of methane conversion with time by 7% in the first 60 min of catalyst operation.

The largest amount of aromatic hydrocarbons during 120 min of operation is formed over a catalyst prepared by mechanical mixing with MoO_3, after which their yield drastically decreases (Fig. 2). During methane conversion over a catalyst produced via impregnation a lower yield of aromatic hydrocarbons is observed as compared to the catalyst prepared by mechanical mixing with the Mo oxide and their amount gradually reduces with reaction time. A catalyst prepared via mixing of a zeolite with the Mo nanopowder is characterised by the highest yield of aromatic hydrocarbons in the first 120 min of catalyst operation.

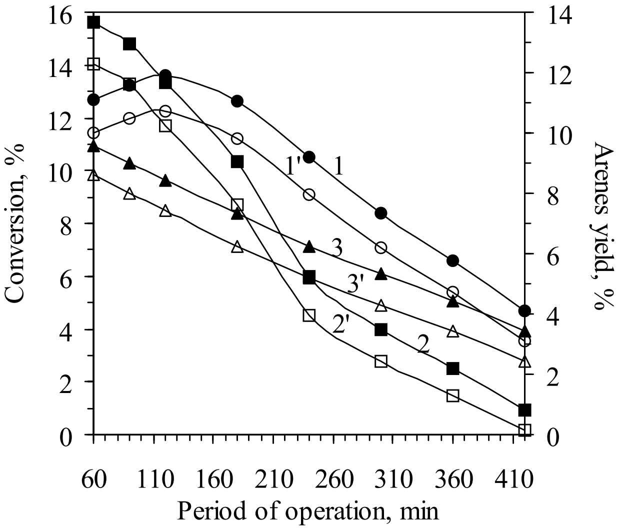

Fig. 2. Methane conversion (1, 2, 3) and arenes yield (1', 2', 3') *vs.* operation period of a zeolite containing 4.0% Mo (calculated as metal): 1, 1' – nanopowder; 2, 2' – MoO_3; 3, 3' – AHM impregnation (T = 750°C; GHSV = 1000 h^{-1}).

Thus, the catalyst prepared by mechanical mixing of a zeolite with the Mo nanopowder exhibits the highest stability in the process of methane conversion into aromatic hydrocarbons within the period of time under investigation.

Figure 3 represents the data on the effect of methane GHSV on the operation stability of a zeolite catalyst containing 4.0% Mo NP at the reaction temperature of 750°C. As seen from the Figure 3, this sample is characterised by a period of gradual activity enhancement, the duration of which increases with the decrease in the contact time. Thus, conversion and yield of aromatic hydrocarbons increase in the first 60 min of catalyst operation at the GHSV of 500 h^{-1}, and in 120 min at GHSV of 1000 h^{-1}. A lower conversion in the initial period of reaction depends on the existence of the induction period determined obviously by the time needed to form active Mo forms both on the surface and in the channels of the zeolite.

Maximal conversion and obtaining of the largest amount of aromatic hydrocarbons are observed over a catalyst containing 4.0% Mo NP at methane GHSV of 500 h^{-1} in 60 min of catalyst operation. These indices are 16.1 and 12.9%, respectively.

The shorter is the contact time, the more drastic is the drop in its degree of conversion. Thus, in 420 min of catalyst operation the conversion and yield of aromatic hydrocarbons reduced by 4.4 and 3.9% at 500 h^{-1}, by 7.3 and 6.6% at 1000 h^{-1}, and by 8.6 and 7.7% at 1500 h^{-1}, respectively. A similar pattern is observed for the selectivity for aromatic hydrocarbons formation: the reduction is 3.5, 14.8 and 39.8% at GHSV of 500, 1000 and 1500 h^{-1}, respectively.

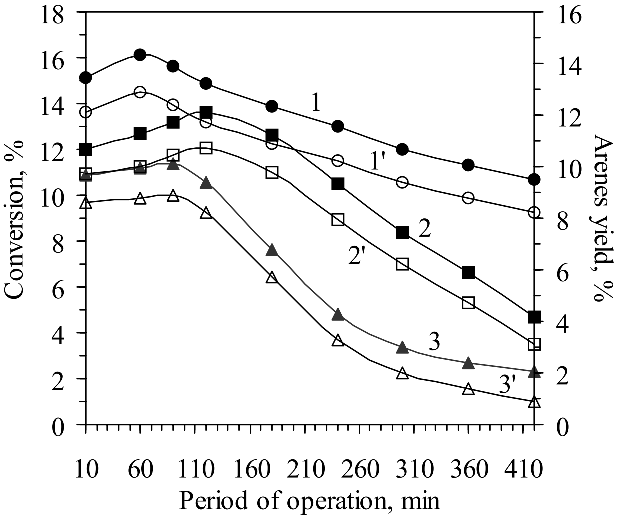

Fig. 3. Methane conversion (1, 2, 3) and arenes yield (1', 2', 3') *vs.* operation period of a zeolite containing 4.0% Mo NP at the following GHSV (h^{-1}): 1, 1' – 500; 2, 2' – 1000; 3, 3' – 1500 (T = 750°C).

Figure 4 shows DTA-DTG patterns (taken on air) of the catalyst samples coked in 420 min of operation at different GHSV (500-1500 h^{-1}). At 110°C an endothermal effect and a corresponding maximum on DTG curve caused by water removal are recorded for each sample. Intensive exothermal effects observed at the temperatures above 380-400°C and the peaks on DTG curves correspond to coke burnout. The comparative analysis demonstrates that the temperatures of removal of the coke formed on the sample increase with the increase in GHSV. Thus, for GHSV of 500 h^{-1} the maximum on DTG curve is at 525°C and exothermal effect on DTA curve is at 500°C, for 1000 h^{-1} – at 545 and 515°C, for 1500 h^{-1} – at 555 and 530°C, respectively. Moreover, it is well seen that at the increase in GHSV of methane the coke being formed becomes more condensed, which is evidenced by the "growth" of the peak shoulder and its displacement into the high-temperature region, from weakly bonded at 500 h^{-1} to more condensed at 690°C for 1000 h^{-1} and to 745°C at 1500 h^{-1}. The amount of the coke formed over the catalyst increases with the methane GHSV from 500 to 1500 h^{-1}. The data on the changes in the mass of the catalyst coked at different methane GHSV relatively to the mass of the "pure" sample (upon coke burnout below 800°C) are given in Table 1.

At present the problem of nature and localisation of active Mo forms is largely discussed in literature. Although there is no unambiguous opinion, most of publications note a bifunctional properties of Mo/ZSM-5 catalysts. Activation of methane molecules occurs over active Mo centres (Mo_2C, MoO_x) followed by CH_x forms formation, and further conversion of these intermediates into benzene and naphthalene takes place over the acidic sites of the zeolite. That is why the acidic properties of zeolites, along with the state and localisation of Mo within the zeolite matrix play an important role in the formation of efficient catalysts of methane conversion.

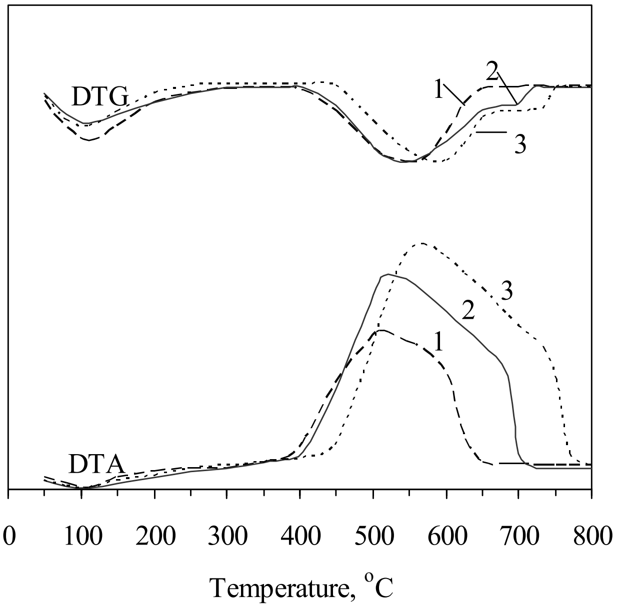

Fig. 4. DTA and DTG curves of coke deposits formed on 4.0% Mo(NP)/ZSM-5 at the following GHSV (h^{-1}): 1 – 500; 2 – 1000; 3 – 1500 (T = 750°C).

Table 1

Changes in mass of 4.0% Mo(NP)/ZSM-5 catalyst coked during methane conversion at different GHSV

GHSV, h^{-1}	Mass change, %		
	Water	Oxygen	Coke
500	-3.00 (110°C)	+0.03 (350°C)	-3.55 (525°C)
1000	-1.90 (110°C)	+0.33 (370°C)	-5.13 (545°C)
1500	-1.30 (110°C)	+0.33 (440°C)	-5.85 (555°C)

Note. The terms in brackets stand for corresponding temperatures of maximums on DTG curves.

The data of Table 2 suggest that the initial zeolite has a great amount of acidic sites, which may be attributed to two types: weak acidic and strong acidic sites. At the introduction of 0.5% Mo in a zeolite a reduction of the concentration of acidic sites of both types occurs. The decrease in the amount of strong acidic sites, especially at Mo NP introduction, is the most significant (Fig. 5). The decrease in the concentration of high-temperature centres is less in the case of the catalyst prepared by zeolite impregnation with ammonium heptamolybdate solution. The change in the concentration of acidic sites corresponding to the low-temperature peak has another behaviour: the maximal decrease in the amount of weak acidic sites is observed for the zeolite impregnated by ammonium heptamolybdate solution.

The strength of the acidic zeolite sites when a small Mo amount (0.5%) is added changes insignificantly, which is pointed out by close temperatures of maxima of the low- and high-temperature peaks.

The increase in Mo content introduced into a zeolite by different methods to 4.0% leads to the decrease in the concentration of acidic sites corresponding to the high-temperature peak and to smoothing of its maximum. The concentration of weak acidic sites increases in the catalysts prepared by impregnation and mixing with MoO_3. When Mo concentration reaches 6.0%, observed is a drastic decrease in the concentration of acidic sites of a zeolite, especially for the samples obtained via impregnation and mechanical mixing with the Mo nanopowder (Table 2). The decrease of the concentration of acidic sites for a sample produced through mechanical mixing of a zeolite with MoO_3 is less pronounced.

Table 2
The influence of the methods for Mo introduction and its concentration (mass.%) into a zeolite on acidic zeolite properties

Method	Mo concentration	t_I, °C	t_{II}, °C	c_I	c_{II}	c
Initial	0	235	450	561	424	985
Mixing with Mo NP	0.5	235	445	546	267	813
	4.0	225	–	510	202	712
	6.0	205	–	147	–	147
Mixing with MoO_3	0.5	235	445	496	280	776
	4.0	225	–	592	188	780
	6.0	220	–	558	–	558
Ammonium heptamolybdate impregnation	0.5	235	450	433	330	763
	4.0	225	–	628	213	841
	6.0	215	–	256	–	256

Note. t_I, t_{II} are the temperatures of maximums of the peaks for forms I and II; c_I, c_{II} and c are the concentrations of acidic sites in the forms I and II, and total concentration, respectively, μmol/g.

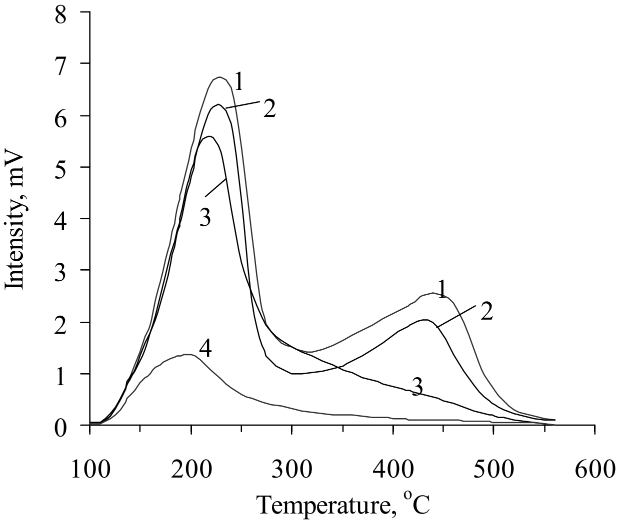

Fig. 5. TD spectra of the initial zeolite (1) and a zeolite containing 0.5% (2); 4.0% (3) and 6.0% (4) of Mo nanopowder.

The decrease in the concentration of acidic sites in modified zeolites is probably determined by the interaction of OH groups connected to the lattice Al with Mo forms during calcination. The results obtained agree well with the data of the studies demonstrating the Mo interaction with the zeolite matrix when treated on air at elevated temperatures [8,9]. Using ^{27}Al NMR and EPR methods, it has been demonstrated that highly dispersed MoO_x forms located on the external zeolite surface penetrates into zeolite channels at high temperatures (>500°C) and generate $(Mo_2O_7)^{2-}$ forms due to the interaction with OH groups. When the Mo concentration in a zeolite surpasses 4.0% and at the treatment temperature above 700°C, a strong Mo interaction with the zeolite matrix occurs, which results in the decomposition of the crystalline zeolite structure followed by the generation of catalytically inactive phases of $Al_2(MoO_4)_3$. Moreover, the elemental analysis of the samples with an increased Mo content has shown that the calcination results in transformation of Mo particles into fine MoO_3 crystals, which, evidently, leads to the decrease in the concentration of acidic sites. To a greater extent this is observed for the samples prepared with the application of Mo nanoparticles. Acidic sites corresponding to the high-temperature peaks are practically absent in zeolites containing 6.0% Mo; a small "tail" behind the low-temperature peak is observed on the TD spectrum in the region of higher temperatures only for the sample obtained via mixing with MoO_3. The data obtained on acidity of the zeolites containing 6.0% Mo agree well with the results of their tests in the process of methane conversion into aromatic hydrocarbons. The catalytic activity of these samples was low. Thus, the modification of a zeolite catalyst by molybdenum results in the change of its acidic properties and to the formation of novel active and inactive sites connected with different Mo forms. The proportion of different molybdenum forms significantly depends on the amount and method of Mo introduction into zeolite catalysts.

Conclusions

On the basis of the results obtained one may draw a conclusion that there exists a certain relationship between the concentration of acidic sites of different types of zeolite and Mo content. In this connection, to produce a catalyst exhibiting a high activity in the process of methane dehydroaromatization, it is necessary to optimise the relationship between the acidic sites number of a zeolite and the number of active sites connected with different Mo forms.

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