ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2016, Vol. 90, No. 12, pp. 2364–2369. © Pleiades Publishing, Ltd., 2016.
Original Russian Text ©A.A. Stepanov, L.L. Korobitsyna, Ya.E. Barbashin, A.V. Vosmerikov, 2016, published in Zhurnal Fizicheskoi Khimii, 2016, Vol. 90, No. 12, pp. 1797–1803.

CHEMICAL KINETICS
AND CATALYSIS

Effect of the Conditions of Thermal Pretreatment on the Properties of Mo/ZSM-5 Catalyst of the Nonoxidative Conversion of Methane

A. A. Stepanov, L. L. Korobitsyna, Ya. E. Barbashin, and A. V. Vosmerikov*
Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, Tomsk, 634055 Russia
**e-mail: pika@ipc.tsc.ru*

Received February 2, 2016

Abstract—Mo-containing zeolite catalysts for the nonoxidative conversion of methane are produced via solid-phase synthesis, followed by thermal treatment at different temperatures. The state of nanosized Mo powders is investigated by means of X-ray diffraction and thermal analysis. The effect the temperature of Mo/ZSM-5 catalyst annealing has on its acidic characteristics and activity in the process of methane dehydroaromatization is established.

Keywords: methane, zeolite, Mo/ZSM-5 catalyst, nanopowder, methane dehydroaromatization, conversion
DOI: 10.1134/S0036024416120281

INTRODUCTION

The nonoxidative conversion of methane into aromatic hydrocarbons on zeolite-containing catalysts modified with transition metals is of great interest as an effective way of utilizing natural gas, which is generally more than 90% methane. High-silica ZSM-5 zeolites modified with molybdenum are the most promising catalysts of nonoxidative methane conversion. Mo-containing zeolite catalysts are usually produced by impregnating zeolite with solutions of ammonium paramolybdate (heptamolybdate), i.e., $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The catalyst is dried after impregnation and annealed in air at temperatures of 500–720°C. The duration of annealing ranges from 4 to 30 h [1–3]. In addition to impregnation, solid-phase synthesis based on the mechanical mixing of a zeolite with molybdenum salt [4] or oxide [5] is used to produce Mo-containing zeolite catalysts. It was shown in [6] that Mo/ZSM-5 catalysts produced by mechanically mixing zeolite with molybdenum nanosized powder (NSP) exhibits higher activity and operating stability in the nonoxidative methane conversion into aromatic hydrocarbons than catalysts produced via impregnation.

In this work, we investigate the effect the temperature of annealing of mechanical mixtures of zeolite and Mo NSP has on the acidic properties and catalytic activity and stability of Mo/ZSM-5 catalyst during methane dehydroaromatization, and present the results from investigating the oxidation of molybdenum nanopowder used in preparing Mo/ZSM-5 catalyst.

EXPERIMENTAL

High-silica zeolite with molar ratio SiO_2/Al_2O_3 = 40 was synthesized by hydrothermal crystallization using hexamethylenediamine (HMDA) as a structure-forming additive. Nanosized molybdenum powder was produced by electrically exploding a conductor in argon. Mo/ZSM-5 catalyst was prepared via the dry mechanical mixing of H-form zeolite and Mo nanopowder in a KM-1 ball vibromill. The content of Mo in the zeolite was 4.0 wt %. The prepared Mo/ZSM-5 catalyst was annealed in air in a muffle furnace at different temperatures in the range of 250 to 650°C for 1 h.

Thermal analysis was performed on a Q-1500 D derivatograph (MOM, Hungary) in the temperature range of 20–800°C. A sample (60 mg) in an alundum crucible was heated in air at a rate of 10 K/min. Aluminum oxide (α-Al_2O_3) was used as the reference sample. X-ray diffraction analysis was performed on a DISCOVER D8 diffractometer (Bruker) using monochromatic CuK_α-radiation and a LynxEye-detector. Scanning was done in the range of $2\theta = 10°–90°$ with a step of 0.02° and an accumulation time for each point of 3 s.

The acidic properties of the samples were investigated via the temperature-programmed desorption (TPD) of ammonia, allowing the distribution of acidic sites to be determined according to their strength and total number [7]. The concentration of acidic centers was determined from the amount of ammonia desorbed at the moment of desorption peak fixing and

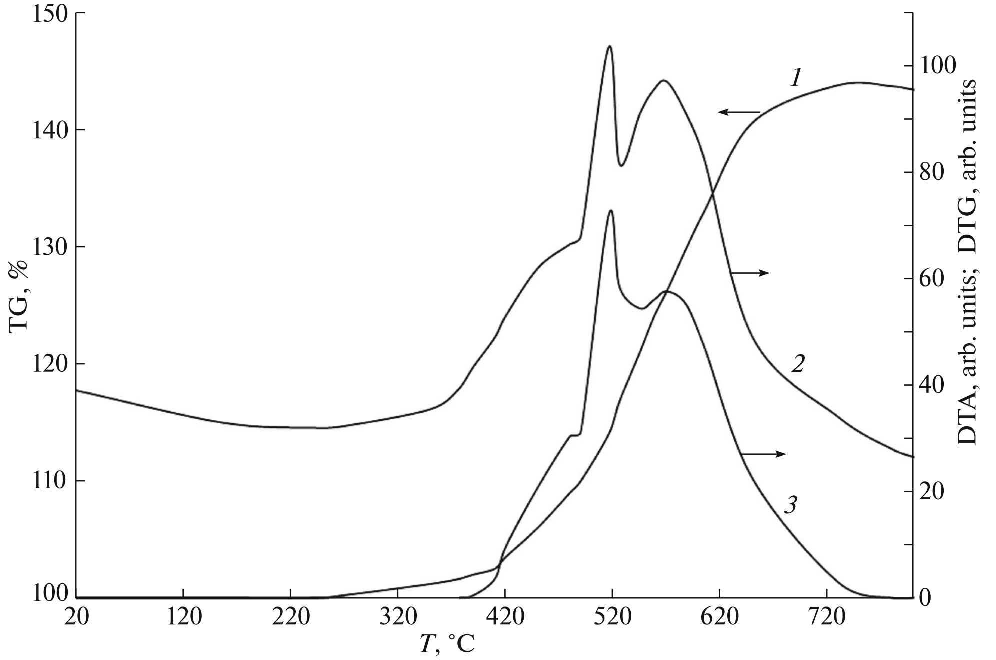

Fig. 1. Thermogram of Mo nanopowders: (*1*) TG, (*2*) DTG, (*3*) DTA.

presented as micromoles per 1 g of catalyst. Mo/ZSM-5 catalyst samples were tested in a flow unit at 750°C, atmospheric pressure, and a volume rate of feed supply of 1000 h^{-1}. A 1.0 cm^3 volume of each sample was placed into a tubular quartz reactor 12 mm in diameter, heated to the reaction temperature in an argon flow. Methane (99.99% purity) was then fed into the reactor. Reaction products were analyzed via GLC on a Khromatek-Kristall 5000.2 chromatograph every 40 min of the process. The degree of methane conversion and the yield of the reaction products were determined to assess the catalytic activity of the samples.

RESULTS AND DISCUSSION

To evaluate the effect the conditions of Mo/ZSM-5 catalyst thermal treatment had on its activity in the process of methane dehydroaromatization, it was necessary first to investigate the change in the state of molybdenum NSP itself in its oxidation during annealing. The behavior of Mo NSP during its oxidation in air in the temperature range of 20–800°C was investigated by means of thermal analysis (Fig. 1). A 0.4% reduction of the sample mass was observed upon heating it from room temperature to 155°C, due to removal of adsorbed compounds (mainly water). Raising the temperature further increases the sample mass, due to the oxidation of molybdenum nanopowder. The data from X-ray diffraction analysis (Fig. 2) of the samples annealed in air indicate that molybdenum oxide MoO_3 formed; in addition, no nitrides were detected in the products.

As can be seen from the data presented in Fig. 1, the process of Mo oxidation is nonlinear as the temperature rises, and four stages can be identified in the process. The first stage is the slow oxidation of Mo observed from 155 to 375°C, accompanied by a 1.7% increase in the sample's mass and the release of a moderate amount of heat. Raising the temperature further sharply increases the rate of Mo oxidation. A shoulder is observed in the DTG curve at 470°C, along with peaks having maxima at 514 and 565°C; this is in good agreement with the exo effects in the DTA curves at 470, 516, and 567°C. The rate of Mo oxidation slows gradually as the temperature rises from 565 to 730°C, and the sublimation of the formed MoO_3 starts at temperatures above 730°C and is accompanied by a reduction in the sample's mass. At the same time, it is likely that heating under nonisothermal conditions does not result in the complete oxidation of molybdenum to stoichiometric MoO_3.

The sample mass grew by 17.5% when the temperature reached 526°C (the inflection point on the DTG curve). According to the equation ($Mo + (1/2)O_2 = MoO$), the mass increase must be 16.7%. The similarity of these values indicates that intermediate oxide MoO forms during the first stage of Mo oxidation, and is then rapidly oxidized to MoO_3. The total increase of the sample mass as a result of heating to 730°C was 48.4%. From the stoichiometry ($2Mo + 3O_2 = 2MoO_3$), it follows that the mass increase should be 50% for the complete transformation of Mo to MoO_3. Deviation from the stoichiometric value is likely explained by the abovementioned incomplete oxida-

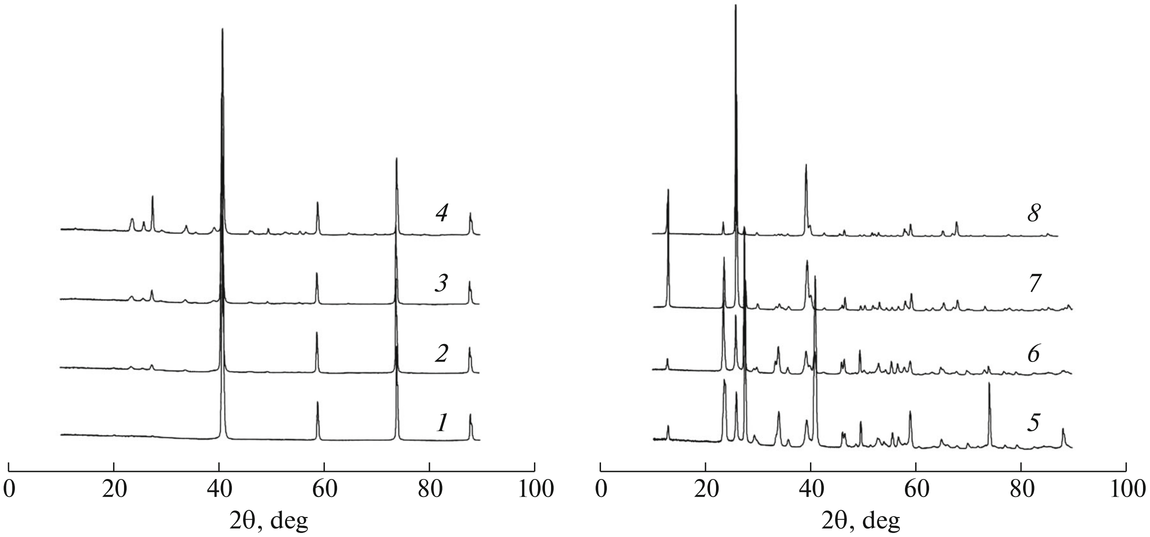

Fig. 2. X-ray diffractograms of Mo NSP annealed at different temperatures: (*1*) 250, (*2*) 300, (*3*) 350, (*4*) 400, (*5*) 450, (*6*) 500, (*7*) 550, and (*8*) 650°C.

tion of Mo under the nonisothermal conditions of thermal analysis, and by the partial loss of Mo oxide due to its sublimation at high temperatures. In addition, the observed difference could be associated with the partial oxidation of the initial molybdenum nanopowder, meaning that it already had certain amount of molybdenum oxide in its composition.

Thermal analysis of 4% Mo/ZSM-5 catalyst showed that the stepwise oxidation of Mo occurred in a manner similar to that of Mo NSP. However, the peaks were observed to shift toward lower temperatures during the process, and oxidation ceased at 630 instead of 730°C, as was the case with the Mo nanopowder. Hence, the stepwise oxidation of Mo occurs in the presence of zeolite, but at lower temperatures, due apparently to the participation of water adsorbed by zeolite during Mo oxidation (since, as is well known, nanopowders of various metals can interact with water [8]).

X-ray diffractograms of the Mo NSP annealed at different temperatures are presented in Fig. 2. The X-ray diffractogram of the sample annealed at 250°C (*1*) exhibits the pattern typical of Mo, indicating that no Mo oxidation occurred at this temperature. Raising the temperature of Mo treatment to 300°C (*2*) results in the emergence of peaks at 22.514°, 25.784°, 27.435°, and 33.383° that correspond to MoO_3 (PDF 00-047-1320). Raising the temperature of Mo treatment further reduces the number of major peaks at 40.750°, 58.774°, and 73.780° that correspond to Mo (PDF 01-076-9187), and increases the number of peaks attributable to MoO_3. Quantitative calculations of the change in the Mo fraction as the annealing temperature changes show that the fraction of MoO_3 in the sample annealed at 250°C is 2%, while in the sample annealed at 350 and 450°C it reaches 26 and 88%, respectively. When treated at 550°C, Mo is virtually 100% oxidized to MoO_3.

It is known that the channel structure and acidity of zeolite, along with the localization and state of molybdenum on its surface, substantially affect the physicochemical and catalytic properties of Mo/ZSM-5 catalysts. The results from investigating the acidic properties of Mo/ZSM-5 catalyst samples produced at different annealing temperatures are presented in the table. It can be seen that introducing Mo NSP into zeolite reduces the strength and concentration of acidic centers of both types, due likely to the localization of Mo nanopowder on the outer surface of the zeolite and the partial blocking of its channels by metal particles. A further drop in the concentration of strong acidic centers is observed for the sample annealed at 250°C. Raising the annealing temperature of the modified zeolite from 300 to 650°C increased the concentration of weak acidic centers, while the content of strong acidic centers in the catalyst passed through its maximum at a treatment temperature of 450°C. The increased concentration of weak acidic centers was probably due to the formation of MoO_3 phase over the outer surface of the zeolite, the amount of which grew along with the annealing temperature [9]. At the same, raising the annealing temperature from 250 to 450°C reduced the strength of the high-temperature acidic centers, as is apparent from the shift of the temperature maxima in the TD spectrum of the investigated samples toward lower temperatures. Annealing the Mo/ZSM-5 catalyst at temperatures above 450°C reduced the concentration and increased the strength of high-temperature acidic centers, due to the considerable increase in the MoO_3 content on the zeolite surface (Mo NSP is completely oxidized to

Acidic properties of the initial zeolite and the Mo/ZSM-5 catalyst annealed at different temperatures (annealing temperatures are given in parentheses)

Sample	$T_{\max}$, °C		Concentration, μmol/g		
	T_{I}	T_{II}	C_{I}	C_{II}	C_{Σ}
Initial ZSM-5	185	440	559	303	862
Mo/ZSM-5 (no annealing)	180	420	525	285	810
Mo/ZSM-5 (250°C)	170	420	552	274	826
Mo/ZSM-5 (300°C)	170	415	608	317	925
Mo/ZSM-5 (350°C)	175	410	624	331	955
Mo/ZSM-5 (400°C)	180	405	653	343	996
Mo/ZSM-5 (450°C)	180	400	658	394	1052
Mo/ZSM-5 (500°C)	190	415	728	296	1024
Mo/ZSM-5 (550°C)	195	425	740	256	996
Mo/ZSM-5 (650°C)	205	425	744	145	889

T_{I}, T_{II} are the temperatures of the maxima of low- and high-temperature peaks, respectively; C_i is the concentration of weak (C_{I}) and strong (C_{II}) acidic centers and their total concentration (C_{Σ}), respectively.

MoO_3 at 550°C) and its growing diffusion into the zeolite channels where it interacts with Brønsted acidic centers.

Different types of interaction between different Mo forms and zeolite are thus possible as a result of Mo/ZSM-5 catalyst annealing at different temperatures during catalyst preparation. Molybdenum can interact with either the acidic centers of the zeolite or the lattice aluminum. In addition, the increased molybdenum oxide concentration in the zeolite and the higher annealing temperature result in the emergence of out-of-lattice Al and the formation of nonactive $Al_2(MoO_4)_3$ crystal phase.

The results from investigating the effect the temperature of Mo/ZSM catalyst annealing has on its activity and stability in the nonoxidative conversion of methane are presented in Fig. 3. The sample not subjected to thermal treatment exhibits very low activity

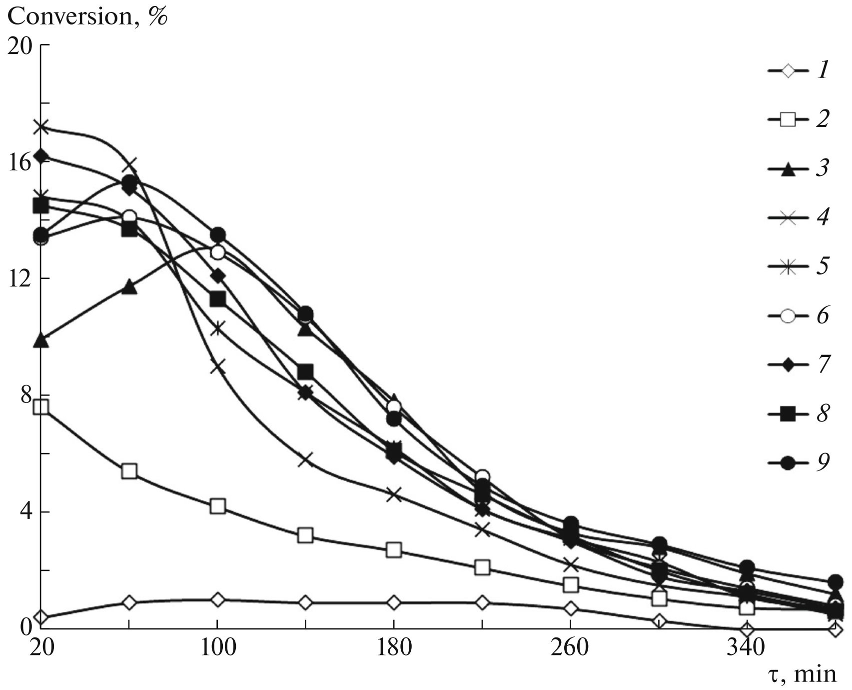

Fig. 3. Change in the degree of methane conversion over time τ of the operation of Mo/ZSM-5 catalyst annealed at different temperatures: (*1*) no annealing; (*2*) 250, (*3*) 300, (*4*) 350, (*5*) 400, (*6*) 450, (*7*) 500, (*8*) 550, and (*9*) 650°C.

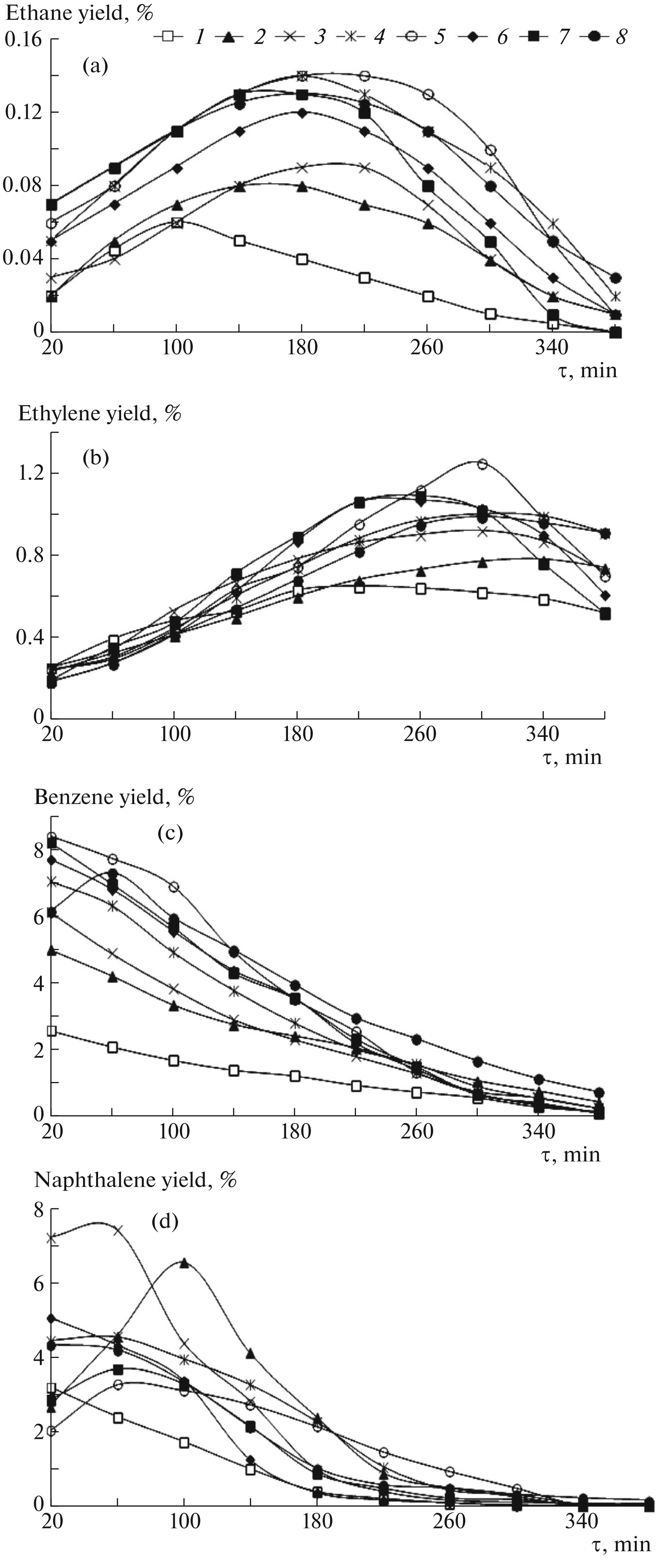

Fig. 4. Change in the yield of (a) ethane, (b) ethylene, (c) benzene, and (d) naphthalene during methane conversion over time τ of the operation for Mo/ZSM-5 catalysts annealed at different temperatures; (*1*–*8*), see Fig. 2.

in this process; the degree of methane conversion on it is no greater than 2%. Methane conversion is 7.8% after the first 20 min of the reaction in the presence of the catalyst sample annealed at 250°C, and it falls gradually during the process. The maximum conversion of methane (17.2 and 15.9%) is reached after the first 20 and 60 min, respectively, of the process conducted with the sample annealed at 350°C. After that, a sharp drop in the degree of conversion is observed. The samples annealed at higher temperatures are less active at the beginning of the process, but over time their activity reaches levels above those for the samples annealed at temperatures below 400°C. The growth in the activity of the Mo/ZSM-5 catalyst as the annealing temperature rises during its production is due to the increase in the fraction of molybdenum oxide and its migration into the zeolite channels. The highest activity and operating stability after 60 min of the reaction was displayed by the sample annealed at 650°C. Raising the temperature of Mo/ZSM-5 catalyst treatment further reduced its activity over the investigated time interval. It was shown in [10, 11] that the zeolite crystal lattice disintegrates completely when the annealing temperature of the Mo-containing catalysts is above 800°C, due to the formation of aluminum molybdate $Al_2(MoO_4)_3$.

Our results from investigating the effect the temperature of Mo/ZSM catalyst annealing has on the composition and yield of the products of methane conversion are presented in Fig. 4. Ethane and ethylene are the main components of the gaseous products; their qualitative composition does not depend on the conditions of catalyst production (Figs. 4a, 4b). The least amount of C_2-hydrocarbons forms on catalysts annealed at 250–350°C. The yield of gaseous hydrocarbons increases in reactions with the catalysts annealed at higher temperatures. The patterns of the changes in the C_2-hydrocarbon yield during the reaction are the same for all investigated samples. The ethane concentration increases with the time of reaction, reaching its maximum level for the samples treated at 400–450°C (Fig. 4a). The greatest amount of ethylene forms on the samples annealed at 450–500°C (Fig. 4b). The amount of ethylene of the reaction products is higher than that of ethane over the duration of the process, and its maximum value does not exceed 1.25%.

Benzene and naphthalene are the main components of the liquid products of methane conversion on Mo/ZSM-5 catalyst. The greatest amount of benzene after first 20 min of the reaction forms on the samples annealed at 450–550°C (Fig. 4c). The benzene yield falls over the time of the process on all of the investigated samples, and the most gradual decrease is observed for the sample annealed at 650°C. The greatest amount of naphthalene is in the reaction products formed in the first 100 min of the reaction on the samples annealed at 300–350°C (Fig. 4d). The benzene/naphthalene ratio in the reaction products formed on all of the investigated samples changes over a wide range during the reaction, but it is close to 2 in most cases.

CONCLUSIONS

The conditions of the thermal treatment of Mo-containing zeolite affect the content of MoO_3 in the catalyst, and consequently its activity in nonoxidative conversion of methane. In order to produce Mo-containing zeolite catalyst that is active in the process of methane dehydroaromatization, it is sufficient to anneal it at 350°C. This indicates that the amount of active phase of MoO_3 formed in annealing the catalysts is sufficient for methane activation and the subsequent conversion of intermediate products on the zeolite acidic centers. Raising the annealing temperature of Mo/ZSM-5 catalyst to 650°C slightly reduces its activity and operating stability. This is likely due to the increased amount of Mo penetrating into the zeolite channels and interacting with its strong Brønsted acidic centers, which in turn lowers the rate of Mo/ZSM-5 catalyst carbonization.

REFERENCES

1. Y. Xu, Y. Shu, S. Liu, J. Huang, and X. Guo, Catal. Lett. **35**, 233 (1995).
2. F. Solymosi, A. Cserenyi, A. Szoke, T. Bansagi, and A. Oszko, J. Catal. **165**, 150 (1997).
3. H. Liu, W. Shen, X. Bao, and Y. Xu, Appl. Catal. A: Gen., No. 1, 79 (2005).
4. B. M. Weskhuysen, D. Wang, M. Rosynek, and J. Lunsford, J. Catal. **175**, 338 (1998).
5. W. Ding, D. Meitzner, and E. Iglesia, J. Phys. Chem. B **105**, 506 (2001).
6. A. V. Vosmerikov, N. V. Arbuzova, L. L. Korobitsyna, G. V. Echevskii, and E. G. Kodenev, RF Patent No. 2271863, Byull. Izobret. No. 8 (2006).
7. A. V. Vosmerikov and V. I. Erofeev, Zh. Fiz. Khim. **69**, 787 (1995).
8. G. I. Volkova, V. G. Ivanov, and O. A. Kukharenko, Khim. Interesah Ustoich. Razvit. **14**, 349 (2006).
9. L. Óvári and F. Solymosi, J. Mol. Catal. A: Chem. **207**, 35 (2004).
10. W. Liu, Y. Xu, S.-T. Wong, L. Wang, and N. Wang, J. Mol. Catal. A: Chem. **120**, 257 (1997).
11. Y. Xu, S. Liu, X. Guo, L. Wang, and M. Xie, Catal. Lett. **30**, 135 (1995).

Translated by L. Brovko