

Deactivation of Molybdenum-Containing Zeolites in the Course of Nonoxidative Methane Conversion

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Abstract—It was found that the nonoxidative dehydroaromatization of methane occurs over Mo-containing pentasil-type zeolites with various framework compositions at 750°C. This reaction is accompanied by catalyst deactivation because of coke formation. The effects of the space velocity of methane and the composition of the zeolite matrix on the amount and properties of the resulting condensation products were studied. It was found that the lowest amount of coke with a relatively low degree of polycondensation was formed on zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$ containing Mo nanoparticles.

INTRODUCTION

Catalysts of a new generation based on pentasil-type zeolites (ZSM-5) have found extensive use in oil and gas-condensate processing [1–7]. After the discovery of the nonoxidative dehydroaromatization reaction of methane in 1993 [8], they became promising for the conversion of oil gas and natural gas into valuable chemical products. It is well known that methane dehydroaromatization over Mo/ZSM-5 occurs with the highest conversion and selectivity at high temperatures of 700–800°C [9–13], which are favorable for intense coking and result in rapid catalyst deactivation. Therefore, one of the most important problems is to increase the catalyst service time between regenerations. For this purpose, the mechanism of catalyst deactivation and the nature of condensation products formed on the outer surface and in zeolite channels, as well as at Mo-containing sites, should be studied. In this work, we studied Mo/ZSM-5 zeolites deactivated in the course of methane dehydroaromatization under various reaction conditions using thermal analysis.

EXPERIMENTAL

The catalysts were prepared by mechanically mixing ZSM-5 zeolite and MoO_3 or nanosized molybdenum powder in a KM-1 vibration ball mill (Germany) for 4 h followed by calcination at 540°C for 6 h. The pentasils with $\text{SiO}_2/\text{Al}_2\text{O}_3$ (M) equal to 30, 40, and 80 were synthesized at the Borekov Institute of Catalysis, Siberian Division, Russian Academy of Sciences (~100% degree of crystallinity). The molybdenum nanopowder was prepared by the electric explosion of a conductor in an argon atmosphere at the Institute of

Strength Physics and Materials Science, Siberian Division, Russian Academy of Sciences (average particle size of 70 nm) [14]. The molybdenum content of the catalysts was 4.0 wt %.

The nonoxidative conversion of methane (99.9% purity) was performed in a flow system at 750°C, feeding space velocities (V_0) of 250–1500 h^{-1} , and atmospheric pressure. The catalyst volume in a quartz reactor was 1 cm^3 , and the catalyst particle size was 0.5–1.0 mm. Before the beginning of an experiment, the catalyst was heated to 750°C in a flow of helium and kept at this temperature for 20 min. To prevent the condensation or strong adsorption of high-boiling hydrocarbons formed in the course of reaction, the reactor outlet tube and the six-way sampling valve were thermostated at a temperature above 200°C. The reaction products (H_2 , ethane, ethylene, benzene, toluene, naphthalene, and C_{11} – C_{12} hydrocarbons) were analyzed by gas chromatography.

The formation and nature of coke deposits were studied by thermal analysis on a C derivatograph (MOM, Hungary) over the range 20–800°C. A sample (400–500 mg), in a platinum crucible, was heated in air at a rate of 10 K/min (sensitivity of 100 mg).

RESULTS AND DISCUSSION

The results given in Table 1 indicate that a catalyst with $M = 40$ containing 4.0% Mo nanopowder was characterized by a development period, the duration of which increased with V_0 . A maximum conversion (X) and the highest yield of aromatic hydrocarbons (Y_{ar}) were achieved on a catalyst at $V_0 = 500 \text{ h}^{-1}$ after 60 min. They were equal to 16.1 and 12.9%, respectively, at a

Table 1. Effect of the space velocity of methane supply on the conversion and the yields of methane conversion products on the 4.0% Mo (nanopowder)/ $M = 40$ catalyst ($T = 750^{\circ}\text{C}$)

t , min	V_0 , h^{-1}	X , %	Product yields, mol %							Y_{ar} , mol %	S_{ar} , %
			H_2	C_2H_4	C_2H_6	C_6H_6	C_7H_8	C_{10}H_8	$\text{C}_{11}\text{--C}_{12}$		
10	500	15.1	2.86	0.12	0.01	5.67	0.16	6.25	0.01	12.1	80.1
	1000	12.0	2.17	0.16	0.03	4.51	0.19	4.87	0.11	9.7	80.8
	1500	10.9	2.08	0.20	0.03	3.80	0.11	4.59	0.12	8.6	78.9
60	500	16.1	2.98	0.15	0.05	6.47	0.18	6.22	0.02	12.9	80.1
	1000	12.6	2.30	0.21	0.10	5.43	0.37	4.02	0.12	9.9	78.6
	1500	11.2	2.01	0.23	0.13	4.97	0.28	3.35	0.19	8.8	78.6
90	500	15.6	2.93	0.22	0.09	6.68	0.21	5.48	0.04	12.4	79.5
	1000	13.2	2.37	0.24	0.14	5.96	0.42	3.94	0.13	10.4	78.8
	1500	11.4	2.08	0.27	0.15	5.37	0.32	3.01	0.19	8.9	78.1
120	500	14.6	2.74	0.24	0.10	6.65	0.23	4.61	0.03	11.5	78.8
	1000	13.5	2.48	0.28	0.16	6.42	0.50	3.55	0.12	10.6	78.5
	1500	10.6	1.90	0.33	0.17	5.19	0.34	2.57	0.08	8.2	77.4
180	500	13.9	2.58	0.27	0.12	6.24	0.26	4.39	0.02	10.9	78.4
	1000	12.6	2.29	0.33	0.18	6.00	0.54	3.13	0.10	9.8	77.8
	1500	7.6	1.29	0.48	0.18	3.89	0.35	1.37	0.05	5.7	75.0
240	500	13.0	2.38	0.30	0.13	6.13	0.33	3.71	0.01	10.2	78.5
	1000	10.5	1.76	0.41	0.19	5.64	0.50	1.91	0.08	8.1	77.1
	1500	4.8	0.72	0.59	0.20	2.33	0.19	0.75	0.03	3.3	68.8
300	500	12.0	2.15	0.33	0.16	6.01	0.31	3.05	0.01	9.4	78.3
	1000	8.4	1.42	0.54	0.22	4.23	0.41	1.53	0.07	6.2	73.8
	1500	3.4	0.42	0.74	0.22	1.45	0.11	0.43	0.01	2.0	58.8
360	500	11.3	2.01	0.37	0.17	5.93	0.30	2.55	–	8.8	77.9
	1000	6.6	1.07	0.61	0.23	2.89	0.30	1.45	0.05	4.7	71.2
	1500	2.7	0.28	0.82	0.24	0.92	0.06	0.42	0.01	1.4	51.9
420	500	10.7	1.90	0.45	0.19	5.80	0.28	2.12	–	8.2	76.6
	1000	4.7	0.55	0.84	0.25	2.16	0.16	0.70	0.03	3.1	66.0
	1500	2.3	0.16	0.97	0.26	0.56	0.04	0.27	–	0.9	39.1

Note: t is the time of catalyst operation; V_0 is the space velocity; X is the conversion; Y_{ar} is the yield of aromatic hydrocarbons; and S_{ar} is the selectivity of formation of aromatic hydrocarbons.

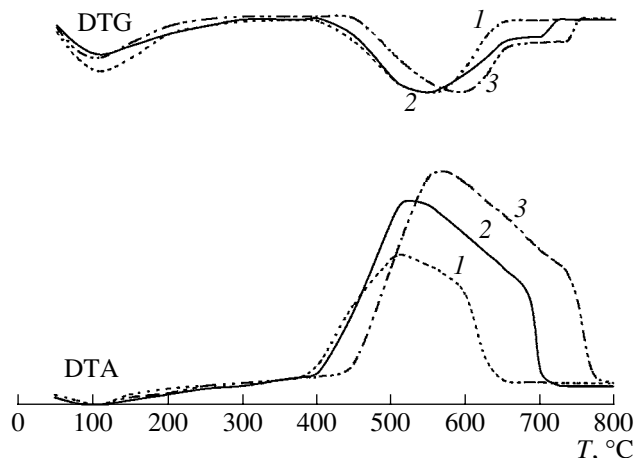


Fig. 1. Thermoanalytical curves of the 4.0% Mo (nanopowder)/ $M = 40$ treated with methane at $V_0 = (1)$ 500, (2) 1000, and (3) 1500 h^{-1} . $T = 750^\circ\text{C}$.

selectivity of formation of aromatic hydrocarbons (S_{ar}) higher than 80%. After a certain time, X and Y_{ar} decreased rapidly at all of the methane space velocities. In this case, the greater V_0 , the more dramatic decrease in the catalytic activity. A similar behavior was observed for S_{ar} : at space velocities of 500, 1000, and 1500 h^{-1} , the selectivity decreased by 3.5, 14.8, and 39.8%, respectively.

Catalyst deactivation in the course of methane dehydroaromatization resulted from coke formation, as supported by X-ray photoelectron spectroscopy and NMR spectroscopy [10, 11, 13]. In the cited publications, it was found that coke was formed as two species on the surface of catalysts. One of these species blocked acid sites in zeolite channels, and the other blocked partially reduced molybdenum clusters; it was mainly localized at the outer zeolite surface. In the course of dehydroar-

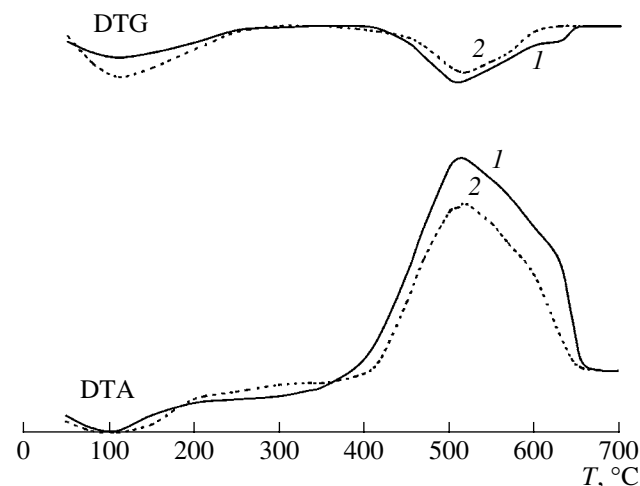


Fig. 2. Thermoanalytical curves of (1) 6.0% $\text{MoO}_3/M = 40$ and (2) 4.0% Mo (nanopowder)/ $M = 40$ catalysts after methane treatment (120 min) at $T = 750^\circ\text{C}$.

omatization, the fraction of the latter coke species rapidly increased.

Figure 1 shows the thermoanalytical curves of a zeolite sample with $M = 40$ after treatment with methane at 750°C (420 min) at V_0 of 500, 1000, and 1500 h^{-1} . The endothermic peak at 110°C and the corresponding DTG peak were due to the removal of water. The intense exotherm and the DTG peaks observed at 380 – 400°C correspond to carbon burning. A comparative analysis demonstrated that the temperatures of coke removal from the surface increased with V_0 . Thus, at $V_0 = 500 \text{ h}^{-1}$, a peak in the DTG curve occurred at 525°C and an exothermic peak in DTA occurred at 500°C . At 1000 and 1500 h^{-1} , the DTG peak and the exotherm occurred at 545 and 515 and at 555 and 530°C , respectively. Moreover, the amount of coke increased with V_0 and more condensed coke was formed. This is evidenced by an increase in a shoulder and a shift of this shoulder toward higher temperatures (690 and 745°C at 1000 and 1500 h^{-1} , respectively). Table 2 summarizes data that indicate changes in the weight of a catalyst after methane dehydroaromatization at various V_0 as compared with the weight of a pure sample (after coke elimination at 800°C). At temperatures lower than that of carbon burning—to 380, 420, and 460°C at $V_0 = 500$, 1000, and 1500 h^{-1} , respectively—an increase in the weights of samples was observed (DTG curves in Fig. 1, Table 2). This increase was likely due to the addition of oxygen and the formation of oxidized coke species on the catalyst surface. The hydrophobicity of samples increases with coke concentration; therefore, the amount of water removed from catalysts decreases.

Table 2. Changes in the weight of the 4.0% Mo (nanopowder)/ $M = 40$ catalyst after the dehydroaromatization of methane at various feeding space velocities

V_0, h^{-1}	Weight 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 corresponding temperatures of peaks in the DTG curves are given in parentheses.

Thus, at short contact times (i.e., great V_0), the carbonization of a sample occurred much more rapidly and

Table 3. Changes in the weight of pentasils with $M = 40$ containing MoO_3 and molybdenum nanopowder after the dehydroaromatization of methane

Catalyst	Weight change, %		
	water	oxygen	coke
6.0% $\text{MoO}_3/M = 40$	-1.00(110°C)	+0.05(320°C)	-3.05(520°C)
4.0% Mo (nanopowder)/ $M = 40$	-3.50(110°C)	+0.10(450°C)	-1.86(525°C)

Note: The catalysts operated for 30 min at each particular space velocity of 500, 750, 1000, and 1500 h^{-1} (total time of 120 min). The corresponding temperatures of peaks in the DTG curves are given in parentheses.

less homogeneous and more condensed coke was formed; this coke blocked the active centers of the catalyst. Because of this, a more rapid loss of activity occurred. In this context, it is preferable to perform the process of methane dehydroaromatization at the relatively low space velocities of 500–750 h^{-1} .

To find the effect of initial Mo-containing substances on the rate of deactivation of modified pentasils, we performed a thermal study of samples with $M = 40$ containing molybdenum trioxide (MoO_3) and molybdenum nanopowder after the dehydroaromatization of methane at 750°C and $V_0 = 500$ –1500 h^{-1} for 120 min (Fig. 2).

The coke formed in the course of methane conversion on zeolites modified with molybdenum nanopowder and MoO_3 differed only slightly in its nature, as evidenced by closely spaced peaks that correspond to coke burning in DTA curves. However, the amounts of oxygen added and, correspondingly, the peak positions in DTG curves were different (Table 3). The amount of coke formed on a catalyst containing MoO_3 was greater than the amount formed on a sample with added molybdenum nanopowder in the same time interval by a factor of more than 1.5.

A comparison of Mo-containing pentasils with various M carbonized in the course of methane conversion demonstrated that two forms of coke were formed on a catalyst with the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$, with the more condensed species being predominant. The DTG curve exhibited a low-temperature shoulder at 420–460°C (Fig. 3), and a carbon-burning maximum corresponded to 555°C. The DTA curve exhibited a doubled broad peak and two exothermic maximums at 450 and 560°C. The coke formed on molybdenum nanopowder-containing zeolites with $M = 30$ and 40 was of the same nature, and its burning occurred in a single step with maximums at 485°C in the DTA curves. Their exothermic maximums in DTA curves are very similar, at 480 and 475°C, respectively. A shift of peak maximums to the low-temperature region, as compared with the above samples, was likely due to the formation of less condensed coke in the course of methane conversion at the low space velocities of 250 and 500 h^{-1} .

On the catalyst with $M = 40$, the amount of coke was the lowest and it burned at a lower temperature than that on the surface of the sample with $M = 80$ (Table 4). The low rate of coke formation on pentasil with $M = 40$, as compared with other catalysts, was responsible for its more stable operation. As in the previous cases, the addition of oxygen was observed in the temperature ranges 300–420 and 290–425°C on catalysts with $M = 80$ and 40, respectively. In the catalyst with $M = 30$, this type of interaction was not detected in the thermal-analysis curve.

Thus, based on this study, we can conclude that the lowest amount of coke was formed on pentasil with $M = 40$ containing 4.0% molybdenum nanopowder at $V_0 = 500$ h^{-1} and 750°C. Under these conditions, a maximum conversion and the highest yield of aromatic hydrocarbons were reached on this catalyst. The coke formed on this catalyst was characterized by a relatively low degree of polycondensation, and it was almost completely removed in the course of oxidative

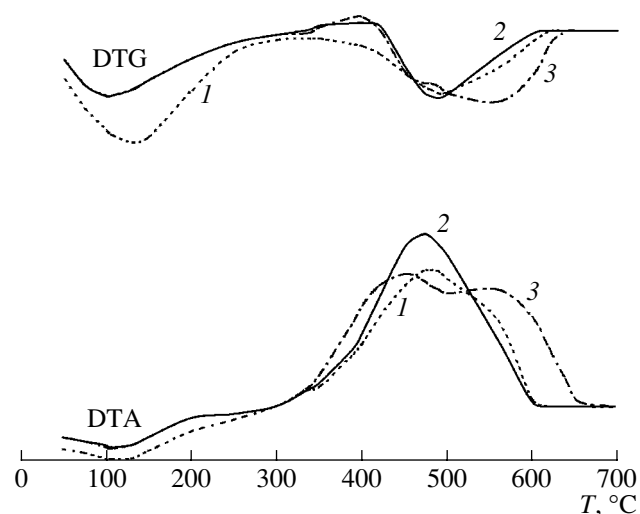
**Fig. 3.** Thermograms of zeolites with $M = (1)$ 30, (2) 40, and (3) 80 containing 4.0% molybdenum nanopowder after 120 min of operation at $T = 750^\circ\text{C}$.

Table 4. Changes in the weight of pentasils with various *M* containing 4.0% molybdenum nanopowder after the dehydroaromatization of methane

<i>M</i>	Weight change, %		
	water	oxygen	coke
80	−2.13(110°C)	+0.31(390°C)	−3.15(460 and 555°C)
40	−2.22(110°C)	+0.23(400°C)	−2.00(485°C)
30	−4.35(125°C)	–	−2.75(485°C)

Note: The catalysts operated for 30 min at each particular space velocity of 250, 500, 1000, and 1500 h^{−1} (total time of 120 min). The corresponding temperatures of peaks in the DTG curves are given in parentheses.

regeneration at temperatures that did not cause the degradation of the zeolite crystal structure.

REFERENCES

1. Minachev, Kh.M. and Kondrat'ev, D.A., *Usp. Khim.*, 1983, vol. 52, no. 12, p. 1921.
2. Radchenko, E.D., Konoval'chikov, L.D., Nefedov, B.K., and Chukin, G.D., *Neftekhimiya*, 1990, vol. 30, no. 3, p. 326.
3. Stepanov, V.G. and Ione, K.G., *Khim. Prom-st.*, 1996, no. 3, p. 59.
4. Nefedov, B.K., *Neftekhimiya*, 1999, vol. 39, no. 5, p. 343.
5. Fal'kevich, G.S., Rostanin, N.N., Vilenskii, L.M., Inyaeva, G.V., Nemira, K.B., and Nefedov, B.K., *Katal. Prom-sti*, 2002, no. 3, p. 12.
6. Echevskii, G.V., Klimov, O.V., Kikhtyanin, O.V., Akse-
nov, D.G., Kodenev, E.G., Yarullin, M.R., Garifzya-
nova, G.G., and Garifzyanov, G.G., *Katal. Prom-sti*,
2003, no. 2, p. 60.
7. Vosmerikov, A.V., Galanov, S.I., and Echevskii, G.V.,
Burenie Neft, 2004, no. 4, p. 16.
8. Wang, I., Tan, L., Huang, J., and Xu, J., *Catal. Lett.*,
1993, vol. 21, p. 35.
9. Wang, D., Lunsford, J.H., and Rosynek, M.P., *J. Catal.*,
1997, vol. 169, no. 1, p. 347.
10. Yide Xu and Liwu Lin, *Appl. Catal., A*, 1999, vol. 188,
p. 53.
11. Shetian Lyu, Linsheng Vang, Ryuitiro Onisi, and Masaru
Ishikawa, *Kinet. Katal.*, 2000, vol. 41, no. 1, p. 148.
12. Young-Ho Kim, Richard, W, Borry III, and Enrique Igle-
sia, *Microporous Mesoporous Mater.*, 2000, vols. 35–36,
p. 495.
13. Yuying Shu and Masaru Ichikawa, *Catal. Today*, 2001,
vol. 71, p. 55.
14. Gusev, A.I., *Nanokristallicheskie materialy: metody
polucheniya i svoistva* (Nanocrystalline Materials: Pre-
paration Methods and Properties), Yekaterinburg: Ural.
Otd. Ross. Akad. Nauk, 1998.