

Carbonization and Regeneration of Mo/ZSM-5 Catalysts for Methane Dehydroaromatization

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Abstract

The character of carbonaceous deposits formed during methane dehydroaromatization reaction in the presence of Mo/ZSM-5 catalysts was studied by differential thermal analysis. The dependence of the concentration and condensation degree (C/H ratio) of the carbonaceous deposits on the catalyst synthesis conditions (Mo content = 1-10%, Si/Al ratio in the initial H-ZSM-5 = 17-45) and reaction conditions (feed flow rate = 405-1620 h⁻¹, methane concentration = 90-98%, reaction temperature = 720-780°C) was investigated. The oxidative treatment conditions of carbonized Mo/ZSM-5 catalysts providing stable operation of the catalysts under multiple reaction-oxidative treatment cycles were selected.

Introduction

Methane is the main component of natural gas, which is considered to be an alternative source for synthesis of valuable products of petrochemistry and organic synthesis [1-3]. Today methane is mostly used as a fuel. Chemical industry uses only 2.5-5% of obtained natural gas [4,5]. Wider use of methane is impeded by its high chemical and thermal stability.

The problem of processing natural gas into organic compounds is usually solved by vapor [6,7], carbon-dioxide [6,7] or oxidative [8] conversion of methane to synthesis gas (CO and H₂ mixture) followed by synthesis of a mixture of alkanes, olefins and alcohols by Fischer-Tropsch method [1,9]. One of the advantages of this method for utilization of natural gas is the possibility to obtain sulfur-free diesel fuel.

The examples of single-stage methane conversion to organic compounds are oxidative dimerization of methane to ethylene or ethane [10,11] and selective oxidation to methanol [12]. However, in the presence of oxygen the obtained hydrocarbons are easily oxidized to carbon dioxide and water leading to a significant decrease of the reaction selectivity at high methane conversion. This causes higher production cost of hydrocarbon fuel prepared from methane in comparison with analogs made of oil.

Lately researchers have paid attention to the search of new methods for utilization of natural gas. One of them is methane dehydroaromatization that is a catalytic method for selective methane conversion directly to aromatic hydrocarbons without participation of oxygen. In 1993 Chinese scientists suggested an efficient Mo-containing catalyst based on ZSM-5 zeolite [13].

Earlier we have showed [14] that the maximum values of methane conversion (14%) and benzene selectivity (70%) in methane dehydroaromatization over Mo/ZSM-5 catalysts are obtained at 2-5% Mo, and they grow when Si/Al ratio goes down from 45 to 17. Under reaction conditions 2-15 nm β-Mo₂C nanoparticles are formed on the zeolite surface, and ~1 nm Mo-containing clusters are formed in the zeolite channels. Carbonaceous deposits in the form of 2 nm thick graphite layers on the surface of molybdenum carbide and loose disordered carbon layer up to 3 nm thick on the zeolite surface are formed during reaction.

According to the literature data [15], molybdenum carbide formed at the initial reaction stages plays an important role in methane activation. However, one of the problems of Mo/ZSM-5 catalysts is their deactivation due to the formation of carbonaceous deposits. This problem can be solved by oxidative regeneration of carbonized catalysts.

In the given work we studied by differential thermal analysis the character of the carbonaceous depo-

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sits depending on the conditions of catalyst synthesis and methane dehydroaromatization. These data made it possible to determine the conditions of oxidative regeneration of Mo/ZSM-5 catalysts.

Experimental

Samples of H-ZSM-5 zeolite with atomic Si/Al ratios 17, 30 and 45 were used for synthesis of Mo/ZSM-5 catalysts. The samples of Mo/ZSM-5 catalysts with 1, 2, 5 and 10 wt.% Mo were prepared by incipient wetness impregnation of the zeolite with ammonium paramolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ solutions of desired concentration and definite pH value [16]. The obtained samples were dried under IR lamp and calcined in a muffle furnace at 500°C for 4 hrs.

The chemical composition of the initial zeolite and molybdenum concentration in the studied catalysts were determined by emission spectroscopy with inductively bound plasma. Differential thermal analysis (DTA) and differential thermogravimetric analysis (DTG) of Mo/ZSM-5 catalysts were carried out using a Q-1500 D derivatograph (Hungary) in the temperature range of 20-600°C in air at 10 °C/min heating rate using 100 mg samples.

The catalytic activity of Mo/ZSM-5 catalysts in methane dehydroaromatization reaction was studied at atmospheric pressure in a flow system with a quartz reactor (inner diameter 9 mm) loaded with the catalyst sample ($m = 0.6$ g, $V \sim 1$ cm³, 0.25-0.5 mm fraction). Before reaction the catalyst was heated in argon flow to 720°C with 10 °C/min heating rate and kept at this temperature during 60 min. Then, the reaction mixture containing 90 vol.% CH₄ and 10 vol.% Ar was introduced with 13.5 ml/min flow rate. To take into account the change of the methane flow due to reaction, argon was used as an internal standard [17].

Reaction products were studied using a Crystal 2000m gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) working simultaneously. Organic reaction products (C₆H₆, C₇H₈ and C₁₀H₈) were separated and analyzed using a steel packed column with 1.5 m length and 3 mm diameter filled with a polymer sorbent DC 550 15% Chromaton N (FID detector, He carrier gas, 30 ml/min flow rate, temperature 165°C). For naphthalene analysis it was collected in an ice trap (~0°C) and dissolved in C₂H₅OH. Separation and analysis of CO₂, C₂H₄ and C₂H₆ was carried out using a steel packed column with 1.5 m length and 3 mm diameter filled with SKT charcoal (TCD

detector, He carrier gas, 30 ml/min flow rate, temperature 165°C). Separation and analysis of CH₄, H₂, Ar and air was carried out using a steel packed column with 2 m length and 4 mm diameter filled with NaX zeolite sorbent (TCD detector, He carrier gas, 30 ml/min flow rate, temperature 165°C).

The activity of Mo/ZSM-5 catalysts was characterized by total methane conversion and methane conversion to benzene vol.%. The benzene selectivity was calculated as the ratio of methane conversion to benzene to total methane conversion.

Results and Discussion

When Mo/ZSM-5 catalysts contact with air at elevated temperatures oxygen may react both with carbon from molybdenum carbide and with carbonaceous deposits C_xH_y, that can be formed during reaction. In the first case, according to the reaction stoichiometry $\text{Mo}_2\text{C}_{(204 \text{ g/mol})} + 4\text{O}_2 = 2\text{MoO}_3_{(288 \text{ g/mol})} + \text{CO}_2$ the sample weight should increase. If all molybdenum were in the form of molybdenum carbide after reaction, the maximum (calculated) weight increase due to the formation of molybdenum oxide by oxidation would be 1.0 and 4.3 wt.% for samples with molybdenum concentrations 2 and 10%, respectively.

Figure 1 (a, b) presents typical TG, DTG and DTA profiles of Mo/ZSM-5 catalysts after methane dehydroaromatization under standard conditions (810 h⁻¹, 90% CH₄ + 10% Ar, 720°C). The samples under study are characterized by an endothermal process at 80-110°C accompanied by 1-5% weight loss due to desorption of adsorbed water vapor [18]. At higher temperatures ($T = 250$ -600°C) an exothermal process is observed, which is, most likely, related to oxidation of carbon-containing components of the sample (C_xH_y and/or molybdenum carbide). Meanwhile, the temperature of the exothermal effect maximum on the DTA curve (T_{DTA}) and the character of weight change (+ Δm or - Δm) depends on the Mo concentration and reaction conditions (Table 1).

The data presented in Table 1 show that the weight loss observed for the catalyst with 2% Mo grows from 1.2 to 7% when the reaction time increases from 0.5 to 20 hrs. This indicates that the concentration of the carbonaceous deposits increases with time on stream. In the meantime, the peak on the DTG curve (T_{DTG}) and the maximum of the exothermal effect related to burning of the carbonaceous deposits shift to higher temperatures (from 455 to 545°C for T_{DTG} and from 455 to 535°C for T_{DTA}). This shift may be caused by

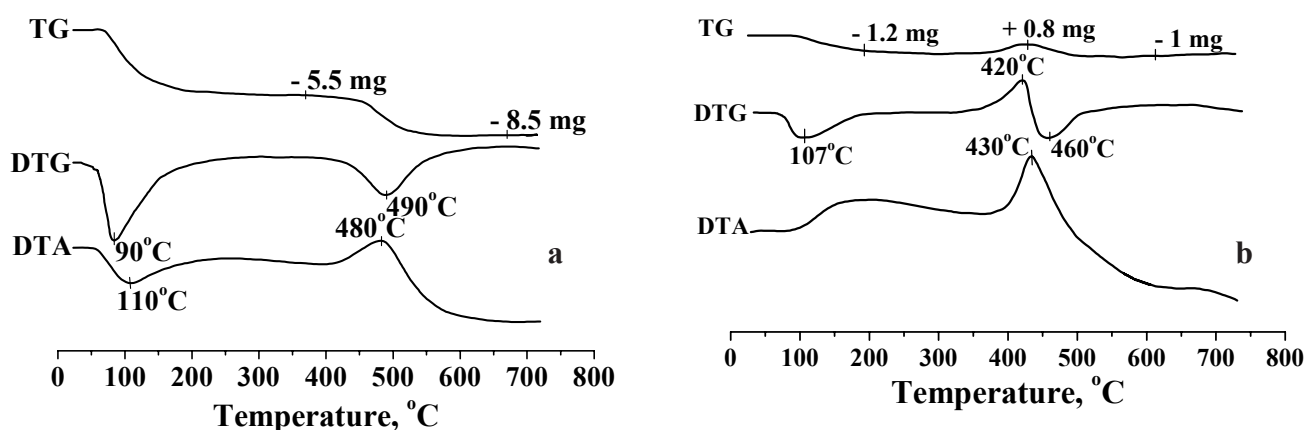


Fig. 1. TG, DTG and DTA profiles of 2% Mo/ZSM-5 (a) and 10% Mo/ZSM-5 (b) catalysts with Si/Al = 17 after 6 hrs on stream. Reaction conditions: 810 h⁻¹, 90% CH₄ + 10% Ar, 720°C.

Table 1

Thermogravimetric analysis data for Mo/ZSM-5 catalysts after methane dehydroaromatization reaction.
Reaction conditions: 810 h⁻¹, 90% CH₄ + 10% Ar, 720°C

Mo content, wt. %	Reaction time, h	Sample weight change (Δm), wt. %	T _{DTG} , °C	T _{DTA} , °C
1	6	- 3.5	525	520
2	0.5	- 1.2	455	455
	1	- 1.5	450*	450*
	6	- 3	490	480
	20	+ 0.3	440*	535
	- 7	545		
5	6	+ 0.5	425*	445
		- 2	460	
	20	+ 0.5	435	485
		- 4	480	
		- 2	520	535
10	0.5	+ 1.3	375	375
	1	+ 1.6	395	395
	6	+ 0.8	420	430
		- 1	460	

* – There is no pronounced maximum (minimum) on the DTG (DTA) profile. The reported temperature corresponds to the change of the sample weight.

increased condensation degree of the carbonaceous deposits (increase of the C/H ratio) [19]. Note that for 2% Mo/ZSM-5 samples after 0.5-6 hrs on stream no weight gain that might indicate the formation of molybdenum carbide is observed. When the reaction is increased to 20 hrs, the sample gains 0.3 wt.% at

410-440°C. Then, 7% weight loss with T_{DTA} = 535°C is observed during further temperature growth. One may suppose that for samples after 0.5-6 hrs on stream the oxidation of molybdenum carbide takes place simultaneously with the burning of the carbonaceous deposits, so that the weight gain due to molybdenum

carbide oxidation is leveled. Increase in reaction time leads to the growth of the condensation degree of the carbonaceous deposits. This results in the increase in their burn-off temperature and, consequently, temperature separation of the oxidation of molybdenum carbide and carbonaceous deposits.

When the molybdenum concentration is increased to 5%, the sample weight loss reflecting the concentration of formed carbonaceous deposits is, on the contrary, somewhat lower than over 2% Mo/ZSM-5 catalyst at the same time on stream (Table 1). Besides, combustion of the carbonaceous deposits from the sample kept in the reactor for extended time (20 hrs) is characterized by two peaks in the DTG and DTA profiles. Both correspond to weight loss. This may indicate either the presence of two different types of carbonaceous deposits in the studied sample [19] or different localization of carbonaceous deposits of one type [20]. For instance, according to the literature data [20], burning of the carbonaceous deposits formed next to metal-containing particles takes place at lower temperatures in comparison with the carbonaceous deposits located on the surface of the support. The weight gain by $\sim 0.5\%$ observed for this sample that corresponds to the oxidation of carbided molybdenum forms is observed already after 6 hrs on stream and remains the same for the sample after 20 hrs on stream.

For the sample with 10% Mo the weight gain due to oxidation of molybdenum carbide is expressed better ($+\Delta m = 0.8\text{--}1.6\%$) and is observed already after 0.5 h on stream. Moreover, no weight loss is observed during analysis of the samples after 0.5 and 1 h on stream. Apparently, the concentration of the carbonaceous deposits is low in this case, and the weight loss due to their combustion is leveled by oxidation of molybdenum carbide. When the reaction time is increased to 6 hrs, both the concentration and condensation degree of the carbonaceous deposits grow, and their T_{DTG} increases. As a result, oxidation reactions of both types take place in a narrow temperature interval with the predomination of molybdenum carbide oxidation at 420°C and burning of the carbonaceous deposits at 460°C (Fig. 1b).

When the Si/Al ratio is increased from 17 to 45, the shape of the DTA and DTG profiles of catalysts with 1–2% Mo after 6 hrs on stream does not change. Somewhat different profiles are observed for samples with 5 and 10% Mo. The thermal analysis data for 10% Mo/ZSM-5 catalysts with Si/Al = 45 are presented in Fig. 2 as a typical example. Two maxima

corresponding to the exothermal burning effects are observed on the DTA curve: $T_{\text{DTA}} = 425^\circ\text{C}$ corresponds to an increase in the sample weight, whereas $T_{\text{DTA}} = 505^\circ\text{C}$ corresponds to its decrease. Similar results were also obtained for sample with 5% Mo and Si/Al = 45 as well as samples with 5 and 10% Mo and Si/Al = 30. Hence, oxidation of molybdenum carbide in these samples takes place at $\sim 420\text{--}430^\circ\text{C}$ similar to catalysts with 5 and 10% Mo and Si/Al = 17 (Table 1). However, combustion of the carbonaceous deposits occurs at a higher temperature ($T_{\text{DTG}} = 515^\circ\text{C}$ versus 460°C). Apparently, carbonaceous deposits formed over Mo/ZSM-5 catalysts with Si/Al = 30 and 45 have higher condensation degrees.

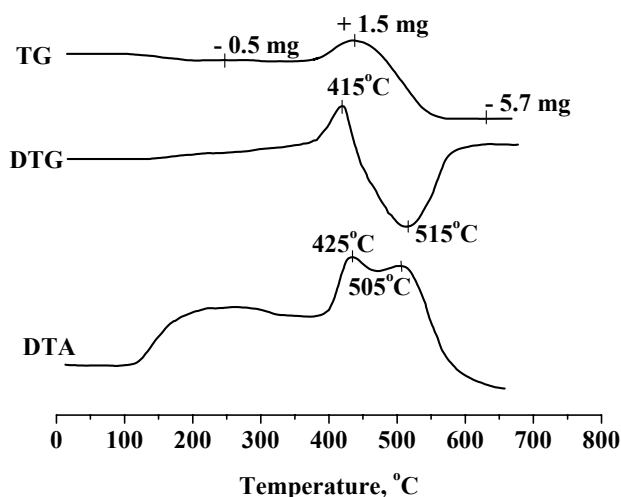


Fig. 2. TG, DTG and DTA profiles of 10% Mo/ZSM-5 catalysts with Si/Al = 45 after 6 hrs on stream. Reaction conditions: 810 h^{-1} , 90% CH_4 + 10% Ar, 720°C .

Figure 3 presents T_{DTG} values of Mo/ZSM-5 catalysts with 1–10% Mo and different Si/Al ratios after 6 hrs on stream. For samples with Si/Al = 17 T_{DTG} shifts to lower temperatures with an increase of Mo concentration from 1 to 5–10%. The observed dependence may be due to the catalytic combustion of carbonaceous deposits in the presence of a metal [20] that becomes more significant when molybdenum concentration increases, or due to lower condensation of carbonaceous deposits over samples with higher Mo concentrations [19]. For Mo/ZSM-5 catalysts with Si/Al = 30 and 45, the burn-off temperature of the carbonaceous deposits decreases first when Mo concentration grows from 1% to 2%. However, further increase of the molybdenum concentration to 5–10% leads to its sharp growth. Apparently, in this case methane dehydroaromatization reaction is ac-

accompanied by the formation of carbonaceous deposits with higher C/H ratio. Besides, the total weight loss of the samples during analysis increases with the Si/Al growth. For example, for 1% Mo/ZSM-5 catalysts after 6 hrs on stream $-\Delta m$ is 3.5, 4.8 and 6.2% for samples with Si/Al = 17, 30 and 45, correspondingly.

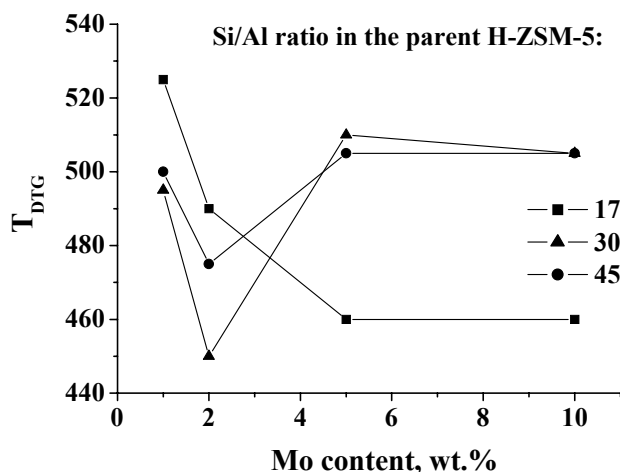


Fig. 3. The effect of Mo content and Si/Al ratio in Mo/ZSM-5 catalysts on the position of the burn-off maximum of the carbonaceous deposits (T_{DTG}) after 6 hrs on stream. Reaction conditions: 810 h^{-1} , 90% CH_4 + 10% Ar, 720°C .

The effect of methane dehydroaromatization conditions (reaction temperature, feed flow rate and composition) was studied for 2% Mo/ZSM-5 catalysts. The reaction temperature increases from 720 to 780°C , that leads to a significant T_{DTA} growth indicating an increased condensation degree of the carbonaceous deposits. A considerable (more than 3-fold) growth of the concentration of the carbonaceous deposits is observed only when the reaction temperature is increased to 780°C (Fig. 4).

When the feed flow rate is increased from 405 to 1620 h^{-1} , the concentration of the carbonaceous deposits and the temperature of their combustion exothermal effect grow (Fig. 4). In this respect, an increase of methane flow rate is similar in its effect to longer reaction time (Table 1). An increase in either of these factor leads to higher load on the catalyst, which results in accumulation of more carbonaceous deposits with higher condensation degree.

If the methane concentration in the feed is increased from 90 to 98%, the DTA and DTG profiles of 2% Mo/ZSM-5 catalysts with Si/Al = 17 after 6 hrs on stream are not changed. The weight loss corresponding to the concentration of carbonaceous deposits is not changed either. Some T_{DTA} growth observed

in this case (Fig. 4) may be due to increased condensation degree of the carbonaceous deposits [19].

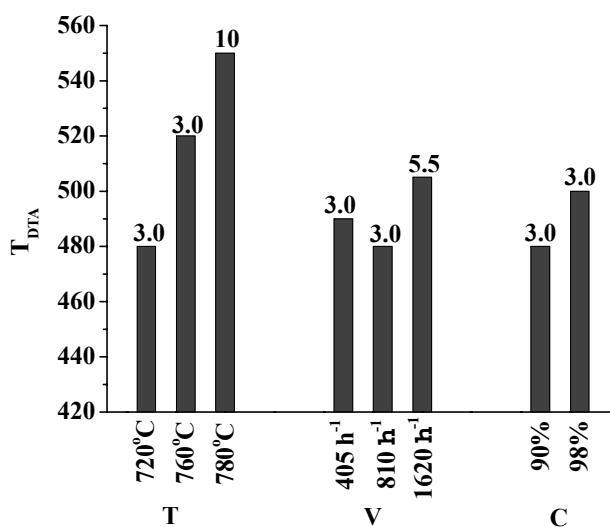


Fig. 4. The effect of reaction temperature (T), feed flow rate (V) and methane concentration (C) on the position of the burn-off exothermal effect maximum (T_{DTA}) and concentration of carbonaceous deposits ($-\Delta m$) in 2% Mo/ZSM-5 catalyst with Si/Al = 17 after 6 hrs on stream.

Thus, according to the thermogravimetric analysis data, the contact of Mo/ZSM-5 catalysts with methane leads to the formation of molybdenum carbide and carbonaceous deposits. For studied Mo/ZSM-5 catalysts, the condensation degree and concentration of the carbonaceous deposits increase during reaction. Oxidation of molybdenum carbide with oxygen takes in the temperature range of $420\text{--}440^\circ\text{C}$ that matches the combustion temperature range of the carbonaceous deposits formed after 6 hrs on stream ($420\text{--}500^\circ\text{C}$). This impedes estimation of the amounts of molybdenum carbide and carbonaceous deposits formed in the course of reaction. A reaction time increase leads to the growth of the condensation degree of the carbonaceous deposits and, consequently, their burning temperature. This makes it possible to estimate quantitatively the amounts of molybdenum carbide and carbonaceous deposits from the thermal analysis data.

Based on the obtained data, oxidative regeneration of 2% Mo/ZSM-5 catalysts after ~ 6 and ~ 20 hrs on stream was carried out at 520 and 600°C , respectively. Figures 5 and 6 present the data on the catalytic activity of 2% Mo/ZSM-5 catalysts in different reaction-oxidative regeneration modes. One can see that after 6 hrs on stream the catalytic activity remains practically constant after 5 reaction-oxidative

regeneration cycles (Fig. 5). Meanwhile, an increase in the reaction time to ~ 20 hrs (Fig. 6) leads to faster catalyst deactivation in the third cycle: methane conversion to benzene goes down to 2% in ~ 15 hrs, whereas after the first reaction cycle such decrease occurs only after ~ 20 hrs on stream.

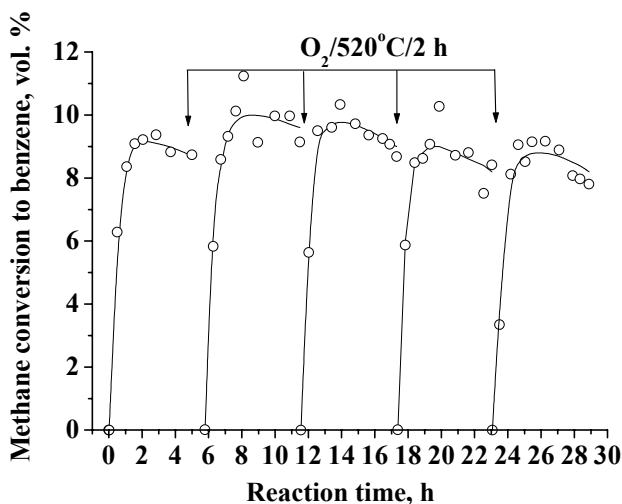


Fig. 5. Catalytic activity of 2% Mo/ZSM-5 with Si/Al = 17 in cycles: reaction (6 hrs)/oxidative treatment (520°C, 2 hrs). Reaction conditions: 810 h⁻¹, 90% CH₄ + 10% Ar, 720°C.

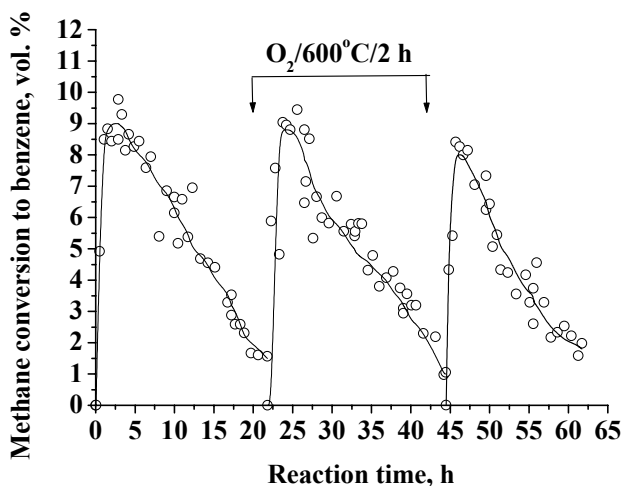


Fig. 6. Catalytic activity of 2% Mo/ZSM-5 with Si/Al = 17 in cycles: reaction (20 hrs)/oxidative treatment (600°C, 2 hrs). Reaction conditions: 810 h⁻¹, 90% CH₄ + 10% Ar, 720°C.

Conclusions

The concentration and condensation degree (C/H ratio) of the carbonaceous deposits increase with an increase of either of the following parameters:

- methane concentration in the feed;
- feed flow rate;
- temperature;
- methane dehydroaromatization reaction time.

The concentration of the carbonaceous deposits grows with an increase of the Si/Al ratio in the initial H-ZSM-5 zeolite. The combustion temperature of the carbonaceous deposits decreases with a molybdenum concentration increase for Mo/ZSM-5 catalysts with Si/Al = 17. Consequently, the temperature required for oxidative regeneration of carbonized Mo/ZSM-5 catalysts is determined by conditions of their synthesis and methane dehydroaromatization reaction. The stability of Mo/ZSM-5 catalysts in reaction-oxidative regeneration cycles is better when time on stream is shorter.

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