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

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Abstract

The methane dehydroaromatization (DHA) was studied over a series of impregnated Mo/ZSM-5 catalysts with different molybdenum contents (1-10 wt.%). It was shown that total methane conversion was decreased by 30% during 12 h of DHA reaction. The benzene formation rate was increased from 0.5 to 13.9 μmol C_6H_6/(g_{Mo}·s) when the molybdenum content in the catalyst was lowered from 10 to 1 wt.%. The deactivated Mo/ZSM-5 catalysts were studied by a group of methods: N_2 adsorption, XRD, TG-DTA, HRTEM and XPS. The content and condensation degree (C/H ratio) of the carbonaceous deposits was found to increase with an increase of either of the following parameters: molybdenum content (1-10 wt.%), reaction temperature (720-780°C), space velocity (405-1620 h^{-1}), reaction time (0.5-20 h). The stability of Mo/ZSM-5 catalysts in reaction-regeneration cycles was better when the time on stream was shorter. The regeneration conditions of deactivated Mo/ZSM-5 catalysts providing their stable operation under multiple reaction-regeneration cycles have been selected.

Introduction

Development of highly effective catalysts for the one-stage conversion of light hydrocarbons to valuable products with high selectivity will solve such problems as efficient utilization of natural and oil-associated gases and environmental protection. Methane dehydroaromatization (DHA) over Mo/ZSM-5 catalysts is a promising process for direct production of valuable aromatic compounds and hydrogen from methane. Bifunctional Mo/ZSM-5 catalysts provide up to 70% benzene formation selectivity with 14% total methane conversion at 720°C [1]. However, the carbonaceous deposits (CD) are formed as a side product in DHA of CH_4, part of them being necessary to assist the reaction, while the others leading to gradual deactivation of the catalysts [2-16]. Thus, it is very important to study the nature of CD formed on Mo/ZSM-5 during reaction – first, in order to possibly minimize their unwanted formation, starting from the rational design of catalysts and, second, to elaborate an appropriate method of catalysts regeneration.

The content and properties of the CD formed on Mo/ZSM-5 samples depend on both catalyst composition and reaction conditions. The formation rate of the CD was found to grow linearly with the molybdenum content in the zeolite matrix increasing from 0 to 2 wt.% Mo and remain almost constant at molybdenum content 2-10 wt.% [2]. The concentration and burn-out temperature of the CD were shown to depend on the type of molybdenum carbide phase formed on the zeolite surface during the reaction [3]. The CD with a lower burn-out temperature preferentially formed over more active and stable α-MoC_{1-x}/ZSM-5 catalyst compared to β-Mo_2C/ZSM-5. However, the total concentration of the CD was twice higher on the α-MoC_{1-x}/ZSM-5 than on β-Mo_2C/ZSM-5.

According to XPS [5], TPO [6] and TGA [3] data, several types of the CD can be found in

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Mo/ZSM-5 catalyst. As a rule, differences in the CD properties (burn-out temperature, structure) result from their different localization. In particular, two types of the CD characterized by low (~470°C [7,8], 503°C [9]) and high (543°C [6], 557°C [8], 592°C [9]) oxidation temperatures were distinguished by TPO. It was supposed [7,10] that the deposits with a lower oxidation temperature were located on the surface of molybdenum carbide, whereas the ones with a higher oxidation temperature were associated with the zeolite Broensted acid sites. The strength of CD has also been correlated with their localization on the external surface or in the pores of zeolite [11,12].

Deactivation of Mo/ZSM-5 catalysts, due to their excessive carbonization is a generally accepted opinion [5, 10, 13]. The time required for the catalyst to loose almost all its activity can be different and equal, *e.g.* to 4 h [13] or 16 h [14]. Several methods were suggested for regeneration of deactivated Mo/ZSM-5 catalysts, e.g. treatment in a NO/air mixture (1/50 vol/vol) at 450°C [15] or in 20% H_2/He mixture at 680°C [16]. The TPH followed by the TPO was shown to be the most acceptable method for regeneration of Mo/ZSM-5 catalysts because it removed all types of the carbonaceous deposits [10]. About 90% of the carbonaceous deposits related to Broensted acid sites and 60% of those related to Mo sites were removed when the catalyst was regenerated only by the TPH. Another suggested approach is an *in situ* catalyst regeneration, by introducing additional components, e.g. CO_2, to the reaction mixture, and thus suppressing the coke formation [17,18].

This paper is devoted to the study of physicochemical properties of CD formed on Mo/ZSM-5 catalysts during DHA of CH_4, depending on the Mo content (1-10 wt.%) and reaction conditions (reaction temperature 720-780°C, space velocity 405-1620 h^{-1}, reaction time 0.5-20 h). The results of the study made it possible to optimize the conditions of oxidative regeneration of Mo/ZSM-5 catalysts.

Experimental

Catalyst preparation

Mo/ZSM-5 catalysts containing 1, 2, 5 and 10 wt.% Mo were prepared by incipient wetness impregnation of H-ZSM-5 zeolite (atomic ratio

Si/Al = 17) with ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solutions of desired concentrations [19]. The prepared samples were dried and calcined at 500°C for 4 h. The catalysts were denoted as x%Mo/ZSM-5, where x is wt.% of Mo.

Catalytic activity measurements

The catalytic activity of Mo/ZSM-5 catalysts in the DHA of CH_4 was studied at atmospheric pressure in a flow setup with a quartz reactor with an internal diameter (i.d.) 9 mm. The reactor was loaded with 0.6 g of a catalyst (0.25-0.5 mm fraction, ca. 1 cm³ volume). Before the reaction, the catalyst was heated in an argon flow to 720°C with a heating rate of 10°C/min and kept at this temperature for 60 min. Then the feed consisting of 90 vol.% CH_4 + 10 vol.% Ar was introduced with a flow rate 13.5 ml/min (810 h^{-1}). Argon was used as an internal standard to account for the changes of methane flow rate due to the reaction [20].

A Kristall-2000M gas chromatograph (Chromatech Ltd., Russia) equipped with two simultaneously operating detectors (TCD and FID) was used for on-line analysis of the reaction products. The aromatic products (C_6H_6, C_7H_8 and $C_{10}H_8$) were separated using a first packed stainless steel column with 1.5 m length and 3 mm i.d. The column was filled with a polymer sorbent DC 550 and 15% Chromatron N (FID, He carrier gas, 30 ml/min flow rate, 165°C column temperature). Naphthalene was collected in an ice trap (T ca. 0°C) and for the analysis dissolved in ethanol. The CO_2, C_2H_4 and C_2H_6 were separated using a second packed stainless steel column with 1.5 m length and 3 mm i.d., which was filled with SKT activated carbon (TCD, He carrier gas, 30 ml/min flow rate, 165°C column temperature). The CH_4, H_2, CO, Ar and air were separated using a third packed stainless steel column with 2 m length and 4 mm i.d. filled with NaX zeolite (TCD, He carrier gas, 30 ml/min flow rate, 165°C column temperature).

The activity of Mo/ZSM-5 catalysts was characterized by methane conversion (%), methane conversion to benzene (%) and benzene formation rate (μmol C_6H_6/(g_{Mo}·s)).

Catalyst regeneration

Regeneration of deactivated (after DHA reaction) Mo/ZSM-5 catalysts was carried out at

atmospheric pressure for 2 h in a flow setup with a quartz reactor (the same one used for the activity measurement, see above). The catalyst was heated in an argon flow to appropriate temperature with a heating rate of 10°C/min. Then the oxygen was introduced with a flow rate of 13.5 ml/min (810 h^{-1}). The regeneration temperature depended on the catalyst composition and conditions of DHA of CH_4, and was varied from 480 to 600°C.

Catalyst characterization

The chemical composition of the parent zeolites and Mo content in the prepared catalysts were determined by means of inductively coupled plasma atomic emission spectroscopy using the Thermo Baird PST instrument.

Textural characteristics (surface area, porosity) of the parent zeolites and Mo/ZSM-5 catalysts were studied on a Micromeritics ASAP 2400 instrument using nitrogen adsorption at 77 K. The specific surface area values were calculated by the BET method.

X-ray powder diffraction (XRD) patterns were obtained using a HZG-4C (Freiberger Praezisionemechanik GmbH) diffractometer with CuK_α radiation, over a 2θ range of 5-50°.

Differential thermal analysis (DTA) was carried out using a Q-1500 D (Hungary) instrument in the temperature range 20-800°C in the air, with the heating rate 10°C/min and initial sample weight 100 mg. In addition, *thermogravimetry (TG)* data were obtained.

High resolution transmission electron micro-scopy (HRTEM) images were obtained using a JEOL JEM-2010 electron microscope with accelerating voltage 200 kV and lattice resolution 0.14 nm. The samples were deposited on perforated carbon supports attached to the copper grids. The local elemental analysis of the samples was carried out by an *Energy Dispersive X-ray Analysis (EDX)* method using an EDAX spectrometer equipped with a Si (Li) detector (energy resolution 130 eV).

X-ray photoelectron spectroscopy (XPS) measurements were performed in the MultiLab 2000 surface analysis system (Thermo Electron Co.). The samples were deposited on Fe-Cr-Ni stainless steel stubs by fixing the powder under hydraulic press at 2 MPa, forming the tablets of about 9 mm diameter and 2 mm height. Before XPS acquisition, the samples were pumped down to 5 x 10^{-8} mbar in the preparation chamber, and then transferred to the analysis chamber, with the base vacuum of 2 x 10^{-10} mbar. Spectra of survey and individual regions (Mo3d, O1s, C1s, Al2p, Si2p) were acquired with MgK_α X-rays (hν = 1253.6 eV) at 20 eV pass energy of hemispherical analyzer, and the photoelectrons were collected from the area of about 1 mm^2 in the center of sample. The binding energy (BE) scale was referenced to Si2p BE value of 103.4 eV characteristic for the H-ZSM-5 support, and verified with expected values of other elements. Spectra were treated with an Avantage v.2.26 software.

Results and Discussion

Catalyst activity and deactivation

Table 1 illustrates the effect of molybdenum content on the activity of catalysts studied in the DHA reaction. According to the presented data, the total methane conversion increases with a Mo content increase from 1 to 2 wt.%. At the same time, the methane conversion to benzene grows when the Mo content is increased from 1 to 2-5 wt.%. Further increase of the Mo content up to 10 wt.% results in a decrease of both the total CH_4 conversion and the methane conversion to C_6H_6. The benzene formation rate is reduced sharply with an increase of Mo content from 1 to 10 wt.%. For example, after 2 h on stream the total CH_4 conversion over the sample with 2 wt.% Mo is ca. 14% and the C_6H_6 formation rate is 10.9 μmol $C_6H_6/(g_{Mo} \cdot s)$, whereas over the sample with 10 wt.% Mo these values are ca. 7% and 0.5 μmol $C_6H_6/(g_{Mo} \cdot s)$, respectively.

The obtained data indicate that for all Mo/ZSM-5 samples, the total CH_4 conversion decreases with time-on-stream. Meanwhile, the methane conversion to benzene initially grows and reaches a maximum value after 75-100 min on stream, and after staying at the plateau slowly decreases (Fig. 1). The total methane conversion decreases by 30% during 12 h of the DHA reaction and becomes equal to 2% after 20 h of the reaction.

Table 1

Total methane conversion and benzene formation rate in the DHA[*] of CH_4 after 2 h on stream over Mo/ZSM-5 catalysts
with different Mo contents (Si/Al = 17)

Molybdenum content (wt. %)	1	2	5	10
Total methane conversion (%)	10.5	13.8	12.2	7.0
Methane conversion to benzene (%)	6.3	9.6	9.5	3.7
Benzene formation rate ($\mu mol\ C_6H_6 / (g_{Mo}\cdot s)$)	13.9	10.9	4.1	0.5

[*] Reaction conditions: 90 vol. % CH_4 + 10 vol. % Ar, 810 h^{-1}, 720°C.

Benzene and hydrogen are the main reaction products of DHA of CH_4. In addition, traces of CO, C_2H_4, C_2H_6, C_7H_8 and $C_{10}H_8$ are formed. The detailed data on the product composition were published earlier [21].

Physico-chemical properties of catalysts

The Mo/ZSM-5 catalysts before and after reaction were studied by a group of methods: N_2 adsorption, XRD, TG-DTA, HRTEM and XPS.

N_2 adsorption

The specific surface area and total pore volume of all the catalysts studied decreased after being on stream. This effect is most pronounced for the sample with the highest Mo content (10 wt.%). Meanwhile, the specific surface area of the sample with 2 wt.% Mo decreases by ca. 15% (from 321 to 271 m^2/g) after 6 h of the reaction. An increase of the molybdenum content to 10 wt.% leads to a

more significant decrease of the specific surface area by ca. 65% (from 254 to 89 m^2/g). An increase of the reaction time leads to further reduction of the specific surface area and total pore volume. For example, the specific surface area of the 2%Mo/ZSM-5 sample decreases by ca. 35% (from 321 to 209 m^2/g) after 20 h on stream. This may be due to the accumulation of CD during the reaction, leading to blocking of the zeolite micropores.

XRD

According to the XRD data, the H-ZSM-5 zeolite is the predominant crystal phase for all studied Mo/ZSM-5 catalysts, both before and after the reaction. The presence of additional X-ray amorphous phases has been shown only for the 10%Mo/ZSM-5 samples after the reaction. These phases are observed after 30 min on stream in the form of a halo with maxima in the 2θ range of 20-25° and 35-42°. Such diffraction picture is retained during the next 6 h of the DHA reaction.
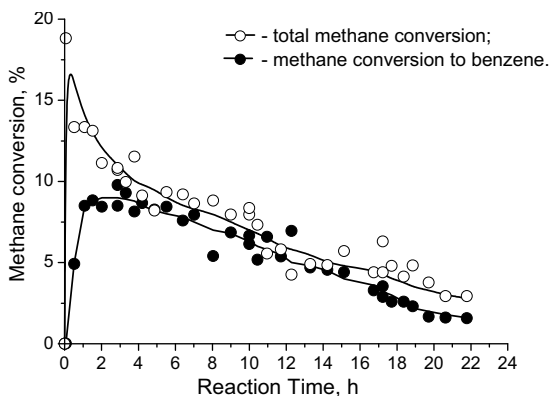

Fig. 1. Activity of 2%Mo/ZSM-5 catalyst (Si/Al = 17) in the DHA of CH_4. Reaction conditions: 90%CH_4 + 10%Ar, 810 h^{-1}, 720°C.
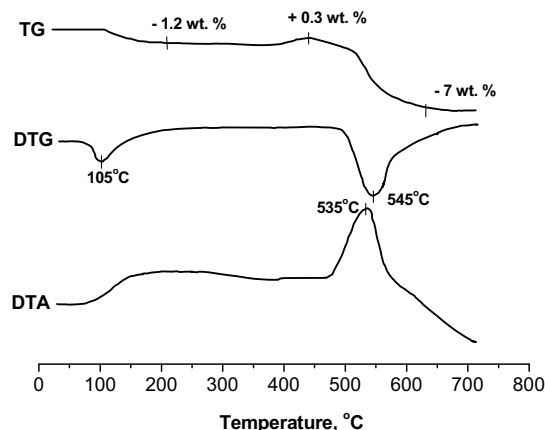

Fig. 2. TG, DTG and DTA curves for 2%Mo/ZSM-5 catalyst (Si/Al = 17) after 20 h of the DHA of CH_4. Reaction conditions: 90 vol. % CH_4 + 10 vol. % Ar, 810 h^{-1}, 720°C.

In accordance with literature, the halo at $2\theta = 20$-$25°$ can be assigned to the formation of CD [22] or amorphous silica [23] in the course of reaction. A halo at $2\theta = 37$-$42°$ can be an evidence of the formation of molybdenum carbide. It is well known that α-MoC_{1-x} is characterized by the diffraction maxima at $2\theta = 36.5$-$36.8°$ and 41.2-$42°$; β-Mo_2C – at $2\theta = 34.4$-$34.7°$; 37.3-$37.8°$ and 39.5-$39.7°$; and η-Mo_3C_2 – at $2\theta = 36.5$-$36.8°$, $39.1°$, $42.5°$; η-MoC – at $2\theta = 36.8°$, $39.3°$, $42.6°$ [24]. In our case, it is most probable that the observed halo ($2\theta = 37$-$42°$) corresponds to η-MoC (JCPDS 8-384) or η-Mo_3C_2 (JCPDS 42-890) phases of molybdenum carbide.

TG-DTA

When the deactivated Mo/ZSM-5 samples are exposed to air at elevated temperatures, oxygen reacts both with carbon of molybdenum carbide and with carbonaceous deposits C_xH_y formed during the reaction. According to the reaction stoichiometry, in the former case the sample weight should increase according to the reaction: $Mo_2C_{(204\ g/mol)} + 4O_2 = 2MoO_{3\ (288\ g/mol)} + CO_2$, whereas in the latter case it should decrease: $C_xH_y + (x + 1/4y)O_2 = xCO_2 + \frac{1}{2}\ yH_2O$.

Fig. 2 presents the typical TG, DTG and DTA curves for Mo/ZSM-5 catalyst after DHA of CH_4. The data of thermal analysis obtained for the 1-10%Mo/ZSM-5 catalysts after 0.5-20 h on stream show an endothermic process at 90-110°C accompanied by a weight loss of 1-5 wt.% that can be attributed to water desorption [25]. At higher temperatures ($T = 370$-$600°C$), an exothermic process is observed. It is related to the oxidation of carbon from C_xH_y and/or molybdenum carbide [4].

The sample weight gains due to the molybdenum carbide oxidation were observed in the temperature range 370-440°C. Then weight loss due to the burning of the carbonaceous deposits is observed during further temperature increase (450-600°C). The position of the exothermic effect maximum on the DTA curve (T_{DTA}) and the sample weight change depend on the Mo content (1-10 wt. %) in the catalyst and the reaction conditions (reaction temperature 720-780°C, space velocity 405-1620 h^{-1}, reaction time 0.5-20 h).

The T_{DTA} value shifts to the lower temperatures with an increase of Mo content from 1 to 10 wt.% (Fig. 3). The observed dependence may be due to the catalytic combustion of carbonaceous deposits in the presence of a metal [26] that becomes more significant when molybdenum concentration increases, or due to lower condensation of carbonaceous deposits over the samples with higher Mo concentrations [27]. Meanwhile, the content of carbonaceous deposits decreases with an increase of the Mo content in the catalyst (Fig. 3). This phenomenon may be explained by several reasons. First, according to the literature [28], acid sites on the external zeolite surface can be the sites of CD formation. It was also shown [29] that concentration of the acid sites decreases when the molybdenum content is increased. It means that a decrease of the CD content with an increased Mo content can be due to the decrease of the concentration of the CD formation sites when the molybdenum content is increased. Second, it is necessary to consider the earlier proposed consecutive mechanism of carbonaceous deposits formation during the DHA of CH_4 [30].
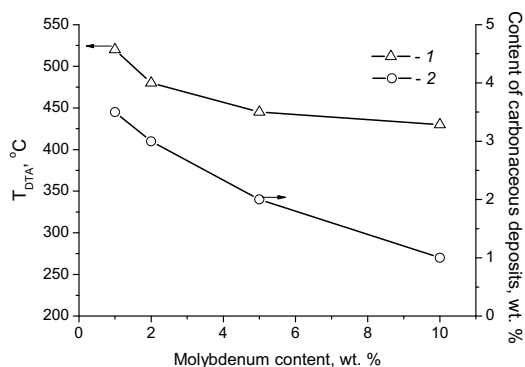

Fig. 3. Effect of the molybdenum content on the position of exothermic effect maximum (1) and content of carbonaceous deposits (2) for the Mo/ZSM-5 catalysts (Si/Al = 17) after 6 h on stream. Reaction conditions: 90%CH_4 + 10%Ar, 810 h^{-1}, 720°C.
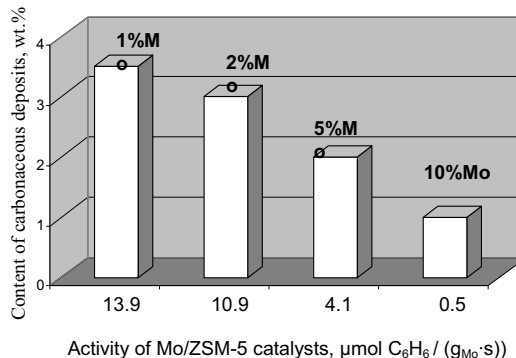

Fig. 4. Correlation between activities of Mo/ZSM-5 catalysts (Si/Al = 17) vs. CD contents formed after 6 h on stream. Reaction conditions: 90 vol. % CH_4 + 10 vol. % Ar, 810 h^{-1}, 720°C.

In accordance with this mechanism, monoaromatics are intermediate compounds in the succession of reactions resulting in the CD formation. Thus, the consecutive mechanism of CD formation allows an assumption that more active catalysts in the DHA of CH_4 should produce monoaromatics at a higher concentration and, consequently, provide a higher rate of polycyclic structures formation. Indeed, Fig. 4 shows that the content of CD increases with the benzene formation rate growth.

Fig. 5 illustrates the effect of the reaction temperature, space velocity and reaction time on the position of exothermic effect maximum and content of carbonaceous deposits over the 2%Mo/ZSM-5 catalysts after the DHA of CH_4. The reaction temperature increase from 720 to 780°C 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 content of the carbonaceous deposits is observed only when the reaction temperature is increased to 780°C (Fig. 4). When the space velocity is increased from 405 to 1620 h^{-1}, the concentration of the carbonaceous deposits and the T_{DTA} grow (Fig. 5). In this respect, an increase of methane flow rate is similar in its effect to a longer reaction time. An increase of either of these factors leads to a higher load on the catalyst, which results in the accumulation of more carbonaceous deposits having a higher condensation degree.

HRTEM

Earlier we have shown [21] that according to HRTEM, under reaction conditions, the 2-15 nm Mo_2C nanoparticles are formed on the zeolite surface, and ~ 1 nm Mo-containing clusters – in the zeolite channels. In the case of Mo/ZSM-5 catalysts after 6 h on stream, the CD were formed as graphite layers with a thickness of ~2 nm on the surface of Mo_2C nanoparticles that were > 2 nm in size, and as friable layers with a thickness of up to 2-3 nm and a disordered structure on the external surface of zeolite. It was proposed [21], that Mo-containing clusters can be the active centers for the DHA of CH_4.

Note that in catalysts after 20 h of the DHA reaction, the thickness of graphite layer on the surface of Mo_2C nanoparticles is practically unchanged. In contrast to CD on the surface of Mo_2C particles, the thickness of CD layer on the zeolite is increasing with time-on-stream and comes to 3-5 nm after 20 h of reaction. These CD are friable and their structure is defective: it consists of the curved graphite-like layers, forming separate islands that do not provide complete coverage of the zeolite surface (Fig. 6). It is most likely that accumulation of friable CD on zeolite with time-on-stream is a main reason of the catalyst deactivation. We suggest that appearance of a single maximum of the exothermic effect during the burn-out of the CD formed on the Mo/ZSM-5 catalysts after 6 h of the reaction (Fig. 2) may be associated either with a small amount or a wide interval of burn-out temperatures of one of the CD types: (1) with graphite structure or (2) friable distorted carbonaceous layer.
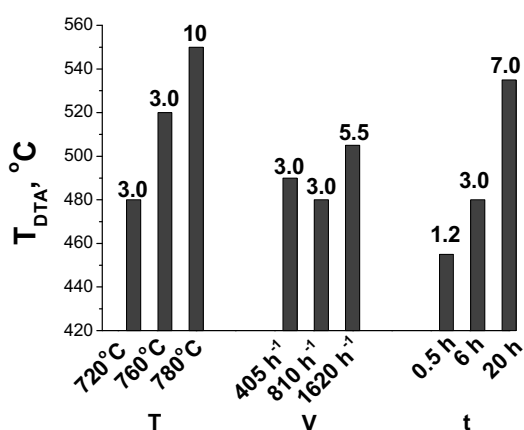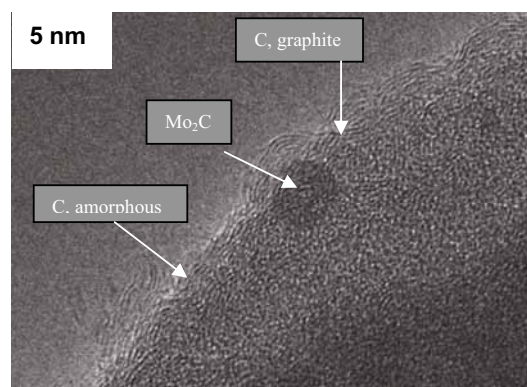
Fig. 5. Effect of the reaction temperature (T), space velocity (V) and reaction time (t) on the position of exothermic effect maximum (T_{DTA}, °C) and content of carbonaceous deposits (wt. %, it is indicated at the top of the bars) for the 2%Mo/ZSM-5 catalysts (Si/Al = 17) after 6 h on stream.

Fig. 6. HRTEM micrographs of CD in 2%Mo/ZSM-5 catalyst after 20 h on stream in the DHA of CH_4: graphite layer on a molybdenum carbide nanoparticle and CD with disordered structure.

XPS

The XPS results for 1-10%Mo/ZSM-5 samples reveal additional details about changes of a surface state of these catalysts during the reaction. It was shown that surface molybdenum (Mo^{6+}) was reduced to lower oxidation states – down to molybdenum oxicarbide MoC_xO_y (BE $Mo2d_{5/2}$ ca. 228 eV) and molybdenum carbide Mo_2C (BE $Mo2d_{5/2}$ ca. 226.8 eV). According to the XPS data, it is possible to distinguish three types of carbon. These include carbide carbon in Mo_2C (C_{1s} 281.9 eV), carbon in pre-graphite carbonaceous deposits (sp-type, C_{1s} 283.4 eV) and carbon in carbonaceous deposits with graphite structure (C_{1s} 284.5 eV), which is in good correlation with literature data [5,6,8,13,14,17]. Detailed quantitative analysis of the XPS spectra will be presented in our next publication [31].

Catalyst regeneration

Oxidative regeneration of Mo/ZSM-5 catalysts after ~ 6 and ~ 20 h on stream was carried out at 520 and 600°C, respectively. It should be noted that the temperature of regeneration was selected in accordance with the values of burn-out temperatures of carbonaceous deposits. The deactivated catalysts were regenerated and one can see (Fig. 7) that catalytic activity of 2%Mo/ZSM-5 remains practically constant after 5 reaction-regeneration cycles. Meanwhile, the catalytic activity of 10%Mo/ZSM-5 was not recovered after regeneration. According to N_2 adsorption, XRD and HRTEM, the state of Mo and structure of H-ZSM-5 were identical in fresh and regenerated 2%Mo/ZSM-5. However, formation of the aluminum molybdate and partial destruction of the H-ZSM-5 structure were observed for the regenerated 10%Mo/ZSM-5 catalyst.
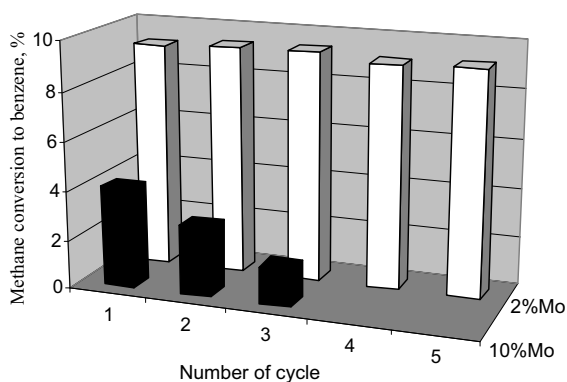

Fig. 7. Catalytic activity of Mo/ZSM-5 catalysts (Si/Al = 17) *versus* number of cycles: reaction (CH_4/720°C/6h) - regeneration (O_2/520°C/2h).

An increase of the reaction time up to ~20 h led to faster 2%Mo/ZSM-5 catalyst deactivation in the third cycle: methane conversion to benzene decreased from 9 to 2% in ~ 15 h, whereas after the first cycle such decrease occurred only after ~ 20 h on stream.

Conclusions

The effect of molybdenum content on the activity and deactivation of Mo/ZSM-5 catalysts in methane dehydroaromatization reaction has been studied. It was shown that total methane conversion decreased by 30% during 12 h of the DHA reaction. The benzene formation rate increased from 0.5 to 13.9 $\mu mol\ C_6H_6/(g_{Mo} \cdot s)$ when the molybdenum content was decreased from 10 to 1 wt. %.

The nature of carbonaceous deposits formed on Mo/ZSM-5 catalysts during the DHA of CH_4 was established. Correlations between the content and physicochemical properties of CD *vs.* catalyst composition and reaction conditions were determined. The content and condensation degree (ratio C/H) of carbonaceous deposits decreases when the Mo content in the catalyst increases from 1 to 10 wt.%.

It was shown that regeneration in oxygen at 520°C during 2 h led to burn-out of all types of carbonaceous deposits formed on Mo/ZSM-5 after 6 h on stream. The stable operation of the 2%Mo/ZSM-5 catalysts under multiple reaction-regeneration cycles was demonstrated.

Acknowledegements

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