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INFLUENCE OF DEEP BED TREATMENT ON THE MO/ZSM-5 CATALYSTS IN METHANE DEHYDROAROMATIZATION

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Abstract

Mo/ZSM-5 catalysts were tested in methane dehydroaromatization reaction. The catalyst samples were pretreated in different ways before the testing. One of the samples was deep bed treated without molybdenum loading, one was deep bed treated after molybdenum loading. In other samples the parent zeolite was desilicated, or the extraframework aluminum was extracted after deep bed treatment. These samples were compared with a catalyst sample, which was not pretreated before the reaction. On all parent zeolites the molybdenum was deposited from the solution of ammonium molybdate. The catalysts were characterized by XRD, TPDA, FT-IR, n-hexane cracking, and the surface properties were measured by nitrogen adsorption.

Keywords: dehydroaromatization; methane; Mo/ZSM-5; zeolites; stabilization.

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1. Introduction

Methane is the simplest alkane, and the main component of natural gas. It is the richest represented organic compound on the Earth. It has a strong greenhouse effect, and it has been mainly used for energetic purposes [1-2]. In 1993 it was reported, that methane could be transformed into benzene and other aromatics in the absence of oxygen [3-4]. Among the catalysts the zeolite ZSM-5 was the best, and the best transition metal component was molybdenum [3]. The methane dehydroaromatization reaction runs at 700°C and by atmospheric pressure [5-7]. In the methane dehydroaromatization reaction at 700°C the main product is benzene and naphthalene. The maximum conversion at 700°C is 12% [8]. The by products are ethane, ethylene, toluene, C8 and C9 aromatics, hydrogen and coke [9].

The zeolite ZSM-5 is the mainly used catalyst in the methane dehydroaromatization reaction. The other catalysts used in this reaction are ZSM-8, ZSM-11, MCM-41 [10], MCM-22 [11-12] and FSM-16 [13-14].

The post synthesis treatment is important to improve the catalyst activity and selectivity. In our paper, we have studied the effect of the hydrothermal dealumination in deep bed before and after molybdenum loading on the catalyst activity and selectivity. Hudec *et. al.* [15] and Bartková *et. al.* [16] tested the activity of zeolites without active metal loading after deep bed treatment and reported, that after deep bed treatment of parent zeolite there are some changes in their activity in n-hexane cracking. Our work is continuation in their research.

The unique catalytic activity of zeolite ZSM-5 is attributed to its low number of strong acid sites, which is related to its high Si/Al ratio [17]. The acid properties and catalytic activity of zeolites are related to the degree of substitution of aluminum for silicon in the framework [18]. Zeolite ZSM-5 is more resistant to dealumination than zeolite Y or mordenites, but the ZSM-5 zeolite lattice can be dealuminated in the presence of steam at high temperatures [17-18]. The extraframework-aluminum, which is produced due to dealumination, can affect the acid properties of the catalyst [17]. The produced extraframework-aluminum can act as Lewis acid center [19]. It has been shown, that both, the amount and the type of extraframework Al and Si/Al species are important for defining the catalytic activity and the acidity of the catalysts [17]. Dealumination and desilication are well known routes to create the additional mesoporosity in zeolite particles [20]. By the dealumination and desilication the Al and Si atoms are removed, or used to form mesopores [19].

Desilication is a method of post synthesis treatment, in which the framework Si is extracted from the zeolite lattice in the presence of OH ions. It is a promising method to create extra porosity in zeolites with high Si/Al ratio. Especially ZSM-5 zeolites are suitable for desilication. By this kind of post synthesis treatment the mesoporous surface area is increasing, which allows better diffusion of reactant molecules to the active sites [19]. Many researchers have shown that desilication of zeolites by alkaline treatment is an economical and effective way to create intraparticle mesopores in zeolites [20].

2. Experimental

2.1 Catalyst preparation

Samples Mo/Z, Mo/(Z)780, (Mo/Z)780, and Mo/(Z)780Ext have the same parent. Mo/(Z)DS was prepared from another parent. Molybdenum was deposited on the parent zeolite in amount of 4,67 wt%. The catalyst preparation was as follows: Mo/Z - the molybdenum was deposited by impregnation from the solution of ammonium molybdate. Mo/(Z)780 – the zeolite matrix was treated in deep bed at 780°C (heating: 2°C/min, 3h), then the molybdenum was deposited by impregnation from the solution of ammonium molybdate. (Mo/Z)780 was prepared in reverse. First, the molybdenum was deposited on the catalyst matrix by impregnation from the solution of ammonium molybdate, and then the catalyst was deep bed treated at 780°C (heating: 2°C/min, 3h). Mo/(Z)780Ext – the matrix was deep bed treated at 780°C, then it was extracted with 0,5M HCl two times to remove the extraframework aluminum and the last step was the molybdenum deposition by impregnation from the solution of ammonium molybdate. Mo/(Z)DS – the matrix was desilicated with 0,5M NaOH, but the catalyst was turned to Na form. To turn the catalyst to NH_4 form, it was washed with NH_4NO_3 four times. Then the molybdenum was deposited on the catalyst from the solution of ammonium molybdate.

2.2 Catalyst characterization

The catalysts were characterized with various physicochemical methods. The TPDA method was used to determine the total acidity. 0.3 g of the samples was treated in situ at 490°C for 1h in a flow of helium. Then they were cooled to 220°C in He and the ammonia was adsorbed from an NH_3/He mixture. Ammonia desorption was done from 220°C to 700°C (heating rate 10.5°C/min) in a flow of He. During the ammonia desorption the outflow was led to a solution of a 0.05M H_2SO_4. The amount of desorbed ammonia was determined by titration of the excess of H_2SO_4 with 0.05M NaOH. Infrared spectra were taken by using FTIR spectrometer to determine the OH groups and the Bronsted and Lewis active sites. Self-supported wafers were treated for 2h at 450°C and 10^{-4} Pa. To identify the type of the acid sites, pyridine was adsorbed on the catalyst at 150°C. The IR spectra were taken between 400 and 4000 $cm^{-1.}$ The catalyst surface was characterized by using BET isotherm and t-plot method. The samples were evacuated overnight at 350°C under the vacuum of 2 Pa and then the nitrogen was adsorbed on the samples at -196°C. The activity and the stability of acid sites were determined in n-hexane conversion. The cracking of n-Hexane was carried out in a glass-flow microreactor at 350°C and 0.1MPa. The reactor was on-line connected to the chromatograph. XRD spectra were taken to the crystalline phase identification and phase purity determination of Mo/ZSM-5 samples under CoKα radiation.

2.3. Catalytic tests

The methane dehydroaromatization was carried out at 700°C and at atmospheric pressure. The reactor was a flow quartz U-shaped fixed bed reactor charged with 0.5g of catalyst. Before the aromatization the catalyst was activated under airflow at 500°C for 3h. After reaching 500°C air was changed to nitrogen, and the catalyst was heated to 700°C. At 700°C the nitrogen was changed to methane. The samples were taken after 10, 30, 60, 120, 180 and 240 min of time on stream. The products were analyzed by gas chromatography. The hydrocarbon components were analyzed in Hewlett Packard 6890 SERIES II chromatograph with PONA capillary column (50m x 0.2mm x 0.5µm) and FID detector. The non-hydrocarbon components were analyzed by using CHROM5 chromatograph with a Porapak Q (80+100 mesh, 1.8 m x 2cm) and with TCD detector.

3. Results and discussion

From the XRD pattern (fig 1) we can see, that the zeolite structure of the sample (Mo/Z)780, which was deep bed treated with impregnated molybdenum, was destroyed. The crystalinity of other samples remain unchanged after deep bed treatment or after Mo loading.

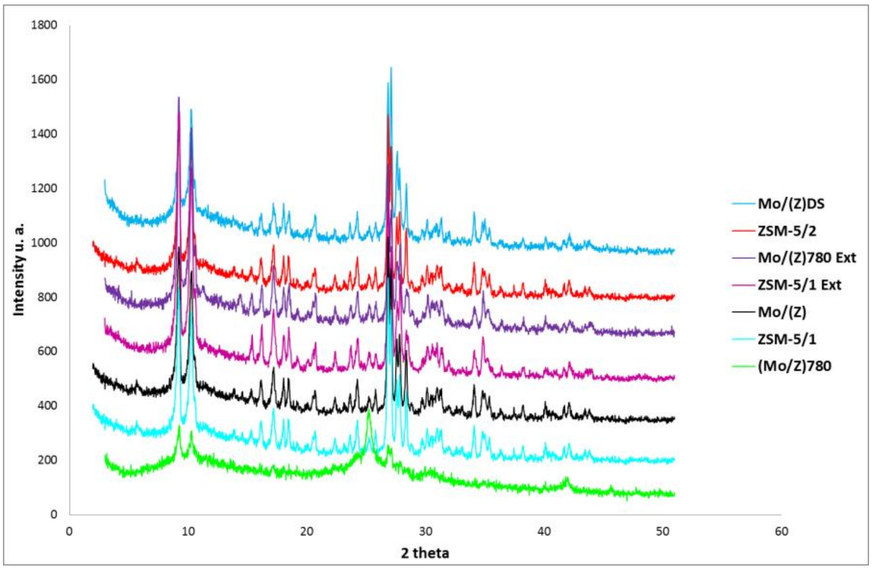

Fig. 1 XRD pattern of Mo/ZSM-5 catalysts

Tab.1 shows the characteristics of the catalyst samples. The specific surface area and the volume of micropores of all samples have decreased after molybdenum loading. The surface properties of the sample, which was deep bed treated after molybdenum loading ((Mo/Z)780) have lowered rapidly. It could be caused by losing the zeolite crystalinity, as we can see it on the XRD pattern (fig1).

Table 1 Characteristic of catalyst sample

Sample	Preparing process	S_{BET} (m^2/g)	S_t (m^2/g)	V_{micro} (m^3/g)	Acidity (mmol/g)	BAS	LAS
ZSM-5/1	Parent 1	313	82	0.117	0.595	0.576	0.019
Mo/Z	Impregnation of Mo form the solution of ammonium molybdate	288	100	0.087	0.292	0.283	0.009
Mo/(Z)780	DB treatment of parent 1 at 780°C+Mo impregnation from solution of ammonium molybdate	249	76	0.091	0.216	0.176	0.04
(Mo/Z)780	DB treatment of the sample after Mo loading	30	9	0.011	0.231	0.049	0.182
Mo/(Z)780Ext	DB treatment of parent + extraction of EFAl + Mo loading	269	72	0.090	0.419	0.267	0.152
ZSM-5/2	Parent 2	389	160	0.121	0.686	0.627	0.060
Mo(Z)DS	Desilication of parent 2 + Mo loading	318	176	0.113	0.575	0.563	0.012

The acidities of the deep bed treated samples dropped by half in comparison with the parent zeolite. The acidity of the sample from which the extraframework aluminum was extracted (Mo/(Z)780Ext) and the acidity of the desili-cated sample (Mo/(Z)DS) decreased slightly in comparison with the parent zeolite after molybdenum loading. The number of Bronsted acid sites of all samples decreased after Mo loading which means, that the Mo is associated with these acid sites. In the case of sample (Mo/Z)780 the number of Lewis acid sites increased. Lewis acid sites could be formed by deep bed treatment, when the Al migrates to the extraframework spaces and forms Lewis acid sites. Lewis acid sites are responsible for coke formation.

Fig 2 represents the n-hexane conversion on catalyst samples. The highest activity in this cracking reaction has the parent zeolites due to their high concentration of Bronsted acid sites. This reaction is used for the comparison of acid sites strength of the catalyst samples. Because of the high acidity and the high concentration of the desilicated sample (Mo/(Z)DS), it has high activity in this cracking reaction. The other samples have lower activity in n-hexane conversion due to their lower acidity and lower concentration of Bronsted acid sites. The sample that was deep bed treated after molybdenum loading has the lowest activity in n-hexane cracking reaction. The n-hexane cracking needs Bronsted acid sites. The samples, in which the Mo is associated with the Bronsted acid sites, are less active in this process.

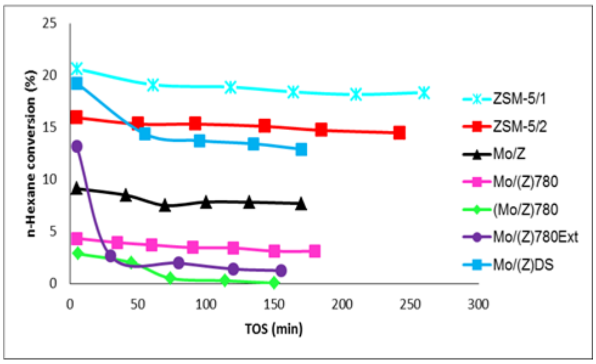

Fig.2 n-Hexane conversion over ZSM-5 type catalysts. Reaction conditions: 350°C, 0.1 MPa, WHSV of n-hexane = 2,61 h^{-1}.

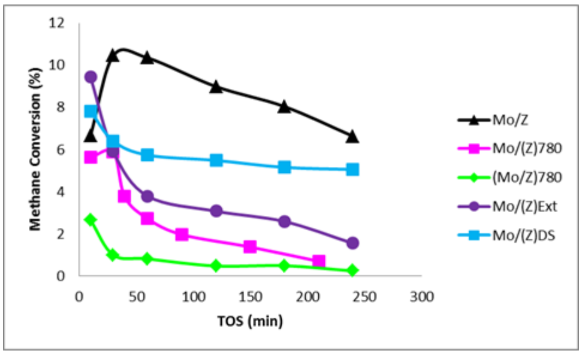

Fig. 3 Methane conversion over Mo/ZSM-5 catalysts. Reaction conditions: 700°C, 0.1 MPa, 3600 mL/h.g.

The activities of the catalyst samples in methane dehydroaromatization are shown on Fig. 3. From the results we can see, that deep bed treatment of the zeolite is not a preferable method for treating the catalysts. According to fig.3 desilication of the parent zeolite seems to be a better treatment than deep bed treatment or extraction of extra-framework aluminum. But nevertheless the catalyst sample without pretreatment has the highest activity among the catalysts. Partly the extraction of the extraframework aluminum can positively influence the aromatization activity of deep bed treated zeolites (see Mo/(Z)780Ext). But on this sample the methane conversion drops very fast. Deep bed treatment with or without the presence of molybdenum has a negative effect on the aromatization activity of the samples. The lowest activity has the sample which was deep bed treated in the presence of molybdenum ((Mo/Z)780) due to loss its crystalline structure. At the deep bed treatment temperature (780°C) Lewis acid sites could form as we can see it from tab.1.

The main product from methane dehydroaromatization is benzene. Toluene, xylenes, C_9 aromatics and naphthalene is formed in small amounts. Fig. 4 shows the selectivities of the catalysts to benzene. Except the sample which was deep bed treated in the presence of molybdenum ((Mo/Z) 780), all catalysts have high selectivity to benzene (over 60%) in the early stage of the reaction. The selectivities of the desilicated sample (Mo/(Z)DS) and the sample without pretreatment (Mo/Z) are decreasing slowlier than the selectivities of the deep bed treated samples (Mo/(Z)780 and (Mo/Z)780) or the sample from which the extraframework aluminum was extracted (Mo/(Z)780Ext). The highest selectivity to benzene has again the catalyst, which was not specially modified before molybdenum loading (Mo/Z). The desilicated sample (Mo/(Z)DS) has comparable selectivity to this catalyst. The loss of crystalline structure of the sample deep bed treated after molybdenum loading ((Mo/Z)780) is reflected on its selectivity to benzene.

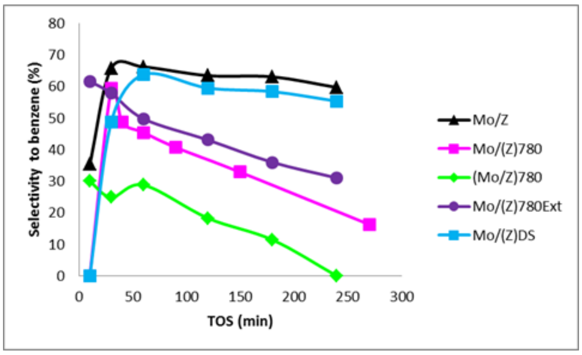

Fig. 4 Selectivity to benzene in methane conversion over Mo/ZSM-5 catalysts. Reaction conditions: 700 °C, 0,1 MPa, 3600 mL/h.g)

During the methane dehydroaromatization reaction not only aromatics are formed but also non-aromatic light products. The decrease in the selectivities to aromatics with the reaction time is accompanied with the production of light products such as nonaromatic C_2-C_3 hydrocarbons, mainly ethylene. Fig. 5 illustrates the selectivity of the catalysts to C_2+C_3 light products and ethylene.

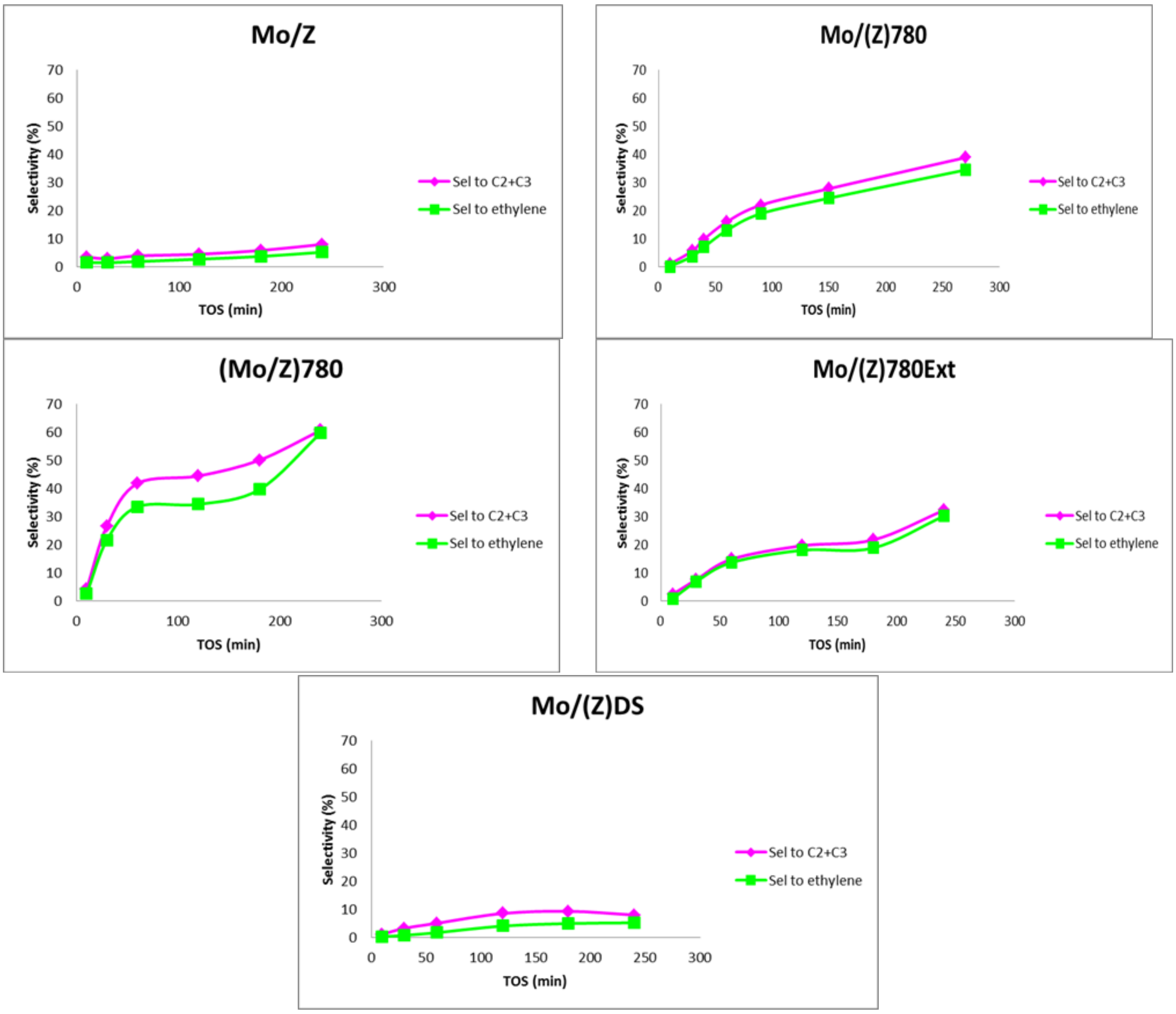

Fig. 5 Selectivity to light products in methane conversion. Reaction conditions: 700°C, 0,1 MPa, 3600 mL/h.g)

The selectivities to the light C_2-C_3 products are increasing with the reaction time. The highest selectivity was reached on deep bed treated catalyst samples (Mo/(Z)780 and (Mo/Z)780). The sample deep bed treated after molybdenum loading has a surprisingly high selectivity to the light products (60%). The lowest selectivity has the desilicated catalyst (Mo/(Z)DS), and the catalyst without pretreatment (Mo/Z) (approximately 10%).

The decrease of activity of all samples is caused by coking which is accompanied by hydrogen creation. Methane decomposes at the beginning of the reaction and molybdenum oxide species form Mo_2C and MoO_xC_y active sites with the produced carbon. This process leads to the increasing of hydrogen amount in the early period of the reaction. The formation of Mo_2C and MoO_xC_y active species is important for the aromatization activity of the catalyst. Fig. 6 compares the quantities of analyzed and calculated hydrogen. The quantity of analyzed hydrogen was obtained from chromatographic analysis of the reaction products. From the reaction stoichiometry was calculated the amount of calculated hydrogen. The amount of analyzed hydrogen is every time higher than the amount of calculated hydrogen.

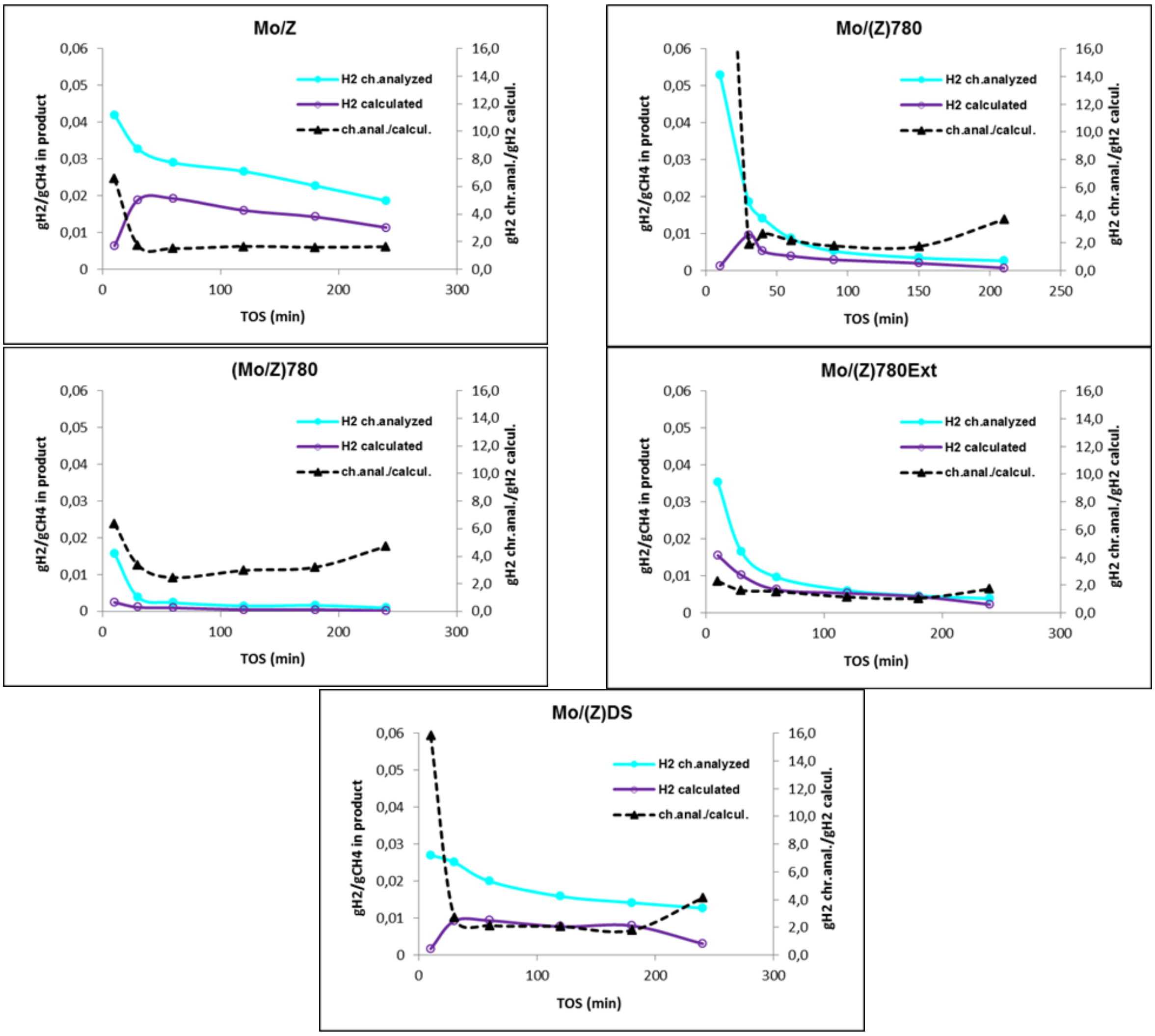

Fig. 6 H_2 in products determined by chromatographic analysis and calculated and the ratio of these values in methane conversion. Reaction conditions: 700°C, 0.1MPa, 3600mL/h g

The catalyst activity is reflected on the hydrogen formation. Catalysts, which are more active in the methane dehydroaromatization reaction, are producing more hydrogen. From the figure it is clear, that the most active catalysts were the sample without treatment (Mo/Z) and the desilicated sample (Mo/(Z)DS). The amount of analyzed hydrogen decreases fast in the induction period, then the decrease is slower. The amount of calculated hydrogen has increasing tendency in the induction period. In case of samples Mo/(Z)780Ext and Mo/(Z)780 the amount of calculated hydrogen decreases from the beginning of the testing. The ratio between the analyzed and the calculated hydrogen amount reflects the coke formation. From fig.6 we can see that the coke formation was the highest in the case of the sample which was deep bed treated in the presence of Mo ((Mo/Z)780). This catalyst was the less active in the methane dehydroaromatization reaction. The highest coke formation at the beginning of the reaction was on samples Mo/(Z)780 and Mo/(Z)DS. It caused the rapid drop in the activity of catalyst Mo/(Z)780. The high coke formation on the desilicated catalyst is reflected on its fast decreasing in activity (fig.3). But then the coke formation is constant and the catalyst activity decreases slightly.

4. Conclusions

Catalysts after deep bed treatment or desilication do not have higher activity in methane dehydroaromatization reaction in comparison with the non-treated sample. Deep-bed treatment or desilication of the zeolite causes the decrease of methane conversion and the selectivity to benzene of MoZSM-5 type catalysts compared with the activity and selectivity of the non-treated catalyst. Remarkable is the selectivity to light products containing mainly ethylene on the deep bed treated catalysts. Deep-bed treatment after Mo loading results in the loss of zeolite crystallinity. This catalyst was the less active in the dehydroaromatization reaction and the less selective to benzene. On the other hand the selectivity to ethylene and to the sum of C_2+C_3 light products was the highest on this sample.

Desilication of the zeolite causes small decrease in catalyst activity and in selectivity to benzene in the dehydroaromatization reaction in comparison to the non-treated sample. The selectivity to the C_2+C_3 light products is almost the same as in the case of non-treated sample.

The deep bed treatment, desilication or extraction of extra-framework aluminum are not appropriate methods for increasing the catalyst activity or stability of activity in methane dehydroaromatization reaction.

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