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Methane aromatization using Mo-based catalysts prepared by microwave heating

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Abstract

Mo/HZSM-5 and Cu–Mo/HZSM-5 catalysts for the non-oxidative aromatization of methane have been prepared by microwave heating method. The effects of Mo loading, the molar ratio of Cu/Mo and preparation method on the catalytic performance of catalysts were studied. The results were compared with those for the methane aromatization over catalysts prepared by conventional heating. Both two kinds of catalysts have the maximum methane conversion when the Mo loading is 6%. The catalysts prepared by microwave heating exhibited higher selectivity to benzene than that prepared by conventional heating. The addition of metal Cu to Mo/HZSM-5 catalyst prepared by microwave heating enhanced the lifetime of catalyst, and gave rise to a little increase in methane conversion. The molar ratio of Cu/Mo influenced the methane conversion, and the maximum value was attained when Cu/Mo = 0.05, whereas no significant influence on the benzene selectivity was observed with the increase molar ratio of Cu/Mo. N_2 adsorption results showed that the catalysts prepared by microwave heating have the larger surface area and the similar pore volume compared with the catalysts prepared by conventional heating. This fact revealed that the more Mo species located on the outer surface of catalysts prepared by microwave heating is the main reason why they have better catalytic performance. XRD analysis indicated that the Mo species are highly dispersed on HZSM-5 zeolite. The addition of Cu influenced the dispersion. The actual active phase Mo_2C can be identified on the catalyst surface after reaction. TEM analysis revealed the carbonaceous deposition to have the form of carbon nanotube after reaction, with a uniform size range of 10–20 nm. TG analysis indicated that carbonaceous deposition on the catalysts prepared by microwave heating is lower than that by conventional heating, and the metal Cu further prompts the stability of catalyst. Most of the carbonaceous deposition on catalysts prepared by microwave heating is formed at low temperature and it is easy to burn-off. Coke accumulation at high temperature is the main reason of catalyst deactivation. The carbonaceous deposition formed on the catalysts for non-oxidative aromatization of methane is different from those formed on the catalysts for partial oxidation of methane.

Keywords: Methane aromatization; Microwave heating; Catalyst preparation; Mo/HZSM-5; Mo–Cu/HZSM-5; Characterization

1. Introduction

The use of aromatics as an important petrochemical feed has always stimulated the research for the production of aromatics. Nowadays, most aromatics are obtained by catalytic reforming of naphthas, but this technology will be abandoned due to the exhausted petroleum reserves. Recently, the direct conversion of natural gas to aromatics such as benzene and toluene has attracted considerable attention because of its merits such as abundant natural gas reserves, higher selectivity to benzene, and easier separation of products.

There is a general agreement that methane non-oxidative aromatization catalyzed by Mo/HZSM-5 has been recognized as a promising route for producing aromatics [1–5]. Recently, extensive studies have been conducted on the modification of Mo/HZSM-5 catalysts by the addition of a second metal promoters [6–9] such as Co, Fe, Cu, Pt, Ru, the adjustment of various supports [10–11] to the catalyst, and the addition of other gases such as H_2, N_2, CO_2, and H_2O [12–14] to the feed. The results showed that these measures improve, to some extent, both the stability and the catalytic performance.

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Despite plentiful studies worldwide, progress in this field has been hampered by low methane conversion and serious catalyst deactivation due to coke formation. It is well known that the preparation method of catalyst can affect the zeolite channel structure, the acid site density, and the oxidation state and location of the molybdenum species. These factors are recognized to affect the catalytic performance of methane conversion [15–19]. Thus, this leads to the investigation of new preparation method and to the further optimization of catalyst performance.

At present, many novel techniques such as microwave heating [20], plasma chemistry [21] have been applied to the field of catalyst preparation. Microwave heating has been shown to be a promising technique for catalyst preparation because of its heating characteristic. The objective of this work was to use microwave heating as an easy and fast method for the preparation of Mo/HZSM-5 and Cu–Mo/HZSM-5 catalysts, and to compare their performance with catalysts prepared by conventional heating. We therefore report here on the use of microwave heating results in the preparation of Mo/HZSM-5 and Cu–Mo/HZSM-5 catalysts with the uniform dispersion of the active species on the outer face of the support, and we also show that these catalysts give an increase in catalytic selectivity and stability towards the non-oxidative aromatization of methane. The dispersion degrees of catalyst surface species were investigated through XRD. The carbonaceous deposition on the used catalysts was also analyzed by TEM and TG techniques.

2. Experimental

2.1. Preparation of a series of Mo/HZSM-5 and Mo–Cu/HZSM-5 catalysts

Commercial HZSM-5 (Si/Al = 25; Nankai University, PR China) was used as a support. Mo catalysts were prepared by impregnating the support with an aqueous solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (99.9%, Jinduicheng Molybdenum Mining Corporation, PR China). The impregnated sample was subsequently dried in air at 393 K for 2 h. A portion of the sample was subsequently calcined in air at 773 K for 4 h (CH catalyst) and the remaining portion was heated in a microwave oven (Galanz Corporation, China) at 100% power (700 W, 2.45 GHz) for 10 min in air (MW catalyst). The 10 min was chosen as the heating time, as in all cases the maximum temperature in the oven was reached within this period. The Cu–Mo/HZSM-5 catalysts were prepared by the consecutive impregnation of 6 wt.% Mo/HZSM-5(MW) with an aqueous solution of $Cu(C_2H_3O_2)_2{\cdot}H_2O$ (99.9%, Beijing Beihua Fine Chemicals Co. Ltd., PR China), followed by drying in air at 393 K and calcination in the microwave oven at 100% power for 10 min in air.

2.2. Catalytic evaluation

Catalytic reactions were carried out at atmospheric pressure by a fixed-bed continuous flow system with a quartz reactor of 8 mm i.d., in which 0.5 g catalyst was loaded. It was connected to a gas feeding unit and the analytical equipment. The reaction temperature controlled by a sheathed thermocouple embedded in the middle of catalyst bed was 973 K. Before exposure to reactant, the catalyst underwent gradual heating under nitrogen in temperature-ramped mode up to 973 K. It was maintained at this temperature for 30 min, then the gas flow was switched to methane and the reaction began. The gaseous reaction products were analyzed by means of a HP4890D gas chromatograph equipped with a flame ionization detector (FID) connected to a PLOT-Q capillary column (30 m long and 50 μm i.d., J&W Scientific Corp.). There were benzene, toluene, naphthalene, ethylene, and ethane in the reactor exit stream. As naphthalene was detected in trace amounts during operation, it was ignored in the carbon balance calculations. The carbonaceous deposits were also discounted in the carbon balance, which were found to be negligible. Methane conversion was thus calculated based on the carbon content of benzene, toluene, ethylene, and ethane. It is important to mention that the blank experiment has shown that no CH_4 conversion occurs in the absence of the catalyst.

2.3. Catalyst characterization

Specific surface area and pore volume measurements were obtained from volumetric nitrogen adsorption using Beckman Coulter Sorption Analysis 3100 Plus instrument.

Powder X-ray diffraction patterns of various catalysts were recorded with a Rigaku D/Max-2400 X-ray diffraction system (made by Rigaku Corporation of Japan) using Cu Kα radiation at 36 kV and 80 mA. Powder diffractograms were recorded at 5°/min scanning speed over a 2θ range of 5–60°.

Transmission electron microscope (TEM) micrographs were acquired with JEM-200CX Transmission Electron Microscope supplied by Electric Corporation of Japan. The samples for this analysis were treated as follows: a suspension was prepared combining 30% ethanol, the catalyst to be analyzed, then ultrasound was applied for 5 min, and when the suspension was homogeneous, one drop was placed over the copper grid for analysis under different magnification.

Thermo-gravimetric (TG) analysis of various catalysts after reaction was carried out on a Perkin-Elmer TG-DTA 2950 instrument in dry air (30 ml/min) with the heating rate 10 K/min. Thermo-gravimetric profiles were recorded automatically over a temperature range of 293–1023 K.

Three changes of the sample mass occurred in original TG profiles. They are the weight loss caused by water before 493 K, the weight loss by coke burn-off between 693 and 1023 K, and the weight gain by the reaction of Mo_2C and

oxygen between 493 and 693 K. The carbonaceous deposition on catalysts comprises the carbon in the Mo_2C and coke deposition. The carbon in the Mo_2C can be calculated by Eq. (1), and the coke formation can be calculated according to Eq. (2)

$$w_1\,(\%) = \frac{m_2 - m_1}{m_2}\frac{M_C}{2M_{MO} - M_{MC}} \times 100 \quad (1)$$

$$w_2\,(\%) = \frac{m_2 - m_3}{m_2} \times 100 \quad (2)$$

In the above equation, w_1 represents the percentage of carbon in the Mo_2C, w_2 represents the percentage of coke formation, m_1 is the weight of the sample after weight loss from 293 to 493 K, and m_2 is the weight of the sample before coke burn-off, m_3 is the weight of the sample after coke burn-off from 693 to 1023 K. M_C, M_{MO}, and M_{MC} represent the molecular weight of C, MoO_3 and Mo_2C, respectively.

3. Results and discussion

3.1. The influence of Mo content on catalytic performance of Mo-based catalysts

The catalytic performance of different Mo loading catalysts prepared by two methods in non-oxidative aromatization of methane at 973 K is reported in Table 1. The methane conversion has the maximum value with the increase of Mo loading. The 6% Mo/HZSM-5 catalyst shows the best catalytic performance on both two kinds of catalysts. The catalytic activity at the same Mo loading is higher for the MW catalysts than for the CH catalysts. The results indicate that the methane aromatization reaction is related to Mo species. The selectivity of all catalysts to benzene is very high, and the overall selectivity of benzene and toluene exceed 98%.

3.2. The influence of preparation method on Mo-based catalysts

A comparison of the activity data, over the first 6 h of reaction, obtained for 6 wt.% Mo/HZSM-5(CH and MW) catalysts is shown in Fig. 1. The MW catalyst appears to achieve the steady state at a higher methane conversion value after 6 h, whereas the CH catalyst suffers a slight loss in initial activity due to carbon deposition. The discrepancy on methane conversion between two catalysts is more obvious with the increase of reaction time. Although the activities of catalysts decrease with an increase of reaction time, the methane conversion over 6% Mo/HZSM-5(MW) catalyst still maintain 18% after 6 h. The steady-state conversion of methane over MW catalyst is higher than that obtained over CH catalyst. It is known that Mo species on the outer surface of catalyst are beneficial to the conversion of methane to benzene [22]. The higher conversion in the case of the MW catalyst implies more Mo species dispersed on the outer surface of catalyst, which is consistent with the effect of the microwave heating.

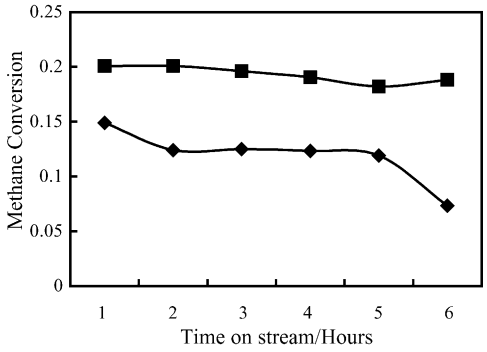

Fig. 1. Time on stream analysis of methane conversion for non-oxidative aromatization over 6% Mo/HZSM-5 catalysts at 973 K: catalyst prepared by conventional heating (◆) and microwave heating (■).

Fig. 2 compares the products selectivity of methane aromatization obtained on the MW and CH catalysts at 973 K. More benzene and less ethene were detected in the case of MW catalyst as compared to the CH catalyst, and no toluene and naphthalene appeared. The reason of this phenomenon is the different location of Mo species due to preparation method.

The nitrogen adsorption results for the parent zeolite HZSM-5, the 6% Mo/HZSM-5(CH) catalysts and the 6%

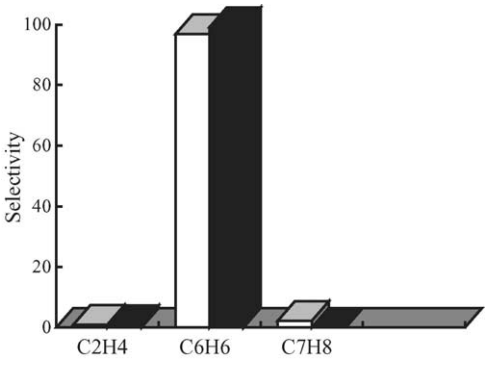

Fig. 2. Products selectivity of methane non-oxidative aromatization over 6% Mo/HZSM-5 catalysts at 973 K: catalyst prepared by conventional heating (□) and microwave heating (■).

Table 1
Catalytic performances of CH_4 aromatization on Mo/HZSM-5 catalysts[a]

W(Mo) (%)	Conventional heating				Microwave heating		
	X(CH_4) (%)	S (%)			X(CH_4) (%)	S (%)	
		C_2H_4	C_6H_6	C_7H_8		C_2H_4	C_6H_6
3	14.1	0.3	94.7	5.0	16.3	3.2	96.8
6	15.9	1.0	91.4	7.6	19.4	0.7	99.3
9	13.2	0.45	96.9	2.6	14.2	1.3	98.7

W(Mo) (%): weight percent of Mo loading; X(CH_4) (%): methane mole conversion; S (%): product selectivity.

[a] The data taken after 3 h on stream.

Table 2
Specific surface area and pore volume for the different catalysts

Catalysts	BET surface area (m^2/g)	BJH pore volumes (cm^3/g)[a]
HZSM-5	328.7	0.031
6% Mo/HZSM-5(CH)	309	0.026
6% Mo/HZSM-5(MW)	327.4	0.025

[a] BJH pore volume relates to the cumulative pore volume.

Mo/HZSM-5(MW) catalysts are listed in Table 2. Comparing the parent HZSM-5 zeolite, the specific surface area of the 6% Mo/HZSM-5(CH) catalyst is reduced after the addition of molybdenum, whereas the surface area of 6% Mo/HZSM-5(MW) catalyst is similar with parent zeolite. The surface area of MW catalyst is larger than that of CH catalyst, however, the pore volume is similar. This fact indicates that the Mo species on CH catalyst migrated into the zeolite channels at high temperature calcination, which led to the decrease of surface area and the lower catalytic performance. Since the microwave heating rate is so fast, most of the Mo species located on the outer surface of catalyst and kept the structure of zeolite. It implies that the better catalytic performance of the MW catalysts is related to the surface area, the dispersion degree of Mo species on the outer surface of catalyst is more important.

3.3. Promotion of the different Cu/Mo on catalytic performance of 6% Mo/HZSM-5 catalysts

As the Mo catalysts prepared by microwave heating exhibited better performance for methane conversion and catalytic stability compared with those prepared by conventional heating, here the promotion of Cu on Mo catalyst (MW) is only discussed. The evolution of the methane conversion and benzene selectivity as a function of reaction time is depicted in Fig. 3. The addition of Cu influenced methane conversion. When the molar ratio Cu/Mo was 0.03–0.05, the methane conversion of Mo–Cu/HZSM-5 catalysts was higher than that of Mo/HZSM-5 catalysts. Furthermore, the stability of catalysts was also promoted due to the addition of Cu. The advantage of Cu was further remarkable with the increase of reaction time. These results reveal that the addition of Cu could depress the Brønsted acid site of carrier, where the carbonaceous deposits are predominantly located. However, when the molar ratio Cu/Mo increased to 0.09, the methane conversion of Cu–Mo/HZSM-5 catalyst showed a significant decline to values, even lower than that of Mo/HZSM-5 catalyst. That is because the existence of Cu leads to the lower activity by over weakening the density of Brønsted acid site. The maximum methane conversion is attained when the molar ratio Cu/Mo is 0.05. The addition of Cu improves the benzene selectivity. However, there is no significant influence on the benzene selectivity with the increase of Cu/Mo molar ratio.

3.4. TEM analysis of catalysts

Fig. 4 shows the micrographs for 6% Mo/HZSM-5 catalyst prepared by microwave heating. Fig. 4a shows the surface state of catalyst sample before reaction. The Mo species sizes are about 20–30 nm, which is much larger than ZSM-5 zeolite channel size (0.54 nm × 0.56 nm). Most of the Mo species spread on the outer surface of the carrier. No fibriform material can be found on the catalyst surface.

Since the methane aromatization is an endothermic reaction, the high temperature is required to yield meaningful conversions into aromatics during the reaction. However, such severe conditions are favorable for carbonaceous deposition. In spite of the stable property of methane, the carbon nanotube can be seen on Ni metal catalyst [23], the similar phenomenon occurred on Mo metal catalysts. The reaction was carried at 973 K; the carbon nanotube was co-products because of carbon deposit during the reaction. Fig. 4b–d shows the carbonaceous deposition of used catalyst under different magnifications. The catalyst surface was covered with many fibriform materials in Fig. 4b, which indicates that the carbonaceous deposition occurred. Fig. 4c shows a weak carbonaceous deposition on the catalyst surface. The fibriform materials are the carbon nanotubes. One end of each carbon nanotube is attached to catalyst, the other end extended to outside. They are slim and have uniformity of diameter. A brunch of carbon nanotubes can be seen clearly in Fig. 4d, which shows a strong carbon

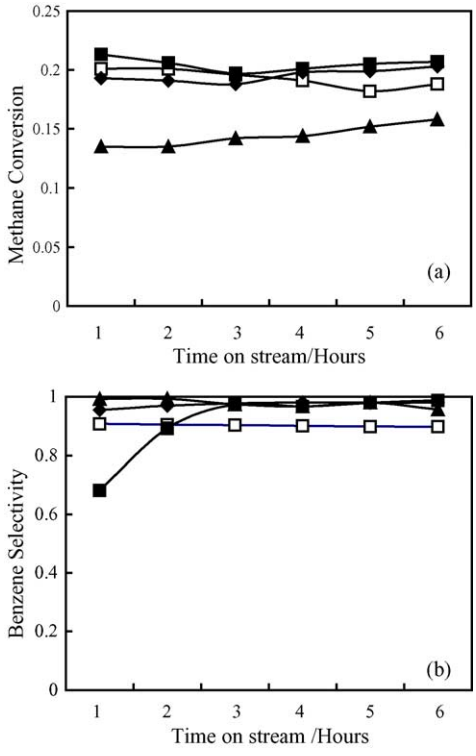

Fig. 3. The influence of Cu/Mo on: (a) methane conversion and (b) benzene selectivity: (■) Cu/Mo = 0.03, (◆) Cu/Mo = 0.05, (▲) Cu/Mo=0.09, and (□) Cu/Mo = 0.

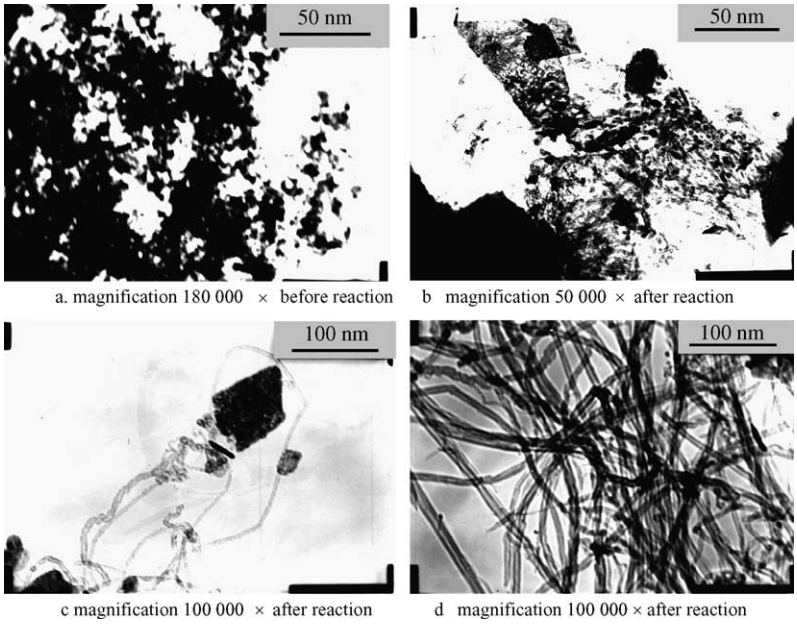

Fig. 4. TEM micrographs of 6% Mo/HZSM-5 catalysts before and after reaction.

deposition. These carbon nanotubes are also slim and have the same size range of 10–20 nm. As the Brønsted acid site is the major position of carbonaceous deposition at high temperature, in addition to the existence of Mo species on the surface of zeolite, the carbon nanotube are generated by the interaction of Mo species and the Brønsted acid site, and then extend to outside.

3.5. XRD analysis

The XRD patterns of a series of 6% Mo catalysts are given in Fig. 5. Compared with the diffraction patterns of MoO_3 and parent HZSM-5 zeolite from literature [24], all the XRD patterns are the composite of the MoO_3 and HZSM-5 diffraction patterns, indicating that the molybdenum was present as MoO_3 (diffraction peaks at $2\theta = 33.2^\circ$, 33.8°, 39.0° and 49.3°).

The MoO_3 diffraction peaks can be clearly found in patterns (a) and (b). This result is different from that of CH catalysts [22], in which no MoO_3 diffraction peaks occurred. It implies that most of MoO_3 species on the MW catalysts dispersed as the crystalloid particle on the outer surface of the zeolite. The microwave heating proceeds with high rate and from inside to outside compared to conventional heating. As a result, the migration of Mo species from the outer surface to inner channels of the zeolite stopped and the blockage of zeolite channels could be avoided. This led to the higher selectivity to benzene of catalysts post-treated by microwave heating. The MoO_3 diffraction peaks of pattern (a) are slight broader than that of pattern (b) especially when at $2\theta = 39^\circ$. The broad peaks indicating that the addition of the metal Cu improved the dispersion of MoO_3.

All intensities of characteristic diffraction peaks of pattern (c) are sharply decreased, and a new characteristic diffraction peak is identified in the 2θ range $38–40^\circ$. The new characteristic diffraction peak can be attributed to the Mo carbide according to literature [25]. This observation is in agreement with earlier proposals indicating that formation of Mo_2C as the actual active site occurs under reaction conditions.

3.6. Thermo-gravimetric analyses (TGA)

The carbonaceous deposition content and catalytic activity of various kinds of catalysts for non-oxidative aromatization of methane at 973 K after 6 h are reported in Table 3. The carbonaceous deposition content on CH catalyst reached 2.9%, and the catalytic activity of catalyst is significantly decreased, amounting to only 7.34%. The carbonaceous deposition on the MW catalysts is lower compared to CH catalyst, and the methane conversions still remain at 18.05 and 20.13% for 6% Mo/HZSM-5(MW) and 0.05Cu–6% Mo/HZSM-5(MW), respectively, after 6 h, where the catalytic performance of 0.05Cu–6% Mo/HZSM-5 catalyst (MW) is better. This implies that the metal Cu depress the carbonaceous deposition.

Fig. 6 shows the derivative thermo-gravimetric (DTG) profile of different catalysts. The content of carbonaceous deposition is equivalent to peak area between DTG = 0 and the corresponding DTG profile. The peak maximum of DTG profiles becomes higher with the increase of carbonaceous deposition content. The amount of carbonaceous deposition decreases in the order sample (1) > sample (2) > sample (3). It reveals that the catalyst prepared by microwave heating have stronger ability to prevent carbonaceous

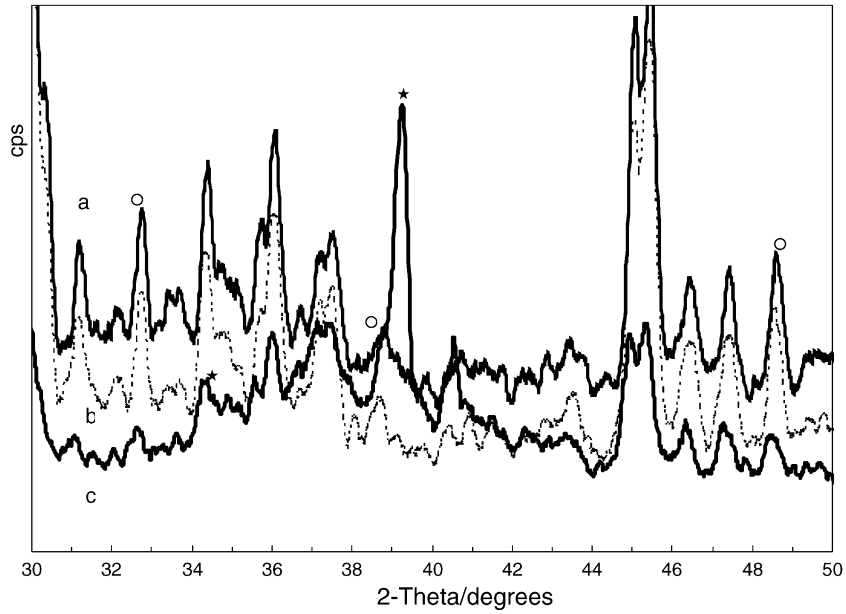

Fig. 5. XRD patterns of Mo catalysts (○) MoO_3 and (★) Mo_2C: (a) 0.05Cu–6% Mo/HZSM-5 catalyst (MW); (b) 6% Mo/HZSM-5 catalyst (MW); (c) used 6% Mo/HZSM-5 catalyst (MW).

deposition compared to that by conventional heating. The addition of Cu further prompts the stability of catalyst. At the same time, the peak maximum temperature of DTG profile for the MW catalysts is lower than that for CH catalyst, it indicates that the carbonaceous deposition on MW catalyst are mainly formed at low temperature, most of them are probably the active site and relatively easy to burn-off, whereas the carbonaceous deposition on the CH catalyst is difficult to eliminate completely even at high temperature. The TG analyses illustrate why the stability of MW catalysts are better than that of CH catalysts. Compared with the literature [26], the carbonaceous deposition of catalysts for non-oxidative aromatization of methane is different from that for the partial oxidation of methane. There are three different peaks in the DTG profiles of catalysts used for the partial oxidation of methane, but in the DTG profiles of catalysts used for the non-oxidative aromatization of methane, only one peak was observed, and the peak maximum temperature is relatively low. The results indicate that the nature of carbonaceous deposition on catalysts for these two reactions is different, probably caused by the dehydrogenation degree of carbonaceous deposition.

Table 3
The carbonaceous deposition and catalytic activity of different catalysts

Catalysts	Carbonaceous deposition fraction (wt.%)	The methane conversion after 6 h, X (%)
6% Mo/HZSM-5(CH)	2.90	7.34
6% Mo/HZSM-5(MW)	2.22	18.05
0.05Cu–6% Mo/HZSM-5(MW)	1.76	20.13

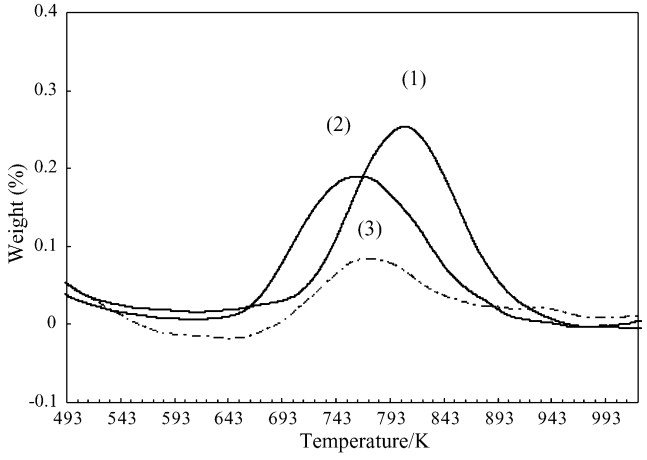

Fig. 6. DTG profile of different catalysts: (1) 6% Mo/HZSM-5(CH) catalyst, (2) 6% Mo/HZSM-5(MW), (3) 0.05Cu–6% Mo/HZSM-5(MW).

4. Conclusion

It could be shown that the preparation method plays a major role for the activity and selectivity of Mo-based catalysts for the non-oxidative aromatization of methane. The catalyst prepared by microwave heating method showed the outstanding benzene selectivity.

The activity of Mo/HZSM-5 catalysts in methane aromatization is related to Mo loading. Methane conversion reaches the maximum value when Mo loading of catalyst is 6%. The corresponding selectivity to benzene calculated on the basis of organic products in the gas phase exceeds 90%. The addition of Cu improves the lifetime of catalyst, gives

rise to a little increase in methane conversion. The best value of Cu/Mo molar ratio for this reaction is 0.05.

The results of BET, XRD and TEM analysis indicated that the Mo species are highly dispersed on the outer surface of carrier for the catalyst prepared by microwave heating method. The addition of Cu influenced the dispersion degree of MoO_3. The actual active phase Mo_2C can be found on the surface of used MW catalyst during reaction. The carbonaceous deposition occurred in the form of carbon nanotubes.

The analyses of TG and DTG profile revealed that the carbonaceous deposition on MW catalyst is obvious decreased and formed at lower temperature compared to that on CH catalyst. The addition of Cu further improved the catalytic stability. The carbonaceous deposition of catalysts for non-oxidative aromatization of methane is different from that for partial oxidation of methane. The former has only one type of carbonaceous deposition, but the latter has three types. The difference is caused by the dehydrogenation degree of carbonaceous deposition.

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