Methane dehydroaromatization over Mo-modified H-MFI for gas to liquid catalysts

Hirofumi Aritani[1,*], Hiromi Shibasaki[1], Hitoshi Orihara[1], Atsushi Nakahira[2]

1. Department of Applied Chemistry, Saitama Institute of Technology, Fukaya 369-0293, Japan. E-mail: aritani@sit.ac.jp
2. Graduate School of Engineering, Osaka Prefecture University, Sakai 599-8531, Japan

Abstract

For direct gas to liquid (GTL), a novel process producing energy sources for methane dehydroaromatization is needed. Supporting MoO_3 on H-MFI zeolite shows the high catalytic capacity and a selective activity for dehydroaromatization of methane to benzene at 973 K in a fixed bed reactor. On the other hand, deactivation by coke on the active sites in all the catalysts is formed during the reaction. H_2 co-feed suppressed the deactivation, which is probably due to the decrease in coking amount. Mo K-edge X-ray absorption fine structure (XAFS) results showed the formation of dispersed Mo_2C species with low crystallinity after dehydroaromatization. Mo L_{III}-edge XANES (X-ray absorption near-edge structure) indicated the formation of active Mo species including Mo_2C and Mo-oxycarbide ($MoOxCy$), where the redox state should be independent in the absence/presence of H_2. It is concluded that Mo-oxycarbide species act as highly active species, and their stability affected the durable activity in the presence of H_2.

Key words: direct gas to liquid; methane dehydroaromatization; Mo/H-MFI; L-XANES; K-XAFS

DOI: 10.1016/S1001-0742(08)62333-5

Introduction

Direct gas to liquid (GTL) process is being considered as a novel energy process. It is conventional and quite selective for liquefaction of natural gases containing methane as a major compound, and is highly and durably active catalysts. Since Wang *et al*. (1997a, 1997b) revealed the methane dehydroaromatization activity over MoO_3/H-MFI catalysts in the absence of oxygen, many research workers have focused on this catalyst system for an application of novel GTL process. Many researchers have revealed that the reduction of Mo^{6+} proceeds in the initial reaction step, and then Mo ions react with methane to form dispersed carbide species (Mériaudeau *et al*., 1999, 2000; Ma *et al*., 2000). It is thus accepted that active Mo species consist of reduced ions, mainly Mo^{2+} (with Mo-carbide and/or oxycarbide species) on H-MFI (Liu *et al*., 1999). However, catalytic deactivation cannot be avoided because carbon deposition and/or coating the dehydroaromatization products proceed on the catalyst surface during the reaction. The detail of the active Mo species on H-MFI and other silica-alumina supports has been unclear because it is hard to characterize the reduced Mo ions (mainly Mo^{2+}). On the other hand, molybdena catalysts supported on silica-alumina-based supports also show the dehydroaromatization activity. It is likely that the activity of methane conversion and its deactivation rate depend on the property of silica-alumina supports (George *et al*., 2000; Tan *et*

al., 2002). In fact, molybdena supported on amorphous silica-alumina also shows dehydroaromatization activity, while it is lower than that on H-MFI (Shu *et al*., 2000a, 2000b; Chen *et al*., 2001; Zhang *et al*., 1998). Therefore, the relation between silica-alumina support (with surface acidity) and active Mo species formed in the reaction is important to clarify the formation process of highly active Mo. In particular, the reduction of Mo ions on H-MFI is brought in contact with methane. Methane react with reduced Mo ions to form molybdenum carbide and/or oxycarbide species (Aritani *et al*., 2006) and their species can be active for methane dehydroaromatization. At the same time, deactivation proceeds by carbon deposition. Liu *et al*. (1999) revealed that hydrogen or carbon dioxide co-feed gives a significant effect on the suppression of coking. On the other hand, excess hydrogen may affect the reduction of Mo species during the reaction, and the decrease of active Mo-oxycarbide species may give a low reactivity. Thus, hydrogen with methane plays an important role in Mo species supporting on H-MFI zeolite.

This study investigated the factors effecting Mo/H-MFI activity. The effects of hydrogen co-feed on methane dehydroaromatization over Mo/H-MFI catalysts were also studied. Mo K-edge XAFS (X-ray absorption fine structure) (Aritani *et al*., 1996) and L_{III}-edge XANES (X-ray absorption near-edge structure) (Evans *et al*., 1991; Aritani *et al*., 2001) studies were introduced to characterize the active Mo species on H-MFI before/after the methane dehydroaromatization in the absence/presence of hydrogen.

* Corresponding author. E-mail: aritani@sit.ac.jp

1 Experimental

1.1 Preparation of catalysts

Mo/H-MFI catalysts were prepared by impregnating H-MFI support with ammonium heptamolybdate solution, and followed by drying overnight and calcination at 773 K for 3 h. H-MFI supports with various silica/alumina ratios (Si/Al_2) were synthesized hydrothermally. In brief, they were prepared by aluminum chloride, sodium silicate, and tetrapropylammonium-bromide (TPABr: as a template for H-MFI). The mixture was stirred for 3 h at ambient temperature to form a gel. The gel was treated hydrothermally at 443 K for 1 week in a stainless autoclave. After the hydrothermal synthesis, the product (Na-MFI) was dried overnight and Na^+ was removed using NH_4Cl solution. Then the product was dried and calcined at 873 K for 3 h. The procedure is shown in Scheme 1. In this article, only the results of MoO_3-modified H-MFI with Si/Al_2 = 40 are shown because of the high activity for methane dehydroaromatization.

1.2 Evaluation of catalytic activity

Catalytic reactivity was evaluated in a fixed bed flow reactor. Each catalyst (0.250 g) was placed in a quartz-tube reactor, and pretreated in He or He-CO flow (30 mL/min) at 973 K for 1 h. Then CH_4 (5%–20%)-H_2(0–3.0%)-He was fed into the reactor at 973 K. The total flow-rate was 30 mL/min (SV = 7.2 L/(g·h)). The products were analyzed by two online gas chromatographs: Shimadzu GC-3BF (with PEG-20M column) and GC-14B (with Gaskuropack-54 column). Methane conversion and benzene yield were obtained by means of C_1-based evaluation on apparent products in this study.
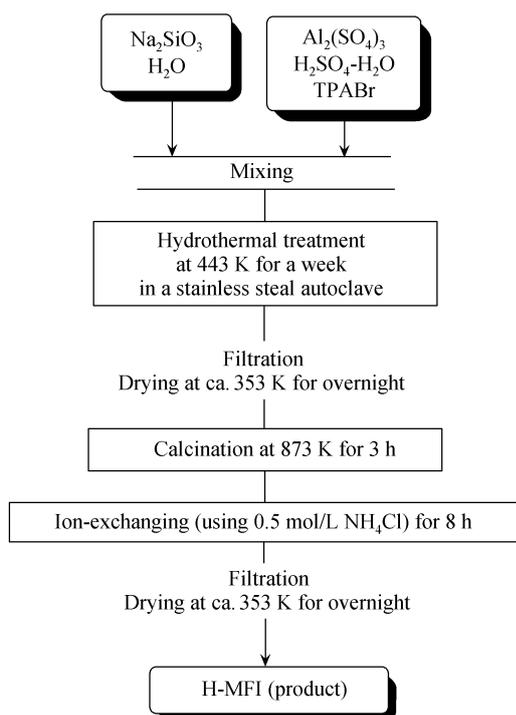
Scheme 1 Procedure of hydrothermal synthesis for the preparation of H-MFI zeolites.

1.3 Characterization of active species

Crystallinity of bulk phase on the whole catalysts before/after the catalytic reaction was evaluated by powdery X-ray diffraction (Rigaku, RINT2300). Mo L_{III}-edge XANES spectra were measured in BL1A of UVSOR-IMS (Okazaki, Japan) in a total-electron yield mode. Photon energy was calibrated using Mo metal-foil at Mo L_{III}-edge, and normalized XANES spectra. Their second derivatives are shown. Mo K-edge XAFS spectra were obtained in BL-7C of KEK-PF (Tsukuba, Japan) in a transmission mode. All XAFS measurements were carried out at room temperature. The analysis of XAFS was performed using REX2000 (Rigaku Co., Japan) program. Amount of coking products was evaluated by TG-DTA (Rigaku TG-8120).

2 Results and discussion

2.1 Catalytic activity

Molybdena supported on several acidic oxide supports are employed to evaluate the catalytic activity for methane dehydroaromatization. Typical results over supported MoO_3 (7.5 wt.%) catalysts are summarized in Table 1. CH_4 (5.0%)-He reactant gas was used at 973 K (as an easily reactive condition). Because deactivation can not be avoided in all catalysts, time on maximum C_6H_6 yield is also shown in Table 1. For molybdena-supported catalysts, H-MFI support shows a notable reactivity for methane dehydroaromatization. Because Mo/H-MFI is a typical catalyst, it may be accepted that dehydroaromatization activity is based on the Mo species and the acidic sites on H-MFI. However, Mo/H-BEA and Mo/silica-alumina catalysts also show an activity even in low benzene yield. This result suggests that acidic sites on H-MFI are not essential, and strong acidic sites are available for methane dehydroaromatization. In the case of Mo/H-MFI, strength and number on acidic sites depend on silica/alumina ratio in H-MFI contents. In addition, the acidic sites may affect the mobility and/or redox behavior of supported Mo species because they can easily be reduced in dehydroaromatization. Deactivation due to coking is likely to relate to the acidity on H-MFI. Table 2 shows the reactivity on Mo/H-MFI with various MoO_3 loading amounts and

Table 1 Reactivity of methane dehydroaromatization over molybdena (7.5 wt.% as MoO_3) catalysts supported on various acidic supports

Catalyst	Time of max. yield (min)	CH_4 conv. (%)	C_6H_6 yield (%)
MoO_3/H-MFI (Si/Al_2 = 1880)	70	1.5	1.3
MoO_3/H-MFI (Si/Al_2 = 90)	35	17.7	17.7
MoO_3/H-MFI (Si/Al_2 = 24)	–	0.0	0.0
MoO_3/H-BEA (Si/Al_2 = 25)	70	7.9	6.1
MoO_3/H-Y (Si/Al_2 = 5.0)	70	0.3	0.0
MoO_3/H-MOR (Si/Al_2 = 72)	70	0.3	0.0
MoO_3/Al_2O_3	–	0.0	0.0
MoO_3/SiO_2-Al_2O_3 (50 wt.%)	105	0.7	0.7
MoO_3/SiO_2-Al_2O_3 (24 wt.%)	140	1.4	1.4
MoO_3/SiO_2-Al_2O_3 (13 wt.%)	175	0.2	0.0
MoO_3/SiO_2-Al_2O_3 (7.0 wt.%)	–	0.0	0.0
MoO_3/SiO_2	–	0.0	0.0

Reactant: CH_4 (5.0%)-He, 30 mL/min.

Table 2   Reactivity of methane dehydroaromatization over Mo/H-MFI catalysts

| Catalyst	Time of max. yield (min)	CH_4 conv. (%)	C_6H_6 yield (%)
MoO_3/H-MFI ($Si/Al_2 = 40$)			
MoO_3 2.5 wt.%	35	7.4	7.3
MoO_3 5.0 wt.%	145	1.7	1.6
MoO_3 7.5 wt.%	250	0.2	0.2
MoO_3/H-MFI ($Si/Al_2 = 72$)			
MoO_3 2.5 wt.%	110	2.8	2.6
MoO_3 5.0 wt.%	215	4.0	3.4
MoO_3 7.5 wt.%	250	2.2	2.2
MoO_3/H-MFI ($Si/Al_2 = 90$)			
MoO_3 2.5 wt.%	110	4.4	4.2
MoO_3 5.0 wt.%	75	4.1	3.8
MoO_3 7.5 wt.%	215	0.8	0.6

Reactant: CH_4 (5.0%)-He, 30 mL/min.

silica/alumina (Si/Al_2) ratios in H-MFI, in which CH_4 (20%)-He reactant gas was used in the reaction at 973 K (as a hard condition). In brief, H-MFI supports with low Si/Al_2 ratios show vary high benzene selectivity and benzene yield. As shown in Fig. 1a, 2.5 wt.% Mo-loading on H-MFI ($Si/Al_2 = 40$) shows a maximum C_6H_6 yield without the addition of CH_4 (20%) reactant. But deactivation cannot be avoided during the reaction because coking carbon may adsorb on the active sites. For obtaining durable reactivity, co-feed gas with CH_4 is added to the reactant. H_2 (1%) co-feed with CH_4 gave low deactivation, indicating the suppression of coking (Fig. 2b). But excess H_2 (more than 1.5%) co-feed gives low activity. It can be suggested that H_2 co-feed affect the suppression of coking for long time reaction, while low reactivity is also given. Thus, the effect of H_2 co-feed is not only based on the coked carbon hydrogenation of catalyst but also on reducing effect. If reductive treatment affects Mo-H-MFI during the reaction, excess reduction of Mo species and/or reconstruction of H-MFI structure is possible. Therefore, the characterization of Mo/H-MFI catalysts was investigated as described in the following sections.

2.2 Characterization of active species

In Fig. 2, the results of XRD patterns over Mo/H-MFI (2.5 wt.% as MoO_3, $Si/Al_2 = 40$ in H-MFI, a highly active catalyst) before/after the reaction indicate a stable H-MFI
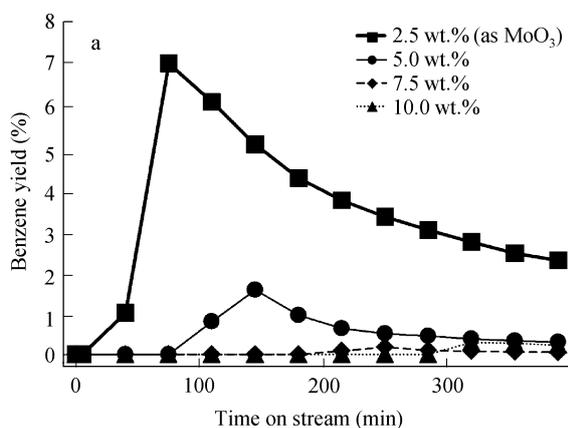
crystallinity and well-dispersed Mo species. It indicates that the decrease of H-MFI crystallinity or aggregation of Mo species has not been occurred during the methane dehydroaromatization. In particular, any phase due to Mo ions is invisible before/after the reaction, which result the well dispersed Mo species formed even after the reaction.

Mo K-edge XANES (Fig. 3) and Fourier-transformed EXAFS (FT-EXAFS; Fig. 4) of MoO_3/H-MFI before/after the dehydroaromatization reaction with methane are shown. XANES shows the reduced state of Mo ions. Mo-carbide (Mo^{2+}) species are formed on H-MFI. The energy of absorption edge (Fig. 3) of Mo/MFI in $Si/Al_2 = 40$ is quite smaller than that before reaction, indicating the reduction of Mo species. However, the edge energy values in Mo species after CH_4 or CH_4-H_2 reaction are larger than that in Mo_2C. This result indicates the existence of more oxidized species than Mo_2C (Mo^{2+}), suggesting the co-existence of carbide (in major) and oxide species (as
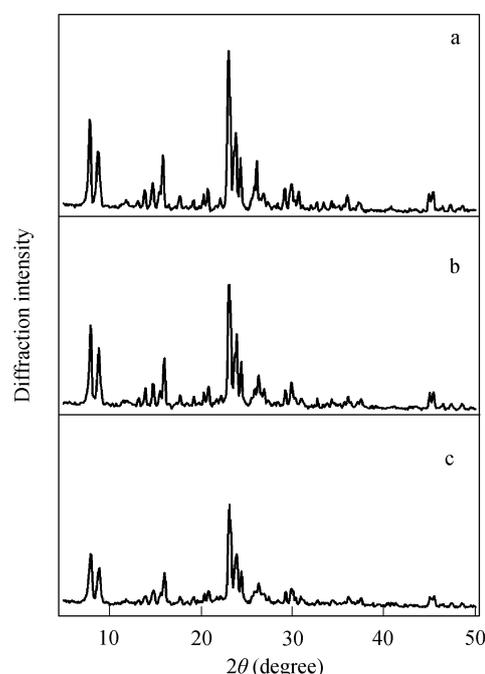

Fig. 2   XRD patterns of MoO_3 (2.5 wt.%)/H-MFI ($Si/Al_2 = 40$). (a) before reaction; (b) after reaction with CH_4 (20%)-He; (c) after reaction with CH_4 (20%)-H_2 (1.0%)-He.
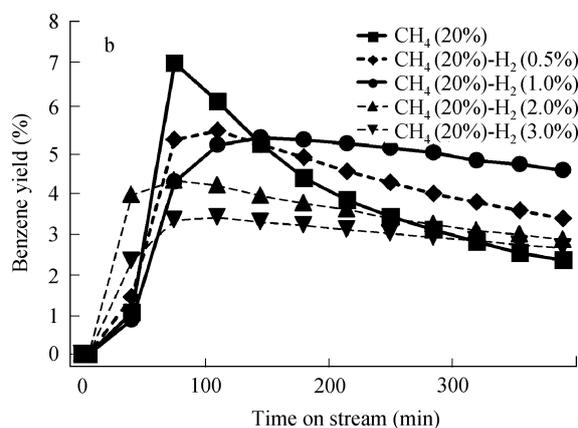

Fig. 1   Time course of CH_4 dehydroaromatization over MoO_3/H-MFI ($Si/Al_2 = 40$) with various Mo contents (a), and over 2.5 wt.% MoO_3/H-MFI ($Si/Al_2 = 40$) in the presence of H_2 (b).
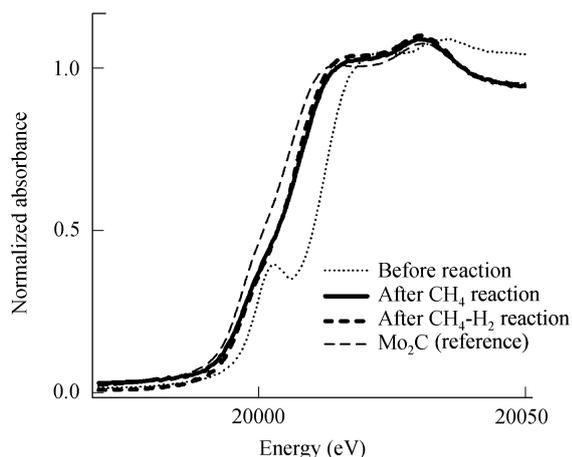
Fig. 3 Mo K-edge XANES of MoO$_3$ (2.5 wt.%)/H-MFI (Si/Al$_2$ = 40) catalysts before/after methane dehydroaromatization.

a minor one). Through FT-EXAFS analyses the details of Mo species are shown in Fig. 4. For FT-EXAFS, both Mo-O/Mo-C and Mo-Mo peaks are visible after the reaction with CH$_4$ or CH$_4$-H$_2$. The Mo-Mo peaks are not due to metallic Mo but Mo-(C)-Mo in Mo-carbide after the both reactions. These results suggest that coking was suppressed at the same time with H$_2$ co-feed without excessive reduction of Mo ions. The FT peak at ca. 2.7 Å

due to Mo-C scattering is clearly be seen in all Mo/H-MFI samples. In the case of Si/Al$_2$ = 90, the Mo-C peak with large intensity is appeared while it is smaller than bulk Mo$_2$C. In addition, a peak at 1.2 Å with small intensity (due to Mo-O) can also be seen. These results strongly suggest the formation of carbide microparticles which is partly oxidized. Thus, "oxycarbide" species is present onto well-dispersed Mo$_2$C on H-MFI as a highly active Mo species.

The suggestion described below is supported by the results obtained by Mo L$_{III}$-edge XANES. Figure 5 shows the L$_{III}$-edge XANES spectra and their second derivatives over MoO$_3$ (2.5 wt.%)/H-MFI catalysts before/after the reaction. The assignment of L$_{III}$-edge XANES is described previously (Aritani *et al.*, 2001). In brief, L$_{III}$-XANES spectra exhibit the coexistence of Mo^{2+} and oxidized ions after the reaction with CH$_4$ or CH$_4$-H$_2$ (1%). If excess reduction is given, a minimum peak at 2524 eV, which is due to metallic Mo, should be shown in second derivative spectra. However, the peak is absent after all the pretreatments and reactions. Thus, their spectra indicate the formation of active Mo species which consists of Mo-oxycarbide (MoO$_x$C$_y$), whose redox state is independent in the absence/presence of H$_2$. It is concluded that Mo oxycarbide species act as highly active ones, and their stability affect the durable activity.
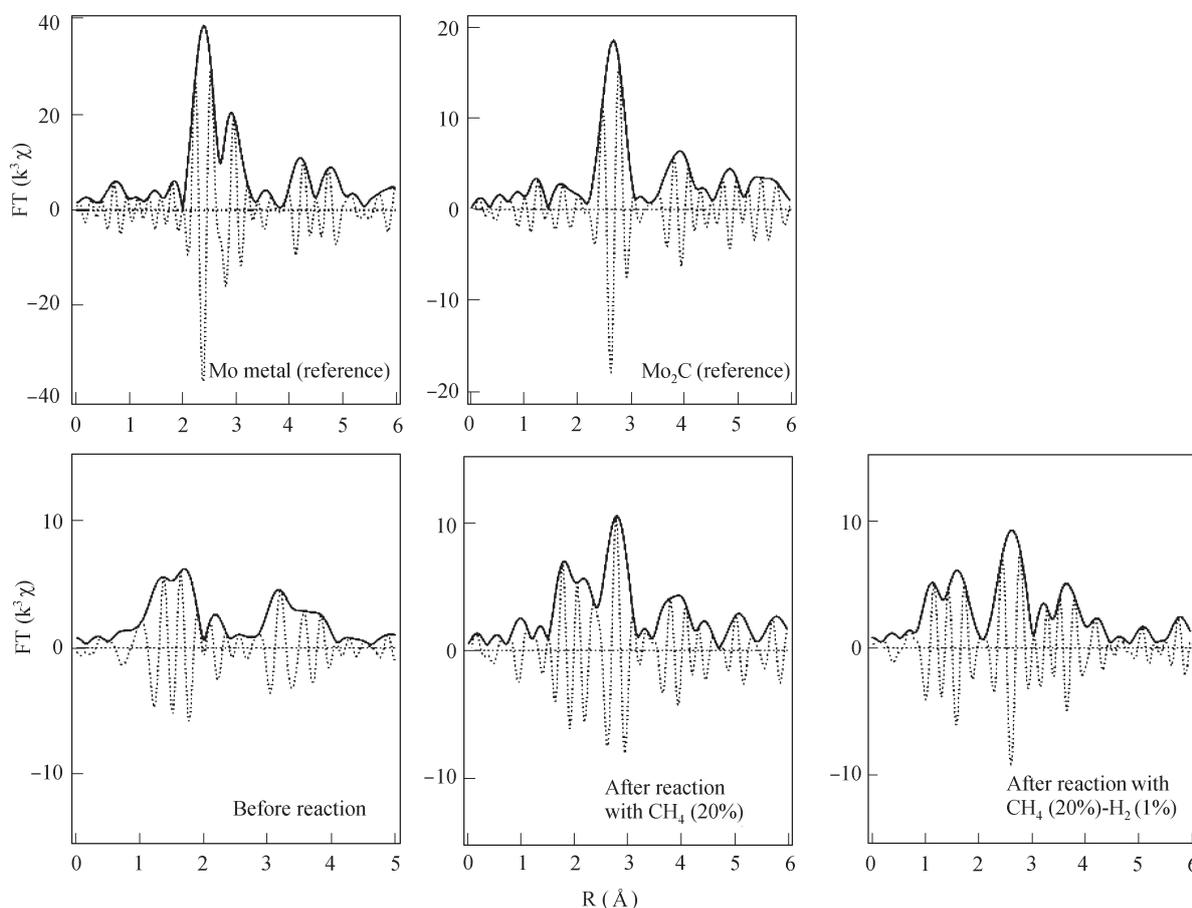

Fig. 4 k^3-weighted FT-EXAFS (at Mo K-edge) of Mo metal, Mo$_2$C (as references), and MoO$_3$ (2.5 wt.%)/H-MFI before/after methane dehydroaromatization in the absence/presence of H$_2$.
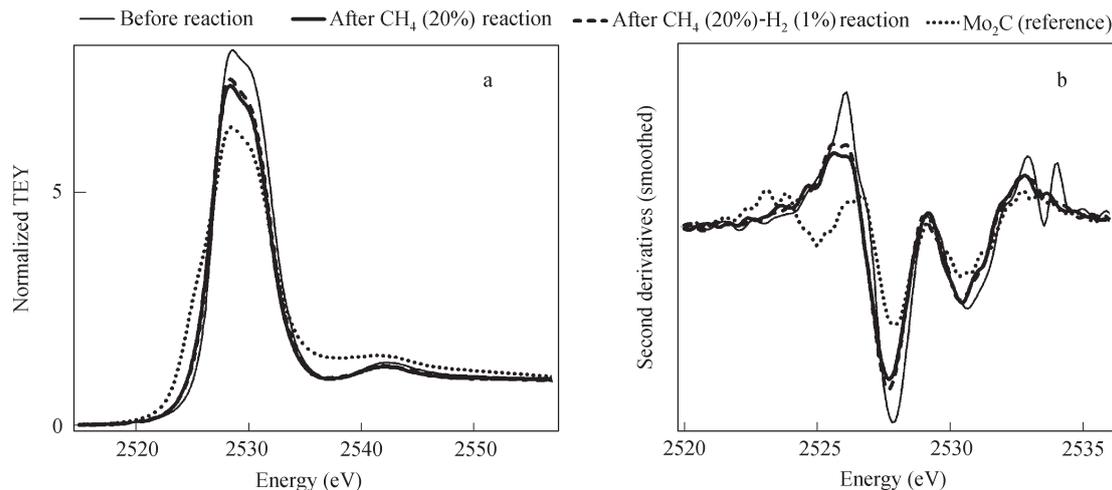
Fig. 5 Mo L$_{III}$-edge XANES spectra (a) and their second derivatives (b) of MoO$_3$(2.5 wt%)/H-MFI (Si/Al$_2$ = 40) catalysts before/after methane dehydroaromatization. The spectrum of Mo$_2$C (as a reference) also contains in the figure.

3 Conclusions

Mo/H-MFI shows catalytically high and selective activity for the dehydroaromatization of methane to benzene at 973 K in a fixed bed reactor. The deactivation is definitely during the reaction because of coking on the active sites in all catalysts. H$_2$ co-feed shows an effect on suppressing the deactivation, which is due to the decrease of coking amount. Mo K-edge XAFS results show the formation of dispersed Mo$_2$C species with low crystallinity after dehydroaromatization. Mo L$_{III}$-edge XANES indicate the formation of active Mo species which consists of Mo$_2$C and Mo-oxycarbide (MoO$_x$C$_y$), whose redox state is independent in the absence/presence of H$_2$. It is concluded that Mo-oxycarbide species act as highly active species, and their stability affect the durable activity in the presence of H$_2$.

References

Aritani H, Shinohara S, Koyama S, Otsuki K, Kubo T, Nakahira A, 2006. Mo L$_{III}$-edge XANES study of catalytically active Mo species on silica-alumina supports for methane dehydroaromatization. *Chemistry Letters*, 35: 416–417.

Aritani H, Tanaka T, Funabiki T, Yoshida S, Eda K, Sotani N *et al*., 1996. Study of the local structure of molybdenum-magnesium binary oxides by means of Mo L3-edge XANES and UV-Vis spectroscopy.

Journal of Physical Chemistry, 100(50): 19495–19501.

Aritani H, Fukuda O, Miyaji A, Hasegawa S, 2001. Structural change of molybdenum on silica-alumina in contact with propene studied by ESR and Mo L$_{III}$-edge XANES. *Applied Surface Scienc*, 80: 261–269.

Chen K, Xie S, Bell A T, Iglesia E, 2001. Structure and properties of oxidative dehydrogenation catalysts based on MoO$_3$/Al$_2$O$_3$. *Journal of Catalysis*, 198: 232–242.

Evans J, Frederick W, Mosselmans W, 1991. L-edge studies on molybdenum. *Journal of Physical Chemistry*, 95: 9673–9676.

George W L, Meitzner D, Borry III R W, Iglesia E, 2000. Raman and X-ray absorption studies of Mo species in Mo/H-ZSM5 catalysts for non-oxidative CH$_4$ reactions. *Journal of Catalysis*, 191: 373–383.

Liu S, Wang L, Ohnishi R, Ichikawa M, 1999. Bifunctional catalysis of Mo/HZSM-5 in the dehydroaromatization of methane to benzene and naphthalene XAFS/TG/DTA/ MASS/FTIR characterization and supporting effects. *Journal of Catalysis*, 181: 175–188.

Ma D, Shu Y Y, Cheng M, Xu Y D, Bao X H, 2000. On the induction period of methane aromatization over Mo-based catalysts. *Journal of Catalysis*, 194: 105–114.

Mériaudeau P, van Tiep L, Ha V T T, Naccache C, Szabo G, 1999. Aromatization of methane over Mo/H-ZSM-5 catalyst: on the possible reaction intermediates. *Journal of Moecular Catalysis A*, 144: 469–471.

Mériaudeau P, Ha V T T, Tiep L V, 2000. Methane aromatization over Mo/H-ZSM-5:on the reaction pathway. *Catalysis Letters*, 64: 49–51.

Shu Y Y, Ma D, Xu L Y, Xu Y D, Bao X H, 2000. Methane dehydroaromatization over Mo/MCM-22 catalysts: a highly selective catalyst for the formation of benzene. *Catalysis Letters*, 70: 67–73.

Shu Y, Ma D, Bao X H, Xu Y D, 2000. Methane dehydro-aromatization over a Mo/phosphoric rare earth-containing penta-sil type zeolite in the absence of oxygen. *Catalysis Letters*, 66: 161–167.

Tan P L, Leung Y L, Lai S Y, Au C T, 2002. Methane aromatization over 2 wt.% Mo/HZSM-5 in the presence of O$_2$ and NO. *Catalysis Letters*, 78: 251–258.

Wang D, Lunsford J H, Rosynek M P, 1997. Characterization of a Mo/ZSM-5 catalyst for the conversion of methane to benzene. *Journal of Catalysis*, 169: 347–358.

Wang L, Xu Y, Wong S T, Cui W, Guo X, 1997. Activity and stability enhancement of Mo/HZSM-5-based catalysts for methane non-oxidative transformation to aromatics and C2 hydrocarbons: Effect of additives and pretreatment conditions. *Applied Cataysis. A*, 152: 173–182.

Zhang C L, Li S, Yuan Y, Zhang W X, Wu T H, Lin A L W, 1998. Aromatization of methane in the absence of oxygen over Mo-based catalysts supported on different types of zeolites. *Catalysis Letters*, 56: 207–213.