

## Mo K-Edge XAFS Study of Active Mo-Carbide Species on H-MFI for Dehydroaromatization

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### Introduction

Many workers have focused on this catalyst system as a novel GTL (Gas-to-Liquid) process from natural gas to petroleum products. They have been revealed that reduction of Mo<sup>6+</sup> ions is brought about in contact with methane in the initial step, and then Mo ions react methane to form carbide species, Mo<sub>2</sub>C, in the next step.<sup>1</sup> It is thus accepted that active Mo species consist of reduced ions, Mo<sup>2+</sup>, with Mo-carbide and/or oxycarbide species on H-MFI. However, deactivation cannot be avoided by carbon deposition on the catalyst surface at the same time. As a responsible Mo species,  $\alpha$ -Mo<sub>2</sub>C (fcc),  $\beta$ -Mo<sub>2</sub>C (hcp), and/or oxycarbide-type species have been proposed. However, detail of the active Mo species on both H-MFI and other silica-alumina supports has been still unclear because of difficulty of reduced Mo ions (Mo<sup>2+</sup>). By XRD, crystallized species can only be seen. XPS analysis is difficult because of reduction during the measurement. Mo K-edge XAFS is very sensitive to reflect the redox behavior of Mo ions between before and after the reaction with methane. In particular, it is important to evaluate the formation of active Mo sites with reduced ions in Mo-carbide and/or oxycarbide species. We characterized Mo species on H-MFI with several SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios before/after the dehydroaromatization of methane (at 973 K for 3 hours) by Mo K-edge XAFS.

### Experimental

Supported molybdena catalysts were prepared by impregnation of each support with an aqueous solution of ammonium heptamolybdate. The supports described in this report were H-MFI with various SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios synthesized by hydrothermal synthesis (at 413 K for 7 days) and followed by calcination (at 873 K) and ion-exchanging by using 0.5 N NH<sub>4</sub>Cl. The impregnate solution of ammonium heptamolybdate was stirred at room temperature and evaporated at 343 K for 6 hours, and then, the paste was dried for overnight and calcined at 773 K for 6 hours. Mo K-edge XAFS spectra were measured at BL-10B of KEK-PF in a transmission mode at room temperature. FT-EXAFS results were obtained by FT of normalized EXAFS (*k*<sup>3</sup>-weighted) spectra in the range of  $\Delta k = 3.5 - 14.5 \text{ \AA}^{-1}$ .

### Results and discussion

Mo K-edge XANES (Fig. 1) and FT-EXAFS (Fig. 2) of MoO<sub>3</sub>/H-MFI before/after the dehydroaromatization

reaction with methane are shown. Maximum activity for benzene production is shown in Mo/H-MFI in Si/Al<sub>2</sub>=90. The XANES shows the reduced state of Mo ions; Mo-carbide (Mo<sup>2+</sup>) species are formed on H-MFI. The energy of absorption edge (in Fig. 1) of Mo/MFI in Si/Al<sub>2</sub>=90 is quite similar than that of Mo<sub>2</sub>C, indicating a formation of carbide species dominantly. It is suggested that H-MFI support in high Si/Al<sub>2</sub> ratio shows the co-existence of carbide (in major) and oxide species. In Fig. 2, the FT peak at ca. 2.7 Å

due to Mo-C scattering is clearly seen in all the Mo/H-MFI samples. In case of Si/Al<sub>2</sub>=90, the Mo-C peak with large intensity is appeared while it is smaller than bulk Mo<sub>2</sub>C. In addition, a peak at 1.2 Å with small intensity (due to Mo-O) can also be seen. These results strongly suggest a formation of carbide micromarticles which is partly oxidized. Thus, so-called oxycarbide species is present onto well-dispersed Mo<sub>2</sub>C on H-MFI. This suggestion is supported by the results obtained by Mo L<sub>III</sub>-edge XANES.<sup>3</sup> Detail of the characterization of active Mo species is now in progress.

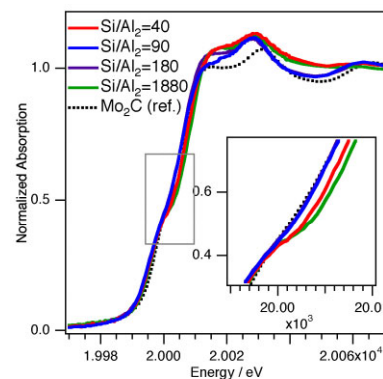


Fig. 1 Mo K-edge XANES of Mo/H-MFI with various Si/Al<sub>2</sub> ratios after methane dehydroaromatization at 973 K.

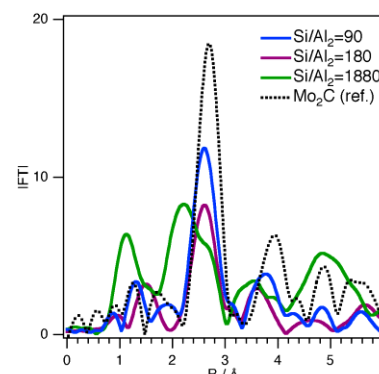


Fig. 2 FT-EXAFS of Mo/H-MFI with various Si/Al<sub>2</sub> ratios after methane dehydroaromatization at 973 K.

### References

- [1] D. Ma, Y. Shu, M. Cheng, Y. Xu, and X. Bao, *J. Catal.* 194, 105 (2000).
- [2] W. L. George, D. Meitzner, R. W. Borry III, and E. Iglesia, *J. Catal.* 191, 373 (2000).
- [3] H. Aritani, S. Shinohara, S. Koyama, K. Otsuki, T. Kubo, A. Nakahira, *Chem. Lett.*, 35 (2006) 416-417.

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