

## ***In situ* XAFS study on molybdenum oxide catalysts supported on zirconia by molten salt preparation**

Nobuyuki MATSUBAYASHI\*<sup>1</sup>, Motoyasu IMAMURA<sup>1</sup>, Koichi SATO<sup>1</sup>, Tomoaki TANAKA<sup>1</sup>, Kyoko K. BANDO<sup>1</sup>, Hiromichi SHIMADA<sup>1</sup> Pavel AFANASIEV<sup>2</sup> and Christophe GEANTET<sup>2</sup>

<sup>1</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan

<sup>2</sup>Institut de Recherches sur la Catalyse, 2 avenue Albert Einstein, 69626 Villeurbanne cedex, France

### **Introduction**

Catalyst preparation by the molten salt method has been shown to produce novel catalysts with high surface areas. In the preparation of molybdenum catalysts, the structures and the reaction mechanisms of the intermediates were not yet clarified. Because these intermediates do not have long-range ordered structures, we applied XAFS to the structural analyses involving composition determination of molybdate species in mixed  $\text{KNO}_3$  and  $\text{NaNO}_3$  salt [1]. In the previous study, we have clarified the changes in the composition of molybdate species during the catalyst preparation procedures [2].

In the present report, the reaction behavior of the preparation of unsupported molybdate catalysts in molten nitrate was investigated by *in situ* EXAFS. For this purpose, XAFS measurements were done using an *in situ* cell at various temperatures between 298 and 773 K.

### **Experimental**

Unsupported molybdate catalysts were prepared from a  $\text{MoO}_3$  precursor (5mg) with 150mg of  $\text{NaNO}_3$  in a quartz reactor. The amount of molten nitrate corresponds to a 10-20 fold molar excess. The mixture was heated up to 773K being kept for 1h stepwise by 50 K during a XAFS measurement as Fig.1. The Mo K-edge XAFS measurements were performed at the Photon Factory (BL10B) using a Si(311) channel-cut crystal monochromator. Fourier transformation was performed for  $\Delta k=80 \text{ nm}^{-1}$  of Mo K-edge EXAFS. The phase shift and backscattering amplitude factor were corrected by using the calculated values of FEFF8 for Mo as an absorber and O as a scatterer in crystalline  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ .

### **Results and discussion**

Figure 1 shows XANES spectra. of Mo K-edge of  $\text{MoO}_3/\text{NaNO}_3$  at 298 – 773 K plotted vs. time. A disorder of the spectra was found at melting point. The edge shape was changed from that of  $\text{MoO}_3$  to that of  $\text{MoO}_4^{2-}$  at the melting point indicating the change of dominant species.

Figure 2 shows the Fourier transforms of Mo K-edge EXAFS of  $\text{MoO}_3/\text{NaNO}_3$  measured at 298-773K. The peak at 0.36 nm is assigned to Mo-Mo scattering of the  $\text{MoO}_3$  structure. This indicates that the local structure of  $\text{MoO}_3$  precursor remains intact before melting. With increasing temperature, the intensities of the peaks at 0.36 nm decrease, whereas the intensities of the peaks at 0.18 nm corresponding to Mo-O scattering in the highly symmetrical tetragonal  $\text{MoO}_4^{2-}$  structure increase. These

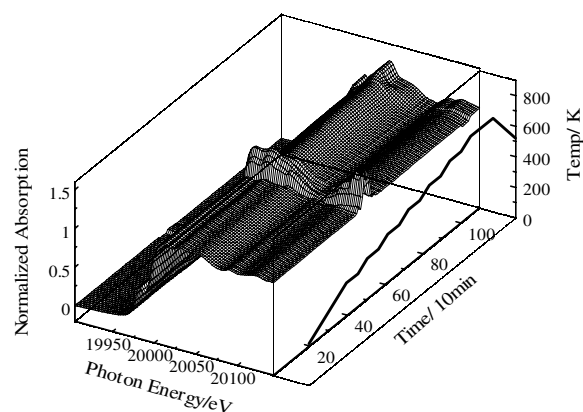


Fig.1 *in situ* XANES spectra. of Mo K-edge of  $\text{MoO}_3/\text{NaNO}_3$  at 298 – 773 K.

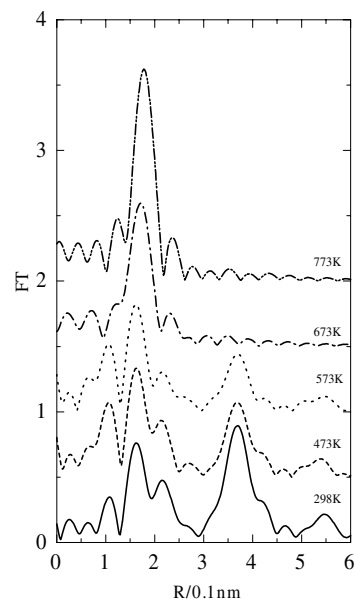


Fig.2 Fourier transforms of Mo K-edge EXAFS of  $\text{MoO}_3/\text{NaNO}_3$  measured at 298-773K.

results show that the  $\text{MoO}_3$  precursor transforms into  $\text{MoO}_4^{2-}$  with increasing temperature.

### **References**

- [1] N. Matsubayashi *et al.*, J. Phys IV France, **7(2)**, 1179 (1997).
- [2] N. Matsubayashi *et al.*, *Journal of Synchrotron Radiation*, **8**, 610 (2001).

\* n-matsubayashi@aist.go.jp