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XAFS Study on the Local Structure of Mo in Molten Nitrates

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Abstract. The local structure of Mo compounds in the intermediate states of the synthesis in molten nitrates media has been studied by the XAFS method. The XAFS results showed that the local structure around Mo changes from distorted octahedral form of MoO_3 to tetragonal form of MoO_4^{2-} via an intermediate phase during the reaction. It has been shown that the intermediate species of Mo oxide exist as a mixture of polymolybdate such as $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_4\text{O}_{13}^{2-}$.

1. INTRODUCTION

Molten nitrates provide an original chemistry and offer new opportunities for the preparation and synthesis of materials[1]. Reaction of MoO_3 in molten nitrates was studied previously[2]. MoO_3 dissolves in the bath and finally MoO_4^{2-} monomers are stabilized but intermediate species are known to be formed. However, the mechanism of stabilization of oxoanions remains unknown. For this purpose, we have studied samples of Mo precursors in nitrate melts quenched at different temperatures by EXAFS.

2. EXPERIMENTAL CONDITIONS

Samples have been prepared from MoO_3 precursor in a 10-fold molar excess of molten nitrates (50wt% KNO_3 and 50 wt% NaNO_3 mixture). The mixture was pre-heated at 150 °C for 2 h under a flow of dry nitrogen to remove water and then the temperature was raised and quenched at various temperatures from 300 to 550 °C.

EXAFS measurements at Mo K-edge (20keV) have been performed at room temperature at the ESRF on CRG-IF beam-line using a $\text{Si}(3\ 1\ 1)$ double crystals monochromator. The ESRF ring was operated with a current of 130-90 mA of 1/3-fill mode at the electron acceleration of 6 GeV. The intensity of the incident x-ray (I_0) and transmitted x-ray (I) were measured by monitoring of scattering x-ray from a Kapton film (thickness: 125 μm for I_0 , 250 μm for I) using silicon photodiodes. MoO_3 , $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were measured as references.

3. RESULTS and DISCUSSIONS

Figure 1 shows Fourier transforms of $k^3X(k)$ of Mo K-edge for samples quenched at various temperatures. The range of $k=3$ to 17 \AA^{-1} were transformed with a Hamming window function at 10 % of the part of the data on both sides. The distance R is shorter by about 0.3 \AA than real distance due to the phase shift in scattering of electron. Peaks at 3.2 and 3.7 \AA in the Fourier transform at 300 °C which are similar to those of MoO_3 indicate that the MoO_3 precursor still remains and the intensity of

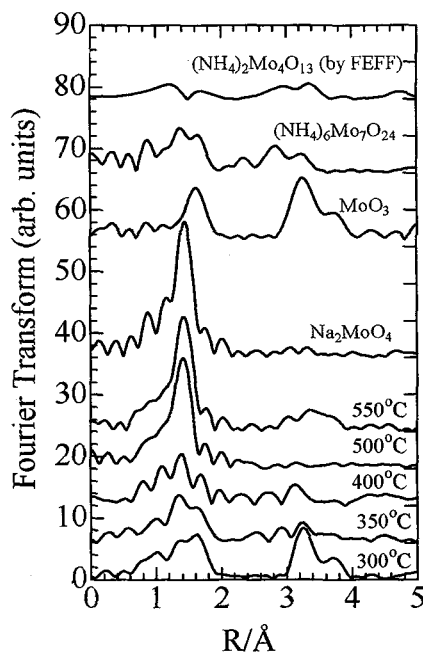


Fig.1 Fourier transforms of Mo K-edge EXAFS for samples obtained from Mo precursors by quenching at various temperatures.

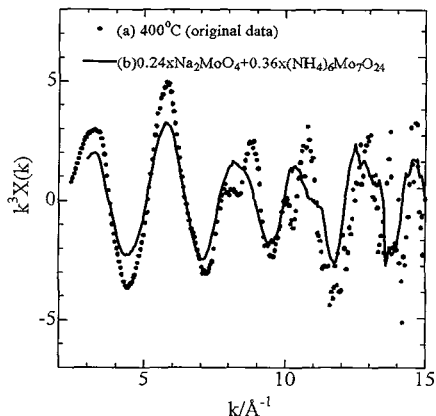


Fig.2. Fitting of EXAFS data in k -space using reference data.

the peaks decrease with increasing temperature. A large peak of 1.4 Å which appears at 500 and 550 °C is corresponding to a high symmetry of tetragonal in MoO_4^{2-} . These results show that MoO_3 precursor transforms into MoO_4^{2-} in progressing reaction. The Fourier transforms at 350 and 400 °C resemble to the spectra of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$.

To discuss quantitatively the $X(k)$ data of these samples were decomposed to those of references by fitting in the range of $k=3$ to 15 \AA^{-1} as shown in Fig.2. The fitting was performed under non-negative constraints for components. The Fourier transforms of residual $X(k)$ after subtraction of contribution from references were compared to those of simulation $X(k)$ for various Mo oxides by FEFF[3]. $\text{Mo}_4\text{O}_{13}^{2-}$ were found to be one of the intermediate species. Adding simulation $X(k)$ of $\text{Mo}_4\text{O}_{13}^{2-}$ the fitting was carried out again.

Figure 3 shows composition of Mo species in the samples quenched at various temperatures obtained from EXAFS data by fitting using experimental data of reference samples and simulated data of $\text{Mo}_4\text{O}_{13}^{2-}$ by FEFF. The concentration of MoO_3 species decreases with increasing temperature and vanishes at 400 °C. Presence of intermediate oxides such as $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_4\text{O}_{13}^{2-}$ is maximum at 350 °C and are transformed to MoO_4^{2-} with increasing temperature. MoO_4^{2-} is the dominant species at 500 and 550 °C. However, at 550 °C the presence of other species than the references can be emphasized.

Figure 4 shows Fourier transform of residual $k^3X(k)$ after subtraction of the fitting result for Mo K-edge EXAFS of the sample at 550 °C. Figure 4 corresponds to Fourier transform for the other Mo species than the references used. The peak of 3.6 Å at 550 °C is relatively long as usual Mo-Mo in Mo oxides. It suggests that another Mo species may be formed at 550 °C.

References

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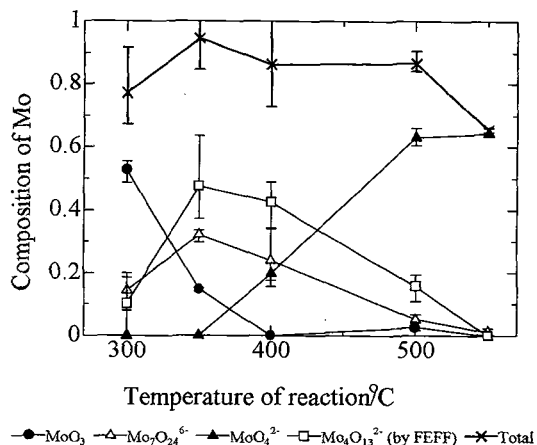


Fig.3 Composition of Mo species in samples obtained from Mo precursors by quenching at various temperatures obtained from EXAFS data by fitting using reference data.

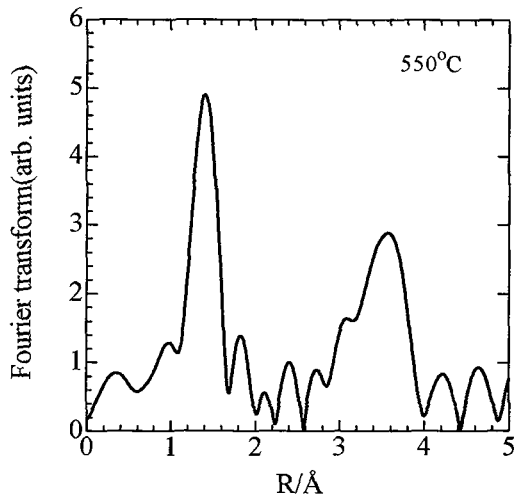


Fig.4 Fourier transform of residual $k^3X(k)$ after subtraction of the fitting result for Mo K-edge EXAFS of the sample at 550 °C.