Multi-component fitting XAFS analysis of molybdate species during catalyst preparation by the molten salt method

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The goal of the present study was to elucidate the formation mechanisms of highly dispersed catalysts by the molten salt method. For this purpose, multi-component fitting Mo K-edge EXAFS analysis was applied to the structure of molybdate catalysts prepared in KNO_3 and $NaNO_3$. The analysis revealed that MoO_3 dissolved in molten salts was at first transformed into polymolybdate anions and finally into MoO_4^{2-} anions. The transformation into MoO_4^{2-} anions took place at a lower temperature when $NaNO_3$ was used as molten salt than KNO_3. In contrast, polymolybdate anions were stable even at higher temperature when ZrO_2 was added as a support of molybdate.

XAFS, Molten Salt, Molybdenum catalysts, Zirconia support

1. Introduction

Catalyst preparation by the molten salt method has been shown to produce novel catalysts with high surface areas (Hamon *et al.*, 1991). The chemical reactions in the molten salts are quite different from those in aqueous solutions and are not yet well understood. In the preparation of molybdenum catalysts, MoO_3 is at first dissolved in the molten nitrate and subsequently transforms into some intermediates before completely changing to MoO_4^{2-} anions (Afanasiev *et al.*, 1995, Afanasiev, 1997, Afanasiev & Geantet, 1998). Although the intermediates play an important role in the formation of the final catalyst, 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 KNO_3 and $NaNO_3$ salt (Matsubayashi *et al.*, 1997).

In the present paper, the effect of the molten salt cation, K or Na, on the reaction behaviour of unsupported molybdate catalysts was investigated. In addition, we dealt with ZrO_2 supported molybdate catalysts that were found to give a high dispersion of molybdate (Afanasiev & Geantet, 1995). For this purpose, XAFS measurements were done on the quenched intermediate samples prepared at various temperatures between 573 and 773 K from either potassium salt or sodium salt. Because many kinds of molybdate anion species coexist during the preparation procedure, XAFS spectra cannot be analyzed by conventional parameter fitting analysis. Therefore, we introduced multi-component fitting analysis using experimentally obtained XAFS data of reference samples. The analysis results clarified the changes in the composition of molybdate species during the catalyst preparation procedures.

2. Experimental

Unsupported molybdate catalysts were prepared from a MoO_3 precursor (0.28 g) with 2 g of molten nitrate (KNO_3 or $NaNO_3$) in a Pyrex glass reactor in a flow of nitrogen. For the preparation of ZrO_2 supported MoO_3 catalysts, MoO_3 (0.15 g) and $ZrOCl_2.8H_2O$ (1 g) were mixed with 3 g of KNO_3 or $NaNO_3$. The amount of molten nitrate corresponds to a 10-20 fold molar excess. The mixture was then heated at 423 K to avoid extreme evaporation of water upon melting of the salt. XAFS samples were obtained by heating the above mixture at various temperatures from 573 to 773 K for 4 hours, followed by quenching. Each sample was pressed into a pellet and kept under inert atmosphere to avoid possible reactions with moisture.

The Mo K-edge XAFS measurements were performed at the Photon Factory (BL10B) (KEK-PF, Tsukuba, Japan) using a Si(311) channel-cut crystal monochromator at room temperature. Fourier transformation was performed for Δk=140 nm^{-1} ($30 < k < 170$ nm^{-1}) of Mo K-edge EXAFS data with a Hamming window function ($W(k)=0.54+0.46\cos((k-k_s)\pi/(k_e-k_s))$) at 10 % of the data on both sides. The phase shift and backscattering amplitude factor were corrected by using the calculated values of FEFF8 (Ankudinov *et al.*, 1998) for Mo as an absorber and O as a scatterer in crystalline $Na_2MoO_4\ 2H_2O$ (Matsumoto *et al.*, 1975).

Multi-component fitting of spectra was done using experimental data of reference samples under non-negative constraint conditions. In particular, the k^3 weighted measured spectra were compared with synthesized spectra of reference spectra in k-space (k=30-170 nm^{-1}) using the chemical composition as the parameter. MoO_3, $Na_2MoO_4.2H_2O$, K_2MoO_4, $K_2Mo_2O_7$ and $Na_2Mo_2O_7$ were chosen as the references.

3. Results and Discussion

3.1 Unsupported molybdate catalyst

Figure 1 shows Fourier transforms of $(k/f(k))\chi(k)$ of Mo K-edge of molybdate catalysts. The peak at 0.36 nm in both of the Fourier transforms of the catalysts quenched at 573 K is assigned

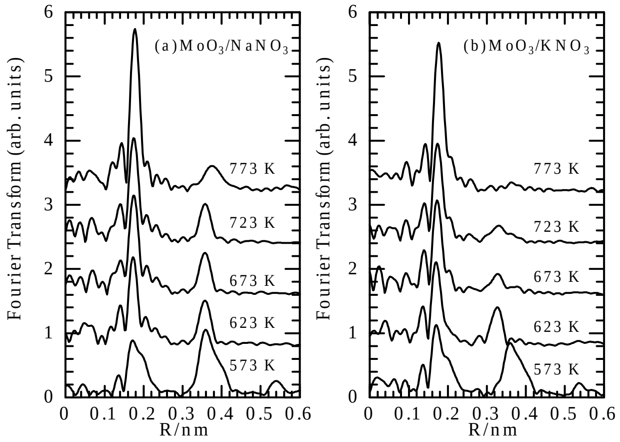

Figure 1
Fourier transforms of (k/f(k))X(k) of the Mo K-edge for (a) $MoO_3/NaNO_3$ and (b)MoO_3/KNO_3 quenched at various temperatures (573-773 K).

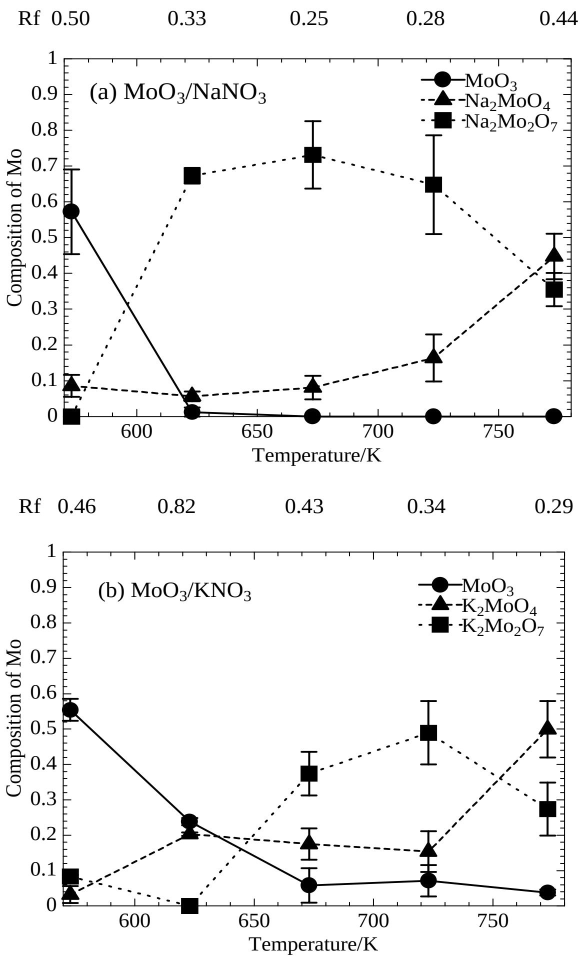

Figure 2

The composition obtained by the fitting for the Mo K edge EXAFS of (a) $MoO_3/NaNO_3$ and (b)MoO_3/KNO_3 quenched at 573 - 773K.

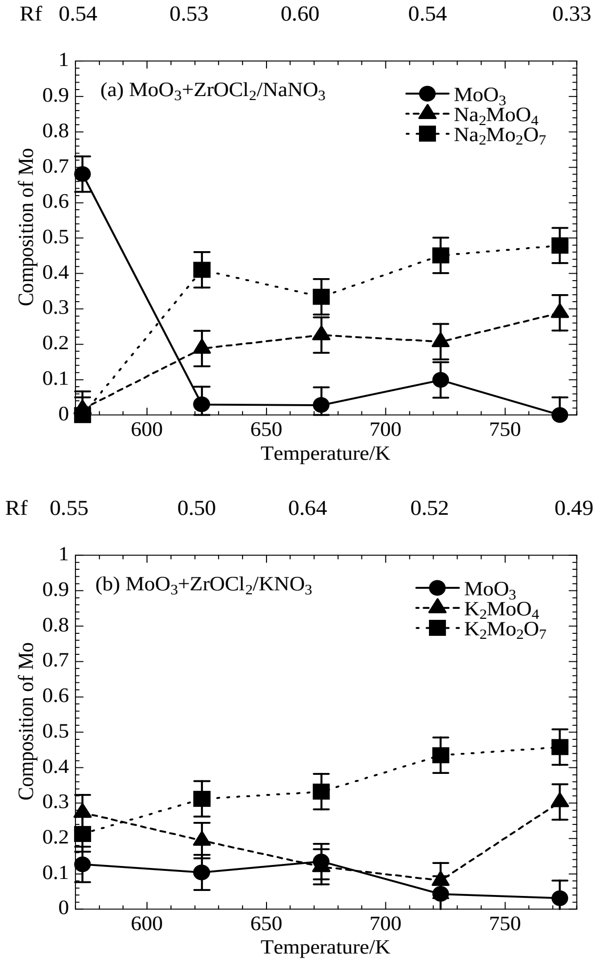

Figure 3

The composition obtained by the fitting for the Mo K edge EXAFS of (a) $MoO_3+ZrOCl_2/NaNO_3$ and (b) $MoO_3+ZrOCl_2$ /KNO_3 quenched at 573 - 773K.

to Mo-Mo scattering of the MoO_3 structure. This indicates that the local structure of MoO_3 precursor remains intact at this temperature. With increasing quench 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 MoO_4^{2-} structure increase. These results show that the MoO_3 precursor transforms into MoO_4^{2-} with increasing temperature.

The comparison of the spectra in Fig. 1 (a) and (b) suggests that the structural changes of molybdate anions with rising temperature depend on the cations of the molten salts. In Fig. 1 (b) when KNO_3 was used, the Mo-Mo peak shifted from 0.36 nm to 0.32 nm at 623 K, whereas the peak in Fig. 1(a) stayed at 0.36 nm independent of the quench temperature up to 723 K. This indicates that the cation affects the formation of the intermediates.

The mixture contains many kinds of molybdate anions in the molten nitrate. We have analyzed the spectra in Fig. 1 using multi-component fitting with the assumption that the Mo species in the mixtures consist of $Mo_2O_7^{2-}$, MoO_4^{2-}, and MoO_3. Figure 2 shows the results of the multi-component fitting analysis of the spectra in Fig. 1 with an R-factor, Rf=$\sqrt{\sum_i \left\{k_i^3\left(\chi(k_i)-\chi'(k_i)\right)\right\}^2 \Big/ \sum_i \left(k_i^3\chi(k_i)\right)^2}$. Other kinds of molybdate species than the above three species may occur in the mixture. Thus, the total composition of the three species is likely below 100%. Strictly speaking, the percentage obtained by this procedure doesn't necessarily correspond to the real percentage of component, but it indicates the relative contribution of the signal of the model to the EXAFS signal. The reliability of this procedure depends on the propriety of the model. The R-factor will be an index of the reliability. The large R-factor indicates existence of other species than the selected models.

Though some reactions occur before the nitrate melting, in $NaNO_3$, 60% of the MoO_3 structure remains unchanged at 573 K. At 623 K, the MoO_3 structure almost disappears, while the percentage of $Na_2Mo_2O_7$ increases. The percentage of $Na_2Mo_2O_7$ decreases above 673 K, when the percentage of Na_2MoO_4 increases. The decrease of MoO_3 in the potassium salt is slower than in the sodium salt, and the percentage of $K_2Mo_2O_7$ is at a maximum at 723 K. $K_2Mo_2O_7$ readily changes into K_2MoO_4 between 723 and 773 K.

1.2 ZrO_2 supported molybdate catalysts

Figure 3 shows the results of the multi-component fitting analysis of the Mo K-edge XAFS of Mo/ZrO_2 catalysts using

$NaNO_3$ and KNO_3. In both molten salts, the percentage of $Mo_2O_7^{2-}$ does not decrease even at 773 K in contrast to those in Fig. 2. This indicates that polymolybdate anions are stabilized by the interaction with ZrO_2 and suggests that this is the reason for the high dispersion of molybdate catalysts on ZrO_2 supports.

4. Conclusion

The EXAFS analysis results confirm that MoO_3 transformed to MoO_4^{2-} via $Mo_2O_7^{2-}$ in molten nitrate. The transformation behavior of molybdate anions depends on the cation present in the molten salt. In addition, it is suggested that the interaction of ZrO_2 with the intermediate, $Mo_2O_7^{2-}$, results in the high dispersion of molybdate catalysts on Zr supports.

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