

DXAFS study on the decarbonylation process of Mo(CO)₆ in NaY supercages

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The decarbonylation process of Mo(CO)₆ in the NaY supercages was studied by means of a time resolved dispersive XAFS method during temperature programmed decarbonylation. XANES analysis demonstrated that the decarbonylation proceeded through two steps and that a stable intermediate existed between 440–490 K. The curve fitting analysis revealed that the intermediate was a molybdenum monomer subcarbonyl species coordinated by three CO ligands and three oxygen atoms of zeolite framework. Molybdenum dimer subcarbonyl species were not observed. This study demonstrated that DXAFS technique is a powerful method to study the dynamic behaviour of the Mo carbonyl species during decarbonylation process.

Keywords: DXAFS, Mo(CO)₆/NaY, CVD, Mo structure, time-resolved structure analysis

1. Introduction

Preparation of highly dispersed uniform metal/oxide clusters and particles at high loadings on robust supports is a key issue to develop efficient catalytic systems. Y-type zeolite is a crystalline porous material composed by supercages with a diameter of 1.3 nm and channels with a diameter of 0.7 nm between the supercages and may be a promising support for homogeneous small clusters and particles at high loadings (Thomas & Thomas, 1997). Chemical vapor deposition (CVD) of metal complexes and clusters into zeolite pores is one of the promising method to achieve high dispersions at high loadings. Mo(CO)₆ is often used to prepare highly dispersed Mo species in the Y-type zeolite and highly dispersed molybdenum species were prepared in the channel of zeolites by the decarbonylation of Mo(CO)₆ (Okamoto *et al.*, 1991, Ozin *et al.*, 1992, Djajanti & Howe, 1995).

In the previous study, we reported that the Mo(CO)₆ species in NaY supercages were decarbonylated at 573 K to form a Mo dimer oxycarbide species (Mo₂(C)O_x) and that upto four Mo₂(C)O_x species can be produced by repeating the CVD-decarbonylation cycles in a supercage without sintering the dimer species (Asakura *et al.*, 1999).

The mechanism of the dimer formation without sintering is interesting to be investigated. One possible explanation is that the dimer species is highly stable and the activation energy for cluster

growth is large. Another possibility is that the decarbonylation process itself prevents the cluster formation.

As a carbon atom bridges the two Mo atoms in the oxocarbide species, it is expected that Mo dimer subcarbonyl species were formed as an intermediate. If the decarbonylation process completes before the formation of the dimer species, it is difficult to explain the existence of the bridging carbon atom.

The decarbonylation process has been investigated by means of IR (Okamoto *et al.*, 1988, Okamoto *et al.*, 1998, Abdo & Howe, 1983, You-Sing & Howe, 1986) and EXAFS (Okamoto *et al.*, 1991) and formation of molybdenum dimer subcarbonyl species was suggested by IR studies (Abdo & Howe, 1983, Yan *et al.*, 1997). However, IR spectra do not give any direct evidence of the formation of the dimer species. Okamoto *et al.* measured EXAFS of Mo(CO)₆ in Y type zeolites evacuated at 373 K and claimed that Mo(CO)₃(O_L)₃ (O_L: oxygen atom of zeolite channel) that Mo dimer was not formed at that conditions. We apply the DXAFS technique, in this study, to elucidate the structural transformation of the molybdenum carbonyl species during the decarbonylation process. As the time resolution of DXAFS is ca. 1 s, this technique is useful to investigate the structure of metastable species.

2. Experimental

Catalyst preparation is described in a previous paper (Asakura *et al.*, 1999). Briefly, NaY zeolite (Tosoh Co.) was pretreated under vacuum (10⁻³ Pa) at 723 K for 15 min and calcined at the same temperature under 26.6 kPa of oxygen for 30 min, followed by evacuation at 723 K for 1 h. Then the zeolite was mounted in a quartz-made chemical vapor deposition (CVD) apparatus without exposing to air. Mo(CO)₆ (Aldrich Co.) was placed in a glass tube connected to the CVD apparatus. The NaY zeolite was exposed to Mo(CO)₆ vapor with stirring at room temperature. After the sufficient exposure time for the saturation of Mo(CO)₆ in zeolite pores (typically 15 h), the sample was evacuated at room temperature to remove the excess Mo(CO)₆. DXAFS spectra were recorded during the decarbonylation under vacuum with ramping temperature (4 K min⁻¹). DXAFS measurement and analysis are described in the previous paper (Yamaguchi *et al.*, 2000). Briefly, a Si(311) bent crystal was used to monochromate X-rays. The X-ray energy was calibrated by a spectrum of Mo foil using a 2nd-order polynomial. Conventional XAFS measurements were carried out at BL-10B at KEK-PF in the Institute of Materials Structure Science. The spectra were analyzed by the UWXAFS package (Stern *et al.*, 1995) and backscattering amplitudes and phase shifts were calculated by the FEFF8 code (Ankudinov *et al.*, 1998).

3. Results and discussion

Figure 1 shows Mo K-edge X-ray absorption spectra of Mo(CO)₆/NaY during temperature programmed decomposition. A clear change in the XANES spectra was observed. The peak at 20025 eV decreased and shift to 20037 eV at 350–400 K. At 550 K, the peak position changed from 20037 eV to 20020 eV. The series of X-ray absorption spectra suggest that there is an intermediate species in ca. 400–550 K. To confirm this idea, the XANES features were fitted by a linear combination of the XANES spectra (eq. (1)) measured at 293, 474, and 623 K, which represent the initial, intermediate, and the final species, respectively.

$$X_{obs} = c_0X_0 + c_1X_1 + c_2X_2 \quad (1)$$

where X_{obs} , X_0 , X_1 , and X_2 represent observed XANES spectrum, and XANES spectra of the initial species, intermediate species, and final product, respectively, and c_0 , c_1 , and c_2 stand for the coefficients for X_0 , X_1 , and X_2 , respectively.

Figure 2 shows c_0 , c_1 , c_2 , $c_0 + c_1 + c_2$, and R_f (%) as a function of evacuation temperature. The value of c_0 began to decrease at 320 K and got to zero at 440 K, accompanied with an increase of c_1 .

In the temperature range between 440–490 K, c_1 was almost unity.

The value of c_1 began to decrease at 490 K and got to zero at 560 K accompanied by increasing of c_2 . The values of $c_0 + c_1 + c_2$ were close to the unity and R_f was less than 0.8 % in the whole temperature range, which indicate that the fitting was done properly. The XANES analysis suggests that a stable intermediate species exists between 440–490 K. The transformation from the initial species to the intermediate species proceeded gradually and it took over 100 K. On the other hand, transformation from the intermediate species to the final product proceeded quickly and completed in the temperature range of 50 K.

Figure 3 shows Fourier transformed k^3 -weighted EXAFS functions obtained by the DXAFS technique as a function of evacuation temperature. Phase shift correction was not carried out

absorbance

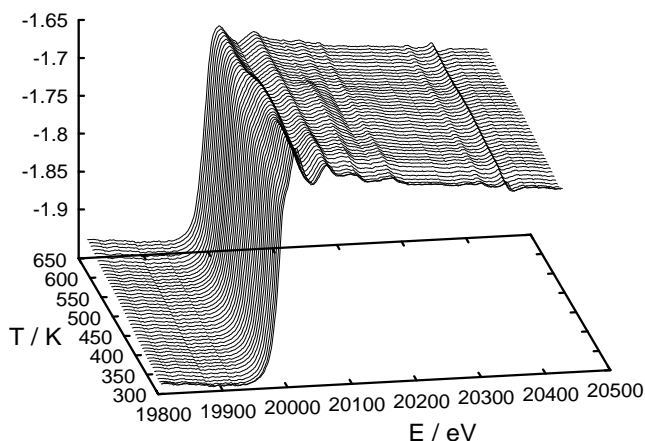


Figure 1. Mo K edge X-ray absorption spectra of molybdenum carbonyl species in NaY as a function of evacuation temperature

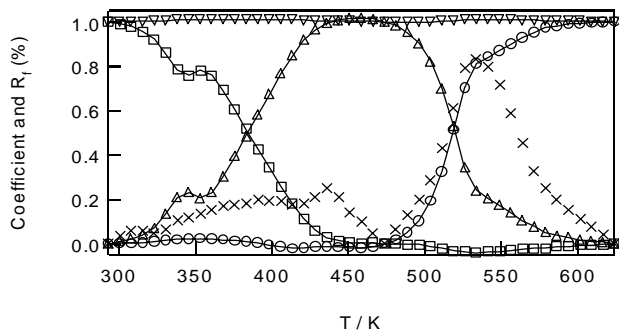


Figure 2. Coefficients (c_0 , c_1 , and c_2) for initial (squares), intermediate (triangles), and final (circles) species as a function of evacuation temperature as well as the sum of the coefficients (inverted triangles) and the residual factors R_f (crosses). The XANES spectra at 293, 474, and 623 K were used as a reference spectra for initial, intermediate, and final species, respectively.

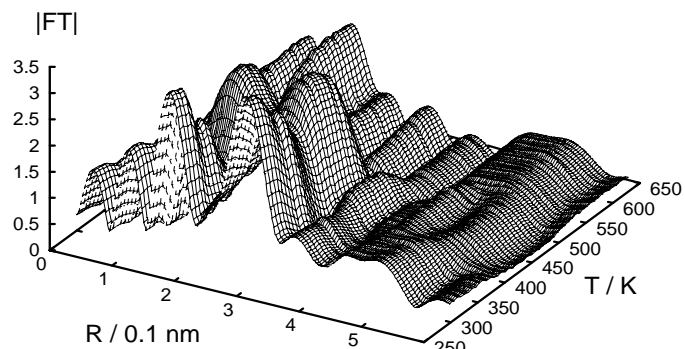


Figure 3. Fourier transformed Mo K-edge k^3 -weighted EXAFS functions of molybdenum carbonyl species in NaY obtained by the DXAFS technique as a function of evacuation temperature.

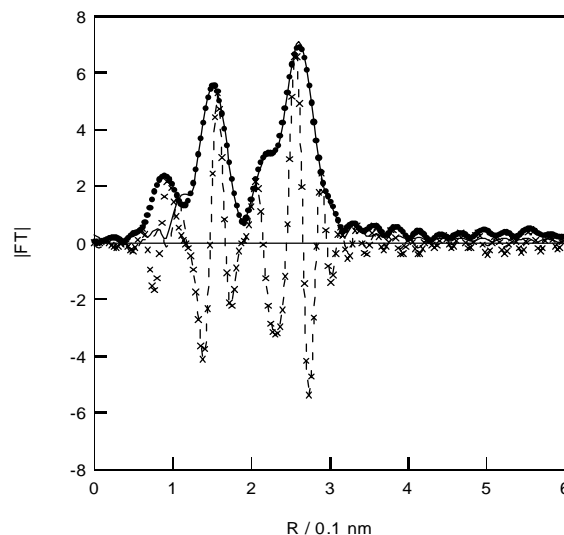


Figure 4. Fourier transformed Mo K-edge k^3 -weighted EXAFS functions of the intermediate molybdenum species in NaY. Circles, crosses, solid line, and broken line represent absolute value of observed EXAFS function, imaginary part of observed EXAFS function, absolute value of calculated EXAFS function, and imaginary part of calculated EXAFS function, respectively.

in these spectra. Two peaks were observed at 0.16 and 0.27 nm at 300 K, which are attributable to Mo-C and Mo-(C)-O contributions of the carbonyl species. These peaks shifted to 0.14 and 0.26 nm when the sample was evacuated at 400 K. Above 550 K, these two peaks disappeared, while peaks attributable Mo-O-(C) and Mo-Mo appeared. Because of limited k range and the limited resolution of the spectrometer, the curve fitting analysis of the DXAFS data are not done at present. Instead, we have analyzed EXAFS data measured by a conventional method to elucidate the structure of the molybdenum species. As the proportion of the intermediate species was unity in a wide temperature range (440–490 K) as shown in Fig. 2, the structural information of the intermediate can be obtained by a conventional XAFS method of the sample evacuated at 440–490 K.

Table 1. Structural parameters for the molybdenum species in NaY.

abs.-scat.	CN	R / nm	$\sigma^2 / 10^{-3} \text{ nm}^2$
at 293 K ($\Delta E_0 = 0.9 \text{ eV}$, $R_f = 3.0 \%$)			
Mo-C	5.1	2.06	1.3
Mo-(C)-O	5.1	3.24	2.6
at 473 K ($\Delta E_0 = 1.9 \text{ eV}$, $R_f = 1.6 \%$)			
Mo-C	3.3	0.192	2.8
Mo-(C)-O	3.3	0.309	3.7
Mo-O	2.9	0.231	9.5
at 623 K ($\Delta E_0 = 2.2 \text{ eV}$, $R_f = 3.1 \%$)			
Mo-C	1.0	0.195	7.0
Mo-O	2.1	0.205	4.7
Mo-Mo	1.0	0.278	10.8

Figure 4 shows Fourier transformed k^3 -weighted EXAFS functions as well as curve fitting results for the intermediate species measured at room temperature. The k and R range of the Fourier transformation and curve fitting were 30-145 nm^{-1} and 0.12-0.32 nm, respectively. As shown in this figure, the observed data were reproduced well by the calculated EXAFS.

Table 1 shows structural parameters for the Mo species evacuated at 300, 473, and 623 K obtained by the curve fitting analysis. When the sample was evacuated at 473 K, the coordination number (CN) of Mo-C and Mo-O for the CO ligands was decreased to 3.3 with decreasing Mo-C and Mo-O distances. The decrease in the Mo-C distance can be attributed to the extension of the $d \rightarrow \pi^*$ back donation (Okamoto *et al.*, 1991). In addition, Mo-(O₁) bondings were observed at 0.231 nm. As shown in Fig. 4, the observed data can be fitted without Mo-Mo contributions, which may exclude the possibility of dimer formation.

As the R_f 's of the XANES fitting in Fig. 2 at 500-600 K are larger than those of other temperatures, an intermediate species is suggested, where the amount may be fractional. Unstable Mo subcarbonyl dimer species are assumed to exist during the transformation from the Mo subcarbonyl monomer to the Mo dimer oxycarbide species, because a carbon atom bridges the two Mo atoms. If the decarbonylation process is completed before two Mo atoms merge, such bridging carbon is difficult to form. The dimer species, however, were not detected in this DXAFS study. This could be attributable to the low stability of subcarbonyl dimer species.

There are two possibilities for the first step of the decarbonylation.

One possibility is that the decarbonylation proceeds gradually and $\text{Mo}(\text{CO})_x$ ($x = 3-5$) species exist in the temperature range of 300-440 K. The other possibility is that three CO's desorb simultaneously from $\text{Mo}(\text{CO})_6$ and only the initial species and the stable intermediate exist in the temperature range 300-440 K. The results of the XANES analysis suggest the latter possibility, though the first possibility is not completely excluded. The good fit with small R_f (ca. 0.2 %) and the sum of $c_0 + c_1 + c_2$ being close to unity indicate that the XANES spectra between 300-440 K were represented well by the linear combination of the XANES of the initial species and the stable intermediate. As the XANES

of $\text{Mo}(\text{CO})_6$ and $\text{Mo}(\text{CO})_3(\text{O})_3$ are different each other substantially, it is reasonable to assume that the XANES of $\text{Mo}(\text{CO})_5$ and $\text{Mo}(\text{CO})_4$ are different from those of $\text{Mo}(\text{CO})_6$ and $\text{Mo}(\text{CO})_3$.

In conclusion, Mo dimer subcarbonyl species were not detected during the decarbonylation process by the DXAFS technique. The subcarbonyl dimer species might be unstable, where the concentration would be low. Further improvement of the DXAFS method is required to elucidate the structure of unstable and low-concentration species such as molybdenum dimer subcarbonyl species.

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