

*J. Synchrotron Rad.* (1999), **6**, 428–429

## XAFS analysis of unsupported MoS<sub>2</sub> catalysts prepared by two methods

Nobuyuki Matsubayashi,<sup>a\*</sup> Hiromichi Shimada,<sup>a</sup> Motoyasu Imamura,<sup>a</sup> Yuji Yoshimura,<sup>a</sup> Akio Nishijima,<sup>a†</sup> Christophe Calais<sup>a</sup> and Christophe Geantet<sup>b</sup>

<sup>a</sup>National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, <sup>b</sup>Institut de Recherches sur la Catalyse, 2 Av. A. Einstein, 69626 Villeurbanne Cedex, France.  
Email: nmatsub@nimc.go.jp

Structural analysis by XAFS method was applied to two kinds of unsupported molybdenum disulfide catalysts. Assuming a structural model consisting of crystalline and non-crystalline parts, curve fitting analysis was performed for the catalysts. The residual XAFS after subtraction of the crystalline contribution showed that the structure of the non-crystalline part was significantly different between the catalysts prepared by the two methods. It was suggested that EXAFS would give the average size of the micro-domains, while other methods such as TEM and TPR would give the size of macro-domains.

**Keywords:** molybdenum disulfide; XAFS; molten salt; unsupported catalyst; fine particle

### 1. Introduction

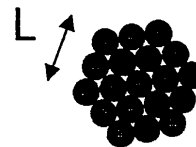
Molybdenum disulfide is extensively used as a catalytically active species on metal oxide supports, however, the precise structure of the active sites still remains ambiguous. We have reported on the determination of particle sizes of unsupported molybdenum sulfides with various specific surface areas prepared by two kinds of methods using many analytical methods such as temperature programmed reduction (TPR), XRD, TEM, and EXAFS in a previous paper (Calais *et al.*, 1998). In the Fourier transform of the Mo K-edge EXAFS, the Mo-S peak intensities at 0.242 nm of unsupported MoS<sub>2</sub> catalysts were almost the same as that of crystalline MoS<sub>2</sub>, while the peak intensities of Mo-Mo at 0.316 nm of the catalysts were obviously small in comparison with that of crystalline MoS<sub>2</sub>. If the decreases of the peak intensities of Mo-Mo were caused only by decreases in the average particle size of crystalline MoS<sub>2</sub>, the crystalline sizes of MoS<sub>2</sub> obtained by EXAFS were significantly smaller than that estimated by the other methods (Bouwens *et al.*, 1990).

In the present study, a new idea for EXAFS analysis combined with FEFF simulation was employed to clarify the reason why the particle size obtained by EXAFS was much smaller than that by other methods.

Table 1 Properties of unsupported MoS<sub>2</sub> catalysts.

Preparation Method	Specific Surface Area (m <sup>2</sup> /g) <sup>a)</sup>	L <sup>b)</sup>
AT	50	8
MS	125	18

a) by BET method, b) by TPR (Calais *et al.*, 1998)



### 2. Experimental

Molybdenum disulfide catalysts were prepared by two methods. One is the thermal decomposition of ammonium thiomolybdate (AT) by heating at 673 K in a 15 vol% H<sub>2</sub>S/H<sub>2</sub> flow (Diemann & Muller, 1973). The other is the molten salt method from molybdenum trioxide and potassium thiocyanide (MS) at 623 K for 48 h in a N<sub>2</sub> flow (Kerridge & Walker, 1977). Both of the catalysts were re-sulfidized at 673 K in a flow of 15 vol% H<sub>2</sub>S/H<sub>2</sub>. The catalysts are specified in Table 1.

The measurement of Mo K-edge EXAFS was performed at the Photon Factory (BL10B) of the National Laboratory for High Energy Physics (Tsukuba, Japan). Fourier Transformation of the EXAFS data for  $\Delta k=140 \text{ nm}^{-1}$  ( $30 < k < 170 \text{ nm}^{-1}$ ) was performed. The phase shift and backscattering amplitude factor were corrected by using the calculated values of FEFF6 (Rehr *et al.*, 1991) for Mo as an absorber and S as a scatterer in crystalline MoS<sub>2</sub> (Bronsema *et al.*, 1986).

### 3. Results and Discussion

We assume a regular hexagon model for the growth of crystalline MoS<sub>2</sub> in the lateral direction. In this model the crystalline size is represented by the number of the molybdenum

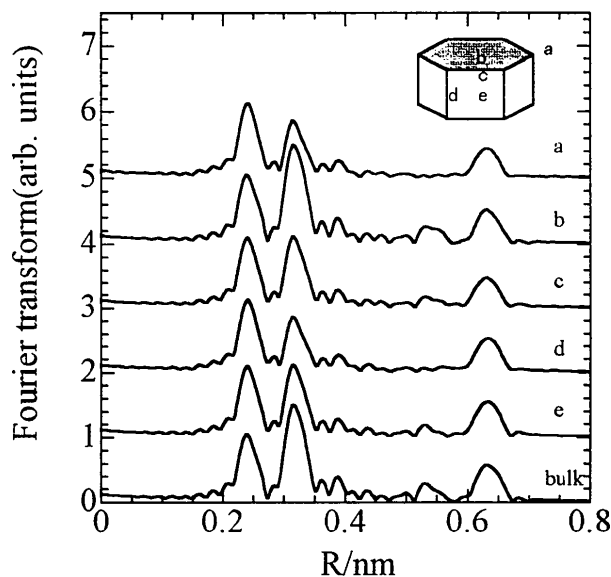


Fig.1 The Fourier transforms of  $X(k)$  simulated by FEFF on Mo at various sites in the regular hexagon model of crystalline MoS<sub>2</sub> ( $Dk=140 \text{ nm}^{-1}$ , the phase shift and backscattering amplitude calculated for Mo-S by FEFF were used).

<sup>†</sup> Present address: Kochi Prefectural Industrial Technology Center, 3992 Nunoshida, Kochi, Kochi 781-5101, Japan

Table 2 EXAFS results of unsupported MoS<sub>2</sub> catalysts by a subtraction analysis.

Prep.	c	R(S <sub>r</sub> )/nm	σ <sup>2</sup> (S <sub>r</sub> )/10 <sup>-4</sup> nm <sup>2</sup>	R(Mo <sub>r</sub> )/nm	N(Mo <sub>r</sub> )	Rf	L
AT	0.54	0.2411	4.1	0.3074	0.4	0.16	4.3
MS	0.61	0.2409	4.2	0.3076	1.6	0.15	5.0

atoms on one side of the hexagon, L. From the hexagon model, the average coordination number of Mo-Mo, N(Mo) can be deduced according to the crystalline size. The value of N(Mo) at 0.316 nm is calculated by simple geometry as follows:

$$N(\text{Mo}) = \frac{24(L-1) + 36 \sum_{i=1}^{L-2} i}{1 + 6 \sum_{i=1}^{L-1} i} \quad \text{for } L \geq 2$$

The N(Mo)s for the catalysts with L of 8 and 18 (Table 1) are, respectively, calculated at 5.4 and 5.8. This is quite inconsistent with the N(Mo)s obtained by EXAFS, 4.0 and 4.5 (Calais et al, 1998).

Figure 1 shows the Fourier transformation of EXAFS which has been simulated on Mo at each site (a - e in the picture shown in Fig.1) of a sulfur terminated particle crystalline MoS<sub>2</sub> by FEFF. The Fourier transform has been performed on X(k) weighted by k|FEFF<sub>Mo-S</sub>(k)| (Δk=140 nm<sup>-1</sup>) using the back scattering amplitude and the phase shift for Mo-S obtained by FEFF under the same conditions as the catalysts. The FEFF simulation clearly shows that the peak intensity of Mo-Mo (0.316 nm) for Mo at the periphery is smaller than that for Mo in the bulk as expected from the geometrical calculation, while the peak intensity of Mo-Mo (0.632nm) does not change as expected. This indicates that the contribution of the multiple scattering is large to the Mo-Mo (0.632nm) but that the multiple scattering does not affect the intensity of Mo-Mo (0.316 nm). Thus, the inconsistency of L obtained by EXAFS and other methods cannot be attributed to the effect of the multiple scattering. There may be a problem of the assumption in the EXAFS analysis that the structures of the unsupported MoS<sub>2</sub> catalysts are homogeneous and the same as that of crystalline MoS<sub>2</sub>.

As a next step, we perform curve-fitting analysis using a structural model consisting of crystalline and non-crystalline parts. The EXAFS, X(k) was divided to a crystalline part, X<sub>cr</sub>(k) and a residual part, X<sub>r</sub>(k) as follows:

$$X(k) = cX_{cr}(k) + (1-c)X_r(k),$$

where c was the ratio of Mo atoms (Mo<sub>cr</sub>) in the MoS<sub>2</sub> crystalline structure relative to total Mo atoms. In the crystalline MoS<sub>2</sub>, both the coordination numbers of Mo-S (0.242 nm), N(S<sub>cr</sub>), and Mo-Mo (0.316nm), N(Mo<sub>cr</sub>), are 6.

By the conventional curve fitting analysis of the EXAFS, the N(S)s of Mo-S(0.242 nm) were calculated at about 6 for both of the catalysts (Calais et al, 1998). Thus, the N(S) is assumed to be 6 for the non-crystalline part as well as for the crystalline part. To reduce the number of parameters, the Debye-Waller factor for Mo-Mo (0.316 nm) of the non-crystalline part, σ<sup>2</sup>(Mo<sub>r</sub>), is assumed to be the same as that of the crystalline part, σ<sup>2</sup>(Mo<sub>cr</sub>). Since the σ<sup>2</sup>(Mo<sub>r</sub>) is likely larger than that for the σ<sup>2</sup>(Mo<sub>cr</sub>), the possible error of σ<sup>2</sup>(Mo<sub>r</sub>) would be reflected on the coordination number of Mo<sub>r</sub>, N(Mo<sub>r</sub>). The structural parameters, N, R, and σ, are determined to minimize the residual value, Rf.

$$Rf = (\sum(Y - Y_c)^2 / \sum Y^2)^{1/2},$$

where Y is experimental X(k) and Y<sub>c</sub> is X(k) calculated by the EXAFS formula including parameters by FEFF.

The c and structural parameters of residual part thus obtained are shown in Table 2. Errors of R, N, and σ<sup>2</sup> in repeated measurements are estimated at ±0.000003 nm<sup>2</sup>, ±0.2, ±0.0002 nm, respectively. On the assumption that the non-crystalline structure occurs at the periphery of crystalline MoS<sub>2</sub>, average particle size, L, is obtained from c in the following equation;

$$L = \frac{3(c-3) - \sqrt{-3c^2 + 42c - 3}}{6(c-1)} \quad L \geq 2 \quad \left( \frac{1}{7} \leq c < 1 \right)$$

The L values calculated by this formula (Table 2), 4.3 and 5.0, were still much smaller than those from TPR. The inconsistency of the particle size determined by EXAFS and other methods can be attributed to the "different definition of the size" by each method. In the unsupported MoS<sub>2</sub> catalysts a macro-domain consists of many micro-domains. EXAFS gives the average size of the micro-domains, while other methods such as TEM and TPR gives the size of macro-domains.

The EXAFS results indicate that the local structure at the periphery of micro-domains depends on the preparation methods. Since the structure of the periphery highly responsible for the catalytic activity and sintering properties of the catalysts, the present result provides important information on the possible difference in the catalytic performances of the two catalysts.

The XAFS measurements were performed under the approval of the Photon Factory Program Advisory Committee (Proposal 92-G195) in the National Laboratory for High Energy Physics.

## Reference

- Bouwens S. M. A. M., Prins R., de Beer V. H. J., Koningsberger (1990), *J. Phys. Chem.*, 94, 3711-3718.
- Bronsema K. D., De=Boer J. L., Jellinek F. (1986), *Z. Anorg. Allgemeine Chemie*, 540, 15-17.
- Calais C., Matsubayashi N., Geantet C., Yoshimura Y., Shimada H., Nishijima A., Lacroix M., and Breyse M. (1998), *J. Catal.*, 174, 130-141.
- Diemann E. & Muller A. (1973), *Coord. Chem. Rev.*, 10, 79-122.
- Kerridge D. H. & Walker S. J. (1977), *J. Inorg. Nucl. Chem.*, 39, 1579-1581.
- Rehr J. J., Mustre de Leon J., Zabinsky S. I., and R.C. Albers, (1991), *J. Am. Chem. Soc.*, 113, 5135-5140.

(Received 10 August 1998; accepted 3 December 1998)