Effect of rhodium modification on structures of sulfided Rh–Mo–K/Al₂O₃ catalysts studied by XAFS

Zhongrui Li,[a] Ming Jiang,[a] Guozhu Bian,[a] Yilu Fu[a] and Shiqiang Wei [b]

[a] Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China, [b] Center of Fundamental Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China.
E-mail: jiangm@ustc.edu.cn

Local structures of the molybdenum sulfide species in the sulfided Rh-Mo-K/Al₂O₃ catalysts with various rhodium loadings have been investigated by XAFS. From the fitting results, the Mo-Mo coordination number for the sample free of rhodium (ca. 3.7) is similar to that for the crystalline MoS₂, indicating that the supported sulfided molybdenum species mainly present as large patches of MoS₂-like slabs. For the rhodium-modified samples, however, the amplitudes of the Mo-S and Mo-Mo coordination shells are sharply reduced, revealing a high dispersion of the MoS₂-like species in the catalysts. The scheme of the microstructures of the sulfided molybdenum species stabilized on the alumina support is discussed based upon the analysis of the EXAFS data.

Keywords: XAFS, Rh-Mo-K/Al₂O₃ catalysts, sulfided molybdenum species, rhodium modification

1. Introduction

The production of C_{2+} alcohols from CO hydrogenation is of practical and academic interests in C_1 chemistry. Sulfided Mo-K/Al₂O₃ catalysts have attracted special attention because of their rather high activities for alcohol synthesis and superior sulfur-resistant property (Murchison et al., 1988; Jiang et al., 1994). Structures and locations of active sites in molybdenum-based catalysts have long been a matter of debate. We have studied the sulfided Mo-K/Al₂O₃ catalysts with different potassium loadings by XAFS and found that a strong interaction occurs between molybdenum and potassium species (Bian et al., 1996). For the sample without addition of potassium, the molybdenum species mainly consist of Mo-S-Mo units, the basic building units of MoS₂, and are dispersed on the support with a higher level of disorder than those in crystalline MoS₂. With potassium promoted, the molybdenum species, though still highly dispersed, are aggregated to some extent and their local structures become more similar to those of MoS₂.

Recently, we have found that sulfided Mo-K/Al₂O₃ catalysts modified by rhodium display drastically improved catalytic properties in CO hydrogenation with the product distribution shifted to $C_{2+}OH$ (Li et al., 1997). The results obtained from the measurements of X-ray diffractions and laser Raman spectra demonstrate that a strong interaction between rhodium and molybdenum species occurs, which causes a dramatic decrease in size of the supported molybdenum species with increasing rhodium loading (Li et al., 1998). In this paper, XAFS is used to study the coordination status of the sulfided molybdenum species affected by the rhodium modification.

2. Experimental

The oxidized Mo-K/Al₂O₃ sample was prepared by a sequential pore volume impregnation method. γ-Al₂O₃ support (BET surface area: 270 m^2 g^{-1}) was first impregnated with K₂CO₃ solution, dried at 393 K for 12 h and calcined in air at 573 K for 1 h, and then impregnated with $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution, dried at 393 K for 12 h and calcined in an oxygen flow of 40 ml min^{-1} at 773 K for 24 h. The resulting sample was further calcined in air at 1073 K for 12 h. The samples modified by rhodium were prepared by impregnating the obtained Mo-K/Al₂O₃ samples with RhCl₃ solution followed by drying at 393 K for 12 h and calcination in air at 773 K for 2 h. The sulfided samples were obtained by heat-treating the oxidized ones in a flow of mixed gas, 8.7% CS₂/ H₂, of 30 ml min^{-1} at 673 K for 6 h. The molybdenum content in the samples, expressed as weight ratio of MoO₃/Al₂O₃, is 0.24, the atomic ratio of K / Mo is 0.8, and the rhodium loading varys from 0 to 1.0% of the total weight of the samples.

The X-ray absorption spectra of Mo K-edge (19,999 eV) were measured at the beamline of 4W1B of Beijing Synchrotron Radiation Facility. The storage ring was operated at 2.2 GeV with a typical current of 50 mA. The fixed-exit Si(111) flat double crystals were used as monochromator. The XAFS spectra were recorded in transmission mode with ionization chambers filled with argon. Data analysis was performed following standard procedures (Sayers et al.,1988). Phase shifts and back-scattering amplitudes of Mo-O, Mo-S and Mo-Mo pairs were extracted from the spectra of Na₂MoO₄·2H₂O and MoS₂ standard compounds.

3. Results

The EXAFS oscillation functions $\chi(k)$ of crystalline MoS₂ and Rh-Mo-K/Al₂O₃ catalysts are shown in Figure 1. It can be seen that the amplitudes of the samples are decreased, but their oscillation features are similar to that of the crystalline MoS₂. Compared with the envelope of the rhodium-free sample, the decreases in amplitude of the rhodium-modified samples are more pronounced in high k region.

The radial distribution functions obtained from the Fourier transform of $k^3\chi(k)$ functions are presented in Figure 2. For the samples, two prominent peaks corresponding to the Mo-S and Mo-Mo shells are observed at about 0.201 and 0.283 nm. They are located almost at the same positions as those for the crystalline MoS₂, indicating the similarity in local structure between the sulfided molybdenum species and MoS₂. However, the magnitudes of the Mo-S and Mo-Mo coordinations are much
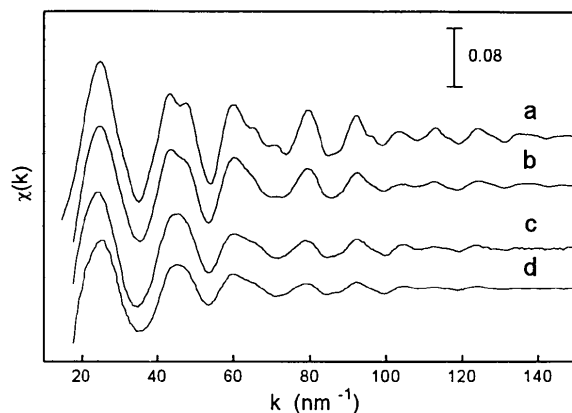
Figure 1

Mo K-edge EXAFS oscillation function $\chi(k)$ of crystalline MoS_2 and the samples. (a) MoS_2, (b) $Mo-K/Al_2O_3$, (c) $Rh(0.5\%)-Mo-K/Al_2O_3$ and (d) $Rh(1.0\%)-Mo-K/Al_2O_3$.

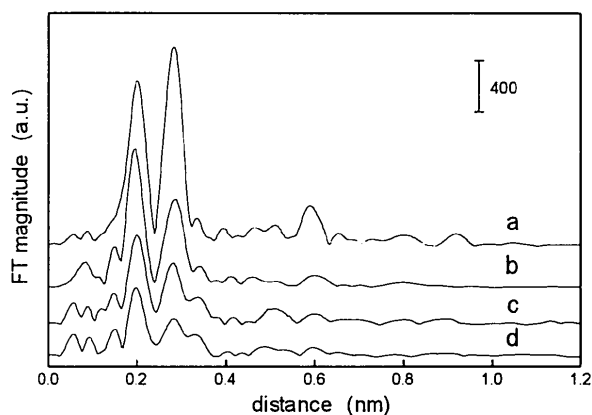**Figure 2**

Fourier transforms of $k^3\chi(k)$ for the crystalline MoS_2 and the samples. (a) MoS_2, (b) $Mo-K/Al_2O_3$, (c) $Rh(0.5\%)-Mo-K/Al_2O_3$ and (d) $Rh(1.0\%)-Mo-K/Al_2O_3$.

lower than those for MoS_2 and the ratios of the magnitude of Mo-Mo shell to that of Mo-S are also smaller. These observations are consistent with the previous XAFS results that the sulfided molybdenum species are highly dispersed in the catalysts and the symmetry of long range-ordered structure of the molybdenum species decreased (Bian *et al.*,1996). It is important to note that the modification of rhodium to the samples brings about a further reduction in the size of the sulfided molybdenum species and symmetry of the coordination shells of the central molybdenum atoms as indicated by the more remarkable decrease in magnitude of Mo-S and Mo-Mo coordinations (Figure 2c and d).

The analysis of Mo-S and Mo-Mo peaks has been carried out by using inverse Fourier transform followed by a fitting procedure on the isolated EXAFS functions. The experimental data are well fitted with the calculated curves as demonstrated in Figure 3. The structural parameters obtained from the fitting results for the Mo coordination shells are presented in Table 1.
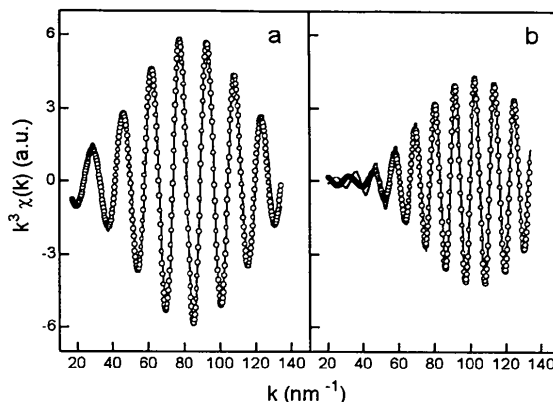

Figure 3

Comparison of inverse transformation of experimental spectra (open circle) and the final fits (solid line) for $Rh(0.5\%)-Mo-K/Al_2O_3$. (a) Mo-S (and Mo-O) shell (r, 0.09 - 0.24 nm) and (b) Mo-Mo shell (r, 0.24 - 0.32 nm).

Table 1

Structure parameters obtained from the Fourier-filtered fitting data for the samples and standard compounds

Samples	Bond	R (nm)	N	$\Delta\sigma^2\times10^{-6}$ (nm^2)*	DE_0 (eV)**
Mo-K/Al$_2$O$_3$	Mo-O	0.177±0.002	0.2±0.0	0±0.1	2.4±0.2
	Mo-S	0.241±0.002	5.1±1.0	2±0.2	0.6±0.2
	Mo-Mo	0.316±0.003	3.7±0.7	1±0.1	1.1±0.2
Rh(0.5%)-Mo	Mo-O	0.197±0.002	1.0±0.2	18±2	2.8±0.2
-K/Al$_2$O$_3$	Mo-S	0.243±0.002	4.0±0.8	11±1	-1.2±0.2
	Mo-Mo	0.315±0.003	2.4±0.5	11±1	1.0±0.2
Rh(1.0%)-Mo	Mo-O	0.200±0.002	1.5±0.3	60±6	-13.4±0.2
-K/Al$_2$O$_3$	Mo-S	0.243±0.002	3.4±0.7	20±2	-0.5±0.2
	Mo-Mo	0.315±0.003	1.9±0.4	24±2	0.3±0.2
Na$_2$MoO$_4$·2H$_2$O	Mo-O	0.177	4.0		
MoS$_2$	Mo-S	0.241	6.0		
	Mo-Mo	0.316	6.0		

* Relative Debye-Waller factor of the sample to that of the standard compounds;

** Correction of the inner-potentials of the samples based upon those of the crystalline MoS_2.

4. Discussions

MoS_2 has a layer lattice and the sulfur-sulfur interaction between sandwich domains of MoS_2 layer is weak. Based upon the results obtained from HRTEM measurements, Hayden *et al.* (1987) concluded that on alumina support MoS_2 crystallites occur in the form of platelets with a height-to-width ratio between 0.4 and 0.7, and some of them are oriented with their basal plane parallel to the Al_2O_3 surface and some oriented at a nonzero angle to the surface. Similar scheme was also proposed by Prins *et al.* (1989). They suggested that the orientation of MoS_2 crystallites on alumina depends upon their size. The crystallites grow on the support with large dimensions parallel to

the basal sulfur planes and a small dimension perpendicular to the basal plane. On a semi-quantitative basis, the Mo-Mo coordination number (N_{Mo-Mo}) has been used by Bouwens *et al.*(1990) as a measure of the size of MoS_2 crystallites. By assuming a S/Mo stoichiometry of 2 and a simple hexagon model to represent a MoS_2-slab as did by Bouwens *et al.*, it can be derived that, *e.g.*, the average local ordered structures of Mo-K/Al_2O_3 (N_{Mo-Mo}=3.7) and Rh(1.0%)-Mo-K/Al_2O_3 (N_{Mo-Mo}=1.9) consist of about 15 and 5 Mo atoms, corresponding to average dimensions of 2 ~ 4 and ~1 nm, respectively. Such an estimation of the size of the sulfided molybdenum species may be plausible considering the results obtained from the measurements of X-ray diffractions and laser Raman spectra (Li *et al.* 1998). Nevertheless, it is clear that the modification of rhodium to the catalysts reduces remarkably the size of the sulfided molybdenum species.

Topsøe *et al.* (1984) claimed that MoS_2 supported on an industrial alumina support can be present as very large patches of a wrinkled, one slab thick MoS_2-like layer, which are stabilized through the weak van der Waals interaction of the basal planes of MoS_2 particles with the surface of the support. For the sulfided sample free of rhodium, it might be the case since the size of the slabs is rather large as indicated by the Mo-Mo coordination numbers. It can be seen from the data shown in Table 1, the contribution of Mo-O coordination is observed for all the samples. As suggested by Prins *et al.* (1990), the supported oxo-molybdenum species should be fully sulfided under the present conditions used for the sulfidation of the catalysts. In such a case, the contribution of Mo-O coordination observed for the catalysts may not arise from the oxygen atoms merely connected with molybdenum atoms due to the incomplete sulfidation of the catalysts, but from the interaction of the molybdenum atoms with the surface oxygen atoms of the alumina support, *i.e.*, the bonding of Mo-O-Al. It implies that the above-mentioned weak van der Waals interaction may not be an appropriate interpretation to the stabilization of the sulfided molybdenum species on the support in the case with Rh-K-Mo/Al_2O_3 catalysts. From Table 1, with the increase of the rhodium loading, *i.e.*, the decrease of the crystallite size of sulfided molybdenum species (vide supra), the contribution of Mo-O coordination increases. Therefore, the configuration of the sulfided molybdenum species supported on alumina may depend upon their size. In order to clarify this point, it is necessary to briefly summarize the possible structural characteristics of edge planes of MoS_2 crystallites interacting with γ-Al_2O_3 surface.

The most stable surface plane of γ-Al_2O_3 (fcc) is (110) plane with oxygen anions closely packed in alternating rows (Wyckoff, 1985). MoS_2 ($P6_3$ / mmc) is of a layer structure with the basal (0002) and the two edge ($10\bar{1}0$) planes exposed as major surface planes, the latter being less stable (Hayden *et al.*, 1987). The molybdenum atoms on ($2\bar{1}\bar{1}0$) surface are arranged in rows, and the Mo-Mo distance within the rows is only 2% less than twice the O-O spacing within the oxygen rows of γ-Al_2O_3 (110) and that between alternate rows on ($2\bar{1}\bar{1}0$) is about 4% greater than the O-O spacing between every third row of γ-Al_2O_3 (110). Every Mo atom in alternate MoS_2 slabs is possible to be

bonded through an Mo-O-Al linkage that leaves the staking of the MoS_2 layers perpendicular to the γ-Al_2O_3 (110) surface. As compared to the MoS_2 ($2\bar{1}\bar{1}0$) edge planes, the bonding between the ($10\bar{1}0$) edge planes and the Al_2O_3(110) surface is not nearly as favorable because of the mismatch in the distance between the Mo atoms in a slab and the O-O distance in the support surface. The geometrical fit between higher index planes of MoS_2 and Al_2O_3(110) is not nearly as good as with ($2\bar{1}\bar{1}0$) either. Therefore, the most excellent geometrical fit is to bond the MoS_2 ($2\bar{1}\bar{1}0$) edge plane to the Al_2O_3 (110) plane and form Mo-O-Al linkages.

From the point of view, the tiny sulfided molybdenum species in the rhodium-modified samples may be mainly stabilized through their edge planes directly interacting with the surface oxygen atoms of the support. If the sulfided molybdenum species interact with the support through their basal plane, the average Mo-S coordination would not change much with decreasing slab size and the contribution of Mo-O coordination would not be so pronounced. The contribution of Mo-O coordination observed for the samples free of rhodium (Table 1) may also result from the interaction of the small crystallites bonded through their edge planes with the alumina surface since the size distribution of the crystallites may not be uniform.

From the above discussion, it is clear that the addition of rhodium to the catalysts significantly modifies the coordination status of the molybdenum atoms in the catalysts. The effect of rhodium will be clarified further by studying the EXAFS spectra of rhodium-edge as presented in a subsequent contribution.

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