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The structure analysis of $MoO_x/TiO_2(110)$ by polarization-dependent total-reflection fluorescence X-ray absorption fine structure

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Abstract

The surface structure analysis of a model catalyst $MoO_x/TiO_2(110)$ was for the first time performed by polarization-dependent total-reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) in three different directions of the crystal surface. Two samples of $MoO_x/TiO_2(110)$ were prepared by an impregnation of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ using ultra high purity water and normal distilled water. The PTRF-XAFS analysis revealed that anisotropic Mo dimer species was preferentially formed on the $TiO_2(110)$ surface, with Mo–Mo bond (0.335 nm) parallel to the $[1\bar{1}0]$ direction when the ultra high purity water was used as the solvent. On the other hand, the Mo oxide on the surface prepared using normal distilled water had a symmetric tetrahedral structure (MoO_4) with Mo–O of 0.176 nm, which was due to the coexistence of alkaline metals at the surface. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Polarization-dependent total-reflection fluorescence XAFS; TiO_2 (110); Mo dimer; Model catalyst

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1. Introduction

Catalytically active metals and metal-oxides supported on oxide surfaces often grow anistoropically or asymmetrically by many factors such as their intrinsic properties, morphology of the support, metal-support interactions, restructuring under the ambient, and coexisting impurities on the surface. The information on anisotropic or asymmetric structures of supported metals and metal oxides may be of great importance in exploring the genesis of catalysis and the relationship between structure and reactivity, and developing new catalytic systems.

Extended X-ray absorption fine structure (EXAFS) has been regarded as a useful method to obtain the information about the local structure and morphology of metal sites in supported catalysts [1,2]. However, conventional EXAFS technique using powder samples gives only the structural information averaged in every direction, impeding the precise structural analysis around active metal sites on supports [2]. The EXAFS oscillation $\chi(k)$ depends on the angle θ_i between the ith bond direction and the polarization electric-field vector of the incident X-ray as shown in Eq. (1);

$$\chi(k) = \sum \chi_i(k)\cos^2\theta_i, \tag{1}$$

where $\chi_i(k)$ is an EXAFS oscillation accompanying the ith bond. When a single crystal oxide is used as a support, structural information on the bonds parallel and normal to the surface can be independently

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obtained. When the polarization vector of the incident X-ray is parallel to the surface (*s*-polarization), only the bondings which lies parallel to the surface contribute to the EXAFS signal. The bondings normal to the surface, i.e., metal-support bonds, are preferentially observed when the polarization vector is perpendicular to the surface (*p*-polarization). However, there are two problems in applying polarization dependent EXAFS to dispersed active species on a flat oxide substrate. First, concentration of the surface species is very low, and hence it is impossible to measure EXAFS spectra in a transmission mode as in case of powder samples. Concentration of monolayer metal on a flat surface ranges 10^{14}–10^{15} atoms cm^{-2}, which is 4–5 orders of magnitude lower than those of metals for conventional catalysts in a powder form. Fluorescence yield detection is more preferable for dilute samples than monitoring a direct absorption [3]. Second, most of catalytically interesting elements have X-ray absorption edges at higher energies. Therefore, fluorescence detection is not available under usual conditions because the penetration depth of the incident X-rays is so large that the scattering X-rays from the bulk substrate suffer detecting surface metal species. In order to reduce the scattering X-rays from the substrate and to improve the surface sensitivity, we adopted the measurements under a total-reflection condition. When the incident X-rays hit a flat substrate below a critical angle (δ_c), the X-rays are totally reflected and can penetrate only a few nm into the bulk [4] resulting in a tremendous decrease in scattering X-rays from the substrate. Combining the total reflection technique and the fluorescence detection technique we can measure the polarization-dependent EXAFS spectra for the active sites on a flat oxide substrate. The technique is called as polarization-dependent total-reflection fluorescence EXAFS (PTRF-EXAFS) method hereinafter. We have determined the asymmetric structures of Co oxides on α-Al_2O_3(0001), Cu oxides on α-quartz (0001) and Pt_4 clusters on α-Al_2O_3(0001) using the PTRF-EXAFS technique [5–7]. The information obtained by PTRF-EXAFS is

1. location of metal atoms on substrate,
2. three-dimensional structure of dispersed and monolayer metal sites,
3. bonding feature at metal-support interface.

Another advantage of this method is in situ observation of catalytically active sites under reaction conditions.

Rutile TiO_2(110) surface has an anisotropic structure with alternative alignment of the bridging oxygen ridge and the groove composed of five-fold coordinated Ti^{4+} rows along the [001] axis [8–13]. Therefore, it is expected that the formation of anisotropic structure of Mo sites supported on the surface. Moreover, TiO_2 is classified as an amphoteric oxide. Thus, alkaline metal impurity may drastically change the surface property. Supported Mo-oxide catalysts, on the other hand, have been investigated by many techniques such as Raman, UV-VIS and EXAFS, in relation to selective oxidation catalysis.

In this study, we have applied PTRF-EXAFS spectroscopy to study the three-dimensional surface structure of MoO_x/TiO_2(110) and the effect of coexisting alkaline metal on the structure of Mo oxides. Because Mo has its K-edge around 20 keV and hence the critical angle becomes as small as 1.7 mrad, it has been considered as an impossible task to measure PTRF-EXAFS for heavy-metals like Mo. The present work is the first to report the successful application of PTRF-EXAFS to a high K-edge energy element.

2. Experimental

2.1. Sample preparation

A polished rutile TiO_2(110) single crystal was annealed at 823 K for 2 h in air. The annealed crystal was impregnated with an ultra-pure aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, followed by calcination at 773 K for 3 h under O_2. The sample thus obtained is denoted as Mo/TiO_2(p) hereinafter. On the other hand, we also prepared a Mo-oxide/TiO_2(110) sample by impregnation of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ using distilled water which contained a trace amount of alkali metals mainly potassium. The sample was calcined at 773 K for 3 h under O_2. The sample thus obtained is denoted as Mo/TiO_2(c). The Mo loading was estimated by XPS. The amount of Mo used for the impregnation corresponded to 0.5 ML for both samples. The final Mo loadings for Mo/TiO_2(p) and Mo/TiO_2(c) were found to be 0.2 ML (1 Mo atom/nm^2) and 0.4 ML (2 Mo atom/nm^2), respectively. During the calcination processes a part of Mo oxides initially impregnated was lost from the $TiO_2(110)$ surface possibly due to sublimation. Total-reflection fluorescence X-ray analysis was performed with TREX610T (Technos I.T. Co., Japan; a W anode operated at 30 kV and 200 mA) to determine the amount of alkali metals on the $TiO_2(110)$ surfaces.

2.2. *PTRF-EXAFS measurement*

PTRF-EXAFS spectra were measured at BL14A vertical wiggler line of the photon factory in the national laboratory for high energy physics (KEK-PF) using a Si(311) double-crystal monochromator. While typical critical angles (δ_c) in the hard X-ray region are several milliradians, e.g. Cu K-edge (8.9 keV): 4.7 mrad, for Mo K-edge at 20 keV the δ_c is so small as 1.7 mrad. In order to adjust the angle of the incident X-rays to the δ_c or less, a four-axis high-precision goniometer with a minimum step of 0.17 mrad was used [14]. Both fluorescent X-ray and reflected X-ray beam intensities were monitored to find an optimum measurement condition. In order to avoid unnecessary irradiation, the beam size was adjusted to ϕ 0.1 mm. The incident X-ray was monitored by a 5 cm long ion chamber filled with Ar. To detect the fluorescent X-ray stemming from the sample we used a pencil-type small NaI(Tl) scintillation counter (ϕ 14 mm), by which we can avoid the Bragg diffraction from the substrate effectively [15]. Since the $TiO_2(110)$ substrate has an anisotropic surface structure, PTRF-EXAFS measurements were carried out under the conditions where the electric vectors of the incident X-rays are parallel to the $[1\bar{1}0]$, [001] and [110] directions of $TiO_2(110)$ as shown in Fig. 1. The EXAFS oscillations were extracted using REX Version 2.1 (Rigaku). Conventional curve fitting analysis was useless because it only gave the one-dimensional local structure. We calculated EXAFS oscillation directly based on the three-dimensional model structure. Calculations were carried out using theoretical amplitude and phase shift functions calculated by FEFF 6.01 [16,17].

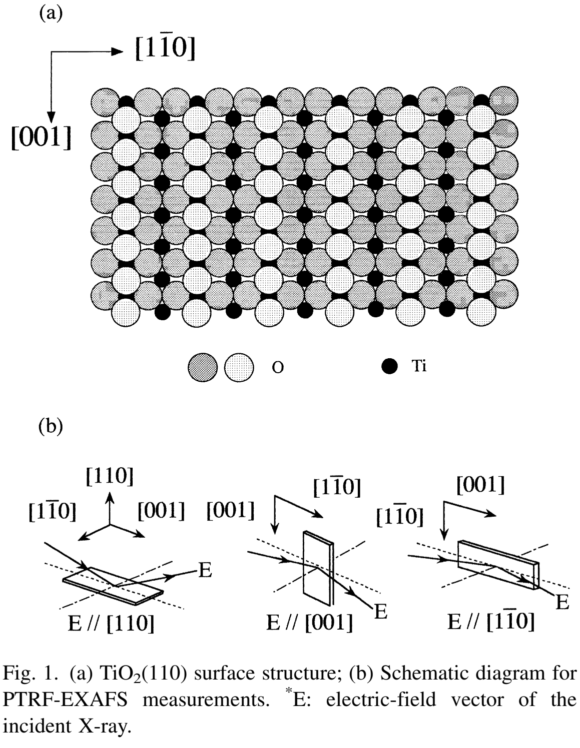

Fig. 1. (a) $TiO_2(110)$ surface structure; (b) Schematic diagram for PTRF-EXAFS measurements. *E: electric-field vector of the incident X-ray.

3. Results and discussion

Mo K-edge PTRF-EXAFS spectra for Mo/TiO_2(p) in the [110], [001] and $[1\bar{1}0]$ directions on the $TiO_2(110)$ plane are shown in Fig. 2. It was found that the EXAFS oscillations in the three directions were obviously different with each other. The results indicate the formation of an anisotropic Mo structure. Especially, the short-period oscillation was observed in the EXAFS spectrum for the $[1\bar{1}0]$ direction. We performed theoretical calculation to reproduce the observed spectra using several plausible models based on known Mo-oxide structures including a MoO_3 layer structure, a heptamolybdate structure, oligomer structures, monomer structures, etc. In consequence, a dimer model possessing Mo–Mo bond at 0.335 nm could reproduce the short-period oscillation for the $[1\bar{1}0]$ direction of $TiO_2(110)$. However, the model did not simulate the oscillation for the [110]. In order to generate the observed EXAFS oscillation for the [110] direction, it was necessary to include the chemical interaction for the Mo dimer with the TiO_2 surface. We have calculated several hundreds of structures attached on the $TiO_2(110)$ surface. All the models never agreed with the experimental results when the Mo dimers unit was placed on the groove over the Ti

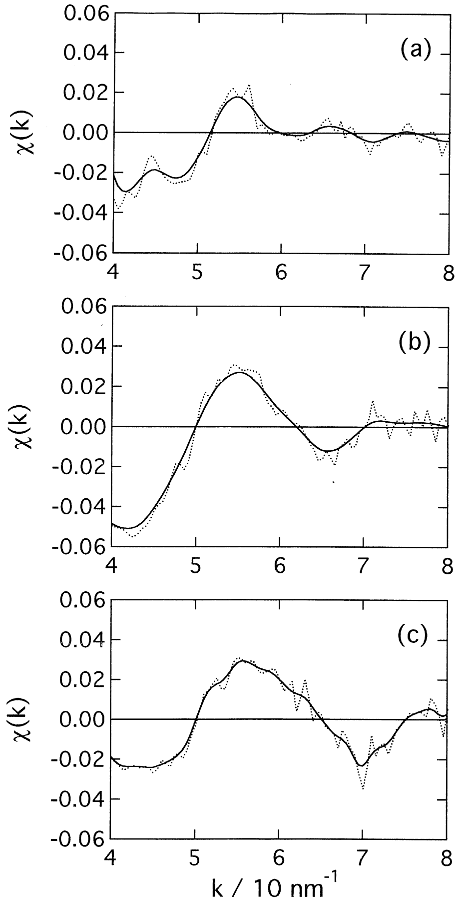

Fig. 2. k^0-weighted, background-subtracted raw Mo K-edge PTRF-EXAFS oscillations for Mo/TiO_2(p): (a) *E // $[1\bar{1}0]$; (b) E//[001]; (c) E//[110]. Dotted line: observed; solid line: smoothing treated. *E: electric-field vector of the incident X-ray.

Table 1
Postulated coordinates for the Mo dimer on TiO_2(1 1 0)

Atoms	x	y	z
Mo	0.0000	0.0000	0.0000
Mo	3.3530	0.0000	0.0000
O	2.9942	0.1148	1.7639
O	4.7261	−0.9644	0.2273
O	1.9289	−1.2658	−0.2859
O	4.1268	1.6091	0.0675
O	1.4241	1.2658	−0.2859
O	0.3588	−0.1148	1.7639
O	−0.7738	−1.6091	0.0675
O	−1.3731	0.9644	0.2273
Ti	1.6765	2.9590	−2.1754
Ti	4.9249	1.4795	−2.1794
Ti	−1.5720	1.4795	−2.1752
Ti	1.6765	0.0000	−2.1792
Ti	4.9249	−1.4795	−2.1831
Ti	−1.5720	−1.4795	−2.1790
Ti	1.6765	−2.9590	−2.1829
O	3.6567	2.9590	−2.1767
O	6.1931	2.9590	−2.1783
O	−2.8402	2.9590	−2.1726
O	−0.3038	2.9590	−2.1742
O	3.6567	0.0000	−2.1804
O	6.1931	0.0000	−2.1820
O	−2.8402	0.0000	−2.1763
O	−0.3038	0.0000	−2.1779
O	3.6567	−2.9590	−2.1842
O	6.1931	−2.9590	−2.1858
O	−2.8402	−2.9590	−2.1801
O	−0.3038	−2.9590	−2.1817

row. Only when two Mo atoms were postulated to be attached on the protruding bridging oxygen atoms, the calculated data agreed well with the observed data as shown in Fig. 3. The postulated coordinates are listed in Table 1 and optimized model structure is depicted in Fig. 3. The two bridging oxygen atoms between two Mo atoms were distorted from the original position [18]. These distortions are induced by the interaction with the Mo dimer structure. It was considered that Mo=O bonds (0.168 nm) placed on the direction between the $[1\bar{1}0]$ and [001] directions of TiO_2(110) surface. The other Mo=O bonding (0.178 nm) was found to be directed towards [110] axis. The results also agreed with the feature of XANES spectra which produced the characteristic pre-edge peak 1s→4d due to Mo=O bonding in all the directions. It was also found that the Mo dimer species was located at 0.220 nm far above the surface. Consequently, we concluded that the Mo dimer structure stepped over the bridging oxygen row with its Mo–Mo distance at 0.335 nm along the $[1\bar{1}0]$ direction of TiO_2(110).

Fig. 4 shows PTRF-EXAFS spectra for Mo/TiO_2(c) in three directions. In contrast to the spectra for Mo/TiO_2(p), the PTRF-EXAFS spectra for Mo/TiO_2(c) showed identical oscillations in every direction. Since only tetrahedral structure has been reported for Mo oxides as a symmetric structure in the literature, we calculated the EXAFS spectra in the three directions using MoO_4 Td structure. It was found that the Mo oxide species was supported on TiO_2(c) in the tetrahedral symmetry with the Mo–O distance of 0.176 nm as shown in Fig. 4. The Mo–O bond length corre-

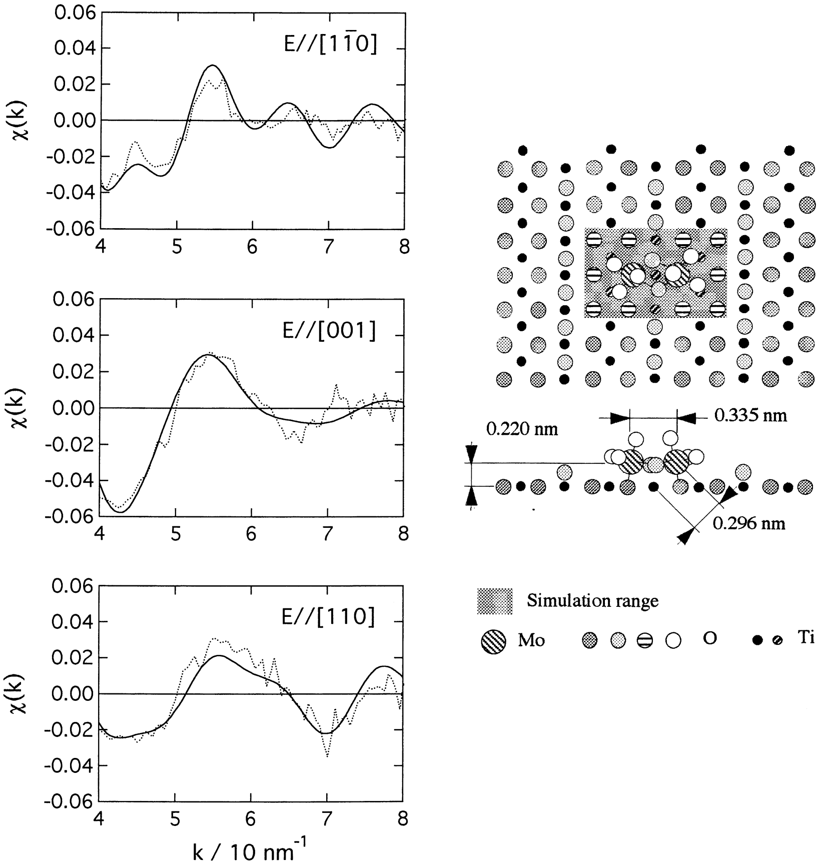

Fig. 3. Mo K-edge PTRF-EXAFS oscillations (dotted lines) for Mo/TiO_2(p) with calculated results (solid lines) and a proposed model structure.

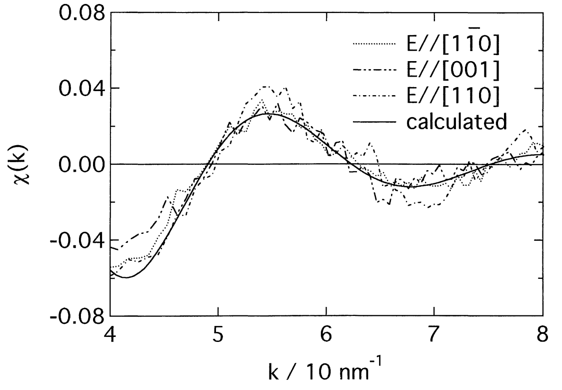

Fig. 4. k^0-weighted, background-subtracted raw Mo K-edge PTRF-EXAFS oscillations for Mo/TiO_2(c) compared to the FEFF simulation with K_2MoO_4.

sponding to a tetrahedral MoO_4 structure. In the Mo/TiO_2(c) system there was no effect of TiO_2(110) surface on the MoO_4 structure, which indicates negligible interaction between the MoO_4 structure and the TiO_2 surface. The difference between the samples Mo/TiO_2(p) and Mo/TiO_2(c) should be due to the solvents. Ultra pure water was used for preparation of Mo/TiO_2(p), while distilled water was used for Mo/TiO_2(c). Thus, the impurity contained in the solvent may affect the structure of supported Mo species. Actually, MoO_4 structure has been reported to be stabilized by the presence of alkali metals [19–22]. Total reflection fluorescence X-ray analysis was employed to check surface impurity. It was observed that potassium was present in the comparable amount of Mo on TiO_2(110)(c). Mo polymeric species are formed at low pH and Mo monomer is stabilized at high pH. The potassium impurity deposited during the impregnation using the distilled water changes the surface acid–base property and stabilizes the structure of Mo oxides as a monomer.

At last we should mention the sensitivity of the PTRF-XAFS technique that we have developed. We can determine the structure of Mo oxide and measure its change at the concentration as low as 0.2–0.4 Ml. This technique does not require any long range order of metal sites which provides wide applications to catalyst model systems.

4. Conclusion

The PTRF-EXAFS measurements revealed that the anisotropic dimer structure of Mo oxide was preferentially formed on the $TiO_2(110)$ surface and its structure changed to a symmetric tetrahedral Mo-oxide structure by coexistence of alkali metals.

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