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Ti-O bond in mesoporous titania with $S_{\mathrm{BET}} = 1256\ \mathrm{m}^2\ \mathrm{g}^{-1}$

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Introduction

In the synthesis of transition metal oxides, the templating method using primary amine directs a mesopore structure with an extremely high surface area. The BET surface area of mesoporous titania synthesized with dodecylamine has been reported to be 1256 m^2 g^{-1}[1], suggesting most of the atoms are exposed at the surface. The chemical bond and coordination structure of the bulk mesoporous titania are likely influenced by the nature of titania surface[2]. In this study we carried out the structural analysis by EXAFS spectroscopy.

Method

Mesoporous titania was prepared according to the literature[1]. X-ray absorption spectra of the Ti K edge were recorded on a BL-7C with a stored current of around 300 - 450 mA. The incident X-ray was focused and the higher harmonics were removed by the total reflection on a Rh-Ni composite mirror and detuning the monochrometer to 50 %. The powder was diluted in boron nitride. A conventional transmission mode with detection using gas ion chambers was employed. The measurement of each spectrum was completed within 30 min. The spectra were acquired five times under the same measuring conditions and from the extracted spectra, the average $\chi(k)$ was calculated. The data were processed by a REX 2000 (Rigaku Co.) program assembly. The EXAFS oscillation was extracted by fitting a cubic spline function through the post edge region. After normalization using the McMaster tables, the k^3–weighted EXAFS oscillation, $k^3\chi(k)$, in the 30 – 125 nm^{-1} region was Fourier transformed into a radial distribution function. The amplitudes and phase-shift functions for Ti-O bond were calculated by FEFF 7.02 code. The amplitude reduction factor (S_0^2) was chosen to be 1 with the lifetime broadening (V_i) equal to 0. The amplitude of $k^3\chi(k)$ at 20 K was considerably suppressed in the spectrum measured at 298 K. In addition, the static disorder and anharmonicity are considered much larger than crystalline titania. We consequently employed the cumulant expansion technique for the determination of the bond length and Debye-Waller factor for the first oxygen shell appearing around 0.1-0.18 nm in the radial distribution functions.

Results and Discussion

Figure 1 shows the EXAFS function of mesoporous titania. A distinct depletion of amplitude is observed at 273 K, which is attributed to the thermal oscillation. The structural parameters are summarized in Table 1. Considering that r(Ti-O) of anatase is 0.196 nm, it is concluded that the bond between Ti and O is abnormally long in mesoporous titania.

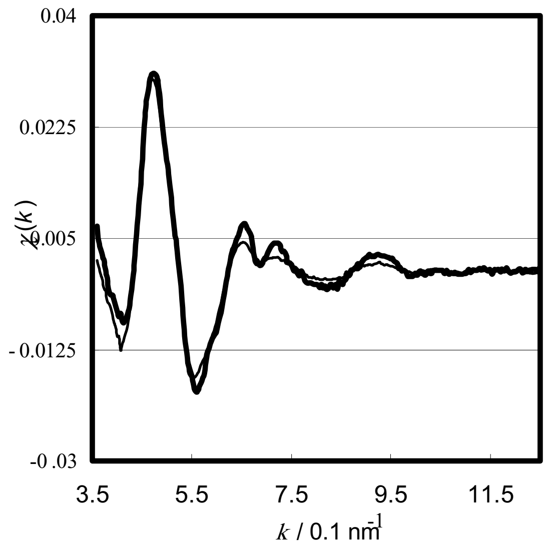

Figure 1 EXAFS oscillations of mesoporous titania before and after template extractions. Thick line : 50 K and thin line : 273 K.

Table 1: Ti K-edge EXAFS Analysis Parameters of the First Oxygen Shell of Mesoporous Titania before and after Template Extraction

sample	T / K	R / nm	σ^2 / 10^{-4} nm^2	C_3 / 10^{-7} nm^3
after template extraction	50	0.1987	0.699	*
	273	0.1998	1.16	3.3
before template extraction	50	0.1984	0.663	*
	273	0.1993	0.798	1.2

N(Ti-O) is fixed to 6. * too small to be calculated.

References

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