Population of 5-fold coordinated Ti in mesoporous titania

Hideaki YOSHITAKE*[1], Tae SUGIHARA[2], Yasuhide GOA[3], Takashi TATSUMI[2]

[1]Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama 240-8501, Japan

[2]Graduate School of Engineering, Yokohama National University, Yokohama 240-8501, Japan

[3]Graduate School of Engineering, University of Tokyo, Tokyo 113-8654, Japan

Introduction

The mesoporous oxides synthesized by a templating method has been studied intensively for high surface areas, narrowly distributed pore sizes and well ordered mesopore channels. The wall structure is, in most cases, amorphous and the local structures of central atoms, such as Si, Al, and transition metals, of these oxides have not studied well.

Since mesoporous titania synthesized with a primary amine template has an extremely large surface area (> 1200 $m^2 \cdot g^{-1}$) and an amorphous nature, the atomic structure can differ in many points from that in all the other known titanium oxides. We applied XAFS spectroscopies to investigating the local structure of Ti.

Method

The mesoporous titania whose structure was directed by dodecylamine template was prepared according to the literature [1]. XANES spectra of the Ti K edge were recorded on a BL-9A. A conventional transmission mode with detection using gas ion chambers was employed.

Since a pre-edge peak due to *p-d* orbital mixing is observed in most titanium oxides, the pre-edge region in XANES has been analyzed for determining the Ti coordinations. The background of XANES was subtracted by a polynomial function followed by a peak deconvolution with Lorentzian functions and arctangents for transitions to a bound state and the continuous state, respectively.

Results and Discussion

Figure 1 shows the result of a deconvolution of the preedge peak of template-extracted mesoporous silica. The absorption at 4968.8 eV is attributed to 6-fold coordination since the peak top of anatase appears at the same position. The another deconvolution component, peak at 4967.6 eV, is assigned to 5-fold coordination. Figure 1 demonstrates that the deconvolution quantifies the population of [5]Ti and [6]Ti. The result is summarized in Table 1. Since normalized absorption of anatase and all [5]Ti in the oxides measured are 0.3 and 0.8, respectively, and [5]Ti turned into [6]Ti of anatase by calcinations, the absorption of [6]Ti and the population of [5]Ti and [6]Ti of mesoporous titania can be calculated. The ratio of [5]Ti/[6]Ti is thus determined to be 0.5.

The most stable low index face of titania single crystals is rutile (110), where [5]Ti and [6]Ti are equally populated. [5]Ti/[6]Ti = 0.5 suggests the three Ti layers. The surface area of this face is 1440 $m^2 \cdot g^{-1}$ while the measured BET specific surface area of mesoporous titania is 1256 $m^2 \cdot g^{-1}$,

ca. 87 % of 1440 $m^2 \cdot g^{-1}$. The disagreement of [5]Ti/[6]Ti with the surface area is attributed to the contribution of micropores.
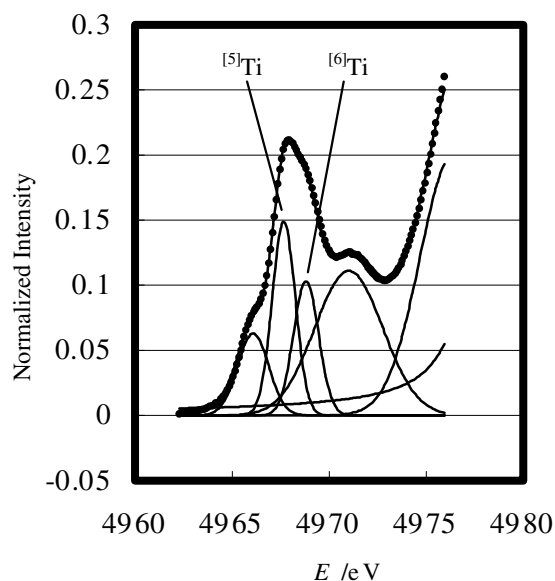

Figure 1. Peak deconvolution of pre-edge peaks of Ti K edge XANES of template-extracted mesoporous silica.

Table 1. Area of Deconvoluted Peaks of XANES Spectra

Sample No.	I (4967.6 eV) arb. unit	I (4968.8 eV) arb. unit	$\dfrac{I\,(4967.6\text{ eV})}{I\,(4968.8\text{ eV})}$
1	1.28	0.77	1.7
2	1.20	0.70	1.7
3	0	1.10	0

Intensity in arbitrary unit. Samples are mesoporous titania before template extraction (1), after template extraction (2), and anatase (3).

The wall structure is, consequently, "porous," which is supported by the FT of FEFF generated EXAFS spectrum for rutile(110), demonstrating that this face is more densely packed than mesoporous titania.

Reference

[1] H. Yoshitake, et. al., *Chem. Mater.* **14**, 1023 (2002).

*yos@ynu.ac.jp