

Local Structure of Titanium in Mesoporous Titania

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Introduction

There has been a great interest in mesoporous oxides with well-defined pore sizes and periodic structure, prepared by templating with surfactant and subsequent calcination. Titanium dioxide is a material of interest for its many applications. We have synthesised mesoporous titania by templating with dodecyl-, tetradecyl-, hexadecyl- and octadecylamines. The surface area of the material is more than $1200 \text{ m}^2\cdot\text{g}^{-1}$, which approaches a theoretical limit of the hypothetical rutile (110) surface. The powder X-ray diffraction shows no patterns, suggesting amorphous nature. The singularity of the solid structure is possibly accompanied with a novel local structure of titanium. XAFS spectroscopy is one of the most appropriate techniques for investigating the chemical bonds of a certain element in the amorphous materials.

Experimental

Mesoporous titania was prepared by the hydrothermal synthesis at 313 K followed by heat treatment at 453 K in an inert condition. The template was extracted with p-toluene sulphonic acid/ethanol. XRD and nitrogen adsorption measurement were carried out to confirm the high surface area with amorphous nature. Some samples were partially destructed by calcination at 623 or 673 K, which resulted in the extinction of the patterns in XRD. The spectra were measured in a transmission mode at BL-9A. The data were analysed by REX2000 and WinXAS2.1.

Results and Discussions

The Ti K-edge XANES spectra of mesoporous titania were processed in background subtraction to be compared each other in fig. 1. The pre-edge peaks of TiO_2 before extraction, that after extraction and that after CVD shift to a lower position by ca. 1eV with enhancement of the intensity. The main peak is assigned to 5 coordinated Ti (IV) by the position and intensity. The intensity in TiO_2 before extraction is larger than the other two, suggesting the conversion of 5-coordinated Ti into O_h Ti by removing the template molecules.

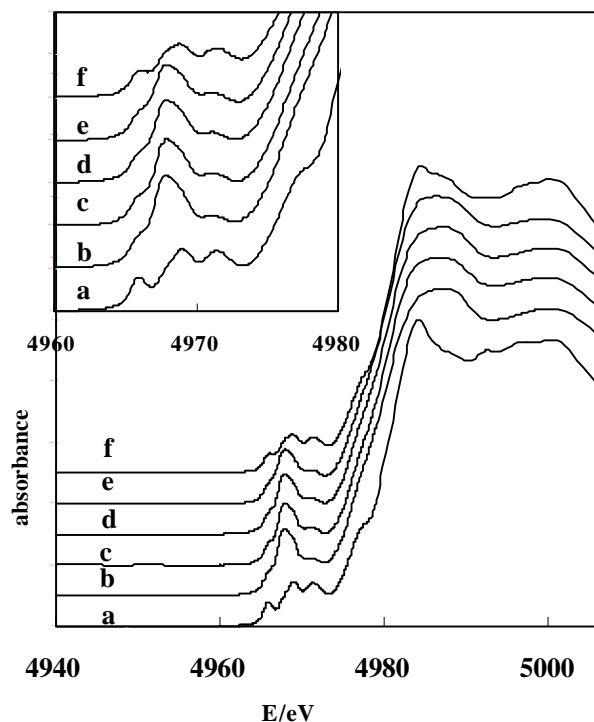


Figure 1. XANES spectra of (a) anatase, (b) mesoporous TiO_2 before extraction of the template, (c) (b)+ extraction, (d) (c)+ CVD treatment, (e) (d) + calcination at 623 K for 24 h and (f) (d)+calcination at 673 K for 1h. The inset is an expansion of pre-edge region.

The calcination at 623 K brought about no change in the XANES. When sample was oxidized at 673 K, the spectrum became similar to that of anatase. However, this dramatic change was not accompanied with the emergence of the diffraction pattern of anatase in XRD. Although the calcination at 623 K decreased the BET surface area from 1150 to $520 \text{ m}^2\cdot\text{g}^{-1}$, the local structure and amorphous nature remained. At 673 K, the former changes into anatase-like but the crystallites are still small enough to smear the diffractions.

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