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Coordination Structure of Ti in the Sols and Gels of Titania Using X-Ray Absorption Spectroscopy

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Introduction

Nanocrystalline titania thin films used as photocatalysis device have been often prepared by sol-gel method. However, the titania films prepared at the same firing temperature have shown different structure each other as studied using XRD and XAFS techniques [1,2]. The coordination structure of Ti in the fired xerogel is predicted to be related with the coordination structure of Ti in the sol, which is prepared under a certain condition. In the present study, we report on the coordination structure of Ti in the sol, gel, xerogel and fired xerogels of titania.

Experimental

Colloidal titania sols were synthesized as described elsewhere [3]. The pH value of the sols was about 2.8. Titania gel was obtained by leaving in a refrigerator for three days prior to measurements. The xerogel was obtained by drying with an evaporator at room temperature after the sols gelled. The xerogel is heated at 200, 300, 400, 500, and 600 °C. Ti K-edge XAFS data were collected all at ambient condition by a transmission method; a mixed gas of 30 % of N_2 gas and 70 % of He gas for the ion chamber (17 cm long) in the front of a sample and a N_2 gas for the ion chamber (31 cm long) behind the sample were used, respectively. Data accumulation time was 1 sec/step for powder samples and 3 sec/step for sol and gel. High harmonic was removed using a focusing double mirror and by detuning appropriately.

Results and Discussion

The XANES spectra near Ti K-edge for the sol, gel, and xerogels of titania are shown in Fig. 1 along with those for the amorphous, anatase, and rutile of titania. The spectral features of the sol, gel, and xerogel without heat treatment are different from those of the xerogels with heat treatment, in addition, from that of the amorphous. On the other hand, the spectral features of the xerogels with heat treatment except for one heated at 200 °C are close to that of the anatase, indicating that the coordination structures of the xerogels is the anatase-like structure. According to Farges's assignment for the peak (A) around 4968 eV [4], the structure around Ti ion in the sol, gel, and xerogel without heat treatment are all six-coordinate Ti species including about 5 % of four-coordinate species. Further, the relative intensity corresponding to each peaks A for the sol, gel, and xerogel without heat treatment is reduced in comparison with that for each xerogel with heat treatment. The reduction of the intensity for peak A suggests that the interaction of one Ti and another Ti, which is cross-linked with O, becomes weak because the peak is assigned to a mixture of the 4p orbital of one Ti and the 3d orbital of another Ti [5]. Hence, the network frame of cross-linked titania with O is considered to be built up for the xerogels with heat treatment, while it is slightly done for the sol, gel, and xerogel without heat treatment. This is also shown in the radial distribution curves obtained by Fourier transforms of the EXAFS spectra; the curves for the xerogels with heat treatment except for one heated at 200 °C are close to that of the anatase, on the other hand, the curves for the sol, gel, and xerogel without heat treatment show the reduction of the intensities in longer distance than first-coordination sphere.

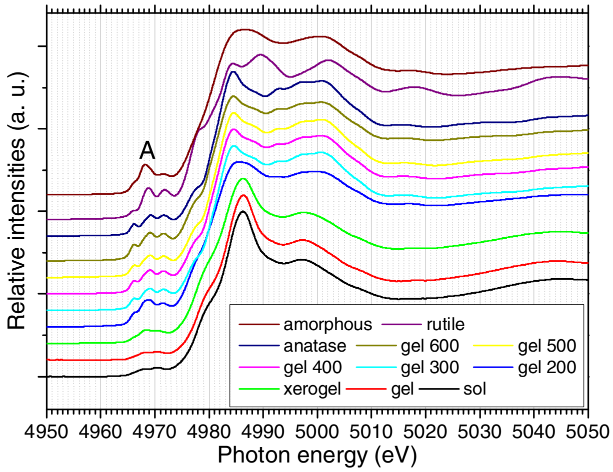

Fig. 1. Ti K-edge XANES spectra for the sol, gel, and xerogels of titania. The amorphous, anatase, and rutile of titania are plotted as references.

References

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