Coordination Structure of Ti in the Xerogel of Metal Ion-Doped Titania by Sol-Gel Methods Using X-Ray Absorption Spectroscopy

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Introduction

The incorporation of transition metal (TM) ion as second metal ions into titania is an excellent method for bringing about new physical and chemical functions. The transparent sols of TM ion-doped titania (TM/titania) have been efficiently prepared by modified sol-gel method [1]; in general, titanium alkoxide (isopropoxide, etc.), alcohol (2-propanol, etc.), and acid (e.g. HCl, HNO_3, and CH_3COOH) are stirred together, and then the acidic solution of chloride, nitride, or acetate of TM ion is added to the stirred solution. The obtained TM/titania sols are dried, and calcined to be grown the crystalline anatase and rutile. We have prepared the TM/titania prepared by our procedure as described below, and obtained transparent Ni/titania, Fe/titania and Cu/titania sols. However, the Fe/titania and Cu/titania sols rapidly gelled. In the present study, we discussed the relation between the coordination structure Ti in these TM/titania and the gelation using XAFS technique.

Experimental

The 5 wt% Ni/titania sol was synthesized as described elsewhere [2], obtained by adding the aqueous solution of nickel nitrate to the solution of the amorphous titania, which is made from Ti(IV) tetraisopropoxide (TIP), 2-propanol (2-PrOH), and pure water, dissolved hydrogen peroxide. The 5 wt% Fe/titania and 5wt% Cu/titania sols were obtained by adding pure water to the mixed solution of TIP dissolved in 2-PrOH and Fe(II) acetate and Cu(II) methoxide dissolved in 2-PrOH, respectively. The xerogel of Ni/titania, Fe/titania and Cu/titania were obtained by drying with an evaporator at room temperature after the sols gelled. After this, they were never calcined. 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. 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 xerogels of Fe/titania, Ni/titania, and Cu/titania are shown in Fig. 1 along with those for the xerogel, amorphous, anatase, and rutile of titania. The spectral features of the xerogel of Ni/titania are close to that of the unmodified titania xerogel, while those of Fe/titania and Cu/titania are close to that of anatase. The radial distribution curves by Fourier transforms of the EXAFS spectra for all samples are shown in Fig. 2, indicating that the features of the curves for the xerogels of unmodified titania and Ni/titania can be distinguished from those of Fe/titania and Cu/titania, which are comparatively resemble to that of anatase. This suggests that the xerogels of Fe/titania and Cu/titania have an anatase-like structure without heating. Thus, Fe(III) and Cu(II) ions can be considered to act as a catalyst for forming an anatase structure in the sol-gel process.

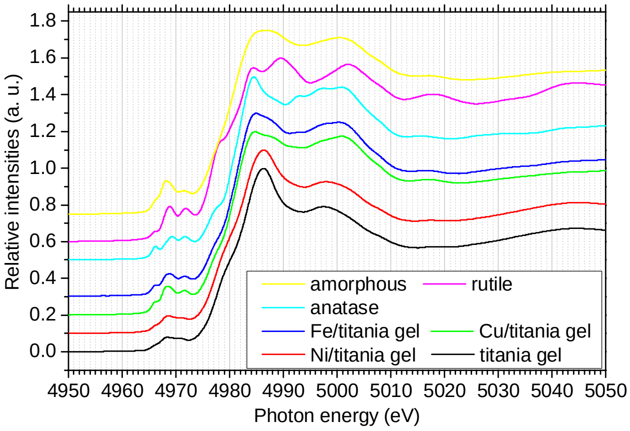

Fig. 1. Ti K-edge XANES spectra for the xerogels of Fe ion-, Ni ion-, and Cu ion-doped titania along with those for the selective references.

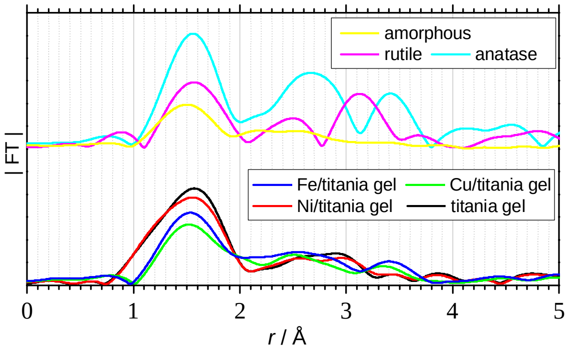

Fig. 2. The radial distribution curves by FT-EXAFS spectra for all samples.

References

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