In situ XANES studies of CuO/TiO₂ thin films during photocatalytic degradation of CHCl₃

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Abstract

Speciation of titanium in the CuO/TiO₂ thin film (synthesized by radio frequency magnetron sputtering) during photocatalytic decomposition of CHCl₃ has been studied by in situ X-ray absorption near-edge structural (XANES) spectroscopy. Little perturbation was observed in the Ti K-edge XANES spectra of the CuO/TiO₂ during photocatalysis. However, by prolonging the UV/ VIS radiation to 90 min, the copper K-edge white line absorbance was enhanced suggesting electron donation (from the encapsulated TiO₂) to surface CuO, which was also observed by electron spectroscopy for chemical analysis (ESCA) spectroscopy.

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1. Introduction

X-ray absorption spectroscopy can be used in the characterization of valence and local structure (<10 Å) of toxic elements in environmental solids (Liu and Wang, 2004). Molecular structure information such as coordination number, bond distance and oxidation state of elements can be determined by X-ray absorption near-edge structural (XANES) and extended X-ray absorption fine structural (EXAFS) spectroscopies. By in situ XANES and EXAFS, we found that copper oxide clusters involved in catalytic reduction of NO (Huang et al., 2003a, b). These molecular-scale data turn out to be very useful in revealing the nature of catalytic active species and the reaction mechanisms involved.

TiO₂, due to unique characteristics of effective band gap, is widely used as a photocatalyst in degradation of toxic organic compounds (Bhatkhande et al., 2001; Hoffmann et al., 1995). Because of the quantum size effect and enlargement of surface-to-volume ratios, nano-TiO₂ can enhance photocatalytic degradation of toxic organic compounds (Kang et al., 2003; Linsebigler et al., 1995). In addition, transition metals (such as Cu, Fe, Ni, Au and Ag) can be dosed onto TiO₂ for promotion of photocatalytic efficiency (Tseng et al., 2002). However, nature of nano-TiO₂ with transition metals is still unresolved. Thus, the main objective of present work was to study speciation of copper and titanium in a CuO/TiO₂ thin film during photocatalytic degradation of CHCl₃ by in situ XANES.
2. Experimental method

The CuO/TiO₂ thin film was synthesized by simultaneous magnetron co-sputtering of copper and titanium targets in O₂ (30 mL/min) and Ar (170 mL/min) mixture gases onto an indium tin oxide (ITO) substrate. The radio frequency and direct current power of Ti and Cu targets were 300 and 50 W, respectively. The nano-TiO₂ photocatalyst was synthesized (by the sol-gel method) with hydrolysis of the precursor material titanium (IV) n-butoxide.

X-ray photoelectron spectra of the CuO/TiO₂ thin film were determined by electron spectroscopy for chemical analysis (ESCA) (VG Scientific, ESCALAB-250) with Mg Kα X-ray (1253.6 eV) excitation source. In situ Ti (4966 eV) and Cu (8979 eV) K-edge XANES spectra of the CuO/TiO₂ thin film were measured during photocatalytic degradation of 100 ppm CHCl₃ on a home-made XANES photoreaction cell (shown in Fig. 1) on the Wiggler beamline (17C) at the Taiwan National Synchrotron Radiation Research Center (NSRRC). Data were collected in fluorescence mode with a Lytle detector for the in situ photoreaction experiments. The electron storage ring was operated at energy of 1.5 GeV (ring current = 120–200 Å). A Si(1 1 1) double-crystal monochromator was used for selection of energy with an energy resolution (ΔE/E) about 1.9 × 10⁻⁴ (eV/eV). The absorption spectra were collected in ion chambers that were filled with helium and nitrogen mixed gases. Beam energy was calibrated by the adsorption edge of Ti and Cu foils at energy of 4966 and 8979 eV, respectively. The raw absorption data in the region from 50 to 200 eV below the edge position was fit to a straight line using the least-square algorithm. The fit pre-edge background curves were extrapolated throughout the whole data range and subtracted and normalized to reduce effects of the sample thickness (Stern et al., 1995).

3. Results and discussion

The XANES spectra of Ti in the CuO/TiO₂ thin film and nano-TiO₂ (8.5 nm) are shown in Fig. 2. An enhanced white line absorbance at 4987 eV was found, suggesting that the grain sizes of TiO₂ in the CuO/TiO₂ thin film might be <8.5 nm (Bazin and Sayers, 1997). The ESCA spectra of the CuO/TiO₂ thin film for Cu 2p and Ti 2p are shown in Fig. 3. Typically, the binding energies of Cu(I) and Cu(II) are found in the ranges of 932.2–932.6 and 933.0–937.0 eV, respectively. The Cu 2p spectrum of the CuO/TiO₂ thin film shows that Cu(II) was the main copper species on the surface of the thin film. Since relatively less TiO₂ was observed on the surface, it is very likely that TiO₂ may be encapsulated in the CuO/TiO₂ photocatalysts.

Speciation of copper in the CuO/TiO₂ thin film is shown in Fig. 4. The pre-edge XANES spectra (8975–8979 eV) of copper in the CuO/TiO₂ thin film exhibit a very weak 1s-to-3d transition forbidden by the selection rule of the perfect octahedral symmetry. An intense band at 8994–9002 eV can be attributed to the 1s-to-4p transition that indicates the existence of the Cu(II) species (Huang et al., 2003a, b; Groothaert et al., 2003). Cu(0) and Cu(I) species were also found in the pre-edge spectrum at 8982 and 8982–8984 eV, which might be attributed to the dipole-allowed 1s-to-4p transition, respectively.

By prolonging the UV/VIS radiation to 90 min onto the CuO/TiO₂ thin film in the presence of 100 ppm CHCl₃, an increase of Cu(II) and decreases of Cu(I) and
Cu(I) contents in the CuO/TiO2 thin film were found. Fig. 5 shows the in situ Ti K-edge XANES spectra of the CuO/TiO2 thin film during photocatalytic degradation of 100 ppm CHCl3. Little perturbation of Ti that might be encapsulated in the thin film was observed during photocatalytic degradation of 100 ppm CHCl3 in water. In addition, the copper K-edge white line absorbance was also enhanced (see Fig. 4). It seems that electron donation (from the encapsulated TiO2) to copper on the surface of the CuO/TiO2 thin film might occur during the photocatalytic degradation of CHCl3.

4. Conclusion

Little perturbation of Ti in the CuO/TiO2 during photocatalytic degradation of 100 ppm CHCl3 was observed. However, by prolonging the UV/VIS radiation to 90 min, an increase of Cu(II) and decreases of Cu(0) and Cu(I) contents in the CuO/TiO2 thin film were found. In addition, the copper K-edge white line absorbance was enhanced suggesting that electron donation (from the encapsulated TiO2) to CuO enriched on the surface of the thin film observed by ESCA during photocatalytic degradation of CHCl3.

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References


