Photocatalytic Activity of Cu/TiO_2 with Oxidation State of Surface-loaded Copper

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Loading of some metals on TiO_2 surface has been known as one of the successful methods for the improvement of photocatalytic oxidation reaction.[1~4] The role of loaded metal is trapping and subsequent transfer of photoexcited electrons on TiO_2 surface. However, all conductive metals are not effective for the improvement of photocatalytic activity of TiO_2. It has been so far reported that Au, Ag and Pd are effective,[2~4] but Pt or Ru is detrimental for the photocatalytic oxidation reaction of TiO_2.[5~7] One of the important properties required to the loaded metal would be a suitable workfunction value. It is proposed that photocatalytic oxidation reaction is an electrochemical reaction among the TiO_2 conduction band, loaded metal, and electrolytes adsorbed on TiO_2 surface. Energy level of the loaded metal may be defined as its workfunction. Then, the position of workfunction will be critical for the effective transfer of electrons on the conduction band of TiO_2 toward adsorbed electrolytes. Secondly, the loaded metals on TiO_2 should be chemically stable during the photocatalytic oxidation reaction or storage in atmospheric condition. If the loaded metals are oxidized, conductivity of metal will be decreased down and their energy level may be altered from its metallic state. Then, the photocatalytic activity will be degenerated, since they cannot trap or transfer the photoexcited electron efficiently.

In this work, we investigate the effect of oxidation state of loaded Cu on the photocatalytic oxidation reaction. Cu is one of extraordinary metals, which exist stably as metallic form as well as metal oxides in atmospheric condition. In addition, it is expected that the loaded Cu may improve photocatalytic activity of TiO_2, since the workfunction of Cu is quite similar to TiO_2 conduction band and the standard reduction potential of oxygen molecule, which is considered to be a probable electron acceptor in TiO_2 aqueous suspension.[8] In addition, little study has so far been carried out on the photocatalytic activity of Cu-loaded TiO_2.[9,10]

Experimental Section

The TiO_2 used in this study was Degussa p25 (47 m^2/g, 70% of anatase). Cu was deposited onto TiO_2 by photochemical decomposition of $CuSO_4 \cdot 5H_2O$. A reagent grade of $CuSO_4 \cdot 5H_2O$ was obtained from Aldrich Chemical Co. and used as received. 1.0 g of TiO_2 was dispersed in aqueous solutions containing various amounts of the $CuSO_4 \cdot 5H_2O$. Distilled water was added to achieve a total volume of 140 mL. In order to expedite the photodecomposition, 10 mL of ethanol was added in this suspension as a hole scavenger. Then the mixture was transferred to the silica reaction vessel and 300W Xe lamp (LX300 UV) without UV cut-off filter was used to irradiate the suspensions. After the irradiation for 30 min, the aqueous suspension was then centrifuged and the recovered precipitates were vacuum-desiccated for several hours. The concentration of $CuSO_4 \cdot 5H_2O$, which was not decomposed during the photochemical decomposition reaction, was evaluated from the characteristic $Cu^{2+}(aq)$ absorption peak at around 800 nm and this result was used for the calibration of the loaded Cu concentration on TiO_2. It was found that most of $CuSO_4 \cdot 5H_2O$ was decomposed to metallic Cu. The deposition of Ag on TiO_2 powders was achieved by photodecomposition of AgF (Aldrich Chemical Co.). Detailed preparation procedure is given in previous work.[3]

For the evaluation of photocatalytic efficiencies of suspended powder samples in the aqueous solution, 1,4-dichlorobenzene (DCB) was utilized as a model compound. 1.5 mg of TiO_2 or metal-loaded TiO_2 powders were added in 100 mL of distilled water and suspended by ultrasonic homogenizer (Cole-Palmer) operated at 20 kHz. 14 mL of dispersed sample was transferred to a Pyrex reactor and 2 mL of 200 μM DCB aqueous solution was added. Total volume of the solution was adjusted to 16 mL and the concentration of DCB to 25 μM. Samples were then irradiated with a 300 W Xe lamp (LX300 UV) with UV cut-off filter. After the irradiation of every 2.5 min, the concentration of remnant DCB in the solution was measured with a Perkin-Elmer 552A UV-visible spectrophotometer.

XRD patterns of TiO_2 powders in glancing angle mode were obtained using a Philips diffractometer (PW3020) with a monochromated high intensity $CuK_{\alpha 1}$ radiation (λ=1.5405 Å). The oxidation state of Cu for the Cu/TiO_2 samples, was examined by X-ray photoelectron spectroscopy (XPS, SSI-2803S). X-ray absorption near edge spectra (XANES) for Cu K-edge were obtained using the 3C1 EXAFS beamline in Pohang Light Source (PLS). Each spectrum was obtained at the fluorescence mode with a solid detector.

Results and Discussion

Photocatalytic activity of Cu/TiO_2 samples with the concentration of loaded Cu is described in Figure 1. Catalytic activity was defined as overall degradation rate constant, since the photocatalytic oxidation reaction of aqueous organic molecules with TiO_2 suspensions approximated to first-order kinetics. The optimum concentration of Cu providing the maximized photocatalytic efficiency is 0.5-1.0 mole percent relative to TiO_2. Photocatalytic activity of

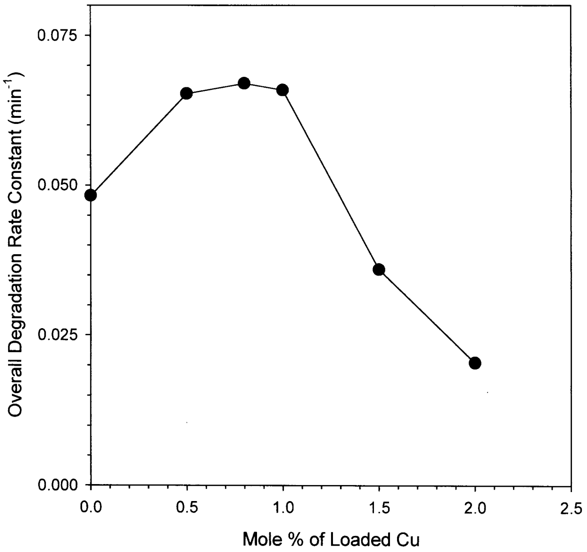

Figure 1. Photocatalytic activity of Cu/TiO_2 samples with the concentration of surface-loaded Cu (Model compound: DCB, 25 μM).

0.8% Cu/TiO_2 is approximately 1.4 times of that of pure TiO_2.

Previously, we reported that Ag is greatly effective in improving photocatalytic activity of TiO_2.[3] Photocatalytic activity of 1.5 mole % Ag/TiO_2 is about 2.0 times of that of pure TiO_2. It is considered that the high efficiency of Ag/TiO_2 originates from the effective electron-transfer capability of Ag clusters. The workfunction of Ag is 4.26 eV. Hence, the energy level of Ag is denoted to –0.24V in NHE, which is located at slightly higher level than the conduction band of TiO_2 (–0.1V in NHE), and in addition it is close to the electrochemical potential of oxygen reduction in aqueous solution [O_2 (aq) + $e^- \rightarrow O_2^-$ (aq), $E^\circ = -0.56V$ in NHE],[11,12] as is described in Figure 2. Thus, it is considered that the loaded Ag on TiO_2 can promote the transfer of electrons in TiO_2 conduction band to outer oxygen, which is dissolved in water. The same argument can also be applied to Cu/TiO_2 system. The workfunction of Cu is 4.65 eV, which is relatively close to that of Ag, much differently from other noble metals such as Pt, Ru, or Rh. Therefore, the role of Cu on TiO_2 surface is considered to be expedition of electron transfer as Ag does. Relatively lower photocatalytic activity of Cu/TiO_2 than that of Ag/TiO_2 is ascribed to the location of Cu energy level, which is not so much appropriate in transferring the electrons to outer oxygen as that of Ag (see Figure 2).

It was observed that Cu/TiO_2 samples left in atmospheric condition were gradually changed in their color from purple to pale-gray, and the photocatalytic efficiencies were accordingly decreased down with the elapse of storing time in air. It is speculated that the decrease of photocatalytic activity is closely related to the oxidation of surface-loaded Cu on TiO_2. In this work, we prepared several Cu/TiO_2 oxidized at different conditions and characterized the oxidation states of Cu for these samples, to investigate the correlation between the oxidation state of loaded Cu and the photocatalytic activity. 0.8 mole % Cu/TiO_2, presenting optimized photocatalytic activity, was annealed at 200 and 300 °C for 30 min in oxygen atmosphere, respectively. Photocatalytic activity of annealed Cu/TiO_2 samples was greatly decreased, compared with that of as-prepared Cu/TiO_2, as is described in Figure 3. The colors of the samples annealed at 200-300 °C in oxygen were changed to gray. Cu clusters on TiO_2 may not be metallic Cu. For the X-ray diffraction measurement, Cu has been loaded on a low-crystallized anatase TiO_2 film, since the crystallographic phase of Cu in 0.8 mole % Cu/TiO_2 can not be identified by XRD and in addition CuO (111) peak is overlapped with anatase (112) peak of TiO_2 powders. As is shown in Figure 4, the loaded Cu in as-prepared Cu/TiO_2 sample is identified to metallic copper. In the XRD patterns for the sample annealed at 200 °C in oxygen, 35.6° peak is indexed to Cu_2O (100) phase and a small peak at around 38.7° is denoted to CuO (111) and anatase (112). For the samples annealed at 300 °C, Cu species on TiO_2 is mainly CuO phase. This indicates that most of metallic Cu clusters

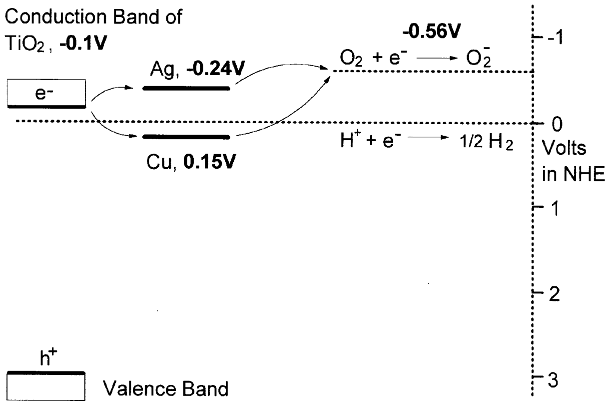

Figure 2. Schematic energy diagram of TiO_2, loaded metals, and several electrolytes.

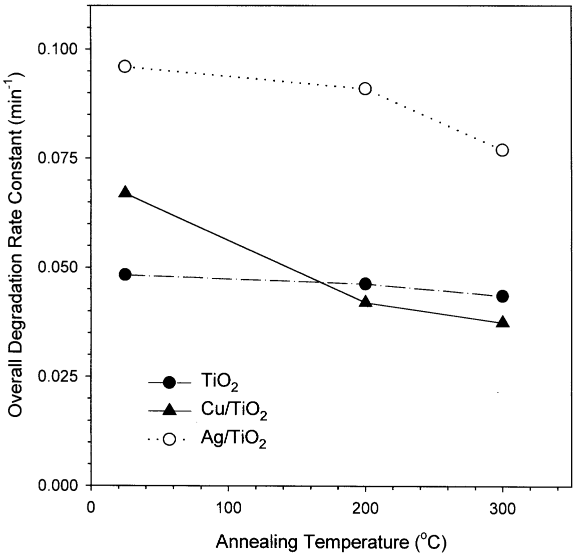

Figure 3. Photocatalytic activity of TiO_2, Cu/TiO_2, Ag/TiO_2 samples with the oxidation temperature (For Cu/TiO_2 the concentration of Cu is 0.8 mole %, and for Ag/TiO_2 that of Ag is 1.5 mole % relative to TiO_2).

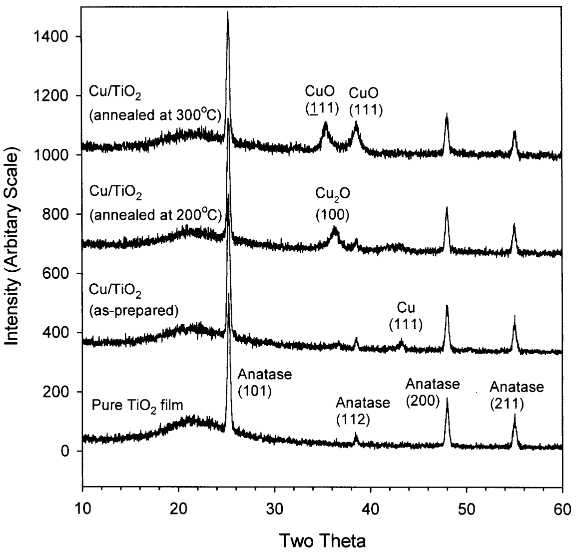

Figure 4. XRD patterns of Cu-loaded TiO_2 films annealed at several temperatures (TiO_2 film in anatase phase was deposited on a silica substrate at 450 °C with MOCVD method. Cu was deposited on TiO_2 film by photodecomposition method with 0.001 M $CuSO_4 \cdot 5H_2O$ aqueous solution.).

in Cu/TiO_2 samples are oxidized to Cu_2O by annealing at 200 °C and they are converted to CuO phase by annealing at 300 °C. However, the XRD results here do not provide the direct proof for the oxidation state of Cu, because the XRD patterns are not obtained from the Cu/TiO_2 powder samples presenting optimized photocatalytic activity. Hence, XPS spectra were obtained for the 0.8 mole % Cu/TiO_2 samples. As is shown in Figure 5 (a), the binding energy of Cu $2p_{3/2}$ for fresh Cu/TiO_2 is 932.7 eV and that of the samples annealed at 200 °C and 300 °C is 933.2 and 933.4 eV, respectively. This indicates that Cu in as-prepared Cu/TiO_2 is metallic and the samples oxidized at 200 °C and 300 °C involve CuO phase. However, the presence of Cu_2O phase is unclear. Oxidation state of Cu was also analyzed by X-ray absorption spectroscopy. XANES spectra of Cu K-edge region were observed for the two Cu/TiO_2 samples (see Figure 6). Compared to fresh Cu/TiO_2, samples annealed at 300 °C show extra absorption peak at around 8978 eV, even though it is not clear with poor intensity of signal, which is caused by the low concentration of Cu in the samples. The peak at around 8978 eV is identified to the transition from 1s to 3d.[13,14] This is another proof that the oxidation state of Cu is +2 for the sample annealed at 300 °C.

As a reference experiment, pure TiO_2 and Ag/TiO_2 samples were annealed at the same condition. Photocatalytic activity of pure TiO_2 was slightly decreased with the annealing process as is shown in Figure 3. Ag/TiO_2 was also decreased in photocatalytic efficiency, but their percentage of decrease is considerably smaller than that of Cu/TiO_2. XPS spectra in Figure 5 (b) present that the binding energies of Ag $3d_{5/2}$ line were not appreciably changed with the annealing treatment at 200 °C or 300 °C. This indicates that the loaded Ag on TiO_2 still exists as metallic state and this explains why photocatalytic activity of Ag/TiO_2 sample is less decreased than that of Cu/TiO_2.

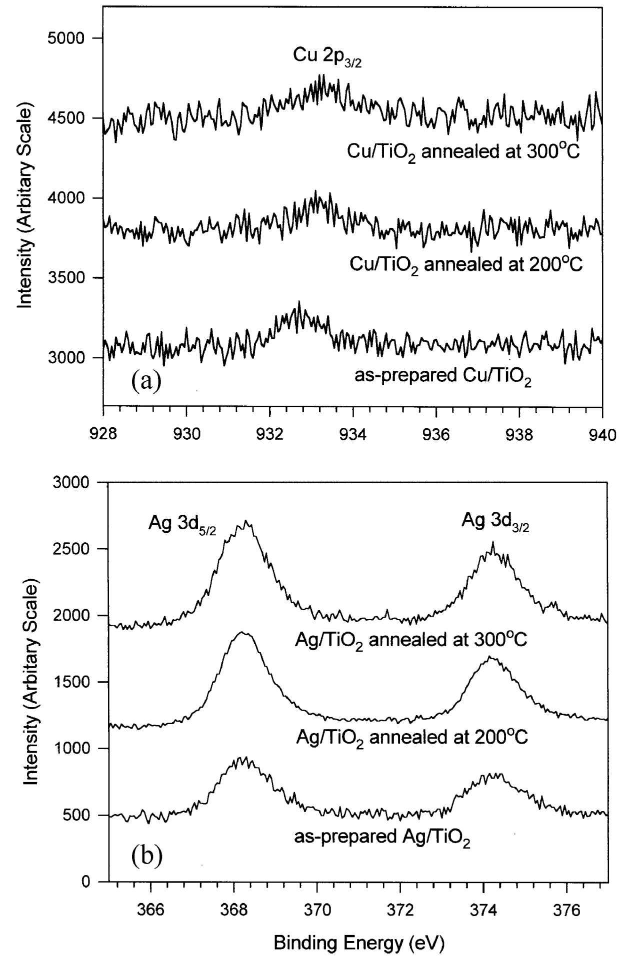

Figure 5. XPS spectra of Cu/TiO_2 and Ag/TiO_2 samples annealed at several temperatures (The concentration of Cu is 0.8 mole % and that of Ag is 1.5 mole %.); (a) Cu/TiO_2; (b) Ag/TiO_2.

It is derived that the metallic Cu on TiO_2 improves photo-

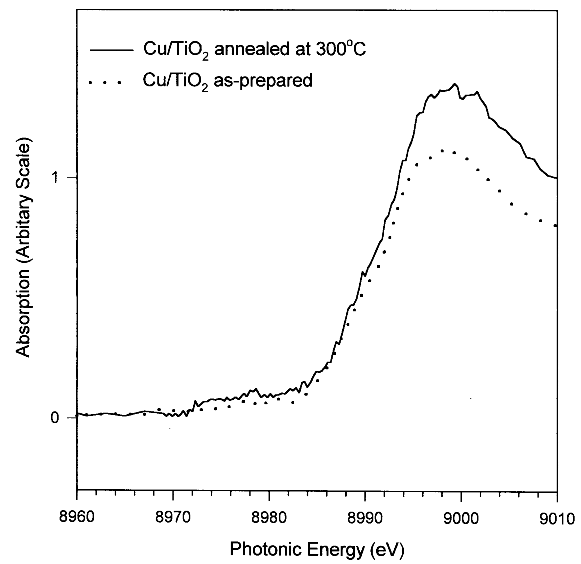

Figure 6. XANES spectra of Cu K-edge region for Cu/TiO_2 samples (The concentration of Cu is 0.8 mole %).

catalytic activity of TiO_2. When Cu is oxidized to CuO, photocatalytic efficiency is greatly decreased down. The activity is even poorer than that of pure TiO_2 sample. It is expected that CuO clusters on TiO_2 are not effective in the transfer of photoexcited electrons on the TiO_2 conduction band. This supports our hypothesis, that is, the role of loaded metal on TiO_2 surface is the expedition of electron transfer from TiO_2 conduction band to outer system.

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