Photocatalytic Degradation of 2-Propanol Diluted in Water with TiO_2 Photocatalyst Loaded on Si_3N_4

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TiO_2 photocatalysts loaded on Si_3N_4 (TiO_2/Si_3N_4) prepared by an impregnation method showed higher photocatalytic activity for the degradation of 2-propanol diluted in water than TiO_2 loaded on SiO_2 (TiO_2/SiO_2). The formation of well-crystallized TiO_2 on Si_3N_4 and the hydrophobic property of Si_3N_4 were found to be related to the efficient photocatalytic activity of TiO_2/Si_3N_4.

The design of highly efficient photocatalytic systems which work for the reduction of global atmospheric pollution and the purification of polluted water is of vital interest and one of the most desirable yet challenging goals in the research of environmentally-friendly catalysts. TiO_2 semiconductor photocatalysts are known as one of the most stable and highly active catalysts. Also the utilization of extremely small TiO_2 particles as photocatalysts has recently attracted a great deal of attention, especially for such environmental applications.[1–5] On the other hand, Si_3N_4 has high mechanical strength and is easy to be molded into a filter.[6] Although it may be a useful support for photocatalysts used in liquid phase, there have been no reports on the properties of TiO_2 photocatalysts loaded on Si_3N_4. In the present study, we deal with the preparation and characterization of TiO_2 photocatalysts loaded on Si_3N_4 and carried out its successful utilization for the photocatalytic degradation of 2-propanol diluted in water. Moreover, the advantages of Si_3N_4 as the support for TiO_2 photocatalysts have been clarified.

Powders of α-Si_3N_4 (Ube-Ind. Co., surface area: $11\,m^2g^{-1}$) and SiO_2 (Aerosil Co., $287\,m^2g^{-1}$) were used as catalyst supports. TiO_2/Si_3N_4 (10 wt % as TiO_2) was prepared by an impregnation method, as follows: Si_3N_4 was impregnated with an aqueous solution of $(NH_4)_2[TiO(C_2O_4)_2]2H_2O$ at 323 K, and then evaporated at 343 K. The obtained sample was dried at 373 K for 12 h and then calcined in air at 773 K for 5 h. TiO_2/SiO_2 (10 wt % as TiO_2) was also prepared by the same method. The XANES spectra were obtained in the fluorescence mode at the BL-9A facility of the Photon Factory at the National Laboratory for High Energy Physics, Tsukuba. The photocatalyst (50 mg) was transferred into a quartz cell with an aqueous solution of 2-propanol ($2.6 \times 10^{-3}\,mol\,dm^{-3}$, 25 mL). Prior to UV irradiation, the suspension was stirred for 1 h under dark conditions. The sample was then irradiated at 295 K using UV light ($\lambda > 250\,nm$) from a 100 W high-pressure Hg lamp with continuous stirring under O_2 atmosphere in the system. The products were analyzed by gas chromatography.

Figure 1 shows the reaction time profiles of the liquid-phase photocatalytic reaction on the TiO_2/Si_3N_4 photocatalyst. In the initial stage of the reaction under dark conditions, the adsorption of 2-propanol onto the photocatalysts can be observed. The amount of adsorbed 2-propanol observed on Si_3N_4 support was 1.8 times (normalized by weight of support) and 45 times (normalized by surface area of support) larger than those of SiO_2 support. When UV light is turned on, 2-propanol is decomposed into acetone, CO_2 and H_2O, and finally, acetone is also decomposed into CO_2 and H_2O.

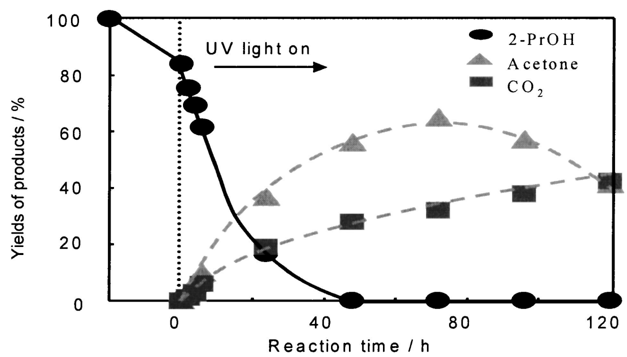

Figure 1. Photocatalytic degradation of 2-PrOH on the TiO_2/Si_3N_4 photocatalyst.

Figure 2 shows the photocatalytic activities for the degradation of 2-propanol diluted in water and the saturated amount of H_2O adsorption at 298 K observed on both the TiO_2/Si_3N_4 and TiO_2/SiO_2 photocatalysts. These activities are the averaged values observed for the initial stage by 50% conversion of 2-propanol. TiO_2/Si_3N_4 clearly exhibits higher photocatalytic activity than TiO_2/SiO_2. The amount of H_2O adsorption on TiO_2/Si_3N_4 is much smaller than TiO_2/SiO_2, suggesting that the hydrophobic property of TiO_2/Si_3N_4 is one of the most important factors in the efficient photocatalytic activity for the liquid phase reaction.[4–7] These results indicate that TiO_2/Si_3N_4 photocatalyst is

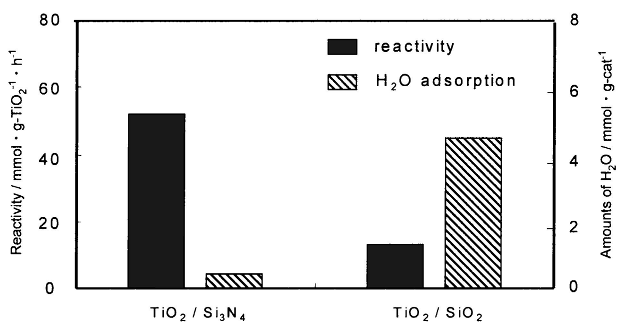

Figure 2. Photocatalytic activity for the degradation of 2-PrOH and the saturated amount of H_2O adsorption at 298 K observed on the TiO_2/Si_3N_4 and TiO_2/SiO_2 photocatalysts.

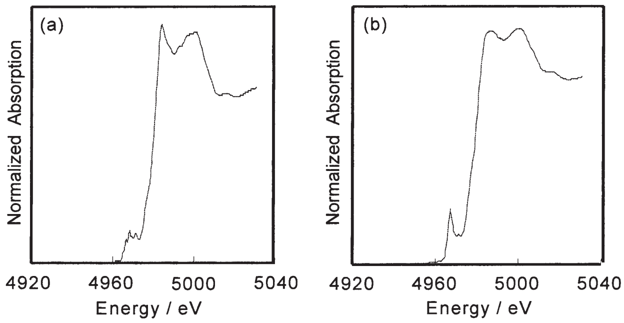

Figure 3. XANES spectra of TiO_2/Si_3N_4 (a) and TiO_2/SiO_2 (b) photocatalysts.

more effective for the degradation of organic compounds diluted in water than the TiO_2/SiO_2 photocatalyst.

In the XRD analysis, both the TiO_2/Si_3N_4 and TiO_2/SiO_2 photocatalysts calcined at 773 K exhibited no peak due to the crystallized phases, indicating that the TiO_2 species exist in an amorphous phase or as ultrafine particles. Figure 3 shows the XANES spectra of TiO_2/Si_3N_4 and TiO_2/SiO_2. The spectra at the Ti K-edge shows several well-defined preedge peaks which are related to the local structure surrounding the Ti atom. The relative intensities of these preedge peaks provide useful information on the coordination number of the Ti atom.[7–9] TiO_2/Si_3N_4 has three small well-defined preedge peaks which can be assigned to the presence of the anatase TiO_2 species (octahedral coordination) with high crystallinity. On the other hand, TiO_2/SiO_2 has only one intense peak, indicating the presence of amorphous TiO_2 species or tetrahedral coordinated titanium oxide species. These results indicate that the titanium oxide species can be crystallized easily to form anatase TiO_2 ultrafine particles on the support of hydrophobic Si_3N_4.

In summary, it has been found that TiO_2/Si_3N_4 exhibits high photocatalytic activity for the degradation of organic compounds diluted in water due to the hydrophobic property of the Si_3N_4 support and the higher crystallinity of the TiO_2 photocatalyst. Since Si_3N_4 is mechanically strong enough to be used as a filter for water purification, it is a good candidate for the support of TiO_2 photocatalysts used in liquid phase reactions.

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