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Photocatalytic degradation of hexachlorocyclohexane (HCH) by TiO_2-pillared fluorine mica

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A significant effect of clay host was observed on the photocatalytic activity of TiO_2; TiO_2-pillared fluorine mica exhibited two orders of magnitude higher activity than TiO_2 and TiO_2-pillared montmorillonite for the photocatalytic degradation of γ-HCH.

Persistent organic pollutants (POPs), including hexachlorocyclohexanes (HCHs), polychlorinated biphenyls (PCBs) and DDT, are long-lived organic compounds.[1] The atmospheric half-live of γ-HCH, for example, was reported to be 2.2–7.3 years.[2] POPs become concentrated as they move through the food chains, and they have toxic effects on animal reproduction, development, and immunological function. Although their use is restricted or banned in many developed countries, POPs are still widely used in developing countries. It is well known that POPs are transportable widely through the atmosphere and the ocean and eventually contaminate all over the world at very low levels of concentration.[1–3] Since normal methods of water treatment are not completely effective in removing these pollutants, it is necessary to develop novel technologies to deal with them. The use of semiconductor photocatalysis is a promising technique for the degradation of environmental pollutants.[4]The complete mineralisation of a variety of aliphatic and aromatic chlorinated hydrocarbons *via* heterogeneous photooxidation on TiO_2 has been reported.[4,5] In general, POPs are highly hydrophobic, and hence they will not be adsorbed on the hydrophilic surface of TiO_2 in aqueous solution. To improve the degradation rate of hydrophobic pollutants, it is desired to design photocatalysts that will adsorb and concentrate the reactants but still allow their diffusion from the adsorption site to the TiO_2 surface.[6] TiO_2-pillared clays have large surface area and pore volume, which will be beneficial for organic compounds to reach and leave the active sites on the surface.[7–9] However, to the best of our knowledge there have been no successful reports demonstrating a significant improvement of photocatalytic efficiency of TiO_2 by including it in the silicate layer of the clays. Here we demonstrate that TiO_2-pillared fluorine mica, which should have hydrophobic interlayer space, is a significantly effective photocatalyst for the degradation of γ-HCH in aqueous solution.

TiO_2 employed for the reaction study was well characterized Degussa P25 (70% anatase, BET surface area = 50 ± 10 m^2 g^{-1}, average particle size = 30 nm). A silica-supported TiO_2 catalyst (TiO_2 /SiO_2) was prepared by impregnating silica (Cab-O-Sil) with an aqueous solution of ammonium titanyl oxalate, followed by evaporation to dryness at 395 K and by calcination in air at 773 K for 4 h. TiO_2-pillared fluorine mica (TiO_2-mica) and TiO_2-pillared montmorillonite (TiO_2-mont) were prepared according to our previous reports.[10–12] XRD patterns of TiO_2-pillared clays showed the typical low angle reflections (001) at around d_{001} = 2.102.45 nm, which were *ca.* 1 nm larger than the d_{001} value of corresponding raw clays, and a broad and very weak anatase (101) diffraction peak (2θ = 25.3°). The crystallite size of TiO_2 pillars determined from line broadening of the anatase peak was around 3 nm. Pore diameter calculated form N_2 adsorption data was 4.2 nm for all the TiO_2-pillared clays. UV-Vis spectrum of the raw mica showed that this material was transparent to UV. Ti K-edge EXAFS and XANES results showed that the local structure of TiO_2 species in different clays is almost the same and is similar to that of anatase.[12]

The photoreactor was a cylindrical flask (500 cm^3) made of quartz. Because of the low solubility of γ-HCH in water, γ-HCH was initially dissolved in acetonitrile and then diluted with water (300 cm^3). The reaction mixture containing γ-HCH (1 ppm), acetonitrile (1%) and the catalyst (0.1 g) was stirred by magnetic stirrer at 303 K in air, and irradiated from the side with a 500 W Xe lamp (Ushio SX-UI500XQ). The concentration of γ-HCH was analyzed by GC-MS equipped with a capillary column DB5ms, and 9-bromoanthracene was used as an internal standard. The reaction solution withdrawn at intervals was extracted with *n*-hexane before GC-MS analysis.

When the reaction mixture containing TiO_2-mica catalyst was stirred in the dark for 24 h, or when the γ-HCH solution was illuminated in the absence of the catalyst for 24 h there was only a slight decrease in γ-HCH concentration (Fig. 1). In the presence of illuminated TiO_2-mica, γ-HCH was 63% degraded in 30 min and 100% degraded in 5 h. In this reaction system, the concentration of Cl^- ion increased as the reaction time passed, and 96% of chlorine was recovered as Cl^- ion after 10 h of irradiation. GC-MS analysis showed no formation of intermediate products in the aqueous phase. From these results, it is shown that γ-HCH was almost completely decomposed by the photocatalysis of TiO_2-mica. The effect of chloride ions on γ-HCH degradation with TiO_2-mica was not significant; in the presence of 200 ppm Cl^- ion as NaCl in the solution γ-HCH was 71% degraded in 30 min and 100% degraded in 7 h. In addition, the photocatalytic efficiency of TiO_2-mica was hardly decreased when a Pyrex reactor was used instead of a quartz reactor.

For a comparison the activity of naked TiO_2 as a conventional photocatalyst was also tested. Unlike most of the organic

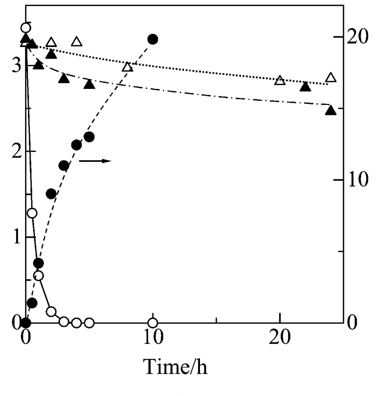

Fig. 1 Photodegradation of γ-HCH (○) and formation of Cl^- ion (●) in the presence of TiO_2-mica. Open triangles and filled triangles correspond to photodegradation of γ-HCH in the absence of the catalyst and adsorption of γ-HCH on TiO_2-mica in dark, respectively.

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Table 1 Characterization results and γ-HCH degradation rates of various photocatalysts

Catalysts	S_{BET}[a]/$m^2\ g^{-1}$	$S_{\mathrm{TiO_2}}$[b]/$m^2\ g^{-1}$	γ-$\mathrm{HCH_{ad}}$ [c]/μmol g^{-1}	Rate/μmol $h^{-1}\ g^{-1}$	Specific activity[e]/nmol $h^{-1}\ m^{-2}$-TiO_2
TiO_2	50	50	0	0.22	4.4
TiO_2(34)[f]-mica	334	23	3.3	17.3[d]	752
TiO_2(20)[f]/SiO_2	126	40	0	0.27	6.7
TiO_2(32)[f]-mont	219	34	0	0.10	2.9

[a] BET surface area measured by N_2 adsorption-desorption at liquid N_2 temperature. [b] Accessible surface area of TiO_2 estimated from benzaldehyde-NH_3 titration..[13,14] [c] Amount of adsorbed γ-HCH per gram of the catalyst after 24 h in dark. [d] The amount of TiO_2-mica used was 0.01 g. [e] The specific activity represents the rate of degradation per unit area of TiO_2 in the catalyst. [f] TiO_2 content (wt.%) determined by elemental analysis using X-ray fluorescence spectroscopy.

pollutants, γ-HCH was found to be stable under the conventional photocatalytic condition; only 31% of γ-HCH was degraded in 24 h in the presence of illuminated TiO_2. It is noteworthy that the photocatalytic efficiency was greatly depended on the type of clay host; the activity of TiO_2-mica was significantly higher than that of TiO_2-mont. The initial rates of γ-HCH decomposition with various TiO_2-containing photocatalysts are summarised in Table 1. TiO_2-mica showed two orders of magnitude higher rate than TiO_2, TiO_2/SiO_2 and TiO_2-pillared montmorillonite. We estimated the accessible surface area of TiO_2 particles on each TiO_2-containing catalysts by benzaldehyde-NH_3 titration[9,13,14] and calculated the specific activity of each catalyst (Table 1). The result shows that TiO_2-mica showed two orders of magnitude higher specific activity than the other catalysts, which confirms that the high efficiency of TiO_2-mica is not due to the high surface area of TiO_2 particles. Taking into account our previous results that the structures of TiO_2 species in different TiO_2-pillared clays are very close to each other and similar to that of anatase,[12]the reaction results indicate that the activity of the present reaction depends strongly on the nature of the clay host.

For each catalyst the dark adsorption experiment of γ-HCH was carried at room temperature for 24 h. As listed in Table 1, γ-HCH was adsorbed only on TiO_2-mica in the dark. The expandable fluorine mica[15] used as a host material has similar properties to swellable clays such as montmorillonite. The most remarkable difference between these clays is their composition.[11] For montmorillonite, a OH^- ion coordinated to Al^{3+} in octahedral site is present at hexagonal cavities consisting of corner-linked SiO_4 tetrahedra. Hence, the interlayer surface of TiO_2-pillared montmorillonite should be rather hydrophilic because of the hydrogen-bonding character of the hydroxy groups on the surface. For fluorine mica, in contrast, most of the OH^- ions present at the hexagonal cavities are substituted by F^- ions. The interlayer surface of TiO_2-pillared mica should be less hydrophilic than that of TiO_2-pillared montmorillonite, and thus, nonpolar substrates, such as γ-HCH, would be more accessible to the hydrophobic silicate layer of TiO_2-mica. It is known that the surface of TiO_2 and SiO_2 also exhibit hydrophilic natures originating from the surface hydroxy groups. This feature could explain the lower activity of naked TiO_2 and TiO_2/SiO_2 than TiO_2-pillared mica.

In conclusion, the activity of TiO_2 photocatalysts for the degradation of γ-HCH is significantly improved by including TiO_2 particles in the interlayer of fluorine mica. The positive effect of mica can be due to a concentration of hydrophobic reactant, γ-HCH, in the interlayer surface. Further work is under way to show the effectiveness of TiO_2-pillared mica for the photocatalytic decomposition of other hydrophobic organic pollutant.

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