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TiO_2–montmorillonite composites *via* supercritical intercalation†

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The successful preparation of TiO_2–montmorillonite mesoporous composites using intercalation of titanium isopropoxide dissolved in supercritical carbon dioxide involved ion exchange of interlayer cations by hydrophobic cations.

TiO_2 has attracted significant attention as a potential photocatalyst in the decomposition of toxic chemicals. TiO_2 composites with porous materials are believed to favour adsorption of some pollutants. Structural design of porous matrices and control of TiO_2 dispersions are important factors in improving the process performance. Higher photocatalytic activity is expected when the TiO_2 is nano-crystalline since then a larger energy band-gap is induced by size quantization effects.[1]

We have developed a new strategy for preparing such composites. The method involves impregnation of titanium alkoxide dissolved in supercritical carbon dioxide ($scCO_2$) followed by hydrolysis of the alkoxide with adsorbed water (or hydroxy groups) in the matrix. The low viscosity and high diffusivity of the supercritical fluid is effective in transporting compounds into small pores.[2] The solubility of titanium alkoxide in $scCO_2$ as a function of pressure is easily controlled in the range from 0.1 wt% to homogeneous mixtures of any desired composition.[3] The hydrophobic properties of $scCO_2$ would restrict the hydrolysis of titanium alkoxide during impregnation and the formation of TiO_2 would be limited to sites of higher moisture content, reflecting the matrix structure. Hence this method yields an advantageous microstructural design and higher dispersion of TiO_2. We have previously demonstrated that preparation of transparent SiO_2–TiO_2 aerogel monoliths is possible.[3,4]

Here we present the preparation of TiO_2–montmorillonite composites using this strategy, *i.e.*, hydrolysis of titanium isopropoxide (TiP) by water adsorbed in the interlayers. Intercalation of colloidal titania into interlayered clay compounds by an ion-exchange mechanism has successfully resulted in high performance photocatalysts.[5,6] Intercalation under $scCO_2$ conditions has already been reported using a dye and montmorillonite. This work demonstrated a higher uptake of the dye into montmorillonite than that in organic solvents.[7] We expected TiP hydrolysis could be controlled in the interlayer space and that the TiO_2 particles would be highly dispersed. Because control of interlayer space has been studied using various pillar compounds, our method has the potential to be a new and useful procedure for designing nanostructures of metal oxide pillared clays.

Na-montmorillonite (MNT, Kunimine Industrials Co. Ltd) was previously washed and swelled by soaking in double distilled water. Tetramethylammonium (C_1TMA) and octadecyltrimethylammonium (C_{18}TMA) ions were selected for control of interlayer space. The interlayer sodium cations were ion-exchanged with the C_1- or C_{18}TMA ions in aqueous solution using a stoichiometric amount of their chloride salts to MNT cation exchange capacity (119 mequiv/100 g). Ion-exchanged samples (C_1TMA–MNT and C_{18}TMA–MNT) were washed until chloride was undetectable in the washing water ($AgNO_3$) and then dried at 333 K. MNT without ion exchange was also prepared by a similar procedure.

Supercritical intercalation was performed using a flow type $scCO_2$ extraction/impregnation system.[4] The apparatus consisted of a high pressure CO_2 pump, a pressurizing vessel (50 cm^3) for the saturation of TiP (10 cm^3 of TiP was introduced under dry conditions) and a pressurizing vessel (1 cm^3) for intercalation (0.2 g of samples were packed) and a back pressure regulator. The temperature of the vessels, pressure in the system and the flow rate of the pump (for liquid CO_2 at 263 K) was fixed at 353 K, 8 MPa and 2 cm^3 min^{-1}. C_1TMA–MNT, C_{18}TMA–MNT and the MNT samples were first washed with pure $scCO_2$ for 5 min. The saturator was connected to the flow line and the samples exposed to the TiP saturated $scCO_2$ for 15 min under the same conditions. Under these conditions, the TiP content of the $scCO_2$ was measured prior to the intercalation, and was *ca.* 0.4 wt%. The saturator was then separated from the flow line again and the sample was washed with fresh $scCO_2$ for 15 min. The $scCO_2$ treated sample was exposed to room air. MNT without ion exchange was more sticky than the other samples at this stage. Yellowish-grey colored samples were obtained after calcination at 823 K for 6 h in air. Final samples are denoted Ti–C_1TMA–MNT, Ti–C_{18}TMA–MNT and Ti–MNT.

The basal spacing of MNT, C_1TMA–MNT and C_{18}TMA–MNT determined from X-ray diffraction analysis of the (100) layered structures (XRD, Rigaku RAX). was 1.22, 1.39 and 2.06 nm, respectively (including MNT layer thickness of 0.96 nm). The XRD peak of the TiP-treated samples before calcination was broadened, however with retention of peak position. Since the (100) XRD peak was not influenced after pure $scCO_2$ treatment under the same conditions, the peak broadening was assumed to be caused by TiP intercalation. The layered structure of calcined samples could not be revealed by XRD analysis.

The titanium contents of the Ti–MNT, Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT samples were determined by inductively coupled plasma spectrometry after dissolving the sample into an aqueous solution of hydrogen fluoride and were 19.7, 12.5 and 28.1 wt%, respectively. This result indicated that the interlayer space did not directly determine the TiO_2 content. XRD patterns of calcined samples were similar to those of previously reported titania-pillared montmorillonite[6] and all samples were shown to contain anatase crystals. Their crystalline sizes, calculated from the (101) diffraction peak using the Scherrer equation, were 14–21 nm. UV–VIS analysis, however, revealed the existence of smaller anatase crystallites in Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT. Fig. 1(a) shows their UV–VIS diffuse reflectance spectra compared to conventional anatase powders having a mean particle diameter of 40 nm (PT-2, Fuji Titan Co. Ltd.). Since montmorillonite is almost transparent in this wavelength region, the adsorption edge of anatase could be observed. In order to clarify the position of adsorption edge Fig. 1(b) shows the differential spectra of those shown in Fig. 1(a). The adsorption edges of Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT samples were blue-shifted compared to PT-2, whereas

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† Electronic supplementary information (ESI) available: Figs. S1 and S2: powder XRD patterns. See http://www.rsc.org/suppdata/cc/b2/b202589b/

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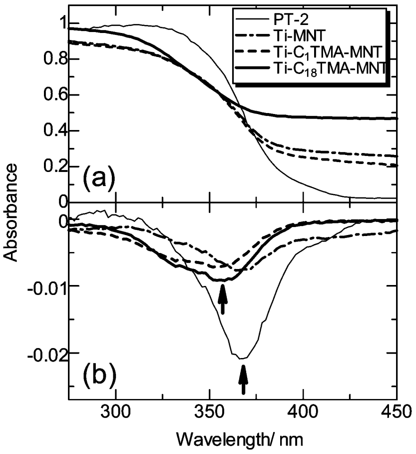

Fig. 1 UV–VIS diffuse reflectance spectra (a) and differential spectra (b) of Ti–MNT, Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT with PT-2 (anatase, mean diameter 40 nm).

that of Ti–MNT sample showed almost the same peak position as PT-2. The blue-shift seems to be caused by a quantum-size effect also seen in anatase crystals of diameters < 10 nm. These results seem to indicate that alkylammonium cations in the interlayers can promote the formation of nano-sized anatase.

Fig. 2 shows TEM (JEOL, JEM 2000FX2) photographs of Ti–C_{18}TMA–MNT samples. An aggregation of anatase particles (diameter 5–20 nm) is seen to be expanding the interlayer space ((a) in Fig. 2). Ordered nanosized particles between the MNT layers, as seen in (b) in Fig. 2, were also observed. TiO_2 aggregates located in the large spaces between the ‘card-house’ structures of the MNT were also observed in all samples. The TiO_2 distribution in the interlayer spaces increased in the following order: Ti–MNT < Ti–C_1TMA–MNT < Ti–C_{18}TMA–MNT.

Fig. 3 shows the nitrogen adsorption–desorption isotherms of the samples at 77 K evaluated using an adsorption analyzer (Belsorp 28, Nippon Bell Co. Ltd.). MNT and Ti–MNT samples showed isotherms similar to the IUPAC type III isotherm,[8] known to characterize non-porous structures. Both Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT showed a much larger nitrogen adsorption capacity. Their isotherms were similar to the IUPAC type IV with adsorption hysteresis (H3) indicating slit type mesoporous structure.[8] The pore size diameter calculated using the D–H method[9] was *ca*. 4 nm for both Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT. It seems reasonable to assign these mesopores to the interlayer space pillared by TiO_2. The development of microporosity in Ti–C_{18}TMA–MNT, as observed in isotherms at low relative pressure, probably originates from interlayer expansion by C_{18}TMA ions.

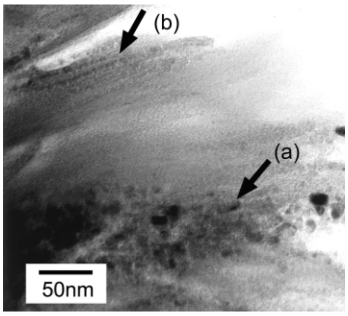

Fig. 2 TEM images of Ti–C_{18}TMA–MNT.

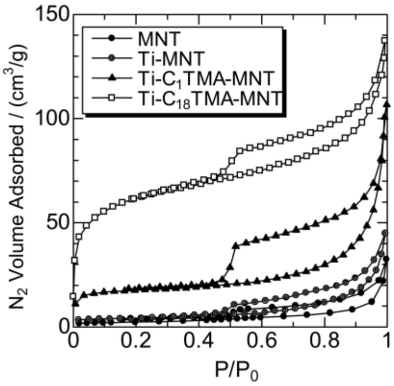

Fig. 3 Adsorption–desorption isotherms for nitrogen on MNT, Ti–MNT, Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT.

We conclude that the key to successful supercritical intercalation is the control of interlayer properties. Diffusion of non-polar TiP into the charged interlayer spaces of MNT seems to be limited and hydrolysis of TiP occurs outside the layered structure for example, in the space between the ‘card house’ structures. Ion exchange of the interlayer cations by alkylammonium ions would partially quench the hydrophilic nature of the interlayer space causing it to show increased affinity towards TiP. Both Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT allow more TiP into the interlayer space than MNT. Consequently, the ratio of interlayered TiO_2 to that located outside the layered structure would be larger in Ti–C_1TMA–MNT and Ti–C_{18}TMA–MNT than in Ti–MNT. Development of mesoporosity in these samples would be caused by the growth of TiO_2 particles. The growth of the interlayer TiO_2 particle size is considered to be restricted compared to that of free TiO_2 particles. The TiO_2 particle size and pore size were not well controlled at the present stage, revealing that controlled delamination during intercalation will be important in designing ordered microstructures.

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