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Synthesis and Photocatalytic Activity of Lamellar Titanium Oxide Formed by Surfactant Bilayer Templating

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Increasing attention has been focused on surfactant-mediated mesoporous materials since Mobil's scientists succeeded in the synthesis of a novel mesoporous silicate called MCM-41,[1] which exhibits highly organized hexagonal packing of cyrindrical channels of 10−100 Å in diameter. A variety of investigations has been carried out for MCM-41 on its preparative techniques,[1,2] as well as modification of its oxide framework and applications such as catalysts.[3−7] However, previous studies on MCM-41 analogues with transition metal oxide frameworks have been mostly limited to synthesis of the hexagonal mesophase.[8] Although syntheses and photocatalytic properties of silicate MCM-41 incorporating crystalline TiO_2 in its channels[9] or with a Ti-doped framework[10] have been previously reported, there has been no report on the photocatalytic activity of a transition metal oxide mesophase synthesized by liquid crystal templating of surfactant micelles. Moreover, despite a number of intensive attempts, no evidence of crystallization of the oxide framework has been presented for MCM-41 itself nor for its transition metal analogues. Here we report that a lamellar mesophase of titanium oxide intercalating surfactant bilayers acquires a photocatalytic activity via crystallization of its oxide framework by hydrothermal post-treatment.

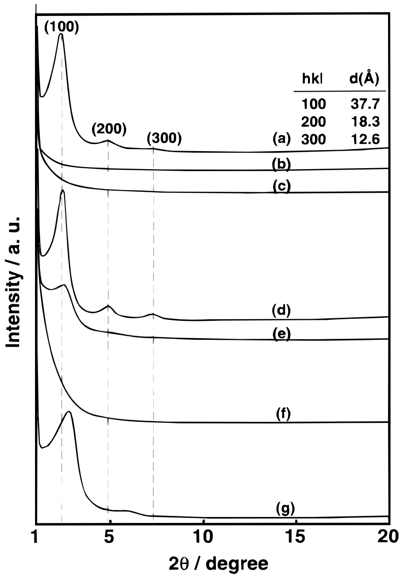

Figure 1. XRD profiles of precipitates obtained from $TiCl_4$ aqueous solutions in the presence of (a) $C_{12}PO$, (b) no surfactant molecules, and (c) $C_{16}TMA$ and after further hydrothermal treatment of the sample with $C_{12}PO$ at (d) 120 °C, (e) 150 °C, and (f) 180 °C for 24 h. The profile of d after photocatalysis is also shown as g.

Sodium dodecyl phosphate ($C_{12}PO$) and cetyltrimethylammonium bromide ($C_{16}TMA$) were employed as anionic and cationic surfactants, respectively. On mixing aqueous solutions of 0.2 mol/dm^3 surfactant and 0.2 mol/dm^3 $TiCl_4$, a white precipitate immediately formed. The molar ratio of the surfactant:$TiCl_4$:H_2O was 1:1:556. The reaction mixture was then neutralized by adding dropwise a 28 wt % NH_4OH aqueous solution. As shown in Figure 1a, an as-synthesized product obtained with $C_{12}PO$ showed a series of XRD peaks in good order at *d* spacings of 37.7, 18.3, and 12.6 Å, which is characteristic of the MCM-41-related lamellar mesophase templated by surfactant bilayer micelles.[1,2] No peak was observed at $2\theta > 10°$, excluding any ordinary crystalline phases of the surfactant or titanium species. On the other hand, a product obtained with $C_{16}TMA$ and that with no surfactant showed no peaks at all, as seen in Figure 1b,c. The largest *d* spacing evaluated from Figure 1a was just 1.7 Å larger than twice the length of the $C_{12}PO$ molecule. This strongly suggests that the product obtained with $C_{12}PO$ is a lamellar mesophase composed of $C_{12}PO$ bilayers (with some tilting in the molecule axis) and thin titanium oxide sheets. Since previously reported metal oxide mesophases all appear to be amorphous, we further carried out hydrothermal post-treatment in an autoclave. As shown in Figure 1d, three peaks in the XRD profile stayed at the same positions even after the hydrothermal treatment (HT) at 120 °C for 24 h, but the lines became much sharper. Nevertheless, the diffraction lines broadened with decreasing the *d* spacing to 35.0 Å after HT at 150 °C to the contrary, and finally, the XRD peaks completely disappeared after HT at 180 °C, as shown in Figure 1e,f. Because an oily substance was found on the surface of the reaction mixture after HT at 150 and 180 °C, $C_{12}PO$ would, at least partially, decompose via HT at ≥150 °C.

The TEM observation clearly confirmed that the product after HT at 120 °C, which showed the most distinct XRD pattern, exhibits a layered image as presented in Figure 2. An EDX

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(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) (a) Beck, J. S.; Vartuli, J. C.; Roth, W.; Leonowicz, J. M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834. (b) Vartuli, J. C.; Kresge, C. T.; Leonowicz, M. E.; Chu, A. S.; McCullen, S. B.; Johnson, I. D.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2070. (c) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2317. (d) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147. (e) Zhang, J.; Luz, Zeev, Goldfarb, D. *J. Phys. Chem. B* **1997**, *101*, 7087.

(3) (a) Corma, A.; Navarro, M. T.; Pariente, J. P. *J. Chem. Soc., Chem. Commun.* **1994**, 147. (b) Reddy, K. M.; Moudrakovski, I.; Sayari, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1059. (c) Fu, G.; Fyfe, C. A.; Schwieger, W.; Kokotailo, G. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1499. (d) Zhao, D. Y.; Goldfarb, D. *J. Chem. Soc., Chem. Commun.* **1995**, 875. (e) Yuan, Z. Y.; Liu, S. Q.; Chen, T. H.; Wang, J. Z.; Li, H. X. *J. Chem. Soc., Chem. Commun.* **1995**, 973.

(4) (a) Junges, U.; Jacobs, W.; Martin, I. V.; Krutzsch, B.; Schuth, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2283. (b) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.

(5) (a) Tanev, P. T.; Chibwe, M.; Pinnavair, T. J. *Nature* **1994**, *368*, 321. (b) Armengol, E.; Cano, M. L.; Corma, A.; Garcia, H.; Navarro, M. T. *J. Chem. Soc., Chem. Commun.* **1995**, 519. (c) Kloetstra, K. R.; Bekkum, H. V. *J. Chem. Soc., Chem. Commun.* **1995**, 1005. (d) Maschmeyer, T.; Ray, F.; Sankar, G.; Thomas, J. M. *Nature* **1995**, *378*, 159. (e) Corma, A.; Grande, M. S.; Gonzalez-Alfaro, V.; Orchilles, A. V. *J. Catal.* **1996**, *159*, 375. (f) Climent, M. J.; Corma, A.; Iborra, S.; Navarro, M. C.; Primo, J. *J. Catal.* **1996**, *161*, 783. (g) Mokaya, R.; William, J. *J. Catal.* **1997**, *172*, 211.

(6) (a) Morishige, K.; Fujii, H.; Uga, M.; Kinukawa, D. *Langmuir* **1997**, *13*, 3494. (b) Ravikovitch. P.-I.; Odomhnaill, S.-C.; Neimark, A.-V.; Schuth, F. *Langmuir* **1995**, *11*, 4765.

(7) (a) Wu, C.-G.; Bein, T. *Science* **1994**, *264*, 1757. (b) Wu, C.-G.; Bein, T. *Science* **1994**, 266, 1013. (c) Huber, C.; Moller, K.; Bein, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2619.

(8) (a) Ciesla, U.; Demuth, D.; Leon, R.; Petroff, P.; Stucky, G.; Unger, K.; Schuth, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1387. (b) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2014. (c) Luca, V.; MacLachlan, D. J.; Hook, J. M.; Withers, R. *Chem. Mater.* **1995**, *7*, 2220. (d) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 426. (e) Antonelli, D. M.; Nakahira, A.; Ying, J. Y. *Inorg. Chem.* **1996**, *35*, 3126. (f) Yada, M.; Machida, M.; Kijima, T. *J. Chem. Soc., Chem. Commun.* **1996**, 769.

(9) Xu, Y.; Langfprd, C. H. *J. Phys. Chem. B* **1997**, *101*, 3115.

(10) Zhang, S. G.; Fujii, Y.; Yamashita, H.; Koyano, K.; Tatsumi, T.; Anpo, M. *Chem. Lett.* **1997**, 659.

S0002-7863(98)00430-2 CCC: $15.00

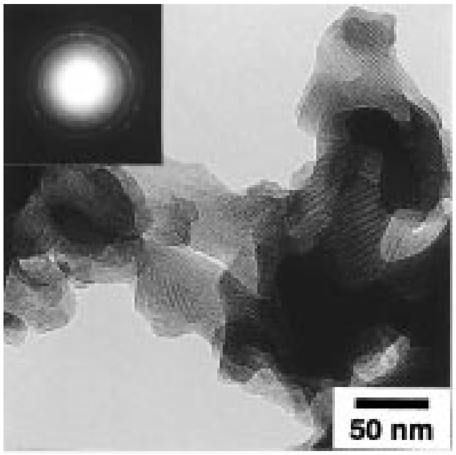

Figure 2. TEM image of lamellar titanium oxide obtained in the presence of $C_{12}PO$ after hydrothermal treatment at 120 °C. The inset shows an electron diffraction pattern of the sample.

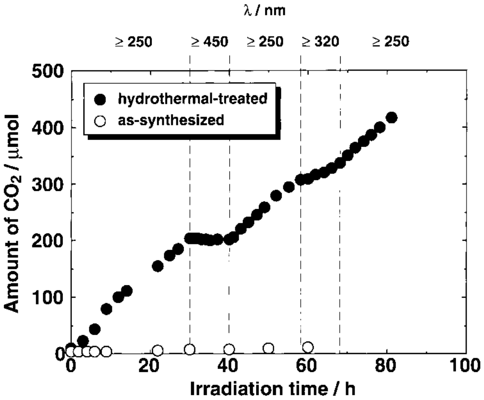

Figure 3. Reaction time courses of the CO_2 evolution from the lamellar titanium oxide suspended in distilled water under light irradiation with various cutoff wavelengths.

analysis revealed that a large amount of Ti and P coexists in the sample at almost the same molar ratio. Moreover, an FT-IR spectrum of this product showed characteristic absorptions due to the CH_2 and CH_3 groups and the P–O and P=O bonds in $C_{12}PO$. Since the *d* spacings of the sample also remained the same even after HT at 120 °C, $C_{12}PO$ is considered to be intact in the mesophase, and hence, the layered image in Figure 2 is attributed to the lamellar nanostructure comprised by thin sheets of titanium oxide and the $C_{12}PO$ bilayers. The thickness of the titanium oxide sheets estimated from the TEM images was ca. 9 Å, being almost the same as that of silicate sheets of lamellar nanocomposites reported by Ogawa.[11] Noteworthily, an electron diffraction pattern of the sample exhibited the Debye–Scherrer rings consisting of a number of small spots as shown in the inset of Figure 2. The diffraction ring pattern and the *d* spacings correspond well to those of the powder XRD profile of rutile-type TiO_2. This is demonstrative of crystallization of the thin titanium oxide sheets into the rutile form. However, no peak was found in the XRD study for the higher angle region, presumably because the size of crystallites is too small.

Crystalline TiO_2 is known to exhibit high activities for photocatalytic decomposition of various surfactants.[12] We hence irradiated the samples suspended in distilled water with a 500-W xenon lamp, monitoring gaseous CO_2. As depicted in Figure 3, whereas virtually no CO_2 evolution was observed for the as-synthesized sample, CO_2 linearly evolved at a rate of 6.9 μmol/h for the sample after HT at 120 °C. This CO_2 evolution should be ascribed to decomposition of $C_{12}PO$, which is the only organic species in the sample. Although the total amount of evolved CO_2 during the irradiation for 80 h corresponds to only 5–6% of total organic carbon in the sample, the XRD profile of the sample was broadened and shifted slightly to the higher angles after the irradiation as shown in Figure 1g. This also confirms that the CO_2 evolution resulted from the surfactant between the layers but not from those at the oxide surfaces or in the outer aqueous phase.

These facts conclude that the light-driven CO_2 evolution should be attributed to photocatalysis induced by a semiconducting nature of the thin titanium oxide sheets having been crystallized. A further confirmation would be drawn from Figure 3. It clearly shows that the decomposition of $C_{12}PO$ does not proceed under light irradiation of $\lambda \geq 450$ nm, whereas shielding the irradiation of $\lambda \leqslant 320$ nm little affects the reaction. This effective window of $320 \text{ nm} \leqslant \lambda \leqslant 450$ nm excellently agrees to the absorption edge of typical crystalline TiO_2. Actually, diffuse reflectance UV measurements followed by the Kubelka–Munk transform and the Tauc plotting for semiconductors with the direct transitions[13] $[(\alpha h\nu)^2$ vs $h\nu]$ revealed that the HT sample has a band gap energy of 3.40 eV (365 nm), while that of conventional crystalline TiO_2 (Aerosil P-25) falls at 3.17 eV (390 nm). The considerably larger band gap of the lamellar TiO_2 is probably due to electron confinement within the thin oxide sheet. Significantly, the band gap energy of the sample before HT was 3.42 eV, the energy becoming 0.02 eV smaller via HT. Furthermore, also the gradient of the Tauc plots was the steepest with almost no tailing for the HT sample. These results are also indicative of the development of the band structure of the lamellar TiO_2 via HT. Further investigations on chemical and structural properties, high-resolution TEM lattice images, and details of photocatalytic activities are now in progress.

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[11] Ogawa, M. *J. Am. Chem. Soc.* **1994**, *116*, 7941.

[12] (a) Hidaka, H.; Zhao, J.; Pelizzetti, E.; Serpone, N. *J. Phys. Chem.* **1992**, *96*, 2226. (b) Fujii, H.; Sato, H.; Ohtaki, M.; Eguchi, K.; Arai, H. *Chem. Lett.* **1998**, 251.

[13] Wang, Y.; Suna, A.; Mahler, M.; Kasowski, R. *J. Chem. Phys.* **1987**, *87*, 7315.