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Non-Silica-Based Mesostructured Materials. 1. Synthesis of Vanadium Oxide-Based Materials

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The invention of a new family of silica-based mesoporous materials, designated as MCM-41, has expanded the range of molecular-sieve (<1.3 nm) materials into the very large pore (2 - 10 nm) regime.[1−5] Although several synthesis mechanisms of MCM-41 have been proposed,[1−4] it is widely accepted that the materials are synthesized by the cooperative assembly of periodic inorganic and surfactant-based structures ("templating"). If the synthetic approach can be employed to synthesize new types of nanocomposite materials of transition-metal oxides, the resulting materials might have applications in many areas such as high surface area catalysts,[6] hosts for inclusion compounds,[7] and electrochemical devices.[8] Indeed, Ciesla et al. have attempted the synthesis of mesostructured materials of WO_3, MoO_3, FeO, and PbO.[9,10] Each material obtained, however, has contained a lamellar phase or another impurity phase other than the hexagonal phase similar to that of the silicate MCM-41, as has been indicated by themselves. At the present, the metal-substituted hexagonal mesoporous silica (metal = Al,[1,2,4,5,11] Ti,[12] and V[13]) can be merely synthesized. Here we wish to report the first example of a non-silica-based mesostructured material which consists of vanadium oxide and phosphorus oxide (designated as VP) and has the pure hexagonal structure.

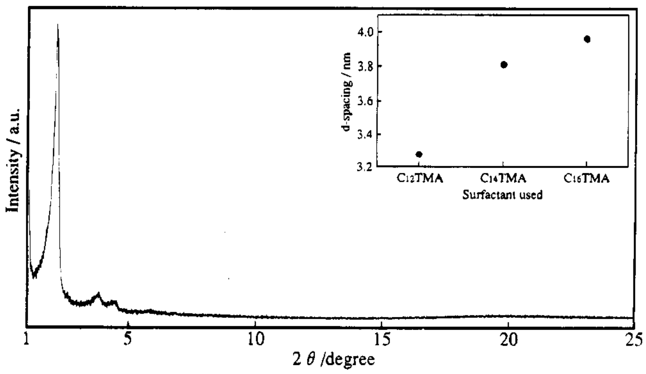

Figure 1. Powder X-ray diffraction pattern of the VP with C_{16}TMA. The pattern was measured by a MAC Science MXP3 with Cu Kα radiation. Inset: change in the *d* spacing of VP as a function of alkyl length of surfactants.

The VP composite materials were synthesized from a mixture of reactants with the following composition: $1.00VOSO_4{\cdot}nH_2O:0.52H_3PO_4:1.10$alkyltrimethylammonium chloride (C_nTMA)$:92.80H_2O$. In this study, C_{12}, C_{14}, and C_{16}TMA were used as the surfactants. The pH of this solution was carefully adjusted at 2.6 by addition of aqueous NaOH solution. The mixture was homogenized at room temperature by stirring. The resulting mixture was loaded into a teflon bottle in an autoclave and statically heated at 403 K for 24 h. The resultant solid product was filtered, washed with deionized water repeatedly, and dried at 353 K.[14] The color of the product was grayish green.

Elemental analysis of the VP obtained with C_{16}TMA by the inductive coupled plasma analysis (ICP, Perkin Elmer Optima 3000) showed the V:P ratio of 2:1. TG-DTA measurement (MAC Science 2000S) in air for the as-synthesized VP with C_{16}TMA gave four distinct stages of weight loss at 273−493, 493−533, 533−673, and above 673 K. Upon being heated at 773 K, the mesostructure was destroyed. In the four TG-DTA stages, the second stage was exothermic and corresponded to the oxidation of the surfactant.[15] The as-synthesized VP contains 15% of the surfactant. It should be noted that the content of the surfactant in the VP does not depend on the concentration of the surfactant in the mixture of reactants and was much smaller than that of the silicate MCM-41 (ca. 50%).[4] Similar results were also observed in the VP products synthesized with C_{12} and C_{14}TMA.

Figure 1 shows the XRD pattern of the VP sample (C_{16}TMA). Three clear peaks were observed at 2.23, 3.87, and 4.44°, and a broad peak appeared around 20°. The first intense peak at 2.23° corresponds to a *d* spacing of 3.96 nm. The whole shape and the respective peak positions of the XRD pattern shown in Figure 1 are completely the same as those of MCM-41[1−5] using the same surfactant. Three peaks can be indexed to (100), (110), and (200), respectively, assuming a hexagonal phase (P_6). In a separated experiment, a product synthesized from a mixture of reactants without C_{16}TMA did not give any peak at 2−10° in the XRD pattern but

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(14) The product yield, defined by the weight of the product/total weight of $VOSO_4$, H_3PO_4, and the surfactant, was in the range 20−30%.

(15) It was confirmed in a separated TG-DTA experiment that the C_{16}TMA itself gave an exothermic peak at ca. 473 K due to the oxidation. The shift of the exothermic peak from 473 to 493−533 K would suggest a strong interaction of C_{16}TMA with vanadium−phosphorus oxide materials.

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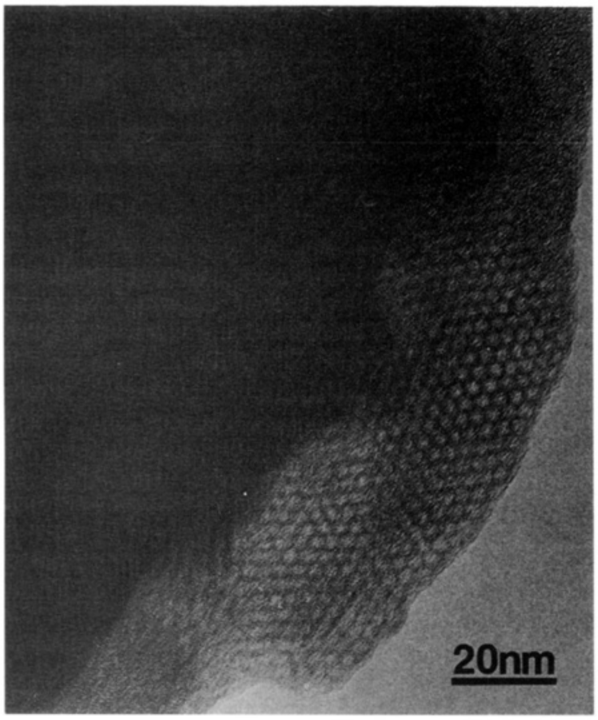

Figure 2. Transmission electron micrograph of the VP with C_{16}TMA. The bar represents 20 nm. The TEM image was obtained on a JEOL JEM-1200EXII at an accelerating voltage of 120 kV.

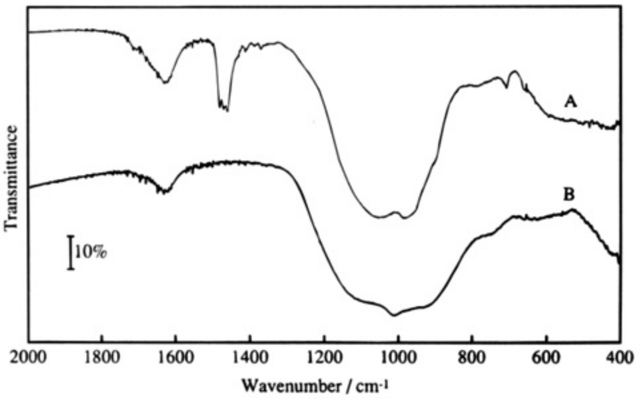

Figure 3. Infrared spectra of (A) the VP with C_{16}TMA and (B) the amorphous vanadium–phosphorus oxide prepared by the melting–quenching method.[18] All spectra were collected on a Perkin-Elmer System 2000 FT-IR.

yielded many peaks at 10–30°. It follows that the existence of a surfactant is essential to the formation of the VP having the MCM-41 structure.

VPs could also be obtained by using C_{12} or C_{14}TMA as a surfactant. The *d* spacings of the VPs determined by the respective first peaks in the XRD patterns were shown in the Figure 1 inset. It is clear that the *d* spacing is dependent on the alkyl chain length of surfactants, which is the same phenomenon as that observed in the silicate MCM-41. This dependence clearly concludes the "templating" effects in the synthesis of the vanadium–phosphorus oxide-based mesostructured material.

Figure 2 shows a typical TEM image of the VP with C_{16}TMA. The regular hexagonal array of the uniform pores, which are probably filled with surfactant, can be recognized. From this figure, the diameter of the pores and the thickness of the wall were determined to be approximately 2.6 and 1.4 nm, respectively. The sum of them, 4.0 nm, is in excellent agreement with the *d* spacing calculated from the XRD pattern. Note that there was also a layered material in the left-hand side of Figure 2. This might be attributed to a side view of the hexagonal array of channels, as suggested by Alfredsson et al.[16]

The wall thickness of the VP obtained was somewhat thicker than that of MCM-41 reported so far. Feuston et al. have calculated the relation between the pattern of XRD and the wall thickness using a molecular dynamics simulation technique with effective interaction potentials.[17] According to their results, the intensity of the (210) diffraction decreases with increasing the wall thickness. The disappearance of (210) peak in Figure 1 is probably attributable to the wall thickness of the VP products.

Figure 3A shows the infrared (IR) spectrum of the as-synthesized VP with C_{16}TMA. The bands around 1500 cm^{-1} are due to the bending of C–H of the surfactant. To assign the absorption bands at 1300–800 cm^{-1}, amorphous vanadium–phosphorus oxide (V_2O_5:P_2O_5 = 2:1) was separately prepared by the melting–quenching method,[18] and its IR spectrum is also shown in Figure 3B. It is evident that the bands corresponding to framework vibrations of the VP were similar to those of the amorphous material. With the crystalline vanadium–phosphorus oxides such as $VOPO_4$ and $(VO)_2P_2O_7$, the stretching frequencies of V=O, V–O–V, P–O–P, and PO_3 groups are at 1020–980, 850–700, 1000–700, and 1150–1000 cm^{-1}, respectively.[18–21] The spectra A and B in Figure 3 are quite different from these. Sakurai and Yamaki found that the increase in content of phosphorus oxide in V_2O_5–P_2O_5 glasses resulted in disappearance of V=O and V–O–V bands and appearance of phosphorus-related bands. Although the assignment of new bands was not carried out in their paper, the great change was observed at or below 78 mol% of V_2O_5 content. Since the present VP materials have the V:P ratio of 2:1 and the spectra in Figure 3 are almost the same as that reported for the glassy V_2O_5–P_2O_5,[18] it follows that the VP consists of amorphous phase of vanadium oxide and phosphorus oxide. This conclusion is further supported by the appearance of the broad peak at 20° in the XRD pattern (Figure 1). The assignment of the bands in Figure 3 remains to be solved in the future.

In conclusion, for the first time, it is clearly demonstrated that vanadium–phosphorus oxide-based mesostructured materials, having the hexagonal array of the pores, could be synthesized by using the "templating" effect of surfactants. Vanadium–phosphorus oxides with high surface area have been of interest in rechargeable batteries[18] and electroconductive materials.[22]

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