Synthesis of a Hexagonal Mesostructured Aluminophosphate

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(Received June 10, 1997; CL-970441)

A hexagonal mesostructured aluminophosphate was successfully synthesized from the mixture of $Al(O^iPr)_3$, 85% H_3PO_4, tetramethylammonium hydroxide, hexadecyltrimethylammonium chloride, and water.

Inorganic-organic mesostructured materials have recently been one of the major research topics among nanoscale materials design. Especially, inorganic-surfactant systems have extensively been investigated because the assembling ability of surfactants is effective for the formation of ordered mesostructured materials.[1] These materials are important not only as the precursors for the formation of mesoporous materials[2,3] but also as the model system for both functional and biomimetic materials design.

Based on the success of microporous $AlPO_4$-n and SAPO-n materials,[4] it is quite reasonable and valuable to attempt to prepare mesostructured aluminophosphates (AlPOs) composed of both AlO_4 and PO_4 units. Although the preparation of lamellar mesostructured AlPOs has recently been reported,[5-9] there has been no indication on the possibility of the formation of hexagonal mesostructured AlPOs. The difficulties would come from the organization of two different units on the surfactant assemblies.

Here, we report the successful formation of a hexagonal mesostructured AlPO by modifying the synthetic conditions reported by Fyfe *et al.* who reported lamellar mesostructured AlPOs.[6]

The synthesis procedure was as follows: hexadecyltrimethylammonium ($C_{16}TMA$) chloride, tetramethylammonium hydroxide (TMAOH, 25 wt% in water), 85% H_3PO_4, and water were mixed for several hours until a clear solution was obtained. Aluminum triisopropoxide ($Al(O^iPr)_3$) was added to this clear solution under vigorous stirring, and the stirring was continued for 24 h. The composition of this starting mixture was $Al_2O_3 \cdot P_2O_5 \cdot C_{16}TMACl \cdot 2.0TMAOH \cdot 65.0H_2O$. The starting mixture was sealed in a teflon tube and heated at 130 ℃ for 5 d. The resultant was dispersed in distilled water, then a white solid was obtained. Because a lamellar mesostructured product was slightly mixed as a byproduct, a lamellar mesostructured product was removed by its slower sedimentation velocity. This solid was washed repeatedly and dried at 80 ℃.

The XRD pattern of the as-synthesized product is shown in Figure 1. The main peak at d-spacing of 4.1 nm was observed. The XRD peaks of 4.1, 2.4 and 2.1 nm are assignable to (100), (110) and (200) of a hexagonal phase, respectively.

The TEM image of the product shown in Figure 2 is quite similar to those observed for hexagonal mesostructured materials with slightly less ordered arrays.[10] The periodical distance of these arrays was *ca.* 4.0 nm, which is smaller than the lattice parameter a_0 (4.8 nm). Though the difference can not be adequately explained at present, the periodical distance might be decreased during the TEM measurement (electron beam irradiation under a very high vacuum condition).

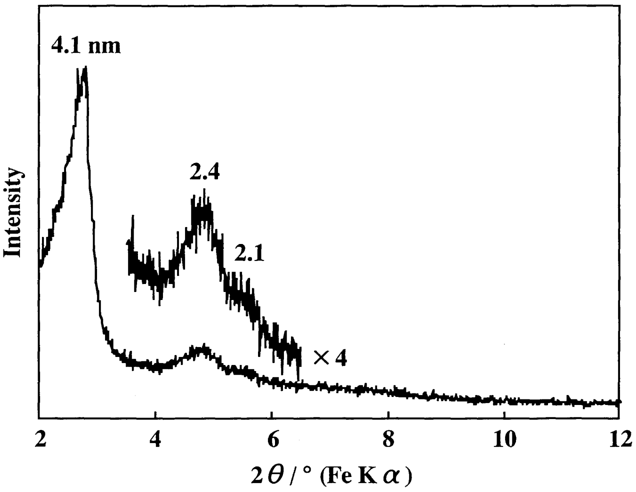

Figure 1. XRD pattern of the as-synthesized product obtained by using a Mac Science M03XHF22 diffractometer with Fe Kα radiation.

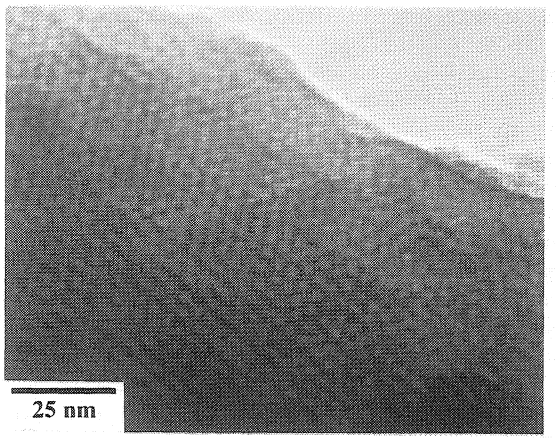

Figure 2. TEM image of the as-synthesized product obtained on a HITACHI H-8100A operated at 200 kV.

The ^{13}C CP MAS NMR spectrum of the product showed that the peak due to methylene groups of $C_{16}TMA$ ions was observed at 31.0 ppm. These methylene groups have a *gauche* conformation, being based on the report by Wang *et al.* who reported the ^{13}C CP MAS NMR spectra of ordered and disordered mesostructured silicates with a hexagonal structure.[11] The profile of the present product agreed with that of the disordered mesostructured silicate.

The ^{27}Al and ^{31}P MAS NMR spectra of the hexagonal mesostructured product are shown in Figure 3. The ^{27}Al MAS NMR spectrum of the product indicates the presence of both 4- and 6-coordinated Al observed at 43.5 and 1.2 ppm, respectively.

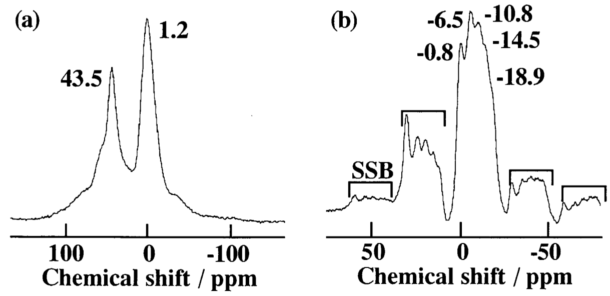

Figure 3. (a) ^{27}Al MAS NMR and (b) ^{31}P MAS NMR spectra of the hexagonal mesostructured product. (These spectra were recorded on a JEOL GSX-400 spectrometer at a spinning rate of 3.5 kHz and a resonance frequency of 104.05 MHz with a pulse length of 4.4 μs and a recycle time of 5 s for ^{27}Al, and 5 kHz, 161.70 MHz, 5 μs, and 20 s for ^{31}P, respectively.)

Four-coordinated Al can be assigned to $Al(OP)_4$ and/or $Al(OH)_x(OP)_{4-x}$ based on this chemical shift and the asymmetric profile.[5,7] Six-coordinated Al can not be definitely assigned at present. However, the ^{27}Al MAS NMR spectrum of the product calcined at 600 ℃ showed the absence of 6-coordinated Al. Therefore, the 6-coordinated Al at 1.2 ppm may be coordinated with not only (OP) groups but also some water molecules. The ^{31}P MAS NMR spectrum of the product showed that several peaks were observed in the range from 0 to -20 ppm possibly due to incomplete condensation of PO_4 units,[12,13] suggesting that these PO_4 units were mainly bonded to one or two Al atoms. The composition of the product was $2.48C_{16}TMA \bullet Al_6P_4O_{19} \bullet 1.42H_2O$. The Al/P ratio of the product is 1.5, being different from unity which should be expected from ideal three-dimensional $AlPO_4$-n.[4] This may be related to the presence of 6-coordinated Al possibly coordinated with water molecules and incomplete condensation of PO_4 units. The molar ratio of C_{16}TMA/(Al+P) was 0.25. These NMR results indicate the hexagonal mesostructured product has incompletely condensed inorganic networks.

When the synthetic conditions (such as the Al/P ratio, the amount of TMAOH, the amount of water, and the reaction temperature) were varied, lamellar mesostructured products mainly formed. Consequently, the formation of the hexagonal mesostructured products is very limited to a narrow range of the synthetic conditions. Further details will be published elsewhere.

The hexagonal mesostructured product was calcined at 600 ℃ for 1 h in air to remove the organic fractions. The IR spectra of the products before and after calcination indicate the absence of C_{16}TMA ions. The d-spacing of the main peak gradually changed from 4.1 nm to 2.6 nm with the increase in the calcined temperature although the intensity of this peak became smaller. The N_2 adsorption isotherm of the calcined product was type I, indicating the presence of micropores. The specific surface area was about 450 m^2/g. The ^{31}P MAS NMR spectrum of the calcined product showed the broad peak centered at -23.6 ppm. The structural change of the hexagonal mesostructured product is caused by the condensation of the inorganic phase. Further study is necessary for the preparation of mesoporous AlPOs.

In conclusion, a hexagonal mesostructured AlPO was prepared from the mixture of $Al(O^iPr)_3$, 85% H_3PO_4, TMAOH, C_{16}TMA chloride, and water. ^{27}Al and ^{31}P MAS NMR results indicate that the hexagonal mesostructured product has incompletely condensed aluminophosphate networks. This material had the possibility for the formation of novel porous materials after calcination.

The authors acknowledge Mr. M. Fuziwara, Materials Characterization Central Laboratory, Waseda University, for his TEM measurements. K.K. acknowledges the financial assistance from Grant-in-Aid for the Special Priority Area by the Ministry of Education, Science, and Culture of the Japanese Government.

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