SYNTHESIS OF A LAMELLAR MESOSTRUCTURED ALUMINOPHOSPHATE

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Abstract A lamellar mesostructured hexadecyltrimethylammonium (C_{16} TMA)-aluminophosphate material was hydrothermally prepared from the mixture of $Al(O^iC_3H_7)_3$, 85% H_3PO_4 , C_{16} TMACl, $(CH_3)_4NOH$, CH_3OH , and H_2O . The XRD pattern of the as-synthesized product indicated that the product had a layered structure, and the SEM and TEM images also supported this result. The ^{27}Al MAS NMR spectrum of the product showed the presence of 4-coordinated Al composed of $Al(OP)_4$, and the ^{31}P MAS NMR spectra showed the presence of 4-coordinated P composed of $O-P(OAl)_3$, including $HO-P(OAl)_3$. Judging from the composition of the product measured by chemical analysis ($1.4C_{16}TMA \cdot Al_3P_4O_{16} \cdot xH_2O$), 4-coordinated P atoms were composed of $HO-P(OAl)_3$ and $C_{16}TMAO-P(OAl)_3$.

INTRODUCTION

Since the role of surfactants for the preparation of mesoporous materials was disclosed,¹ silica-based mesoporous molecular sieves and inorganic-organic mesostructured materials have recently been investigated. However, there have been only several reports on mesostructured surfactant-aluminophosphates,²⁻⁸ and no reports on mesoporous aluminophosphates, although $AlPO_4$ -n and $SAPO$ -n molecular sieves are well known.⁹⁻¹⁰ Since the tetrahedral networks can be constructed by utilizing both AlO_4 and PO_4 units, it is quite reasonable to attempt to prepare a variety of mesophase materials composed of aluminophosphate networks. Previously reported mesostructured aluminophosphates have layered structures,²⁻⁸ whereas we have succeeded in synthesizing hexagonal mesostructured aluminophosphates by modifying the synthetic conditions reported by C. A. Fyfe *et al.*¹¹ Based on our research on the hexagonal mesophases, we have noticed that lamellar and hexagonal mesophases form in very closely interrelated synthetic conditions. Therefore, it is necessary to examine the formation conditions of lamellar mesostructured aluminophosphates in more detail. Thus, a lamellar mesostructured alkyltrimethylammonium-aluminophosphate was synthesized hydrothermally and characterized in order to elucidate the feature of the lamellar mesophases.

EXPERIMENTAL PROCEDURE

The synthesis procedure was followed by a report of C. A. Fyfe *et al.*,⁸ although methanol was added to the starting mixture as cosolvent. Hexadecyltrimethylammonium (C₁₆TMA) chloride, tetramethylammonium hydroxide (TMAOH, 10wt% in methanol), 85% phosphoric acid, and water were mixed for a few minutes. Aluminum triisopropoxide was added to this solution under vigorous stirring, and the reaction mixture was stirred for 24 hr. The molar ratio of the starting gel was 0.3Al₂O₃ • P₂O₅ • C₁₆TMA • 1.6TMAOH • 15H₂O • 40.9CH₃OH. This starting gel was hydrothermally treated at 130°C for 120 hr. The resultant product was washed repeatedly with distilled water, and dried. The resultant inorganic-organic mesophase material was analyzed by powder XRD, ²⁷Al MAS NMR, ³¹P MAS NMR, SEM, TEM, and chemical analysis.

RESULTS AND DISCUSSION

The XRD pattern of the as-synthesized product is shown in Fig. 1. The main peak at d-spacing of 3.29 nm and the peaks of higher order reflections were observed, indicating that this product had a layered structure, which is consistent with a report of C. A. Fyfe *et al.*⁸ The SEM image shown in Fig. 2 indicates this product obviously has platy crystals. The TEM image shown in Fig. 3 also exhibits the layered nature of the product.

FIGURE 1. XRD pattern of the as-synthesized product.

FIGURE 2. Scanning electron micrograph of the product.

FIGURE 3. TEM image of the product.

Figures 4 and 5 show the ^{27}Al MAS NMR and ^{31}P MAS NMR spectra, respectively. As to the environment of Al atoms, the chemical shift of 42.0 ppm indicates the presence of tetrahedral Al sites composed of $\text{Al}(\text{OP})_4$. For P atoms, the ^{31}P CP MAS NMR spectrum shows two signals at -17.8 and -20.2 ppm, indicating the presence of tetrahedral P sites composed of $\text{OP}(\text{OAl})_3$.¹⁰ A signal at -20.2 ppm is assignable to $\text{HO-P}(\text{OAl})_3$, because this signal remarkably decreased in the ^{31}P MAS NMR spectrum. Judging from the composition of the product measured by chemical analysis ($1.4\text{C}_{16}\text{TMA} \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot x\text{H}_2\text{O}$), a signal at -17.8 ppm would be assignable to $\text{C}_{16}\text{TMAO-P}(\text{OAl})_3$.

FIGURE 4. ^{27}Al MAS NMR spectrum of the product.

FIGURE 5. ^{31}P MAS NMR spectra of the product.

With the increase in the concentration of C_{16}TMA ions, no ordered structures were observed. While, $\text{AlPO}_4\text{-20}$ coexisted with a lamellar mesophase when very low amount of C_{16}TMA was employed. Although the addition of methanol as cosolvent to the reaction system leads the variation of surfactant assemblies, the as-synthesized product had a lamellar structure, being in agreement with a report of C. A. Fyfe *et al.* who used the same starting mixture except methanol.⁸ They have reported the formation of lamellar mesophases under the conditions with a small amount of water. Besides, we found that lamellar mesostructured aluminophosphates were obtained under the conditions with a large amount of water.¹¹ Based on these results, $(\text{Al}+\text{P})/\text{C}_{16}\text{TMA}$ ratio rather than C_{16}TMA concentration influences the structure of mesophases. On the other hand, a possible amount of remaining TMA ions in the product is very low based on the CHN analysis. However, TMAOH may act as an basic source, not only because no layered aluminophosphates were obtained under TMAOH free conditions, but also because a layered aluminophosphate was obtained under the conditions without TMAOH when $\text{C}_{16}\text{TMACl}/\text{OH}$ was used instead of $\text{C}_{16}\text{TMACl}$.

CONCLUSIONS

A lamellar mesostructured C₁₆TMA-aluminophosphate was obtained by hydrothermal synthesis from the mixture of Al(OⁱC₃H₇)₃, 85%H₃PO₄, C₁₆TMACl, (CH₃)₄NOH, CH₃OH, and H₂O. The composition of the aluminophosphate layers was thought to be Al₃P₄O₁₆, being constructed of Al(OP)₄, HO-P(OAl)₃, and C₁₆TMAO-P(OAl)₃. The structure of the mesophases of the C₁₆TMA-aluminophosphates was influenced by several interrelated parameters such as Al/P ratios, (Al+P)/C₁₆TMA ratios, C₁₆TMA concentrations, and so on.

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