Synthesis of Thermally Stable Hexagonal Mesostructured Aluminophosphate-based Materials Modified with Organoalkoxysilanes

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Hexagonal mesostructured aluminophosphate (AlPO)-based materials with higher thermal stabilities have been successfully synthesized by the modification with organoalkoxysilanes.

Nonsiliceous mesostructured and mesoporous materials prepared by using amphiphilic molecules have much potential in a wide variety of applications.[1] However, the mesostructures of almost nonsiliceous materials are collapsed and/or turn out disordered during the removal of the amphiphilic molecules used or the utilization as catalysts and adsorbents. Therefore, it is strongly required to prepare nonsiliceous mesostructured and mesoporous materials with high stabilities. Organic modifications are useful for controlling the surface properties of ordered mesoporous silicas (FSM-16, MCM-41, etc.).[2,3] In this manner, the stability of the mesoporous silicas is significantly improved with the increase in hydrophobicity and the formation of new siloxane bonds at the surface of silicate frameworks.[4] Nevertheless, there have been no reports on the preparation of organically modified nonsilica-based mesostructured materials. Here, a new method for enhancing thermal stabilities of nonsilica-based mesostructured materials is presented through the preparation of hexagonal mesostructured AlPO-based materials containing organic groups.

Hexagonal mesostructured AlPO-based materials were synthesized by using hexadecyltrimethylammonium chloride (C_{16}TMACl) in the presence of methyl- (Me-TMS), ethyl- (Et-TMS) and butyltrimethoxysilanes (Bu-TMS). According to the literatures,[5] a precursor solution (Al_2O_3 : P_2O_5 : C_{16}TMACl : 2.0 $(CH_3)_4$NOH : 65.0 H_2O, pH = ca. 10) was prepared by using $Al(O\text{-}i\text{-}C_3H_7)_3$, 85% H_3PO_4, C_{16}TMACl, 25% $(CH_3)_4$NOH, and distilled water. Organoalkoxysilanes were added to the precursor solution (Si/Al+P) = 0.25) and the stirring was kept for 30 min. After the dispersion of the mixtures in distilled water, the resultants (denoted as Me-, Et and Bu-APW-2) were washed with distilled water repeatedly, and dried at 50 °C. The products were heated at 550 °C for 1 h in N_2, followed by calcination at 550 °C for 2 h in O_2.

The powder X-ray diffraction (XRD) patterns of Me-, Et- and Bu-APW-2 are shown in Figure 1, indicating that all the peaks were assignable to (100), (110), (200), and (210) reflections of 2d-hexagonal structures (*p6m*) with lattice constants a = 4.6–4.7 nm (d_{100} = 4.0–4.1 nm). Both relatively ordered hexagonal and striped images were observed in all the modified APW-2 by transmission electron microscope (TEM). The d_{100} values were almost constant and similar to that of an unmodified APW-2 (4.0 nm), meaning that organic groups in organosilica species are pointing into C_{16}TMA assemblies due to the hydrophobicity as in the case of silica-based materials,[6] but not
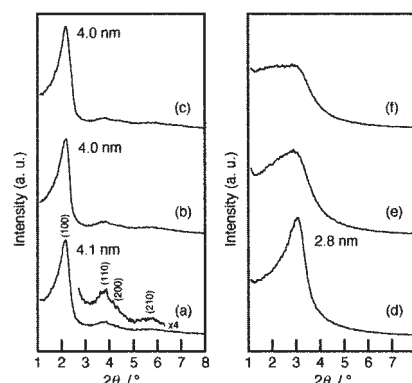
solubilized.

Figure 1. XRD patterns of (a) Me-, (b) Et- and (c) Bu-APW-2 and (d), (e), (f) the corresponding calcined products.

The ^{27}Al MAS NMR spectra of Me-, Et- and Bu-APW-2 showed the presence of both AlO_4 and AlO_6 units observed at 43 and -1.6 ppm, respectively. In the ^{31}P MAS NMR spectra of the modified APW-2, several peaks were detected in the range of 0 to -20 ppm (mainly 0 to -10 ppm). The NMR results reveal that the modified APW-2 have less condensed AlPO frameworks observed for the unmodified APW-2.[5] The ^{29}Si CP/MAS NMR spectra of the modified APW-2 proved the presence of Si species with T^n (n = 1–3) environments (R–Si(OT)$_n$(O$^-$)$_{3-n}$, T=Al, Si or P) observed at -48, -55 and -60 ppm. The Si/(Al + P) molar ratios of the modified APW-2 was 0.07–0.14. Being different from crystalline AlPO$_4$-n and SAPO-n, it cannot be explained by the ^{27}Al, ^{29}Si and ^{31}P MAS NMR data whether silicate groups in organosilica species are incorporated into the AlPO frameworks because of the less condensed AlPO frameworks with various PO$_4$ units. However, it is reasonable that the organosilica species are homogeneously distributed in the AlPO frameworks because the water adsorption isotherms confirmed that a hydrophilic nature of the unmodified APW-2 is retained after calcination of the modified APW-2.

The Al/P molar ratios of the modified APW-2 (1.53–1.79) were deviated from that of the unmodified APW-2 (1.50). This would be related to the presence of a small amount of alumina impurity. For Me-APW-2 (Al/P = 1.79), the ^{27}Al MAS NMR spectrum indicates that the amount of 6-coordinated Al species was somewhat larger than that in the unmodified APW-2. Organic contents in Me-, Et- and Bu-APW-2 were 49.6, 52.1 and 54.8 mass%, respectively. These values are consistent with the presence of organic groups in the incorporated organosilica species though 53.0 mass% of C_{16}TMA molecules were present

in the unmodified APW-2.

The IR spectra of the calcined products showed the complete removal of organic fractions. On the basis of the ^{29}Si CP/MAS NMR data, all the Si species were changed into Q^n ($n = 2$–4) species $Si(OT)_n(O^-)_{4-n}$, T=Al, Si or P). The ^{27}Al MAS NMR showed the increase in the amount of 4-coordinated Al species. In the ^{31}P MAS NMR spectra, a broad peak centered at -15 ppm was observed. Both ^{27}Al and ^{31}P MAS NMR data suggest that AlPO frameworks were shrank by calcination.[5] The d_{100} values decreased to 2.8 nm according to the substantial shrinkage of the less condensed AlPO frameworks. When organosilica species with shorter alkyl chain lengths are present in the AlPO framework, stronger peaks remained after calcination. The surface areas, pore volumes and pore diameters of the calcined products are listed in Table 1. The surface area and the pore volume of the calcined Me-APW-2 are comparatively larger than those observed for the other calcined products. These results suggest that thermal stability of hexagonal mesostructured AlPOs is largely improved by the modification with Me-TMS. Although the complete removal of C_{16}TMA molecules from the mesostructured materials has not been achieved by extraction yet, those materials are useful as precursors of organically modified mesoporous AlPO-based materials.

Table 1. Structural properties of calcined APW-2 containing organic groups

	Surface area /m^2 g^{-1}	Pore volume /cm^3 g^{-1}	Pore size /nm
Me-APW-2	818	0.39	1.8
Bu-APW-2	526	0.29	—
unmodified APW-2	488	0.27	—

The ordering of hexagonal mesostructured AlPO-based materials reported so far is collapsed and/or turns out disordered during calcination, which is mainly caused by the formation of water molecules from the combustion of surfactant molecules.[7] In this study, the destruction of mesostructures is restricted by the hydrophobicity owing to the presence of the organic groups at the surface of AlPO frameworks. The TG-DTA measurements revealed that the combustion of Me-, Et- and Bu groups starts at around 360 °C, 400 °C and 460 °C in air, respectively, meaning that organic groups with shorter alkyl chains are thermally stable. Nevertheless, the combustion of the organic groups cannot be separated from that of C_{16}TMA molecules during the calcination of the modified APW-2. Consequently, the combustion of the C_{16}TMA molecules (at around 220 °C) induces the following combustion of Me-, Et- and Bu groups. Therefore, combustible organic groups such as Bu groups are not useful to enhance the thermal stability of mesostructured AlPO-based materials.

In conclusions, hexagonal mesostructured AlPO-based materials containing organic groups are successfully synthesized by using organoalkoxysilanes. This is the first example for an organic modification of nonsilica-based mesostructured materials prepared by using surfactant assemblies. The incorporation of noncombustible organic groups in the AlPO-based materials is capable to enhance the thermal stability. This method is easily applicable to the preparation of nonsilica-based mesostructured materials and the derivative mesoporous materials will show interesting properties depending on the nonsilica-based framework structures.

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