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Mesoporous Aluminium Organophosphonates Functionalized with Chiral L-Proline Groups in the Pore

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Mesoporous aluminium organophosphonates with chiral L-proline groups in the pore were synthesized for the first time through surfactant-assisted one-pot co-condensation of $Al(OsBu)_3$ with a mixture of 1-phosphonomethylproline (*S*)-$H_2PO_3CH_2NC_4H_7COOH$ (H_3PMP) and phosphoric acid (H_3PO_4) [$H_3PMP/(H_3PMP + H_3PO_4)$ = 50, 75, 100 mol-%] under basic conditions in the presence of cetyltrimethylammonium bromide.

Introduction

Recently, the interest in the design and fabrication of organic-inorganic materials with high surface area and hierarchically ordered porous structure is growing because of their potential applications in the fields of optics, electronics, membranes, catalysis, biology and etc.[1,2] The periodic mesoporous organosilicas (PMOs) with organic bridging groups in the framework were regarded as one of the recent breakthroughs in the fields of hybrid organic-inorganic mesoporous materials.[3,4] Compared with the silica-based materials, metal organophosphonates are more promising in respect of their unique properties, such as proton conductivity, nonlinear optical effects, electron transfer, topochemical reactivity, and photochromism.[5–7] Inspired by the success of PMOs, a pure mesostructured aluminium organophosphonate (AOPs) containing internal methylene groups was first reported by Kimura in 2003.[8] To the best of our knowledge, only limited types of organic groups (alkyl, alkylene and phenyl) were incorporated in the mesoporous metal organophosphonates,[8–12] however, mesoporous AOPs functionalized with chiral organic groups have not been reported so far.

Amino acids are the principal building blocks of proteins and enzymes. Among them, L-proline is one of the cyclic aliphatic amino acids that is a major component of the protein collagen. Also, L-proline is an efficient catalyst for the asymmetric catalysis and chiral selector for the chiral separation.[13,14] The combination of the mesoporous AOPs with L-proline will be interesting in view of the enzyme adsorption, chiral synthesis etc. Here, we report for the first time the synthesis of mesoporous AOPs containing chiral L-proline groups in the pore by a one-pot synthetic method.

Results and Discussion

Mesoporous AOPs with different amounts of L-proline were synthesized through the "atrane route" previously reported for the synthesis of aluminium phosphonates and diphosphonates with slight modification.[11] During the synthesis, the pre-hydrolysis of aluminium species is essential for the formation of pure mesoporous AOPs, otherwise pure mesoporous AOPs cannot be obtained. The mesoporous AOPs with different amounts of L-proline in the pore are designated as MAOP-*n*, while *n* (= 50, 75, 100) is the mol-% value of $H_3PMP/(H_3PMP + H_3PO_4)$ in the initial mixture.

The powder XRD patterns of all as-synthesized MAOPs-*n* display a single broad diffraction peak at low diffraction angle, suggesting that these hybrid materials have a "worm-like" mesoporous structure (Figure 1). The TEM images of as-synthesized MAOPs-*n* clearly show the "worm-like" pore arrangement throughout the materials, which is consistent with the XRD results (Figure 2). It is noteworthy to mention that the mesoporous structure could be formed even for MAOP-100, synthesized from 100 mol-% of H_3PMP. With the amounts of organophosphonic acid, H_3PMP, in the initial mixture increasing, the intensity of the diffraction peak decreased. The XRD patterns of MAOPs-*n* remain almost the same before and after the surfactant extraction, showing that the mesoporous structure of MAOPs-*n* is stable enough to survive during the surfactant removal process. Additionally, the diffraction peaks shift toward lower 2θ angles after removal of the surfactant, which is in agreement with the results of previous reports on mesoporous ALPOs.[11,15,16] All surfactant-extracted MAOP-*n* solids present typical type IV isotherms with H2

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hysteresis loop according to IUPAC classification, characteristic of the mesoporous material with "ink-bottle" pores (see Supporting Information). The BET surface area, the pore volume, and the pore diameter of MAOP-100 are lower than those of MAOP-50 and MAOP-75. The results of XRD and N_2 sorption isotherms imply that the mesoporous structure of MAOPs-*n* are disturbed by the incorporation of L-proline groups in the materials. This can be explained by the fact that it is difficult for the monophosphonic acid to construct the mesoporous framework[11] and the steric hindrance resulting from the large L-proline group.

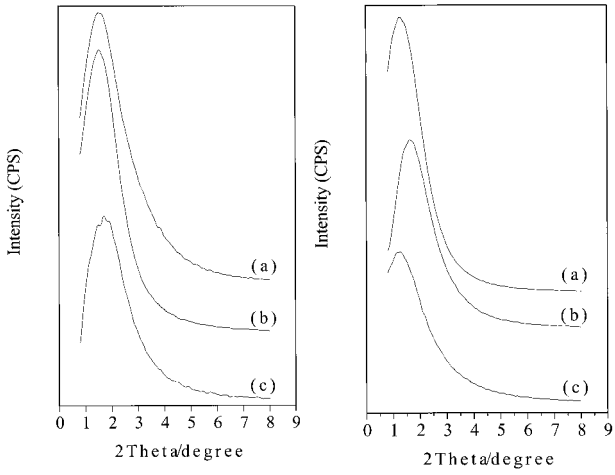

Figure 1. Powder X-ray diffraction patterns of (left) as-synthesized and (right) surfactant-extracted MAOPs-*n*: (a) MAOP-50; (b) MAOP-75; (c) MAOP-100.

The ratio of Al/P for the mesoporous aluminium phosphates varies in the range of 1.0 to 5.5 depending on the synthetic conditions.[17] The ratio of Al/P for MAOPs-*n* is about 3, which is higher than the ideal stoichiometric value of 1 (Table 1). This fact shows that the extra aluminium species participate in the formation of the mesoporous framework. During the synthesis, the reaction rate between the aluminium species and H_3PMP is retarded because of the steric restriction derived from the L-proline group. Also, before the addition of H_3PMP/H_3PO_4, the aluminium precursor was allowed to pre-hydrolyze. As a result, the interaction of the hydrolyzed aluminium species with H_3PMP and the condensation between the hydrolyzed aluminium species occurred simultaneously. The excess aluminium species that could be incorporated in the mesoporous framework of MAOPs-*n* in a controllable way can act as a stabilizer in the pore wall to stabilize the mesoporous framework of MAOPs-*n*.

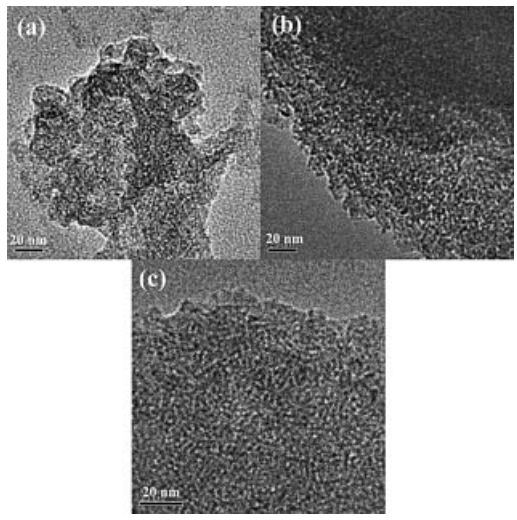

Figure 2. TEM images of as-synthesized MAOPs-*n*: (a) MAOP-50; (b) MAOP-75; (c) MAOP-100.

^{31}P MAS NMR spectra of the surfactant-extracted MAOPs-*n* show that the organophosphonate groups are actually incorporated in the materials (Figure 3). MAOP-100 displays a broad peak centered at δ = 2 ppm with a shoulder at δ = 6 ppm, which could be assigned to P atoms of RPO_3^{2-} and RPO_3H^-, respectively. The presence of RPO_3H^- in MAOP-100 is also supported by the FT-IR. The stretching vibration of the P–OH band was clearly observed at 950 cm^{-1} (see Supporting Information). A broad signal centered at δ = –12 ppm was observed in ^{31}P MAS NMR spectra of MAOP-50 and MAOP-75. After deconvolution by computer simulation, the broad peak was divided into two singals. The signal at δ = –12 ppm is attributed to the inorganic phosphorus species according to ref.[18], while the singal at δ = 2 ppm is derived from the organic phosphorus species, RPO_3^{2-}. From the ratio of P_{inorg}/P_{org} (calculated from the peak area, Table 1), we could see that only 10 and 22 mol-% of H_3PMP could be incorporated in MAOP-50 and MAOP-75, respectively. This is probably due to the severe steric hindrance of H_3PMP.

^{13}C MAS NMR spectrum of MAOP-100 also confirms that L-proline groups have been incorporated in the material (Figure 4). The signals at δ = 174 and 179 ppm are associated with the C atoms of CO_2H and CO^{2-}, respectively. The resonance at δ = 72 ppm can be assigned to the C atom of

Table 1. Physicochemical data for surfactant-extracted MAOPs-*n*.[a]

Sample	H_3PMP in the solution [mol%]	H_3PMP in the solid[b] [mol%]	*d*(100) [nm]	Al/P[c]	S_{BET} [m^2g^{-1}]	Pore volume [cm^3g^{-1}]	BJH pore diameter[d] [nm]
MAOP-50	50	10	6.7 (5.8)	3.22	373	0.43	3.5
MAOP-75	75	22	5.3 (5.1)	3.41	422	0.54	3.7
MAOP-100	100	100	6.9 (5.5)	2.78	215	0.13	2.9

[a] Data in parentheses are for the as-synthesized materials. [b] Based on ^{31}P MAS NMR spectroscopy. [c] Calculated from ICP analysis. [d] Calculated by using the BJH model on the adsorption branch of the isotherm.

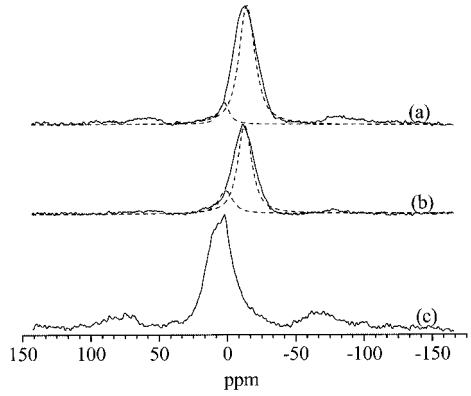

Figure 3. ^{31}P MAS NMR spectra of surfactant-extracted MAOPs-*n*: (a) MAOP-50; (b) MAOP-75; (c) MAOP-100.

the CH group connected with the carboxy group, while the signal at δ = 56 ppm is attributed to the C atom of CH_2 group connected with the phosphonic group. The signals related to the CH_2 group of the pyrrolidine ring are observed at δ = 23, 29 and 59 ppm. The ^{13}C MAS NMR spectrum shows that organophosphonic acid, H_3PMP, retains its integrity in the mesoporous solid. In addition, the peak at $\delta \approx 15$ ppm, associated with the C atom of the terminal CH_3 group of the surfactant CTAB, cannot be observed in the spectrum, which illuminates that the surfactant is almost completely removed using the extraction method.

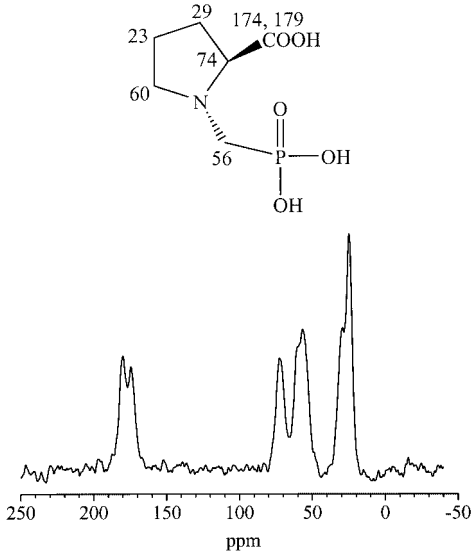

Figure 4. ^{13}C MAS NMR spectra of surfactant-extracted MAOP-100.

The ^{27}Al MAS NMR spectra of surfactant-extracted MAOPs-*n* give information of the aluminium coordination environment (see Supporting Information). Two signals at δ = 0 and 50 ppm are observed in the spectra of MAOP-50 and MAOP-75, which could be assigned to octahedral and tetrahedral Al centers, respectively. The peak at δ = 0 ppm is dominant, showing that almost all aluminium species are six-coordinate. Only a six-coordinate Al species is observed for MAOP-100. This may be due to the large influence of the charge balance of MAOPs-*n* on the coordination environment of the Al species. The different charges between H_3PO_4 and H_3PMP may be the main reason for the different aluminium coordination environments in MAOPs-*n*.

The chirality of L-proline in the solid product was analyzed by CD spectroscopy (see Supporting Information). A positive Cotton effect was observed for MAOP-100, which is consistent with that of H_3PMP. From the CD results, we can draw the conclusion that L-proline groups retain their chirality during the synthesis and subsequent surfactant-removing process.

Conclusion

In summary, mesoporous AOPs with different amounts of chiral L-proline groups in the pore were synthesized for the first time through the surfactant-templated method. The existence of extra aluminium species in the mesoporous framework (formed through "pre-hydrolysis" of the aluminium precursor) plays an important role in stabilizing the mesoporous structure of the materials. The integrity and chirality of L-proline were retained in the mesoporous AOPs. The successful synthesis of mesoporous AOPs containing chiral molecules may provide a new method for the design and synthesis of chiral solid materials.

Experimental Section

MAOP-*n* Materials: In a typical synthesis, Al(O*s*Bu)$_3$ (0.985 g, 4 mmol) was added dropwise to a solution of triethanolamine (2.389 g, 16 mmol) at 160 °C. After cooling to 120 °C, cetyltrimethylammonium bromide (0.364 g, 1 mmol) was added to the above mixture. The solution was further cooled to 70 °C and distilled water (20 mL) was added. The mixture was stirred for a few minutes to "pre-hydrolyze" the aluminium precursor (this "pre-hydrolysis" process for the aluminium precursor is essential, otherwise pure mesoporous AOPs cannot be obtained). An aqueous solution (20 mL) containing a mixture (6 mmol) of phosphoric acid and 1-phosphonomethylproline [(*S*)-$H_2PO_3CH_2NC_4H_7COOH$, H_3PMP] was added to above mixture under vigorous stirring. The mixture was kept at 70 °C for 30 min. After filtration, the resulting white powder was dried under vacuum at 60 °C. The surfactant was extracted using an acetic acid/ethanol solution (1 g of powder in 130 mL of ethanol containing 16 mL of acetic acid) at room temperature.

Supporting Information (see footnote on the first page of this article): N_2 sorption isotherms, FT-IR spectra, and ^{27}Al MAS NMR specra of MAOPs-*n*; CD spectrum of MAOP-100.

Acknowledgments

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