The First Pure Mesoporous Aluminium Phosphonates and Diphosphonates − New Hybrid Porous Materials

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Organophosphorus moieties have been incorporated into mesoporous ALPOs through a one-pot surfactant-assisted procedure leading, for the first time, to periodic mesoporous aluminium phosphonates and diphosphonates. The number of organic groups on the surface or in the network can be modulated continuously up to the maximum incorporation level of the respective organophosphorus entities (100 %). (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Since the discovery of three-dimensional aluminium phosphates (ALPOs),[1] the chemistry of open metal phosphates and phosphonates was extensively explored in the search for expanding microporous availability.[2] Organophosphorus reagents have been used as both anionic species able to construct layered or open structures[2] (one-pot) and coupling agents[3] for the preparation of hybrid materials based on metal oxides (grafting). Interest in these materials is currently related to the broad range of their potential applications in fields such as catalysis, molecular sieves and biomedical sciences.[4] The current trend of expanding pore sizes by using supramolecular templates has been successfully adapted for obtaining MCM-41-like aluminium phosphates.[5] Notwithstanding, reports on organically modified mesoporous phosphates are very scarce when compared to those dealing with hybrid organosilicas.[6] In fact, once the preparation of mesoporous silicas began to be controlled, a key objective was the functionalisation of the walls with organic groups (housed in the pore space or embedded in the walls).[6] In contrast, as far as we know, there are only three publications in which mixed mesoporous phosphate-phosphonate (containing Ti[7] and Zr[8]) or mesoporous phosphate-diphosphonate (based on Al[9]) materials are described. In the case of the Ti[7] and Zr[8] derivatives, by using terminal RPO_3 substituting groups, the phosphonate incorporation to the final materials is limited ($< 50\,\%$) and restricted to the pore surface. Dealing with the Al-containing solid, although diphosphonate moieties with bridged methylene groups have been used to connect the Al centres (in the mesostructured solid), the thermal evolution of the surfactant to prepare the corresponding mesoporous material leads to a significant degradation of diphosphonate moieties that decompose into terminal RPO_3 and phosphate groups. Hence, this solid must be understood as a mixed phosphate−phosphonate−diphosphonate mesoporous material constructed, as stated by the author, from aluminophosphate-like domains interconnected through bridged organic groups instead of a pure mesoporous aluminium-diphosphonate.[9]

Results and Discussion

We report here a generalised one-pot method that has allowed us to prepare for the first time pure mesoporous aluminium phosphonates and diphosphonates (henceforth denoted as UVM-9 for University of Valencia Materials) showing that a good selection of reagents, conditions and procedures allow the full extension of the ALPO derivatives to as broad a family as mesoporous organosilicas. In fact, a great variety of terminal organic groups $[(RO)_{4-n}Si{-}R'_n,\ 1 \le n \le 3]$ have been incorporated into the silica matrix through cohydrolysis or post-treatments. In any case, these terminal groups are usually housed in the pore space.[6] As an alternative, a novel strategy based on the use of bridge-bonded silsesquioxanes $[(RO)_3{-}Si{-}R'{-}Si(OR)_3]$ leads to the incorporation of the organic functional groups embedded in the silica walls (PMO materials).[11] Thus, surface and framework organic modifications have been carried out by using RPO_3^{2-} terminal phosphonates [instead of $R'Si(OR)_3$][6] or $^{2-}O_3P{-}R{-}PO_3^{2-}$-bridged diphosphonates [instead of $(RO)_3{-}Si{-}R'{-}Si(OR)_3$],[10] respectively. Our method al-

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lows the progressive incorporation of organic groups, which originates from organic-free ALPOs to pure mesoporous aluminium phosphonates or diphosphonates (100 % of organophosphorus groups) through ALPOs with organically modified surfaces (terminal phosphonates) and/or frameworks (bridged diphosphonates).

The procedure is based on the use of a simple and commercial structural-directing agent (CTABr = cetyltrimethylammonium bromide) and a complexing polyalcohol (2,2′,2′′-nitrilotriethanol = TEAH3), which has proved its capability to harmonise the rates of the hydrolytic reactions of the aluminium species in water−phosphoric acid media and the subsequent processes of self-assembling with the surfactant aggregates.[11] The same general procedure has been used for obtaining solids with diphosphonates (using ethylenephosphonic acid), phosphonates (using methylphosphonic acid) or mixed phosphate−phosphonate/diphosphonate derivatives (starting from mixtures of phosphoric and organophosphorus acids; see Exp. Sect.). In all cases, the molar ratio of the reagents was adjusted to 2 Al/3 P (H_3PO_4 + phosphonic acid)/8 TEAH3/0.52 CTABr/270 H_2O. Table 1 summarises the main synthesis variables and physical data.

EPMA shows that all UVM-9 samples are chemically homogeneous (spot area ca. 1 μm) and have a constant and well defined composition. In all cases, UVM-9 solids containing diphosphonate groups show Al/P proportions close to the idealised Al/P molar ratio (1:1), typical of stoichiometric ALPOs, in contrast to the aluminium phosphate−phosphonate materials previously described (Al/P = 1.37[9]), while deviations from the Al/P ratio have been observed when monophosphonate groups were present. This fact indicates that the UVM-9 solids may basically be regarded as aluminophosphonates rather than a compound consisting, to a significant degree, of alumina domains connected through organophosphorus moieties. Moreover, the high-angle XRD patterns do not show peaks associated to segregated bulk phases. Based on these facts and taking into account the difficulty to condense phosphate, phosphonate and/or diphosphonate groups among them (leading to P−O−P bonds) under aqueous conditions, we can propose that the UVM-9 materials display a regular distribution of Al and P atoms along the pore walls. The high chemical homogeneity and dispersion achieved for Al and P atoms indicates that the good reactivity control previously reached with Al-TEAH3 complexes as an aluminium source in water/phosphoric media is maintained when phosphoric acid is partially or totally replaced by phosphonic or diphosphonic acids.

Elemental CNH analysis of all mesoporous UVM-9 samples reveals that they are nitrogen-free materials. This fact confirms the efficiency of the soft surfactant extraction procedure we have used. Moreover, the absence of signals associated to surfactant molecules in the ^{13}C NMR spectra supports the total CTA^+ evolution. Thus, CNH analysis allows an estimation of the content of organic groups in the final mesoporous materials to be calculated (see Table 1). The phosphonate/phosphate molar ratio in the materials containing diphosphonate species is close to that present in the mother liquor (samples 5 and 7), but it significantly drops when monophosphonates are involved (samples 2 and 3). Very likely, this difference is related to the capability of the phosphate and diphosphonate groups to act as network building blocks (bridging Al atoms); a role that monophosphate groups do not play (RPO_3^{2-} groups are necessarily terminal). As in the case of the PMO organosilicas, the bridging nature of the diphosphonates and their ability to interact through six O atoms allows their easy incorporation as network-forming groups. For this reason, the isolation of practically stoichiometric (Al/P = 1) diphosphonate materials is possible. Without prejudice to the observed preferential incorporation of the phosphate groups vs. monophosphonate groups, the existence of pure Al-monophosphonates (sample 4) and Al-diphosphonates (sample 7) is proof of the cooperative ability of the organophosphorus and aluminium moieties to construct stable networks around the surfactant aggregates. This last result accords well with previous results on organosilicas (with terminal organic groups), suggesting an upper functionalisation limit of about 40 %;[12] probably because at least 50 % of SiO_4^{3-} units is required to stabilise the pore wall network. Effectively, the intrinsic compositional nature of the UVM-9 materials (Al/P ≈ 1:1) warrants the presence of a similar amount of network-forming groups. Indeed, the slightly higher aluminium content in the Al-monophosphonates (Al/P = 1.15−1.25:1), should be viewed as a requirement for the pore wall stabilisation.

^{31}P MAS NMR spectra (Figure 1) confirm the incorporation of phosphate and phosphonate groups and provide useful information on their evolution as the functionalis-

Table 1. Selected synthetic and physical data for UVM-9 mesoporous organophosphonates

Sample	Phosphonic acid used	Solution (%)[a]	Solid (%)[b]	Al/P[c]	d_{100} (XRD)/nm	S_{BET} ($m^2 \cdot g^{-1}$)	BJH pore (nm)	Pore vol. ($cm^3 \cdot g^{-1}$)
1	–	–	–	1.10(2)	4.86	633.2	3.23	0.70
2	$CH_3PO(OH)_2$	50	22.3	1.25(2)	4.95	703.6	2.84	0.75
3	$CH_3PO(OH)_2$	75	45.8	1.15(2)	5.09	793.9	2.69	0.71
4	$CH_3PO(OH)_2$	100	100	1.24(2)	6.13	674.9	3.33	0.75
5	$(OH)_2OP\text{-}(CH_2)_2-PO(OH)_2$	50	54.2	0.97(2)	4.96	655.0	3.41	0.86
6	$(OH)_2OP\text{-}(CH_2)_2-PO(OH)_2$	75	78.1	1.00(2)	5.33	712.8	3.26	0.85
7	$(OH)_2OP\text{-}(CH_2)_2-PO(OH)_2$	100	100	1.11(2)	6.09	674.9	3.32	0.63

[a] P(phosphonate)/P(total) molar ratio (%) in the starting solution. [b] Values estimated from CNH analysis and referred to the P(phosphonate)/P(total) molar ratio (%) in the final UVM-9 solids. [c] Values averaged from EPMA of about 50 particles.

ation level increases. The spectrum of sample 1 (ALPO) shows a broad signal centred at −25 ppm, which can be attributed to tetrahedral phosphates connected to aluminium centres.[5] As expected, according to the CNH analysis, the spectra clearly show the evolution of the P environments as the phosphonic/phosphoric acid ratio increases (samples 2−4 and 5−7); the intensity of the signals associated with the phosphate groups decreases while that of the signals characteristic of the phosphonate increases (10−22 ppm range).[13] Finally, the spectra of samples 4 and 7 (Al-methylphosphonate and Al-ethylenediphosphonate, respectively) only display the ^{31}P signal typical of phosphonate groups. Hence, while samples 2, 3, 5 and 6 present two different phosphorus environments, the UVM-9 materials with a functionalisation level of 100 % (samples 4 and 7) show only one environment for the P atoms both before and after (mesoporous) surfactant evolution. The small ^{31}P signal shifts observed in the NMR spectra can be associated to different parameters such as the proportion of octahedral aluminium sites and OH groups bonded to the P atoms and also to the presence of variable water amounts inside the mesopores.[14] In our case, the soft chemical treatment used to extract the surfactant allows us to maintain the chemical integrity of methylphosphonate and ethylenediphosphonate groups in the final mesoporous solids. This strategy avoids the degradation of the bridged diphosphonate.[9] All UVM-9 materials have ^{27}Al MAS NMR spectra that include two resonance signals at approximately $\delta = 0$ and 50 ppm (see Supporting Information; see also the footnote on the first page of this article). These signals are indicative of six- and four-coordinate Al centres, respectively. In the case of ALPO (sample 1), the majority of the Al centres are in tetrahedral sites. The proportion of octahedral Al sites increases as more of the phosphonate or diphosphonate groups are incorporated, and finally they become dominant in samples 4 and 7 where a significant amount of hydroxyl groups, probably bonded to aluminium atoms, would be required to balance the charge. Moreover, the coordination of the aluminium atoms at the pore surface should be increased by water molecules.

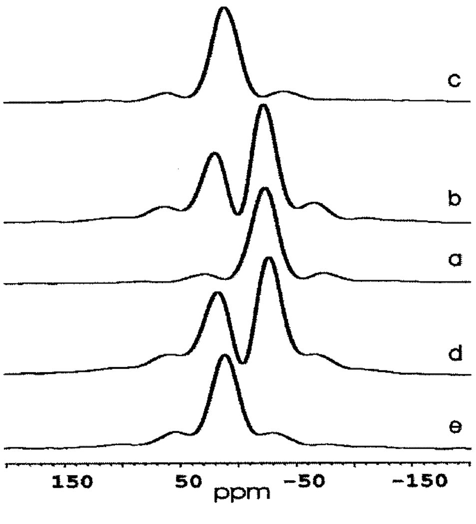

Figure 1. ^{31}P MAS NMR spectra of selected dehydrated samples: (a) sample 1; (b) sample 3; (c) sample 4; (d) sample 5; (e) sample 7

Selected XRD patterns of UVM-9 samples are shown in Figure 2. All materials display XRD patterns with at least one strong peak at low 2θ values (associated with the [100] reflection if a hexagonal cell is assumed), which is typical of periodic mesoporous materials. The shift of the d_{100} peak at low 2θ values as the content of organophosphorus groups increases suggests that both phosphonates and diphosphonates should be effectively incorporated into the inorganic walls. The resolution from the background of this intense peak decreases with increasing functionalisation level. Such an evolution indicates that incorporation of phosphonate or diphosphonate groups implies a progressive lowering of order in the pore system from hexagonal partially ordered (sample 1) to clearly disordered materials (samples 4 and 7). TEM micrographs (Figure 3) fully correlate to

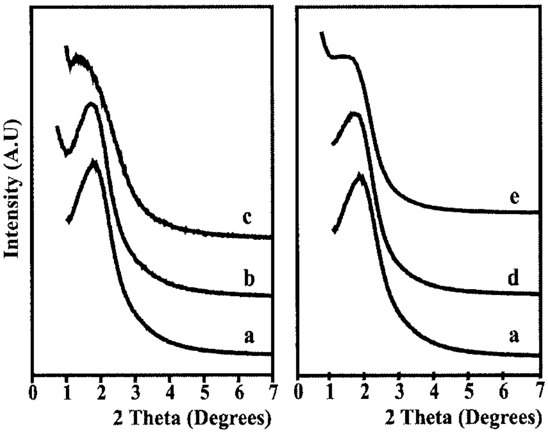

Figure 2. Selected XRD patterns of UVM-9 materials: (a) sample 1; (b) sample 3; (c) sample 4; (d) sample 5; (e) sample7

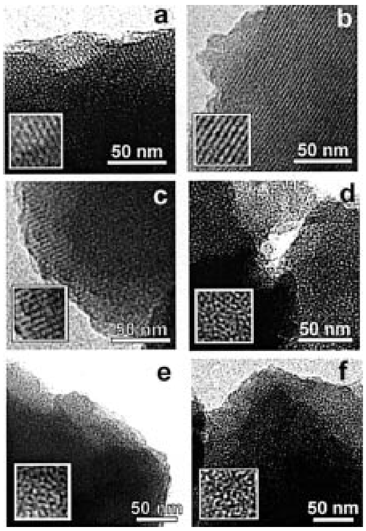

Figure 3. Representative TEM images of UVM-9 materials: (a) sample 1; (b) sample 2; (c) sample 5; (d) sample 3; (e) sample 4; (f) sample 7; the insets show enlarged (× 2) images

XRD observations. Whereas small domains with partially ordered hexagonal (H_d) mesopore arrays are observed in the ALPO (sample 1) and materials with low amounts of organophosphorus moieties, the solids having medium and high proportions of phosphonate or diphosphonate groups show disordered topologies. On the other hand, all UVM-9 samples show one well-defined step in their N_2 adsorption−desorption curves, characteristic of type IV isotherms (see Supporting Information). Although XRD and TEM data suggest that a progressive loss of order occurs as the amount of organophosphorus moieties increases, the relatively sharpness of these steps (unusual in nonsilica based materials) indicates a reasonable uniformity of the mesopores. A high surface area and pore volume are retained in all UVM-9 solids.

Conclusion

In short, periodic mesoporous aluminium phosphonates and diphosphonates (100 % of organophosphorus groups) have been synthesised for the first time through a generalised surfactant-assisted procedure. This method is applicable to the preparation of materials including other cations (different from Al) and/or phosphonic acids, which implies in turn new opportunities for applications of mesoporous phosphates. The control of the pore size and the wall properties such as hydrophobicity and the easy incorporation of organic functional groups attached to the P atoms confers on this new family of hybrid porous materials potential interest in areas such as chemical sensors, separations, catalysis and environmental sciences.

Experimental Section

UVM-9 Mesoporous Hybrid Materials: A typical synthesis leading to sample 7 (a pure Al-diphosphonate) is as follows: 1) $Al(OBus)_3$ (12.7 mL) was slowly added to liquid TEAH3 (26.2 mL) and heated at 150 °C to give aluminium atrane complexes (compounds containing TEAH3 ligands); 2) after cooling this solution to 110 °C, CTABr (4.68 g) were added; 3) the resulting solution was cooled to 60 °C and mixed with a solution of 1,2-ethylenediphosphonic acid (7.03 g in 120 ml water). After a few minutes a white powder precipitated out and was filtered off, washed with water and ethanol and air dried. Finally, the surfactant was extracted from the obtained powder with an acetic acid/ethanol solution (ca. 1 g of powder, 16 mL of acetic acid and 130 mL of ethanol; $t = 24$ h, at room temperature). The final porous material was separated by filtration, washed with ethanol and air dried.

All samples were characterised by CNH elemental analysis and electron probe microanalysis EPMA (Philips SEM-515), ^{13}C, ^{27}Al and ^{31}P MAS NMR (Varian Unity-300), XRD (Seifert 3000TT diffractometer using Cu-K_α radiation), TEM (JEOL JEM-1010 operating at 100 kV) and N_2 adsorption-desorption isotherms (ASAP2010).

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