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Communication

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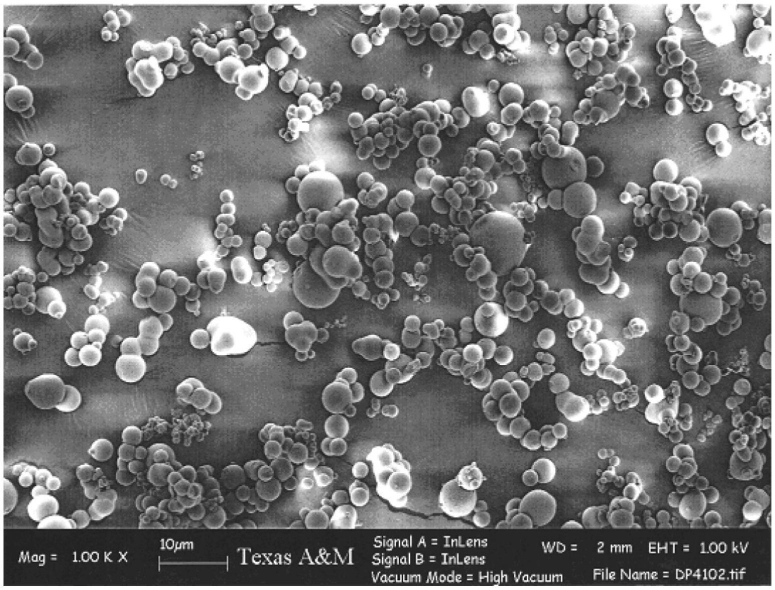

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A Family of Microporous Materials Formed by Sn(IV) Phosphonate Nanoparticles

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We report here a new family of microporous materials, the tin(IV) phosphonates, that derive their porosity from the aggregation of their nanosized particles. In a sense, the search for new micro- and mesoporous materials is derived from the examples provided by zeolites. The zeolites are among the most important and varied group of porous materials which have found many different applications. Their limitation is that the very useful members have channels and pore sizes or openings into the pores no larger than about 10 Å. Our research has been directed toward obtaining materials with high surface areas, where the pores are in the 10−20 Å range. Such materials would bridge the gap between the zeolites and the newer mesoporous materials.[1] One such group of compounds with the requisite type of pores recently reported by us are mixed oxides of ZrO_2, TiO_2, SiO_2, and $Al_2O_3-SiO_2$, containing high levels of transition-metal oxides.[2] A family of organic−inorganic hybrids having pores in the 8−20 Å range are the zirconium aryl bisphosphonates of ideal formula $Zr[O_3P(C_6H_4)_n\text{-}PO_3]$.[3] The ZrO_3P groups form zirconium phosphate-like layers that are cross-linked into three-dimensional structures by the aryl groups.

Our research has, for many years, been concerned with metal phosphonate chemistry.[4] The prototype compound is zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$.[5] It is a layered compound[6] with an interlayer spacing of 14.82 Å, with the Zr atoms in the center of the plane in a near hexagonal array. These metal atoms are bridged by the phosphonate oxygens in much the same way as in α-zirconium phosphate.[7] This compound is nonporous with relatively low surface areas. Therefore, it was of great interest to us when it was reported that both titanium and tin(IV) phenylphosphonate have high surface areas.[8] In previous reports,[9a] the surface area of titanium phenylphosphonate was attributed to the ease with which the phenylphosphonate groups were hydrolyzed in aqueous solution. The pores were in the mesopore range with a wide distribution of pore sizes.[9b] However, when the titanium phenylphosphonate was prepared in the presence of sodium dodecyl sulfate (SDS), the surface area was 264 m^2/g and the isotherm was type I, indicative of microporosity.[10] In the case of tin(IV) phenylphosphonate, once again, the sample prepared in the presence of SDS was found to be microporous, but samples for which SDS was not present gave mesopores with a broad distribution of pore sizes characteristic of interparticle porosity.[11] We repeated the preparations without the presence of any surfactant and obtained quite different results. The sorption−desorption isotherm for N_2 at 77 K is shown in Figure 1a and the pore size distribution as determined by the MP method in Figure 1b. The surface area was 367 m^2/g, and the peak in the pore size distribution curve is at ∼9 Å. A small portion of the pores are in the 18−27 Å range. An X-ray pattern of the tin phosphonate has a major peak at 15.2 Å and weaker reflections that index as 002 and 003 if the first peak is considered to be the 001 reflection. This X-ray powder pattern is similar to that of zirconium 4,4′-biphenyldiphosphonate, which does have a layered structure with as little as seven layers.[3b] Analytical data indicated a near 2:1 ratio of phenyl groups to Sn with a small amount of F$^-$ present because HF was used as a tin solubilizing agent. With these indications that we are dealing with a layered tin(IV) phosphonate structure similar to that of zirconium phenylphosphonate, the question is how to account for the very high surface area.

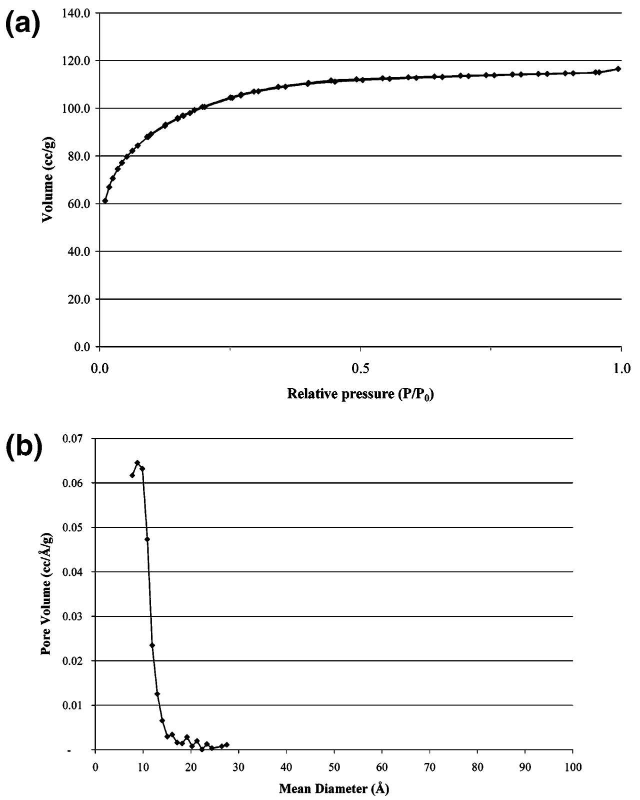

Figure 1. (a) Nitrogen sorption−desorption isotherm for Sn(IV) phenylphosphonate. (b) Pore size distribution curve derived from the isotherm in 1a.

Scanning electron micrographs (Figure 2) revealed unusual features of the powdered solid. The particles appear as micron-sized spheres, but on very high magnification, the spheres exhibit pores almost like a sponge due to the aggregation of small rods. These pores must run through the spheres in perhaps a tortuous

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Table 1. Ideal Formulas and Properties of Selected Tin (IV) Phosphonates

ideal formula	d_{001} (Å)	Surface Area (m^2/g) total	Surface Area (m^2/g) micro	max in pore size distribution curve (Å)	TGA wt. loss (%)
$Sn(O_3PC_6H_5)_{1.95}F_{0.05}\cdot H_2O$	15.35	367	350	9	34.09
$Sn(O_3PC_6H_5)_{0.95}(O_3PCH_3)_{0.95}F_{0.10}\cdot 0.4H_2O$	15.22	514	493	11	24.05
$Sn(O_3PCH_3)\cdot 0.4H_2O$	9.74	68	0		6.8
$Sn(O_3PC_{12}H_8PO_3)\cdot 0.8H_2O$	13.8	416	388	17	36.0
$Sn(O_3PC_{10}H_{21})_2$	28.07	264	220	9	47.6
$Sn(O_3PCH_2CH_2COOH)_2\cdot 0.8H_2O$	11.07	224	102	27	33.09

fashion to provide the observed very high surface areas. Substitution of methylphosphonic acid for half the phenylphosphonic acid increases the surface area to 514 m^2/g and the pore maximum to ~11 Å. The X-ray powder pattern (XRPD) for the mixed phenyl−methyl derivative is very similar to that of the pure phenylphosphonate, indicating that the mixed derivative is a single phase. The pure methylphosphonate has an initial reflection at 9.74 Å, which does not appear in the XRPD of the mixed derivative. Furthermore, the spherical spongelike topology persists in the mixed derivative but not in the tin methylphosphonate.

Table 1 summarizes the data for a number of tin(IV) phenylphosphonates. All of them except the methyl derivative behave the same way. They form the spherical morphology, have high surface areas, and are largely microporous. We have chosen only a small selection for the table out of 20-some compounds we have prepared, but of sufficient variety to demonstrate that these characteristics apply to a broad family of tin phosphonates.

To further characterize these tin phosphonates, small angle neutron scattering data were obtained at IPNS. The curves of intensity as a function of Q in $Å^{-1}$ are presented in Figure 1S in the Supporting Information. Measurements were carried out for $Sn(O_3PC_6H_5)_2$, $Sn(O_3PC_6H_5)(O_3PCH_3)$, $Sn(O_3PC_{12}H_8PO_3)$, and $Sn(O_3PC_6H_4C_6H_5)(O_3PCH_3)$. The curves could be fit with a rodlike model for the particles. For the phenylphosphonate, the rod was 11 Å for the cross-sectional radius of the rod and 44 Å for the length of the rod. For the mixed methyl−phenyl derivative, these values increased to 15 and 78 Å, respectively.

Further characterization of the tin(IV) phosphonates has been obtained from solid-state MAS NMR. Spectra for ^{119}Sn have been obtained for a number of the phosphonates and in each case. The ^{119}Sn chemical shifts lie between −817 and −822 ppm. This compares to the six-coordinate tin in SnO_2 at −603 ppm and values for eight-coordinate Sn(IV) in a number of coordination compounds near −800 ppm. Therefore, it is likely that these tin phosphonates are eight-coordinate and dictates that the structure of the tin(IV) phosphonate layers are considerably different from their zirconium analogues.

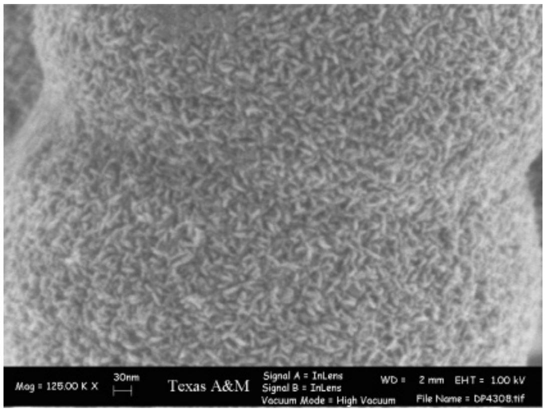

Figure 2. SEM of Sn(IV) phenylphosphonate showing the micron-sized spheres and the porosity of the surface.

In conclusion, we report the synthesis and characterization of a broad family of tin(IV) phosphonates that are nanoparticles, not by design but by their very nature. A consequence of their very small particle size is that the particles aggregate into micron-sized spheres that create tunnels that represent micropores. The cross-sectional diameters of the tunnels ranged from about 11 to 24 Å with maxima in the pore size distribution curves in the 10−27 Å range, depending on the size of the R group in RPO_3H_2. Thus, it may possible to control the pore sizes by choice of the phosphonic acid and the time and temperature used in the synthesis, from small micro to the mid-meso range. This characteristic suggests their use in separations, not only by size but also by control of hydrophilic−hydrophobic character or by chemical character. The presence of amino or carboxylic acid groups can allow their use as metal complexing agents and for incorporation of catalytically active metals. Sulfonation of the phenyl rings may yield strong Bronsted acidity.[3] One can think of the walls of the pores lined with functional groups in a similar sense to decorating the walls of mesoporous silicas to add chemical reactivity to the host.

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Supporting Information Available: Figure 1S. This material is available free of charge via the Internet at http://pubs.acs.org.

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