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[16] X-ray crystal data for **1**: $C_{36}H_{63}CrN_6$, $M_r = 589.85$, triclinic, $P\bar{1}$, $a = 9.9754(17)$, $b = 12.707(2)$, $c = 16.687(3)$ Å, $\alpha = 77.228(3)$, $\beta = 75.734(3)$, $\gamma = 70.655(4)^\circ$, $V = 1911.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.025$ g cm^{-3}, $\mu = 0.326$ mm^{-1}, 8755 independent reflections harvested from 2450 frames of data collected at 20 s per frame and 0.2° between frames yielded 13711 integrated intensities, $R_{int} = 0.029$. All data were included in the refinement. For $I > 2\sigma(I)$, $R_1 = 0.0685$ and $wR_2 = 0.1856$; including weak data $R_1 = 0.1585$ and $wR_2 = 0.2141$. Siemens/Bruker P4-CCD, $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å), graphite monochromator, $2\Theta_{max} = 56.5^\circ$, $T = 295(2)$ K. Suitable crystals for single-crystal X-ray analysis were selected and mounted inside thin-walled capillaries in a dry box under nitrogen atmosphere. Data collection and integration used the Bruker SMART and SAINT software. Empirical absorption corrections were calculated using the program SADABS.[17] Solution and refinement used the programs SHELXS[17] and SHELXL-93.[17] All non-hydrogen atoms were described anisotropically. Hydrogen atoms were placed in calculated positions. The 3,5-di-*tert*-butylpyrazolato ligands typically show severe disorder in the *tert*-butyl groups, which results in modeling difficulties and high *R* values. However, other criteria of chemical and crystallographic reasonableness show these to be acceptable structural models. CCDC-175570 (**1**) and CCDC-175571 (**2**$\cdot(C_6H_{14})_{0.5}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Hexagonal and Cubic Thermally Stable Mesoporous Tin(IV) Phosphates with Acidic and Catalytic Properties[**]

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Since the initial work of Mobil researchers on the synthesis of mesoporous silica,[1] a lot of work has been devoted to extend the composition of mesoporous materials to metal oxides other than silica for applications in acid, redox catalysis, or photocatalytic processes.[2–4]

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To date, a wide range of non-silica based mesostructured solids such, as metal oxides[5–10] of Al, Ti, Nb, V, W, and Sn or metal phosphates of Al, Zr, or V have been reported.[11–13] Most of these materials are, however, not stable to the removal of the surfactant and/or lack of long-range order. To our knowledge, cubic mesoporous solids are still scarce in spite of promising results with oxides of Nb,[14] Sb,[15] Al-B,[16] Ti,[6b] and Zr[17]. The first mesotextured metallophosphate with a cubic structure was described recently by Mizuno et al.[18] However, its framework collapses after the removal of the surfactant.

We recently reported new hexagonal or lamella titanium(IV) fluorophosphates synthesized by the fluoride route.[19] By extending this pathway to the tin(IV) system, we obtained hexagonal and cubic thermally stable porous tin(IV) fluorophosphates. Several mesotextured tin oxides were reported previously,[10] however, our solids are the first tin-based mesoporous materials exhibiting both a high thermal stability, long-range order, and high surface areas. The cubic phase is also the first thermally stable cubic mesoporous non-silicated metallophosphate reported to date. Finally, the acidic character determination as well as deNO_x catalytic tests (catalysts for the removal of NO_x) are reported.

The existence of either hexagonal or cubic phases is strongly dependent on synthesis parameters, such as concentration, P/Sn, S/Sn ratios (where S = surfactant), and the alkyl chain lengths. Hexagonal solids are obtained for long alkyl-chain surfactants ($n > 14$) while cubic phases appear for short-chain surfactants ($n < 14$). With $n = 14$, either hexagonal or cubic solids are obtained by tuning the P/Sn and/or S/Sn ratios. At a fixed surfactant concentration (S/Sn = 0.5), two phosphoric acid contents, P/Sn = 4 or 16, lead, respectively, to the formation of hexagonal and cubic solids while at a fixed phosphoric acid ratio (P/Sn = 16), hexagonal and cubic solids are obtained, respectively, at S/Sn = 1 and 0.5. At $n = 16$, changing the steric hindrance of the surfactant polar head by using cetyldimethylethylammonium bromide instead of cetyltrimethylammonium bromide (CTAB), leads either to hexagonal or cubic solids depending on the P/Sn ratio.

Both quantitative and thermal analysis reveal that both as-synthesized solids are tin fluorophosphates with P/Sn, F/Sn, and S/Sn (calculated) ratios close to 1.35, 1, and 0.65 (hexagonal) or 1.55, 0.65 and 0.45 (cubic), respectively. These results give approximate compositions of $Sn_3(PO_4)_4F_3 \cdot 2TTAB$ (TTAB = tetradecyl trimethylammoniumbromide) and $Sn_2(PO_4)_3F \cdot TTAB$, respectively, for the two phases. Both solids are calcined under air at 400 °C, and on cooling to room temperature, the calcined forms rehydrate to some extent without modification of the framework. Quantitative analysis and solid state ^{19}F, ^{31}P, and ^{119}Sn NMR spectra indicate that the resulting solids are rehydrated tin(IV) phosphates that contain only traces of fluorine. Mössbauer experiments indicate also that the two solids possess only octahedrally coordinated tin centers in the +IV oxidation state.

The X-ray patterns (Figure 1) of the as-synthesized TTAB solids ($n = 14$) are characteristic of the hexagonal MCM-41 compound,[1] and of the cubic micellar mesoporous solid SBA-1,[15, 20] respectively. Both structures are, on the whole, retained upon calcination. Their thermal stability, up to 600 °C, is almost identical. Calcined solids still exhibit a long-range organization since second-order diffraction peaks ((110) and (200) for H and (321) for C) are still visible in the X-ray patterns even if their intensity has slightly decreased. The pore contraction is within the 8–10 Å range in both cases.

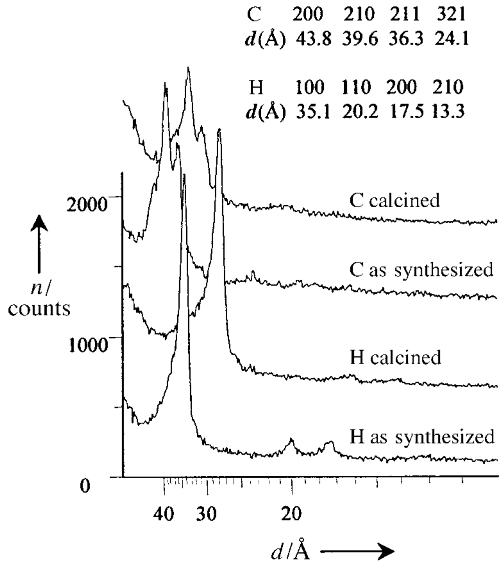

Figure 1. X-Ray powder diffraction patterns of the as-synthesized and calcined forms of the hexagonal (H) and cubic (C) tin(IV) phosphates obtained using TTAB surfactant. A peak index of the as-synthesized solids is given at the top of the Figure.

Brunauer–Emmet–Teller (BET) experiments, performed on the TTAB hexagonal (H) and cubic (C) solids calcined under air at 400 °C, indicate specific surface areas of 350 (H) and 425 (C) $m^2 g^{-1}$, respectively. These values are consistant since tin phosphates exhibit a much higher framework density than pure SiO_2. Both N_2 adsorption–desorption isotherms are of type I and do not show hysteresis loops (Figure 2). Schüth and co-workers observed similar isotherms with mesoporous titanium oxophosphates and explained this through the presence of "supermicropores" within the 15–20 Å range.[6e] Transmission electron microscopy (TEM) experiments (see below) indicate that the pore wall thickness is about 15 Å in both cases; considering the important pore contraction that occurs upon calcination, this gives an estimated pore size for each solid of below 20 Å. This size is consistent with results obtained previously with SBA-1 where

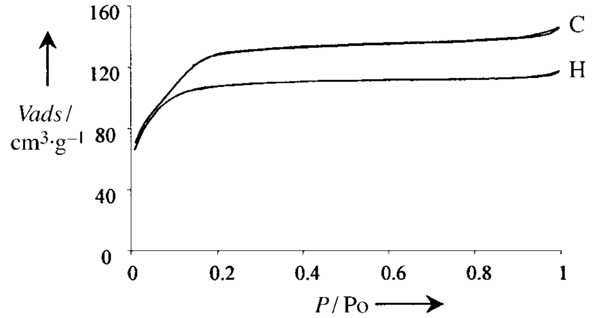

Figure 2. N_2 adsorption–desorption isotherm of the TTAB hexagonal (H) and cubic (C) tin(IV) phosphate solid calcined at 400 °C under air.

the pore size was estimated at about 20 Å for a sample displaying a very narrow hysteresis loop. Finally, by changing the nature of the surfactant (alkyl chain length, polar head), cubic or hexagonal solids, with surface areas between 200 and 630 $m^2 g^{-1}$ and pore sizes within the 12–25 Å range, are obtained.

High resolution TEM was performed on two solids: an H sample (CTAB-hexagonal) and a C sample (TTAB-cubic). Images show that the two materials, hexagonal and cubic, are not amorphous but clearly organized. Each of the grains is made of one or several randomly oriented small domains with a periodicity of the order of several nanometers. For the H sample, the electron-microscopy images exhibit a contrast which can be described as an unperfected honeycomb-like arrangement of six-fold faceted spheroids (Figure 3). The average periodicity of the close-packed spheroids is close to 45 Å, which is consistent with the X-ray diffraction results: $a = d(100)\frac{2}{\sqrt{3}} \approx 45.5$ Å.

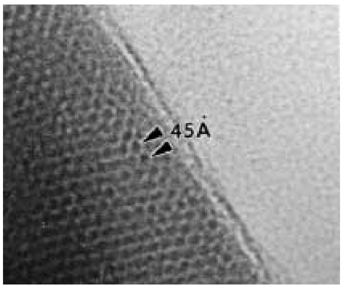

Figure 3. High-resolution electron micrograph showing the organized CTAB hexagonal domains of the as-synthesized tin(IV) phosphate solid.

Concerning the C system, globular cages, such as those observed with SBA-1 are present (Figure 4).[15] The cages are surrounded by dark rings because of the higher electron density of the tin phosphate framework. Within each organized arrangement of particles, we can distinguish the bright core of the particles, correlated with a zone of low electron density corresponding to the surfactant moieties. Numerous high resolution images were recorded. No preferential orientation of the grains is observed and the images suggest that the symmetry is of a P-type ($hk0$: no condition, $h0l$: $l = 2n$ and hhl: $l = 2n$). This symmetry is consistent with a pseudo-cubic (or tetragonal) lattice of a P-type symmetry with $a \approx c \approx$ 80 Å. This value is smaller than the parameter reported for the as-synthesized SBA-1: $a \approx 89$ Å,[20] but in agreement with the use of a smaller alkyl-chain surfactant ($n = 14$) compared with SBA-1 (CTAB ($n = 16$)).

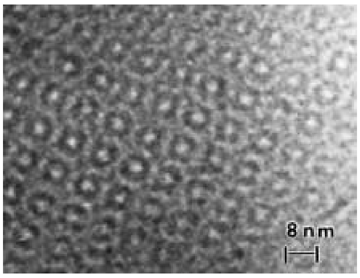

Figure 4. High resolution electron microscopy micrograph of the organized pseudo-cubic domains of the as-synthesized TTAB-cubic tin(IV) phosphate solid.

Electron microscopy images also show that, in both cases, no system of sharp reflections is detectable by working in selected-area electron diffraction (SAED) mode. Thus, the pore walls of these solids exhibit no crystallinity unlike the hexagonal titanium fluorophosphates reported.[19] Energy dispersive spectroscopy (EDS) indicates for both solids (H and C) that the pore walls exhibit a stoichiometry of three tin atoms per four phosphorus centers (Sn/P = 0.75). This result is in relatively good agreement with quantitative analysis results (Sn/P ≈ 0.73 and 0.65, respectively, for phases H and C).

Tin(IV) is well-known for its acidic properties. Therefore, a microcalorimetric study of the NH_3 adsorption was performed on the calcined forms of H and C TTAB solids. The proportion of acidic sites as a function of the binding energy was determined for each solid, which indicated (Figure 5) that both solids are strongly acidic with a large proportion of sites presenting a heat evolved above 100 kJ mol^{-1}. These solids and especially the hexagonal phase, are thus more acidic than MCM-41 and on the whole as acidic as some H-ZSM-5.[21] The hexagonal form is more acidic than the cubic phase. The number of acidic sites, the strength of which is between 100 and 150 kJ mol^{-1}, is two times higher for the hexagonal phase than for the cubic phase. However, the number of weak sites is similar for the two samples.

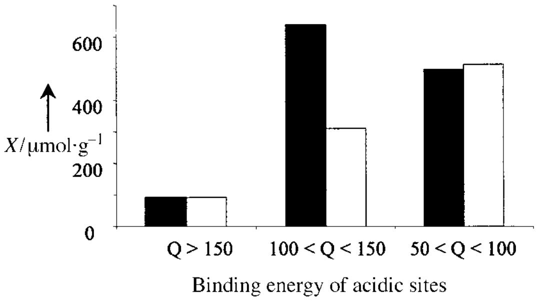

Figure 5. Comparative amount of the acidic sites of the calcined TTAB hexagonal (■) and cubic (□) solids as a function of their binding energy.

Since a $deNO_x$ catalytic activity requires acidic properties and as tin(IV)-containing amorphous oxides are well known for their activity in the reduction of NO by hydrocarbon,[22, 23] $deNO_x$ catalytic tests were performed on these mesoporous solids.

The two samples were evaluated in the NO-C_2H_4-O_2 reaction performed in lean conditions (in excess oxygen). Significant conversion of NO into N_2 as well as of C_2H_4 into CO_2 were detected between 400 and 600 °C. Plotting N_2 yield versus temperature gave a Volano-shaped curve, as usually observed for most $deNO_x$ catalysts.[23] The maximum amount of N_2 produced was observed around 475 °C for both the samples, hexagonal tin phosphate being more active than the cubic tin phosphate (30 and 20% of N_2 formation, respectively). To indicate the differences between the two samples, Figure 6 shows the profiles of N_2 formation expressed in terms of activity per surface unit obtained for the two samples in the whole temperature range investigated. The better activity of the hexagonal form of tin(IV) phosphate

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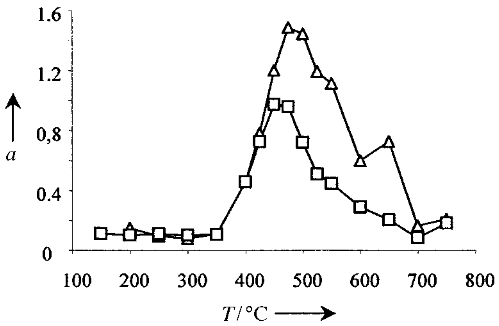

Figure 6. Intrinsic activity *a* (10^5 μmol N_2 m^{-2} min^{-1}) of N_2 formation from NO reduction by C_2H_4 in oxygen atmosphere on TTAB hexagonal (△) and cubic (□) tin phosphate solids.

could arise from different coordination of the tin(IV) centers and/or a higher amount of tin(IV) species exposed at the surface with respect to the cubic phase.

Besides nitrogen, by-products, such as nitrous oxide and nitrogen dioxide, were present in the reactor outlet at very low concentration, around 10–15 ppmv of NO_2 and 40-50 ppmv for N_2O. This behavior indicates a good selectivity of the samples.

Finally, a synthesis route in aqueous medium leading to thermally stable hexagonal and cubic mesoporous tin(IV) phosphates has been developed. These solids exhibit strong acidic properties and first catalytic tests have shown positive results especially for the hexagonal phase. Comparing their catalytic performances with those of known amorphous catalysts,[22] it seems that these new compounds could represent an interesting family of materials with good catalytic properties. Other catalytic experiments are currently in progress to evaluate the catalytic behavior of these new mesoporous solids.

Experimental Section

These solids were prepared by mixing SnF_4 with an aqueous solution of phosphoric acid with a final P/Sn ratio between 4 and 16. Then, the surfactant (cetyl or tetradecyl trimethylammoniumbromide (CTAB or TTAB)) solution was added to the stirred first solution (S:Sn ratio: 1:2). The final tin concentration was 0.1 Mol L^{-1}. The suspensions were aged at 90 °C overnight in a Teflon-lined PARR bomb and cooled to room temperature. The solids, filtered, washed, and dried were calcined under air at 150/400 °C for 1 and 8 h, respectively.

X-ray powder diffraction was conducted on a conventional high resolution (θ-2θ) Siemens D5000 diffractometer using $\lambda_{\mathrm{Cu}_{K\alpha}}$. Tin, phosphorus, fluorine, carbon, nitrogen, and hydrogen contents were determined at the C.N.R.S. Central Laboratory of Analysis of Vernaison (69, France). The surface area measurements were measured with a Micromeretics ASAP 2010 apparatus using nitrogen (N_2) as the adsorbed gas. The high resolution electron microscopy (HREM) was performed with a TOPCON 002B microscope (point resolution of 1.8 Å) equipped with an energy dispersive spectroscopy (EDS) analyzer. Samples were prepared by dispersing the powder in alcohol without grinding.

The microcalorimetric studies of ammonia adsorption were performed at 353 K in a heat-flow calorimeter of the Tian-Calvet type (C80 from Setaram) linked to a conventional volumetric line. Before each experiment the samples were outgassed overnight at 673 K. The differential heats of adsorption were measured as a function of coverage by repeated addition of amounts of gas until an equilibrium pressure of about 66 pa was reached. Then, the samples were evacuated for 1 h at the adsorption temperature and a second adsorption was carried out to allow the determination of chemisorption uptakes.

The catalytic tests were carried out with samples of mass 0.15 g contained in a quartz tubular microreactor (5 mm internal diameter). The reactant stream was provided from a set of mass-flow controllers (Bronkhorst, Hi-Tec) supplying 1000 ppmv NO and 1000 ppmv C_2H_4, and 20000 ppmv O_2 in helium at a total flow rate of 50 cm^3 (standard temperature and pressure) min^{-1}, with the reactor at close to atmospheric pressure. Contact time was maintained constant at 0.168 kg s L^{-1}. The exit gas stream from the reactor flowed through a gas cell (path length 2.4 m, multiple reflection gas cell) in the beam of an FTIR spectrometer (Bio-Rad with DTGS detector), to give analyses for NO, N_2O, and NO_2 for N-containing species, and C_2H_4, CO, and CO_2 for C-containing species. The measurements were carried out at 0.50 cm^{-1} resolution with an accuracy of ±10 ppmV for NO, and 4 for N_2O and NO_2 using lines at 1876, 2225, and 1619, respectively.

The samples were contained in the reactor between plugs of quartz wool and initially pretreated in flowing 20% O_2/He while the temperature was raised in stages up to 350 °C and maintained it for 4 h. The tests were repeated three times using fresh portions of catalyst and working in low (200–500 °C), high (450–750 °C), and medium (350–600 °C) zones of reaction temperature, respectively.

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