Experimental Section

Cage **3** was prepared as described.[7] Setup and procedures for spectrophotometric and potentiometric titration experiments have been reported elsewhere.[14] Equilibrium constants were determined by a nonlinear least-squares method.[15]

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[8] X-ray data for $[\mathrm{Cu}_2^{\mathrm{II}}(\mathbf{3})(\mathrm{Br})](\mathrm{ClO}_4)_3$: a crystal of approximate dimensions $0.20 \times 0.35 \times 0.40$ mm was mounted on a glass rod protected from the air by a thin film of perfluoric oil. Diffraction data were collected on a Philips PW1100 diffractometer equipped with a normal focus 2.0-kW sealed-tube X-ray source operating at 50 kV and 20 mA with graphite-monochromated $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined by least-squares refinement on 30 $I_{hkl}(\theta, \kappa, \varphi)$ reflections found in a random search on the reciprocal lattice in the range $10 < \theta < 18°$. The intensities were determined by profile analysis[9] and corrected for Lorentzian and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu were taken from the International Tables for X-Ray Crystallography.[10] The structure was solved by direct methods with SIR92[11] and then completed by cycles of Fourier ΔK and refined by full-matrix least-squares methods on F^2 by using SHELXL-96.[12] The parameters refined were the overall scale factor and the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included in their calculated positions with the geometrical constraint $d(\mathrm{X{-}H}) = 0.96$ Å and refined in the riding model. All calculations were carried out on a Digital Alfa255 workstation. Crystal data: $M_r = 1074.109$; monoclinic, space group $P2_1/c$, $a = 16.603(5)$, $b = 9.972(5)$, $c = 27.760$ (5) Å, $\beta = 101.26(2)°$, $V = 4508(3)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.583\,\mathrm{g\,cm^{-3}}$, $F(000) = 2192$, $T = 293$ K. 6823 ($\pm h$, $+k$, $+l$) reflections were collected, of which 6205 were unique ($R_{\mathrm{int}} = 0.04$) and 3329 observed ($F_o > 4\sigma(F_o)$). The refinement converged at $R1 = 0.058$, $wR2 = 0.17$ (all data), GOF: 0.86. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139472. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Unprecedented Expansion of the Pore Size and Volume of Periodic Mesoporous Silica**

Abdelhamid Sayari*

The synthesis of materials with designed pore structures is of paramount importance for many applications in areas such as catalysis, adsorption, and separation.[1] In designing such materials, several characteristics of the pore structure may be addressed, which include their shape, size, and connectivity. Since the discovery of the M41S periodic mesoporous silicas in the early 1990s,[2] a number of synthesis strategies to control their pore size have been developed. With only a few exceptions,[3, 4] all of the reported investigations dealt with MCM-41 silica whose pore structure consists of hexagonally packed unidimensional cylindrical channels (*p*6*mm*). In the latter case, the pore sizes may be adjusted from the lower end of the mesoporous range (about 2.0–2.5 nm) to well into the macroporous range. A summary of these approaches along with pertinent references is provided elsewhere.[5] In our earlier work,[6, 7] we found that treatment of as-synthesized 3.5 nm pore MCM-41 silica with long chain trialkylamines or *N*,*N*-dimethylalkylamines, typically at 100–130°C for 2–3 days, increased the pore size to a maximum of about 11 nm. The pore volume also increased threefold from 0.8 to 2.4 $\mathrm{cm^3\,g^{-1}}$. In this paper, we report an unprecedented pore size expansion from approximately 3.15 to 25 nm with conservation of the surface area and pore wall thickness.

The filled symbol in Figure 1 shows the nitrogen adsorption–desorption isotherm for MCM-41BT (BT = before treatment) with a sharp nitrogen condensation step at a

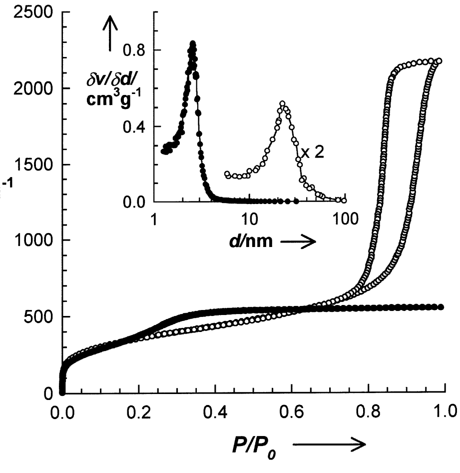

Figure 1. Nitrogen adsorption–desorption isotherms for MCM-41BT (●) and MCM-41AT (○). Inset: Corresponding PSDs (×2 indicates enhanced by a factor of 2).

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[*] Prof. A. Sayari
Department of Chemical Engineering and CERPIC
Université Laval
Ste-Foy, Qc, G1K 7P4 (Canada)
Fax: (+1)418656-5993
E-mail: sayari@gch.ulaval.ca

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relative pressure of 0.2, characteristic of mesoporous materials with a narrow pore-size distribution (PSD). The PSD (Figure 1, inset) exhibited a maximum at 3.15 nm. The BET (Brunauer-Emmett-Teller) surface area and the total pore volume were 1316 $m^2 g^{-1}$ and 0.86 $cm^3 g^{-1}$. Figure 2 shows a typical transmission electron micrograph (TEM) image for calcined MCM-41BT, which confirms the presence of hexagonally packed channels. As for the morphology of this material, scanning electron microscopy (SEM) showed it consisted of facetted tubules of approximate dimensions 45 × 10 μm (Figure 3, above).

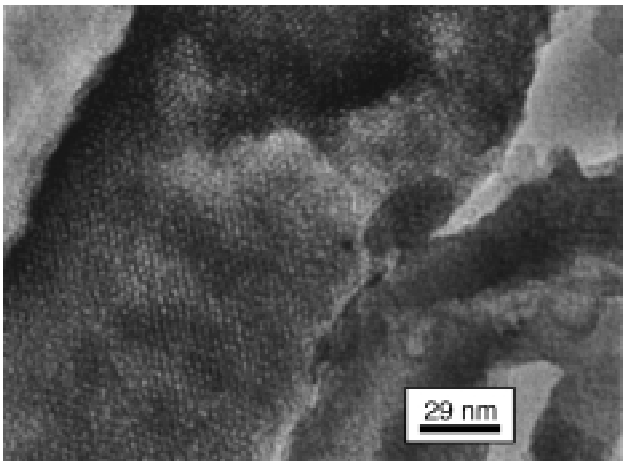

Figure 2. TEM image of MCM-41BT.

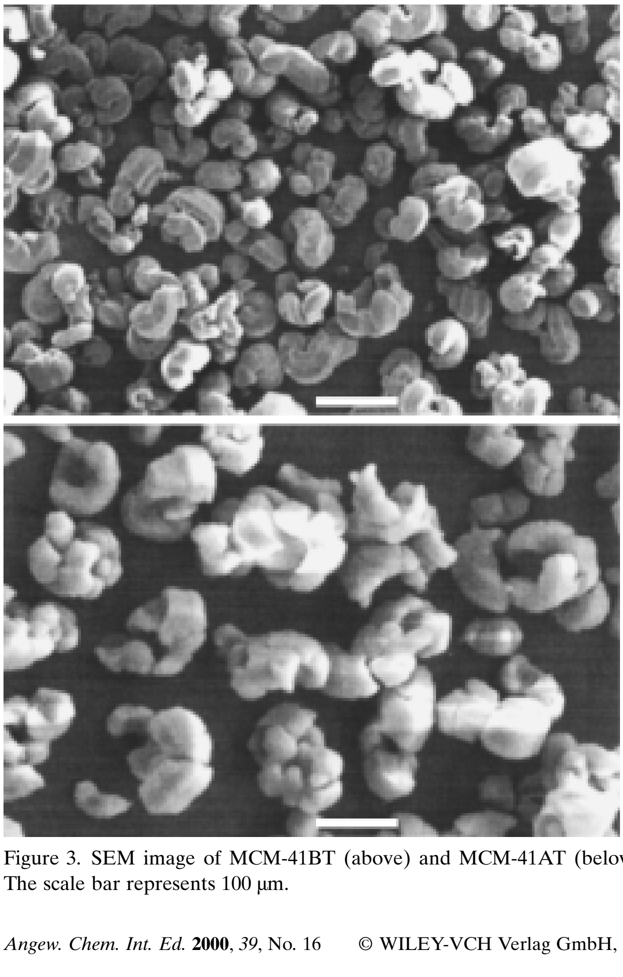

Figure 3. SEM image of MCM-41BT (above) and MCM-41AT (below). The scale bar represents 100 μm.

The nitrogen adsorption–desorption isotherm for the material after treatment in the presence of *N,N*-dimethyldecylamine (DMDA) at 120 °C for 48 h, MCM-41AT (AT = after treatment), is shown as open symbols in Figure 1. The nitrogen condensation and evaporation steps were shifted strongly to higher relative pressures, which indicates the occurrence of an unprecedented pore size expansion. The PSD was relatively narrow with a maximum at 25 nm (Figure 1, inset). The pore volume also increased tremendously, from 0.85 to 3.31 $cm^3 g^{-1}$, whereas the surface area remained almost constant at 1268 $m^2 g^{-1}$. This indicates that the pore wall thickness did not undergo any significant changes and shows the extreme structural flexibility of the MCM-41 silica. The pore structure, however, was no longer ordered as inferred from the absence of X-ray diffraction (XRD) lines and the lack of sufficient contrast to obtain good quality TEM images. In addition, as seen by SEM, the facetted tubular shape of the particles (Figure 3, lower) did not change during the amine treatment but the particles were swollen and exhibited a high density of cracks, most likely due to the stress generated by the expansion process.

Several experimental parameters may be adjusted to fine tune the pore size and volume of MCM-41 silica through postsynthesis treatment with DMDA or other appropriate amines.[7] First, since the degree of silica condensation in the starting material is likely to depend on the synthesis temperature, therefore, under otherwise identical DMDA treatment conditions, materials prepared at higher temperature are expected to expand to a lesser extent. For example, a MCM-41 silica prepared at 100 °C had a pore size of 3.3 nm and a pore volume of 1.17 $cm^3 g^{-1}$, which, upon amine treatment under the same conditions as above, the pore size increased to only 14 nm and the pore volume to 2.62 $cm^3 g^{-1}$. This is in contrast to the the MCM-41 silica prepared at 80 °C, in which values of 25 nm and 3.31 $cm^3 g^{-1}$, respectively, were obtained. The amine to silica ratio is also important. For example, treatment of the same amount of MCM-41 silica (0.8 g) prepared at 100 °C for 48 h at 120 °C for two days in the presence of 0.3 or 0.5 g of DMDA, instead of 1 g, increased the pore size to only 6.9 or 9.4 nm, respectively, while the pore volume increased to 1.64 or 2.18 $cm^3 g^{-1}$. Additional parameters for adjusting the pore size and volume are the temperature and duration of the postsynthetic treatment.

A tentative representation of the pore size expansion process is shown schematically in Scheme 1. Although the neutral amine may self-assemble into inverse cylindrical micelles due to hydrophobic interactions between the carbon chains, no direct proof of this effect on the pore size expansion

Scheme 1. Representation of the pore size expansion process using postsynthetic hydrothermal treatment in the presence of DMDA.

can be provided at this time. Work devoted to this issue is being carried out using labeled DMDA.

To our knowledge, the pore volume of the current MCM-41AT material (3.31 $cm^3 g^{-1}$) is the highest ever reported. Materials such as aerogels,[8] mesocellular silica foams,[9] and some hexagonal mesoporous silica prepared in the presence of amphiphilic triblock copolymers ("SBA-15")[10] exhibit pore volumes of up to 2.5 $cm^3 g^{-1}$, which is more than 30% less than that of the current MCM-41AT. Because of its particularly narrow pore size distribution and very high surface area, this material has potential applications in separation or catalysis involving large molecules. Several important applications of such materials ranging from adsorption to catalysis and stabilization of nanoparticles are being developed in our laboratory. In addition, similar pore size expansion procedures using cubic MCM-48 silicas as starting materials are in progress.

Experimental Section

MCM-41 silica was prepared as follows: 3.848 g of tetramethylammonium hydroxide (TMAOH; 25%) was diluted with water (37.1 g) before adding cetyl trimethyl ammonium bromide (CTAB; 5.466 g) under vigorous stirring. After 15 min, silica (Cab-O-Sil; 2 g) was added. The overall mixture composition was 1.0 SiO_2:0.317 TMAOH:0.45 CTAB:67 H_2O. The gel obtained after stirring for an additional 30 min was transferred into a Teflon-lined autoclave and heated statically under autogenous pressure at 80°C for 40 h. The obtained materials were filtered, washed extensively, dried, and calcined at 540°C, first in flowing nitrogen then in air. For post-synthetic pore size expansion, 0.8 g of the as-prepared sample was added to an emulsion of DMDA (1 g) and water (30 g) at RT. After about 1 h of stirring, the mixture was heated at 120°C for 2 days under autogenous pressure. Further separation and calcination were carried out as described above.

Adsorption measurements were performed using a Coulter Ominorp 100 gas analyzer. Pore size distributions were calculated using the Kruk-Jaroniec-Sayari method.[11] XRD spectra were obtained on a Siemens D5000 diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 0.15418$ nm). SEM images were recorded on a JEOL 840A microscope operated at an accelerating voltage of 10–20 kV. TEM images were obtained using a Philips 430 instrument operated at 100 kV. The specimen were embedded in an epoxy resin and ultrathin sections (approximately 60 nm) were cut and examined.

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Template Synthesis of the First 1,4,7-Triphosphacyclononane Derivatives**

Peter G. Edwards,* Paul D. Newman, and
K. M. Abdul Malik

The small-ring tridentate macrocyclic ligands 1,4,7-triazacyclononane (tacn) and 1,4,7-trithiacyclononane have occupied a central role in the development of macrocyclic coordination chemistry.[1] Surprisingly, the related homoleptic phosphorus compound, 1,4,7-triphosphacyclononane is unknown in the literature and prior to our present study, the smallest triphosphorus macrocyclic ring system known is 11-membered and was prepared by a nonstereoselective, high-dilution method.[2] To date, the smallest (and indeed only) triphosphorus macrocycle prepared stereoselectively is based upon the 1,5,9-triphosphacyclododecane ([12]-ane-1,5,9-P_3) core by Norman and co-workers who developed a $Mo(CO)_3$ template-assisted synthesis[3] which has led to a number of derivatives and in the free ligand being released subsequently by us.[4] This method has not allowed formation of smaller ring systems;[5] we have consequently chosen to investigate alternative templates that may provide stereospecific routes to smaller facially capping triphosphorus macrocycles.

In this respect, we have studied reactions of cyclopentadienyliron "piano-stool" complexes which appear ideally suited to the formation of *fac*-trisphosphane derivatives. In addition, the sequential selective incorporation of diphosphanes followed by monophosphanes (which is difficult to control in the $M(CO)_3$ templates) is well established;[6] this should give rise to far greater flexibility in the synthetic methodology. Herein we report on the synthesis of the first triphosphacyclononane (9aneP_3) derivatives by an iron(II)-mediated intramolecular cyclization of 1,2-bis(phosphanyl)ethane and trivinylphosphane.

The new compounds and synthetic methodologies reported herein are summarized in Scheme 1. The precursor complex $[Fe(CH_3CN)(CO)_2(\eta^5\text{-}Me_5C_5)]BF_4$ (**1**) was prepared by the oxidative cleavage of the dimer $[\{Fe(CO)_2(\eta^5\text{-}Me_5C_5)\}_2]$ by $Cp_2Fe^+\ BF_4^-$ as described by Astruc and Catheline.[7] UV photolysis of a 1:1 mixture of **1** and 1,2-bis(phosphanyl)ethane gives the diprimary phosphane acetonitrile cation **2** as the tetrafluoroborate salt. The $^{31}P\{^1H\}$ spectrum of **2** shows the expected singlet at $\delta = 7$, which appears as a triplet ($^1J_{P,H} = 343$ Hz) in the proton-coupled spectrum. Heating **2** with an equimolar quantity of trivinylphosphane in 1,2-dichloroethane or chlorobenzene at 70–80°C over 2 h gave the diprimary monotertiary phosphane complex **3**. The latter was identified by the presence of a doublet at $\delta = 15.5$ and a triplet at $\delta = 49.5$ ($^2J_{P,P} = 47$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. When **3** was heated at 80°C in 1,2-dichloroethane or chlorobenzene

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[*] Prof. P. G. Edwards, Dr. P. D. Newman, Dr. K. M. A. Malik
Department of Chemistry
Cardiff University
PO Box 912, Cardiff, CF10 3TB (UK)
Fax: (+44) 29-20874083
E-mail: Edwardspg@cardiff.ac.uk

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