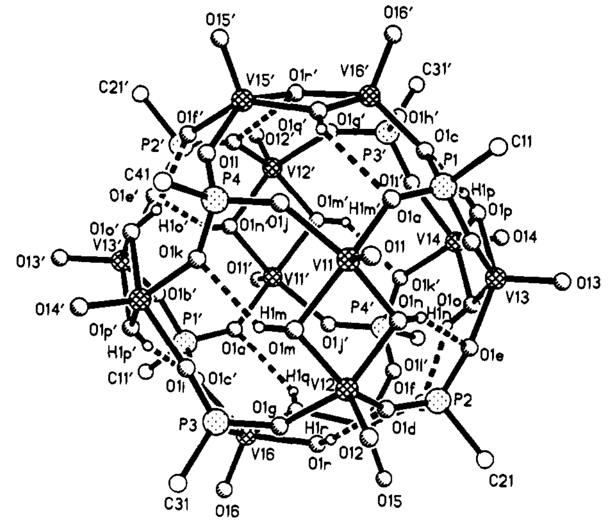

Figure 1. Perspective plot of one of the two crystallographically independent $[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]^{4-}$ anions in **1** with the phenyl groups omitted for clarity. Hydrogen bonds are represented by dashed lines. Atoms labeled with a prime are related to nonprimed atoms by the crystallographic inversion center. Bond distances (Å) and angles (deg) of interest: V–V, 3.082 (2)–3.106 (1); V–O_{term}, 1.568 (6)–1.590 (7); V–(μ_2-O(H)), 1.936 (6)–1.980 (6); V–(μ_2-O), 1.942 (5)–1.986 (4); O_{term}–V–(μ_2-O(H)), 105.7 (2)–110.7 (2); O_{term}–V–(μ_2-O), 103.6 (2)–108.9 (3); (μ_2-O)–V–(μ_2-O), 74.4 (2)–76.1 (2); (μ_2-O)–V–(μ_2-O(H)), 89.5 (2)–92.4 (2) and 140.7 (2)–150.5 (2); (μ_2-O)–V–(μ_2-O(H)), 82.9 (2)–84.3 (2).

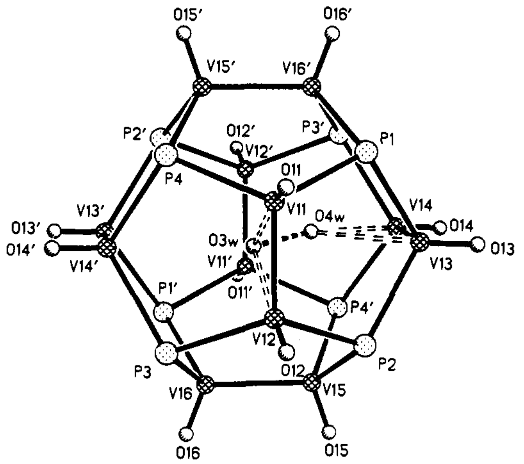

Figure 2. A drawing of the dodecahedral arrangement of the 12 vanadium and eight phosphorus atoms in the $[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]^{4-}$ anion of Figure 1. The terminally bonded oxygen on each vanadium is also shown as is one pair of included and weakly complexed water molecules (O_{3w} and O_{4w}).

water molecules during synthesis. However, the presence of additional atoms in the $\{V_{12}P_8O_{48}\}$ sphere results in a larger central diameter and consequently a greater free volume. The average distance from the center of the sphere to an oxygen atom is 4.4 Å compared to the value of 3.675 Å observed in $[H_4V_{18}O_{42}(X)]^{9-}$ (X = Br, I), suggesting that the inclusion of still larger molecules or ions by the vanadium organophosphonate structure may be possible.

Supplementary Material Available: Crystal structure analysis report including Tables I–VIII containing atomic coordinates for non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for anion hydrogen atoms, bond lengths and angles for the anion and cation non-hydrogen atoms, and close contacts involving hydrogen atoms for compound **1** (38 pages); table of observed and calculated structure factors for compound **1** (43 pages). Ordering information is given on any current masthead page.

Preparation of Molecular Sieves from Dense, Layered Metal Oxides

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We now report a novel pillaring procedure to convert dense, layered metal oxides and silicates into high surface area molecular sieves with large interlayer separations. The procedure is applicable to a wide variety of layered phases and allows for the engineering of microporous materials with diverse compositions and physical properties.

Over the past three decades, zeolite catalysis has had a dramatic impact upon petroleum refining and petrochemical processing.[1] Catalytic differences among zeolites are typically manifested by differences in product distributions as a consequence of unique zeolite channel or pore size and their framework aluminum content. To exploit the selectivity differences possible with different pore geometries and catalyst compositions, other classes of molecular sieves have been prepared which include aluminum phosphates ($AlPO_4s$)[2,3] and silica- and metal-modified $AlPO_4s$ such as SAPOs[4] and $MeAPO_4s$.[5] Pillared or intercalated clays,[6] layered phosphates,[7] and a layered tetratitanate[8] are other classes of molecular sieves. Historically, these have been synthesized by incorporating cationic precursors to stable metal oxide pillars.[6] The pore sizes of these pillared materials are determined by the size of the exchanging cation and are typically in the 8–9-Å range.[6,7]

The pillaring procedures developed for smectite clays are not generally applicable to the wide variety of laminar metal oxides that do not spontaneously delaminate in water. To tailor-make materials with varied but controllable pore sizes from metal oxides with unique chemistries, a new synthetic approach was created.

We found that pillaring could be facilitated by utilizing a preswelling step in which the interlayer is exposed to organoammonium ions. According to procedures developed earlier, layered metal oxides[9] and silicates[10] were first intercalated with an aqueous solution of long-chain organoammonium salt or amine. An organic pillar precursor, such as tetraethyl orthosilicate (TEOS), was then absorbed into the organophilic interlayer region, where it was converted to a metal oxide pillar. Typically, the organoammonium ion exchanged product was stirred with excess TEOS for 1–3 days at 25–80 °C, filtered, and dried. The final microporous material was produced by calcination for several hours in air at 538 °C, which removes the water, preswelling organoammonium ion, and organic byproducts from TEOS hydrolysis, affording a silica-pillared product. Using this procedure, we have prepared porous products from a wide variety of layered oxides, including alkali titanates,[11] alkali metal-substituted titanates

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(1) (a) Meisel, S. L.; McCullough, J. P.; Lechthaler, C. H.; Weisz, P. B. *Chem. Technol.* **1976**, *86*, 6. (b) Chen, N. Y.; Gorring, R. L.; Ireland, H. R.; Stein, T. R. *Oil Gas J.* **1977**, *75*, 165.

(2) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *105*, 1146.

(3) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C. *Nature* **1988**, *331*, 698.

(4) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6092.

(5) Flanigen, E. M.; Lok, B. M.; Patton, R. L.; Wilson, S. T. *Stud. Surf. Sci. Catal.* **1986**, *28*, 103.

(6) (a) Pinnavaia, T. J. *Science* **1983**, *220*, 365. (b) Vaughan, D. E. W.; Lussier, R. J. In *Proceedings of the 5th International Conference on Zeolites*; Rees, L. V. C., Ed.; Hyden: London, 1980; p 94. (c) Vaughan, D. E. W. *ACS Symp. Ser.* **1988**, *368*, 308.

(7) Clearfield, A.; Roberts, B. D. *Inorg. Chem.* **1988**, *27*, 3237.

(8) Cheng, S.; Wang, T.-C. *Inorg. Chem.* **1989**, *28*, 1283.

(9) Weiss, A. *Angew. Chem.* **1960**, *413*.

(10) (a) Lagaly, G.; Beneke, K.; Weiss, A. *Am. Mineral.* **1975**, *60*, 650. (b) Beneke, K.; Legaly, G. *Am. Mineral.* **1983**, *68*, 818.

0002-7863/91/1513-3189$02.50/0

Table I. Physical Properties of Pillared Layered Oxides

layered precursor	basal d spacing, Å initial[b]	basal d spacing, Å final[c]	surface area, m²/g initial	surface area, m²/g final	cyclohexane adsorptn,[a] wt % initial	cyclohexane adsorptn,[a] wt % final
titanates $Na_2Ti_3O_7$	8.4	20	<5	280	<1	9
Metal titanate $Cs_{0.7}(Ni_{0.35}Ti_{1.65})O_4$	8.4	22	<5	300	<1	10
magadiite	11.5	33	<20	530	<2	14
kenyaite	17.5	36	≤20	600	<5	21

[a] At 25 °C, 40 Torr. [b] Dehydrated phase. [c] Swollen with octylammonium, pillared with silica.

Table II. Properties of Pillared Alkali Titanates with Varying d spacings

swelling agent	surface area, m²/g	increase in d spacing,[a] Å	cyclohexane adsorptn, wt %
starting material $Na_2Ti_3O_7$	<5	<1	<1
propylammonium	50	2–3	<3
hexylammonium	200	9	6
octylammonium	280	12	9
dodecylammonium	470	21	16

[a] The increase in d spacing is calculated by the formula d_{001}(pillared) − d_{001}(layered phase), where d_{001}(layered phase) = 8.4 Å.

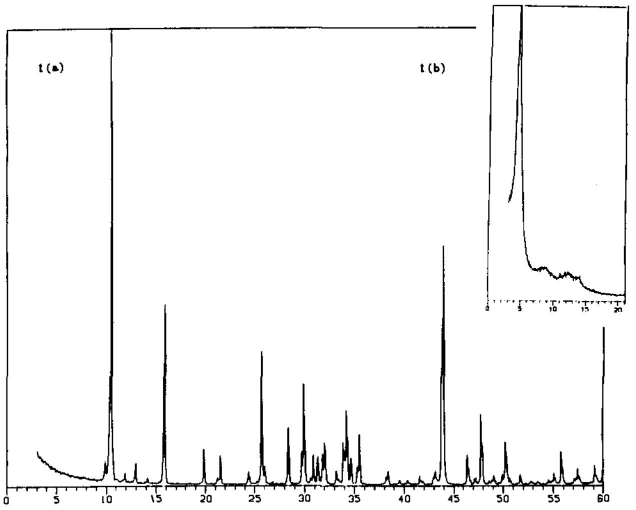

Figure 1. X-ray diffraction pattern of sodium titanate (**1a**) and silica-pillared sodium titanate (**1b**).

$A_x[MTi]_2O_4$,[12] and layered silicates such as magadiite, $Na_2Si_7O_{15}$, and kenyaite, $K_2Si_{14}O_{29}$. Table I outlines the starting materials and relevant physical properties of the porous silica-pillared products.

Evidence for the creation of pillared, microporous products follows. First, X-ray diffraction patterns (Figure 1) of a dense, layered titanate, $Na_2Ti_3O_7$ (**1a**), and its silica-pillard product[13] (**1b**) after calcination at 538 °C indicate a large increase in basal spacing (~12 Å). Secondly, this silica-pillared titanate, containing only 23 wt % silica, shows an increase in surface area from <5 m²/g in the starting $Na_2Ti_3O_7$ to 280 m²/g in the product. SEM photographs do not reveal significant amounts of amorphous silica external to the titanate crystallites. Also, a dense silica phase completely filling the interlayer region would not give rise to the observed high surface areas. Finally, this product adsorbs 9 wt % cyclohexane (Table I), characteristic of microporous solids such as zeolites.

This novel pillaring technique allows for tailoring of pore sizes as exemplified in Table II for a series of pillared titanates. As the alkyl chain length of the preswelling organic is increased, the observed d spacing, reflective of the pore size, also increases. Surface area and cyclohexane adsorption also increase with increasing interlayer separation. These examples illustrate preparation of stable pillared products with interlayer separations of 3–20 Å, determined by the size of the swelling agent. By careful choice of the organic preswelling agent, an even broader range of pore sizes are accessible. Thus, this new procedure not only allows for pillaring of diverse layer compositions but also permits the synthesis of materials with a wide range of pore sizes.

The ability to controllably modify chemical composition as well as pore size provides the flexibility to tailor catalysts for specialized end uses, and the catalytic potential of these materials is actively being explored.

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(11) Anderson, S.; Wadsley, A. D. *Acta Crystallogr.* **1961**, *14*, 1245.

(12) Reid, A. F.; Mumme, W. G.; Wadsley, A. D. *Acta Crystallogr.* **1968**, *B24*, 1228. Groult, D.; Mercey, C.; Raveau, B. *J. Solid State Chem.* **1980**, *32*, 289.

(13) The X-ray diffraction pattern of the calcined silica-pillared product is very similar to that of its organoammonium precursor.

NMR Determination of the Bond Lengths in C_{60}

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Several years ago, the idea that 60 carbon atoms could form a molecule with icosahedral symmetry was conceived as a purely theoretical possibility.[1] Subsequently, mass spectrometric evidence indicated that microscopic quantities of this fascinating molecule could be produced in cluster beam experiments.[2] More recently, success in generating C_{60} molecules in macroscopic amounts[3] has stimulated intense interest and activity, and a number of spectroscopic studies of C_{60} have confirmed that the molecular symmetry is indeed icosahedral (I_h).[4] We have carried out solid-state ^{13}C NMR experiments which showed that although C_{60} reorients rapidly in the solid state at ambient temperatures, the motion can be slowed sufficiently by lowering the temperature that a measurement of the ^{13}C chemical shift anisotropy can be made.[5] The observed line shapes also indicate that the reorientational dynamics for C_{60} is not uniform throughout the sample, which contained ~10% C_{70}.[5,6]

Although the icosahedral symmetry of C_{60} is now established with reasonable certainty, the detailed electronic and geometric structures of this molecule are still of considerable interest. Many

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(1) For this history, see: Kroto, H. W. *Science* **1988**, *242*, 1139.

(2) Heath, J. R. *Spectroscopy* **1990**, *5*, 36. Curl, R. F.; Smalley, R. E. *Science* **1988**, *242*, 1017.

(3) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(4) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983. Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *Chem. Commun.* **1990**, *20*, 1423. Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167. Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. *Chem. Phys. Lett.* **1990**, *174*, 219. Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J.; Golden, W. G.; Seki, H.; Brown, C. A.; DeVries, M. S. *Chem. Phys. Lett.* In press.

(5) Yannoni, C. S.; Johnson, R. D.; Meijer, G.; Bethune, D. S.; Salem, J. R. *J. Phys. Chem.* **1991**, *95*, 9.

(6) The same inhomogeneity in dynamics appears to hold in a sample of pure C_{60}; see: Tycko, R.; Haddon, R. C.; Dabbagh, G.; Glarum, S. H.; Douglass, D. C.; Mujsce, A. M. *J. Phys. Chem.* **1991**, *95*, 518.

0002-7863/91/1513-3190$02.50/0