Ligand-Assisted Liquid Crystal Templating in Mesoporous Niobium Oxide Molecular Sieves

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A systematic study of the factors governing the formation of Nb-TMS1, a niobium-based mesoporous hexagonally-packed transition metal oxide molecular sieve, is reported. The synthesis of this material was achieved through a novel ligand-assisted liquid crystal templating mechanism in which a discrete covalent bond is used to direct the templating interaction between the organic and inorganic phases. In general, the synthesis of Nb-TMS1 is more strongly affected by starting conditions such as temperature, surfactant-to-metal ratio, pH, and solvent than by temperature and time of aging after the initial hydrolysis step. The results also show that Nb-TMS1 can be synthesized under conditions which strongly disfavor the formation of micelles. This suggests that Nb-TMS1 is formed via a mechanism involving self-assembly with concomitant condensation. It was found that with increasing surfactant-to-metal ratios, new hexagonal *P*63/*mmc* (Nb-TMS2) and layered (Nb-TMS4) phases could be formed, while increasing the surfactant chain length led to a new cubic phase (Nb-TMS3). Crystals of Nb-TMS1 of up to several mm in dimensions were also grown. These crystals are larger than the biggest mesoporous crystals reported by a factor of 3 orders of magnitude. These crystals retain their structure on micelle removal by acid treatment and are thus of great interest as hosts for quantum wires.

Introduction

Recently we reported the synthesis of a new family of materials, termed M-TMS1,[1−4] which represented the first examples of a hexagonally-packed mesoporous transition metal oxide molecular sieves. Prior to this discovery, hexagonally-packed mesoporous materials were confined to the silica- and aluminosilica-based MCM-41 family of materials first prepared by Mobil in 1992.[5−12] Mesoporous materials are of great interest to catalysis[13−17] because of their large and uniform pore sizes (20−100 Å), which allow sterically-hindered molecules facile diffusion to internal active sites. They are also important

because the regular pore structure can serve as a support for conductive and magnetic materials, leading to quantum wires for smart electronic devices.[18−20] The extension of MCM-41-like structures into the realm of pure transition metal oxides represents an important leap from both the catalytic and electronic standpoints because transition metal oxides have variable oxidation states, which are lacking in aluminum and silicon oxides, useful towards tailoring catalytic, conductive, and magnetic properties. Although molecular sieves doped with small amounts of transition metals have been studied for several decades, there is a great paucity of materials constructed solely from oxides of these metals.
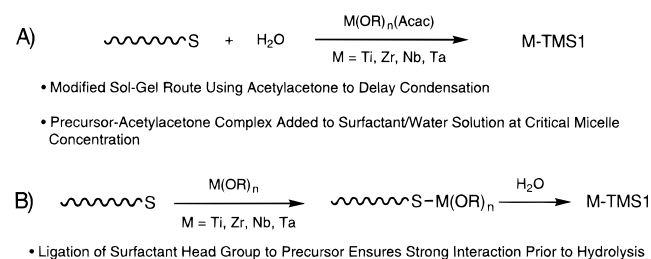
MCM-41 is synthesized using a micelle-based liquid crystal templating method[21] at a variety of pH values from a source of silica and a cationic trimethylammonium bromide surfactant at concentrations under which micelle formation of the organic phase is favorable.[22] This approach relies on the Coulombic

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Scheme 1. Two Approaches to the Synthesis of Transition Metal Oxide Mesostructures

A) $\text{\raisebox{0pt}{$\sim\!\!\sim\!\!\sim\!\!\sim$}}S$ + H_2O $\xrightarrow[\text{M = Ti, Zr, Nb, Ta}]{\text{M(OR)}_n\text{(Acac)}}$ M-TMS1

• Modified Sol-Gel Route Using Acetylacetone to Delay Condensation

• Precursor-Acetylacetone Complex Added to Surfactant/Water Solution at Critical Micelle Concentration

B) $\sim\!\!\sim\!\!\sim\!\!\sim S$ $\xrightarrow[\text{M = Ti, Zr, Nb, Ta}]{\text{M(OR)}_n}$ $\sim\!\!\sim\!\!\sim\!\!\sim S\text{–M(OR)}_n$ $\xrightarrow{H_2O}$ M-TMS1

• Ligation of Surfactant Head Group to Precursor Ensures Strong Interaction Prior to Hydrolysis

attraction between the inorganic phase, consisting of polysilicate anions, and the organic template.[23] Early attempts to prepare transition-metal oxide analogues of MCM-41 employed this approach to successfully synthesize mesostructures of tungsten, lead, antimony, and iron oxides[24] as well as a vanadyl phosphate structure.[25] While the template in MCM-41 is readily removed by calcination to leave hollow porous channels of silica with surface areas of over 1000 m^2/g, this strategy led to structural collapse in the case of transition metal oxides. Recognizing that this micelle templating route relied on the existence of a soluble inorganic anion which could charge match with the cationic template, we anticipated that it would not be generally applicable to the synthesis of early transition metal oxides, because the large ionic radius of the early transition metals favors the formation of insoluble oxide oligomers[26] which are unable to interact sufficiently with the template to form the desired mesostructures. Under this assumption, we developed two routes to hexagonally-packed mesoporous early transition-metal oxides in order to avoid the formation of these insoluble oxide species while allowing the appropriate interaction between the inorganic phase and the template for self-assembly (Scheme 1). Method A was successful in the synthesis of Ti-TMS1,[1] a hexagonally-packed titanium oxide mesoporous molecular sieve, and involved a modified sol–gel method employing acetylacetone[27] to slow down the condensation of the titanium alkoxide precursor, thus allowing the metal to interact with the organic template before the metal alkoxide formed an insoluble titanate.[28] This exciting new material maintained its structure upon calcination to yield the first example of a hexagonally-packed mesoporous transition metal oxide. The second method (Scheme 1B) we developed bypassed the need for a chelating agent to slow down the condensation and relied instead on the formation of a discrete covalent bond between the metal alkoxide and the organic template prior to hydrolysis.[2–4] Using this approach we have been able to prepare samples of M-TMS1 (M = Ti, Nb, Ta, Zr, Ce) with ultrahigh surface areas, distinct hexagonal X-ray diffraction (XRD) patterns, and narrow pore size distributions. Nuclear magnetic resonance (NMR) evidence[2] suggests that this chemical bond was maintained throughout the entire aging process and was finally cleaved chemically to yield the structurally intact hexagonally-packed molecular sieve, free of any residual organic material. The thermal stability of these

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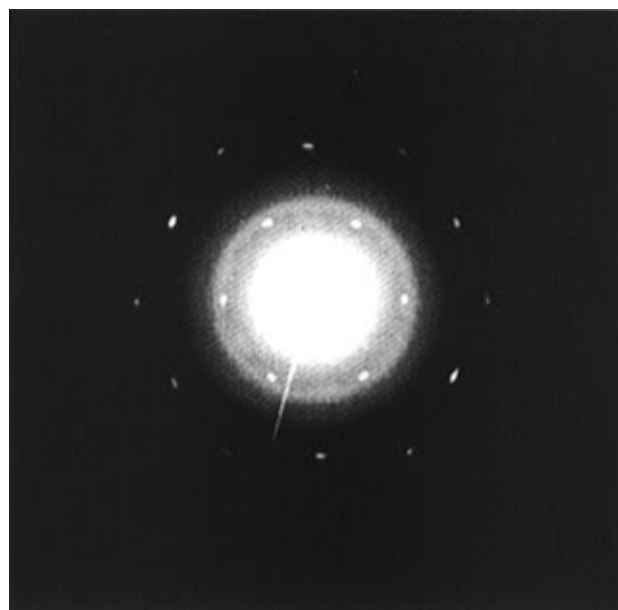(28) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1991.

Figure 1. Electron diffraction pattern of a crystal of Nb-TMS1 synthesized at a 0.5:1 dodecylamine-to-metal ratio and treated with HNO_3 showing the hexagonal symmetry of the unit cell.
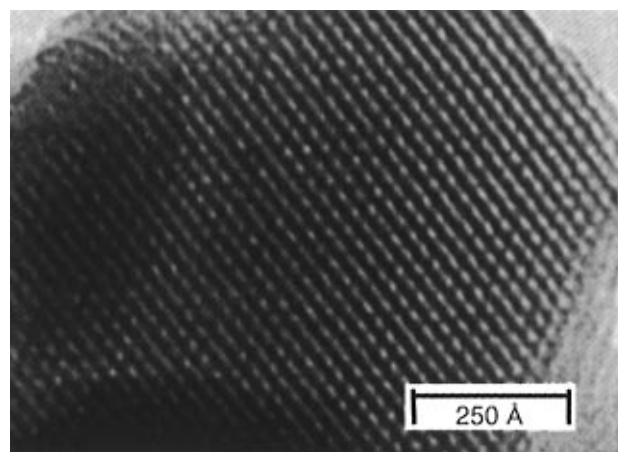

Figure 2. TEM of Nb-TMS1 synthesized at a 0.5:1 dodecylamine-to-metal ratio and treated with HNO_3 showing the hexagonal array of 24 Å pores with ca. 10 Å thick walls.

materials after template removal ranges from 300 to at least 800 °C,[29] and varies with the composition and the thickness of the walls. Figure 1 shows a hexagonal electron diffraction pattern of a highly crystalline sample of Nb-TMS1 after template removal, and Figure 2 shows a transmission electron micrograph (TEM) of this same sample, clearly displaying the hexagonal array of mesopores.

Herein we report the synthesis optimization of Nb-TMS1 and provide evidence that the mechanism proceeds without the formation of micelles prior to condensation. The quality of the materials obtained depends largely on the synthesis parameters, and by adjusting the conditions appropriately, crystals of Nb-TMS1 large enough for single-crystal X-ray diffraction studies can be obtained. We also report Nb-TMS2, a new niobium oxide mesostructure which crystallizes in the hexagonal $P6_3/mmc$ space group, a cubic niobium oxide mesostructure (Nb-TMS3), as well as Nb-TMS4, a layered material closely related to MCM-50. These materials have significant potential for a variety of catalytic and electronic applications.

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Results and Discussion

By analogy with the method of Firouzi *et al.*,[30] we initially attempted to synthesize mesostructures of Nb oxide from niobate polyanions and trimethylammonium bromide surfactants at a wide variety of pH values. The literature reports[31] that soluble niobates can be generated by fusing an alkali hydroxide with niobium oxide and dissolving the melt in water at pH 7−14. Although the solubilities were extremely low, we were able to obtain dilute aqueous solutions of niobates at pH above 14. Addition of cetyltrimethylammonium bromide to this solution above the critical micelle concentration (cmc) of this surfactant followed by aging at 80−180 °C for 1−7 days yielded only niobates with no mesostructure formation. We also tried the modified sol−gel route (Scheme 1A) employed successfully in the synthesis of Ti-TMS1. Nb(OEt)$_5$ was added to 10−25 wt % solutions of a variety of surfactants at metal-to-surfactant ratios ranging from 3:1 to 1:1 at pH values between 2 and 9. Cationic surfactants were used at basic pH values, and anionic surfactants were used at acid pH values. All materials formed were amorphous. Employment of Nb(OEt)$_4$(acac) (acac = 2,4-pentanedione) as a precursor gave similar results. The reason for this is not fully understood but may be related to the fact that Nb(OEt)$_4$(acac) is coordinatively saturated and hence cannot interact strongly with the surfactant head groups. This hypothesis is supported by the observations in the formation of Ti-TMS1 by an analogous sol−gel route. The precursor complex Ti(OCH(CH$_3$)$_2$)$_3$(acac) is coordinatively unsaturated and leads to formation of Ti-TMS1 with biphosphate surfactants under appropriate conditions. The fact that replacement of biphosphate with sulfate in this system leads to amorphous materials suggests a ligand interaction between the head group and the inorganic phase exist in the former, since under the conditions studied these two ions are roughly the same charge density and should thus lead to similar materials if this were an important factor. Addition of excess acac to this system inhibits Ti-TMS formation, presumably due to formation of a coordinatively saturated tris(acetylacetonate), complex which is unable to interact with the phosphate head groups of the surfactant. Thus, acac is only helpful in situations where it slows down hydrolysis while still leaving a vacant coordination site with which to bind to the surfactant head group.

Owing to these unsuccesful attempts, we systematically developed a new general approach to transition metal oxide mesostructures on the hypothesis that the two requirements for the synthesis of such materials were as follows: (a) a strong interaction between the inorganic precursor and the surfactant; and (b) condensation under condition favorable for liquid crystal formation, i.e. polar solvents and surfactants with a nonpolar tail group. Prior to our work, both Coulombic[7] and hydrogen bonds[8] were used to mediate the templating process; however, the use of discrete precursor units in which the surfactant head group and the inorganic moiety are covalently bound to each other in such a way that they are a part of *the same molecule* had never been explored. This strategy would also allow for facile spectroscopic studies of the intimate interaction between the head group and metal center throughout the synthesis process. Scheme 2 illustrates these two previous strategies alongside our new ligand approach. Claims of a ligand interaction have been made for systems involving polydentate silicate anions and quaternary ammonium surfactants; however,

Scheme 2. Illustration of the Three Types of Liquid Crystal Templating: Our New Ligand-Assisted Approach, the Charge-Matching Approach, and the Hydrogen-Bonding Approach
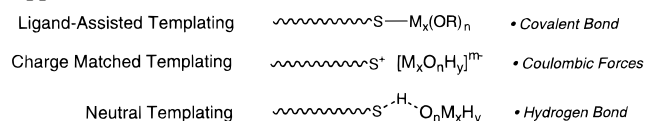
a true ligand interaction is unlikely in this case because the quaternary nitrogen center has no vacant orbitals for bonding with the silicate siloxide units.[7] We termed this novel approach the ligand assisted templating (LAT) approach.[2−4] Because of the coordinative unsaturation, high Lewis acidity, rapid hydrolysis, and ease of availability of niobium ethoxide, in conjunction with the variable oxidation states (-3 to +5) of Nb[32] and the chemical inertness, high melting point, and thermal stability of niobium oxide,[33] we reasoned that it would be an ideal candidate for such an approach. Since niobium ethoxide readily forms octahedral adducts with Lewis bases[34] and the ancillary alkoxide ligands readily condense in the presence of water to form oxo bridges, it would make a perfect precursor to mesostructures as long as a surfactant was found which forms a strong, moisture-resistant bond with the Nb center which would maintain its integrity throughout the selective hydrolysis/ condensation of the alkoxide ligands. Thus, we undertook a systematic screening of surfactants to determine which head group formed the strongest interaction while also allowing facile chemical removal without damage to the mesostructure after aging. We also investigated other factors such as surfactant chain length, pH, use of co-solvent, concentration of precursor, method of water introduction, temperature of formation and aging, relative metal-to-surfactant ratios and method of surfactant removal.

Variation of Head Group. In order to determine the optimal head group for the formation of hexagonally-packed niobium oxide mesostructures, a wide variety of surfactants were screened and the resulting materials formed were analyzed by XRD. In all cases the chain length of the surfactant was held constant at 12 carbon atoms. All materials were prepared by melting the surfactant together in its neutral protic form with Nb(OEt)$_5$ in a 0.5:1 ratio followed by addition of excess water at room temperature. After being left overnight, the mixtures were further aged at 100 °C for 5 days. The quality of the materials were judged by both the sharpness and intensity of the (100), (110), (200), and (210) reflections displayed in the XRD patterns.

The head groups examined in this study were carboxylate, phosphate, sulfate, sulfonate, hydroxyl, 2,4-pentanedionate, amino, methylamino, dimethylamino, 4-anilino, 4-pyridino, and dimethylphosphino. The sulfate, sulfonate, and hydroxyl surfactants phase separated and floated to the top of the reaction mixture after less than 1 h of heating at 100 °C, yielding amorphous aerogels with high surface areas of 400−600 m^2/g, broad pore size distributions and no distinct XRD pattern. Dimethylphosphino, methylamino, dimethylamino, 4-pyridino, and 2,4-pentanedionate surfactants were retained in the structure even after aging at 100 °C for 5 days, but yielded materials with no crystalline XRD pattern. Treatment of these materials

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with HNO$_3$/EtOH at 50 °C leached out the surfactant and gave materials similar to those isolated in the case of sulfate, sulfonate, and hydroxyl surfactants. Carboxylate and 4-anilino surfactants gave materials with a broad amorphous hump centered at 2° 2θ which gave amorphous xerogels after acid treatment. The only head groups which produced discernible hexagonal phases were amino and phosphate. Phosphate surfactants were found to be optimal for the formation of as-synthesized Ti-TMS1;[1] however, amino surfactants are more desirable because of their ease of removal by solution techniques[2] and general availability in a wide variety of chain lengths.

In general, the best materials were formed from the most basic head groups and those with greater hapticity. These two points are illustrated by the fact that dodecylamine gives far better materials than 4-dodecylaniline and that although alkoxides are more basic than carboxylates, monohapto dodecyl alcohol gives inferior materials with respect to those obtained using dihapto tridecanoic acid. Substitution at the head group with one or two alkyl groups leads to lower quality materials in the case of amines. This fact indicates that the alkyl groups, although increasing the basicity of the nitrogen, introduce an undesirable steric interaction through the larger cone angle with respect to the unsubstituted amine. This larger cone angle weakens the Nb−N bond and leads to materials with no discernible structure. The case of 4-dodecylpyridine is less clear. Although pyridine is a weaker base than an amine, it often forms more stable transition metal complexes because of the π conjugation effects of the aryl ring. Niobium alkoxides readily form stable complexes with a wide variety of pyridine derivatives. Also, although the cone angle of pyridine is larger than that of a primary amine, the fact that pyridine is flat and only occupies space in one plane reduces the steric tension around the metal center. Because of these two effects, pyridine is often a much better ligand than most secondary amines. It is also expected that the increase of steric bulk in the head group would favor a hexagonal phase as normally observed[35] and lead to higher levels of crystallinity than materials made with primary amines because of improved packing of aryl rings with respect to aliphatic chains. This was surprisingly not the case, as 4-dodecyl pyridine, although completely retained in the resulting solid, gave materials with no discernible XRD pattern. The only possible reason for this is that an X-type ligand, capable of forming a discrete σ bond with the Nb center, is required rather than a datively bonding Lewis basic L-type ligand.[36] This hypothesis would also explain why dimethyldodecylamine gives amorphous materials. The fact that methyldodecylamine gives amorphous materials suggests, in the absence of steric effects, that capacity to form a N−Nb double bond may be required. Such bonds are thermally robust,[37] and evidence for their role in the formation of Nb-TMS1 has been seen in the lack of proton couplings in the ^{15}N-NMR spectrum of a niobium ethoxide−dodecylamine dimer in deuterotoluene at −40 °C.[2] A thorough NMR investigation of Nb-TMS1 and its formation is the subject of an separate study.[38]

In conclusion, both phosphate and primary amino surfactants form high-quality hexagonal niobium oxide mesostructures.

Amino surfactants are desirable over phosphate surfactants because they are more easily removed than phosphate surfactants to yield the desired hexagonally-packed niobium oxide molecular sieves. This study revealed three major trends in the formation of Nb-TMS1: (a) The fact that substituted amine and pyridine surfactants give poor materials suggests that multiple bonding may be important in the Nb-N interaction. (b) Since 4-dodecylaniline gives inferior materials to more basic aliphatic amines, we can conclude that in the absence of steric effects stronger bases give better materials than weaker bases. (c) The higher quality of carboxylate-formed Nb-TMS1 over more strongly basic hydroxyl-formed materials demonstrates that chelating head groups are superior to nonchelating head groups.

Variation of Surfactant-to-Metal Ratio. Since the liquid crystal-type phases of silica-based mesoporous materials are sensitive to the relative ratios of silicon and the surfactant employed,[5c] we undertook a study of the effect of the variation of surfactant-to-Nb ratios on the phase isolated. For silica-based materials, the general trend is the derivation of hexagonal (MCM-41), cubic *Ia3d* (MCM-48), and finally lamellar (MCM-50) phases with increasing surfactant-to-Si ratios. In general, MCM-41 is favored for ratios below 0.6:1, while MCM-48 is observed at ratios between 1.0 and 1.2:1, and MCM-50 is favored at ratios higher than 1.2:1. The phase obtained also depends on the concentration, head-group size, and chain length of the surfactant, the ionic strength and pH of the medium, and the aging temperature, all factors which are known to perturb liquid crystal formation.[39] At very low concentrations of trialkylammonium surfactant, for example, only individual surfactant molecules are observed. At higher concentrations, spherical and rodlike micelles are formed. These micelles order as the concentration increases to hexagonally-packed rods and then cubic and lamellar phases. The exact structure of the cubic liquid crystal phase Ia3d is not fully understood, but it is believed that it consists of an intricate three-dimensional bicontinuous arrangement of these micellar rods.[40] At very high surfactant concentrations the rodlike micelles become unstable, and layered phases are observed. While we were able to prepare well-defined Nb-TMS1 with hexagonally-packed mesopores, we were interested to see if variation of these factors mentioned above could lead to mesostructured layered and cubic phases of niobium oxide related to MCM-48 and MCM-50. Thus a systematic survey of synthesis parameters was conducted in which the surfactant-to-metal ratio, temperature, concentration, pH, surfactant chain length, and aging conditions were varied. Our approach uses moisture-sensitive organometallic surfactant−precursor complexes and differs from that used in the synthesis of MCM-41, where the weight percentage of the surfactant in water is adjusted before addition of the precursor. Thus, we were unable to adjust the weight percentage of the surfactant in the same way that was done in the case of the silica materials. Instead, we examined the effect of the dilution in alcohol of the precursor−surfactant complex prior to addition of water.

Using dodecylamine as a precursor with no added ethanol, the ratio of surfactant-to-Nb(OEt)$_5$ was varied. In general, 25 mL of water/g of niobium(V) ethoxide was added to the homogeneous liquid precursor at room temperature, resulting in the immediate precipitation of a white solid. This solid was then broken up and left in the water overnight at room temperature followed by 5 days of further aging at 80 °C. The quality and phases of the materials were determined by XRD

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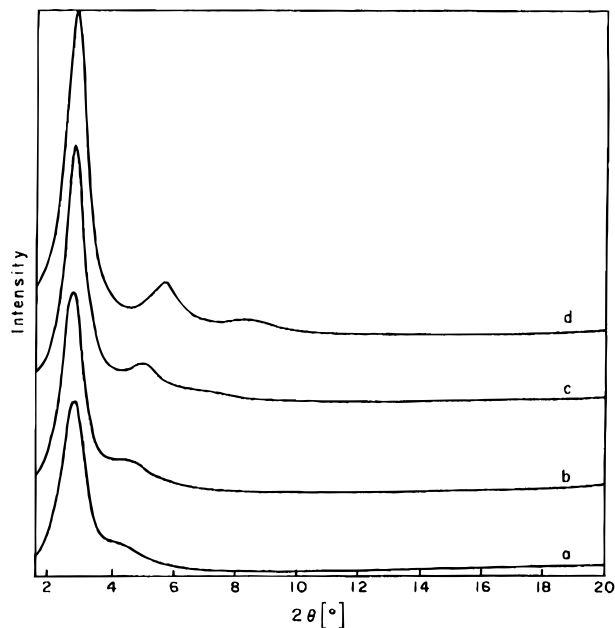
Figure 3. XRD patterns of Nb-TMS samples prepared with no additional ethanol at dodecylamine-to-Nb(OEt)$_5$ ratios of (a) 0.3:1, (b) 0.5:1, (c) 0.75:1, (d) 1.0:1, (e) 1.25:1, (f) 1.5:1, and (g) 2.0:1 showing the progression from Nb-TMS1 (a−e) to Nb-TMS2 (f) and Nb-TMS4 (g) with increasing surfactant concentration.

and TEM. Figure 3 shows the XRD patterns for materials thus prepared for surfactant-to-Nb(OEt)$_5$ ratios of 0.3:1, 0.5:1, 0.75:1, 1.0:1, 1.25:1, 1.5:1 and 2.0:1. The materials obtained for the 0.3:1, 0.5:1, and 0.75:1 ratios are hexagonal and the intensity and sharpness of the (100), (110), and (200) peaks increases with increasing surfactant ratio, although the (110) and (200) peaks were not clearly resolved. The latter phenomenon has been attributed in samples of MCM-41 to either small areas of hexagonal packing in the material or thin walls leading to a diminishing in the intensity of the (210) peak as shown for MCM-41.[41] The hexagonal nature of the pore structure was
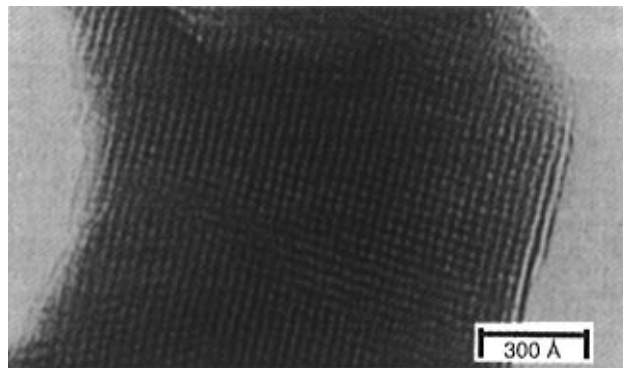
(41) Feuston, B. P.; Higgins, J. B. *J. Phys. Chem.* **1994**, *98*, 4459.

Figure 4. TEM of as-synthesized Nb-TMS2 synthesized at a dodecylamine:Nb(OEt)$_5$ ratio of 1.5:1 showing the ordered array of 24 Å pores.
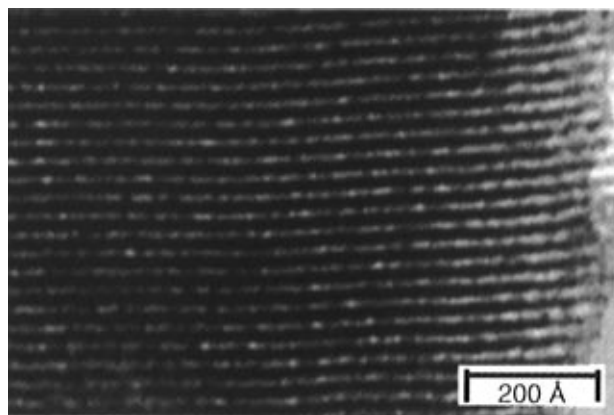

Figure 5. TEM of as-synthesized Nb-TMS4 synthesized at a dodecylamine:Nb(OEt)$_5$ ratio of 2.0:1 showing the layered structure of this new phase.

confirmed by TEM studies.[2] The sample prepared at a 1.5:1 surfactant-to-alkoxide ratio is a hexagonal phase (Nb-TMS2) which can be indexed to a *P63/mmc* unit cell. A related mesostructured silica phase, SBA-2, prepared by Stucky[42] was also indexed in this space group. Figure 4 shows a TEM of Nb-TMS2 synthesized from dodecylamine showing the ordered array of 24 Å pores. The samples prepared at 1.0:1 and 1.25:1 ratios appear to be either mixed phases or a single phase which is less well crystallized than that obtained at a 1.5:1 ratio. At a 2.0:1 ratio, the materials obtained are layered MCM-50 analogues (Nb-TMS4). Figure 5 shows a TEM micrograph of Nb-TMS4 synthesized at a surfactant-to-Nb(OEt)$_5$ ratio of 2.0:1. The interlayer spacing is 25 Å, and the thickness of the walls is approximately 8 Å.

This same set of experiments was conducted by first dissolving the precursor complex in ethanol (10 mL/g of niobium (V) ethoxide) at room temperature and allowing moisture from the atmosphere to diffuse into the mixture at a set temperature, followed by further aging at 80 °C after precipitation was judged complete. Only hexagonal phases are observed in this case for varying dodecylamine surfactant content. Figure 6 shows the XRD patterns of samples prepared in this manner from surfactant-to-Nb(OEt)$_5$ ratios of 0.3:1, 0.5:1, 0.75:1, 1.0:1, 1.25:1, and 2.0:1 at 50 °C. The intensity and sharpness of the patterns increases with increasing proportions of surfactant. Another observation was that at a given surfactant-to-Nb(OEt)$_5$ ratio where the hexagonal phase was formed by both the alcohol-free and vapor diffusion methods, the XRD patterns are comparable in intensity and sharpness. Thus,

(42) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.

The table within Figure 3:

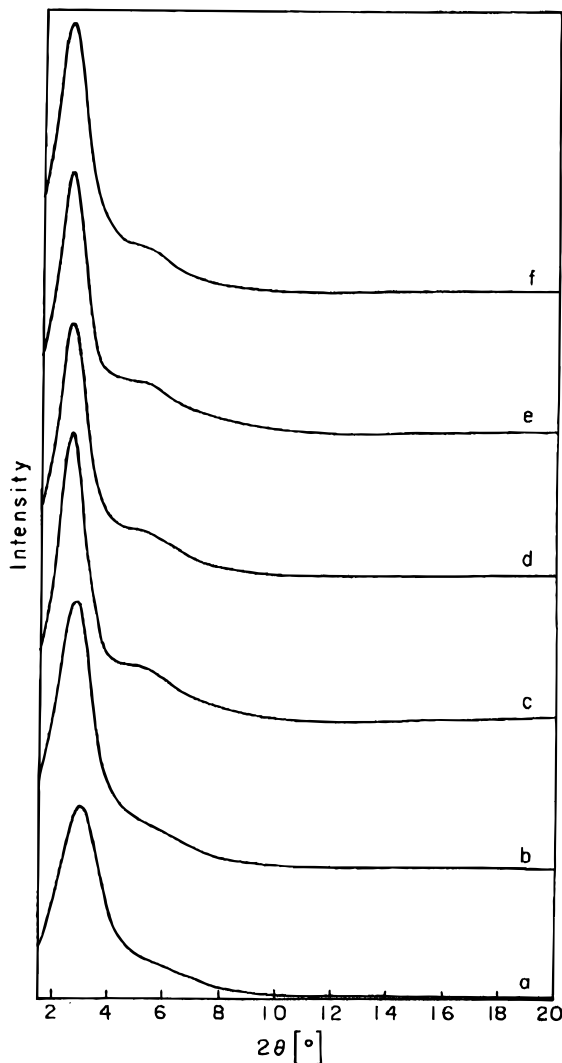| P6$_3$/mmc	hkl	d(Å)
	100	33.0
	002	31.6
	101	29.3
	110	19.5
	103	17.6
	112	16.5
	211	12.3

Figure 6. The XRD patterns of Nb-TMS1 samples prepared by vapor diffusion into ethanol with dodecylamine-to-Nb(OEt)$_5$ ratios of (a) 0.3:1, (b) 0.5:1, (c) 0.75:1, (d) 1.0:1, (e) 1.25:1, and (f) 2.0:1, at 50 °C.

ethanol inhibits the formation of Nb-TMS2 and Nb-TMS4, but does not affect the quality of Nb-TMS1. Surprisingly, it was also found that the concentration of the precursor in ethanol does not influence the quality of Nb-TMS1 either. For precursor concentration studies with 1 g of Nb(OEt)$_5$ in 0 mL of ethanol to 1 g of Nb(OEt)$_5$ in 200 mL of ethanol at a given surfactant-to-metal ratio, neither the phase nor the crystallinity of the bulk material formed was affected in any way. The mechanistic implications of this observation are important, because under high dilution in ethanol with water present only at steady-state concentrations, preformed micelles are not known to form at all. Thus, the most likely mechanism for the formation of Nb-TMS1 is one involving self-assembly through condensation, as opposed to precondensation micelle formation, as proposed by Chen *et al.*[22] for the case of MCM-41 formation. This mechanism may be related to that proposed by Huo *et al.*[23] for MCM-41 in which the self-assembly of the charged surfactants is mediated by the aggregation of condensing inorganic anions around the charged head groups. The latter relies on charge density matching to initiate and direct the self-assembly process. The major difference between our mechanism and that of Huo *et al.* is that our approach starts from a discrete monomer in which there is a chemical bond between the head group and the inorganic moiety whereas the latter approach relies on Coulombic forces to hold together the inorganic and organic
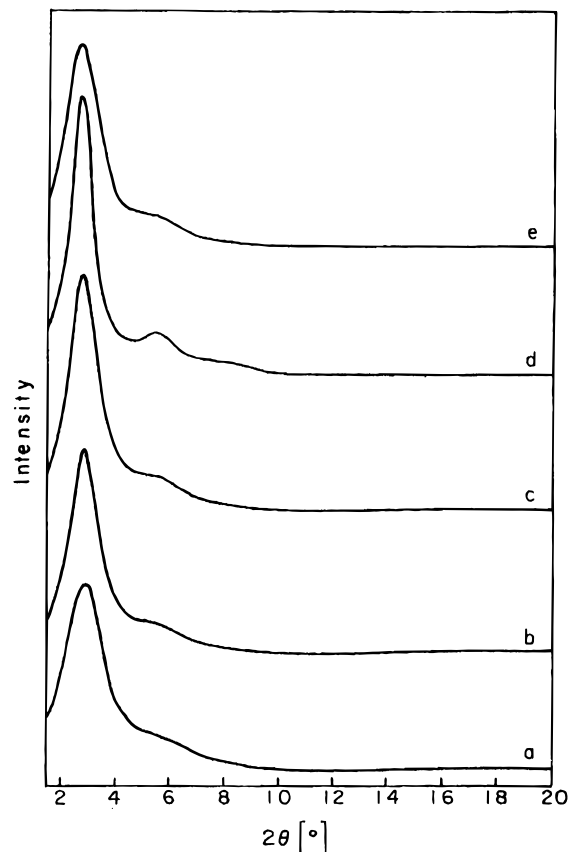

Figure 7. XRD patterns of Nb-TMS1 prepared by vapor diffusion into ethanol with a dodecylamine-to-Nb(OEt)$_5$ ratio of 0.75:1 at (a) −78 °C, (b) 0 °C, (c) 25 °C, (d) 50 °C, and (e) 78 °C.

phases. This establishes that neither preformed micelles nor charge density matching is a requirement for self-assembly via our new approach.

The effect of temperature on the quality of Nb-TMS materials obtained via vapor diffusion was also studied. Diffusion was allowed to proceed at a given temperature until visible formation of precipitate or solid was judged complete, and then more water was added and the solutions were allowed to stand at room temperature for one day, and then heated at 80 °C for 5 days. Figure 7 shows XRD patterns for those materials obtained by vapor diffusion of water into solutions of 1 g of Nb(OEt)$_5$ in 10 mL of ethanol at a surfactant-to-Nb(OEt)$_5$ ratio of 0.5:1 at temperatures of −78, 0, 25, 50, and 78 °C. The phase obtained in all cases examined is hexagonal, however the crystallinity of these materials increases steadily from −78 to 50 °C and then drops off at 78 °C. This increase of crystallinity with temperature below 50 °C is also surprising because micelle formation is favored at lower temperatures.[43] This may be explained by the solubility of the partially hydrolyzed precursor at lower temperatures in ethanol. As hydrolysis proceeds at low temperature, there is a tendency for an incompletely hydrolyzed gel to separate from the solution. Only when the solution is allowed to warm to room temperature and more water added does this gel completely solidify. When diffusion of moisture into the ethanol solution occurs at high temperature, a solid readily separates with no observation of any of the incompletely hydrolyzed gel observed at lower temperatures. At 78 °C, however, no incompletely hydrolyzed gel is formed, but the material is less crystalline than that obtained at 50 °C, most likely because the increased temperature interferes with the self-assembly process. Thus, these results are consistent

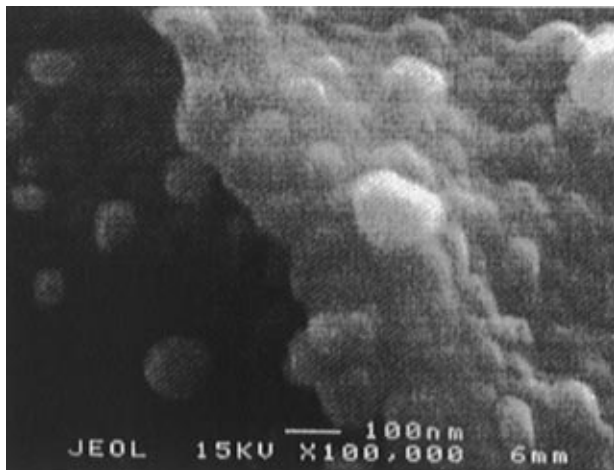(43) Reiss-Husson, F.; Luzzati, V. *J. Phys. Chem.* **1964**, *68*, 3504.

Figure 8. SEM of an as-synthesized sample of Nb-TMS1 prepared with a dodecylamine:Nb(OEt)$_5$ ratio of 0.5:1 showing the hexagonal shape of the small crystallites.

with the temperature-dependence of self-assembly when the precipitation of the incompletely hydrolyzed amorphous gel at lower temperatures is taken into account.

When water is allowed to diffuse slowly into ethanol solutions of the Nb(OEt)$_5$−dodecylamine complex, single crystals of up to several millimeters in length can be grown. These crystals are almost 3 orders of magnitude larger than the largest crystals of MCM-41, which are on the micrometer level, or any related material reported, and the electron diffraction patterns obtained for samples of this material are sharper and more intense than those obtained for bulk powder materials. In previous studies[8] it had been suggested that charged head groups were necessary in the formation of large crystalline domains in hexagonally-packed mesoporous oxides. Our results show that this is not the key to crystal growth for TMS materials. The factors governing the formation of these crystals is under active investigation, but it was found that addition of 0.1−0.3 equiv of water to the ethanol before introduction of the Nb(OEt)$_5$ precursor enhanced crystallization. Also, the ease of formation of crystals is related to the order of crystallinity shown in Figure 7. Thus crystals are most easily grown at 50 °C as opposed to cooler temperatures where the incompletely hydrolyzed gel can separate from the mixture and interfere with the crystallization process, or higher temperatures which can inhibit self-assembly and thus also retard crystal growth. Figure 8 shows a scanning electron micrograph (SEM) of microcrystallites of Nb-TMS1 of ca. 100−200 nm in size, and Figure 9 shows a digital optical micrograph of a ∼2.5 mm crystal of Nb-TMS1. The hexagonal symmetry of the unit cell is reflected in the macroscopic morphology of the crystals in which all angles are roughly 120°. In general, the nanostructured ordering of the individual tubes in a sample of Nb-TMS1 crystals is far greater than that found in the powder samples, which have areas of hexagonal order in the 100 nm range. Large crystals of Nb-TMS1 show greater resistance to structural collapse in surfactant removal by acid treatment than powder samples with smaller domains of hexagonal packing. This suggests that the acid-catalyzed degradation of microcrystalline samples of Nb-TMS1 may be related to cleavage of more strained Nb−O bridges in the less ordered structure.

Conducting this diffusion process in different alcohols was also investigated. Figure 10 shows the XRD patterns of materials precipitated by vapor diffusion of water from a 0.5:1 ratio of dodecylamine-to-Nb(OEt)$_5$ in ethanol, 2-propanol and 2-methylpropan-2-ol. Although the hexagonal phase was isolated in each case, there is a clear trend towards higher
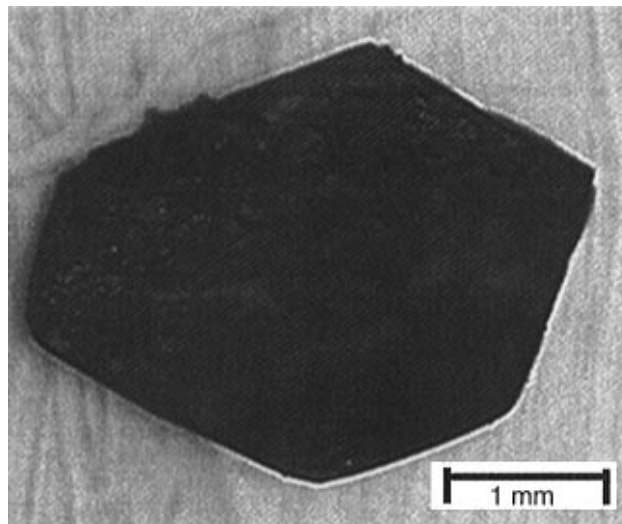

Figure 9. Digital optical micrograph of a crystal of Nb-TMS1 grown by vapor diffusion of water into an ethanol solution of dodecylamine and Nb(OEt)$_5$ at room temperature.
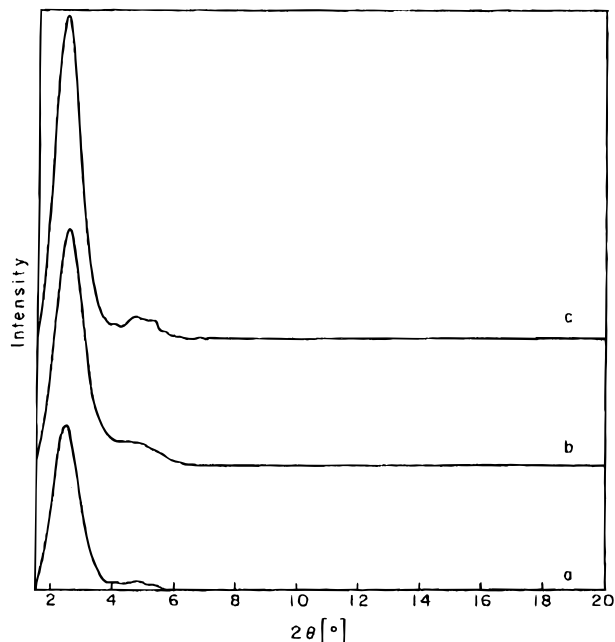

Figure 10. XRD patterns of Nb-TMS1 prepared by vapor diffusion into (a) tertiary butanol, (b) 2-propanol, and (c) ethanol with a dodecylamine-to-Nb(OEt)$_5$ of 0.5:1 at room temperature.

crystallinity from tertiary to secondary and then to primary alcohol groups. Changing from ethanol to methanol has little effect. These results are best rationalized by taking into account the steric influence of the larger isopropyl and *tert*-butyl groups on not only the rate of hydrolysis but also the binding constant of the amine to the metal center. Under the conditions studied, exchange between the alcohol and ethoxide ligands readily occurs. The acidity of the Nb decreases as does the Nb−N bond strength going from primary to tertiary alcohols not only because of the well-documented steric effect of ancillary ligands on metal−ligand bond strengths[44] but also because of the increased electron-donating capacity of more highly substituted alkyl chains over primary alkyl chains. Thus, the amine template would have a weaker affinity for the Nb center when the reaction is carried out in 2-propanol or 2-methylpropan-

(44) Rothwell, I. P. in *Activation and Functionalization of Alkanes*; Hill, C. G. Ed.; Wiley: New York, 1989; Chapter 5.

Scheme 3. Equilibrium in Ethanol Solutions of Nb(OEt)$_5$ and Amine Surfactants Showing the Proposed Pathways (A−D) of Formation of Nb-TMS1, Nb-TMS2, and Nb-TMS4 from the Different Species (1−5) Present
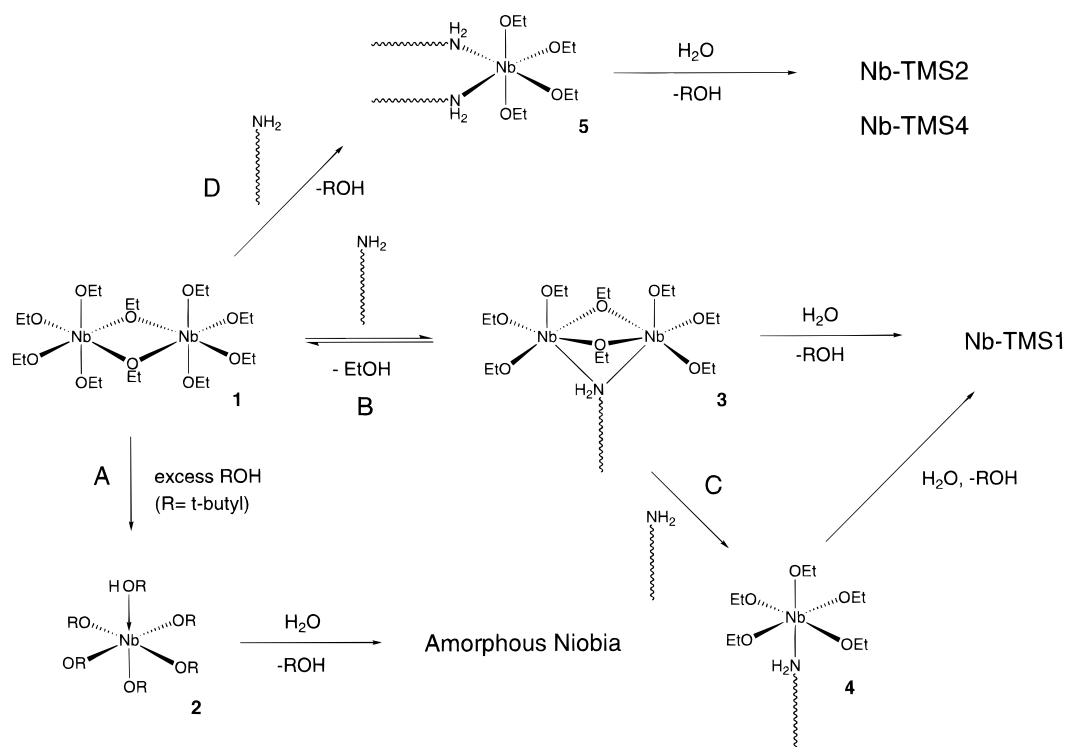
2-ol, decreasing the strength of this templating interaction. This is illustrated in Scheme 3, pathway A.

As stated earlier, the mechanistic implications of these results are under investigation by NMR to determine from a molecular standpoint what factors govern the formation of each phase. Scheme 3 shows a suggested reaction pathway rationalizing the solution studies discussed above. The solution dynamics of Nb-(OEt)$_5$ amine complexes are complicated[45] and may involve several species, including free ligand, Nb$_2$(OEt)$_{10}$ (species 1), Nb(OR)$_5$(ROH) (species 2), the octahedral ligand−Nb(OEt)$_5$ complex (species 4), and possible other species involving two amines per Nb (species 5) or two Nb per amine (species 3), with different N−Nb bond orders as well as bridging, rather than only terminal, amino functionalities. The observation that once precipitation of Nb-TMS materials from water vapor diffusion into ethanol occurs no further phase changes take place on aging to 150 °C suggests that the formation of these materials is controlled by kinetic rather than thermodynamic factors. Thus, the initial concentrations of the various components and the temperature of precipitation are more important than the aging process in determining the phase isolated. The bis(amine) adduct (species 5) favors the layered and possibly *P63/mmc* phases via pathway D, while complexes 3 and 4 promote the hexagonal phase through pathways B and C. The conditions leading to the formation of the *P63/mmc* phase (1.5:1 dodecyl-amine-to-Nb(OEt)$_5$ with no ethanol) are those in which a mixture of species 5 and 4 are both potentially present. Thus, it seems that the *P63/mmc* phase may be favored by a mixture of these two complexes. Excess ethanol inhibits formation of the bis-(amine) adduct 5 by shifting equilibrium A towards complex 2, thus inhibiting pathway D. This explains why there are no layered, *P63/mmc*, or cubic phases observed in the presence of

alcohol. When the R group on the alcohol is bulkier, the hexagonal phase is also disrupted. Although this effect could be related to the dielectric constant of the medium disrupting self-assembly, it could also be rationalized on the basis of bulkier R groups interfering with amine coordination both sterically and electronically, the latter because the stronger electron-donating ability of larger alkyl chains would tend to decrease the Lewis acidity of the niobium center. This would lead to a decreased affinity for the amine template and favor the formation of variations of complex **2**. A complete NMR investigation to confirm this pathway and fully characterize all species present in solution is underway.[38]

Effect of Surfactant Chain Length and Mesitylene Addition. Increasing the surfactant chain length favored the formation of layered and cubic phases. Figure 11 shows the XRD patterns for Nb-TMS materials synthesized by vapor diffusion of water into ethanol solutions of the octadecylamine precursor complex. The sample prepared at an octadecylamine-to-Nb-(OEt)$_5$ ratio of 0.75:1 is hexagonal; the sample prepared at a ratio of 1.0:1 ratio is cubic and can be indexed to a *Pm3n* space group (Nb-TMS3), while that prepared at a ratio of 1.25:1 is layered (Nb-TMS4). The effect of increasing the chain length from 12−18 carbon atoms is thus dramatic because under identical conditions only hexagonal phases are observed with dodecylamine (Figure 6). The effect of changing phases with changing surfactant chain lengths has been observed before, as increasing the surfactant chain length or tail-to-head group size ratio favors the layered and *P63/mmc* phases over the hexagonal phase.[5c] This can also be used to rationalize why the bis-(surfactant) complex **5** from Scheme 3 favors the layered and cubic phases. By ligation of two surfactant chains onto one metal center, the net ratio of the space occupied by the surfactant relative to the head group increases in the same way as it does when the size of the tail group on a monoligated complex is increased.

(45) (a) Puri, D. M.; Pandey, K. C.; Mehrotra, R. C. *J. Less-Common Met.* **1962**, *4*, 393. (b) Mehrotra, R. C.; Kapoor, R. N.; Prakash, S.; Kapoor, P. N. *Aust. J. Chem.* **1966**, *19*, 2079. (c) Kapoor, R. N.; Prakash, S.; Kapoor, P. N. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1384.
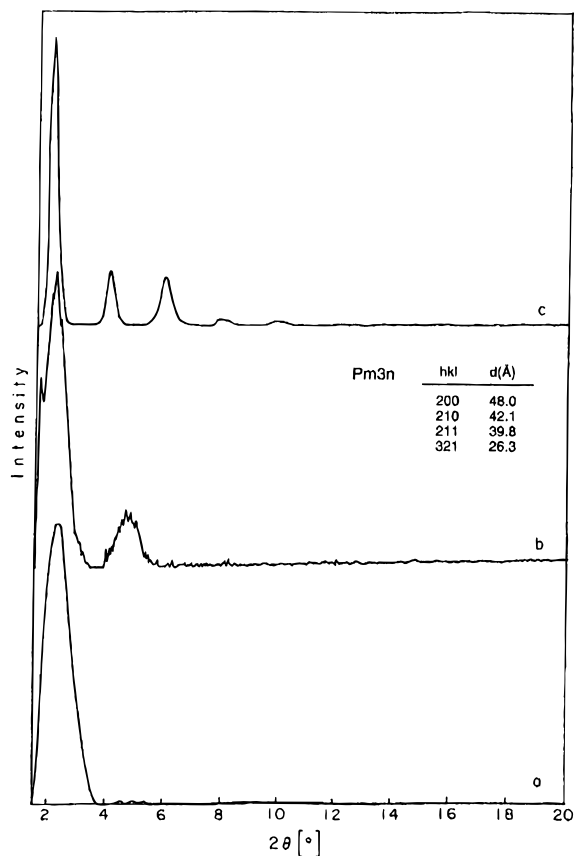
Pm3n	hkl	d(Å)
	200	48.0
	210	42.1
	211	39.8
	321	26.3

Figure 11. XRD patterns of Nb-TMS materials prepared by room temperature vapor diffusion into ethanol with octadecylamine-to-Nb-$(OEt)_5$ ratios of (a) 0.75:1 (Nb-TMS1), (b) 1.0:1 (Nb-TMS3), and (c) 1.25:1 (Nb-TMS4).

Table 1. Variation of Pore Size with Chain Length and Mesitylene of Nb-TMS1[a]

chain length	d(100) (Å)	repeat distance (Å)[b]	pore size (Å)	wall thickness (Å)
12	28	32.3	22	10.4
14	33	38.2	27	11.1
16	36	41.7	29	12.7
18	40	46.0	33	13.0
18 + 2 mesitylene	45	51.8	39	12.8

[a] Samples were prepared by direct addition of water to 0.5:1 amine–Nb$(OEt)_5$ mixtures followed by aging for 1 day at ambient temperature, 1 day at 80 °C, 1 day at 100 °C, and 4 days at 150 °C. The template was removed by treatment with HNO₃/2-propanol as described in the experimental section. No change in the d(100) peak was observed upon template removal. [b] $a_0 = 2d(100)/\sqrt{3}$.

Table 1 shows the XRD d-spacings of the (100) peaks in as-synthesized samples of Nb–TMS1 prepared at a 0.5:1 surfactant-to-Nb$(OEt)_5$ ratio for chain lengths of 12, 14, 16, and 18 carbon atoms as well as a sample prepared with octadecylamine at this same ratio with 2 equiv of mesitylene. The samples were prepared by adding mesitylene to the precursor mixture before introduction of water. The resulting precipitate was then aged for 1 day at room temperature followed by 9 days at elevated temperatures. The d-spacings for the hexagonal-structured template-free material, average BJH pore size from nitrogen adsorption data, and the wall thickness (calculated from repeat distance a_0 and pore size) are also shown. The values obtained are similar to those obtained for Ta-TMS1.[4] The surprising result of this study is that addition of the mesitylene swelling agent only increases the pore size up to approximately 39 Å. Once this pore size is attained, addition of excess swelling agent makes little difference. This contrasts to what has been

seen for MCM-41 synthesis in which samples with pore sizes of up to 100 Å have been observed.[5a] This indicates that the individual nanotubes can only absorb so much mesitylene before they reach a saturation point. As in the case of MCM-41, swelling agent can only be added before initial precipitation of the gel. This suggests that once initial self-assembly has occurred in Nb-TMS1, the pore sizes are relatively fixed and cannot be changed by addition of a swelling agent.

Aging Temperature, pH, and Addition of Salts. A real-time XRD study was conducted on the formation of Nb-TMS1 from a 0.5:1 dodecylamine-to-Nb$(OEt)_5$ precursor mixture from slow hydrolysis by ambient moisture. As found for MCM-41, the initial mixture was amorphous, and over several days at room temperature the hexagonal phase grew in with no observation of any intermediate layered phase. Once initial precipitation occurs, the quality, crystallinity, and stability towards subsequent acid treatment, but not the liquid crystal phase of the material, can be altered. In general, aging up to 180 °C increases the structural stability of Nb-TMS materials, most likely due to increased crystallinity and condensation in the walls. This condensation leads to a degree of pore shrinkage, such that template-free materials produced with octadecylamine and aged at 180 °C for 10 days have XRD (100) peaks at $d = 34$ Å, as opposed to $d = 40$ Å as observed for those same samples aged at only 100 °C for 5 days. The materials aged at higher temperature, however, show greater stability after template removal as discussed later. Aging at basic or acidic pH values has a detrimental effect on the materials and leads to amorphous niobia at the upper and lower ends of the pH scale. This can be rationalized by the competition of hydroxide with the template for the coordination site on Nb on the one hand and the formation of noncoordinating ammonium surfactant salts in the presence of acid on the other. Even addition of 1 equiv of ammonium chloride to the aging mixture can lead to substantial leaching out of the surfactant as the ammonium salt can cleave the surfactant-to-Nb bond in the structure by protonolysis, liberating the ammonium form of the surfactant and free ammonia, which can leave the system. Addition of alkali metal halides, on the other hand, can lead to higher level of crystallinity and structural stability, possibly due to salt-promoted higher order condensation of the walls. This effect has also been observed in zeolites and in Ti-TMS1 synthesis.[1]

Surfactant Removal. The amine template can readily be removed from Nb-TMS1 by protonation in organic solvents to yield pure niobium oxide phases as determined by infrared spectroscopy, thermogravimetric analysis, and elemental analysis[2] with surface areas of over 600 m²/g and well-defined hexagonal pore structure as determined by nitrogen adsorption, TEM, and XRD. The surfactant is best removed from Nb-TMS1 by acid treatment in organic solvents as described for Ta-TMS1.[4] The best method involves the treatment of Nb-TMS1 with 1 molar equiv of triflic acid with respect to nitrogen content (as measured by elemental analysis) in dimethoxyethane at −78 °C, followed by filtration and subsequent stirring overnight in isopropanol. Other methods include heating in ammonium tetraphenylborate/isopropanol and either stirring in a large excess of HNO₃ in isopropanol for 1 h at room temperature followed by filtration and washing in isopropanol, or stirring in a pH 2 solution of isopropanol/water at 50 °C for 1–2 weeks. The most important factor in retaining the structure while maximizing surfactant removal is to minimize the exposure to acid. This is done by using only 1 equiv (with respect to nitrogen) of a very strong acid and shortening the exposure times to solutions of excess acid or by using weaker acids or more dilute solutions of strong acid for longer contact

times. When care is taken and the samples are prepared properly with optimal aging times, no damage to the mesostructure is observed. It must be added, however, that any sample of Nb-TMS1 is acid-sensitive and can be damaged by treatment with concentrated nitric acid solutions of pH less than zero. Thus, Nb-TMS1 differs from Ta-TMS1, which shows acid resistance even toward acid solutions of negative pH.

Other methods of template removal were also tried, including pyrolytic sublimation and calcination in dioxygen. Both methods lead to structural collapse. In the first of these methods, the as-synthesized sample is heated to temperatures above the sublimation point of the surfactant under high vacuum. Although most of the surfactant is removed at temperatures lower than 400 °C, a temperature at which Nb-TMS1 would be stable after template removal, the XRD pattern is not retained in pyrolytic sublimation of surfactants. We attribute this to the fact that pyrolytic rupture of the ligated amine−Nb bond generates a high concentration of open coordination sites on the inner surface of the material. This leads to rearrangement of the structure to a lower energy form. When the surfactant is removed by chemical methods, this is not a problem as water or solvent is present to block the open coordination site. When the sample is calcined in dioxygen this is also a potential problem, since a light-off of the transition metal oxide would be induced by surfactant combustion causing strong local heating and structural rearrangement. The combustion process can also liberate high levels of carbon dioxide which can insert into the Nb−O bonds, thus degrading the framework of the structure.

In general, those template-free materials synthesized at surfactant-to-Nb(OEt)$_5$ ratios of 0.75:1 or less retain their XRD pattern and well-defined mesoporosity, and show no hysteresis in their nitrogen adsorption/desorption isotherms. Those materials synthesized at ratios of 1.0:1 or greater give rise to non-distinct XRD patterns but high surface areas and narrow pore size distributions as calculated by nitrogen adsorption. These materials also have a small degree of hysteresis in their nitrogen adsorption/desorption isotherms. These observations are consistent with partial pore collapse due to acid etching of the thin walls of these samples prepared at high surfactant-to-Nb(OEt)$_5$ ratios. Elemental analysis of as-synthesized samples of Nb-TMS1 produced from dodecylamine:Nb(OEt)$_5$ ratios of 0.5:1 and 1:1 give wt. % carbon values of 30.87 and 38.42 respectively, with wt % Nb (ash method) of 38.72 and 32.57 respectively. This establishes that materials with higher carbon content have less niobium oxide and hence thinner and weaker walls. For example, a sample of Nb-TMS1 prepared at a 1:1 dodecylamine-to-Nb ratio has walls ca. 8 Å thick, while a sample prepared at a 0.5:1 ratio has walls ca. 11 Å thick. This is consistent with the partial structural degradation observed upon surfactant removal by acid treatment from those samples produced with higher ratios of dodecylamine to Nb(OEt)$_5$, and the structural retention upon surfactant removal by materials with lower dodecylamine:Nb(EtO)$_5$ ratios.

The resistance of Nb-TMS1 materials to acid can be greatly increased by doping with a wide variety of transition metals, lanthanides and actinides. Like pure Ta-TMS1, Nb-TMS1 doped with 5−10% Zr or Hf shows stability to acids at pH values approaching zero. These materials also show greater thermal and hydrothermal stability (ca. 500 °C) after template removal than pure Nb-TMS1, which is stable to ca. 400 °C in nitrogen and ca. 360 °C in nitrogen saturated with water vapor. However, even more thermally stable than Zr/Hf-doped Nb-TMS1 are samples of Ta-TMS1 doped with 5−20% Hf. These materials retain their XRD pattern, ultrahigh surface areas, and mesoporosities to temperatures of at least 700 °C in N$_2$ saturated

Scheme 4. Rational Design of Organometallic Precursors for Tailoring of Unique Mesostructures.[a]
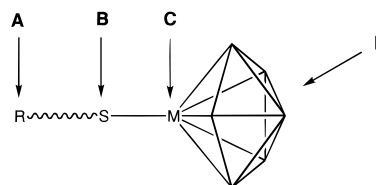
[a] Key: (A) variation of the number of tail groups per metal alkoxide cluster and the size and shape of the tail group determining the resulting liquid crystal phase; (B) choice of the appropriate head group leading to optimal strength of interaction between the organic and inorganic phases; (C) choice of appropriate size and composition of the metal cluster from one to several atoms determining the final composition, thickness, and crystal structure of the walls (tailoring of active catalyst sites possible); (D) choice of appropriate solvent and ancillary ligand type and size to control rate of hydrolysis and crystal growth.

with water, rivaling that observed for aluminosilicate samples of MCM-41. This indicates that these and related materials may be extremely useful in high-temperature catalytic process such as NO$_x$ decomposition.

Samples of Nb-TMS4 treated with acid lose their structure as expected, since the removal of the pillaring surfactant molecules leads to collapse of the layered structure. This has also been observed for MCM-50.[5c] The stability of Nb-TMS2 and Nb-TMS3 toward acid is under investigation; however, preliminary results show that they both collapse upon treatment with HNO$_3$.

Conclusion

In summary, we have demonstrated that by varying the synthesis parameters of the formation of niobium oxide meso-structures, new *P*63/*mmc* hexagonal (Nb-TMS2), cubic P*m*3*n* (Nb-TMS3), and layered (Nb-TMS4) phases can be obtained in addition to the original hexagonal phase (Nb-TMS1). We have also shown that the mechanism of formation is more dependent on starting conditions and kinetic factors than thermodynamic ones, and that formation of Nb-TMS meso-structures most likely proceeds without the assistance of preformed micelles, and through a mechanism involving a cooperation between self-assembly and condensation, as proposed previously for MCM-41 charge-matched templating. The use of the ligand interaction was found to be crucial for mesostructure formation as previously reported pathways were unsuccessful. We attribute this to the rapid hydrolysis of the early transition metal precursors to form highly insoluble species which are unable to interact with the inorganic phase by either a Coulombic or hydrogen-bonding interaction. Scheme 4 shows a general strategy for applying the ligand approach to a wide array of meso- and microstructures by variation of A, the template(s) shape and size, B, the template(s) ligand head group-(s), C, the ligated metal(s), and D, the metallic composition of the inorganic cluster and its ancillary ligands.

The thermal stability of these exciting new materials and the ease of compositional doping make them excellent candidates for a wide variety of high- and low-temperature catalytic applications, as well as porous hosts for mediating the synthesis of quantum wires and smart electronic materials.

Experimental Section

Materials. Niobium ethoxide and niobium oxide were obtained from Strem Chemicals. Mono-*n*-dodecylphosphate was obtained and used without further purification from Lancaster Synthesis. ^{15}N-enriched dodecylamine was obtained from Cambridge Isotopes and used without further purification.

Sodium dodecylsulfate, sodium dodecylphosphonate, undecanoic acid, dodecanol, and dodecyl trimethylammonium bromide were also obtained from Lancaster Synthesis, as were dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine. Dimethyldodecylphosphine was prepared according to the literature procedure[46] from Mg (Aldrich), dodecylbromide (Aldrich), and chlorodimethylphosphine (Strem). 4-dodecylaniline was obtained from Aldrich. Mono- and dimethyldodecylamine were obtained from Johnson Mathey, while 4-dodecylpyridine was prepared according to the literature procedure[47] from 4-picoline (Aldrich), lithium diisopropylamide (Aldrich), and dodecyl bromide (Aldrich). 3-Tetradecyl-2,5-pentanedione was prepared according to the literature procedure[48] from base-catalyzed condensation of acetylacetone and 1-bromotetradecane (Lancaster Synthesis) and distilled under vacuum at 149 °C before use. Ammonium tetraphenylborate was obtained from Aldrich and used without further purification. Sulfuric acid, nitric acid, and hydrochloric acid were obtained from J. T. Baker Chemical Co. Triflic acid, potassium chloride, and potassium hydroxide were obtained from Aldrich.

Instrumentation. X-ray powder diffraction data were recorded on a Siemens D-5000 $\theta-\theta$ diffractometer using Cu Kα radiation and a scintillation detector at 2.2 kW. High resolution transmission electron microscopy (TEM) images and electron diffraction patterns were obtained on JEOL 200 CX or a JEOL 2010 transmission electron microscope operated at 200 kV. Samples were prepared by extensive grinding, sonication in isopropanol and suspension on carbon-coated copper grids. Field emissions SEM images were taken on a JEOL (6320 FV). Nitrogen, water, and hydrocarbon adsorption data were collected on a Micromeritics ASAP 2000 Adsorption Analyzer. Samples were degassed at 170 °C at 10^{-3} Torr before running. Thermogravimetric analysis was conducted on a Perkin-Elmer TGA-7. Elemental analyses were performed by Huffman Laboratories. MAS-NMR and solution NMR experiments were conducted by Spectral Data Services, Inc.

Synthesis. (a) Nb-TMS1. In a typical preparation, niobium ethoxide (1.0 g, 3.14 mmol) was warmed with dodecylamine (0.292 g, 1.57 mmol) until a homogeneous colorless solution was obtained (ca. 1 min, 50 °C). To this solution was added 25 mL of water with stirring. Precipitation occurred immediately. The heavy solid was broken up with a spatula and allowed to sit at room temperature in the supernatant for 24–72 h before heating to 80° C for 24 h, 100 °C for 24 h, and 180 °C for 7 days. Alternatively, dodecylamine (0.292 g, 1.57 mmol) and niobium ethoxide (1.0 g, 3.14 mmol) were melted together and diluted in ethanol (10 mL), with water being introduced either with stirring (10 mL) or by vapor diffusion in air from −78 to 50 °C. After precipitation occurred (immediately when water was added directly to the solution or over several days when water was introduced by vapor diffusion), the white solid was allowed to sit at room temperature in the supernatant for 24–72 h before heating to 80° C for 24 h, 100 °C for 24 h and 180 °C for 7 days. The product in all cases was collected by suction filtration and washed with three 100 mL portions of water, one 100 mL portion of ethanol, and one 100 ml portion of diethyl ether. The solid was then dried at 120 °C for 1 day. Elemental analysis of this material gave 30.94% C, 6.48% H, 2.41% N (Kjeldahl), and 38.52% Nb (ash) by weight. This sample (1.00 g, 1.72 mmol of N) was suspended in dimethoxyethane at −78 °C under a nitrogen

atmosphere, treated with triflic acid (0.151 mL, 1.72 mmol), and stirred for 1 h at this temperature before allowing the solution to warm to ambient temperature with stirring for an additional 2 h. The solid was then collected by suction filtration, washed once with isopropanol (100 mL) before it was transferred to a new flask and stirred at ambient temperature in isopropanol for 24 h. The solid was collected by suction filtration and washed with water (100 mL), ethanol (100 mL), and ether (100 mL), and then dried in vacuo at 100 °C. The resulting solid had a (100) peak centered at 29 Å, distinct (110), (200), and (210) peaks, and a BET surface area of 617 m^2/g with a BJH adsorption pore size of 23 Å. Elemental analysis gave 0.43% C, 0.97% H, 0.05% N, 67.21% Nb (ash) by weight. Alternatively, the surfactant was removed by stirring in 200 mL of 4:1 isopropanol:water at pH 0.5 with nitric acid for 24 h at 80 °C, followed by extensive washing with water and ethanol before drying. This material was essentially the same as that described above; however, the (110), (200), and (210) reflections in the XRD were less well-defined, and the BET surface area was 468 m^2/g.

(b) Nb-TMS1 with Swelling Agent. The synthesis of Nb-TMS1 with a swelling agent is essentially the same as that described above; however, mesitylene was added to the organometallic mixture before addition of water. In a typical preparation, niobium ethoxide (5.0 g, 15.71 mmol) was warmed with octadecylamine (2.11 g, 7.8 mmol) and mesitylene (3.08 mL, 12.30 mmol) until a homogeneous solution was obtained (ca. 2 min, 50 °C). To this solution was added 25 mL of water with stirring. The thick oil suspended in the aqueous phase solidified over 5 min. The heavy solid was broken up with a spatula and allowed to sit at room temperature in the supernatant for 24 h before heating to 80 °C for 24 h, 100 °C for 24 h, and 150 °C for 7 days. The product was collected by suction filtration and washed with three 100 mL portions of water, one 100 mL portion of ethanol, and one 100 mL portion of diethyl ether. The solid was then dried at 120 °C for 1 day. The isolated sample had a (100) peak centered at 45 Å. The surfactant was removed as described above in section a.

(c) Nb-TMS2 and Nb-TMS4. These materials were synthesized by a method analogous to that described in part a in which water was added to the neat niobium ethoxide–amine melt; however, a 1.5:1 dodecylamine-to-niobium ethoxide ratio was used for Nb-TMS2, and a 2.0:1 ratio was used for Nb-TMS4.

(d) Doping of Nb-TMS1 was achieved by a method directly analogous to that described in part a; however a dopant was either added to the niobium ethoxide before addition of the amine in 1–25% molar quantities in the form of a metal alkoxide or conversely added as a metal salt solution to the niobium ethoxide amine melt. The latter method is not applicable when water is introduced by vapor diffusion into an ethanol solution of the precursor. All other procedures were the same as those reported for pure Nb-TMS1.

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