

# Synthesis and Characterization of Hexagonally Packed Mesoporous Tantalum Oxide Molecular Sieves

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Received October 9, 1995. Revised Manuscript Received February 5, 1996<sup>8</sup>

The synthesis and characterization of Ta-TMS1, a new member of a growing family of hexagonally packed transition-metal oxide mesoporous molecular sieves (termed TMS1) is described. Ta-TMS1 exhibits a hexagonal array of pores which can be varied in size from 20 to 40 Å and surface areas of over 500 m<sup>2</sup>/g. The thermal and hydrothermal stabilities of Ta-TMS1 are 500 and 450 °C, respectively, making this system the most stable transition-metal oxide molecular sieve yet isolated. The high hydrocarbon adsorption capacities of this material make it a promising candidate as a catalyst support for hydrocarbon re-forming processes. The synthesis of this material was achieved by a novel approach involving the careful hydrolysis of long-chain primary amine complexes of Ta(OEt)<sub>5</sub>. This ligand-assisted templating mechanism represents a new approach to the synthesis of porous materials in that the inorganic precursor is covalently bonded to the template throughout synthesis. The high thermal stability, ease of synthesis and doping, and high surface areas of this material make it competitive with zeolitic molecular sieve materials and may lead to a wide variety of commercial applications.

## Introduction

Since Mobil first demonstrated in 1992<sup>1,2</sup> that hexagonally packed mesoporous silicate and aluminosilicate materials (MCM-41) with uniformly sized pores and surface areas approaching 1400 m<sup>2</sup>/g could be synthesized by a micelle-assisted crystallization of the inorganic phase, there has been a great deal of interest in synthesizing transition-metal analogues of this material.<sup>3,4</sup> These materials would be attractive as adsorbents and in a wide variety of catalytic processes including partial oxidation of methane to methanol,<sup>5</sup> NO<sub>x</sub> decomposition,<sup>6</sup> hydrodesulfurization,<sup>7</sup> solid acid catalysis,<sup>8</sup> and photocatalytic decomposition of organic

halides.<sup>9</sup> This is because the large and uniform pore sizes should lead to fast diffusion to the active sites during catalysis, even for large molecules. Our group recently reported the first successful synthesis of the first thermally stable titanium oxide<sup>10</sup> and niobium oxide<sup>11</sup> analogues of MCM-41 (Ti-TMS1 and Nb-TMS1). The former was prepared using a modified sol-gel method using titanium acetylacetone isopropoxide precursors and aliphatic phosphate surfactants, while Nb-TMS1 was synthesized via a novel mechanism in which the surfactant head group was covalently bonded to the inorganic precursor prior to hydrolysis and condensation. While Nb-TMS1 shows remarkable stability to at least 400 °C, we reasoned that its Ta analogue should be even more thermally robust due to the greater stability of Ta<sub>2</sub>O<sub>5</sub> as compared to Nb<sub>2</sub>O<sub>5</sub>.<sup>12</sup> Ta<sub>2</sub>O<sub>5</sub> is useful in storage capacitors in large-scale integrated memory cells and as a gate insulator in MOS devices because of its large dielectric constant.<sup>13</sup> It is also useful in optical applications because of its high refractive index and very low light absorption coefficient<sup>14</sup> and in the production of ultrastable ceramics

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<sup>8</sup> Abstract published in *Advance ACS Abstracts*, March 15, 1996.

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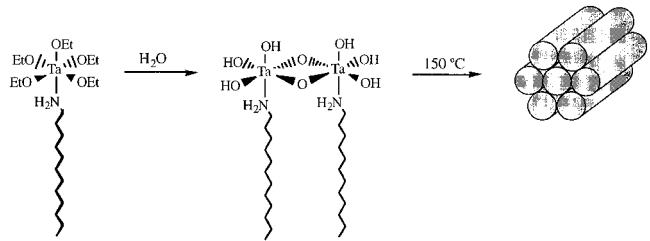
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**Scheme 1. Synthesis Approach for Ta-TMS1<sup>a</sup>**

<sup>a</sup> The tantalum ethoxide amine complex is treated with water to force condensation of the individual Ta centers. After self-assembly and further aging, the hexagonally packed mesoporous material is isolated.

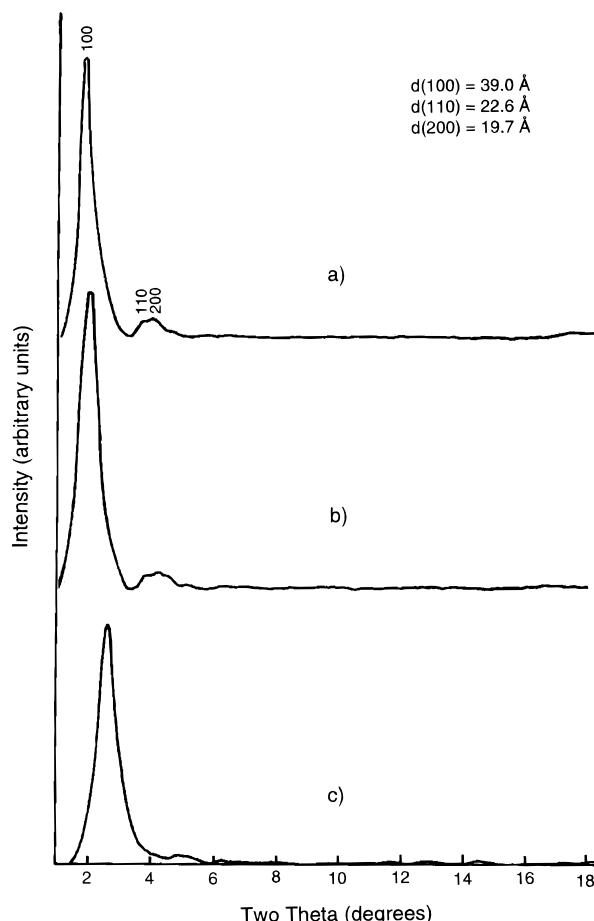
because of its high melting point, acid resistance, and thermodynamic stability.<sup>15</sup>

Herein we report the first synthesis of hexagonally packed tantalum oxide molecular sieves (Ta-TMS1) through a synthesis route analogous to that used to prepare Nb-TMS1. This material retains its mesoscopic order to higher temperatures than its Nb analogue and thus shows even greater promise as a catalytic support material than its lighter congener.

## Results and Discussion

**Synthesis and Characterization.** Initial attempts to synthesize hexagonal mesoporous tantalum oxide via hydrothermal methods directly analogous to those described by Mobil<sup>1b</sup> in the synthesis of MCM-41 did not succeed. When sodium metatantalate was heated at basic pH in the presence of tetraalkylammonium bromide surfactants with chain lengths ranging from 12–18 carbon atoms, only the precursor, the corresponding stoichiometric oxide, or a layered phase were obtained. Owing to the failure of these initial approaches, we pursued the alkoxide-based gel route successful in the synthesis of hexagonal  $TiO_2$ <sup>10</sup> mesoporous structures. Initial attempts at hydrolysis of tantalum ethoxide in the presence of trimethylammonium bromide surfactants at pH 8–10 produced only amorphous  $Ta_2O_5$  after calcination. Similarly, hydrolysis at lower pH with trimethylammonium bromide surfactants, or anionic sulfate, carboxylate, and phosphate surfactants gave either  $\beta$ - $Ta_2O_5$  or amorphous tantalum. While it was found that addition of acetylacetone promoted the formation of Ti-TMS1 using a related sol–gel route, this agent had no effect on the synthesis of hexagonally packed mesoporous tantalum oxide. Thus, the use of tantalum acetylacetone ethoxide in place of tantalum ethoxide led only to the formation of an amorphous phase over the synthesis conditions described above.

The synthesis of Ta-TMS1 was successfully achieved using the ligand-assisted templating approach (Scheme 1) with amine surfactants as described for Nb-TMS1.<sup>11</sup> Thus when  $Ta(OEt)_5$  was combined with one equivalent of a long-chain aliphatic amine such as octadecylamine and hydrolyzed from –20 to 180 °C, a white solid (Ta-TMS1) was obtained. The powder X-ray diffraction (XRD) pattern for this isolated as-synthesized Ta-TMS1



**Figure 1.** XRD patterns for (a) as-synthesized Ta-TMS1 made with octadecylamine, (b) triflic acid-treated Ta-TMS1 made from octadecylamine, and (c) triflic acid-treated Ta-TMS1 made from octadecylamine after heat treatment in  $N_2$  at 500 °C for 1 h. The pattern for the as-synthesized material is assigned and indexed to a hexagonal unit cell, although the broadness of the 110 and 200 peaks indicates that the regions of mesoscopic order are smaller than in samples of MCM-41.

made with 1 mol equivalent of octadecylamine and aged for 1 week at 180 °C had a (100) peak at a  $d$  spacing of 39 Å. The low-intensity (110), (200), and (210) peaks became more distinct when the sample was aged for longer periods, though they never achieved the high degree of resolution observed for samples of MCM-41. The material isolated after only 1 day of aging at room temperature gives a diffraction pattern in which the (100) peak is broad and the smaller peaks are not clearly distinguished. This phenomenon has been observed before in MCM-41 and has been attributed to disordered packing of the individual silicate tubes in the mesostructure.<sup>4a</sup> Figure 1a shows the XRD data of as-synthesized Ta-TMS1 with a first  $d$  spacing of 39 Å, obtained using an amine surfactant with a chain length of 18 carbon atoms. As with MCM-41, shorter chain lengths give materials with smaller pores and the addition of swelling agents yields materials with larger pores. Table 1 lists XRD  $d$  spacings for the (100) peak observed for samples of Ta-TMS1 synthesized with amine surfactants with chain lengths of 12, 14, 16, and 18 carbon atoms, as well as those values obtained from samples made from octadecylamine with 1 and 2 equiv of mesitylene. Different precursors and surfactants were also used in the synthesis of Ta-TMS1, but none

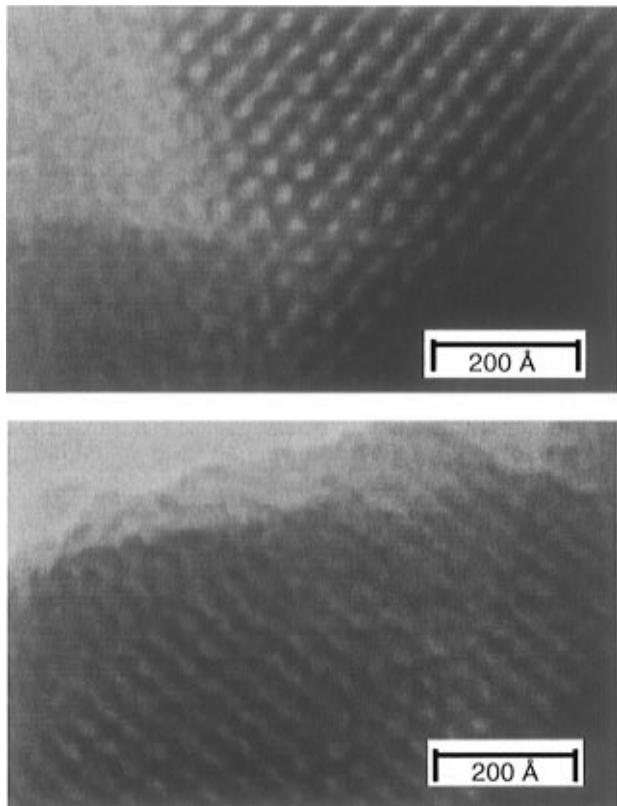
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**Table 1.** *d* Spacings, Repeat Distances ( $a_0$ ), Pore Sizes, and Wall Thicknesses for Triflic Acid-Treated Ta-TMS1 Synthesized with Surfactants of Chain Lengths of 12, 14, 16, 18, and 18+Mesitylene Swelling Agent

chain length	<i>d</i> (100) (Å)	repeat distance (Å) <sup>a</sup>	pore size (Å)	wall thickness (Å)
12	29	33.5	22	11.5
14	32	36.9	25	11.9
16	35	40.5	28	12.5
18	39	44.8	32	12.8
18 + mesitylene	43	49.5	34	13.5

<sup>a</sup>  $a_0 = 2d(100)/\sqrt{3}$ .



**Figure 2.** TEM micrographs of (a, top) as-synthesized Ta-TMS1 containing octadecylamine and (b, bottom) triflic acid-treated Ta-TMS1 synthesized from octadecylamine. As the broad XRD pattern of Ta-TMS1 shown in Figure 1a suggests, regions consisting of lower degrees of mesoscopic order, where the individual tubes are more randomly packed, also exist in samples of Ta-TMS1. No layered regions were observed.

of these systems investigated yielded materials superior to those derived from  $Ta(OEt)_5$  with primary amino surfactants. Thus, *N*-methyl dodecylamine, *N,N*-dimethyldodecylamine, 4-dodecylpyridine, and dodecylammonium bromide were combined with  $Ta(OEt)_5$  and subsequently hydrolyzed and aged to give materials with either weakly hexagonal or amorphous XRD patterns. The bulkier amino head groups apparently do not interact as effectively with the Ta center, possibly for steric reasons. The use of  $Ta(OEt)_4$ (acetylacetone) in place of  $Ta(OEt)_5$  led only to amorphous materials. This is consistent with the need for a vacant coordination site on the Ta center for the amino group to bind with. The acetylacetone complex is coordinatively saturated and thus acts as a poorer ligand acceptor than the ethoxide complex.

The TEM (Figure 2a) of as-synthesized Ta-TMS1 with a *d* spacing of 39 Å further confirms our results. Although obtaining a high-resolution image is difficult

due to the high density and electron absorption capacity of the material, the fringe regions of many particles are thin enough to obtain quality micrographs without microtoming. These micrographs show the hexagonal array of stacked tubes of approximately 32 Å in pore diameter. The inorganic walls of this material are ~13 Å thick, corresponding to what is expected on the basis of the XRD data, and agreeing well with the TEM observation of MCM-41 samples. The domain sizes of regular hexagonal packing are ca. 50 nm, although samples aged at lower temperatures for shorter times exhibit regions where the individual tubes are packed with a lower degree of mesoscopic order.

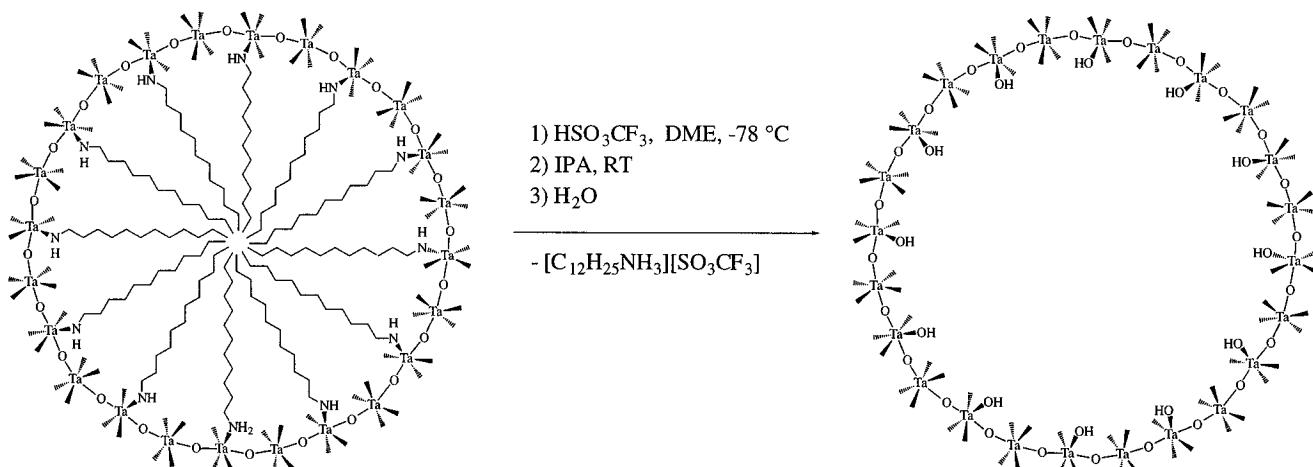
Elemental analysis of as-synthesized samples of Ta-TMS1 indicated ca. 30% surfactant by weight with a 2.2:1 Ta:N molar ratio. Samples made using only 0.5 mol equiv of surfactant had compositions with only slightly less surfactant in them and a Ta:N ratio of 2.35:1. This differs from the behavior observed for Nb-TMS1<sup>16</sup> where samples synthesized with a 1:1 Nb:surfactant molar ratio have a final Nb:N ratio of 1.7:1, while those synthesized with a 2:1 Nb:surfactant ratio have Nb:N ratios of 2.32:1 in the product. Thus, Ta-TMS1 exhibits less compositional flexibility than Nb-TMS1 with respect to weight percentage of the surfactant. Samples of Ta-TMS1 made from Ta:surfactant ratios of 1:1.5 do not differ in final composition or phase from those made from 1:1 ratios. No layered or cubic phases have yet been observed for Ta-TMS1 as have been noted for MCM-41 or unstable mesophases of W, Sb, and Pb.<sup>17</sup> Surfactants with carboxylate and acetylacetone head groups were also tried and gave only amorphous materials. Different ratios of Ta:surfactant ranging from 3:1 to 1:1.5 were tried and had little effect on the XRD of the final product. In all cases the synthesis was carried out at near neutral conditions. Addition of acid to the synthesis mixture before heating led to protonation of the amine functionality and formation of amorphous materials; while addition of base led to poorly crystalline products at pH 8–10, amorphous materials at pH 10.5–13, and partial dissolution of the inorganic phase above pH 14. This is consistent with the formation of water-soluble tantalates at high pH.<sup>18</sup>

**Surfactant Removal.** The surfactant in Ta-TMS1 cannot be removed by simple ethanol washing as observed for mesoporous silica and alumina materials<sup>4</sup> synthesized from neutral amine surfactants. To achieve removal of surfactants, a proton source is required. This behavior has also been observed in Nb-TMS1 and suggests a strong Ta–N bond in the as-synthesized structure. Surfactant removal from Ta-TMS1 was achieved chemically by one of the three following methods. The first and best of these methods is illustrated in Scheme 2 and involved the treatment of Ta-TMS1 with stoichiometric quantities of triflic acid in dimethoxyethane at –78 °C followed by extensive washing with 2-propanol at room temperature. In the second method, Ta-TMS1 is treated with nitric acid at pH 1 and 80 °C in 2-propanol for several days and finally washed with water and ethanol. The third technique

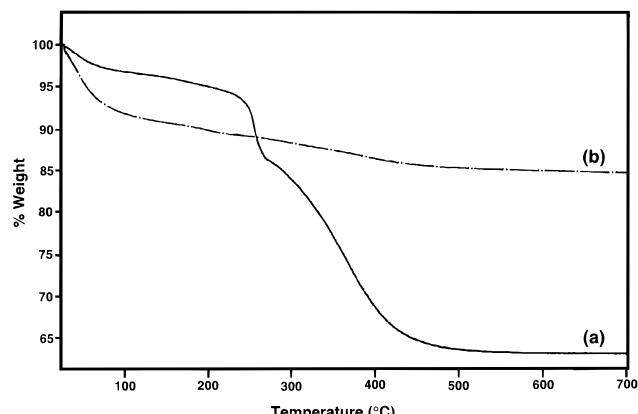
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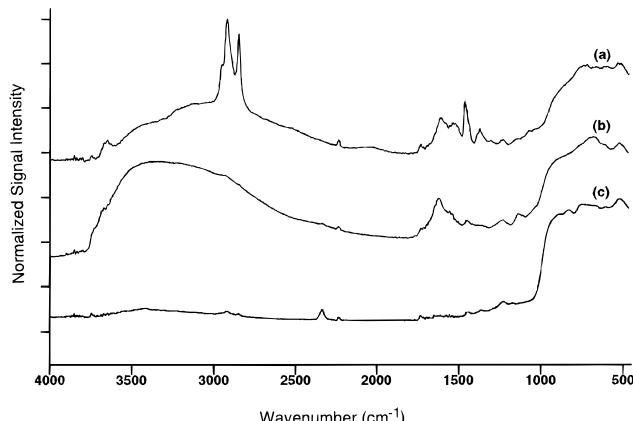
**Scheme 2. Illustration of Surfactant Removal from Ta-TMS1 by Treatment with Triflic Acid<sup>a</sup>**

<sup>a</sup> The N-Ta bond is cleaved by protolysis at  $-78^{\circ}\text{C}$  in the first step. The protonated surfactant is then removed by washing the material in dry 2-propanol (IPA) at ambient temperature for 24 h. Washing with water gives the final hydrated product.



**Figure 3.** TGA of (a) as-synthesized Ta-TMS1 containing octadecylamine and (b) triflic acid-treated Ta-TMS1 synthesized from octadecylamine.

uses ammonium tetraphenylborate ( $\text{NH}_4\text{BPh}_4$ ) as a proton source in dimethoxyethane at  $80^{\circ}\text{C}$ . In the triflic acid method, the triflic acid first protonates the amine surfactant at  $-78^{\circ}\text{C}$ . This is carried out in the absence of water which may lead to hydrolysis of Ta–O–Ta bridges. Treatment of the supernatant dimethoxyethane with thymol blue 5 minutes after addition of the triflic acid shows that no excess acid is present, indicating that the surfactant has consumed 1 equiv of acid. Warming to room temperature followed by filtration and stirring in 2-propanol for several hours removed the protonated surfactant. Analysis of the material before washing showed that the surfactant was still in the structure. The fact that aprotic dimethoxyethane did not wash out the protonated surfactant but 2-propanol did suggests that the surfactant may be hydrogen bonded to the structure. This first method is preferable over the second and third because it can be carried out without heating above room temperature and leads to the most complete removal of the organic phase of the three methods as determined by weight loss in the thermogravimetric analysis (TGA, Figure 3) and disappearance of the C–H stretches in the photoacoustic Fourier transform infrared (PA-FTIR) spectrum of the material (Figure 4). The TGA in Figure 3 compares the weight loss as a function of temperature of as-synthe-



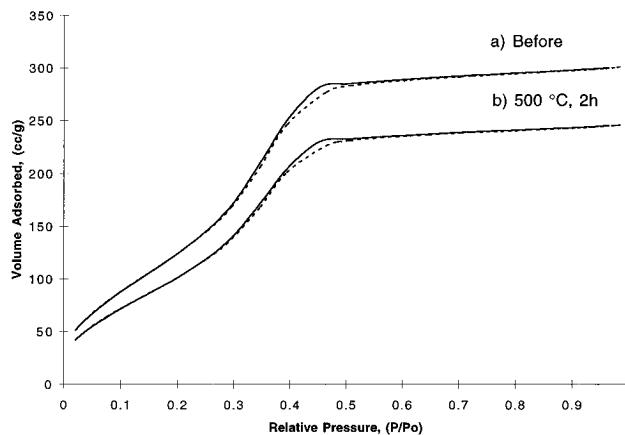
**Figure 4.** PA-FTIR spectra of (a) as-synthesized Ta-TMS1 containing octadecylamine, (b) triflic acid-treated Ta-TMS1 synthesized from octadecylamine, and (c) an anhydrous  $\text{Ta}_2\text{O}_5$  sample obtained from Strem Chemicals.

sized Ta-TMS1 to that of the triflic acid-treated material. The sharp weight changes between 250 and  $400^{\circ}\text{C}$  due to organics removal in the TGA of as-synthesized Ta-TMS1 are not present in the acid-treated sample, confirming that the surfactant has been effectively removed. Figure 4 compares the PA-FTIR spectra of as-synthesized Ta-TMS1, triflic acid-treated Ta-TMS1, and pure  $\text{Ta}_2\text{O}_5$ . The lack of C–H stretches at  $2800\text{--}3000\text{ cm}^{-1}$  in the acid-treated sample demonstrates that triflic acid has effectively removed the surfactant. The broad band at  $3000\text{--}3500\text{ cm}^{-1}$  and the peak at  $1620\text{ cm}^{-1}$  in this spectrum are not present in that of pure  $\text{Ta}_2\text{O}_5$  and are respectively attributed to the hydrogen-bonded and molecular  $\text{H}_2\text{O}$  in the acid-treated sample.<sup>19</sup> Thus, surfactant-free Ta-TMS1 is composed of a hydrated  $\text{Ta}_2\text{O}_5$  surface and can be successfully isolated by treatment of the as-synthesized Ta-TMS1 with 1 equiv of triflic acid. The only drawback of this method of surfactant removal is that the material must first be dried and analyzed for content of nitrogen to determine the appropriate amount of acid to add. It also must be carried out using anhydrous dimethoxyethane in an inert atmosphere to prevent moisture from entering the

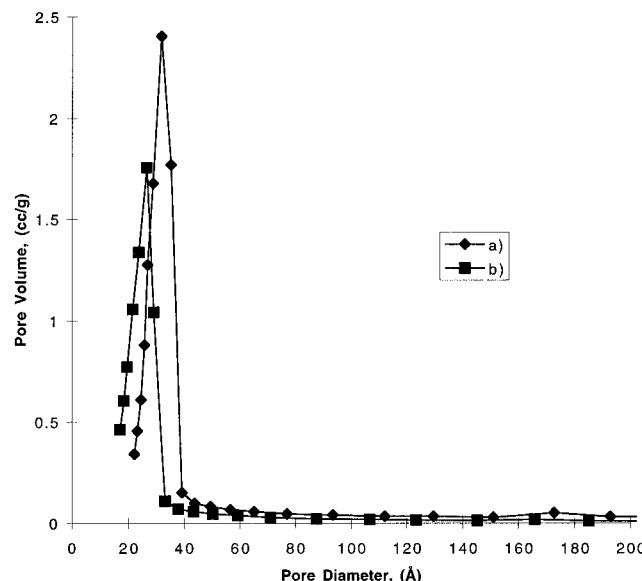
system and weakening the strength of the proton source. This is because the hydronium triflate formed in the presence of water is a weaker acid than triflic acid. The advantage of the ammonium tetraphenylborate method is that it can be carried out in the presence of water and does not require the use of highly corrosive and moisture-sensitive materials. Ammonium nitrate works less well, presumably because the nitrate salt of the ammonium surfactant cation is less soluble in organic media and takes longer to diffuse out of the structure and into the solvent. The nitric acid method is advantageous simply because of its convenience, but care must be taken in controlling the conditions to balance between complete surfactant removal and structural damage, which occurs at lower pH values.

The degree of which the material retains its structure depends mostly on the thickness of the walls and the aging temperature of the as-synthesized material. Samples aged to 150 °C or higher show signs of pore shrinkage due to higher-order condensation reactions. These processes stabilize the structure from further hydrolysis and increases the thermal stability of the surfactant-free material. Samples aged at 150 °C or higher invariably retain their structure when subjected to any of the three recommended methods of surfactant removal described above. Samples aged to 80–100 °C preserve their structure when using the triflic acid route but not the higher temperature routes, which lead to materials with diminished sharpness and intensities in the XRD pattern. In general, materials synthesized with less than 2:1 Ta:surfactant ratios are less stable to surfactant removal than those made at higher ratios. This could be attributed to thinner walls in these materials as compared to those synthesized with higher Ta:surfactant ratios. There is a tradeoff, however, because those samples made with less than 3:1 Ta:surfactant ratio have lower degrees of mesoscopic order as evidenced by broader XRD patterns. The optimal materials are synthesized with a 2:1 Ta:surfactant ratio and have the surfactant removed by the triflic acid method. The surfactant-free material normally weighs 60–70% the weight of the as-synthesized material.

Figure 1b shows the XRD pattern of a sample of surfactant-free Ta-TMS1 made from 2:1 Ta:surfactant ratio with octadecylamine at 180 °C for 1 week followed by surfactant removal via the triflic acid technique. There was little or no change in the crystallinity of the structure upon acid treatment. The BET surface area of this sample as determined by nitrogen adsorption was 510 m<sup>2</sup>/g. Accounting for the ratios of molar masses (220.94/60.09), 510 m<sup>2</sup>/g is comparable to 1850 m<sup>2</sup>/g for a SiO<sub>2</sub> system with similar mesoporous structure (e.g., MCM-41 with 32 Å pore sizes). Such high surface area was not achieved in MCM-41 synthesis. The adsorption and desorption isotherms (Figure 5) show no hysteresis and have a steep incline at about 0.4  $P/P_0$ , indicating uniform cylindrical mesopores.<sup>20</sup> The narrow pore size distribution of this material is shown in Figure 6a and is centered around 32 Å. This gives a wall thickness of ca. 13 Å as expected from the TEM of this sample shown in Figure 2b. Table 1 lists the  $d$  spacing, repeat distance ( $a_0$ ), pore size, and wall thickness of a series of samples made from C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, and C<sub>18</sub> amine surfactants as



**Figure 5.** Nitrogen adsorption (—) and desorption (—) isotherms for triflic acid-treated Ta-TMS1 synthesized from octadecylamine (a) before and (b) after heat treatment to 500 °C for 1 h in N<sub>2</sub>. The BET surface areas were 510 m<sup>2</sup>/g before and 436 m<sup>2</sup>/g after the heat treatment.



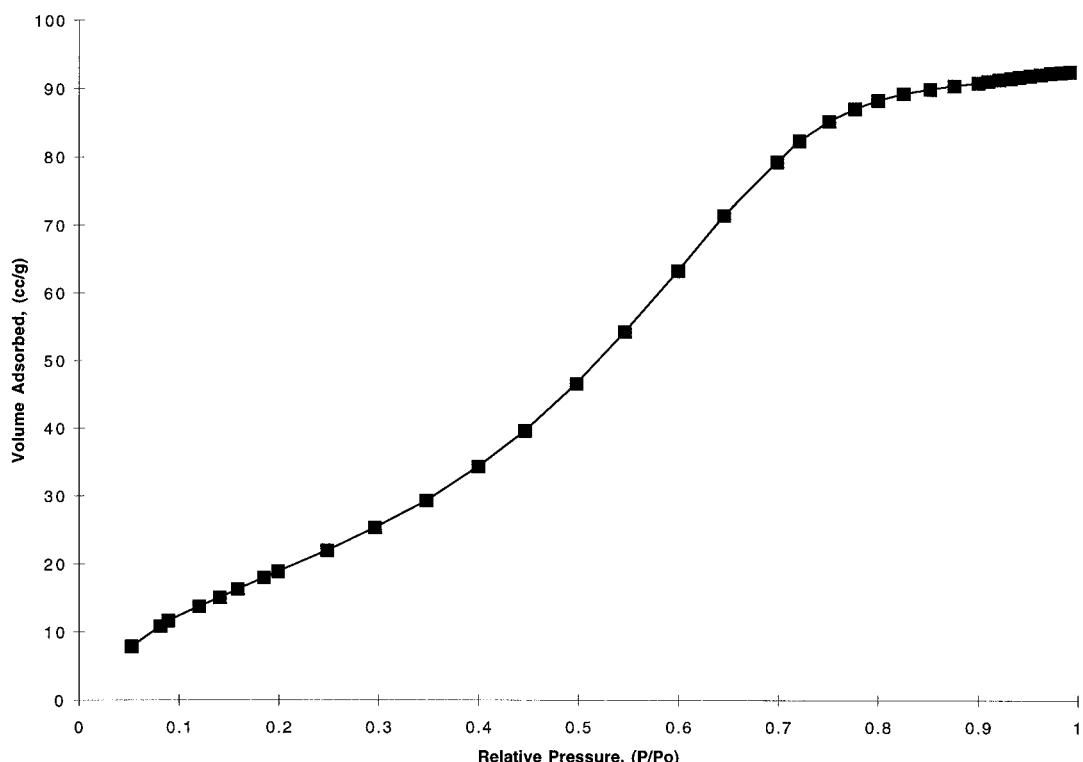
**Figure 6.** BJH pore-size distributions of triflic acid-treated Ta-TMS1 synthesized from octadecylamine (a) before and (b) after heat treatment to 500 °C for 1 h in N<sub>2</sub>. Data were calculated from adsorption isotherms in Figure 5.

well as two samples made with C<sub>18</sub> surfactants with 1 and 2 equiv respectively of mesitylene. In all cases the wall thickness is about 10 Å which is consistent with about three Ta–O units per wall, assuming a ca. 2 Å Ta–O bond length.<sup>21</sup>

**Thermal Stability and Sorption Capacity.** Samples of surfactant-free Ta-TMS1 prepared with a Ta:surfactant ratio of 2:1 and aged for 1 week at 150 °C retained a hexagonal XRD pattern after heat treatment in N<sub>2</sub> at 500 °C. Prolonged heating at this temperature leads to gradual structural degradation over 12 h as determined by reduction in intensity and sharpness of the XRD pattern. The hydrothermal stability is only slightly lower as samples slowly lose their well-defined XRD pattern after heating to 450 °C. This high stability demonstrates that Ta-TMS1 would make an excellent support material in catalytic processes. Figure 1c shows the XRD pattern of a sample

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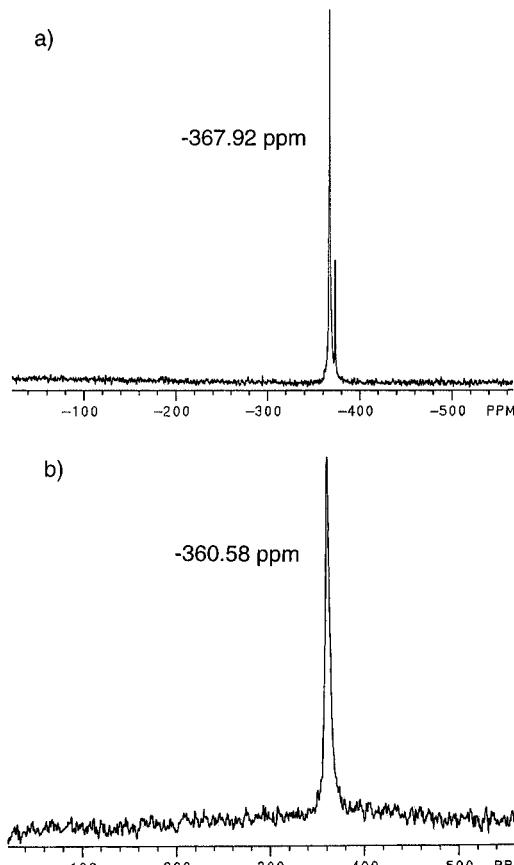


**Figure 7.** Butane adsorption isotherm at 0 °C for triflic acid-treated Ta-TMS1 synthesized from octadecylamine.

of surfactant-free Ta-TMS1 made with 0.5 mol equiv of octadecylamine relative to  $\text{Ta}(\text{OEt})_5$  after heat treatment to 500 °C in  $\text{N}_2$  for 1 h. The (100) peak has shifted to a lower *d* spacing, indicating that some pore shrinkage due to condensation of the walls. The nitrogen adsorption–desorption isotherm of Ta-TMS1 heated to 500 °C in  $\text{N}_2$  for 1 h is shown in Figure 5b and demonstrates that the mesoporosity has been retained with only a slight reduction of surface area from 510 to 436  $\text{m}^2/\text{g}$ . The pore size distribution of this same sample is shown in Figure 6b. The peak shift of the pore size distribution from 32 to 26 Å is expected on the basis of the pore shrinkage indicated by the XRD patterns of this sample. When as-synthesized samples of Ta-TMS1 are calcined in dioxygen from 350 to 550 °C, the structure is not retained. The reason for this is not fully understood but may be related to the large amounts of  $\text{CO}_2$  and water liberated in the combustion of the surfactant as well as the strong local heating that occurs during this process. Metal oxides are known to react with  $\text{CO}_2$  to form carbonates and with water to form hydroxides.<sup>22</sup> Such reactions could be responsible for the structural degradation observed.

Figure 7 shows a butane adsorption isotherm for a sample of Ta-TMS1 with 32 Å pores synthesized from a 2:1 Ta:surfactant ratio. The maximum adsorption capacity was 95  $\text{cm}^3/\text{g}$  or 0.28 g/g at STP which compares favorably to what has been observed for MCM-41 hydrocarbon adsorption. The water adsorption capacity was 0.23 g/g. The higher adsorption capacity of Ta-TMS1 for butane as compared to water has also been noted for samples of MCM-41<sup>1b</sup> and suggests that Ta-TMS1 might be useful in hydrocarbon isomerization and cracking reactions.

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**Figure 8.** MAS- $^{15}\text{N}$ -NMR of (a) 100% enriched  $^{15}\text{N}$ -dodecylamine, and (b) as-synthesized Ta-TMS1 prepared with 100% enriched  $^{15}\text{N}$ -dodecylamine. Spectra were recorded at ambient temperature and 36.82 MHz.

**Mechanistic Considerations.** Figure 8 shows the MAS  $^{15}\text{N}$  NMR spectra of 100%  $^{15}\text{N}$ -enriched dodecylamine and Ta-TMS1 synthesized from such  $^{15}\text{N}$ -en-

riched dodecylamine. As in the case of Nb-TMS1, the  $^{15}\text{N}$  resonance in the as-synthesized Ta-TMS1 ( $-360.58$  ppm) shifts downfield with respect to free dodecylamine ( $-367.92$  ppm). The line-broadening in the  $^{15}\text{N}$  resonance for  $^{15}\text{N}$ -enriched Ta-TMS1 is ca. 350 Hz at half-width, which strongly suggests the influence of the  $^{181}\text{Ta}$  ( $I=7/2$ ) quadrupole or a local disorder in the amine group structure. A quadrupolar interaction would most likely be due to a Ta–N bond in the as-synthesized samples Ta-TMS1, suggesting that the Ta–N bond has been retained throughout the synthesis process.

The mechanism of formation of Ta-TMS1 and Nb-TMS1<sup>23</sup> represents a novel approach to the synthesis of mesoporous materials in that the surfactant is covalently bonded to the metal atom in the precursor and possibly throughout the entire aging process. This mechanism contrasts to that proposed for the synthesis of MCM-41, where a ligand interaction between the tetraalkylammonium surfactant head group and the Si center is neither present nor possible. For this latter case, it is proposed, as in the synthesis of zeolitic materials, that the surfactant phase templates the assembly of the inorganic phase by electrostatic charge matching between the silicate oligomers and the individual surfactant head groups.<sup>3</sup> Neutral templating of amine surfactants to silicates has also been used to synthesize these structures;<sup>4</sup> however, in these systems covalent bonds between the amine and the silicate wall are also not possible and hydrogen bonds have been invoked to explain this process.

Strong evidence for the templating mechanism leading to the formation of MCM-41-like materials is drawn from the observation that all the known phases of silicate materials isolated through this process correspond exactly to one of the three liquid crystalline phases—cubic, hexagonal, or layered—observed for the pure surfactant phase by light scattering experiments.<sup>24</sup> The main source of controversy in this mechanism centers around the issue of the involvement of preassembled organic micelles in the formation of the as-synthesized materials. Davis and co-workers have proposed a mechanism where the inorganic phase crystallizes around preformed micelles, and higher ordering of these silicate-coated rods occurs at elevated temperatures to give the hexagonally packed arrays of tubes that constitute MCM-41.<sup>25</sup> An alternate mechanism suggests that the ordering of the surfactant/inorganic composite into rod-shaped agglomerates and finally into MCM-41 is directed by the charge-matching of the inorganic species and the surfactant head groups and does not involve preformed micelles. Support for this mechanism was mainly based on the observation that MCM-41 can be synthesized at temperatures and surfactant concentrations at which preassembled organic micelles do not exist.<sup>3a</sup>

In the synthesis of M-TMS1 (M = Nb, Ta) it is unclear how and at what stage of the synthesis process self-

assembly occurs, although preliminary results suggest that preformed micelles are not involved. We also propose that the templating forces required in self-assembly of these materials originate from the covalent bond rather than Coulombic forces or hydrogen bonding. Nb and Ta ethoxide complexes are known to form amine adducts.<sup>26</sup> This, however, does not rule out the transmetalation of the surfactant from one Ta center to an adjacent one during this process. Such fluxional processes are common in transition-metal clusters<sup>27</sup> and may be an important part of the crystallization process where a substantial degree of reordering is necessary to achieve highly regular structures. Furthermore, if electrostatic forces rather than discrete chemical bonds are required to template the synthesis of Ta-TMS1, the ammonium form of the surfactant would be expected to play an important role in the process. If this were true, there would be soluble alkylammonium salts in the supernatant during the aging process. Aliquots of the supernatant taken during aging contain no detectable quantities of such species. We have also investigated surfactants with mono- and dimethyl amine head groups and found that they do not work in the synthesis of Ta-TMS1. These more sterically hindered surfactants would not form as strong a bond with the Ta center and hence would not be effective in the synthesis of mesoporous materials if the ligand-assisted mechanism were indeed operative. Also, the surfactant is removed best under the low-pH conditions which normally favor the cleavage of Ta–N bonds. This suggests that such bonds may be intact in the as-synthesized material until the removal of surfactants. The mechanism of this process is currently under investigation and is the subject of an independent report.<sup>23</sup>

These results strongly indicate that a new mechanism involving a strong ligand interaction between the organic and inorganic phase is operative in our system. Our novel approach to synthesizing these exciting new materials is summarized in Scheme 1. In step 1, a surfactant-to-precursor bond is formed. In step 2, the new complex is selectively hydrolyzed under conditions which favor the rupture of the alkoxide Ta–O bonds but not the metal-to-surfactant Ta–N bonds. The material is aged in step 3 to optimize the mesoscopic order and stability of the mesostructure. Scheme 2 illustrates our new approach to surfactant removal. In step 1, the surfactant is protonated by a strong acid at low temperature and under anhydrous conditions with 1 equiv of acid to minimize structural damage. In step 2, the ammonium triflate form of the surfactant is repeatedly washed out with 2-propanol. Presumably 2-propanol replaces the surfactant after protonation of the amine by coordinating to the surface Ta centers. In step 3, water introduction replaces the surface isopropoxy with hydroxy groups to leave the final product with the structure intact with a hydrated tantalum oxide surface.

## Conclusion

In this study we have extended the synthesis of Nb-TMS1, the first hexagonally packed transition-metal

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oxide molecular sieve, to Ta and shown that it is even more stable than its lighter congener. The synthesis of these novel systems proceeds via a new mechanism in which the metal is incorporated in the surfactant head group through a ligand interaction. This approach should be extendable to a wide range of mesoporous and microporous materials well beyond the typical aluminosilicate based compositions. Such transition-metal oxide-based porous systems are not widely available, and these new materials should have applications in a variety of areas, including catalysis, molecular adsorption, nonlinear optics, and thermal or acoustic insulation. Studies are ongoing to further verify the mechanism, extend the synthesis to other metals, and explore the exciting new applications.

## Experimental Section

**Materials.** Tantalum ethoxide and sodium metatantalate were obtained from Strem Chemicals. Mono-*n*-dodecylphosphate was obtained and used without further purification from Lancaster Synthesis. <sup>15</sup>N-enriched dodecylamine was obtained from Cambridge Isotopes and used without further purification. Sodium tetradecyl sulfate, tridecanoic acid, and tetradecyltrimethylammonium bromide were also obtained from Lancaster Synthesis as were dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine. 3-Tetradecyl-2,5-pentanedione was prepared according to the literature procedure<sup>28</sup> 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 Company. Triflic acid, potassium chloride, and potassium hydroxide were obtained from Aldrich Chemicals.

**Instrumentation.** X-ray powder diffraction data were recorded on either a Siemens D-5000  $\theta$ – $\theta$  diffractometer using CuK $\alpha$  radiation and a scintillation detector at 2.2 kW or a Rigaku RU-300  $\theta$ – $2\theta$  with a rotating anode using Cu K $\alpha$  radiation at 10 kW. High resolution transmission electron microscopy (TEM) images 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. 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 experiments were conducted by Spectral Data Services, Inc. and recorded on a Nicolet NT-360 NMR spectrometer.

**Synthesis.** (a) *Ta-TMS1*: In a typical preparation, tantalum ethoxide (5.0 g, 12.30 mmol) was warmed with octadecylamine (1.65 g, 6.15 mmol) until a homogeneous colorless solution was obtained (ca. 5 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 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. Elemental analysis of this material gave 23.64% C, 4.77% H, 1.79% N, and 53.12% Ta (ash) by weight. This sample (1.00 g, 1.28 mmol N) was suspended in dimethoxyethane at –78 °C under a nitrogen atmosphere, treated with triflic acid (0.113 mL, 1.28 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 and washed once with 2-propanol (100 mL) before it was transferred to a new flask and stirred at ambient temperature in 2-propanol 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 39 Å, distinct (110), (200), and (210) peaks, and a BET surface area of 510 m<sup>2</sup>/g with a BJH adsorption pore size of 32 Å. Elemental analysis gave 1.07% C; 1.43% H; 0.09% N; 73.12% Ta (ash) by weight. Alternatively, the surfactant was removed by stirring in 200 mL of 4:1 2-propanol: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 420 m<sup>2</sup>/g. Stirring 1.0 g of the as-synthesized sample for 24 h in dimethoxyethane (200 mL) with 1.0 g of NH<sub>4</sub>BPh<sub>4</sub> at 80 °C followed by extensive washing with water, ethanol, and diethyl ether gave a sample with a BET surface area of 386 m<sup>2</sup>/g and a XRD pattern similar to that obtained with the nitric acid method with poorly resolved (110), (200), and (210) peaks.

(b) *Ta-TMS1 with swelling agent*: The synthesis of Ta-TMS1 with a swelling agent is essentially the same as that described above; however, mesitylene is added to the organometallic mixture before addition of water. In a typical preparation, tantalum ethoxide (5.0 g, 12.30 mmol) was warmed with octadecylamine (1.65 g, 6.15 mmol) and mesitylene (2.42 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 43 Å. Elemental analysis of this material gave 27.87% C, 5.89% H, 1.98% N, 51.22% Ta (ash) by weight. The surfactant was removed as described above in section a.

**Acknowledgment.** The National Science Foundation (CTS-9257223, CTS-9411901) is acknowledged for its financial support. The authors thank T. A. Gubiotti and D. Levin for their assistance in obtaining PA-FTIR and TGA data and in butane adsorption analysis, respectively. M. Frongillo (MIT CMSE) is acknowledged for his help in the TEM experiments.

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