

## Synthesis and Characterization of Mesostructured Vanadium Oxide

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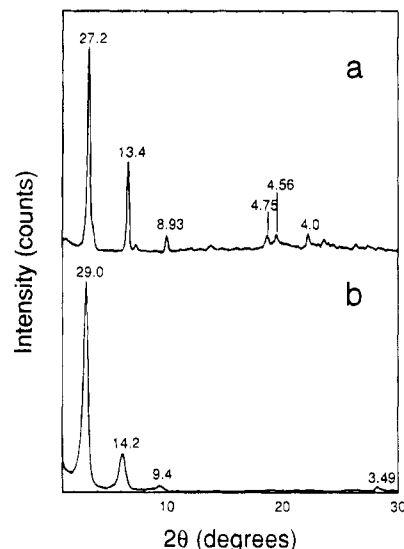
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The use of organic molecules as templates for the synthesis of zeolites and molecular sieves<sup>1</sup> as well as simple porous oxides has a long history. Although micellar and reverse micellar systems have often been used to synthesize finely divided silicas,<sup>2</sup> their use as templates in the synthesis of mesoporous silicates and aluminosilicates with regular pore structure has occurred only recently.<sup>3-7</sup> This represents a landmark event in molecular sieve technology and demonstrates how the propensity of organic molecules to form macromolecular ordered assemblies might be exploited to fashion uniform nanoscale inorganic oxide cavities.

Most synthetic and characterizational studies to date have focused on the hexagonal mesoporous silicate phase MCM-41 first synthesized by workers at Mobil Corp. Because of the obvious allure of transition-metal oxides in catalysis, there have been a number of recent attempts to synthesize transition-metal oxide analogues of MCM-41.<sup>8-11</sup> For instance, using a cationic surfactant and an aqueous solution containing tungsten polyanions, an ostensibly phase-pure mesostructured tungsten oxide has been synthesized hydrothermally.<sup>11</sup> Mesostructured lead and iron oxide phases have also been successfully synthesized hydrothermally from aqueous solutions. However, the conventional hydrothermal aqueous preparations using various surfactants that have been reported to date yield predominantly



**Figure 1.** X-ray powder patterns of (a) CTA-vanadate and (b) layered CTA-vanadium oxide intercalate synthesized in an autoclave at 150 °C (LVO1). Numbers indicated on figures are  $d$  spacings in angstroms. Patterns recorded in reflection geometry on Siemens D5000 diffractometer using Cu K $\alpha$  radiation.

layered rather than mesostructured phases<sup>8</sup> (e.g., the oxides of molybdenum and zinc). Because the oxides and phosphates of vanadium are exceedingly important in catalysis, especially for the selective oxidation and reduction of hydrocarbons, considerable effort has been expended in synthesizing zeolites and simple oxides in which vanadium is substituted into the oxide framework.<sup>12-16</sup> There have not yet been however any reports of the successful synthesis of mesostructured vanadium oxide even though vanadium, like tungsten and molybdenum, gives rise to a variety of generally anionic solution species of various nuclearities over a broad pH range.<sup>17</sup> In this communication we report for the first time the synthesis of mesostructured vanadium oxide via a novel route that features the use of cetyltrimethylammonium (CTA) vanadate in alcoholic medium at ambient temperature.

In a typical synthesis, the vanadate salt of the cetyltrimethylammonium cation was isolated by adding excess cetyltrimethylammonium (CTA) chloride (Fluka) to a 0.115 M solution of ammonium vanadate (Aldrich). The resulting white precipitate was filtered, washed thoroughly with distilled water, and dried at 50 °C. The product has the composition  $C_{19.5}H_{46.9}N_{1.0}V_{0.92}O_{4.6}$ , indicating that there is one vanadium per surfactant anion; chloride was absent. The X-ray diffraction (XRD) pattern of the CTA-vanadate salt (Figure 1a) is similar to that of CTA-bromide and shows a series of 00 $l$  reflections with the most intense and lowest order reflection that we could observe occurred at 27.2 Å,

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compared to 52 Å for the bromide salt.<sup>18</sup> Dissolution of CTA–vanadate in ethanol, gave essentially a single <sup>51</sup>V NMR resonance at  $\delta = -556$  ppm, and this has been assigned to  $H_xVO_4^{3-x}$  monomers where  $x$  is between 1 and 2 at pH = 7.0.<sup>19</sup> Additional weak peaks at  $-569.8$ ,  $-576.1$ , and  $-603.3$  ppm representing 7% of the total spectrum assigned to small polymeric species up to possibly  $H_xV_6O_{13}^{6-x}$ . It is interesting to note that while the aqueous vanadate solution used for the synthesis of CTA–vanadate contained predominantly tetramers and pentamers as shown by the <sup>51</sup>V NMR spectrum, dissolution of CTA–vanadate in ethanol results in only vanadate monomers.<sup>20</sup>

The solid CTA–vanadate (3.21 g) was dissolved in ethanol (240 mL) to give a solution with initial pH of 8.4 which was then titrated at ambient temperature with 0.20 M HCl past the equivalence point (pH = 4.5) to a pH of 2.2. Continued addition of acid past a pH of 2.2 yielded X-ray amorphous products. After completion of the titration the red-brown precipitate that formed was filtered, washed thoroughly, first with ethanol, and then distilled water, and finally air-dried. This red-brown product has the composition  $C_{20.1}H_{48.0}N_{1.0}V_{2.9}O_{11.4}$  with approximately three vanadiums per surfactant molecule and will be denoted MVO. This V/N ratio of 2.9 is not too different to the Si/N ratio of 3.4 found in MCM-41.<sup>21</sup> The XRD pattern of the MVO material (Figure 2a) possesses only three broad reflections in the  $1-10^\circ 2\theta$  range in contrast to four for MCM-41 and six for mesostructured tungsten oxide. No attempt was made to index the pattern of air-dried MVO because of the broad and overlapping peaks.

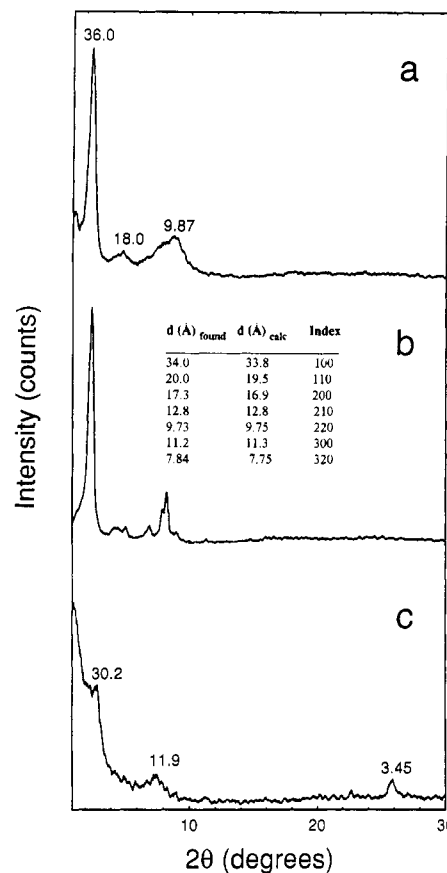
For comparison purposes, we synthesized a lamellar vanadium oxide phase by reacting a decavanadic acid solution that was 0.115 M in vanadium with CTA–chloride hydrothermally at 160 °C for 24 h. This temperature was chosen because it has been shown that synthesis of MCM-41 at temperatures exceeding 140 °C, where surfactant assemblies are not observed, produce either zeolitic or lamellar oxide phases.<sup>8</sup> The resulting dark green product has the composition  $C_{26.8}H_{50.5}N_{1.0}V_{4.42}O_{15.0}$  and its XRD pattern (Figure 1b) contains a main peak at  $d = 29.0$  Å and a series of high-angle peaks that are integral multiples of the main peak confirming that the product has a layered structure. This material will be denoted LVO1. In addition, CTA intercalation of preformed layered vanadium pentoxide gels that were synthesized by protonation of ammonium vanadates<sup>17</sup> was performed by stirring the vanadium pentoxide gel in water containing an appropriate amount of CTA–chloride overnight at room temperature. This material is denoted LVO2 and has a similar X-ray diffraction pattern to the LVO1 materials.

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(20) We have repeated the synthesis of CTA–vanadate on numerous occasions and found that the upper limit of these higher polymeric impurities is 7%. On some occasions higher polymers were not evidenced at all in the <sup>51</sup>V NMR spectrum. The quantities of higher polymers probably depends on parameters such as reaction time, the amount of excess surfactant added to the aqueous ammonium vanadate solution, etc. We are presently studying such variables and will report the results of our findings in a forthcoming publication.

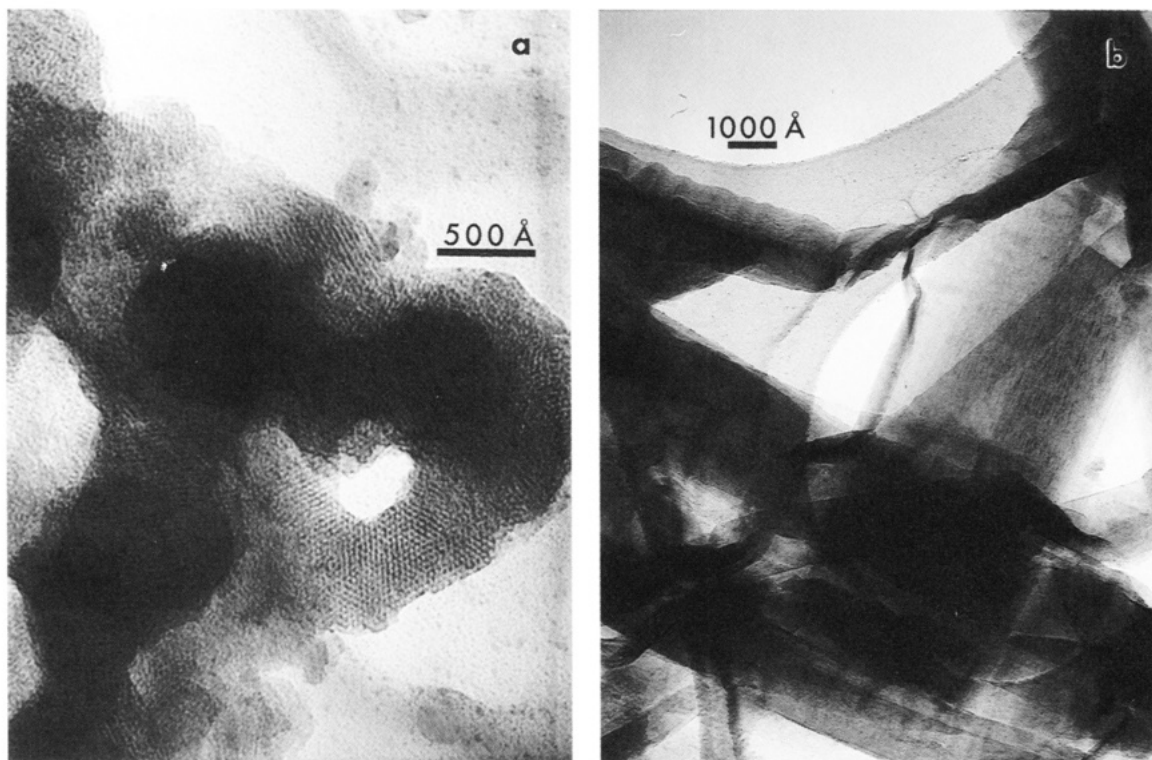
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**Figure 2.** X-ray powder patterns of (a) uncalcined MVO, (b) sample from (a) after calcination at 200 °C in air for 2 h, and (c) sample from (b) after calcination in air at 330 °C for 2 h.

Suspecting that a mesostructured vanadium oxide should have a greater thermal stability than a CTA–intercalated oxide as is the case in aluminosilicates,<sup>22</sup> we calcined the various samples in air at increasing temperatures. Calcination of the MVO sample to 200 °C for 2 h gave the XRD pattern of Figure 2b. Heating at this temperature results in a decrease in the  $d$  spacing of the main peak from 36 to 34 Å representing a lattice contraction of about 2 Å. This is comparable to the 3 Å contraction observed in silica MCM-41 samples after calcination.<sup>6</sup> Judging by the narrowing of peaks above  $3^\circ 2\theta$ , heating at 200 °C also induces an improvement in crystallinity as it does for MCM-41. The XRD pattern of MVO shown in Figure 2b resembles closely that of mesostructured tungsten oxide<sup>11</sup> and can be similarly indexed on a hexagonal cell with  $a = 39$  Å ( $2d_{100}/\sqrt{3}$ ). The composition of the material after this thermal treatment is  $C_{14.6}H_{48.4}N_{1.0}V_{4.0}O_{15.3}$  indicating a partial destruction of the surfactant ( $C/V$  ratio of 3.7 compared with 6.9 for the uncalcined sample). When the calcination temperature was raised to 330 °C, a marked reduction in crystallinity occurred (Figure 2c). Thermogravimetric analysis showed that the weight loss at this temperature was about 40% while the sample composition is  $C_{12.3}H_{21.9}N_{1.0}V_{5.1}O_{24.4}$ . The nitrogen adsorption isotherm of a sample that was calcined at 250 °C in air was of type II<sup>23</sup> and gave a surface area of

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**Figure 3.** Transmission electron microscope images of (a) MVO and (b) LVO1. Images obtained on a JEOL 100CX microscope of powder samples dispersed on holey carbon grids.

about 60 m<sup>2</sup>/g confirming that the surfactant is only partially removed at this calcination temperature.

In contrast, the hydrothermally synthesized lamellar oxide LVO1 and the CTA-intercalated preformed vanadium pentoxide gel LVO2 were markedly less stable than the MVO phase and decomposed to amorphous materials well below 200 °C. Calcination of these LVO phases at progressively higher temperatures up to eventual decomposition at about 150 °C resulted in a corresponding slight expansion of the interlayer space. This effect, together with the generally low thermal stability of CTA-intercalated V<sub>2</sub>O<sub>5</sub> gels has been described by Bouhaouss and Aldebert,<sup>24</sup> who found that heating to 150 °C resulted in amorphous phases which crystallized to orthorhombic V<sub>2</sub>O<sub>5</sub> on further heating.

Transmission electron micrographs of MVO and LVO1 samples are shown in Figure 3, parts a and b, respectively. These two materials have quite different morphologies, the MVO material having a platy morphology while the LVO materials have the characteristic ribbon morphology of vanadium pentoxide gels.<sup>25</sup> The MVO sample shows lattice fringe images that are 34–36 Å apart (Figure 3a) in agreement with the spacing of the most intense reflection in the X-ray powder diffractogram of the uncalcined sample. These fringe images are very similar in appearance to those of MCM-41<sup>6,7</sup> and the mesostructured tungsten oxide synthesized by Cielsa and co-workers.<sup>11</sup> Although extensive regions of the MVO sample appear as a honeycomb of hexagonal perforations that are characteristic of mesostructured oxide phases, regions of less well ordered material may also be discerned (e.g., bottom left of Figure 3a). Such

less well ordered material is also observed in many MCM-41 samples. In contrast, no fringe images were observed for the LVO materials. The striking similarity of images of the MVO samples with those of mesostructured tungsten oxides and MCM-41 together with the X-ray data and the enhanced thermal stability relative to the layered intercalates shows that the MVO samples are mesostructured surfactant–vanadium oxide composites similar in structure to MCM-41.

To further characterize the inorganic component of the mesostructured surfactant vanadium oxide composite we used a variety of spectroscopic techniques. Diffuse-reflectance UV–vis spectra of the CTA–vanadate salt and the mesostructured vanadium oxide phase along with data for a selection of model compounds taken from refs 26 and 27 are reported in Table 1. These data show that a more completely condensed structure in which vanadium is in distorted octahedral coordination is signalled by the appearance of a band around 450 nm. Such a band is present in the MVO product but not in the CTA–vanadate starting material. The increased connectivity of vanadium polyhedra after reaction is further highlighted by the presence of an infrared band at around 1000 cm<sup>-1</sup> that has been assigned to the V<sup>5+</sup> = O vibration in both crystalline and gel forms of vanadium pentoxide.<sup>28</sup> No such band is observed in the infrared spectrum of the CTA–vanadate precursor. Additional evidence for a vanadium pentoxide-like wall structure for the mesostructured product is obtained from the static and MAS <sup>51</sup>V NMR spec-

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**Table 1. Diffuse Reflectance UV/Vis Data of Reference Compounds Taken from Refs 26 and 27 Together with Data for the CTA–Vanadate and Mesostructured Vanadium Oxide**

sample	band positions/nm					coordination and geometry <sup>a</sup>
Na <sub>3</sub> VO <sub>4</sub>	238	290	357			4, tetrahedral, monomers
NaVO <sub>3</sub>		275	340			4, tetrahedral, 1-D chains
α-VPO <sub>5</sub>				412		5, square pyramidal, 2-D layers
V <sub>2</sub> O <sub>5</sub>	238	323	385		467	6, octahedral, multi-layer lattice
CTAV	229 <sub>28</sub>	302 <sub>54</sub>	360 <sub>18</sub>			
meso-V	238 <sub>6</sub>	309 <sub>29</sub>			441 <sub>24</sub> 914 <sub>40</sub> <sup>b</sup>	

<sup>a</sup> See ref 27 for a more detailed account of band assignments. <sup>b</sup> V(V)–V(IV) intervalence band. <sup>c</sup> Subscripted numbers are the percentage peak areas for the spectral decomposition.

trum.<sup>29</sup> This shows an essentially axial chemical shielding tensor with  $\delta_{11} = \delta_{22} = -341$  ppm and  $\delta_{33} = -1043$  ppm and an isotropic chemical shift deduced from the MAS spectrum at  $-618$  ppm. Such features are characteristic of the square pyramidal or distorted octahedral vanadium geometry in vanadium pentoxide.<sup>30</sup>

Our results are to be compared and contrasted with those published recently by Stein et al.,<sup>31</sup> who prepared surfactant–tungsten oxide composite materials from Keggin ion salts of cetyltrimethylammonium, (CTA)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>. The TEM images of these materials resemble those of MCM-41, but the XRD pattern was best indexed on a monoclinic unit cell and not a hexagonal cell as is MCM-41. The Keggin ion salts appeared to be composed of a puckered layer arrangement of disconnected Keggin ions that create a roughly spherical cavity for the surfactant cations. We do not believe that the mesostructured vanadium oxide prepared in this work has a structure similar to the Keggin ion composites for the following reasons. First, the preparation of mesostructured vanadium oxide does not employ a stable polyoxometalate salt but rather the cetyltrimethylammonium vanadate salt (CTA–H<sub>2</sub>VO<sub>4</sub>) in which VO<sub>4</sub> tetrahedra are essentially disconnected. This is confirmed by the diffuse reflectance, NMR, IR, and also Raman data. Second, our data indicate that

after reaction a more completely condensed structure reminiscent of V<sub>2</sub>O<sub>5</sub> and not decavanadate is formed. In fact the FTIR spectrum of MVO did not show a strong band at 960 cm<sup>-1</sup> that is characteristic of the decavanadate anion.<sup>32</sup> The vanadium–surfactant composites synthesized here seem to be more akin to the tungsten–surfactant composites synthesized by Ceilisa et al. which in turn appear to be different from those of Stein et al. This difference is clear from the XRD patterns of the tungsten–surfactant composites synthesized by these two groups.

On the basis of the above observations and discussion, we advance the following tentative mechanism for the formation of mesostructured vanadium oxide. Discrete vanadate species are initially present at the micelle interface as the only anionic species. Controlled addition of HCl initiates condensation reactions in a regime where the anion concentration initially favors vanadium and not the spectator anion, in this case chloride. This careful addition of HCl to the nonaqueous medium perhaps serves to better control what might otherwise be a cascade of runaway polymerization/condensation reactions. We surmise that increased connectivity of vanadium polyhedra occurs at the micelle interface and that the eventual condensation of vanadium-coated micelles leads to a wall structure resembling vanadium pentoxide. Studies aimed at testing the above hypothesis are currently in progress.

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