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Evidence for Decavanadate Clusters in the Lamellar Surfactant Ion Phase

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There has been much interest in the formation of transition metal oxides using soft chemistry approaches.[1] Hydrothermal techniques, in particular, have been extensively studied[2] for tungsten,[3,4] molybdenum,[5] and most recently vanadium oxides.[6] The discovery of a new class of mesoporous aluminosilicate materials by Beck et al.[7] provoked extensive studies of whether similar transition-metal oxides could be formed.[8−10] Stucky et al. proposed[8] mechanisms for formation of both lamellar and hexagonal phases of these types of surfactant templated transition-metal oxides. In a detailed study of tungsten and niobium materials templated with hexadecyltrimethylammonium, Stein et al. proposed[10] that tungsten oxides reacted with the surfactant ions to form unconnected Keggin clusters, rather than a continuous transition-metal oxide network. Recently the formation of vanadium oxide dodecylamine compounds was discussed,[11] and the unit cell of the lamellar phase was reported. Here we confirm, using the first single-crystal study of such materials, that the lamellar compounds at least in the case of vanadium oxide material contain discrete clusters between which reside the long-chain cationic surfactant; the clusters are joined via hydrogen bonding from water molecules.

In an earlier report we discussed[11] the synthesis and characterization of a material synthesized from V_2O_5 and dodecyltrimethylammonium bromide, DTABr, which formed transparent orange, platelike crystals that ranged from 1 × 1 to over 5 × 5 mm in size with a thickness of less than 0.5 mm. That material was synthesized either at room temperature, which resulted in smaller crystal dimensions, or by crystallization from the supernatant liquid after hydrothermal reaction. We have now found that we can form even larger crystals by heating the reactant materials on a hot plate, and changing the order and rate of reactant addition. DTABr (4 g) was first dissolved in 40 mL of water on a stir plate at room temperature. Sodium hydroxide (1 mL, 5 M) was then added to this solution for pH adjustment. The optimum pH for the final solution, after V_2O_5 addition, is about pH 6. Finally V_2O_5 was added to the solution at around 65 °C to give a 1:2 molar ratio of DTABr to V_2O_5. After mixing for about 1 h at 65 °C, the residual amorphous solid material was separated by gravity filtration. Crystal formation occurred overnight at room temperature as opposed to days or weeks for the hydrothermal method described previously.

This material readily dehydrates after removal from the reaction medium, and this dehydration led to our inability to gain good single-crystal data in the earlier study.[11] The structure presented in this report was made possible both by encasing the sample in a glue which stabilized the crystal and in particular by running the experiment on a high-speed diffractometer, thereby significantly shortening the data collection time and enabling *R* factors of around 10% to be obtained.

The structure determination was done on a Scintag XDS 2000 powder diffractometer and a Siemens Smart CCD single-crystal X-ray diffractometer. CSD software[12] was used for data analysis and structure refinement. The structure was solved using direct methods. The best solution gives all the vanadium and part of oxygen on the E-map. The remaining oxygen in the cluster, the carbon and nitrogen in the long-chain amine as well as the water oxygens were found from sequential difference Fourier maps alternating with least-squares refinement of the known part of the structure in isotropic and then anisotropic approximations.

The structure of the surfactant−V_2O_5 compound is a large unit cell of dimensions $a = 9.8945(3)$ Å, $b = 11.5962(1)$ Å, $c = 21.9238(2)$ Å, $\alpha = 95.153(2)°$, $\beta = 93.778(1)°$, $\gamma = 101.360(1)°$, similar to our earlier preliminary data.[11] The crystal class is triclinic and the space group $P\bar{1}$. On refinement, the unit cell was found to contain the decavanadate cluster, $V_{10}O_{28}^{6-}$, and not the dodecavanadate cluster originally proposed, which is charge balanced with four DTA molecules and two hydrogen atoms (possibly in the form of H_3O^+). Electron microprobe study showed no sodium in the material. The structural analysis indicated eight water molecules in the unit cell, giving a formula of $DTA_4H_2V_{10}O_{28}\cdot 8H_2O$; TGA showed[11] that six of these were removed by 200 °C with the other two being lost along with the organic species. Figure 1 shows a view down the *a* axis with all the DTA chains parallel to one another, with their trimethylammonium headgroups oriented in opposite directions. The vanadium cluster is at the center of the cell and not directly bonded to any other cluster but surrounded by DTA ions and water molecules. The inorganic layers in the structure are formed by decavanadate clusters hydrogen bonding together with water

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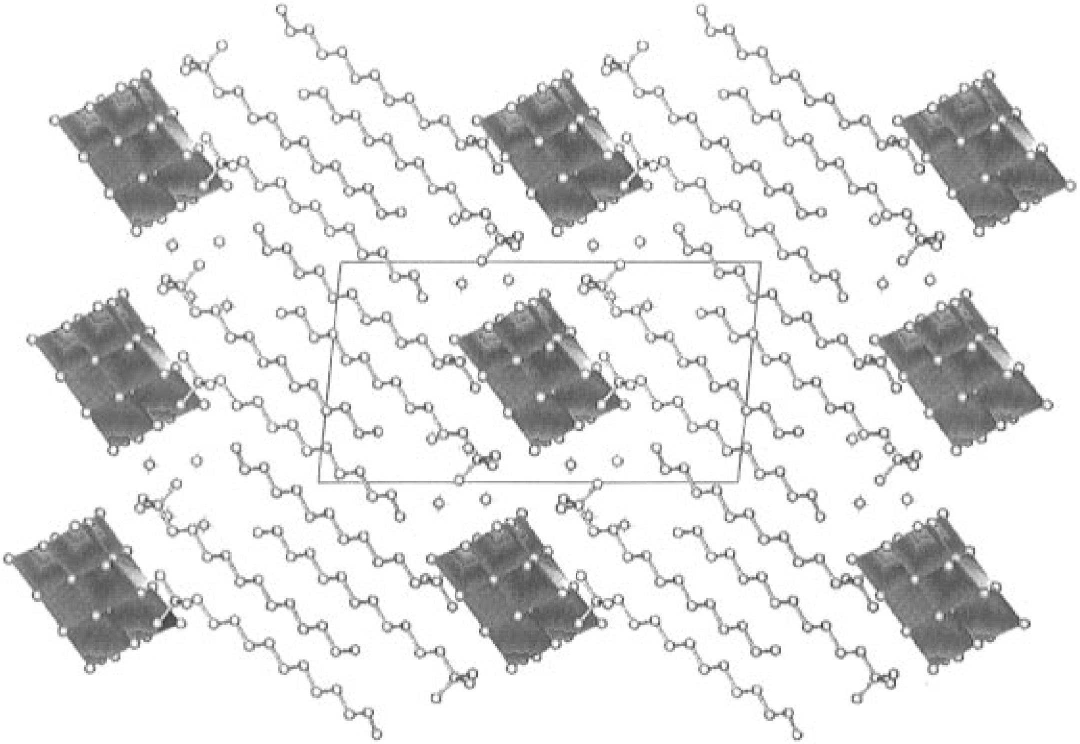

Figure 1. Packing of the decavanadate clusters and dodecyltrimethylammonium cations viewed along the *a* axis.

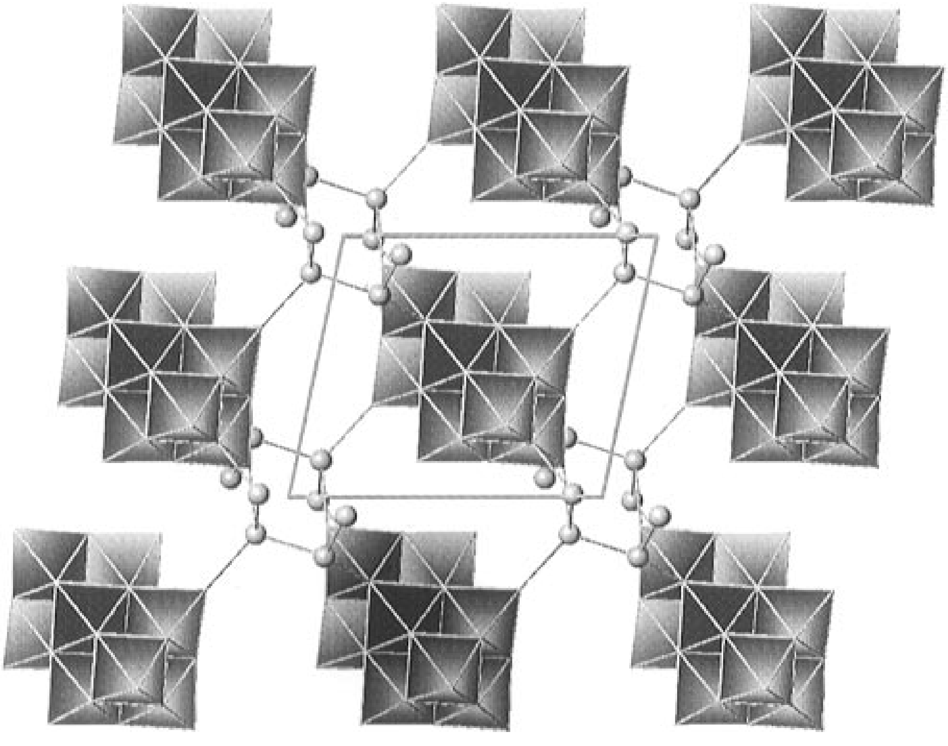

Figure 2. Decavanadate clusters and water molecules joined by H-bonds viewed along the *c* axis.

molecules. These hydrogen bonds are shown in a view of the *ab* plane in Figure 2; their lengths are in the range 2.64–3.06 Å. Attempted removal of the surfactant ions by heating caused the collapse of the structure.

The decavanadate crystals dehydrate rapidly under room conditions causing a decrease in the *d* spacing of the sample. This contraction of the unit cell by approximately 3 Å corresponds to a loss of six water molecules incorporated in the unit cell. The dehydration of the DTA–vanadate was monitored via X-ray powder diffraction. A hydrated sample was prepared and put into the diffractometer which had been purged with dry nitrogen for 2 h to expedite water transport from the sample. Short scans of the low angle region were taken over a period of 2 h with 2 min between scans. These data, shown in Figure 3, revealed the disappearance of the peak at 21.7 Å and the corresponding appearance of a peak at 18.9 Å as the water was removed from the structure. About half of the original intensity of the peak due to the wet interlayer spacing, 21.7 Å, has disappeared after 20 min, whereas the peak corresponding to the dry material, 18.9 Å, has begun to grow in.

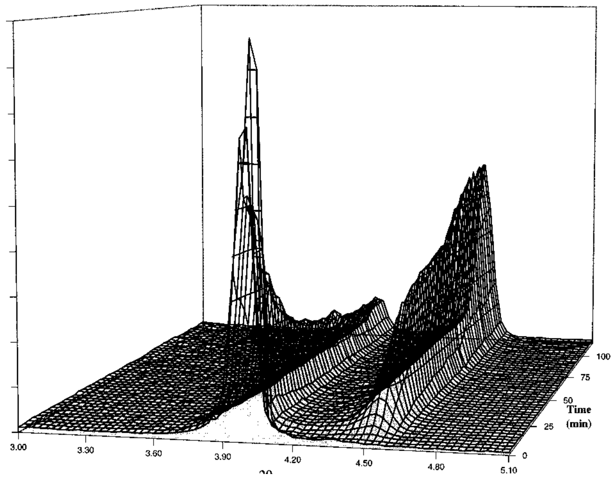

Figure 3. Real-time view of the dehydration process; lower angle peak from the hydrated phase, and the higher angle peak from the dehydrated phase.

The weight loss corresponding to the loss in water is consistent with the loss of six water molecules per unit cell, as discussed in our previous work.[11]

It was found that addition of methanol or ethanol also expanded the lattice to 22.7 and 24.9 Å, respectively. Both alcohols were absorbed into the unit cell at a rate similar to that with which water absorption was observed, and similarly desorbed in a solvent-free atmosphere reverting to the 19 Å "dry" phase. An attempt to insert *tert*-butyl alcohol, however, resulted in a permanent change to the structure.

In conclusion the crystal structure reported here, the first on a surfactant transition-metal oxide, clearly shows that the lamellar surfactant vanadium oxide phase contains discrete vanadium oxide clusters and not a continuous transition-metal oxide lattice. This lamellar phase has a variable water content, and the water molecules can be exchanged for other solvent molecules.

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Supporting Information Available: X-ray crystallographic data (12 pages). Ordering information is given on any current masthead page.

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