

NMe₄V₃O₇: critical role of pH in hydrothermal synthesis of vanadium oxides

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pH is critical in the formation of new mixed-valence vanadium oxides, NMe₄V₃O₇, NMe₄V₄O₁₀ and the dioxide Li_xV₂O₄·H₂O, with NMe₄⁺ cations or water molecules residing between vanadium oxide layers.

In the last few years there has been much effort placed on the synthesis of new transition-metal oxides that might be active hosts for intercalation reactions. There is particular interest in oxides that react readily with lithium and might find application as cathodes in advanced lithium batteries.¹ Reis *et al.*² built on the pioneering work of Gunter *et al.*³ and showed that two different tungsten oxides could be formed by hydrothermal reaction, and that pH controlled the phase formed. Subsequently, Guo *et al.*⁴ expanded this work to molybdenum and discovered a new layered molybdenum oxide when tetramethylammonium ions were in the reaction medium. Most recently, several new vanadium oxide structures were formed also using the tetramethylammonium ion, including a new layered vanadium dioxide and NMe₄V₄O₁₀, both of which contain vanadium in square pyramids.⁵ These two phases have now been completely characterized.^{6–8}

In a systematic study of the impact of the pH of the reaction medium on the vanadium oxides formed, we have found that a whole range of new materials are formed. In this study the reactants V₂O₅, NMe₄OH, and LiOH in a molar ratio of 1 : 2 : 1 in water were acidified with acetic acid and heated at 185 °C in a Teflon-lined Parr reactor for 3 days; typically 20 g of reactants were reacted in 70 ml of water. X-Ray diffraction of the products formed showed that at least six different phases were formed depending on the initial pH. The pH range for the products is shown in Fig. 1. At the highest pH, 10, the known Li₃VO₄ is formed;⁹ in this structure all the metal atoms are in tetrahedral sites. As the pH is lowered the new phase NMe₄V₃O₇ is formed whose structure is described below. This phase is also formed in the absence of lithium ions. At a pH of *ca.* 5 the new layered vanadium dioxide compound Li_xV₂-₈O₄₋₈·H₂O is found, as reported earlier.^{5–7} Lowering the pH further leads to the formation of another tetramethylammonium vanadate, NMe₄V₄O₁₀ whose structure we reported recently.^{5,8} At the highest acidities two new compounds are formed, both of which contain tetramethylammonium ions; they appear to have layer structures with repeat distances of 11.5 Å and 19.1 Å at pH 3.3 and 2.6 respectively. We are presently trying to determine their structures from powder diffraction data.

Crystals of the trivanadate, NMe₄V₃O₇, have a lath-like appearance and their structure was determined by Rietveld analysis of powder diffraction data. It is related to that recently reported for (DABCO)V₆O₁₄,^{10,11} (DABCO = 1,4-diazabicyclo[2.2.2]octane) but has some significant differences. The structure contains zigzag strings of edge-sharing VO₅ square pyramids; these strings are joined together by VO₄ tetrahedra,

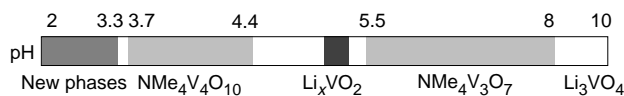


Fig. 1 Structures formed as a function of the pH of the reaction medium

as indicated schematically in Fig. 2. The structure has lattice parameters of $a = 18.478$, $b = 6.552$, $c = 8.427$ Å and $\beta = 91.1^\circ$, in space group P2₁/n; b is the dimension along the chain, c that perpendicular to the chain but in the plane of the vanadium oxide sheet, whereas a is twice the distance between the sheets. The tetramethylammonium ions reside between the vanadium oxide layers, as indicated in Fig. 3. The sheets are almost planar in direct contrast to those of the DABCO hexavanadate C₆H₁₄N₂V₆O₁₄·H₂O which are highly puckered, leading to a longer a and a shorter c axis, $a = 19.20$, $c = 7.547$ Å and $\beta = 111.3^\circ$, whereas the dimension along the chain remains almost unchanged, $b = 6.625$ Å.¹⁰ This buckling is common for vanadium oxides, being also observed for the alkali-metal vanadium oxides.

The tetramethylammonium ions are lost on heating the trivanadate to 350 °C, with loss of the structure. However, at

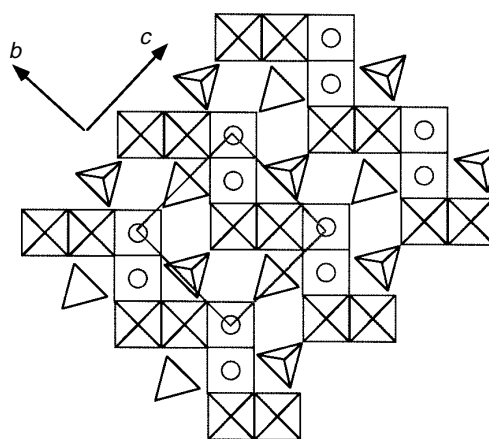


Fig. 2 Schematic representation of the structure of NMe₄V₃O₇, showing the zigzag chains of VO₅ square pyramids, joined together by VO₄ tetrahedra. The tetrahedra are shown separated from the chains for clarity. ⊠ = VO₅ pyramid, apex up; □ = VO₅ pyramid, apex down; △ = VO₄ tetrahedron, apex up; and ▽ = VO₄ tetrahedron, apex down.

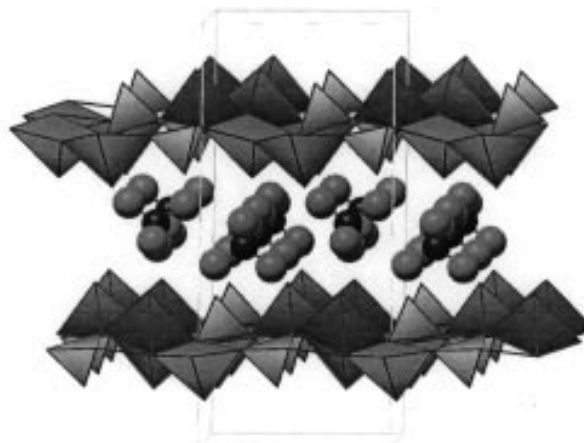


Fig. 3 Side-view of NMe₄V₃O₇ looking down the b axis

around 200 °C prior to the loss of the organic cations the structure takes up an additional oxygen atom to give the fully oxidized phase $\text{NMe}_4\text{V}_3\text{O}_8$. This appears to have a triclinic structure. Just like the tetravanadate, $\text{NMe}_4\text{V}_4\text{O}_{10}$, we have been unable so far to ion-exchange the tetramethyl ammonium ions out of the structure. In contrast the tetramethylammonium ions are expelled from the layered vanadium dioxide, $\text{Li}_x\text{V}_{2-8}\text{O}_{4-8}\cdot\text{H}_2\text{O}$, during synthesis; the structure is not formed in the absence of tetramethylammonium ions. This dioxide readily and reversibly undergoes dehydration and redox reactions with lithium⁷ and organic molecules.

Some trends in the structures formed can be seen. Li_3VO_4 has all the vanadium in tetrahedral sites. As the pH is lowered the first phase formed, $\text{NMe}_4\text{V}_3\text{O}_7$, has vanadium in both tetrahedral and square-pyramidal sites. At still lower pH all the vanadium is found in square pyramids. Although the structures of the two phases formed under the most acidic conditions are not known it is probable by comparison with cluster complexes formed under similar acidic conditions that some of the vanadium will be found in octahedral sites. These cluster complexes often remain in solution during the hydrothermal reaction, and precipitate from the filtrate after standing under ambient conditions for several days; an example is $[\text{NMe}_4]_4\text{-Li}_2\text{V}_{10}\text{O}_{28}\cdot 12\text{H}_2\text{O}$, whose structure is also layered. It contains $\text{V}_{10}\text{O}_{28}$ clusters arranged in sheets together with $\text{Li}(\text{H}_2\text{O})_4$ tetrahedra; the tetramethylammonium ions reside between these sheets.¹²

In conclusion, change of pH of the reaction medium in the hydrothermal synthesis of vanadium oxides results in a wide range of new structures, indicating the richness of the hydrothermal approach.¹³ The first layered vanadium oxide⁵ containing an organic species, $\text{NMe}_4\text{V}_4\text{O}_{10}$, has spawned a wide range of new compounds, including the dioxide Li_xVO_2 and $\text{NMe}_4\text{V}_3\text{O}_7$ whose structure is reported here. In addition, Nazar has recently found¹⁴ an additional compound, $[\text{NMe}_4]_5\text{V}_{18}\text{O}_{46}$, which we have not yet seen in this investigation. Within the last year a number of other organic molecule–vanadium oxide complexes have been reported,¹⁵ but so far only the tetramethylammonium ion has been found to form more than one structure type.

This work was supported by the National Science Foundation through grant DMR-9422667 and by the Department of Energy through Lawrence Berkeley Laboratory (Office of Transportation Technologies).

Footnote

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Received, 3rd October 1996; Com. 6/06772G