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HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION
OF NH₂CH₂CH₂CH₂NH₂²⁺ [(VO₄)₃(VO₆)₂]⁻
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Introduction

In the past decade, the design and synthesis of organic-inorganic hybrid materials has received considerable attention, not only to the variety of structural types and bonding geometries but also due to potential applications in fields such as catalysis [1], electronic conductivity [2], magnetism [3], medicine [4] and others. One of the most potent methods for the preparation of these hybrid materials and other important solids is the hydrothermal synthesis technique. The hydrothermal method is particularly suitable for fabrication of organic-inorganic metal metal oxide materials since the traditional methods of synthesizing the metal oxide frameworks rely on high temperatures which would destroy the organic template molecule. Organometallics have been used extensively as templates for preparation of many of these hybrid materials under hydrothermal conditions. The organic moiety is generally both a charge-compensating anion and a space-filling moiety, and may also function as a ligand to the metal.

Experimental

The synthesis of NH₂CH₂CH₂CH₂NH₂²⁺ [(VO₄)₃(VO₆)₂]⁻ was carried out under hydrothermal conditions; a mixture of V₂O₅ (0.8000 g), CoCl₂·6H₂O (0.541 g), 1,3-DAP (0.607 g), HCl (1.000 g), and H₂O (20.4 ml) in a molar ratio of 1:0.5:5:51 was stirred for 30 min in a test tube with a stirrer and heated in a 125 ml teflon-lined stainless steel autoclave (Parr bomb), and heated to 180°C under autogeneous pressure for 4 days before cooling to room temperature. The acidity of the medium was constant pH of 7-8 before and after the reaction. Flower-like crystals were filtered off, washed with water, and stored at room temperature. The composition is unidentifiable in view of common organometallics.

The morphology of the crystal-line product (Figure 1) was observed by scanning electron microscopy (model ISM-6600 SEM) equipped with an energy dispersive x-ray fluorescence microanalyzer (WDS-100 EDS attachment). The IR spectrum was recorded in the range 400-4000 cm⁻¹ on a Perkin-Elmer spectrometer using a KBr pellet. The FTIR analysis was carried out on a Perkin-Elmer TGA 7 Thermal Analyzer in flowing N₂ with a heating rate of 10°C min⁻¹. X-ray crystallographic data were collected from a hexagonal crystal with a Brucker-Nordico KappaCCD four-circle diffractometer equipped with a graphite monochromator and 0.5 mm 0.0 exposure capillary collimator.

Results, Discussion and Conclusions

The RDX spectrum indicates the presence of both vanadium (IV) and cobalt (IV). There is no evidence for carbon in the structure from the crystallographic model, and the crystals seem to be related in the same morphology as the data crystal. It is possible that there is a third solid state product that either deposits on the surface of the crystals or forms in a non-isolated crystal along with the crystals.

The crystal structure consists of two dimensional monoclinic vanadium oxide networks separated by organic layers of 1,3-DAP ions as illustrated in Figure 2. The vanadium oxide layers are constructed from equal mixtures of VO₄ tetrahedrons each containing one vanadium (IV) atom and VO₃ square pyramids with vanadyl oxygen atoms at the apical positions. The square pyramids occur in edge-sharing units with the vanadyl groups occupying opposite sides of the vanadyl-based planes. Each oxygen atom shared between the two square pyramids is also shared with one VO₄ tetrahedron (µ-O). The remaining four oxygen atoms of the basal planes are also shared with VO₄ tetrahedrons (µ-O). The resulting network is illustrated as a polyhedral representation in Figure 3(a). It can be seen that the underlying apical positions (the vanadyl groups) of both the tetrahedron and the square pyramids alternate above and below the plane in an mcm symmetry layer.

The vanadyl groups are good hydrogen bond acceptors, and it is surprising to find that all nine hydrogen bond donors from hydroxyl groups on the vanadyl groups as illustrated in Figure 2(a). Three of the hydrogen bonds involve two vanadyl groups (bidentate hydrogen bonds) and three involve single vanadyl groups.

The IR spectrum is shown in Figure 4. The strong bands at 871 cm⁻¹ are assigned to the terminal V=O stretching mode and the bands at 1015, 1041 and 1069 cm⁻¹ are associated with symmetric and asymmetric M-O-M stretching vibrations. Bands at 1590, 1645 and 1717 cm⁻¹ are characteristic of 1,3-DAP, and the bands in the 2820 and 2920 cm⁻¹ region can be attributed to O-H stretching.

The TG curve is shown in Figure 5 and can be divided into two stages. In the first stage from 270°C to 570°C, a 33% weight loss occurs, corresponding to the release of 1,3-DAP. A second stage in the temperature range of 650°C-920°C shows a gradual weight gain of 2.9% consistent with volatilization of the vanadyl-based structure. From Figure 5(b).

Discussion

References


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Figure 1. SEM picture of one crystal of (3,4-DAP) [(VO₄)₃(VO₆)₂]

Figure 2. (a) Projection drawing parallel to the (00) polyhedral network. (b) Projection drawing parallel to the (110) polyhedral network showing the three-dimensional vanadium oxide and organic layers. (c) Perspective drawing showing the vanadyl-based layers.

Figure 3. FTIR spectrum

Figure 4. TG spectrum

Figure 5. DTA curve

Figure 6. X-ray powder diffraction pattern

Figure 7. Transmission electron microscopy (TEM) micrograph

Figure 8. High-resolution transmission electron microscopy (HRTEM) image

Figure 9. Selected area electron diffraction (SAED) pattern

Figure 10. Raman spectrum

Figure 11. Raman spectrum of the vanadyl-based layer