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HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF A MICROPOROUS COBALT VANADIUM OXIDE FRAMEWORK COMPOUND

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ABSTRACT An organic-inorganic hybrid of cobalt vanadium oxide has been made by hydrothermal synthesis from a 1:1:2:1:593 molar mixture of V_2O_5, $CoCl_2 \cdot 6H_2O$, 1,3-diaminopropane (DAP), HCl, and water, reacted at 180 °C for 4 days. Infrared analysis shows the presence of the 1,3-diaminopropane template, and energy dispersive x-ray fluorescence shows the presence of vanadium and cobalt. Single crystal x-ray structural characterization shows the black crystals to be monoclinic, P21/n (No. 14), with unit cell parameters at 298 K of a = 7.975(3), b = 9.986(2), c = 15.629(3) Å, β = 100.66(3), and V = 1223.4(5) Å^3. The crystal structure consists of two dimensional metal oxide layers with 1,3-DAP molecules separating adjacent layers. Characterization by thermal analysis (TG) is also described.

1. INTRODUCTION

In the past decade 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 application in fields such as catalysis [1], electronic conductivity [2], magnetism [3], medicine [4] and others. One of the most powerful methods for the preparation of these hybrid materials and other important solids including microporous crystals [5], complex oxide ceramics [6], magnetic materials [7], chemical sensors, and electronically conducting solids [8], is the hydrothermal synthesis technique. There are many variables in the hydrothermal process, such as the type of starting materials, pH, solvent, reaction time, and temperature [9] that can affect the reaction system and/or the formation of products. The hydrothermal method is particularly suitable for fabrication of organic-inorganic hybrid metal oxide materials since the traditional methods of synthesizing the metal oxide frameworks rely on high temperatures which would destroy the organic template molecules.

Porous vanadium oxides are being studied for their potential use as secondary cathode materials for advanced lithium batteries [10] and their importance in industrial oxidative catalysis [11]. Organic amines have been used extensively as templates for preparation of many of these hybrid materials under hydrothermal conditions. The organic amine may adopt a variety of roles depending on its structure, charge, and the presence of a secondary transition or post-transition metal cation in addition to the vanadium component [12]. The role of the organic amine is generally a charge-compensating, space-filling, and structure-directing cation. It also may act as a ligand bound to a secondary metal site to form a metal-ligand complex which may also be directly coordinated to the vanadium oxide through bridging oxo- groups to form a bimetallic phase. Recent examples of such bimetallic complexes include {[Mn(2,2′-bipy)$_2$]$_2$V$_4$O$_{12}$} [13] with a [V$_4$O$_{12}$] ring linked through oxo groups of adjacent vanadium sites to two [Mn(2,2′-bipy)$_2$] moieties, [Cu(phen)V$_4$O$_{10}$]$_\infty$ [14], consisting of inorganic vanadium oxide layers decorated with Cu(phen) coordination fragments, each linked to an inorganic layer through three oxygen atoms, [(NH$_3$(CH$_2$)$_3$NH)Zn]$_2^{3+}$[V$_4$O$_{13}$]$^{6-}$ [15], consisting of ZnO$_3$N and VO$_4$ tetrahedral units corner connected into a unique layered architecture, with the amine molecule directly bonded to the Zn center pointing in a direction perpendicular to the plane of layer, and others. Herein we report the synthesis by a hydrothermal process of a new organic-inorganic hybrid of cobalt vanadium oxide and 1,3-diaminopropane.

2. EXPERIMENTAL

2.1 Materials and physical measurements

The reagents used were vanadium pentoxide (99%, Carlo Erba), cobalt dichloride hexahydrate (99%, Carlo Erba), 1,3-diaminopropane (99%, Fluka), and hydrochloric acid (Merck). All chemicals were commercially purchased and used without further purification. The synthesis was carried out in a 125 mL Teflon-lined stainless autoclave (Parr bomb). The morphology of the crystalline product was observed by a scanning electron microscope (Jeol model JSM-6400 SEM) equipped with an energy dispersive x-ray fluorescence microanalyzer (WDX-100 EDX attachment). The IR spectrum was recorded in the range 400-4000 cm^{-1} on a Perkin-Elmer model Spectrum GX FTIR spectrometer using a KBr pellet. TG analysis was carried out on a Perkin-Elmer TGA7 Thermal Analyzer in flowing N_2 with a heating rate of 10 °C min^{-1}.

2.2 Hydrothermal synthesis

The synthesis of the hybrid cobalt vanadium oxide compound was carried out under hydrothermal synthesis conditions. A mixture of V_2O_5 (0.5002 g), $CoCl_2 \cdot 6H_2O$ (0.6541 g), 1,3-DAP (0.4097 g), HCl (0.1003 g), and H_2O (29.4 g) in a molar ratio of 1:1:2:1:593 was stirred for 30 min in air. The solution/mixture was transferred and sealed in a 125 ml Teflon-lined stainless steel autoclave (Parr bomb), and heated to 180 °C under autogenous pressure for 4 days before cooling to room temperature. The acidity of the medium was at constant pH of ~7-8 before and after the reaction. Black crystals were filtered off, washed with water, and air-dried at room temperature. The compound is insoluble in water and common organic solvents.

2.3 X-ray crystallography

A single crystal of the compound with size, 0.28 x 0.30 x 0.32 mm was selected and glued to the end of a hollow glass fiber with cyanoacrylate adhesive. Reflection intensities were collected on a Bruker-Nonius KappaCCD four-circle area-detector diffractometer [16] equipped with a graphite monochormator, a 0.5 mm *ifg* capilliary collimator, and a fine focus x-ray tube (Mo Kα radiation, λ = 0.71073 Å) operating at 40 kV and 20 mA. The frame images were reduced to intensity data using the EvalCCD package and corrected for Lorentz, polarization, and absorption effects [17]. Crystal data and details of the data collection and structure refinement are summarized in Table 1.

3. RESULTS AND DISCUSSION

3.1 Structure description

The crystal structure consists of two dimensional metal oxide layers with 1,3-DAP molecules separating adjacent layers. As shown in Fig. 1, the layer are constructed from equal number of VO_4 tetrahedral and VO_5 square pyramidals. The VO_4 tetrahedra are isolated from each other, the VO_5 square pyramids exist in pairs sharing on edge. Each polyhedron has terminal oxygen; the others are shared between two or three polyhedra. In each pair of edge-sharing pyramids the two terminal oxygen atoms are oriented to ward opposite sides of the plane of the layers. Two square pyramids share an edge in such a way that in one pyramid the terminal oxygen and below it in the second one. These two different positions are labeled "up" and "down", for the pyramids and the tetrahedral. The last vertex of each tetrahedron is common with the two-dimensional inorganic network with the compositions. In rows of tetrahedra the arrangement of tetrahedra is up/down/up/down... In rows of the pyramidal units the arrangement of the pyramids is alternatively up/down/up/down...

3.2 SEM-EDX

The morphology of the crystal is show in Fig. 2. The EDX spectrum indicates the presence of V and Co in the compound.

Table 1.

Crystal data and structure refinement of compound.

Crystal color	Black
Crystal size (mm)	0.28 × 0.30 × 0.32
Crystal system	Monoclinic
Space group	P2$_1$/n (No. 14)
Unit cell parameters	
a (Å)	7.975(3)
b (Å)	9.986(2)
c (Å)	15.629(3)
V (Å^3)	1223.4(5)
Z	4
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
Temperature (K)	293
Diffractometer	Nonius Kappa CCD
Range of h, k, l	$10 \le h \le 0$, $12 \le k \le 0$, $19 \le l \le -20$
Refinement	Full-matrix least-squares on F^2
R_1	0.0957
wR_2	0.1598

$\{R_1 = \Sigma \| F_o| - |F_c| | / \Sigma |F_o|;\ wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}\}$, $W = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$.

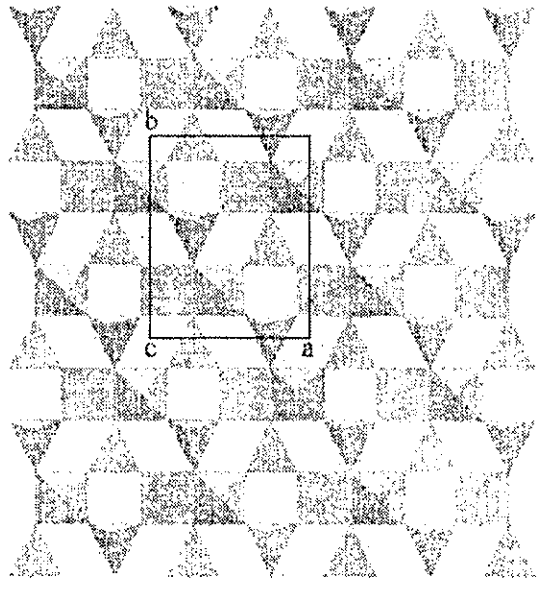

Fig. 1. Polyhedral representation of one two-dimensional metal oxide layer viewed parallel to the c axis.

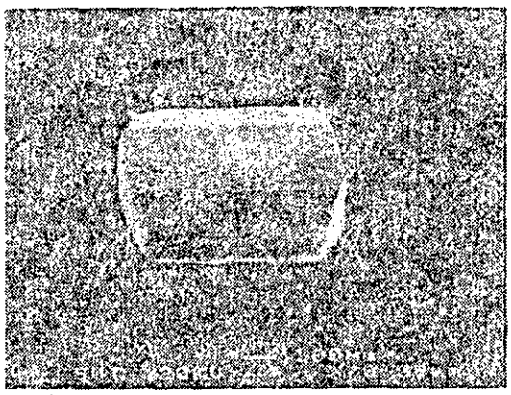

Fig. 2. The SEM picture of compound.

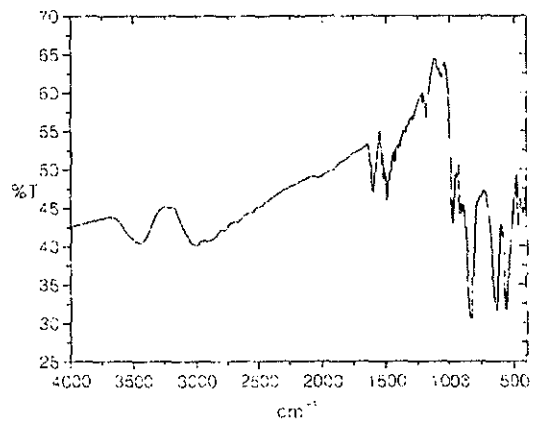

Fig. 3. The IR spectra of compound.

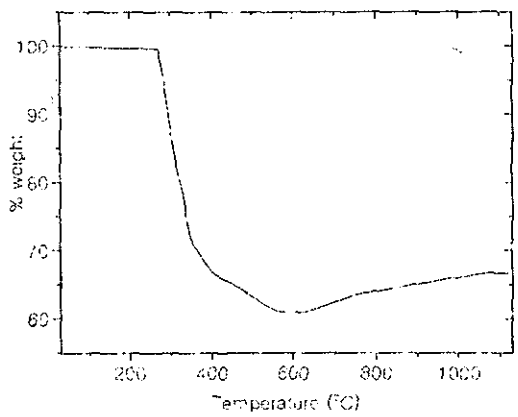

Fig. 4. TG curve of compound.

3.3 FTIR

The IR spectrum of compound is shown in Fig. 3. The strong bands at 971 cm^{-1} is assigned to terminal V=O stretching and bands at 830, 631 and 560 cm^{-1} are consistent with symmetrical and asymmetrical M–O–M stretching. Bands at 1599, 1488 and 1187 cm^{-1} are characteristic of 1,3-DAP, and bands in the 3009 and 3450 cm^{-1} region can be attributed to N–H stretching, and/or possibly water OH stretches, respectively.

3.4 Thermal Analysis

The TG curve is shown in Fig. 4 and shows a 39% weight loss from 270 to 570 °C, corresponding to the release of 1,3-DAP.

4. CONCLUSIONS

Hydrothermal synthesis provides a convenient tool for the preparation of organic-inorganic hybrid vanadium oxide. This new structure showed the mixed polyhedra of tetrahedra and pyramidal. Two tetrahedra and pyramidal, one up and the other down, share the two oxygen let appear a square vacancy within the secondary building unit. The holes through the layer are bounded by –SqPy–Td–SqPy–Td–.

5. ACKNOWLEDGMENT

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