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A new metallate phase of V_2O_5 crystalline microstructure achieved in a facile route: Synthesis, characterization, and measurement in catalytic reactions

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ABSTRACT

Experiencing a series of complicated changes, abundant orange crystals of novel metallic phase of vanadium pentoxide were obtained by a mild chemical method, the formula of which is defined as $[V_3(\mu_3\text{-}O)_2\cdot(\mu_1\text{-}OH)\cdot O_5]\cdot H_2O$. Differ from the synthesis methods of vanadium oxide published, we have adopted a simple solution method that mixed starting materials are refluxing in the system of ethanol–water under a relatively lower temperature. Symmetry of the crystals is Monoclinic, with cell unit dimensions: $a = 4.9978(10)$ Å, $b = 8.4273(17)$ Å, $c = 7.8669(16)$ Å, $\beta = 96.44(3)^\circ$ and space group of $P2_1/m$. The structure of the complex was characterized by elemental analysis, IR, UV–vis spectroscopy and single-crystal diffraction analysis. Powder X-ray diffraction (PXRD) was used to detect the purity of the crystals, and crystal morphology was detected by the scanning electron microscope (SEM). In addition, in order to extend application of oxidovanadium complexes, bromination catalytic activity about the complex in a single-pot reaction of the conversion of phenol red to bromophenol blue in a mixed solution of H_2O–DMF at a constant temperature of 30 ± 0.5 °C with a buffer solution of NaH_2PO_4—Na_2HPO_4 (pH = 5.8) was evaluated firstly, indicating that the complex can be considered as a potential functional model of bromoperoxidase, in the meantime, we have conducted the bromination catalytic reaction to simulate and measure the changes in reaction process indirectly. Besides, catalytic oxidation activity of the complex is also evaluated in the oxidation of cyclohexane (Cy) and cyclopentane with hydrogen peroxide promoted under mild conditions, showing potential catalytic activity of the complex by comparing TON (total turnover number) ratios of CyO/CyOH (CyO is the abbreviation of cyclohexanone and CyOH represents cyclohexanol) in the oxidation results.

1. Introduction

In the family of 3d transition metal complexes, vanadium oxides have received considerable attentions owing to their outstanding properties in physical and chemical research field [1–3], for example: electrical, optical, magnetic and environmental area [4–16]. Numerous researchers have also studied their behaviors when the oxides were designed as cathode material for rechargeable Li^+ battery [17], or have reported their excellent performance as catalysts in oxidation reactions [18–20] to further drive for practical capacities of vanadium oxides. It is to be noted that the interest in catalytic oxidation carrying on with the presence of metallic vanadium complex as catalyst has increased recently [21,22]. By checking the literatures [23], there are mainly two factors influencing the catalytic performance of vanadium oxides, one is the oxidation states of the vanadium ion, and the other is the configuration of the molecule. As far as we know, vanadium usually adopts valence states from +3 to +5 in the complexes; different valence state and various coordination environment determine the geometry of vanadium oxides, by sharing corners, edges and faces, leading to variable structural configurations of vanadium oxides (tetrahedron, trigonal bipyramid, square pyramid, regular octahedron, and distorted octahedron), which is the source of abundant catalytic agents. Until now, several kinds of geometries of V—O systems have been reported [24–33], characters of molecular structures, natures of the complexes and meaningful studies of the properties are involved among those researches. Vanadium Oxides have been prepared by a variety of synthetic ways in amorphous or crystalline forms [34–37]; for example, Popuri et al. [38]

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have provided a rapid way to obtain VO_2 using a hydrothermal process with V_2O_5 and citric acid as precursors; Wu et al. [30] used an available pathway to accomplish paramontroseite VO_2 by a simple chemical reaction of sodium orthovanadate ($Na_3VO_4 \cdot 12H_2O$) and thioacetamide (TAA). Besides, V_2O_5 is also a widely studied hotspot topic, since it is a common material for synthesis and catalysis system. Vanadium oxides possess different elemental composition forms, and various coordination polyhedra, which build up the tremendous structural diversity of vanadium oxides and bring the unique electrochemical and optical properties of vanadium oxides [39–42].

Traditional synthetic approach for vanadium oxides is hardly to reach, high cost and strict experimental conditions, sometimes high temperature and means of calcination are needed. While in our work, we have easily achieved abundant crystals of vanadium pentoxide in a mild condition refluxing in water–alcohol system at a relatively lower temperature, the method is facile and environmental. To our knowledge, it is found that molecular structure of the as-prepared complex and synthetic method has not been reported so far. Here, the new vanadium oxide is characterized by elemental analysis, IR spectra, UV–vis spectroscopy, single-crystal X-ray diffraction, SEM and Powder X-ray diffraction. In order to extend application of the vanadium oxide, we tested firstly for its catalytic activity both in bromination catalytic system with phenol red as organic substrate and in catalytic oxidation with hydrogen peroxide promoted. The results indicate that the complex can be considered as a potential functional model of bromoperoxidase (V-BrPO), and a promising catalytic agent used for obtaining clean energy source. In the meantime, the transformation mechanism from NH_4VO_3 to vanadium pentoxide is proposed; furthermore, we make full use of catalytic bromination reaction to track the species in solution during the synthetic reaction in situ.

2. Experimental section

2.1. Materials and methods

All the other chemicals used were of analytical grade and without further purification. Elemental analyses for C, H and N were carried out on a Perkin Elmer 240C automatic analyzer, and content of V was measured by a Plasma-Spec(I)-AES model ICP spectrometer. Infrared spectra were recorded on a JASCO FT/IR-480 spectrometer in the range of 200–4000 cm^{-1} with pressed KBr pellets. UV–vis absorption spectra were recorded on a JASCO V-570 spectrometer (200–2500 nm, in the form of a solid sample). X-ray powder diffraction (PXRD) patterns were obtained on a Bruker Advance-D8 equipped with Cu Kα radiation, in the range $5^\circ < 2\theta < 60^\circ$, with a step size of 0.02° (2θ) and an count time of 2 s per step. The SEM samples were performed with a SU8000 field emission scanning electron microscope. A 30% aqueous solution of hydrogen peroxide was used as primary oxidant in the cyclohexane oxidation reaction. The products of cyclohexane (Cy) oxidation were analyzed by a GC-9790 series gas chromatograph equipped with a flame ionization detector (FID) and a capillary column (PG2000, column length: 30 m; internal diameter: 0.25 mm).

2.2. Preparation of $[V_3 \cdot (\mu_3\text{-}O)_2 \cdot (\mu_1\text{-}OH) \cdot O_5] \cdot H_2O$

NH_4VO_3 (0.1 mmol, 0.0117 g), triflusal (0.05 mmol, 0.0124 g) and some carboxylic acids as auxiliary ligands (1,3,5-Benzenetricarboxylic acid, 1,2,4,5-Benzenetetracarboxylic acid, salicylic acid, benzenesulfonic acid, malic acid, aminoacetic acid and so on; 0.1 mmol) were dissolved in 15 mL $CH_3CH_2OH—H_2O$ system (the ratio of volume is 2:1), instantaneously giving an opaque orange solution which was stirred at room temperature for 3 h. Then, the solution was transferred into pyxides with refluxing for 3 h at a temperature of 80 °C. The orange bulk crystals were obtained in ca. 68% yield based on V(V). Anal. calc. for $H_3O_9V_3$: H, 1.00; V, 51.00. Found: H, 0.70; V, 50.17%. IR (KBr, ν, cm^{-1}): 3412, ν(O—H); 1629, 1418, δ(O—H); 1007, ν(V=O); 625, ν_s(V—O—V); 475, δ(V—O—V). UV–vis (λ_{max}, nm): 406(LMCT), 790(d–d*).

2.3. X-ray single crystal structural determination

The crystal was mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite–monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a ω scan mode. All the measured independent reflections ($I > 2\sigma(I)$) were used in the structural analyses, and semi-empirical absorption corrections were applied using SADABS program [43]. The structure was solved by the direct method and refined using SHELXL-97 [44]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the lattice water were found in the difference Fourier map. The hydrogen atom of hydroxyl group was not located. Crystal data, details of the data collection and the structure refinement of complex are given in Table 1, the parameters of selected bond lengths, bond angles and hydrogen bonds are listed in Table 2. Figs. S1 and S2 present the infrared spectra and UV–vis spectra of the as-prepared complex, respectively.

2.4. Measurement of the bromination activity in solution

Bromination reaction activity test for the product was carried out in a mixed solution of $H_2O—DMF$ at a constant temperature of 30 ± 0.5 °C. The complex was dissolved in the addition of 25 mL $H_2O—DMF$ mixture (DMF: 1 mL; H_2O: 24 mL). The solutions used for the kinetic measurements were maintained at a constant concentration of H^+ (pH 5.8) by the addition a buffer solution of $NaH_2PO_4—Na_2HPO_4$ [45]. The reactions were conducted in the addition of a phenol red solution. Solutions of the complex with five different concentrations were confected in five different

Table 1
Crystallographic data for the complex.*

Formula	$H_3O_9V_3$
M (g mol^{-1})	299.84
Crystal system	Monoclinic
Space group	$P2(1)/m$
a (Å)	4.9978(10)
b (Å)	8.4273(17)
c (Å)	7.8669(16)
α (deg)	90
β (deg)	96.44(3)
γ (deg)	90
V (Å^3)	329.24(12)
Z	2
Dcalc (g cm^{-3})	3.025
Crystal size (mm)	0.28 × 0.17 × 0.11
F(000)	288
μ(Mo Kα)/mm^{-1}	4.188
Reflections collected	3200
Independent reflections ($I > 2\sigma(I)$)	804
R_{int}	0.0417
Parameters	62
$\Delta(\rho)$ (e Å^{-3})	0.525, −0.633
Goodness of fit	1.166
θ (°)	3.55–27.44
R[a]	0.0272(0.0290)[b]
wR_2[a]	0.0750(0.0787)[b]

[*a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2/\Sigma(w(Fo^2)^2)]^{1/2}$; $[Fo > 4\sigma(Fo)]$.
[b] Based on all data.