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Phase evolution of vanadium oxides obtained through temperature programmed calcinations of ammonium vanadate in hydrogen atmosphere and their humidity sensing properties



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HIGHLIGHTS

• Validated the theoretical mass losses at each temperature of NH₄VO₃ with TGA.

• Confirmed mechanisms of formation of various stoichiometries of VO_x from NH₄VO₃.

• Determined the evolution of VO₂, V₆O₁₃ and V₂O₅ with temperature.

• Phase diagram of VO₂, V₆O₁₃ and V₂O₅ by VSM, XPS/EDS, XRD and Raman spectra.

 \bullet Comparative response of VO2, V_6O_{13} and V_2O_5 to humidity.

A R T I C L E I N F O

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ABSTRACT

The possibility of obtaining vanadium dioxide (VO₂) [wherein the vanadium ionic state is 4⁺] from a precursor of ammonium metavanadate (NH₄VO₃) bearing the ion V⁵⁺ is investigated. The reduction is carried out by calcining the NH₄VO₃ powders in similar concentrations of H₂ flow at varying temperatures. The resulting powders have been studied by several techniques including XRD, Raman spectroscopy, FTIR, TEM, BET and DSC. It is found that remnants of bright yellow V⁵⁺ still exist up to calcination temperatures of 100 °C after which the sky-blue VO₂ dominates at calcination temperatures of 150 °C –250 °C. There is a population surge of metastable dark-blue V₆O₁₃ (where V is in between V⁴⁺ and V⁵⁺ ionic states) between 250 °C and 300 °C. However above 350 °C the material reverts to the stable V⁵⁺ in the yellow–orange V₂O₅. XPS/EDS and VSM confirm the order of appearance to be VO₂(150 °C) \rightarrow V₆O₁₃(200 °C) \rightarrow V₂O₅ (350 °C).

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1. Introduction

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An oxidation state is influenced by ionization energy while ionization energy depends on the shielding effect between the orbital electron and the nucleus of an atom. In transition metal elements, the electrons enter an inner-shell electron orbital as opposed to other groups where electrons enter the outer-shell electron orbital [1]. The substitution of electrons in the inner-shell in case of transition metals consequently increases the shielding effect, decreases the effective nuclear charge and thereby weakening the ionization energy. All transition metals (Ti, W, Mn, V, Cr, Pd, Pt, Co, Zn, Fe, Cd, Cu, etc.) have low ionization energy, and

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this makes it less costly to remove more than one electron from their orbitals than it is from compounds with completely filled 3s or 3d orbitals such as alkali metals and alkali earth metal elements. Vanadium is one of these transition metals, it usually presents synthesis difficulties due to its existence in several oxidation states by forming a variety of binary oxides with the following general formulas for $n = 1, 2, 3 ... (1) V_nO_{2n+1}$ e.g. V_2O_5 , V_3O_7 , V_4O_9 , V_6O_{13} , (2) V_nO_{2n-1} e.g. VO, V_2O_3 , and (3) V_nO_{2n} also with VO₂ and V_2O_4 [2]. Among these oxides, V_2O_3 , VO₂, V_6O_{13} and V_2O_5 possess many interesting characteristics that can be used in various applications because of their tendency to undergo metal to insulator phase transition commonly known as MIT transition [3–12].

Vanadium dioxide (VO₂) is unique among these oxides because of the abrupt changes in its crystal structure that usually follow the phase transition around 68 °C. The transition temperature is considerably low and close to room temperature. This MIT property was first observed by F.J. Morin 1959 and later widely studied by Magneli, Mott Hubbard, Peirels, Goodenough, Adlar, Paquet and Fujimori [3–12]. VO₂ has 4⁺ oxidation state oxide of vanadium with a monoclinic (insulating/semiconducting) before transition temperature and tetragonal (metallic) above the transition temperature. Changes in crystal structure explained by Peierls as electron-phonon interaction or coupling, or band structure shift explained by Mott as electron-electron correlation is usually accompanied by a number of physical properties [13]. Such properties are changes in electrical resistance or conductance, optical transmittance or reflectance, phonon frequencies from Raman spectroscopy and FTIR. surface plasmon resonance from absorption spectra and light scattering studies [14,17–21]. The optical property of VO₂ is also found to be dependent on the surface roughness by AFM studies [15,16]. All these properties make VO₂ feasible for practical application purposes and have been applied in various technological devices. Such devices include smart or switchable window glass panes (thermo-chromic and photo-chromic property) [22–26] as well as gas chemical sensing (gaso-chromic property) [22,27]. Uses of VO₂ in the fabrication of electrochemical devices (electro-chromic property) have also been recorded [28].

Other oxides such as V_6O_{13} and vanadium pentoxide (V_2O_5) are also relevant as they are close to VO_2 in stoichiometry. V_2O_5 is a V^{5+} oxidation state oxide and is the most stable oxide of vanadium. Its orthorhombic crystal structure usually undergoes metal to insulator phase transition at 375 °C. V_2O_5 is used as a passive electrode with WO_3 as an active electrode in electro-chromic glass application [28,29]. It has been reported for gas chemical sensing capabilities [30] and also found applications in the lithium ion batteries [31]. V_6O_{13} is known as a mixed valence oxide as it exists between the V^{4+} and V^{5+} oxidation states [32]. It is monoclinic in crystal structure at both high and low temperature with a characteristic zigzag chain running along the b-axis with mono V^{4+} and mixed V^{4+} and V^{5+} [32]. Its transition temperature is -143 °C and finds application in lithium ion batteries.

Ammonium meta-vanadate (AMV, NH₄VO₃) has been widely used as a source material for the syntheses of vanadium oxides by various deposition/synthesis techniques, such as chemical precipitation [33,34], thermal annealing [35], spray pyrolysis [36,37], and autoclave hydrothermal treatment [38].

In all these synthesis techniques, the phase diagram of V–O system was not followed. As a result, many such reports indicated either single phase VO₂ or V₂O₅ without validation. In this work, we started by thermogravimetry of NH₄VO₃ in nitrogen. Instead of mass loss alone, we also observed mass increase. This prompted further systematic study of phases at various temperatures in hydrogen atmosphere. This paper reports the quantitative study of phases of VO_x at various temperatures. This study sheds more light on the existing phase diagrams of VO_x.

2. Experimental techniques

Ammonium metavanadate powder (NH₄VO₃, purity 99.99%, molecular weight of 116.98 a.m.u, density of 2.3 g cm⁻¹ and melting (or decomposition) temperature of 200 °C) was purchased from Sigma–Aldrich Chemical Co. Differential scanning calorimetry (DSC) analysis was performed on the powder using DSC 02000 V24.4 Build 116 to measure the amount of heat flow into and out of the sample relative to the reference pan with a linear temperature ramp under nitrogen gas. A series of heat treatments were performed for better understanding of the decomposition and phase change in the material. Firstly, heat treatment of the NH₄VO₃ powder was carried out for 400 and 500 °C in chemical vapour deposition (CVD) reactor under nitrogen flow. This experiment was followed by the TGA measurement of the resulting powder (5.096 mg) and that of standard NH₄VO₃ (4.726 mg) to study the thermal decomposition process in the materials under nitrogen atmosphere. The instrument used is TGA Q500 V20.10 Build 36 by Anton Paar Inc. Further a comprehensive CVD calcinations of NH₄VO₃ powder under 20 mL min⁻¹ hydrogen flow was performed in two different sections, firstly at 100, 150, 200 and secondly at 250, 300, and 350 °C for 2 h.

The powder was characterized using an X-Ray diffraction (Panalytical X' pert Pro PW 3040/60 XRD equipped with Cu Ka $(\lambda = 0.154 \text{ nm})$ monochromatic radiation source). XRD patterns were recorded in the scanning range of 5°-90°. DSC of these calcined powders was also studied. Raman spectroscopic studies were conducted using a Jobin–Yvon T64000 Raman spectrograph with a 514.5 nm excitation wavelength from an argon ion laser. The power of the laser at the sample was low enough (0.384 mW) in order to minimise localised heating of the sample. The T64000 was operated in a single spectrograph mode, with the 1800 lines/mm grating and a 100× objective on the microscope, and further optical measurements were performed with standard spectrum 100 PerkinElmer FT-IR spectrometer. The microscopic studies and quantitative elemental composition studies were carried out using IEOL 2100 Transmission Electron Microscopy (TEM) (from Tokyo Japan) equipped with LaB6 filament and a Gartan U1000 camera of 2028×2028 pixels, and high quality inbuilt Energy dispersive Xray spectroscopy (EDS).

X-ray photo-electron spectroscopy (XPS) was also performed on a reference sample containing V₂O₅, VO₂, V₆O₁₃ as well domains of WO₃. EDS taken from VO_x domains (excluding the WO3 domains) in HRTEM was also performed on the same reference sample. The XPS determinations of the proportion of V^{3+} , V^{4+} and V^{5+} were used to calibrate the EDS spectra and this information was then employed in the determination of the proportions of V^{3+} , V^{4+} and V⁵⁺ for the current set of samples. X-ray photoelectron spectroscopy analyses were carried using a PHI 5000 Versaprobe- Scanning ESCA Microprobe. The survey scans were recorded with a 100 µm, 25 W, 15 kV beam using monochromatic Al K_{α} radiation (hv = 1486.6 eV) and for the higher resolution spectra the hemispherical analyzer pass energy was maintained at 514 eV-520 eV (C 1s, O 1s, V 2p) for 50 cycles. Measurements were performed using either a 1 eV/step and 45 min acquisition time (binding energies ranging from 0 to 1000 eV) for survey scans or a 0.1 eV/step and 20-30 min acquisition times for the high-resolution scans. The pressure during acquisition was typically under 1 \times 10 $^{-8}$ Torr. The surfaces were also sputtered clean for 30 s using an Ar ion gun (2 kV energy ions) and measurements were repeated.

The field dependent magnetic characterization was performed using Lakeshore 735 vibrating sample magnetometer (VSM) at room temperature. It is vital to point out that because this type of sample exhibits small magnetization signals, special care was taken during measurements as to avoid any trace magnetic Download English Version:

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