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Characterization and Thermodynamic Analysis of VO₂ Synthesized by NH₄VO₃*

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Abstract

A new process was developed for synthesizing vanadium dioxide (VO₂) by pyrolyzing ammonium metavanadate (NH₄VO₃) in nitrogen flow. The chemical reaction in the synthesizing process was analyzed by thermodynamic calculations. X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) were applied to characterizing the product. The experimental results indicated that VO₂ microcrystal particles were successfully synthesized. The product VO₂ presents two kinds of micro morphologies, torispherical and pentagonal prism. The phase transition mainly takes place at 337.8K and 341.8K. The average enthalpy of phase transition is 28.82 J/g.

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Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).*Keywords:* vanadium dioxide, ammonium metavanadate, phase transition, microstructure, pyrolysis

1. Introduction

Vanadium dioxide presents a first-order phase transition, from a semi-conducting state to a metallic state at temperature around 341K^[1]. The phase transition of VO₂ is reversible from a monoclinic crystal structure at low temperature to a tetragonal structure at high temperature, accompanied by changes of optical and electrical properties^[2]. Monoclinic VO₂ is highly transparent in the infrared spectral band between 2.5 and 11.5μm, and at radio and microwave frequencies. The tetragonal structure at high temperature, however, strongly attenuates incident electromagnetic radiation at all frequencies^[3]. It is of practical interest since its transition point occurs at a relatively low temperature of about 341K, which can be easily reached by physical warming, heat dissipation, or laser excitation at a sufficient level^[4]. A great deal of attention has been paid to vanadium dioxide due to various technological applications such as

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optical switching devices, optical recording materials and infrared sensors, passive solar-energy control of buildings, and switchable/tunable microwave devices [5]. In the previous research works [6-10], VO₂ films were prepared by a complicated process, such as a strict reducing atmosphere under vacuum conditions and for long periods of time. There were some reports regarding synthesizing VO₂ (B) nanobelts and nanorods [11-13]. It was noted that VO₂ (B) is a metastable allotropic phase of vanadium dioxide [14]. On the basis of our previous work [15, 16], the authors developed the novel and simple process to synthesize thermochromic VO₂ micro-crystal particles by pyrolyzing ammonium metavanadate. In this paper, we report the synthesizing process, thermodynamic analysis and characterization of the product VO₂.

2. Experimental

2.1 Preparation of vanadium dioxide

The VO₂ particles were synthesized by controlled pyrolyzing ammonium metavanadate (NH₄VO₃). 800mg NH₄VO₃ (99.0%, Shanghai Chemical Limited Company of China, Analytical Reagent) were loaded in a ceramic container. The container loaded with NH₄VO₃ was placed into a tube furnace. The technical process of synthesizing VO₂ was illustrated as Fig. 1. A flow of N₂ (99.99%, 20ml/min) passed through the furnace and the heating rate was set on 15K/min. The water was used to absorb the exhausted gas from the furnace. After the temperature reached 1000K, the temperature was kept constant for 1.5 hours. The furnace was naturally cooled to 500K in the N₂ flow and the sample was ready for characterizations.

2.2 Characterization of the product sample

The phase and crystallinity of VO₂ were characterized by using a XRD-6000 X-ray diffractometer (Shimadzu, Japan) in a reflection mode with Cu K_α(λ=0.154nm) radiation and a graphite monochromator. The 2θ scanning rate was 4 deg/min. SEM images were obtained by a JSM-5600LV scanning electron microscope (JEOL, Japan) operated at 15 kV. Thermal properties of VO₂ were measured in a nitrogen atmosphere by DSC 204 (Netzsch, Germany) in the temperature range of 305-375K. A heating rate of 5 K/min and the air-dried sample were used for DSC.

3. Results and Discussion

3.1 Thermodynamic analysis of synthesizing VO₂ by NH₄VO₃ pyrogenation in N₂ gas

Thermodynamic properties of the pure substances in their standard states, including standard enthalpies of formation $\Delta_f H_m^\circ$, standard Gibbs free energy of formation $\Delta_f G_m^\circ$ and absolute entropies S_m° at 298.15K, were taken from the literature [17]. Enthalpies of formation allow us to calculate enthalpies of any reaction, provided that we know $\Delta_f H_{m(T)}^\circ$ values for all the reactants and products [18]. The $\Delta_r H_{m(T)}^\circ$ for any reaction is the difference between the sum of $\Delta_f H_{m(T)}^\circ$ values for all the products and the sum of the $\Delta_f H_{m(T)}^\circ$ values for all the reactants. The relationship was shown in equation (1). In the same way, if the absolute entropies of all the substances in a chemical reaction are known, it is then a simple matter to calculate the entropy change in the reaction. The relationship was shown in equation (2). The thermodynamic parameters for the reactions at other temperatures except 298.15K were calculated by the equations (3)-(5), where “ v_B ” are the stoichiometric coefficients for the substances in the reactions, “ T ” denotes the reaction temperature, “ m ” the molar value, “ $^\circ$ ” indicates that the reactants and products are in their standard state, “ r ” denotes the parameters for reaction processes and “ f ” the data in

the formation process of the substances, $C_{p,m}^\circ$ is heat capacity. In addition, the correlation between heat capacity $C_{p,m}^\circ$ and temperature T was shown as equation (6), where the values of a, b, c, d, e for the pure substances in the reactions were given in Ref. [17].

$$\Delta_r H_m^\circ(T) = \sum \Delta_f H_m^\circ(T)(p) - \sum \Delta_f H_m^\circ(T)(r) \tag{1}$$

$$\Delta_r S_m^\circ(T) = \sum S_m^\circ(T)(p) - \sum S_m^\circ(T)(r) \tag{2}$$

$$\Delta_r H_m^\circ(T) = \Delta_r H_m^\circ(298.15K) + \int_{298.15K}^T \sum v_B C_{p,m}^\circ dT \tag{3}$$

$$\Delta_r S_m^\circ(T) = \Delta_r S_m^\circ(298.15K) + \int_{298.15K}^T \frac{\sum v_B C_{p,m}^\circ}{T} dT \tag{4}$$

$$\Delta_r G_m^\circ(T) = \Delta_r H_m^\circ(T) - T\Delta_r S_m^\circ(T) \tag{5}$$

$$C_{p,m} = a + bT + cT^2 + dT^3 + eT^4 \tag{6}$$



The decomposition reaction of NH_4VO_3 was given in (7). The consequent reactions in the process of NH_4VO_3 pyrogenation were shown in (8) and (9). Firstly we calculated $\Delta_r H_m^\circ(298.15K)$ and $\Delta_r S_m^\circ(298.15K)$ for the reactions (8) and (9) by equations (1) and (2). Secondly we calculated $\Delta_r H_m^\circ(T)$ and $\Delta_r S_m^\circ(T)$ by substituting $C_{p,m}^\circ$ in equations (3) and (4) for the correlation equations (6). The integrating process in equations (3) and (4) included two parts: (1) for the temperature range from 298.15K to 373.15K, $C_{p,m}^\circ$ where H_2O was taken to be liquid $H_2O(l)$, and (2) for the temperature range from 373.15K to 1000K, $C_{p,m}^\circ$ where H_2O was taken to be gaseous $H_2O(g)$. The phase transition enthalpy for H_2O was considered in the calculations for equations (3) and (4). Finally Gibbs free energy $\Delta_r G_m^\circ(T)$ for the reactions was calculated using equation (5). The results are shown in Table 1.

Table 1 $\Delta_r G_m^\circ(T)$ for reactions (7-9) at the indicated temperatures

T (K)	$\Delta_r G_m^\circ(T)$ (kJ/mol)		
	Reaction (7)	Reaction (8)	Reaction (9)
298.15	87.36	-585.32	-491.92
400	49.18	-586.88	-494.38
500	5.09	-603.40	-514.25
511.37	0	-605.24	-516.55
600	-40.38	-619.13	-534.90
700	-87.67	-633.68	-556.63
800	-137.20	-646.68	-579.93
900	-189.20	-657.68	-605.38
1000	-244.10	-666.21	-633.70
1100	-302.40	-671.80	-665.68
1119.80	-314.40	-672.51	-672.51
1200	-364.30	-673.94	-702.12

A negative $\Delta_r G_{m(T)}^\circ$ for a reaction means that the process is spontaneous. The data in Table 1 shows that the reactions from (7) to (9) are spontaneous in standard state over 511.17K. Actual reactions always take place in nonstandard state. The relationship between $\Delta_r G_{m(T)}$ and pressure quotient (Q) for the reactions in nonstandard state was shown in equation (10). The pressure quotient Q for the reactions from (7) to (9) are given by equations (11) and (12).

$$\Delta_r G_{m(T)} = \Delta_r G_{m(T)}^\circ + RT \ln Q \tag{10}$$

$$Q_{(7)} = \frac{P_{\text{NH}_3}^2 P_{\text{H}_2\text{O}}}{(P^\circ)^3} \tag{11}$$

$$Q_{(8)} = Q_{(9)} = \frac{P_{\text{H}_2\text{O}}^3 P_{\text{N}_2}}{P_{\text{NH}_3}^2 P_{\text{O}_2} P^\circ} \tag{12}$$

Where R is universal gas constant, $P_{\text{H}_2\text{O}}, P_{\text{N}_2}, P_{\text{NH}_3}$ are the partial pressures of $\text{H}_2\text{O}, \text{N}_2, \text{NH}_3$, respectively, and P° is the standard atmosphere pressure (101325 Pa).

Table 1 also shows that when the reaction temperature is lower than 1119.8K, $\Delta_r G_{m(T)}^\circ$ for reaction (8) is smaller than that for reaction (9). Equation (10) shows that $\Delta_r G_{m(T)}$ for reaction (9) can be adjusted by increasing the pressure quotient $Q_{(9)}$ to a value greater than zero, and at same time $\Delta_r G_{m(T)}$ for reaction (8) will be <0 . These are the requirements for forming pure VO_2 free V_2O_3 . When the reaction temperature is higher than 1119.8K, $\Delta_r G_{m(T)}^\circ$ of the reaction (8) is greater than that of the reaction (9). There is no ways to meet the requirements of forming pure VO_2 . Therefore, the ranges of the pressure quotient $Q_{(7)}$ and $Q_{(8)}$ for synthesizing pure VO_2 were deduced and shown in Table 2.

In the present work the keeping temperature was designed at 1000K between 511.37K and 1119.8K. Table 2 shows that at 1000K when the pressure quotient $Q_{(7)} < 5.66 \times 10^{12}$ and $Q_{(8)} = Q_{(9)} = 1.27 \times 10^{33} \sim 6.32 \times 10^{34}$, reaction (7) and (8) were spontaneous and reaction (9) was not. This is the reason why pure VO_2 crystal particles are produced in the present work.

Table 2 Q ranges for synthesizing VO_2 by NH_4VO_3 pyrolysis

T (K)	$Q_{(7)} = \frac{P_{\text{NH}_3}^2 P_{\text{H}_2\text{O}}}{(P^\circ)^3}$ (Pa/Pa)	$Q_{(8)} = Q_{(9)} = \frac{P_{\text{H}_2\text{O}}^3 P_{\text{N}_2}}{P_{\text{NH}_3}^2 P_{\text{O}_2} P^\circ}$ (Pa/Pa)
600	$< 3.28 \times 10^3$	$3.70 \times 10^{46} \sim 7.98 \times 10^{53}$
700	$< 3.49 \times 10^6$	$3.45 \times 10^{41} \sim 1.94 \times 10^{47}$
800	$< 9.02 \times 10^8$	$7.36 \times 10^{37} \sim 1.68 \times 10^{42}$
900	$< 9.56 \times 10^{10}$	$1.37 \times 10^{35} \sim 1.49 \times 10^{38}$
1000	$< 5.66 \times 10^{12}$	$1.27 \times 10^{33} \sim 6.32 \times 10^{34}$
1100	$< 2.29 \times 10^{14}$	$4.09 \times 10^{31} \sim 7.98 \times 10^{31}$

3.2 The structure, morphology and phase transition of the product VO_2

The XRD pattern of the product sample was shown as Fig. 1. By comparing the results with standard JCPDS card (PDF ID number 43-1051) of XRD data documents, the sample was a match to VO_2 pure

phase. There were no impurity peaks to be found in the diffraction pattern.

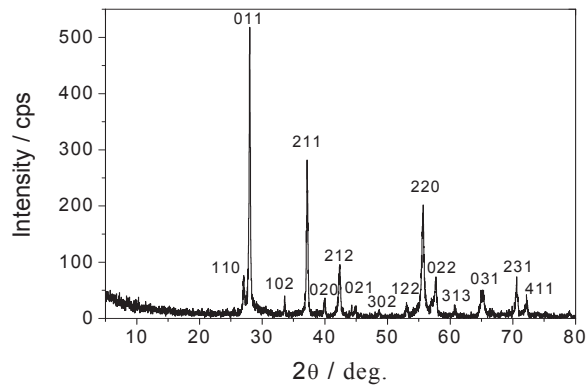


Fig. 1 X-ray diffraction pattern of the product VO₂

Scanning electron microscope (SEM) results showed that the grain size distribution of the VO₂ microcrystal is in the range from several micrometers to several decade micrometers as seen in Fig. 2 and Fig. 3. The morphologies of the VO₂ particles are spherical and pentagonal prism.

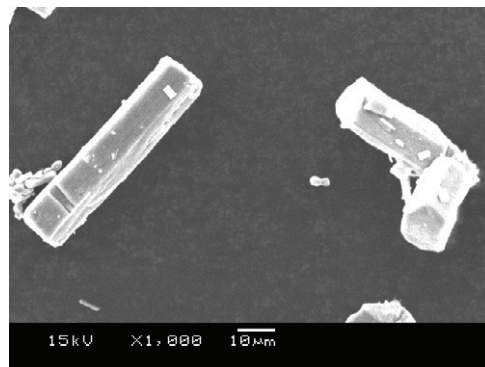


Fig. 2 SEM image (1000×) of the product VO₂

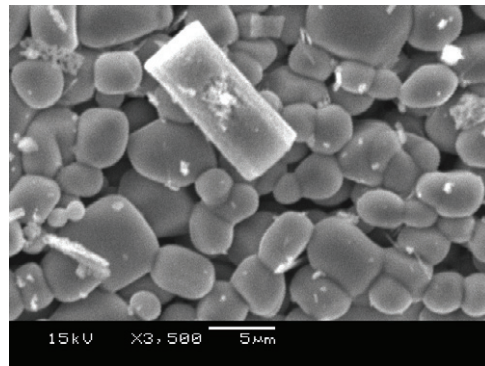


Fig. 3 SEM image (3500×) of the product VO₂

Differential scanning calorimetric (DSC) studies indicated that the phase transition is endothermic process. The phase transition takes place mainly at 341.7K and 337.8K. Integration takes place between 315K and 355K, and the average enthalpy of the phase transition is 22.82J/g as shown in Fig. 4. In Fig. 3 two kinds of VO₂ morphologies had been found and in Fig. 4 two peaks had been found. It indicated that the grain morphologies may be the main factor to affect VO₂ phase transition parameters. It is agreeable to the recently published literature [19].

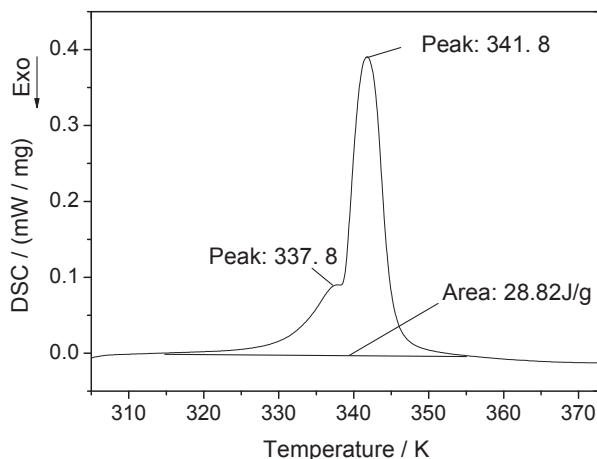


Fig. 4 DSC curve of the product VO₂

4. Conclusions

A facile process was developed for synthesizing thermochromic VO₂ microparticles by pyrolyzing NH₄VO₃ in tube furnace from room temperature to 1000K with a rapid heating rate of 15K/min and a slow N₂ (containing about 0.01% O₂) flow rate of 5ml/min, and kept at 1000K for 1.5h. The conditions of pyrolyzing NH₄VO₃ were designed through thermodynamic modeling of chemical reaction process and analyzing the process of NH₄VO₃ pyrogenation in N₂ gas, and optimized by experiments. The experimental results indicated that the present process is a convenient and low cost method to synthesize thermochromic VO₂ crystal particles. As prepared VO₂ particles have two types of morphologies, spherical and pentagonal prism. The phase transition takes place mainly at 341.7K and 337.8K. The average enthalpy of the phase transition is 22.82J/g.

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