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Synthesis and characterization of V_2O_3 microcrystal particles controlled by thermodynamic parameters

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A facile process is developed for the synthesis of pure vanadium(III) oxide by thermal reduction of vanadium pentoxide (V_2O_5) in ammonia gas. The process of thermal reduction of V_2O_5 was optimized by experiments and by modeling of thermodynamic parameters. The obtained V_2O_3 was characterized by X-ray diffraction, X-ray photoelectron spectrometry, scanning electron microscopy and thermogravimetric analysis. The experimental results indicated that crystal particles of pure V_2O_3 were successfully synthesized within a short reaction period of 1 h and at a relatively low temperature of 903 K. The content of V_2O_3 in the product sample higher than 99 wt. %. The grain size of V_2O_3 ranged from several hundred nanometers to several micrometers. The morphologies of the V_2O_3 particles were micrometer layers in nanometer sheet structure.

Keywords: *vanadium oxides; chemical synthesis; thermodynamic parameters; X-ray diffraction; scanning electron microscopy*

1. Introduction

The V_2O_3 system has been the subject of many investigations because it exhibits at least one, if not several, spectacular metal–insulator transitions [1]. The most notable one is that pure vanadium(III) oxide displays a single metal–insulator transition (MIT) around 160 K, changing from a low-temperature antiferromagnetic insulator to a high-temperature paramagnetic phase [2]. Vanadium oxide V_2O_3 was chosen as the conductive ceramic oxide because of previous research on the properties of composite thermistors [3]. V_2O_3 is a potential material for many functional devices such as temperature sensors and current regulators [4]. V_2O_3 powder can also be used in conductive polymer composites [5], in catalysts [6], etc. V_2O_3 is the most unstable material among V_2O_5, VO_2 and V_2O_3. Fabrication of pure V_2O_3 is not straightforward because

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it forms in conditions similar to those of formation of VO_2 [7]. In past years, many methods for preparing V_2O_3 powder have been studied. Spherical V_2O_3 particles were prepared by the O_2–H_2 flame of V_2O_3 at 2273 K [8]; spherical and necking V_2O_3 powder was synthesized by reducing V_2O_5 in a H_2 flow at 1123 K for 6 h [9]. V_2O_3 powder was also fabricated by pyrolyzing hydrazine containing vanadium salt and by reducing the sol-gel synthesized V_2O_5 in a H_2 stream [10]. Furthermore, V_2O_3 nanoparticles were synthesized by laser induced vapour phase reaction [11], by reductive pyrolysis of ammonium oxovanadium (IV) carbonate hydroxide, $(NH_4)_5[(VO)_6\ (CO_3)_4(OH)_9]\cdot 10H_2O$, under H_2 atmosphere [12], by thermal decomposition of vanadium oxalate [13], by reacting vanadium(V) oxoisopropoxide with benzyl alcohol at 473 K in a solvothermal process [14]. Sediri et al. synthesized V_2O_3 by the reduction of V_2O_5 with 1,6-diaminohexane under hydrothermal conditions [15]. In this paper, we report on a novel and efficient method of synthesizing pure V_2O_3 microcrystal particles by reducing V_2O_5 in ammonia gas. For the first time, the synthesis was optimized by thermodynamic modelling. The method has a short reaction period at a relatively low temperature of 903 K. Compared with previous reports, the synthesis process is more reasonable with respect to thermodynamic parameters, simpler to perform and easier to control, more suitable for large scale processing because it is less harmful to the environment. Furthermore, obtained V_2O_3 has a higher purity of 99.8 wt. %.

2. Experimental

Design of the technical process. The scheme of technical process of synthesizing V_2O_3 is shown in Fig. 1. In order to recycle ammonia gas, protect the environment and reduce material cost, the column for deoxygenation and dehydration was designed to remove the exhaust NH_3 gas from the tube furnace. The principle of the deoxy and drying column is that MnO (green) is oxidized by oxygen (O_2) to MnO_2 (brown) at room temperature. Water is adsorbed on dry microparticles of SiO_2 coated with MnO. The column was fabricated by the method described in the literature [16].

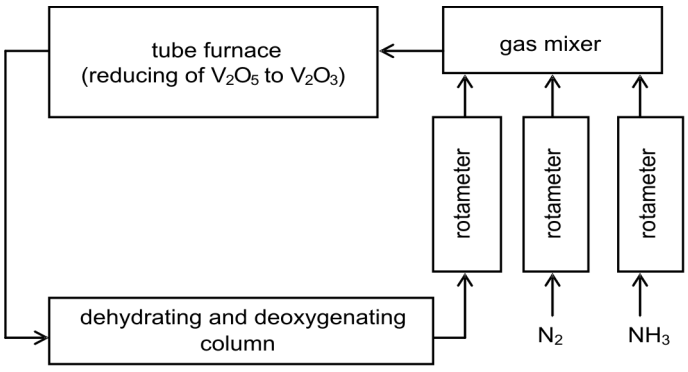

Fig. 1. Technical process of synthesis of V_2O_3 by thermal reduction of V_2O_5 in NH_3

Synthesis by thermal reduction. V_2O_3 particles were synthesized by thermal reduction of V_2O_5 in ammonia. 1 g of V_2O_5 (99.5%, Chinese Shanghai Chemical Limited Company, Analytical Reagent) was loaded into a ceramic container without a cover. The container loaded with V_2O_5 was placed into a tube furnace. After the temperature had reached 903 K, a mixture flow of NH_3 (5 cm^3/min) and N_2 (110 cm^3/min) was passed through the furnace. The furnace was naturally cooled to ambient temperature after 1 h and the sample was then ready for characterization.

Characterization of the sample. The phase composition and crystalline form of V_2O_3 were characterized by using a D/MAX-2400 X-ray diffractometer (Rigaku, Japan) in a reflection mode with Cu K_α (λ = 0.154 nm) radiation and a graphite monochromator. The 2θ scanning rate was 4 deg/min. Thermogravimetric (TG) data were acquired with a thermogravimetric analyzer, Mettler-Toledo TGA/SDTA 851e (Mettler-Toledo GmbH, Schwerzenbach, Switzerland) in the temperature range of 300–850 K at the heating rate of 5 K/min in an ambient atmosphere. X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Analytical Amicus XPS instrument (Perkin-Elmer Corporation, USA) with a MgK_α X-ray source operating at 160 W (8 kV, 20 mA). SEM images were obtained with a JSM-5600LV scanning electron microscope (JEOL, Japan) operating at 20 kV.

3. Results and discussions

3.1. Thermodynamic analysis of the synthesis of V_2O_3 by reducing V_2O_5 in NH_3

The thermodynamic properties of 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 298.15 K, were taken from the literature [17]. Enthalpies of formation allow us to calculate the enthalpies of any reaction, provided that we know $\Delta_f H_{m(T)}^\circ$ values for all the reactants and products [18]. The value of $\Delta_f H_{m(T)}^\circ$ for any reaction is the difference between the sum of the $\Delta_f H_{m(T)}^\circ$ values for all the products and the sum of the $\Delta_f H_{m(T)}^\circ$ values for all the reactants. The equations used are as follows:

$$\Delta_r H_{m\,(T)}^\circ = \sum \Delta_f H_{m\,(T)(\text{products})}^\circ - \sum \Delta_f H_{m\,(T)(\text{reactants})}^\circ \tag{1}$$

$$\Delta_r S_{m\,(T)}^\circ = \sum S_{m\,(T)(\text{products})}^\circ - \sum S_{m\,(T)(\text{reactants})}^\circ \tag{2}$$

$$\Delta_r H^\circ_{m\ (T)} = \Delta_r H^\circ_{m\ (298.15\ \mathrm{K})} + \int_{298.15\ \mathrm{K}}^{T} \sum v_B C^\circ_{P,\,m} dT \tag{3}$$

$$\Delta_r S^\circ_{m\ (T)} = \Delta_r S^\circ_{m\ (298.15\ \mathrm{K})} + \int_{298.15\ \mathrm{K}}^{T} \frac{\sum v_B C^\circ_{P,\,m}}{T} dT \tag{4}$$

$$\Delta_r G^\circ_{m\ (T)} = \Delta_r H^\circ_{m\ (T)} - T\Delta_r S^\circ_{m\ (T)} \tag{5}$$

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

$$3V_2O_5 + 2NH_3 = 6VO_2 + N_2 + 3H_2O \tag{7}$$

$$6VO_2 + 2NH_3 = 3V_2O_3 + N_2 + 3H_2O \tag{8}$$

If absolute entropies of all reactants are known, it is a simple matter to calculate the change of entropy in the reaction (Eq. (2)). The thermodynamic parameters for the reactions at various temperatures except 298.15 K were calculated according to Eqs. (3)–(5), where v_B are the stoichiometric coefficients for the substances in the reactions, T denotes the reaction temperature, m is the molar value, the symbol ° indicates that the reactants and products are in their standard states, r denotes the reaction and f denotes the reactions of formation of the substances, $C^\circ_{p,\,m}$ is the heat capacity. The temperature dependence of the heat capacity $C^\circ_{p,\,m}$ is given in Eq. (6), where the coefficientsf a, b, c, d, e for pure reactants were taken from Ref. [17].

The reactions in the process of reduction of V_2O_5 under NH_3 are given in Eqs. (7) and (8). First we calculated $\Delta_r H^\circ_{m\ (298.15\ \mathrm{K})}$ and $\Delta_r S^\circ_{m\ (298.15\ \mathrm{K})}$ for the reactions (7) and (8), by applying Eqs. (1) and (2). Then we calculated $\Delta_r H^\circ_{m\ (T)}$ and $\Delta_r S^\circ_{m\ (T)}$ by substituting $C^\circ_{P,\,m}$ in Eqs. (3) and (4) for Eqs. (6). The integrations in Eqs. (3) and (4) included two parts: for liquid (l) and gaseous (g) water. The enthalpies and entropies of phase transitions for H_2O were included in the calculations for Eqs. (3) and (4), respectively. Finally the Gibbs free energy $\Delta_r G^\circ_{m(T)}$ for the reactions was calculated using Eq. (5). The results are shown in Table 1.

A negative value of $\Delta_r G^\circ_{m(T)}$ means that the reaction is spontaneous. The data in Table 1 shows that both the reactions (7) and (8) are spontaneous at the indicated temperatures. Actual reactions always take place in nonstandard state. The relationship between $\Delta_r G_{m(T)}$ and the pressure quotient (Q) for the reactions in a nonstandard state is given in Eq. (9). The pressure quotient Q for the reactions (7) and (8) is given by Eq. (10):

$$\Delta_r G_{m(T)} = \Delta_r G^{\circ}_{m(T)} + RT \ln Q \tag{9}$$

$$Q = \frac{P^3_{H_2O} P_{N_2}}{P^2_{NH_3}} \left(P^{\circ}\right)^{-2} \tag{10}$$

Here R is the universal gas constant, P_{H_2O}, P_{N_2}, P_{NH_3} are the partial pressures of H_2O, N_2, NH_3, respectively, and P° is the standard pressure (1.01×10^5 Pa).

Table 1. $\Delta_r G^{\circ}_{m(T)}$ [kJ·mol^{-1}] for reactions (7) and (8) at various temperatures

Temperature [K]	Reaction (7)	Reaction (8)
298.15	–398.72	–184.12
400	–417.50	–323.77
500	–448.13	–364.43
600	–476.51	–407.56
700	–501.65	–454.26
800	–522.43	–505.94
830	–527.62	–522.68
842	–529.55	–529.55
903	–537.88	–566.27
1000	–545.42	–631.63

Table 2. Ranges of he pressure quotient Q for synthesizing V_2O_3

Temperature [K]	$Q = \frac{P^3_{H_2O} P_{N_2}}{P^2_{NH_3}} (P^{\circ})^{-2}$
298.15	$<1.81\times10^{32}$
400	$<1.91\times10^{42}$
500	$<1.18\times10^{38}$
600	$<3.04\times10^{35}$
700	$<7.91\times10^{33}$
800	$<1.08\times10^{33}$
830	$<7.85\times10^{32}$
842	$<7.12\times10^{32}$
903	$<1.30\times10^{31}$
1000	$<3.10\times10^{28}$

Table 1 also shows that when the reaction temperature is lower than 842 K, $\Delta_r G^{\circ}_{m(T)}$ for reaction (7) has more negative values than that for reaction (8), whereas

according to Eq. (9) the values of $\Delta_r G_{m(T)}$ for reaction (8) seem to change first into positive ones upon increasing the pressure quotient Q. When the reaction temperature is higher than 842 K, the value of $\Delta_r G^{\circ}_{m(T)}$ in reaction (7) is less negative than its corresponding value in reaction (8), and $\Delta_r G_{m(T)}$ for reaction (7) upon increasing the pressure quotient Q will change first to a positive value. In non-standard state, the required pressure quotient Q for V_2O_3 formation leads to $\Delta_r G^{\circ}_{m(T)} < 0$, for both reactions (7) and (8). The required pressure quotient ranges, which are dependent on temperatures, were calculated and are shown in Table 2. The only requirement is that $\Delta_r G^{\circ}_{m(T)} < 0$ for reactions (7) and (8).

3.2. Structure and properties of V_2O_3

The XRD pattern of the product sample is shown in Fig. 2. By comparing the results with standard JCPDS card (PDF ID No. 34-0187) of XRD data documents, the sample was found to be a V_2O_3 pure phase. No impurity peaks were found in the diffraction pattern.

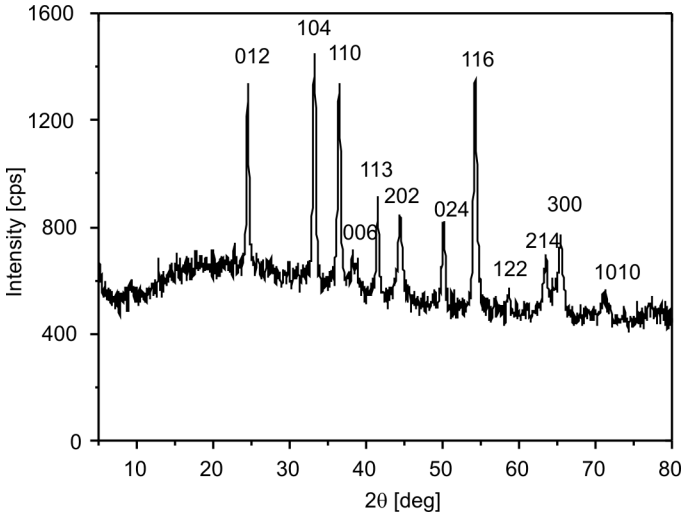

Fig. 2. X-ray diffraction pattern of the obtained V_2O_3

The results of thermogravimetric (TG) analysis (Fig. 3) showed that there was an initial weight loss below 363K, a slow weight increase above 423 K and a notable weight increase above 600 K. The weight loss between 300 K and 363 K was due to the elimination of water adsorbed on the particle surfaces, the weight increase between 423 K and 600 K indicated that V_2O_3 was oxidized to VO_2 above 423 K in ambient

atmosphere, and the rapid weight increase between 600 K and 723 K showed that further oxidation to V_2O_5 above 600 K was accelerated and complete at 723 K. This agrees with the result given in Ref. [16], stating that VO_2 is not stable above 600 K. The balance weight between 363 K and 423 K was 13.373 mg, and the balance weight from 723 K to 850 K was 16.225 mg. TG analysis confirmed that the following reactions took place:

$$2V_2O_3+O_2 = 4VO_2 \tag{11}$$

$$4VO_2+O_2 = 2V_2O_5 \tag{12}$$

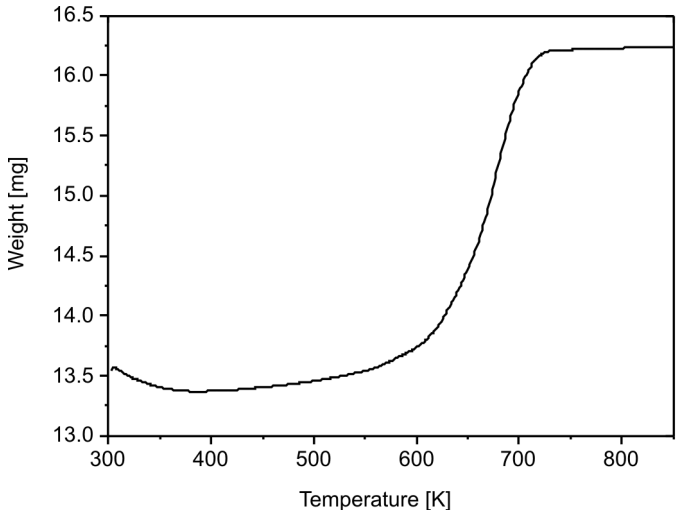

Fig. 3. Thermogravimetric curve of the product V_2O_3. The initial sample mass – 13.537 g, temperature range 300–850 K, the heating rate 5 K/min in an ambient atmosphere

It was calculated that 13.346 mg of V_2O_3 and 0.027 g of VO_2 were oxidized to 16.225 mg V_2O_5 on the assumption that only V_2O_3 and VO_2 were present in the sample. The TG data and the calculations of the V_2O_3 content in the sample are given in Table 3.

Table 3. Results of TG analysis and the calculated V_2O_3 contents in the sample

Parameter	Sample	V_2O_3	VO_2	H_2O	V_2O_5
Molar weight [g·mol^{-1}]	–	149.88	82. 94	18.01	181.88
Initial mass [mg]	13.537	13.346	0.027	0.164	
Mass change from 300 K to 363 K	–0.164				
Balance weight between 363 K and 423 K [mg]	13.373	13.346	0.027		
Balance weight between 723 K and 850 K [mg]	16.225				16.225
Mass change from 423 K to 723 K [mg]	2.852				
V_2O_3 content [wt. %] in the sample		99.8	0.2		

In Figure 4, the X-ray photoelectric energy spectrum is shown. It indicates that the binding energy of $V_{2P3/2}$ is 516.8 eV, that of $V_{2P1/2}$ is 524.2 eV and that of O_{1s} is 530.3 eV. This result is consistent with the literature data [19], and suggests that V ions exist in 3+ valence states. Multipeak data fitting was applied to the XPS in Fig. 4. No results suggested that V at any other valence state was present.

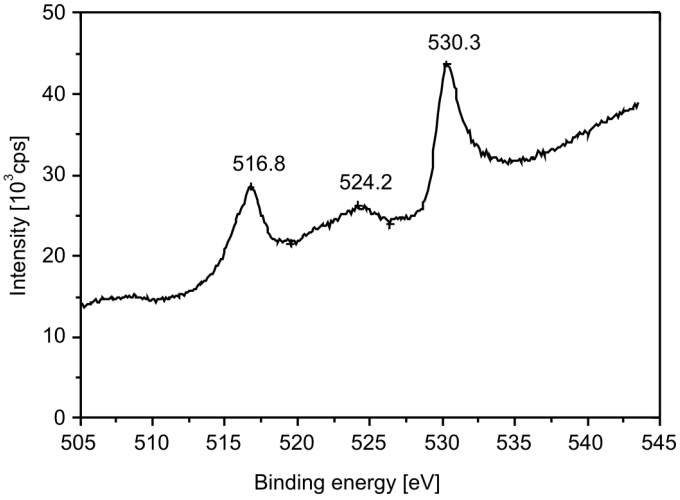

Fig. 4. XPS spectrum of the product V_2O_3

The scanning electron microscopy (SEM) results of V_2O_3 sample are shown in Fig. 5. The grain size distribution of the V_2O_3 microcrystal ranges from several micrometers to tens of micrometers. V_2O_3 particles consist of layers which are several micrometers thick. Each layer is made up of sheet structures, each sheet measuring several nanometers in thickness.

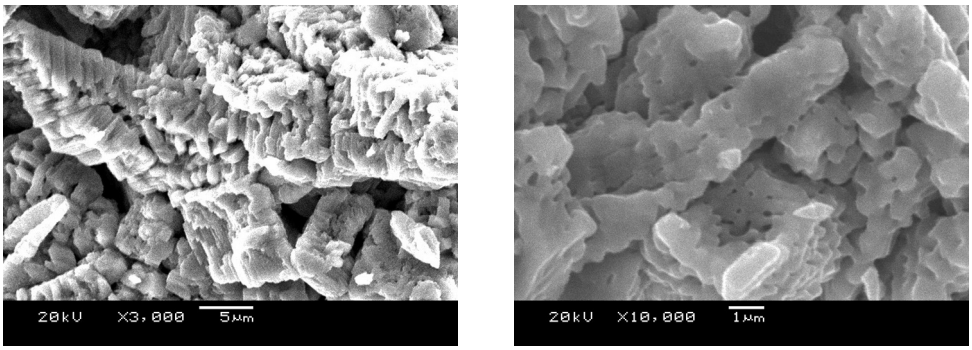

Fig. 5. SEM images of the product V_2O_3 with magnification 3000× (left) and 10 000× (right)

All the experimental results showed that high purity V_2O_3 microcrystal particles have been successfully synthesized.

4. Conclusions

A novel process was developed for synthesizing high purity V_2O_3 particles by thermal reduction of V_2O_5 under gaseous ammonia. The experimental results indicated that the process described in this paper is a convenient and efficient approach to synthesis of pure V_2O_3 crystal particles. The reduction parameters of V_2O_5 in ammonia were optimized by thermodynamic calculations for the relevant chemical reactions. Analysis of the reaction process suggested that the reaction temperature and pressure quotient are the key factors for producing pure vanadium(III) oxide. When the temperature of synthesis is 903 K, the required pressure quotient for vanadium formation is lower than 1.30×10^{31}, the reaction period is 1 h, the purity of the V_2O_3 product sample is higher than 99 wt. % and the grain size ranges from several hundred nanometers to several micrometers.

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