J. of Supercritical Fluids 56 (2011) 194–200

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Preparation of V_2O_3 nanopowders by supercritical fluid reduction

Xinghai Liu[a,b], Yifu Zhang[a], Shengping Yi[c], Chi Huang[a,c,*], Jun Liao[c], Houbin Li[b], Di Xiao[a], Hongyun Tao[a]

[a] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China*
[b] *College of Packing and Printing, Wuhan University, Wuhan 430079, PR China*
[c] *Engineering Research Center of Organosilicon Compound and Material, Ministry of Education of China, Wuhan 430072, PR China*

ARTICLE INFO

Article history:
Received 21 June 2010
Received in revised form 30 October 2010
Accepted 19 November 2010

Keywords:
Supercritical fluid
Vanadium sesquioxide
Nanoparticles
Ethanol
Reduction
XRD

ABSTRACT

V_2O_3 nanoparticles, with diameters of 30–60 nm, have been synthesized by supercritical ethanol fluid reduction of VOC_2O_4. It was found that the reaction time has little influence on the purity and morphology of as-prepared products. And carbon oxides decomposed from $C_2O_4^{2-}$ were conducive to the formation of the uniform sphere-like nanoparticles. The reaction mechanism of synthesizing uniform V_2O_3 nanoparticles is believed to be the redox reaction between VOC_2O_4 and ethanol in the supercritical condition. The crystal growth mechanism was proposed on the basis of the discussion about the formation process of the uniform sphere-like nanoparticles.

1. Introduction

Vanadium sesquioxide (V_2O_3) exhibits a metal-to-insulator transition (MIT) [1] as a function of temperature, pressure, and doping concentration [2]. It undergoes a first-order transformation from a rhombohedral paramagnetic metallic (PM) to a monoclinic antiferromagnetic insulator (AFI) phase at $-113\,^\circ C$, with a jump in the resistivity of about seven orders of magnitude. And a broad second-order transition occurs at $227\,^\circ C$ from the metallic to a semiconducting state [3]. When V_2O_3 is doped with a few percents of Cr [4], Al [5], Mo [6], and Rare earth elements [7], the transition temperature may be controlled by changing the proportion of the doped metals. These properties allowed V_2O_3 and doped V_2O_3 to have potential applications in different areas, such as temperature sensors, optical device, conductive composite polymer and catalyst [8–11].

Over two decades, number of techniques for preparing V_2O_3 powder have been reported in literatures. For instance, spherical V_2O_3 particles were formed using O_2–H_2 flame fusion of V_2O_3 at $2000\,^\circ C$ [12]. Spherical V_2O_3 powders were prepared by reduction of V_2O_5 in H_2 atmosphere at $850\,^\circ C$ for 6 h [13]. V_2O_3 powders were formed as well using pyrolyzing the hydrazine containing vanadium salt [14] and reduction of the V_2O_5 gel in H_2 stream [15]. However, only micrometer scale powders are obtained by these methods. Few preparation methods of the V_2O_3 nanoparticles have been developed, including laser-induced vapor-phase reaction [16], pyrolysis of $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot 10H_2O$ [17], the reaction between metal alkoxides and benzyl alcohol [18], thermal decomposition of the oxalate [19], and ultrashort pulsed deposition of vanadium oxides [20]. Several disadvantages exist in these systems, such as complicated process, unavailable to disperse nanoparticles, and expensive costs.

Supercritical fluids (SCF) processes have been applied to producing inorganic materials [21,22]. Various oxide nanoparticles such as Fe_2O_3, CeO_2, ZnO, CuO, CoO, and $CoFe_2O_4$, have been synthesized using supercritical hydrothermal technique [23–27]. It is well known that the temperature and pressure of supercritical water are very high ($T_c > 374\,^\circ C$, $P_c > 22.1$ MPa). However, those of ethanol are relative low ($T_c = 240.85\,^\circ C$, $P_c = 6.1$ MPa) [28]. Chhor et al. had developed both batch and semicontinuous reactors for the crystallization of metal oxide powders through supercritical alcohol fluid drying process of sol–gel of the alkoxide precursors [29,30]. Nano-sized silica has been produced by supercritical methanol drying process of methanol silica gel from tetramethoxysilane. However, preparation of vanadium oxide using this method is quite difficult and expensive. Moreover, few reports have been published yet on the formation of nanoparticles using supercritical ethanol synthesis.

In this paper, a novel method for preparing V_2O_3 nanoparticles with spherical morphology was developed by supercritical ethanol fluid reduction of VOC_2O_4. The use of this reaction was particularly attractive because the obtained products are phase-pure and spher-

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[*] Corresponding author. Tel.: +86 27 68752701; fax: +86 27 68754067.
E-mail address: chihuang@whu.edu.cn (C. Huang).

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doi:10.1016/j.supflu.2010.11.012

ical; the process is a simple and reaction temperature is relatively low. That could easily be scaled-up and there was no contamination with other inorganics, such as halides or alkaline ions. Especially, this method prevented effectively these sphere-like nanoparticles from aggregation compared with other methods.

2. Experimental

2.1. Experimental procedure

The synthesis of V_2O_3 nanoparticles was performed in three steps. First, vanadyl oxalate (VOC_2O_4) was prepared according to literature [31]: 18.91 g of $H_2C_2O_4{\cdot}2H_2O$ and 9.09 g of V_2O_5 were dispersed into 50 mL of ethanol and the mixture was refluxed for 2–5 h, then the blue solution was obtained. It should be noted that if some precipitation was obtained in the blue solution, the process of filtration must be carried out. Second, the above blue solution and additional 200 mL of ethanol were transferred into a 500 mL autoclave. The autoclave was sealed and heated to get supercritical ethanol conditions 250 °C, 7.2 MPa with a needle-like valve to release the supercritical fluid. When the autoclave was maintained for 1 h under supercritical conditions, the supercritical ethanol was released from needle-like valve of the autoclave during 5–8 h. Then the autoclave was cooled to room temperature to obtain the black powder. Third, the as-obtained black powder was calcined at different temperatures ranging from 350 to 750 °C under high purity N_2 (99.999%) atmosphere to synthesize V_2O_3 powder.

2.2. Characterization methods

X-ray diffraction (XRD) measurements were carried out on a Shimadzu XRD-6000 diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54060$ Å). Transmission electron microscopy (TEM) experiments were carried out on a JEM-100CXII transmission electron microscope with an accelerating voltage of 100 kV. Scanning electron microscopy (SEM) image was collected by employing a Quanta 200 scanning electron microscope operated at 30 kV. X-ray photoelectron spectra (XPS) were obtained on a VGESCALAB MK II X-ray photoelectron spectrometer with an exciting source of Mg Kα (1253.6 eV).

The carbon oxides were analyzed by gas chromatography (GC, Lulan SP6980, China) with the column of 5A molecular sieve. The oxidation of ethanol was confirmed by silver mirror reaction. The mass-balance of each species was quantitatively checked as follows: (1) the reactant of ethanol and its corresponding products was analyzed by GC, (2) vanadium oxides were measured by their weight, (3) the carbon dioxide was absorbed by solution of sodium hydroxide to turn into carbonate, and then was titrated quantify of carbon dioxide [32], (4) the ratio of carbon monoxide to carbon dioxide was confirmed by FTIR on a Nicolet 360-SXB spectrometer from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} [33], and the quantitative analysis of carbon monoxide can be calculated according to the ratio and the results of step (3).

3. Results and discussion

3.1. Crystallographic analysis

Crystallization of the synthesized V_2O_3 samples was examined using X-ray diffraction. Fig. 1 shows the powder diffraction patterns of the sample calcined at different temperatures. All diffraction peaks can be assigned to the V_2O_3 Karelianite phase, which corresponds to the V_2O_3 (JCPDS, No. 34-187) already described in the literature [34]. No peaks of any other phases were detected, indicating the product with high purity. It was interesting that the as-obtained products were crystalline when they were taken from autoclave (Fig. 1a). Moreover, the higher the calcinating temperature increases, the more crystallized products were formed. Based on the Scherrer equation [35] ($D = k\lambda/(\mathrm{FWHM}/\cos\theta_{hkl})$, where k was 0.89 and λ was 1.54060 Å), the average size of V_2O_3 nanoparticles were 33.7 nm, which could be calculated according to the peaks (0 1 2), (1 0 4), (1 1 0), and (1 1 6).

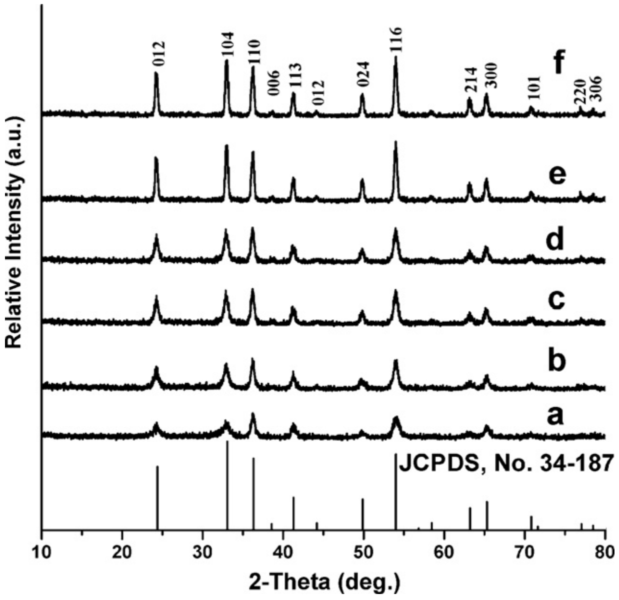

Fig. 1. The XRD pattern of samples calcined at different temperature: (a) non-calcined V_2O_3 sample, (b) 350 °C, (c) 450 °C, (d) 550 °C, (e) 650 °C, and (f) 750 °C.

3.2. Compositional analysis

To determine the composition and valence state of vanadium atom of the products, XPS measurements were carried out. As shown in Fig. 2a, no peaks of elements other than C, O, and V were observed on the survey spectrum. Peaks for O could be attributed to the V_2O_3, and O_2, CO_2, or H_2O absorbed on the surfaces of the sample. The high resolution XPS region spectrum (Fig. 2b) further confirmed that vanadium oxide consists of V(III). According to the literatures [15,36–40], the $V^{3+}_{2p3/2}$ peak was located at 515.5 eV, 515.7 eV, or 515.3 eV and the $V^{3+}_{2p1/2}$ peak was located at 523.1, 523.3, or 523 eV; the $V^{5+}_{2p3/2}$ peak was located at 516.95, 516.9, or 517.1 eV and the $V^{5+}_{2p1/2}$ peak was located at 524.3 eV; the $V^{4+}_{2p3/2}$ peak was located at 516.3, 516.2, or 515.9 eV and the $V^{4+}_{2p1/2}$ peak was located at 523.8 eV. Peaks at 515.5 eV and 523 eV can be attributed to $V^{3+}_{2p3/2}$ and $V^{3+}_{2p1/2}$ peaks, respectively. It is further confirmed that the as-obtained nanopowders were V_2O_3.

3.3. Morphology

The size and morphology of the typical products were examined using TEM and SEM. The TEM images (Fig. 3a and b) revealed that V_2O_3 nanoparticles are sphere-like with diameters of 30–60 nm. Nanoparticles were also observed in typical SEM image (Fig. 3c and d), which was in agreement with the TEM and XRD results. The reaction conditions for the formation of V_2O_3 nanoparticles and the corresponding diameters of the products are shown in Table 1. The influence of synthetic parameters including preparation of the precursor, reaction time, the supercritical conditions, and the drying process was systematically investigated to control the purity and morphology of V_2O_3.