Synthesis of single crystalline (NH₄)₂V₆O₁₆·1.5H₂O nest-like structures

Pallellappa Chithaiah, Gangaiyah Vijaya Kumar, Gowdiahnapally Puttaiah Nagabhushana, Ganganagappa Nagaraju, Gujjarahalli Thimmanna Chandrappa

Department of Chemistry, Bangalore University, Bangalore 560001, India
Laboratory of Molecular Catalysis, Institute of Chemistry, UFRGS, Porto Alegre, Brazil

HIGHLIGHTS

- Nest-like (NH₄)₂V₆O₁₆·1.5H₂O structures have been facilely synthesized.
- A hydrothermal method has been employed.
- A reaction mechanism for the formation of (NH₄)₂V₆O₁₆·1.5H₂O structures is discussed.

ABSTRACT

Novel nest-like (NH₄)₂V₆O₁₆·1.5H₂O structures made of nanobelts have been synthesized by a facile hydrothermal approach. The powder X-ray diffraction pattern of the sample reveals the monoclinic crystalline phase of (NH₄)₂V₆O₁₆·1.5H₂O. The scanning electron microscopy images of the sample obtained at 130 °C for 3 days exhibit nest-like morphology. The transmission electron microscopy result reveals that the nanobelts have a smooth surface. The selected area electron diffraction pattern of the nanobelts indicates single crystalline nature. The two major weight losses occur in thermogravimetric analysis which correspond to the removal of water and ammonia molecules. Further, calculation of the (NH₄)₂V₆O₁₆·1.5H₂O product results in the formation of orthorhombic phase of shcherbianite V₂O₅.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Over the past few years, considerable attention has been devoted to the synthesis of one-dimensional (1D) nanostructured materials such as nanotubes, nanorods, nanowires and nanobelts, because of their novel physical and chemical properties [1–3]. Among various metal oxide nanostructures, one-dimensional vanadium oxide-based nanostructured materials have interested many researchers over the last few decades due to their outstanding structural flexibility [4], diverse technological applications in catalysis [5,6], rechargeable lithium ion batteries [7], chemical sensors or actuators [8,9], electrochemical pseudo-capacitors [10] and electro-chromic coatings [11]. Several synthesis methods, such as thermal evaporation, surfactant-assisted solution, hydrothermal and solvothermal have been employed to prepare 1-D nanostructured vanadium oxides and their compounds [12–16]. However, there have been a few reports on the synthesis of 1-D nanostructured vanadates. For example, Durupthy et al. synthesized the crystalline NaV₃O₈·1.5H₂O at room temperature on acidification of a metavanadate solution [17]. Yu et al. and Zhou et al. have synthesized Na₂V₆O₁₆·3H₂O nanobelts and nanowires in the presence of F⁻ and SO₄²⁻ anions, respectively [18,19]. Mai et al. reported the synthesis, electrical transport measurements, and conduction mechanism on nanobelts of NH₄V₃O₈ vanadate [20]. Wang et al. reported that the one-dimensional ammonium vanadates are semiconductors at room temperature [2]. More recently, we reported the synthesis of Na₂V₆O₁₆·3H₂O belts/rings and suggested that the Na₂V₆O₁₆·3H₂O rings were made of self-coiling nanobelts [21]. However, it is still a big challenge for materials scientists to fabricate 1D nanostructured materials through a simple and facile route. In the present study, we report the synthesis of nest-like (NH₄)₂V₆O₁₆·1.5H₂O architectures made of nanobelts by the hydrothermal method and the possible reaction mechanism for the formation of (NH₄)₂V₆O₁₆·1.5H₂O architecture is discussed. The orthorhombic phase of shcherbianite V₂O₅ is obtained on calcination of (NH₄)₂V₆O₁₆·1.5H₂O at 350 °C for 2 h.
2. Experimental

2.1. Synthesis

All reagents were of analytical grade and used as received without further purification. Distilled water was used throughout. 0.5 g of NH₄VO₃ (4.27 × 10⁻³ mol) powder was added into 25 mL of distilled water and 0.2 mL of orthophosphoric acid (H₃PO₄, 88%, pH ~ 1.5) was also added, resulting in the formation of a wine red solution. The solution was stirred for about 15 min and transferred to a 60 mL Teflon lined stainless steel autoclave, which was maintained at 130 °C for 3 days and then cooled to room temperature. The red product was collected and washed with distilled water and absolute alcohol and then dried at 60 °C for 2 h.

2.2. Characterization

Powder X-ray diffraction (PXRD) data were recorded on a Philips X'pert PRO X-ray diffractometer with graphite-monochromatized Cu Kα radiation (λ = 1.541 Å) operated at 40 kV and 30 mA. The Fourier transform infrared (FTIR) spectrum of the sample was collected using a Thermo Nicolet FTIR spectrometer. The water content in the sample was investigated by thermogravimetric analysis (TGA) using a SDT Q600 thermomicrobalance in N₂ atmosphere from room temperature to 600 °C at a heating rate of 10 °C min⁻¹. The morphologies of the products were examined by a Quanta-200 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX). The nano-/microstructure of the product was observed by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) which were performed with a Hitachi model H-600 instrument operating at 100 kV.

3. Results and discussion

The PXRD pattern of the as-prepared sample is shown in Fig. 1a. All the diffraction peaks in the pattern can be readily indexed to a pure monoclinic crystalline phase of (NH₄)₂V₆O₁₆·1.5H₂O (JCPDS Card no. 51-0376). No reflections of impurity are found in the pattern, which proves that pure (NH₄)₂V₆O₁₆·1.5H₂O has been successfully synthesized.

The FTIR spectrum of the as-prepared sample is shown in Fig. 1b. The bands at 1004 cm⁻¹ and 964 cm⁻¹ correspond to V=O stretching of distorted octahedral and distorted square-pyramids respectively; the bands at 733 and 534 cm⁻¹ are ascribed to asymmetric and symmetric stretching vibrations of V–O–V bonds. The two bands at 3501 and 1617 cm⁻¹ are attributed to O–H stretching and H–O–H bending vibrations of water molecules respectively. The bands at 3154 and 1402 cm⁻¹ are respectively assigned to the

![Fig. 1. (a) PXRD pattern (b) FTIR spectrum and (c) TG-DTA curves of (NH₄)₂V₆O₁₆·1.5H₂O.](image-url)
Fig. 2. SEM images of the (NH₄)₂V₆O₁₆·1.5H₂O product prepared at (a) 120 °C, 24 h; (b) 130 °C, 3 days; low magnification (c) 130 °C, 3 days; high magnification (d) 160 °C, 3 days.

Fig. 3. (a) TEM image (b) SAED pattern of an individual (NH₄)₂V₆O₁₆·1.5H₂O nanobelt and (c) EDX spectrum of (NH₄)₂V₆O₁₆·1.5H₂O.
asymmetric stretching and the symmetric bending vibrations of NH₄⁺ [20].

The TG-DTA curves of the as-prepared sample are shown in Fig. 1c. The first weight loss of 5.6% from 100 °C to 255 °C mainly resulted from the evaporation of NH₃ and water. The second weight loss of 8.0% from 260 to 375 °C was caused by the de-intercalation of strongly-bounded water. The exothermic peak at 412 °C can be assigned to the oxidation of V (IV) to V (V) [22].

The morphology and structure of the (NH₄)₂V₆O₁₆·1.5H₂O product were investigated by SEM and TEM. The product obtained at 120 °C for 1 day (Fig. 2a) does not indicate any regular, well-defined shaped structure and is composed of a mixture of nanorods and nanobelts. When the reaction was performed at 130 °C for 3 days, the product exhibits nest-like morphology made of nanobelts (Fig. 2b and c). When the reaction was performed at 160 °C for 3 days (Fig. 2d), the dispersed nanobelts were obtained. The obtained nanobelts have the smooth surface with an average width of 300–400 nm and the length of several tens of micrometers. Fig. 3a shows the TEM image of selected individual (NH₄)₂V₆O₁₆·1.5H₂O nanobelts. The SAED pattern (Fig. 3b) shows clear diffraction spots, indicating a single crystal structure. The result from EDX shows (Fig. 3c) that the product contains only V, N, and O.

The effect of calcination on the crystallization and morphology of (NH₄)₂V₆O₁₆·1.5H₂O was investigated. After calcination of (NH₄)₂V₆O₁₆·1.5H₂O at 350 °C for 2 h, pure crystalline V₂O₅ was obtained. Fig. 4a and b shows representative low and high magnification SEM images of postcalcined V₂O₅ sample, indicating that the nest-like morphology of the precalcined (NH₄)₂V₆O₁₆·1.5H₂O does not change after calcination. All the PXRD peaks shown in Fig. 4c could be readily indexed to the orthorhombic shcherbianite V₂O₅ phase (JCPDS Card no. 86-2248). The EDX spectrum analysis (inset of Fig. 4a) of V₂O₅ confirms that the product contains only V and O elements. The calcined sample was gold coated prior to the EDX analysis. The FTIR spectrum (Fig. 4d) of the calcined vanadium pentoxide is characterized by four absorption bands centered at 1028 cm⁻¹, 829 cm⁻¹, 630 cm⁻¹ and 474 cm⁻¹. The first band at 1028 cm⁻¹ is assigned to V=O stretching (Vanadyl oxygen) and the last three bands at 829 cm⁻¹, 630 cm⁻¹ and 474 cm⁻¹ are due to V–O–V deformation modes. The two bands at 3459 and 1642 cm⁻¹ are attributed to O–H stretching and H–O–H bending vibrations of water molecules respectively [23].

The basic reactions for the formation of (NH₄)₂V₆O₁₆·1.5H₂O phase can be tentatively proposed in a similar way as previously proposed for Na₂V₆O₁₆·3H₂O [21].

$$3\text{NH}_4\text{VO}_3 + \text{H}_3\text{PO}_4 \rightarrow 3\text{VO}_3^- + (\text{NH}_4)_3\text{PO}_4 + 3\text{H}^+ \quad (1)$$

$$11\text{VO}_3^- + 8\text{H}^+ + \text{H}_2\text{O} \rightarrow [\text{H}_2\text{V}_{10}\text{O}_{28}]^{4+} + [\text{VO}_2(\text{H}_2\text{O})_4] \quad (2)$$

$$[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4+} + 4\text{H}^+ + 32\text{H}_2\text{O} \rightarrow 10[\text{VO(OH)}_3(\text{H}_2\text{O})_2] \quad (3)$$

$$[\text{VO}_2(\text{H}_2\text{O})_4]^{4+} \rightarrow [\text{VO(OH)}_3(\text{H}_2\text{O})_2] + \text{H}^+ \quad (4)$$
During the reaction process, decavanadate \([\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}\) resulting solution was subjected to the hydrothermal treatment. Undergoes deprotonation (Eq. (4)) in order to provide a neutral \([\text{VO(OH)}_3(\text{H}_2\text{O})_2]^{-}\) precursor. Then, \((\text{NH}_4)_2\text{V}_6\text{O}_{16}\) and the \(\text{NH}_4^+\) could be escaped as \(\text{NH}_3\) gas through the formation of bubbles and PO_4^{3-} and Na_2V_6O_{16} in a similar manner as previously proposed for the formation of layers. Furthermore, tunnels in order to compensate for the negative charge of the crystal structure parameters between \((\text{NH}_4)_2\text{V}_6\text{O}_{16}\) and \(\beta\text{V}_3\text{O}_8\), leading to the formation of \(\beta\text{V}_3\text{O}_8\) phase results from polycondensation of the neutral \([\text{VO}_2(\text{H}_2\text{O})_4]^{3+}\) species undergoes deprotonation (Eq. (4)) in order to provide a neutral \([\text{VO(OH)}_3(\text{H}_2\text{O})_2]^{-}\) precursor. Then, \((\text{NH}_4)_2\text{V}_6\text{O}_{16}\) and \(\beta\text{V}_3\text{O}_8\) (Eq. (5)) phase results from polycondensation of the neutral \([\text{VO(OH)}_3(\text{H}_2\text{O})_2]^{-}\) precursor, leading to the formation of \(\beta\text{V}_3\text{O}_8\) layers, and the \(\text{NH}_4^+\) ions can accommodate within these \(\beta\text{V}_3\text{O}_8\) framework tunnels in order to compensate for the negative charge of the layers.

The formation of \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) nanobelts can be explained in a similar manner as previously proposed for the formation of \(\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}\). Since these two compounds have a similar crystal structure and the same growth direction, the difference of these crystal parameters between \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) and \(\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}\) lies in the different length of the \(c\)-axis and the different \(\beta\) angles [24]. The \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) structure consists of \(\beta\text{V}_3\text{O}_8\) layers. \(\text{NH}_4^+\) ions and water molecules are intercalated between these layers. During the hydrothermal process, the presence of anions plays an important role in the formation of nanobelts in a similar way as observed previously for the formation of vanadates [21]. Therefore, in the present work, we assume that the PO_4^{3-} anions are crucial for the growth of \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) nanobelts, because PO_4^{3-} has a stronger coordination ability and may adsorb selectively to the special crystal facets, leading to the formation of \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) belts. Further, the residual \(\text{NH}_4^+\) ions from the solution could be escaped as \(\text{NH}_3\) gas through the formation of bubbles and the \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) belts reside on the gas bubble. Finally, the bubble could be destroyed and leads to the formation of nest-like morphology. However, further study is needed to precisely understand the formation mechanism of the nest-like morphology.

4. Conclusions

In conclusion, \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) nest-like morphology has been successfully prepared by the simple hydrothermal route. Nest-like morphology was formed due to the self-assembly of individual nanobelts. After calcination at 350 °C, \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) leads to pure crystalline V_2O_5.

Acknowledgments

The authors gratefully acknowledge the DST, New Delhi, India for financial support and Prof. Sarala Upadhya, UVCE, Bangalore for the SEM measurements.

References