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ScienceDirect

Ceramics International 36 (2010) 807–809

CERAMICS INTERNATIONAL

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Short communication

Soft chemistry preparation of layered $Al_{0.3}V_2O_5{\cdot}5H_2O$

Zaynab M. Elhadi [a], Khaled Melghit [a,*], Issa Al-Amri [b], Mohammed A. Al-Kindi [b]

[a] *Chemistry Department, College of Science, Sultan Qaboos University, P.O. Box 36, Al-Khodh 123, Oman*
[b] *Electron Microscope Unit, College of Medicine and Health Sciences, Sultan Qaboos University, P.O. Box 36, Al-Khodh 123, Oman*

Received 4 May 2009; received in revised form 15 May 2009; accepted 21 September 2009

Abstract

A novel layered compound $Al_{0.3}V_2O_5{\cdot}5H_2O$ was successfully prepared and characterized using powder X-ray diffraction, Thermal analysis, scanning and transmission electron microscopes. The new layered $Al_{0.3}V_2O_5{\cdot}5H_2O$ has like-nanowires shape and the layered structure was stable until 400 °C. At higher temperature (500 °C), it decomposes to orthorhombic $Al_xV_2O_5$ and triclinic $AlVO_4$.

Keywords: Nanosize materials; Layered compound; Aluminum vanadate

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1. Introduction

Mixed oxides based on vanadium have many applications in numerous areas such as heterogeneous catalysis and lithium ion batteries [1,2]. Recently layered compounds based on vanadium $M_xV_2O_5{\cdot}nH_2O$ (M = metal) have been obtained by a simple soft chemistry method [3,4]. These layered products are similar to electrolyte vanadium oxide (e-V_2O_5) [5] and are showing interesting nanosize shape. Different metals were used (M = Mg, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) and many of them were found to form $M_xV_2O_5{\cdot}nH_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn) layered compounds. Following our investigation, we explore in this paper the preparation of layered $Al_xV_2O_5{\cdot}nH_2O$.

2. Experimental procedure

All chemicals were obtained commercially and used as received unless otherwise stated. Vanadium (V) oxide was purchased from BDH Chemicals Ltd. Hydrogen peroxide (30%) was obtained from Fluka Chemika, Aluminum chloride anhydrous was purchased from Sigma–Aldrich, whereas 33% ammonia used was supplied by Reidal-de Haën and was diluted to 10% before use. A solution of vanadium oxide is prepared according to the method described elsewhere [3]. Boehmite or AlO(OH) was prepared by dissolving $AlCl_3$ in distilled water. To this solution ammonium hydroxide (10%) was added dropwise causing a gel-like opaque precipitate to form at pH 10. The precipitate was filtered and left to air dry overnight. To the boiling yellow vanadium oxide solution obtained above, AlO(OH) was added with an initial stoichiometry of V/Al = 1. The resultant solution was then left under heating at 85–95 °C and magnetic stirring for about 20 h. Then the solution was allowed to evaporation until only about 50 ml of the solution remained. Thereafter, the precipitate was isolated by filtration and left to air dry overnight. The crystalline structures of the as-prepared samples and the thermally treated samples were analyzed with powder X-ray diffraction (XRD) using Philips 1710 diffractometer, using Cu Kα radiation ($\lambda = 1.54056$ Å) and a graphite monochromator. The XRD measurements were carried out by a step scanning method (2θ range from 3° to 70°) with a scanning rate of $0.02\ s^{-1}$ and a step time of 1 s. The morphology of the samples and composition were investigated using JEOL JSM-5600LV scanning electron microscope equipped with an Oxford energy dispersive spectroscopy detector and JEOL 1234 transmission electron microscopy. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were run from room temperature to a temperature of 800 °C with a heating rate of $10\ ^{\circ}C\ min^{-1}$ at normal air atmosphere. DTA and TGA was measured using SDT 2960 Simultaneous DSC-TGA instrument.

3. Results and discussions

Fig. 1(a) shows X-ray diffraction (XRD) pattern of as-prepared sample. Its XRD pattern suggests a structure similar to

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* Corresponding author. Tel.: +968 24142449; fax: +968 24413415.
E-mail address: melghit@squ.edu.om (K. Melghit).

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doi:10.1016/j.ceramint.2009.09.043

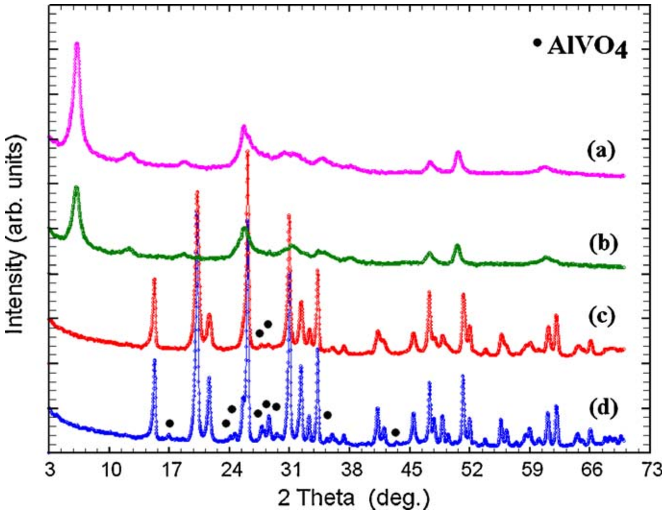

Fig. 1. XRD patterns of (a) as-prepared sample, (b) heated at 400 °C (4 h), (c) heated at 500 °C (4 h), (d) heated at 600 °C (4 h).

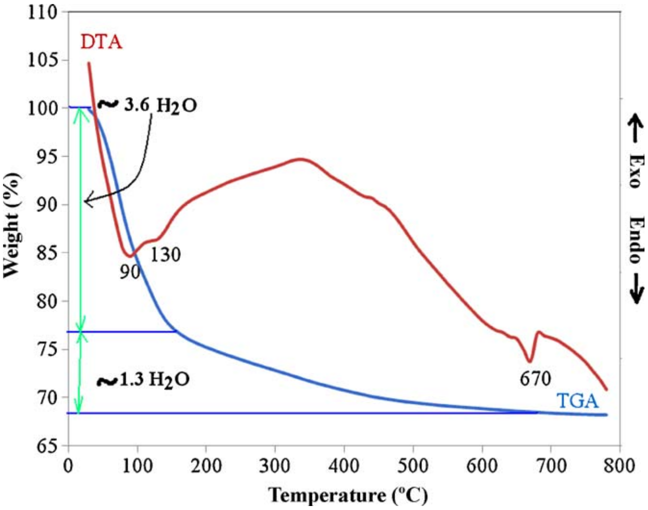

Fig. 2. TGA and DTA curves of as-prepared sample.

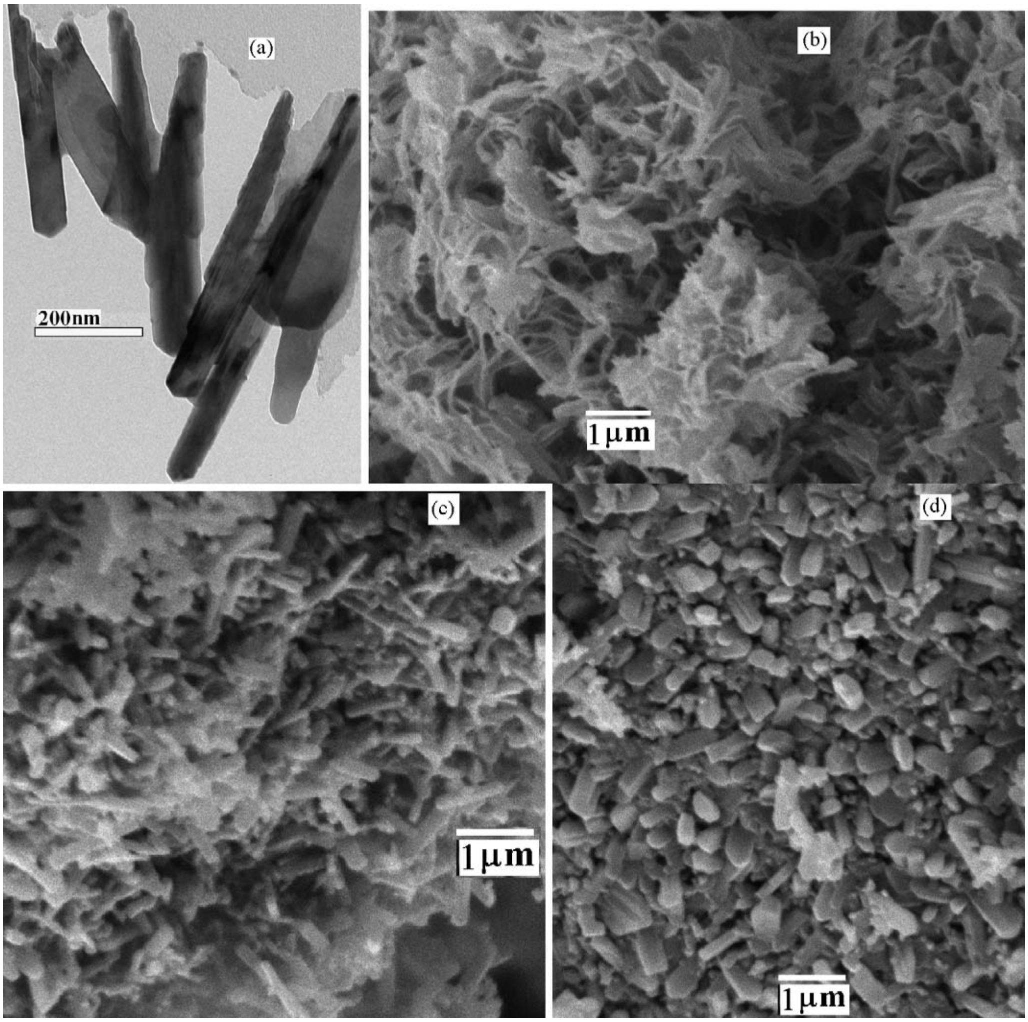

Fig. 3. (a) TEM micrograph of as-prepared sample; (b) SEM micrograph of as-prepared sample; (c) SEM micrograph of as-prepared sample heated at 500 °C (4 h); (d) SEM micrograph of as-prepared sample heated at 600 °C (4 h).

e-V_2O_5 [5] as well as $M_xV_2O_5 \cdot nH_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn) [3,4]. Fig. 1(b)–(d) show X-ray diffraction patterns of as-prepared sample upon thermal treatment at 400, 500 and 600 °C, under air, for 4 h. The XRD peaks that can be attributed to $AlVO_4$ are marked by a circular marker. The remaining peaks (Fig. 1(c) and (d)) belong to orthorhombic V_2O_5 crystal structure. The amount of aluminum ion incorporated in as-prepared layered $Al_xV_2O_5 \cdot nH_2O$ sample as found by energy dispersive X-ray spectroscopy (EDX) was determined to be 0.3 Al/2 V. Fig. 2 depicts the thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) curves of as-prepared sample. The TGA curve shows two clearly distinct dehydration steps, one due to the loss of adsorbed or weakly bonded water (about 3.6 H_2O) and starts from room temperature until about 160 °C. The DTA curve shows two endothermic peaks, at 90 and 130 °C. The other loss occurs over a broad range of temperature from 160 °C to about 650 °C and is more gradual. This water loss (about 1.3 H_2O) takes place at relatively high temperature and will correspond to the bonded water with probably some amount of hydroxide groups. No clear exothermic peak could be seen in the DTA curve. The DTA curve also shows an endothermic peak at 670 °C that corresponds to the melting point of vanadium pentoxide. According to the present results the chemical formula of as-prepared sample could be $Al_{0.3}V_2O_5 \cdot 5H_2O$. Probably small amount of vanadium 4+ along with hydroxide groups (OH^-) would balance the highly charged aluminum (Al^{3+}) and probably would play a role in the stability of the layered phase. It is interesting to note that the layered structure was found to be thermally stable until 400 °C, which is higher compared to the thermal stability reported for $Mg_{0.15}V_2O_5 \cdot 2.4H_2O$ and $Mn_{0.2}V_2O_{5.4} \cdot 2.1H_2O$ prepared in a similar method [3]. As the temperature increases (500 °C), the bonded water is lost and the layered phase changes to $Al_xV_2O_5$ orthorhombic along with small amount of triclinic $AlVO_4$ (Fig. 1(c)). More $AlVO_4$ is formed at higher temperature (600 °C). Probably, at that high temperature, the hydroxides (OH^-) present are removed from the structure and the orthorhombic $Al_xV_2O_5$ phase becomes unstable to accommodate aluminum, which leads to more separation of aluminum as $AlVO_4$. The values of the unit cell calculated using dicvol04 program [6] (Table 1) indicate that the sample heated at 500 °C (Fig. 1(c)) has smaller interlayer spacing between VO_5 layered sheets (b = 4.353 Å), compared to the sample heated at 600 °C (b = 4.362 Å) (Fig. 1(d)). This is consistent with the result published for the copper doped vanadium oxide [7]. This is explained by the shielding that metal ions exert on the apical oxygen of the VO_5 pyramids. Such effect reduces the electrostatic repulsion between oxygen and allows the distance between the vanadium oxide layers to shrink. Fig. 3(a) shows that $Al_{0.3}V_2O_5 \cdot 5H_2O$ is made of like-nanowires particles, with diameters in the range of 60 nm and few hundred of nm in length. SEM micrograph of $Al_{0.3}V_2O_5 \cdot 5H_2O$ (Fig. 3(b)) shows strongly aglomerated like-nanowires. At 500 °C (Fig. 3(c)), the nanowires change to nanorods with about 150 nm diameter and about 760 nm in length. At 600 °C (Fig. 3(d)) the particles' shape became shorter and wider with about 370 nm in diameter and 750 nm in length. It is worthnoting that the same behavior, of shape change, was observed for the nanorods TiO_2 upon annealing [8].

Table 1
Unit cell parameters of $Al_xV_2O_5$ at 500 and 600 °C.

Unit cell parameters	500 °C	600 °C
a (Å)	11.501	11.487
b (Å)	4.353	4.362
c (Å)	3.553	3.556

4. Conclusion

This study shows that aluminum is successfully inserted between vanadium layers and formed layered compound $Al_{0.3}V_2O_5 \cdot 5H_2O$. The present structure shows a good thermal stability and the amount of aluminum incorporated is the highest compared to the other layered compounds $M_xV_2O_5 \cdot nH_2O$ (M = Mg, Mn, Co, Ni, Cu, Zn) prepared by similar method. Probably, this is related to the small size and highly positive charge of aluminum ions.

Acknowledgements

This work was financially supported by the Sultan Qaboos University. The authors would like to thank Ms. Samira Al-Kharousi for XRD measurements and Mr. Nasser Al-Mandhary for TG/DTA measurements.

References

[1] S. Blanco, S.R.G. Carrzan, V. Rives, Appl. Catal. A: Gen. 342 (2008) 93.
[2] C. Ban, M.S. Whittingham, Solid State Ionics 179 (2008) 1721.
[3] K. Melghit, I. Al-Amri, Solid State Sci. 10 (2007) 607.
[4] K. Melghit, M. Al-Balushi, Mater. Lett. 62 (2008) 3358.
[5] E. Potiron, A. Le Gal La Salle, A. Verbaere, Y. Piffard, D. Guyomard, M. Tournoux, J. Phys. Chem. Solids 62 (2001) 1447.
[6] A. Boultif, D. Louer, J. Appl. Cryst. 37 (2004) 724.
[7] F. Coustier, J. Hill, B.B. Owens, S. Passerini, W.H. Smyrl, J. Electrochem. 145 (1999) 1355.
[8] K. Melghit, K. Bouziane, J. Alloys Compd. 453 (2008) 102.