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Short communication

Short reaction time preparation of zinc pyrovanadate at normal pressure

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Abstract

Zinc pyrovanadate with a good yield was prepared successfully with a short reaction time (few minutes) at normal pressure by using a simple method of preparation which consists of mixing a boiling solution of vanadium oxide (obtained by reacting V_2O_5 with few millilitres of 30 vol.% H_2O_2 following dilution with distilled water) with zinc nitrate solution. The zinc pyrovanadate precipitates at pH 5.6 after adding the appropriate amount of ammonium hydroxide. The solution temperature was found to affect the crystallinity and purity of zinc pyrovanadate. Zinc pyrovanadate was obtained with high level of purity and good crystallinity when ammonium hydroxide was added to the solution at boiling temperature (about 100 °C).

Keywords: A. Powders: chemical preparation; B. X-ray methods; D. Zinc pyrovanadate

1. Introduction

Zinc pyrovanadate $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$ was first discovered in 1997. It was prepared under hydrothermal conditions at 438 K [1]. Zinc pyrovanadate has an interesting crystalline structure. It has a porous framework assembled from layers of Zn octahedra connected by pyrovanadate groups (Fig. 1). Water molecules fill the large cavities; they are attached by hydrogen bonds to hydroxyl groups present in the structure. With such a structure, this material is a potential candidate for many applications in different areas. Also, as a metastable phase, it can be used as an active starting material for preparing other new advanced mixed oxides based on vanadium and zinc. In 1999, zinc pyrovanadate was prepared at normal pressure by using a mixture of zinc oxide powder and solution of vanadium oxide xerogel $V_2O_5{\cdot}2H_2O$ [2]. Although zinc pyrovanadate was obtained at normal pressure, the reaction time remains 2 days, similar to the previous method [1]. Very recently in 2004, two families of zinc vanadates, with structures derived from zinc pyrovanadate, were obtained by hydrothermal reaction with 1-day reaction time [3]. In general, research in material chemistry is undertaken with two aims: to prepare materials with new chemical and physical characteristics, and to find new method of preparation for interested materials, which can save time and energy. The experiments [1–5] show that by changing the starting materials, even a small change, it is possible to change the experimental conditions: temperature, pressure and reaction time. This study reports a new simple method for preparing pure zinc pyrovanadate with a short reaction time (only few minutes) and at normal pressure.

2. Experimental

It is known that V_2O_5 reacts with hydrogen peroxide [6], and recently this method was used to prepare a gel of vanadium oxide by reacting 1 g of V_2O_5 with about 50 mL of 30 vol.% H_2O_2 (20 g V_2O_5/1 L H_2O_2) [7]. This mixture progressively turns into a red gel after 24 h. In this work, we slightly modified this procedure; about 0.250 g of V_2O_5 (BDH, England) was mixed with about 3 mL of 30 vol.% H_2O_2 (Fluka). We started with a solution more concentrated on V_2O_5 (83 g V_2O_5/1 L H_2O_2); an exothermic reaction took place immediately. After few minutes about 400 mL of distilled water was added to this mixture, and this solution was heated until boiling, which leads

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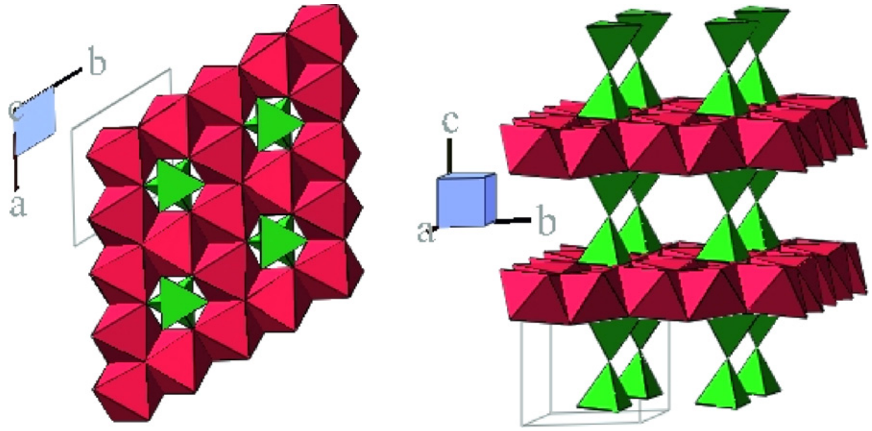

Fig. 1. Crystal structure of zinc pyrovanadate.

to yellow orange clear solution with pH around 2. At that temperature, the appropriate amount of Zn $(NO_3)_2{\cdot}6H_2O$ (S.d. Fine-Chem. Ltd) was added. The solution remains clear without any precipitate until adding 10% NH_4OH (aq). The obtained product was analyzed by different techniques as powder X-ray diffraction (Philips 1710, diffractometer), thermogravemetric analysis (SDT instruments 2960 TGA-DTA), infrared spectroscopy (Ncolet Impact 400D, the sample powder was dilute with KBr), scanning electron microscope (JEOL JSM-5600LY with an Oxford EDS detector) and transmission electron microscope (Jeol 1234).

3. Results and discussion

As it was reported in previous study [1,2], zinc pyrovanadate preparation is sensitive to the pH of solution. It was reported that zinc pyrovanadate was formed at pH 5.6. Because the pH of this vanadium oxide solution was low, after adding zinc nitrate to this solution, no precipitate forms. It takes place only after adding ammonium hydroxide. In order to control the pH of the solution, ammonium hydroxide was added drop by drop. After adding about 3 mL of 10% ammonium hydroxide, the pH of the solution was 5.6 and the yellowish color disappears completely from the solution with apparition of a white precipitate. This could indicate a transfer of vanadium ions V^{5+} to the precipitate by chemical reaction with the zinc ions Zn^{2+} present in the solution. In this range of pH, presence of vanadium ions within the solution gives yellowish color. In order to know the ratio of zinc to vanadium in the precipitate formed, it was analyzed by an Oxford EDS detector connected to scanning electron microscope (JEOL JSM-5600LY). The ratio obtained Zn/V = 1.6 is very close to the theoretical ratio of zinc pyrovanadate Zn/V = 1.5. In order to check the purity and the crystalline structure of this product, it was investigated by powder X-ray diffraction. A calculation of cell parameters was carried out using a computer-indexing program Dicvol04 [8]. All diffraction peaks are indexed in hexagonal unit cell similar to the reported unit cell for zinc pyrovanadate [1]. A Reitveld refinement was conducted on the as-prepared sample using Fullprof program [9]. As a starting model, zinc pyrovanadate coordination parameters from literature were used [1], the proton not included in the refinement. The obtained refinement (Fig. 2) shows a satisfactory agreement between the observed and calculated spectra ($R_p = 9.61$, $R_{wp} = 12.4$). The occupancy of water oxygen in the refinement was found to be higher than the expected value, around three molecules of water instead of two. In order to have precise information of the water amount present in the product, thermogravimetric analysis (TGA) was carried out. The TGA curve in Fig. 3 shows two breaks: the first one at 258 °C which indicates loss of 2.5 H_2O molecules; this corresponds to the removal of hydration water, and the second break occurs at 558 °C which corresponds to the removal of hydroxide groups (lost as one H_2O molecule). Thus, thermogravemity analysis confirms the presence of more than two molecules of water in as-prepared zinc pyrovanadate lattice; however, the amount is slightly less than what was predicted by Reitveld refinement. Thus, the formula of zinc pyrovanadate prepared by this work is $Zn_3V_2O_7(OH)_2{\cdot}2.5H_2O$. Fig. 4 depicts the infrared spectroscopy of the as-prepared zinc pyrovanadate. The first vibration bands (3510, 3190 and 1622 cm^{-1}) correspond to water and hydroxyls vibration modes, and the last vibration bands (930, 800 and 484 cm^{-1}) can be attributed to tetrahedral VO_4 and octahedral ZnO_6 vibration modes in the network. It shows similar vibration bands reported in the

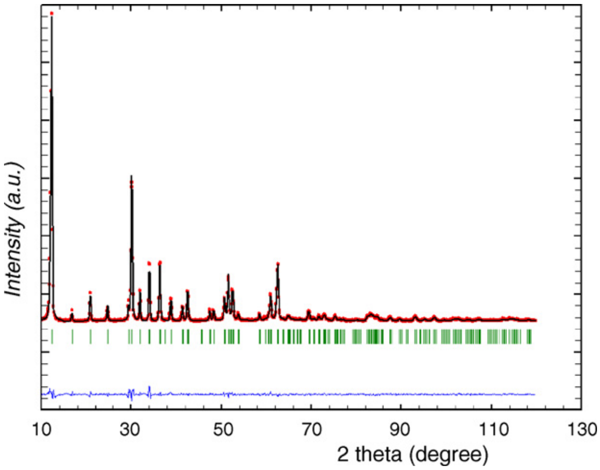

Fig. 2. The observed and calculated X-ray powder diffraction patterns for the as-prepared zinc pyrovanadate.

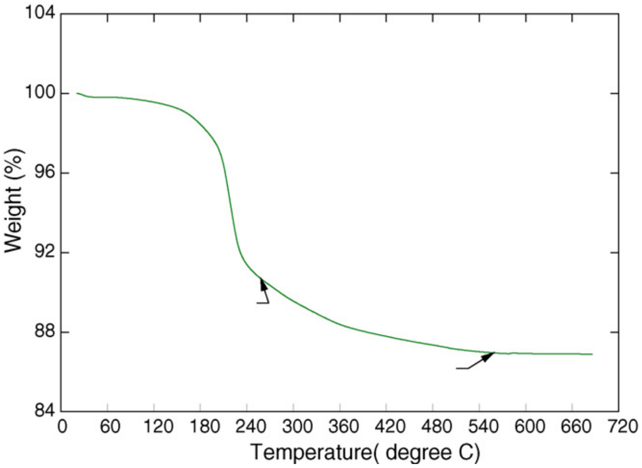

Fig. 3. TGA curve of the as-prepared zinc pyrovanadate.

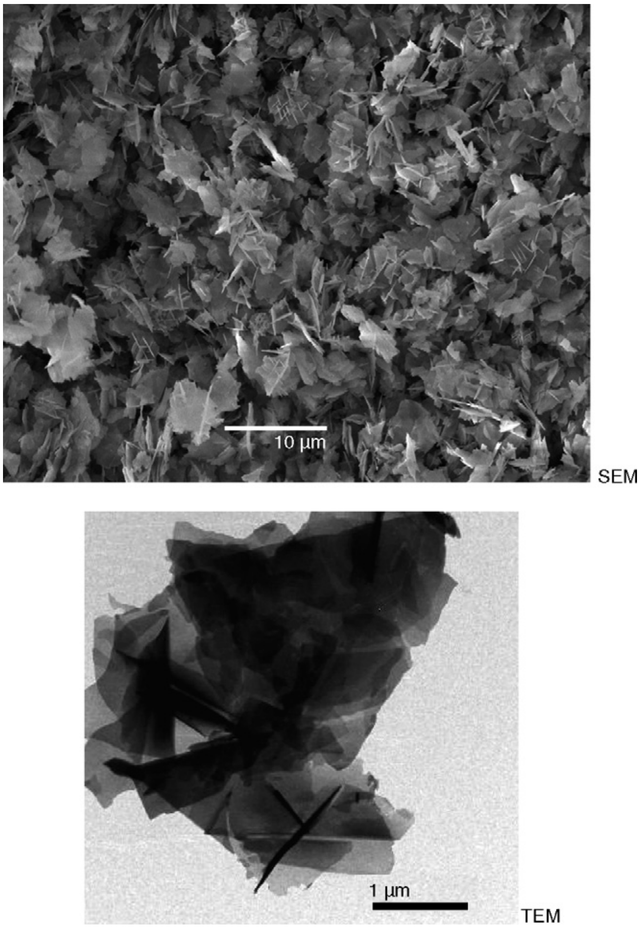

Fig. 5. SEM and TEM of the as-prepared zinc pyrovanadate.

literature for zinc pyrovanadate [5,10]. Fig. 5 shows the scanning and transmission electron microscope of the as-prepared zinc pyrovanadate, respectively. They show a homogenous pure product composed of thin-plate particles. To study the effect of temperature on this preparation, the following reaction was carried out: after mixing vanadium oxide with hydrogen peroxide and distilled water, the resulting solution was stirred and heated until boiling. Before adding zinc nitrate and ammonium hydroxide, this solution was first cooled down until room temperature then the corresponding amount of zinc nitrate was added. The solution remains yellowish transparent without any precipitate until the appropriate amount of ammonium hydroxide was added. A yellowish-brown precipitate was obtained. The pH of the solution was 6.6, and the solution remains yellowish that indicates an uncompleted reaction. Fig. 6 depicts the powder X-ray diffraction patterns of the as-prepared zinc pyrovanadate and the precipitate obtained at room temperature. It shows a high-pattern background with some diffraction peaks which indicate probably a mixture of two phases: one with low crystallinity and another amorphous. It seems that the zinc pyrovanadate formed, in this preparation, is less crystallized (broad diffraction peaks with lower intensities) and mixed with another amorphous phase. Fig. 7 depicts the infrared spectrum of the as-prepared zinc pyrovanadate and the precipitate obtained at room temperature. The IR curve of the precipitate obtained at room temperature shows some differences compared to the IR curve of the as-prepared zinc pyrovanadte;

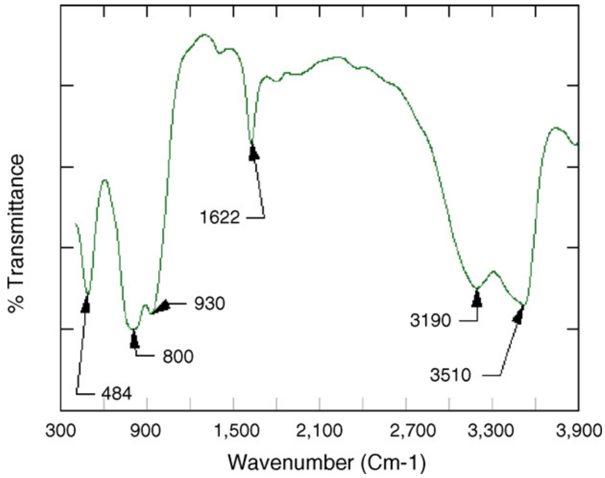

Fig. 4. FTIR spectroscopy of the as-prepared zinc pyrovanadate.

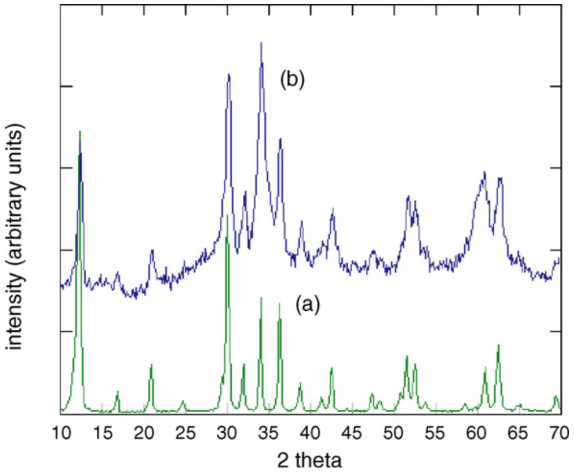

Fig. 6. Powder X-ray diffraction pattern: (a) zinc pyrovanadate obtained at 100 °C and (b) precipitate obtained at room temperature.

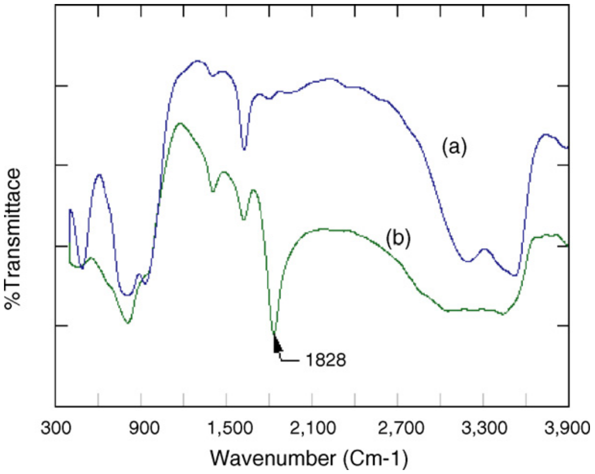

Fig. 7. FTIR-spectra: (a) zinc pyrovanadate obtained at 100 °C and (b) precipitate obtained at room temperature.

a new vibration band appears at 1828 cm^{-1}, which probably correspond to the new phase formed. The vibration bands around 900 cm^{-1} that correspond to the vibration modes of zinc pyrovanadate network are less resolved, which probably is the consequence of low crystallinity of the phase. From these observations, it is clear that the precipitate obtained in this experiment is composed of zinc pyrovanadate with low crystallinity mixed with a new phase amorphous to X-ray diffraction analysis.

4. Conclusion

By using a new simple method of preparation, pure zinc pyrovanadate was prepared with a short reaction time and good yield (more than 85%) at normal pressure. This study shows how the starting materials can affect the experimental conditions of the reaction. With different starting materials, zinc pyrovanadate can be obtained at different experimental conditions: (1) at higher pressure (hydrothermal reaction) and longer reaction time (1 or 2 days) [1,3]; (2) normal pressure and longer reaction time (2 days) [2]; and (3) with the present method at normal pressure with a shorter reaction time (few minutes, less than 1% of the previous reaction time). This will reduce the time and the cost of preparing zinc pyrovanadate for different purposes.

Acknowledgement

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