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The effect of starting materials on the morphology and particle size of copper pyrovanadate $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$

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Abstract

Copper pyrovanadate with spherical nanosize particles was successfully prepared from a mixture of vanadic acid solution and copper(I) oxide. Comparisons of X-ray diffraction profiles, scanning and transmission electron micrographs of particles of copper pyrovanadate obtained by using vanadic acid solution and xerogel of vanadium oxide solution were reported.

Keywords: B. Microstructure; Copper pyrovanadate; Morphology

1. Introduction

Soft chemistry or chimie douce is now widely used to prepare new materials especially with controlled morphology and particle size which cannot be obtained by the classical method (ceramic route). In such techniques, the final product is found to be sensitive to a slight change in the method of preparation. Small change in the process of preparation can affect the final product and can leads usually to three cases: (1) a product completely different (different composition and crystalline structure); (2) a metastable product (the same chemical composition with different crystalline structure) or (3) a product with the same chemical composition and the same crystalline structure but with different particle size and morphology. For example, in previous works, in synthesis of indium and chromium vanadates [1–3], it was shown that the stirring time of the reaction alone can affect the final product. A pure amorphous or crystalline phase is obtained with different stirring times.

Recently, we showed that copper pyrovanadate $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ could be prepared using a chimie douce process at room temperature by mixing copper(I) oxide, Cu_2O, powder to a solution of vanadium oxide xerogel [4]. A solution of vanadium oxide xerogel is obtained by dissolving xerogel of vanadium oxide, $V_2O_5 \cdot 2H_2O$, in distilled water. Preparation of vanadium oxide xerogel is well known [5]. It can be prepared at ambient condition by passing a solution of sodium vanadates through an acidic ion exchange resine. A yellow vanadic acid solution is obtained which spontaneously gives the gel of vanadium oxide. If the gel is dried at room temperature, xerogel of vanadium oxide, $V_2O_5 \cdot 2H_2O$ (a semi-crystalline product relatively soluble in water) can be obtained. In this paper, we introduce a small change in the method of preparation of copper pyrovanadate previously described [4], i.e., in place of using xerogel of vanadium oxide solution, the vanadic acid solution was used. This paper investigated the effect of this change on the final product.

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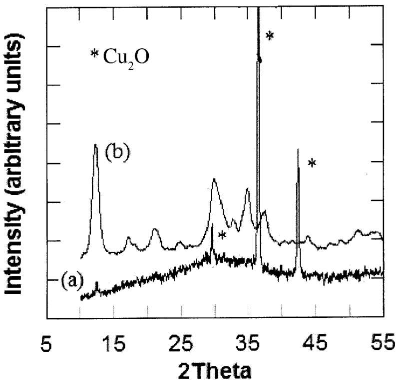

Fig. 1. XRD patterns of (a) the product obtained after 40 h stirring (the first peak at 12.38° 2θ of copper pyrovanadate can be seen) and (b) copper pyrovanadate obtained after 10 days stirring.

2. Experimental

Vanadic acid was obtained by passing a solution of sodium vanadate $NaVO_3$ (Fluka) through a cation (H^+) exchange resin. Copper pyrovanadate was prepared by mixing vanadic acid with copper(I) oxide, Cu_2O, powder (Fluka). This reaction can be schematized by the following equation:

$$\underset{\text{yellow solution}}{\text{Vanadic acid}(H_3VO_4)} + Cu_2O\ \text{powder} \xrightarrow[\text{stirring}]{\text{room temperature}} \text{Copper pyrovanadate} \qquad (1)$$

The stirring time was varied for different times. The solid phase was separated by filtration and dried at room temperature.

The solid phases were analyzed by X-ray diffraction (Shimadzu XRD 6000), FTIR spectrophotometer (Perkin-Elmer Model 1725x), scanning electron microscope (SEM-Philips XL 30) and transmission electron microscope (Leo 912AB, 120 kV)

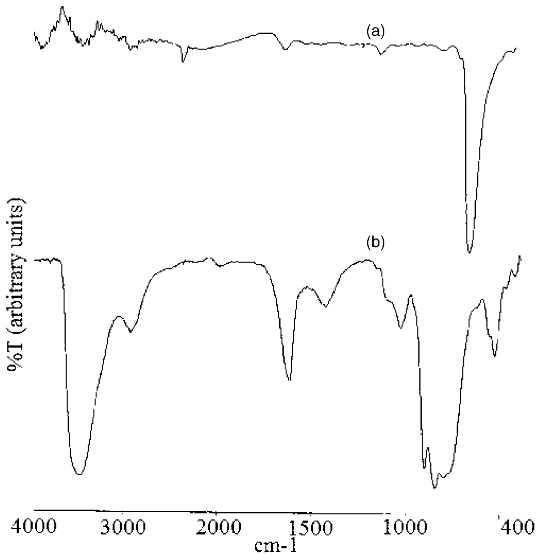

Fig. 2. FTIR spectra of (a) copper(I) monoxide and (b) copper pyrovanadate prepared from vanadic acid using 10 days stirring.

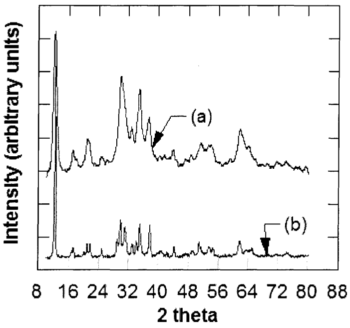

Fig. 3. XRD patterns of copper pyrovanadate obtained after 10 days of stirring using (a) vanadic acid solution and (b) vanadium oxide xerogel solution.

3. Results and discussions

In this reaction, different stirring times were used. The evolution of the reaction was followed with powder X-ray

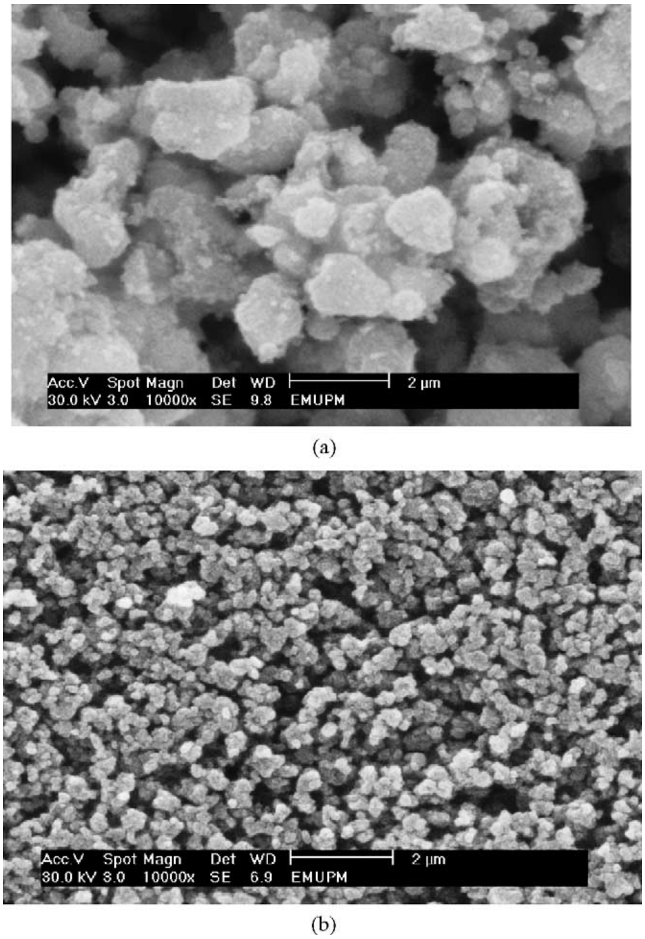

Fig. 4. SEM pictures of copper pyrovanadate obtained after 10 days of stirring using (a) vanadic acid solution and (b) vanadium oxide xerogel solution.

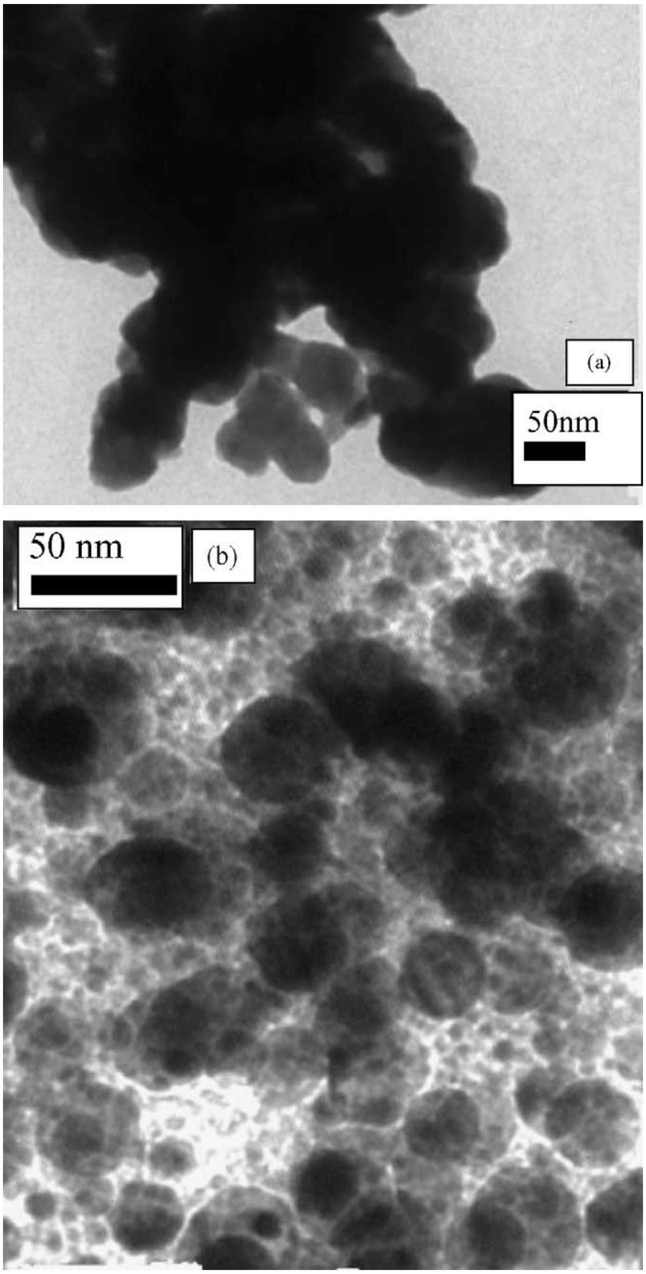

Fig. 5. TEM pictures of copper pyrovanadate obtained after 10 days of stirring (a) using vanadium oxide xerogel solution and (b) using vanadic acid solution.

diffraction. After few hours of stirring, the X-ray diffraction pattern shows only copper monoxide peaks as a crystalline phase, i.e., no product is formed. However, the change of the pH of the solution which increases from pH 2 to 4 indicates changes of species present in the solution. Thus, longer stirring time was used. The main peak of copper pyrovanadate at 12.38° appears only after 40 h of stirring (Fig. 1). With more stirring, more product is formed. Fig. 1(b) shows the X-ray diffraction pattern of the product obtained after 10 days of stirring. It consists of pure copper pyrovanadate. Compared with copper pyrovanadate obtained by using xerogel of vanadium oxide with 4 days of stirring [4], the diffraction peaks looks more broad. Fig. 2 shows the FTIR spectra of copper(I) oxide powder and as prepared copper pyrovanadate by 10 days of stirring. Two spectra are totally different and the FTIR spectrum of copper pyrovanadate is similar to copper pyrovanadate previously reported using xerogel of vanadium oxide solution [4]. This confirms the result of X-ray diffraction. Thus, using vanadic acid solution instead of vanadium oxide xerogel solution, the preparation needs more stirring time. In order to make a better comparison between the two preparation methods, copper pyrovanadate was prepared from xerogel of vanadium oxide solution using the same stirring time (10 days). Fig. 3 depicts its X-ray diffractogram. The peaks look sharper than those of copper pyrovanadate obtained from vanadic acid solution (Fig. 3). This result could be a consequence of difference in their particles size and morphology. Fig. 4 shows the scanning electron microscope of the two copper pyrovanadate obtained from (a) vanadic acid and (b) vanadium oxide xerogel solutions. Both pictures show agglomeration of small particles and two materials show different shapes. To get deeper understanding of this difference, a transmission electron microscope was used (Fig. 5 (a and b)). Copper pyrovanadate prepared from xerogel of vanadium oxide shows strongly agglomerate particles about 50 nm, however, copper pyrovanadate prepared with vanadic acid shows less agglomeration in spherical particles with smaller size ranging from 2 to 40 nm. Thus, the small particles size may be responsible of X-ray diffraction pattern broadening.

4. Conclusions

By using vanadic acid solution, more time of stirring was needed but smaller and less agglomerated particles with different morphology of copper pyrovanadate were obtained compared to the particles obtained by using xerogel of vanadium oxide solution. Thus, with a right change, even a small change in the soft chemistry preparation, it is possible to control the characteristics of final product such as morphology and particle size, which could affect reactivity and physical properties.

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