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Precipitation synthesis and characterization of cobalt molybdates nanostructures

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ABSTRACT

$CoMoO_4$ nanorods have been successfully synthesized by precipitation method using $Co(C_7H_5O_2)_2{\cdot}4H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ as starting materials. The effect of some parameters including reaction time, temperature, concentration, and surfactant were investigated to reach optimum condition. The as-synthesized nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmittance electron microscopy (TEM), photoluminescence (PL) spectroscopy, Fourier transform infrared (FT-IR) spectra, and energy dispersive X-ray microanalysis (EDX). Facile preparation and separation are important features of this route. This work has provided a general, simple, and effective method to control the composition and morphology of $CoMoO_4$ in aqueous solution, which revealed potential new insight into inorganic synthesis methodology.

1. Introduction

Metal molybdates, as two important families of inorganic materials, have a potential application in various fields such as magnetic, catalysis [1], photoluminescence [2], and humidity sensors [3]. $CoMoO_4$ is well known as an active and selective catalyst in the oxidation of hydrocarbons. It is accepted that these reactions proceed via the redox mechanism. First, the hydrocarbon molecule is

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oxidized by an oxygen ion from the catalyst lattice and then it is reoxidized by oxygen from the gas phase [4].

$CoMoO_4$ may exist in several phases: the low temperature α-phase, the high temperature β-phase, the high pressure hp-phase, and the hydrate [5]. Generally, $CoMoO_4$ can be prepared by two ways [6]: (i) the reaction between molybdenum trioxide [7] and (ii) by soft chemical, e.g. precipitation from aqueous solutions of soluble salts of Mo and Co [8,9]. Most of the previous reported approaches to obtain molybdates need high temperature and harsh reaction condition, such as a solid state reaction at 1000 °C [10] or the sol–gel method [11]. It has already been demonstrated that the soft chemistry routes can be as an appropriate method for controllable synthesis of this group of materials, such as two dimensional $CdWO_4$ nanocrystals [12].

In current investigation, a simple and facile precipitation method to prepare the $CoMoO_4$ nanostructures at mild temperature under atmospheric pressure by employing $Co(C_7H_5O_2)_2$ as a new precursor was developed. The presented approach is not restricted to complicated instruments, difficult processes, extra additives, and harsh conditions such as high temperature and pressure. The effect of different synthetic conditions such as reaction time and concentration of precursors, different surfactants, and different temperatures on the morphology and size of the final products were investigated.

2. Experimental

2.1. Materials and physical measurements

All the chemical reagents used in the experiment were of analytical grade and used as received without further purification. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. TEM image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on Nicolet Magna-550 spectrometer in KBr pellets. Room temperature PL was studied on a Perkin Elmer (LS 55) fluorescence spectrophotometer that with an excitation slit width of 5 nm.

2.2. Preparation of $CoMoO_4$ nanostructures

In a typical procedure, 0.048 mmol of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ was dissolved in 30 ml of distilled water and then was added dropwise to 30 ml solution containing 0.3 mmol of $Co(C_6H_5O_2)_2$ under magnetic stirring. This solution was stirred till a homogeneous solution obtained. The final solution was heated at 70 °C for 30 min under stirring. During these processes no sediment was observed. Then the temperature was increased to 90 °C and kept constant at 90 °C for 1 h which led to formation of a violet precipitate. Finally, the precipitates were separated and dried under vacuum at 60 °C for further characterization. To reach optimum condition for synthesis, the same process was repeated which each different condition is presented in Table 1 with more details. To investigate the surfactant role, appropriate amount of the surfactant was added after mixing precursors.

3. Results and discussion

The crystal structure and purity of the products were characterized by powder X-ray diffraction pattern. Fig. 1 shows the XRD pattern of $CoMoO_4$ prepared at 90 °C for 1 h. The diffraction peaks are in good agreement with the literature data (JCPDS No. 15-0439), and with those reported previously in ref [13]. Besides, several weak diffraction peaks were attributed to $CoMoO_6{\cdot}0.9H_2O$. The small crystallite size and poor crystallization are evidenced by the broad and weak diffraction peaks.

Chemical composition of the as prepared products was confirmed by EDX. As can be observed in Fig. 2, Co and Mo signals are detected in the collected peaks of the products. No impurities were detected in the EDX survey.