



Short communication

Synthesis and characterization of ferric molybdate nanoparticles in reverse micelles nanoreactors

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ABSTRACT

Ferric molybdate nanoparticles were successfully synthesized via microemulsion method. Ferric chloride and ammonium heptamolybdate were used as starting materials. A microemulsion system comprised from cationic surfactant (CTAB), isooctane as oil phase, n-butanol as co-surfactant and aqueous solution of ferric chloride was employed. Direct addition of aqueous solution of ammonium heptamolybdate to the microemulsion solution produced amorphous ferric molybdate nanoparticles. Crystallization of the product was performed by calcinations at 450 °C. Physicochemical characterization of the prepared nanomaterial was achieved by FT-IR and UV–vis spectroscopies, X-ray diffraction, scanning and transmission electron microscopies, and thermogravimetric analyses. The product was found to be consisted of relatively monodispersed nanoparticles with 80–90 nm in size.

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1. Introduction

In recent years, the control of the morphology and size of inorganic materials with nanoscale dimensions have been rapidly developed and become of promising field in material chemistry. It has been well known that micelles and microemulsions can be used as soft templates for controlling the size and shape of inorganic nanomaterials [1–6]. A microemulsion is thermodynamically stable, transparent and isotropic mixture with nanosized water pools, which has been widely used as nanoreactors for controlled synthesis of nanostructured materials.

Ferric molybdate, $\text{Fe}_2(\text{MoO}_4)_3$, is an important material in the fine chemical industry due to its catalytic activities in methanol conversion to formaldehyde and oxidation of propylene to propylene oxide [7–10]. Despite some reports on the preparation of metal molybdates such as solvothermal/hydrothermal [11–13], molten salt [14] and ultrasonic assisted synthesis [15], there are few methods for preparation of nanostructured $\text{Fe}_2(\text{MoO}_4)_3$ in the literature, such as hydrothermal synthesis [16–18], and liquid phase deposition of Fe^{3+} onto MoO_3 single crystal nanorods formed by heat treatment of the core/shell nanorods [19,20].

To the best of our knowledge there is no report about preparation and characterization of ferric molybdate nanoparticles with microemulsion method. So, in this paper we present the results on the synthesis of $\text{Fe}_2(\text{MoO}_4)_3$ crystallites in water-in-oil microemulsion. The

advantage of this approach is the better control over the size and shape of the final nanoparticles in comparison to other methods.

2. Experimental

All chemical reagents were purchased from Merck Chemical Company. Bulk ferric molybdate was prepared according to literature method [8]. FT-IR spectra were recorded with a Perkin-Elmer Spectrum RXIFT-IR spectrometer using pellets of the materials diluted with KBr. UV–vis spectra were recorded with a PG Instrument Ltd T90 + UV/VIS spectrometer. X-ray diffraction (XRD) patterns were recorded with a Siemens D5000 diffractometer using a $\text{Cu K}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$). The morphology and particle size of the materials were observed by using a transmission electron microscope (Philips EM 208 S instrument with an accelerating voltage of 100 kV) and a scanning electron microscope (ZEISS-DSM 960A microscope with attached camera operating at 30 kV). Thermogravimetric measurements were made on a Perkin Elmer Diamond Thermogravimeter in static air. The temperature was increased to 700 °C using a rate of 10 °C/min.

The synthesis of $\text{Fe}_2(\text{MoO}_4)_3$ nanoparticles was achieved via a microemulsion-mediated route. In a typical procedure, microemulsion solutions were prepared by adding 3 ml of 0.5 M FeCl_3 aqueous solution to a mixture of n-butanol (7.4 ml)/cetyltrimethyl ammonium bromide (3 g)/isooctane (17.4 ml) and stirring for 10 min at room temperature until the mixture becomes transparent. After that, 3 ml of 0.053 M $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ aqueous solution was slowly added to the microemulsion solution under vigorous stirring. After total addition of ammonium heptamolybdate solution, the resulting yellow suspension was kept for 24 h under stirring. The obtained precipitate was separated

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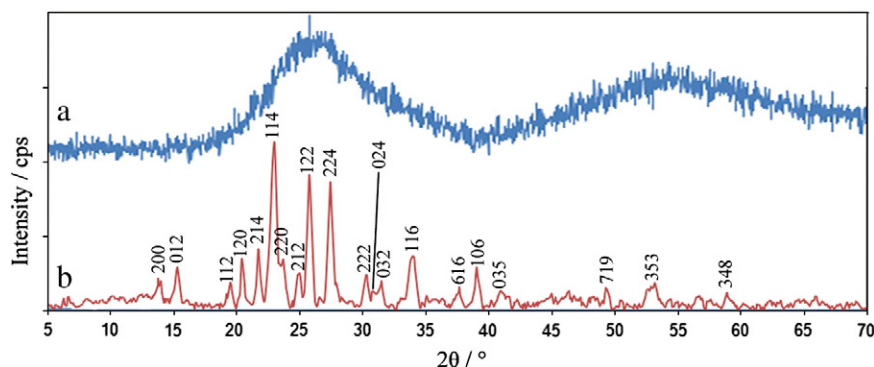


Fig. 1. XRD patterns of samples (a) before and (b) after calcination.

by centrifugation and washed with ethanol several times and then dried at 120 °C for 24 h. Finally, the resulting precipitate was calcined at 450 °C for 8 h.

3. Result and discussion

Phase identification of the products was performed using X-ray diffraction analysis. X-ray diffraction patterns of as-prepared and calcined ferric molybdate materials were presented in Fig. 1a–b. The XRD pattern of the as-prepared material before calcination (Fig. 1a) is marked by the absence of any sharp diffraction lines. The broad peaks indicate the relatively amorphous nature of the material obtained with direct precipitation of ferric molybdate in microemulsion system. The observation of double hump in this pattern suggests some intermediate range order in the resulted material. In the XRD pattern of the product after calcination (Fig. 1b) the nearly sharp diffraction peaks implies its good crystallinity. As can be seen, all the diffraction peaks of the calcined material can be indexed as monoclinic $\text{Fe}_2(\text{MoO}_4)_3$ (JCPDS Card Number: 35-0183) without any evidence of the presence of free MoO_3 in the calcined material. This is an indication that crystallization of ferric molybdate has occurred during the heat treatment of as-prepared product at 450 °C.

The process of surfactant degradation was studied by thermogravimetric analyses. Fig. 2 presents the results of TGA–DTA analyses of the as-prepared ferric molybdate. In the TGA curve two peaks can be found. The peak between the temperature range 50–200 °C could be attributed to removal of water molecules adsorbed on the surface of prepared material. The corresponding DTA curve shows endothermic process which is in agreement with this explanation. The next

TGA peak is observed at about 350–400 °C and is related to combustion of the organic surfactant, CTAB. This process is exothermic which is in good agreement with the corresponding DTA curve in this region. The thermal degradation of surfactant was completed by 450 °C so the prepared material was calcined at this temperature.

Fig. 3a–b shows the FT-IR spectra of the obtained materials before and after calcination as well as bulk ferric molybdate. In the FT-IR spectrum of the as-prepared material (Fig. 3a) the observed bands in 2851 and 2922 cm^{-1} are attributed to the asymmetric and symmetric C–H stretching vibrations of CH_2 groups of CTAB species, respectively. Also, the bands at 1400–1486 cm^{-1} were assigned to the symmetric and asymmetric C–H deformations. More specifically, the bands at 1467 and 1486 cm^{-1} have been assigned to C–H deformation of CH_2 groups. The observed bands at 1420 and 1378 cm^{-1} are attributed to asymmetric and symmetric C–H deformation of CH_3 groups, respectively. On the other hand, the broad and strong band in the range of 600–1000 cm^{-1} and the band at 562 cm^{-1} can be ascribed to stretching vibrations in amorphous ferric molybdate. Thus FT-IR spectrum of the as prepared material showed the existence of the ferric molybdate material associated with CTAB coating.

In the FT-IR spectrum of the product after calcination (Fig. 3b) the bands due to the presence of the C–H groups were disappeared as a result of the combustion and removal of CTAB species. The observation of a broad band between 700 and 900 cm^{-1} is ascribed to the stretching vibration of Mo–O bonds in nonequivalent tetrahedral positions. The band in 593 cm^{-1} corresponds to stretching vibrations of octahedral six coordinated molybdenum species in the ferric molybdate. The narrow peak observed at 961 cm^{-1} and 999 cm^{-1} is attributed to Fe–O–Mo and terminal Mo=O stretching vibrations, respectively [21]. Compared with

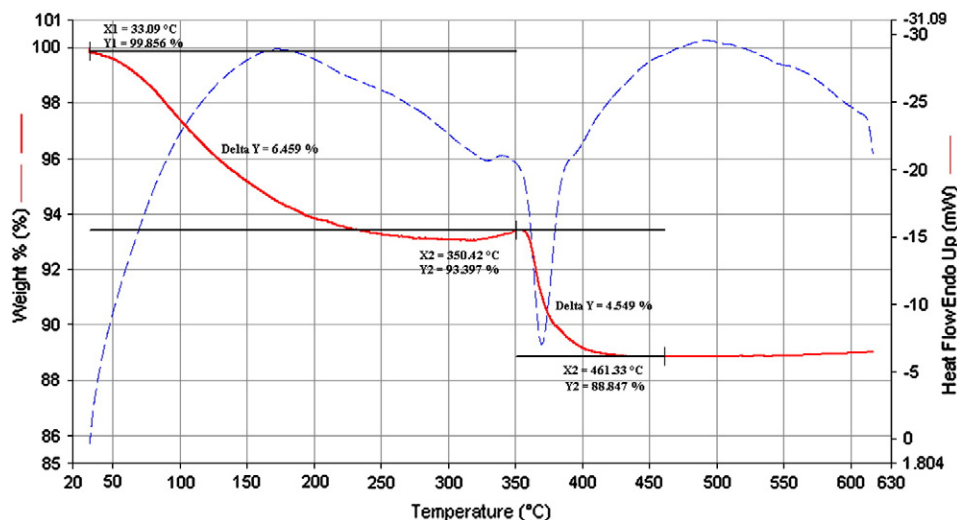


Fig. 2. TGA–DTA curves of the as-prepared ferric molybdate.

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