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Synthesis and structural characterization of MoO_3 phases obtained from molybdic acid by addition of HNO_3 and H_2O_2

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Orthorhombic (α) MoO_3 and monoclinic (β) MoO_3 were successfully synthesized by cation-exchange of sodium molybdate solution applying three different routes: ***i)*** pure precursor molybdic acid solution (H_2MoO_4), ***ii)*** addition of HNO_3 to a precursor and ***iii)*** addition of 35% H_2O_2 to a precursor. By route ***i)*** pure orthorhombic (α) MoO_3 was synthesized. Pure monoclinic (β) MoO_3 was obtained in the presence of HNO_3. A polyphase product containing 72% monoclinic (β) MoO_3 and 28% orthorhombic (α) MoO_3 was obtained in the presence of 35% H_2O_2. The products obtained were characterized by XRD, IR and SEM analysis. The morphology of MoO_3 strongly depended on the synthesis method applied. Smaller crystals with uniform shape were obtained in the presence of HNO_3 and 35% H_2O_2.

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1. Introduction

The investigations on the microstructure of the crystalline materials received considerable attention during the last years in connection with the preparation of nanostructured materials. The microstructure influences the properties of the materials and can be controlled by different synthesis methods.

Transition metal oxides like MoO_3 have numerous industrial applications due to their optical, electrical and thermal properties [1]. Molybdenum oxide exhibits catalytic properties and is the major component of the catalysts for the oxidation of methanol to formaldehyde [2].

Various MoO_3 microstructures, such as: rods [3-6], wires [7], belts [8,9], flowers [9,10] and platelets [11] were synthesized by different methods. The most popular are: hydrothermal synthesis [3,4,6,9,12], vapor-deposition [8], vapor-transportation [5], hydro/solvothermal treatment [11], chemical precipitation [13] and sol-gel method [14-22].

Depending on the experimental conditions, different MoO_3 polymorphs can be obtained: thermodynamically stable orthorhombic (α) MoO_3, metastable monoclinic (β) MoO_3 or hexagonal (h) MoO_3. For example, M. Nagano et al. [14] and W. Dong et al. [15] synthesized orthorhombic (α) MoO_3 by precursors of metal alkoxides. R. Murugan et al. [16] and M. A. Camacho-Lopez et al. [1] obtained this phase by acidification of sodium molybdate (Na_2MoO_4) solution through a proton-exchanged resin. G. Li et al. [10] applying a peroxo method synthesized orthorhombic (α) MoO_3. The peroxo sol-gel route is also suitable for the preparation of orthorhombic (α) MoO_3 thin films at low temperature [17]. In the above studies hydrogen peroxide was used as a precursor for the synthesis of MoO_3 nanostructures and films [10,17], but its application as additive in cation-exchange method still was not investigated.

The metastable monoclinic (β) MoO_3 was also synthesized by different methods: McCarron et al. [18] applied spary-dried of the amorphous molybdate acid obtained via cation-exchange of sodium molybdate (Na_2MoO_4) solution. F. Harb et al. [19] prepared monoclinic (β) MoO_3 by cation-exchange of sodium molybdate (Na_2MoO_4) solution and heat-treatment in autoclave. The obtained product was characterized by rectangular platelet particles. According to T. Mizushima et al. [1,21] the key for the preparation of monoclinic (β) MoO_3 is the addition of a small amount of HNO_3 to the precursor molybdic acid solution (H_2MoO_4). X. M. Wei et al. [11] obtained monoclinic (β) MoO_3 by hydro/solvothermal treatment of inorganic-organic hybrid precursors $MoO_3(4,4'\text{-bipyridyl})_{0.5}$. In the above results there are not sufficient data about the morphology of the monoclinic (β) MoO_3 particles.

S Komaba et al. [12] obtained hexagonal (h) MoO_3 by a hydrothermal reaction. Using chemical precipitation, the same phase with unique rod-like morphology was synthesized by J. Song et al. [13]. Z. S. Guan et al. [22] obtained a nanodisk of hexagonal (h) MoO_3 by heat-treatment of rhodamine B/ molybdic acid aggregates (RBMA).

The above possibilities to modify the microstructure and the type of the polymorphs varying the experimental conditions initiated our research interest in this field. The aim of this work was to study the structure and morphology of MoO_3 phases obtained from molybdic acid precursor in the presence of two different additives - HNO_3 and H_2O_2.

2. Experimental

The cation-exchange synthesis was carried out following the procedure described by T. Mizushima et al. [21]. The molybdic acid (H_2MoO_4) solution was prepared by successively passing 50 ml aqueous solution of $Na_2MoO_4.2H_2O$ (Merck) (1mol/dm^3) through two columns of a cation-exchange resin (Aldrich, Amberlite IR120). This treatment allowed removing of Na^+ ions from the solution. The concentration of Na^+ ions in the final solution, measured by ICP-AES, was below 2 mg/cm^3**.** The solution of H_2MoO_4 obtained was evaporated, then heat-treated at 200 ^{o}C and 250 ^{o}C according to three different routes**:**

i) using pure H_2MoO_4 solution (without any additives); ***ii)*** adding HNO_3 to a H_2MoO_4 solution; ***iii)*** adding 35% H_2O_2 to a H_2MoO_4 solution:

i) pure H_2MoO_4 solution: 30 cm^3 of molybdic acid solution (H_2MoO_4) formed via cation-exchange were placed in a 50 cm^3 vessel, evaporated to near dryness in a vacuum drying oven at room temperature for one week and after that in a dessicator over concentrated sulphuric acid. The powder obtained was heated successively for 2 h at 200 ^{o}C and 250 ^{o}C, in an oxygen flow [16,20].

ii) adding HNO_3 to a H_2MoO_4 solution: To 30 cm^3 of the cation-exchanged solution, 0.060 cm^3 of concentrated HNO_3 were added. The solution was evaporated to dryness by vacuum drying at room temperature. The drying was completed in three weeks and obtained powder was heated successively for 2 h at 200 ^{o}C and 250 ^{o}C in an oxygen flow [21].

iii) adding 35% H_2O_2 solution to a H_2MoO_4 solution. The influence of H_2O_2 was studied by addition of 0.020 cm^3 of 35% H_2O_2 to 20 cm^3 of the molybdic acid (H_2MoO_4) solution. The solution containing (0.1% H_2O_2) was evaporated by vacuum drying at 60 ^{o}C. The powder obtained was heated successively for 2 h at 200 ^{o}C and 250 ^{o}C in air.

The samples obtained were characterized by X-ray diffraction (XRD-Bruker D8 Advance, Cu K_α radiation) and Infrared spectroscopy (IR-Nicolet-320 FTIR spectrometer). The X-ray diffraction data were analysed using the "PowderCell" program to determine the volume percentage of the phases present in the samples [23]. The morphology of the MoO_3 phases obtained was investigated by scanning electron microscopy (SEM-JEOL 5300). For comparison, the structure of as-purchased orthorhombic (α) MoO_3 was presented.

3. Results and discussion

Fig. 1 (a-d) shows the X-ray patterns of: as-purchased orthorhombic (α) MoO_3 (fig.1a); monophase orthorhombic (α) MoO_3 prepared by route ***i)*** (JCPDS-35-0609) (fig.1b); monophase monoclinic (β) MoO_3 (JCPDS-47-1081) obtained by route ***ii)*** (fig.1c) and polyphase sample obtained by route ***iii)*** (fig.1d).

Heat treatment at 200 ^{o}C of the samples obtained by ***i)*** and ***ii)*** routes led to partial crystallization. The amorphous phase was observed only when we used H_2O_2 as additive (route ***iii***). By "PowderCell" program, it was estimated that after heat-treatment at 250 ^{o}C the crystallization was accomplished and polyphase product was obtained, containing monoclinic (β) MoO_3 (72%) and orthorhombic (α) MoO_3 (28%) (fig.2).

The intensity of the main diffraction lines of orthorhombic (α) and monoclinic (β) MoO_3 phases was very close to JCPDC data (JCPDS-35-0609 and JCPDS-47-1081; fig.1b-c)**.** It is worth nothing that in as-purchased MoO_3 the crystals were mostly oriented along 0*l*0 planes (*l*=2, 4, 6 and 10) (fig.1a).

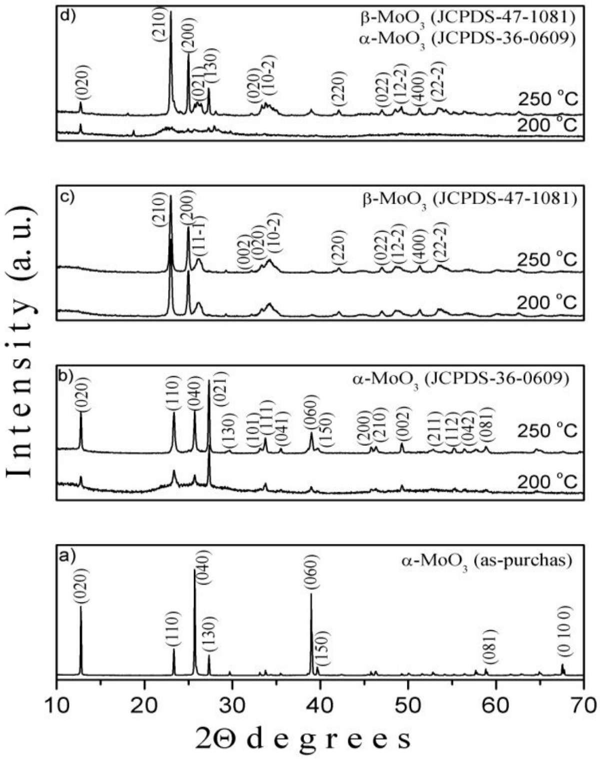

Fig.1. X-ray patterns of: a) as-purchased orthorhombic (α) MoO_3; b) orthorhombic (α) MoO_3 obtained by route i); c) monoclinic (β) MoO_3 obtained by route ii); d) sample obtained by route iii).

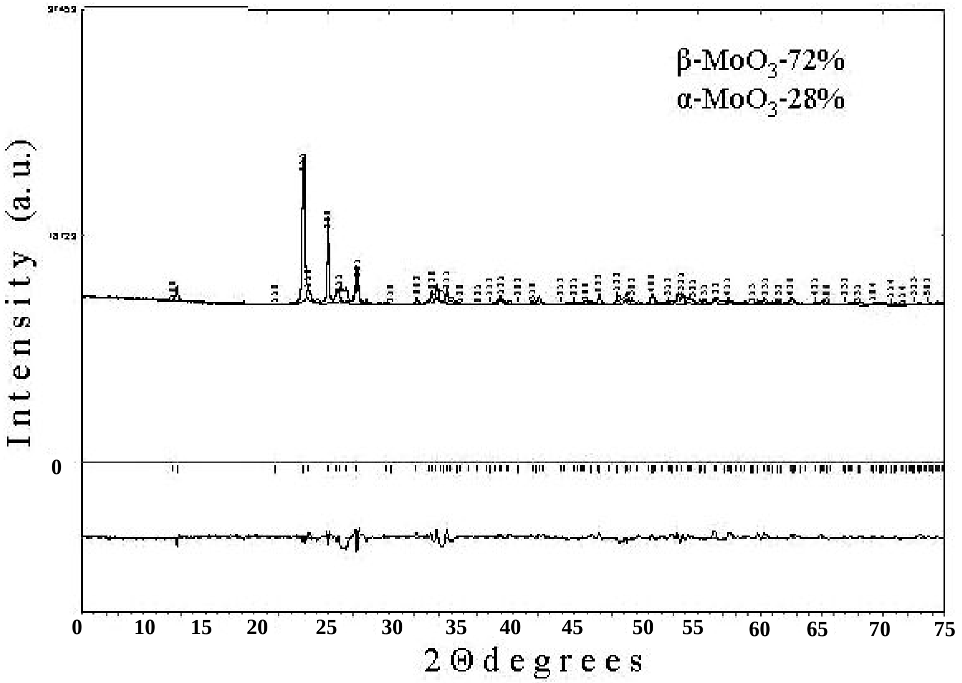

*Fig. 2. Result of the phase refinement for X-ray data of the sample obtained by route **iii)**.*

IR spectroscopy was used to obtain additional information on the phases and structure transformations of MoO_3 phases. Fig. 3 presents the IR spectra of the different samples. The assignment of the observed absorption bands was made in the framework of the local point-symmetry approach [24]. The main difference was found in the absorption regions around 600 cm^{-1} and at 990 cm^{-1}. The band at 600-630 cm^{-1} is typical of the vibration of the Mo_2O_2 entity formed by edge shared MoO_6 polyhedra building the orthorhombic (α) MoO_3 structure. The band at 990 cm^{-1} is characteristic of the vibration of the Mo=O terminal bond (fig.3a-c) [25,26]. The dominant band at 870 cm^{-1} is associated with the vibration of Mo-O-Mo bridging bonds [19,25-28]. The decrease in intensity of the band at 600 cm^{-1} may be considered as a result of the decreasing number of edge shared bonds (Fig.3c). Shifting of the band position to high frequency is probably due to a change in symmetry of the Mo_2O_2 entity.

In the IR spectrum (Fig.3d) of monoclinic (β) MoO_3 there are no absorption bands at 990 cm^{-1} and bands around 600 cm^{-1} because Mo=O and Mo_2O_2 entities are absent in this polymorph [19,25,28]. Obviously, the IR spectra can be a useful tool by which one can get in a short time information about the transition of polymorphs.

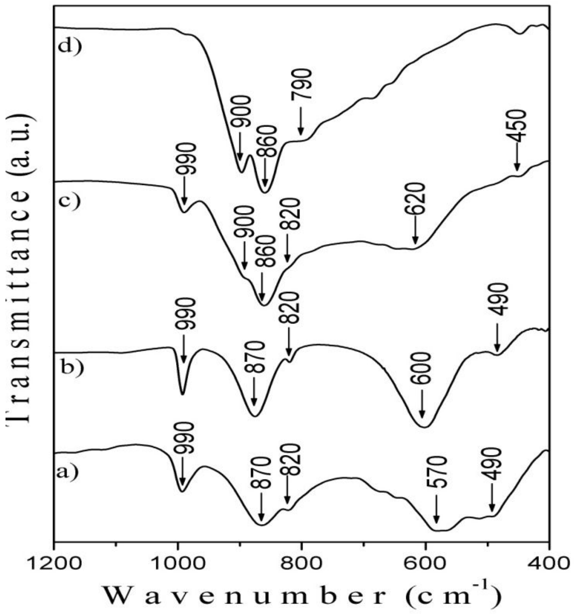

Fig. 3. IR spectra of: a) as-purchased orthorhombic (α) MoO_3; b) orthorhombic (α) MoO_3 obtained by route i); c) sample obtained by route iii); d) monoclinic (β) MoO_3 obtained by route ii).

Figs. 4-7 show the SEM images of the different MoO_3 phases. The particles of as-purchased orthorhombic (α) MoO_3 are of elongated needle-type with an average size of about 5÷50 µm (fig.4).

In the SEM images of orthorhombic (α) MoO_3 (route ***i***) nearly isometric crystals with an average size of 1 µm (primary particles), with a strong tendency to agglomeration were observed. These secondary particles were sized between 10÷20 µm (fig.5).

The sample containing pure monoclinic (β) MoO_3 is composed of small crystals below 0.5 µm, with a lower tendency to agglomeration (fig.6). The SEM image of the sample containing 72% monoclinic (β) MoO_3 and 28% orthorhombic (α) MoO_3 (route ***iii***) shows also a decrease in average size of the particles below 0.5 µm (fig.7).

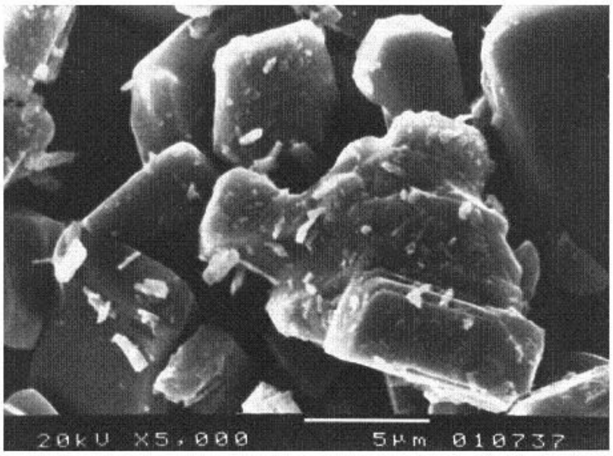

Fig. 4. SEM image of as-purchased orthorhombic (α) MoO_3.

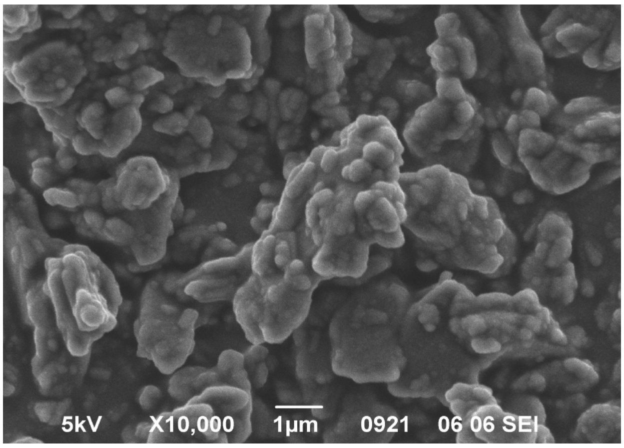

Fig. 5. SEM image of orthorhombic (α) MoO_3 obtained by route ***i)***.

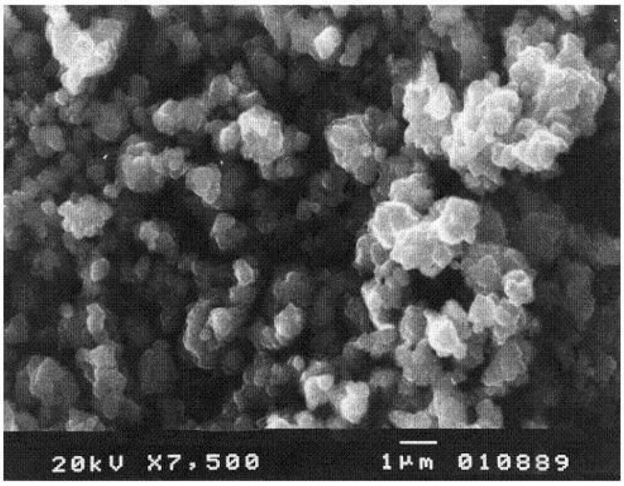

Fig. 6. SEM image of monoclinic (β) MoO_3 obtained by route ***ii)***.

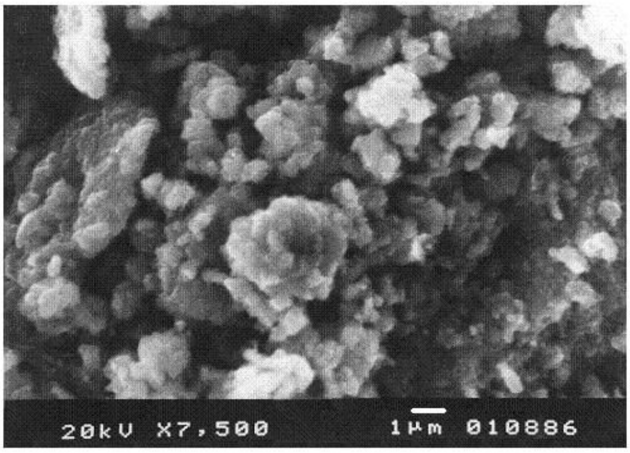

Fig.7. SEM image of sample obtained by route ***iii)***.

4. Conclusion

A new approach to the preparation of monoclinic (β) MoO_3 was suggested. A small amount of H_2O_2 (0.1%) as additive contributed to the formation of this phase. It is estimated that the addition of H_2O_2 hampered crystallization processes in comparison to the addition of HNO_3. At 200 °C the amorphous phase was predominant.

In the presence of HNO_3 and H_2O_2 as additives, after heat treatment, both MoO_3 polymorphs are characterized by isometric crystals and lower tendency for agglomeration. The least tendency for agglomeration was observed in pure monoclinic (β) MoO_3 phase obtained by route ***ii)***.

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