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Influence of chelating agent on the morphological properties of α-$CuMoO_4$ powder synthesized by sol–gel method

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Abstract

In this work, we have synthesized precursor gels of copper molybdate with various chelating agents (glycine, polyacrylic acid, citric acid). After heating at adequate temperatures, the obtained precursors led to the pure phase α-$CuMoO_4$, whose morphology and grain size depend on the chemical nature of the chelating agent used.

Keywords: Copper molybdate, Sol-gel, Grain size, Morphology

Introduction

The copper molybdate $CuMoO_4$ has been extensively studied in recent years, in particular because of its thermochromic, piezochromic and tribochromic effects [1-3], as well as its use as catalyst in the oxidation of organic compounds [4-6]. This molybdate exhibits a polymorphism with a stable phase at low pressure and high temperature named α and another stable phase at high pressure and low temperature named γ. In the polymorph α-$CuMoO_4$, the Cu ions present two types of coordinance: octahedral (CuO_6) and pyramidal (CuO_5) [7-9], whereas molybdenum is in tetrahedral environment (MoO_4). In the polymorph γ-$CuMoO_4$, both metallic cations are in octahedral environment [7-9]. The transition α ↔ γ is obtained by increasing/decreasing the temperature or the pressure. Both polymorphs present different colors, green and red-brown respectively for α and γ. It is therefore possible to envisage the use of this molybdate as marker of pressure and/or temperature. Recent studies have shown that the temperatures / pressures of transition α↔γ are adjustable by chemical doping [1].

Various methods have been developed to prepare $CuMoO_4$. The traditional method of synthesis involves solid state reactions between copper and molybdenum oxides at temperatures close to 750°C. The powders obtained by this method are composed of large size particles with low specific surface area [10]. The soft chemistry methods are particularly adapted to obtain fine powders. They generally lead to homogeneous powders with nano-sized grains. Among the methods of soft chemistry used for the elaboration of $CuMoO_4$, the co-precipitation method [11], spray pyrolysis [12] and solvothermal process may be mentioned [13]. Recently, we have been able to obtain this molybdate by the sol-gel process [14, 15].

This work proposes to study the influence of the chelating agent used (citric, acrylic acid, glycine) on the micro-structure of the obtained powder.

2. Materials and methods

The reagents used for the synthesis of various precursors of $CuMoO_4$ are: ammonium-heptamolybdate $(NH_4)_6Mo_7O_{24}$, $4H_2O$ (Sigma-Aldrich, 99%), copper nitrate $Cu(NO_3)_2$, $3H_2O$ (Acros organics, 99.9%), glycine Gly (Sigma Aldrich, 98.5%), polyacrylic acid PAA (Sigma Aldrich, Mw =1800 g/mol, 98 %) and citric acid CA (Acros, 99.5%).

The procedure adopted for the synthesis of $CuMoO_4$ is schematically shown in Fig.1. Aqueous solutions of copper nitrate and ammonium heptamolybdate are mixed in stoichiometric proportions. The aqueous solution of the chelating agent is then introduced. The chemical composition of different reaction mixtures is given in Table 1. The evaporation of the solution at 80°C led to the formation of gels. These gels were dried at 120 °C for 24h and then pre-calcined at 300°C in air for 12 h.

Table 1: Chemical composition of different reaction mixtures

Precursor	*Chelating agent*	*Composition*
P_{Gly}	*glycine (Gly)*	*1.3 Gly :Cu :Mo*
P_{PAA}	*polyacrylic acid (PAA)*	*7 PAA* : Cu :Mo*
P_{CA}	*citric acid (CA)*	*3 AC: Cu :Mo*

* *Concentration of acrylic acid monomer unit of PAA*

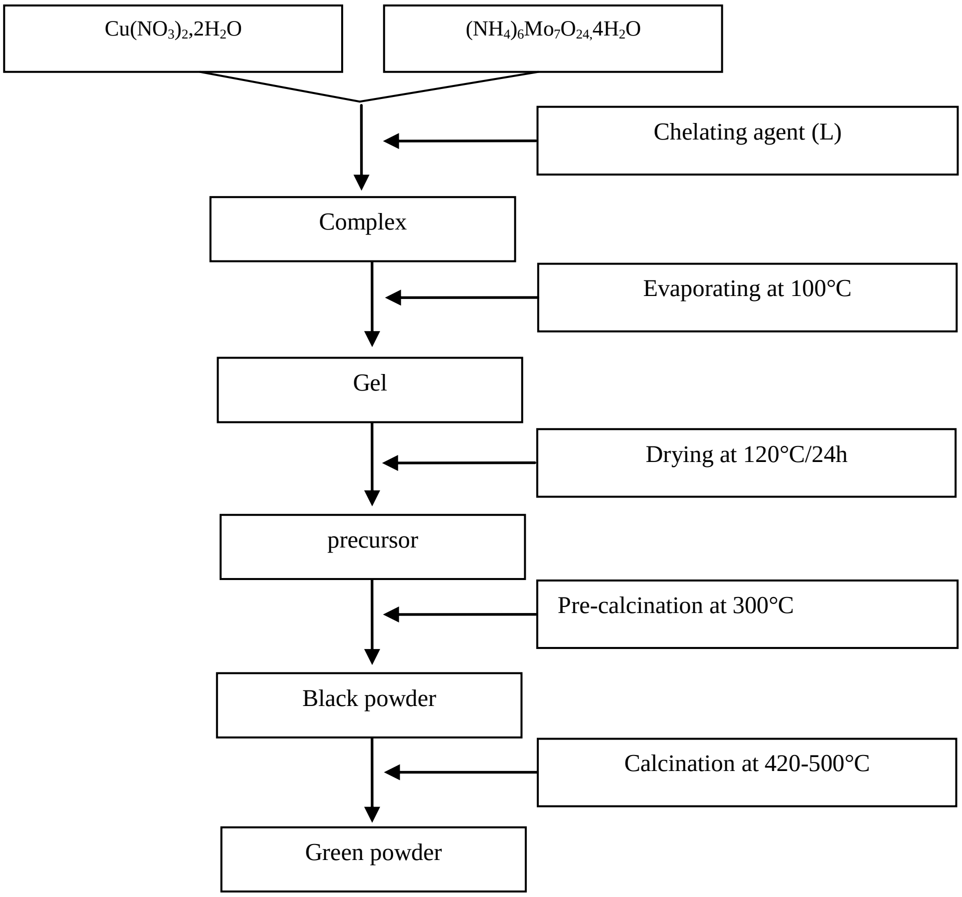

Figure1: Flowchart of the synthesis of $CuMoO_4$ powder

The thermal decomposition of the precursors was studied by thermogravimetric analysis (SETARAM TAG 1750). The phase existing in the particles after heat-treatment was identified by X-ray diffraction (Brucker AXS D4, λCuK_α=1.5418 Å). Scanning (JEOL JSM 6400) and transmission (JEOL 1011) electron microscopies were used to observe and to analyze the morphology and the particle size of the powders. Specific surface areas were determined using a BET (Micrometrics Flowsorb II 2300).

3. Results and discussion

The thermosgravimetric curves of the precursors performed in air were very different and revealed several decomposition steps (fig. 2). It is found that the temperature of the end of decomposition is decreased according the sequence citric acid (P_{CA}), glycine (P_{Gly}), and polyacrylic acid (P_{PAA}). The mass loss and the temperature of the end of decomposition are given in Table 2.

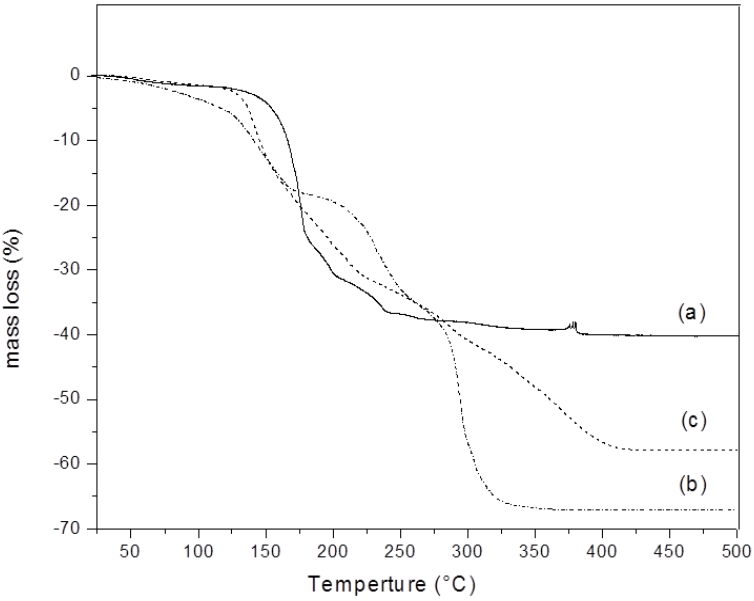

Figure 2: Thermogravimetric analysis of the precursors P_{Gly}(a), P_{PAA}(b) and P_{CA}(c)

Table 2: Temperature of the end of decomposition and mass loss of the different phenomena determined by TGA

Precursor	*Temperature (°C)*	*mass loss(%)*
P_{Gly}	*380*	*40.3*
P_{PAA}	*350*	*67.0*
P_{CA}	*420*	*58.6*

The X-ray diffraction patterns of the precursors calcined at various temperatures (Fig.3) show that the formation of molybdate α-$CuMoO_4$ depends on the nature of the chelating agent used. Indeed, after heat treatment at 420°C for 2 h, the X-ray diffractogram of P_{CA} only contains the characteristic peaks of copper molybdate α-$CuMoO_4$ (JCPDF 073-0488) whereas, the X-ray diffractograms of calcinations the residue of P_{PAA} and P_{Gly} precursors contain, in addition to the characteristic peaks of the α-$CuMoO_4$, peaks of low intensity attributed to molybdenum oxide MoO_3 (JCPDS076-1003) and copper oxide CuO (JCPDS 074-1021). A calcination at 500°C for 6 hours is necessary to make disappear these parasitic phases. The α-$CuMoO_4$ powders obtained, by calcination of the precursors at different temperatures were examined by scanning electron microscopy (Fig. 4). The powder obtained with the precursor P_{Gly} consists of porous agglomerates (Fig. 4-a). This porosity comes from the rapid departure of the gaseous products formed during the combustion. The agglomerate size varies between 5 and 40 μm, the primary particles appears to have merged thus revealing a certain degree of sintering. The primary particle size is between 300 and 600 nm and the specific surface area is close to 3.5 m^2 / g.

The precursor prepared with polyacrylic acid P_{PAA} (Fig. 4-b) leads to a powder formed of agglomerates more or less voluminous. These later are constituted of fine mono-crystalline grains, which size does not exceed 500 nm. The specific surface area is about 6.3 m^2/g (table 3).

In the case of molybdate prepared from citric acid P_{CA} (Fig. 4-c), the agglomerates forming the powder are less dense and trained elementary grains mono-crystalline, of size between 100 and 200 nm. The specific surface area of these particles is about 8.3m^2/g (table 3).

The crystallite sizes (calculated according to the Scherrer equation [16] from the broadening of X-ray diffraction peaks) of different powders are of the same order of magnitude as sizes of grains measured on TEM micrographs (table 3). In this study, it emerges that the powder obtained with citric acid has the narrowest particle size distribution.

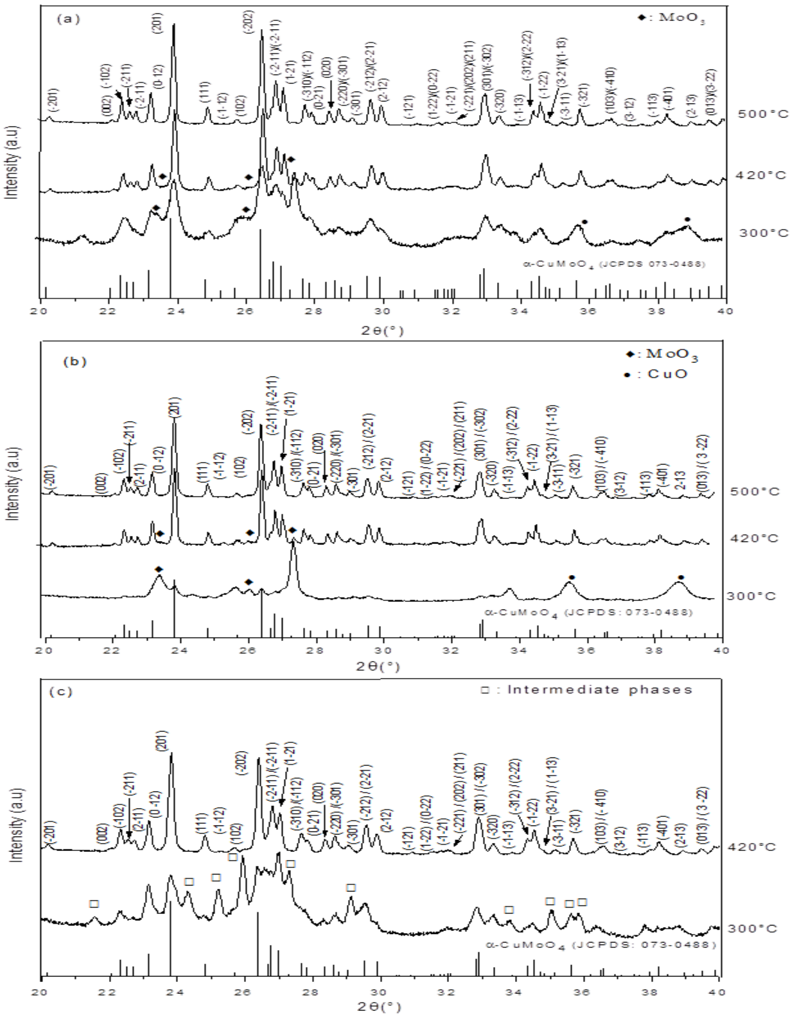

Figure 3: XRD patterns of precursors treated at different temperatures: (a) P_{Gly} treated at 300, 420 and 500°C, (b) P_{PAA} treated at 300, 420 and 500°C, and (c) P_{CA1} treated at 300 and 420°C.

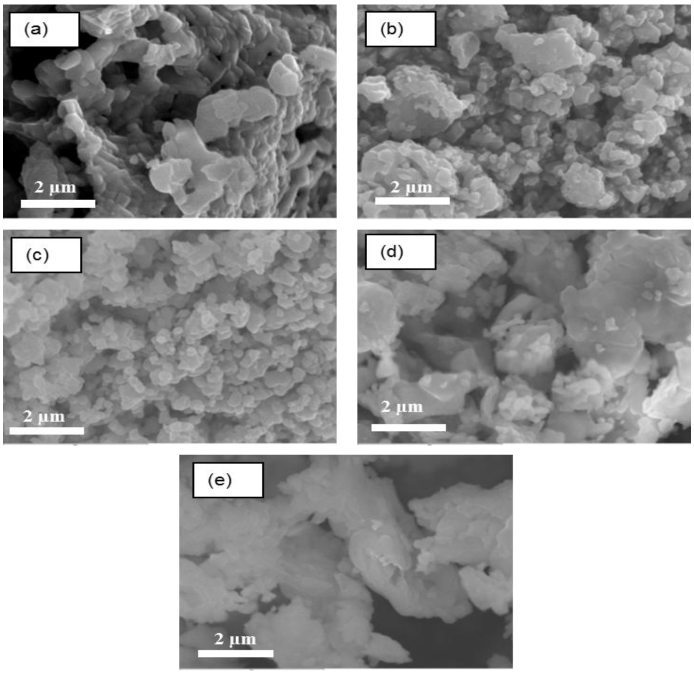

Figure 4. SEM micrographs of $CuMoO_4$ powders obtained from different precursors: (a) P_{Gly}, (b) P_{PAA}, (c) P_{CAS1}, (d) P_{CAS4} and (e) P_{CAS7}.

To investigate the influence of pH on the morphology of the powders obtained from P_{CA}, we have prepared precursors at different pH values. These precursors are named P_{CAi} (i is the pH, i= 1, 4 and 7). The SEM micrographs (Fig.4) show that the α-$CuMoO_4$ powders obtained by calcination of precursors P_{CAi} are formed of irregular shaped agglomerates. The size of these agglomerates increases dramatically with pH. The examination by transmission electron microscopy (Fig.5) indicates these agglomerates are constituted of elementary grains with more or less elongated shape. The TEM micrographs show that the grain size increases with pH and the specific surface area decreases (table 3).

Table 3: Morphological characteristics of $CuMoO_4$ powders

Precursor	*Temperature (°C) /time*	Crystallite size *DRX*(nm)*	Grain size *MET (nm)*	*BET (m^2/g)*
P_{Gly}	*500°C/6h*	*325*	*300-600*	*3.2*
P_{PAA}	*500°C/6h*	*218*	*200-500*	*6.3*
P_{CA1}	*420°C/2h*	*103*	*100-200*	*8.3*
P_{CA4}	*450°C/6h*	*125*	*150-300*	*5.9*
P_{CA7}	*450°C/6h*	*156*	*350-550*	*5.3*

* Size of crystallites calculated from XRD peaks broadening

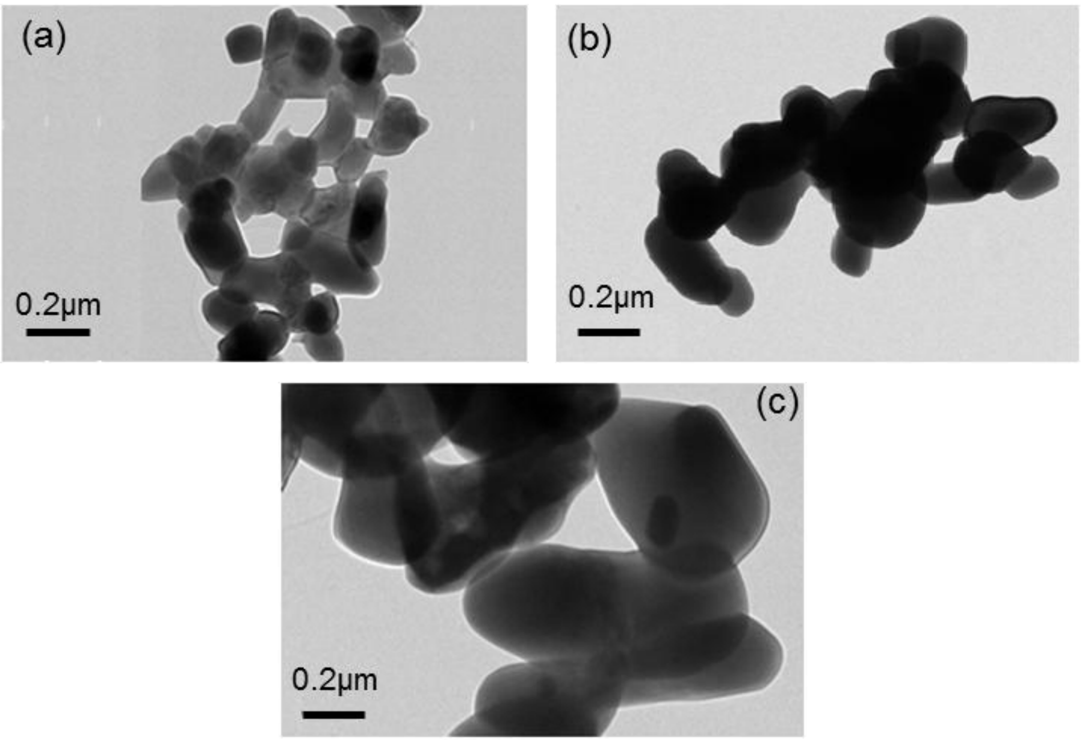

Figure 5: TEM micrographs of $CuMoO_4$ powders obtained from different precursors: (a) P_{CA1}, (b) P_{CA4} and (c) P_{CA7}.

Conclusion

The copper molybdate α–$CuMoO_4$ was obtained by pyrolysis, at temperatures ranging from 420 to 500°C, of precursors prepared with different chelating agents (glycine, poly acrylic acid and citric acid). The morphology and the particle size of obtained powder depend on the complexing agent used. Indeed, the grain size is increased following the sequence citric acid (0.1-0.2 µm), poly acrylic acid (0.2-0.5µm) and glycine (0.3-0.6 µm). The effect of the pH on the formation of $CuMoO_4$ with citric acid was studied. The particle size decreases with pH.

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