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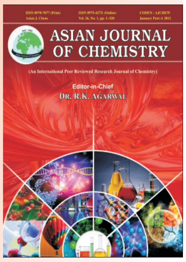

General Synthesis and Phase Control of Different Copper Molybdate Structures†

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Different phases and morphologies of copper molybdate have been successfully prepared *via* a simple hydrothermal process. The pH and reaction tempertaure of the solution have a crucial influence on the synthesis and shapes evolution of the final copper molybdate products. At the same time, surfactants PEG-400 and PEG-20000 have also been used to control the formation of copper molybdate.

Keywords: Copper molybdate, Hydrothermal method, pH, PEG.

INTRODUCTION

Polymetallic oxygen sour salt (POMS) included with the polymetallic oxygen sour salt (isopoly anion) and heteropoly acid metal salt (heteropoly anion). Berzelius reported the first polymetallic oxygen sour salt $(NH_4)_3PMo_{12}O_{40-n}H_2O$ in 1826[1]. Metal molybdate belongs to a branch of the polymetallic oxygen sour salt. Molybdates has a potential application in various fields, such as in photoluminescence, catalysis, magnetic properties and humidity sensor[2-5]. Most previous approaches to obtain molybdates need harsh reaction conditions and very high temperature, such as solid-state reaction at 1000 ºC[6]. Recently, increasing interests have been focused on the formation of metal molybdate, such as Yu group has reported a general method for hydrothermal synthesis of a family of molybdate nanorods/nanowires such as $Ag_6Mo_{10}O_{33}$ and $Fe_2(MoO_4)_3$[7,8].

In this paper, we report systematically on how to selectively synthesize a family of copper molybdate with well defined nanostructures and high yield by a simple hydrothermal approach. The influence of pH, temperature, reaction time, growth mechanism and surfactant PEG on the phase transformation was discussed.

EXPERIMENTAL

All chemicals used in our experiments were purchased and used as received without further purification. In a typical procedure, 1 mmol of $Na_2MO_4 \cdot 2H_2O$ was dissolved in 15 mL distilled water and 1 mmol of $CuSO_4 \cdot 5H_2O$ was dissolved in 15 mL deionized water, respectively (the mole ratio of Mo to metal is 1.0). Then, the $Na_2MO_4 \cdot 2H_2O$ solution was slowly added into the $CuSO_4 \cdot 5H_2O$ solution under magnetic stirring to form a homogeneous solution at room temperature. The pH was adjusted to a specific value using $NH_3 \cdot H_2O$ (25 wt %) or HNO_3 (1 mol L^{-1}) solution. The resulting precursor solution was transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and maintained at 180 ºC for 12 h, then allowed to cool to room temperature in air. After the reaction, the solution was filtered, washed by deionized water and absolute ethanol, respectively and dried in a vacuum at 80 ºC for 6 h.

Characterization: X-Ray powder diffraction patterns (XRD) of the products were obtained on a Japan Rigaku Dmax-gA rotation anode X-ray diffractometer equipped with graphite monochromatized CuK_α radiation ($\lambda = 1.54178$ Å). The field-emission scanning electron microscope (FE-SEM) measurements were carried out with a field-emission microscope (JEOL, 7500B) operated at an acceleration voltage of 10 kV.

RESULTS AND DISCUSSION

Hydrothermal treatment of a amorphous particulate dispersion made of $CuSO_4 \cdot 5H_2O$ and $Na_2MO_4 \cdot 2H_2O$ at 180 ºC for 12 h led to the formation of pure phase $CuMoO_4$ with well crystallinity as shown in Fig. 1. All reflection peaks of the different products prepared at pH 5 can be easily indexed as $CuMoO_4$ (JCPDS Card No.: 85-1529).

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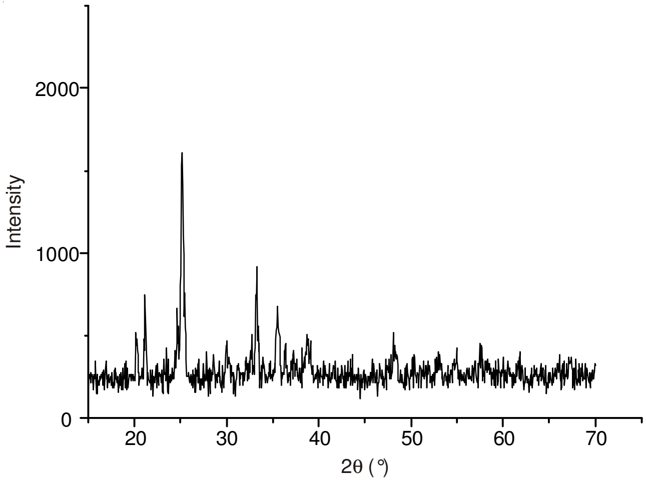

Fig. 1. XRD pattern of the as-synthesized copper molybdate

As shown in Fig. 2, FE-SEM images of the $CuMoO_4$ show different morphologies. Fig. 2a,b shows that the product of $CuMoO_4$ is in a form of micro-spheres with a diameter of about 20 μm and these micro-spheres are composed of packed nanoflake as shown in a magnified SEM image in Fig. 2c,d.

The pH of the precursor solution has an important effect on both the formation of the molybdate phase in the synthetic process. The controlled experiments were carried out to investigate the influence of pH on the synthesis of $CuMoO_4$ and the phase evolution.

A highly supersaturated solution was adopted and amorphous fine particles acted as the precursor for the synthesis of crystallized $CuMoO_4$ architectures. At first, the formation of tiny crystalline nuclei in a supersaturated solution occurred and then followed by crystal growth. Because of different solubility between relatively bigger particles and smaller particles according to the well-known Gibbs-Thomson law the bigger particles grew at the cost of the smaller ones[9].

The alignment of thin flakes in the radial way could fit aligned with the electric line principles as proposed previously in the mineralization of metal carbonates and hydroxyapatite[10-12].

Hydrothermal treatment of a amorphous particulate dispersion made of $CuSO_4{\cdot}5H_2O$ and $Na_2MO_4{\cdot}2H_2O$ at 180 ºC for 12 h, prepared at pH 1, led to the formation of pure phase MoO_3 with well crystallinity as shown in Fig. 3. All reflection peaks of the different products can be easily indexed as MoO_3 (JCPDS Card No.: 85-2045).

Hydrothermal treatment of a amorphous particulate dispersion made of $CuSO_4{\cdot}5H_2O$ and $Na_2MO_4{\cdot}2H_2O$ at 180 ºC for 12 h, but prepared at pH 11, led to the formation of pure phase CuO with well crystallinity as shown in Fig. 4. All reflection peaks of the different products can be easily indexed as CuO (JCPDS Card No.: 80-0076).

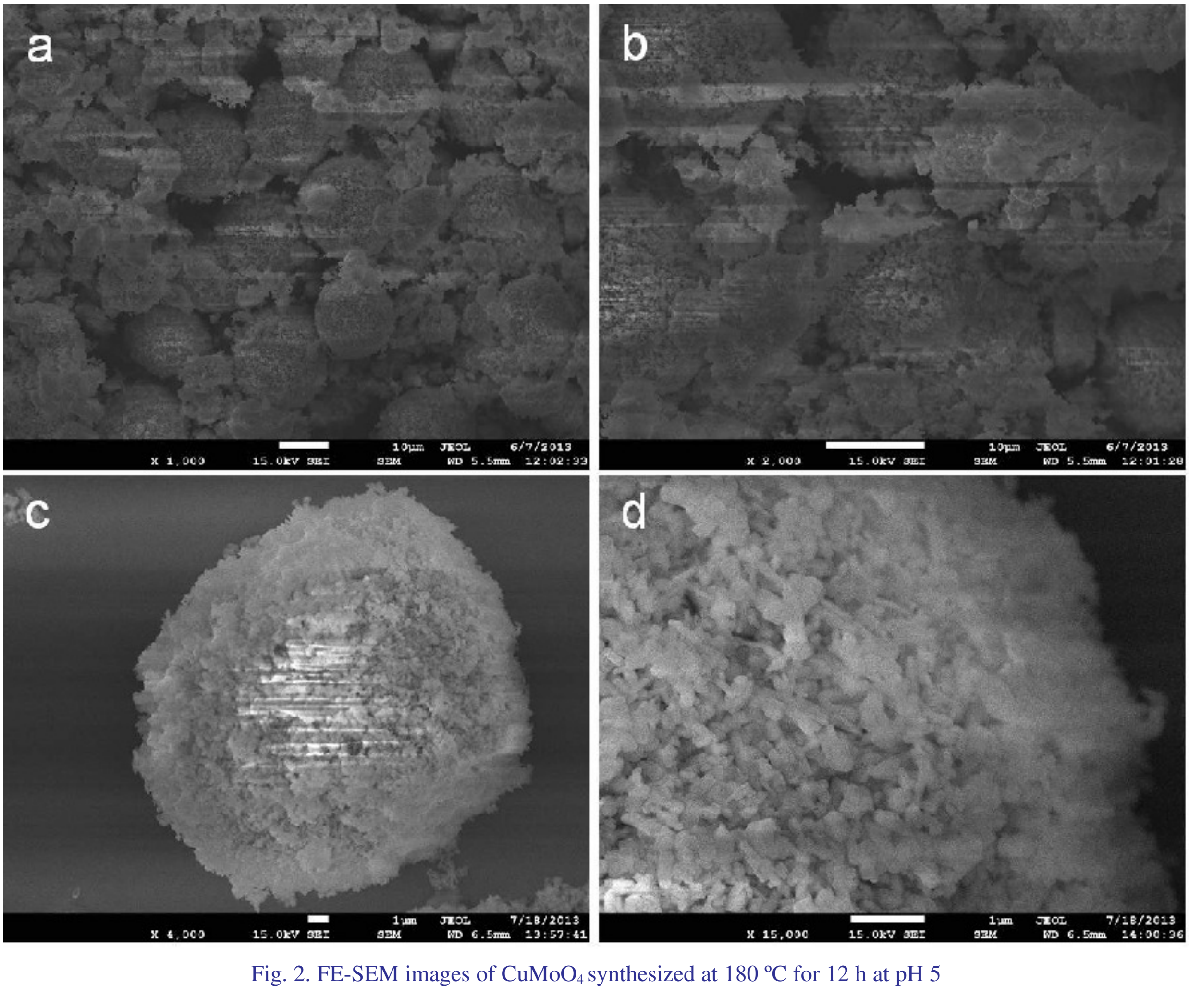

Fig. 2. FE-SEM images of $CuMoO_4$ synthesized at 180 ºC for 12 h at pH 5

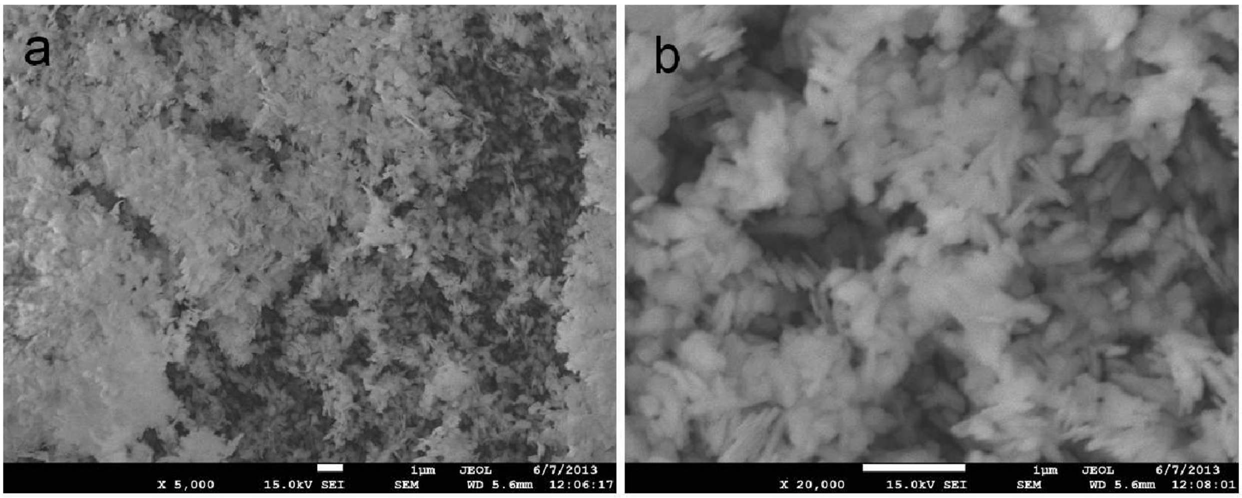

Fig. 5. FE-SEM images of $CuMoO_4$ synthesized at 180 °C for 12 h at pH 5

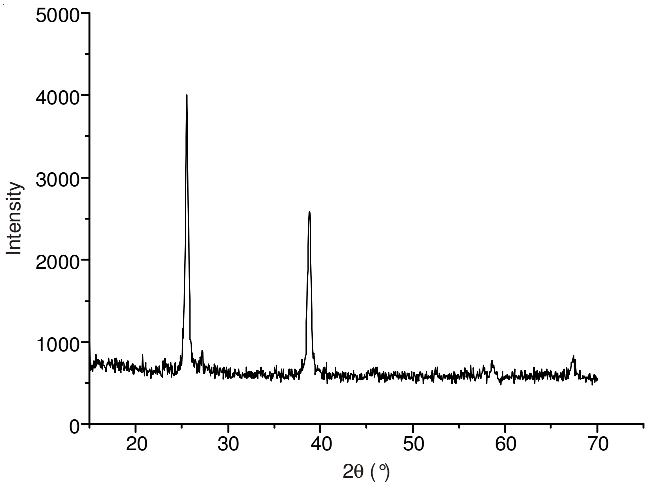

Fig. 3. XRD pattern of the as-synthesized MoO_3

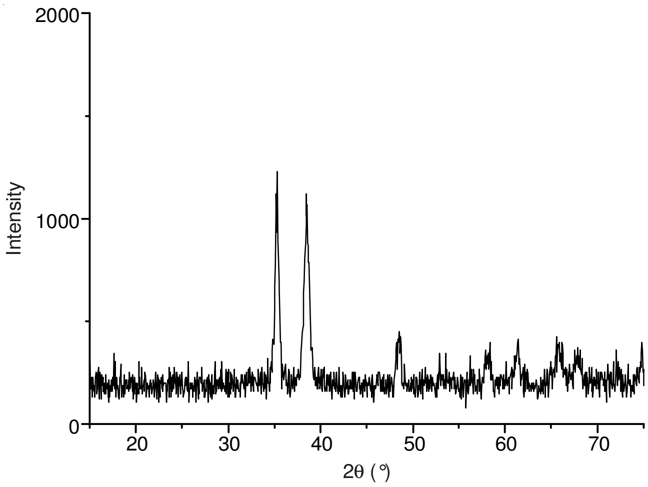

Fig. 4. XRD pattern of the as-synthesized CuO

The volume ratio of PEG-20000 to water has some effects on the morphologies of copper molybdate.

FE-SEM images in Fig. 5 shows the morphologies of $CuMoO_4$ particles. Fig. 5a shows that the obtained $CuMoO_4$ is high yield. Similar rod-like CuMoO4 particles are observed and they have a diameter of 1 μm and lengths of 10 μm as shown in Fig. 5b.

Conclusion

$CuMoO_4$ was obtained *via* a simple hydrothermal process with micro-spheres and the surfactant of PEG-20000 was used as a crystal growth modifier for effectively controlling growth. The morphologies have been changed with the presence of PEG-20000 and the uniform Submicron of $CuMoO_4$ was obtained.

ACKNOWLEDGEMENTS

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REFERENCES

1. M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Berlin, (1983).
2. J.C. Sczancoski, M.D.R. Bomio, L.S. Cavalcante, M.R. Joya, P.S. Pizani, J.A. Varela, E. Longo, M.S. Li and J.A. Andrés, *J. Phys. Chem. C*, **113**, 5812 (2009).
3. J.C. Jung, H. Kim, Y.S. Kim, Y.M. Chung, T.J. Kim, S.J. Lee, S.H. Oh and I.K. Song, *Appl. Catal. A*, **317**, 244 (2007).
4. Y. Ding, Y. Wan, Y.-L. Min, W. Zhang and S.-H. Yu, *Inorg. Chem*., **47**, 7813 (2008).
5. J.H. Bi, L. Wu, Y.F. Zhang, Z.H. Li, J.Q. Li and X.Z. Fu, *Appl. Catal. B*, **91**, 135 (2009).
6. H.E. Swanson, M.C. Morris, R.P. Stinchfield and E.H. Evans, *NBS Monogr. (USA)*, **25**, 24 (1963).
7. X. Cui, S.-H. Yu, L. Li, L. Biao, H. Li, M. Mo and X.-M. Liu, *Chem. Eur. J.*, **10**, 218 (2004).
8. Y. Ding, S.H. Yu, C. Liu and Z.A. Zang, *Chem. Eur. J.*, **13**, 746 (2007).
9. J.W. Mullin, Crystallization, Butterworth-Heinemaan, Oxford, edn 3 (1997).
10. H. Cölfen and L.M. Qi, *Chem. Eur. J.*, **7**, 106 (2001).
11. S.H. Yu, H. Cölfen, J. Hartmann and M. Antonietti, *Adv. Funct. Mater*., **12**, 541 (2002).
12. H. Tlatlik, P. Simon, A. Kawska, D. Zahn and R. Kniep, *Angew. Chem. Int. Ed*., **45**, 1905 (2006).