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研究简报

$MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$ 的水热合成及反应时间对其形貌的影响

朱黎霞*,[1] 岳 涛[3] 高世扬[1,2] 夏树屏*,[1]

([1] 中国科学院青海盐湖研究所西安二部, 西安 710043)

([2] 陕西师范大学应用化学研究所, 西安 710069)

([3] 兰州大学化学系, 兰州 730000)

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Hydrothermal Synthesis and the Effect of Reaction Time on Morphology of $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$

ZHU Li-Xia*,[1] YUE Tao[3] GAO Shi-Yang[1,2] XIA Shu-Ping*,[1]

([1] *Xi'an Branch, Institute of Salt Lakes, Academic, Sinica, Xi'an* 710043)

([2] *Institute of Applied Chemistry, Shaanxi Normal University, Xi'an* 710069)

([3] *Department of Chemistry, Laozhou University, Lanzhou* 730000)

Both whisker and nanometer $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$(MOS) were prepared by hydrothermal method at 140℃ for different times, using NaOH and $MgSO_4 \cdot 7H_2O$ as raw materials. The $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$ particles were characterized by powder X-ray diffraction(XRD), thermal analysis(TGA-DSC), infrared spectroscopy (FT-IR), transmission electron microscopy(SEM) and scanning electron microscopy(TEM). The size distribution in whisker-like and nanocrystalline materials are in the range of 10 ~ 50μm and 10 ~ 20nm respectively. The whisker MOS is metastable phase in $MgSO_4$-NaOH-H_2O system at 140℃, whereas nanometer MOS is stable phase.

Keywords: hydrothermal synthesis magnesium oxysulfate morphology

0 Introduction

Whiskers with high aspect ratio have been extensively used as composite materials in alloys, ceramics, cement and plastic[1~5], since they have specific desire properties such as high melting point, low density and high modulus[6]. Magnesium oxysulfate (MOS) compound shows the high crystallinity and aspect ratio to make it a potential reinforcing material for plastics, resin and rubber[7,8]. In past years, $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$ has been synthesized by hydrothermal reaction using magnesium hydroxide and magnesium sulfate as raw materials[9]. In the present paper, we report a new method for synthesis of whisker and nanometer MOS using sodium hydroxide and magnesium sulfate. The objective of this study is to look for a cheaper method of

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* 通讯联系人。E-mail: gsyabc@pub.xaonline.com

第一作者:朱黎霞,女,36岁,在职博士生;研究方向:硼酸盐化学及晶须材料。

preparing μm and nm size products, and to provide an effective way for the comprehensive utilization of the magnesium resources in salt lake.

1 Experimental

1.1 Synthesis of $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$

The $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$(MOS) was prepared by a hydrothermal reaction as described. A mixture of NaOH, $MgSO_4$ (Analytic reagent, Xi' an Chemical Factory, China) and H_2O in the mole ratio of 1: 2: 36 was put in a 2 litre autoclave which was heated and kept at 140℃ from 2 to 24h, after which the autoclave was naturally cooled to room temperature. The product was separated, washed thoroughly with distilled water, absolute alcohol, and finally ether, then stored in a desiccator.

1.2 Analysis

The MOS sample is dissolved in a given excess standard HCl solution which is prepared with azeotropic hydrochloric acid and deionized water, and its concentration is determined by titration with standard borax. Magnesium is titrated by a standard solution of Na-EDTA in an alkaline, pH = 10 buffer solution (ammonium hydroxide + ammonium chloride). SO_4^{2-} is determined by the $BaSO_4$ gravimetric method and OH^- is determined by titrating the excess H^+ with standard NaOH solution. H_2O is determined by difference.

1.3 Characterization

The powder X-ray diffraction data of the synthesized products were obtained using D/MAX-2400 with Cu $K\alpha$ radiation ($\lambda = 1.5418$Å). The IR spectra was recorded by a Pekin-Elmer 683 using KBr pellets. Thermogravimetric analysis(TGA) and DSC were conducted on a NETZSCH-Geratebau STA 449c, in a flow of N_2 with a heating rate of 10℃ · min^{-1}. For crystal morphology and size studies, a scanning electron microscope SEM Hitachi, S-2700 and transmission electron microscope TEM JEM-200CX were used.

2 Results and Discussion

The typical chemical analyses results of the synthesized products: $MgSO_4$: 25.83%, $Mg(OH)_2$: 62.39%, H_2O: 11.79% are in agreement with the theoretical values for $MgSO_4$: 25.83%, $Mg(OH)_2$: 62.58%, H_2O: 11.59%, and correspond to an empirical molar ratio $MgSO_4$: $Mg(OH)_2$: H_2O = 1: 5: 3.

The XRD patterns of MOS samples synthesized at 140℃ for different times (shown in Fig. 1) reveals that the crystallinity and integrity of $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$ is maintained. There is no characteristic diffraction peak of $Mg(OH)_2$. Thus MOS samples prepared here are pure magnesium oxysulfate compound with the composition of $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$. When the MOS is synthesized at 140℃ for 2 ~ 15h, the characteristic peaks of MOS are sharp with narrow half-widths. However, the MOS is prepared at 140℃ for 18 and 24h, the two characteristic double peaks at 22.90° and 22.38° (2θ), 45.14° and 45.68° (2θ) merge into one peak (22.94° and 45.12° respectively), and the half-widths have clearly increased. The relative intensity also changed with reaction time. The $I/I_0 = 100$ peak at $2\theta = 17.28°$ for samples heated for 2 ~ 15h changed to $I/I_0 = 76$ after 24h heating, whereas the peak with $I/I_0 = 50$ at $2\theta = 40°$ for samples heated for 2 ~ 15h became the $I/I_0 = 100$ peak after 24h heating. These results showed that the parti-

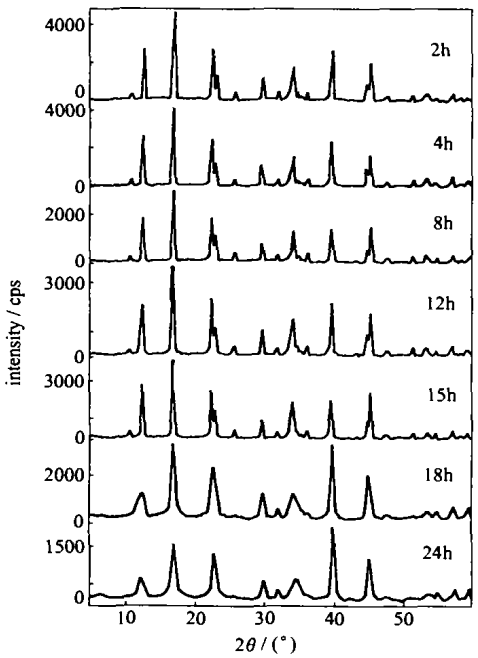

Fig. 1 XRD patterns of MOS samples for different times

cle size of MOS decreased with prolonged reaction time. The crystallite size of sample prepared for 24h is 20nm by calculated Scherrer formula: $D = k\lambda/(\beta\cos\theta)$, where $\lambda = 1.5418$Å, k is a constant, β is the half-width, θ is diffraction angle.

As shown in Fig. 2 the SEM and TEM photographs suggested that when the reaction time is 2, 4, and 8h respectively, the size distribution of MOS is in the range of 10 ~ 50μm, however, by heating in excess of 15h, the structure of the MOS whiskers begin to break up, and after 18h, the MOS crystalline size decreases markedly. From the observed TEM photograph, it have round shape, and their mean grain size is 16nm. These results are agreement with XRD.

We think that whisker MOS is metastable phase in $MgSO_4$-NaOH-H_2O system at 140℃, nanocrystalline MOS is stable phase. For this reason, MOS whiskers broke up with prolonged reaction time. When reaction time was 24h, the products wholly changed into nanocrystalline MOS.

Fig. 3 shows the infrared spectra of MOS in the region 4000 ~ 400cm^{-1}. The main IR absorption peaks for all synthesized MOS are the same, which means that chemical composition of samples are identical. The absorption bands appear at 3656, 3620, 3540, 1119, 817 and 642cm^{-1}. The IR absorption spectra of MOS

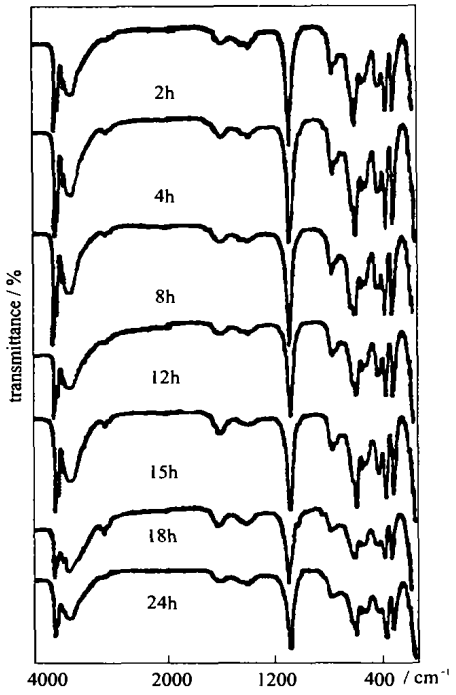

Fig. 3　IR spectra of MOS samples

can be assigned as follows: 3656, 3620 and 3540 cm^{-1} bands are attributed to O-H bond stretching vibration, while those at 1119 and 642cm^{-1} are attributed to the SO_4^{2-} stretching vibration.

The TGA curve of MOS (Fig. 4) can be divided into two stages. The first one occurs from ~148 to ~360℃ is attributed to the loss of free water

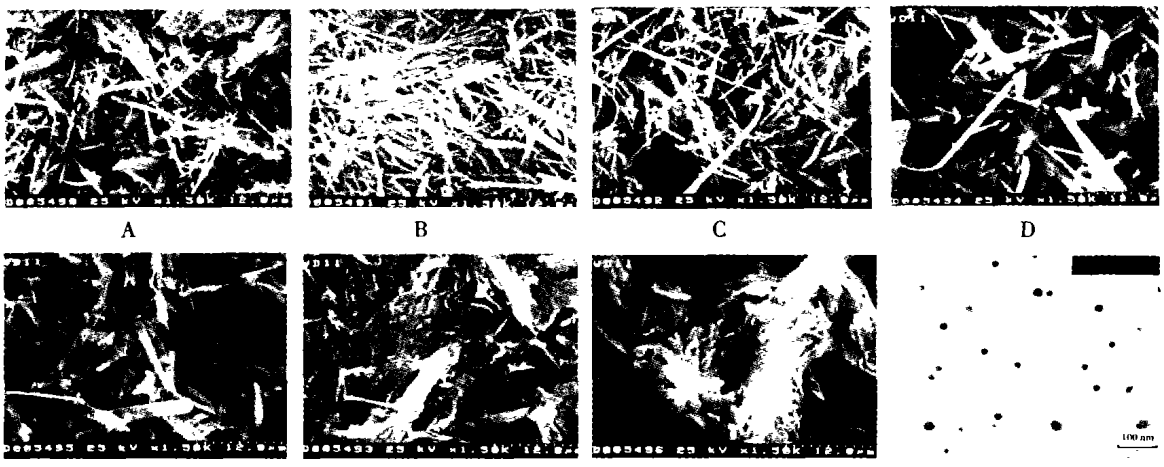

Fig. 2　SEM and TEM of synthesized MOS samples at 140℃ for different times
A: SEM for 2h; B: SEM for 4h; C: SEM for 8h D: SEM for 12h;
E: SEM for 15h; F: SEM for 18h; G: SEM for 24h; H: TEM for 24h

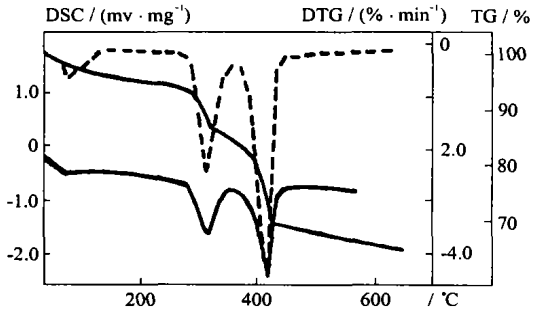

Fig. 4 TG-DTG-DSC curves of MOS

molecules, and the observed weight-loss(11.47%) is in good agreement with calculated value (11.59%). The second stage between ~360 to ~680℃ would be due to the release of five water molecule coming from the reaction $MgSO_4 \cdot 5Mg(OH)_2 \rightarrow MgSO_4 + 5MgO + 5H_2O$. The observed weight- loss(19.75%) in this stage compares well with calculated value 19.31%. There appear two endothermal peaks on the DSC curve at 314.6 and 420.0℃ respectively. The ΔH values were determined to be 22774.94kJ · mol^{-1} and 38987.62kJ · mol^{-1} respectively.

3 Conclusions

From the above results, it may be concluded that the whisker MOS is metastable phase in $MgSO_4$-NaOH-H_2O system at 140℃, whereas the nanometer MOS is stable phase. Nanocrystalline $MgSO_4 \cdot 5Mg(OH)_2 \cdot 3H_2O$ was prepared by the hydrothermal reaction at 140℃ for 24h, its size distribution is in the range of 10 ~ 20nm and the mean size is 16nm.

References

[1] Albert P. L. *Whisker Technology*, John Wiley & Sons Inc: New York, **1970**, p1.

[2] Hoshino S., Tanaka H., Kimura T. *J. Plastics Engineering*, **1983**, **39**, 37.

[3] Yoshida M., Takeuchhii S. *J. Applied Composite Materials*, **1999**, **8**, 259.

[4] Tsutsui K., Ueno K., Kagawa A. *EP* 382229, **1990**.

[5] Asagami O., Igarashi H. *JP* 10297951, **1998**.

[6] Brenner S. S. *Factors Influencing the Strength of Whiskers in Fiber Composite Materials*, American Society for Metal: New York, **1965**, p11.

[7] Watanabe K. *JP* 1036586, **1998**.

[8] Nomura M., Wada K. *EP* 319924, **1989**.

[9] Shuji Y., Fumio S., Masahara K. *JP* 01126218, **1989**.