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RESEARCH ARTICLE

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Preparation of nanometer MgO by sol-gel auto-combustion

Abstract Nanometer MgO was prepared via a sol-gel auto-combustion technique using magnesium nitrate as raw material and citric acid as chelating agent. IR spectra of the dried gel were used to investigate the structure of the precursors. By studying the different TG curves of magnesium citrate gel prepared by different methods, we found that a combustion process occurred and the nitrate ions acted as an oxidant in the combustion process. TEM photographs of synthesized powders from the sol-gel auto-combustion showed that the crystallites were uniform in size. In addition, the XRD pattern of this sample showed that the particle size was 8.9 nm. The BET curves, in turn, showed that the specific surface of the sample was 26.34 m^2/g. The mechanism of the frothing process in restraining agglomeration is discussed.

Keywords sol-gel auto-combustion, nanometer magnesia, citric acid

1 Introduction

Many methods have been developed to prepare nano-scale MgO. Generally, according to the state of the starting material, they can be divided into three kinds: the solid-phase method, the gas-phase method and the liquid-phase method. The solid-phase method involves a mechanical method and a solid state reaction. However, the mechanical method cannot obtain particles smaller than 100 nm, and the particle sizes obtained from the solid state reaction are not uniform.

The gas-phase method includes physical and chemical vapor deposition methods. With such a method, the grain size can be well controlled and large-scale production can be achieved. Unfortunately, it has limitations such as difficulty in gathering the product, expensive equipment, energy waste, and environmental pollution. Therefore, it would be difficult for it to achieve the requirements of industrial application. The liquid-phase method, which is widely adopted, involves direct-precipitation, co-precipitation, sol-gel and so on. The product prepared by direct-precipitation has large grain size and wide particle size distribution. The precipitate obtained via co-precipitation is uniform and compact, which is easy to wash and filtrate. In addition, nanoparticles with small average diameter and good uniformity can be obtained, but the production rate is low. The sol-gel technique is a method to prepare oxides or other nanometer materials using metal organic or inorganic matter as raw materials. The microstructure of product can be better controlled in the initial stage of the process and particle size is homogenous [1]. Recently, the sol-gel technique has been gradually combined with auto-combustion, which has extensive applications in the synthesis of nano-phase materials, especially in nano-scale oxides.

Sol-gel auto combustion is a novel method of preparing nanometer materials. Combustible organics such as citric acid, urea, glycine and nitrate are used as raw materials, gel is formed after continuous stirring and exhibits self-propagating combustion behavior. At a certain ignition point, the gel will burn in a self-propagating combustion manner until it completely burns out to form fluffy powders, which is called sol-gel auto combustion [2].

The combustion can be considered a thermally induced redox reaction. The energy from the exothermic reaction between oxidant and reductant can be high enough to form nanometer particles which mingle with organic compounds decomposed from the raw material and need further heat treating [3].

Here, we will report the synthesis of nanometer MgO using the sol-gel auto combustion technique in which magnesium nitrate and citric acid act as chelating agent, and also a comparison study with the product prepared using the traditional sol-gel technique.

2 Experimental

Citric acid was added to a 0.4 mol/L solution of $Mg(NO_3)_2$ (magnesium nitrate) to make the molar ratio of citric acid

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to nitrates 4:1. A small amount of ammonia was added to the solution to adjust the pH value to about 4, then the solution was evaporated at 80°C in a thermostatic water bath followed by drying at 120°C in a vacuum oven, until it turned into dry gel. The dried gel was precalcined at 350°C for 1.5 h, and then calcined at 600°C for 3 h.

In the other method, analytically pure MgO was used as raw material and chelated with citric acid, and then the same preparation process as above was followed except for the auto-combustion, which did not take place. This is a conventional sol-gel technique and the aim is to compare the results with sol-gel auto combustion.

3 Characterization of nanometer MgO and precursor

Infrared spectra (IR) was used to study the components of the gel precursors by the KBr pellet method. Dried gels were characterized via thermogravimetry (TG) at a heating rate of 10°C/min and a flow rate of 10 mL/min under air atmosphere; the average crystallite size of the sample was determined using a Rigaku D/Max-RD X-ray with Kα radiation. Transmission electron microscopy (TEM) was used to observe the microstructure of the sample. The surface area and porosity of the sample were determined by the Dubinin method, from nitrogen absorption data obtained at low temperature (77 K) by a standard volumetric procedure.

4 Results and discussion

4.1 IR spectrum of the precursor

Figure 1 shows the IR spectrum of the dried gel. It can be clearly seen from the figure that dried gel shows an absorption band at about 3420 cm^{-1}, corresponding to the O–H group. The appearance of the characteristic band of O–H indicates that the acidic O–H group in the citric acid structure did not take part in the reaction. The bands at 1420 cm^{-1} and 1617 cm^{-1}, which can be assigned to the symmetric and asymmetric stretching vibration absorption of carbonyl, were moved to a lower wavenumber due to the formation of magnesium citrate [4].

The IR spectra of the dried gels and as-burnt powders are generally used to investigate the chemical and structural changes that take place during the combustion process and to reveal the mechanism of self-propagating combustion. In the typical IR spectra of dried nitrate gel the characteristic absorption bands of NO_3^- ion exist but disappear in the IR spectra of the powders after combustion. Due to the fact that the NO_3^- ion played a very important role in this reaction, TG curves were used in this work to investigate the mechanism of the self-propagating combustion. $Mg(NO_3)_2$ and MgO were used respectively as raw material and chelated with citric acid, and their corresponding dried gels were characterized via TG.

Figure 2 shows the TG plot of the precursor prepared by MgO and citric acid. Figure 3 shows the TG plot of the precursor prepared by $Mg(NO_3)_2$ and citric acid.

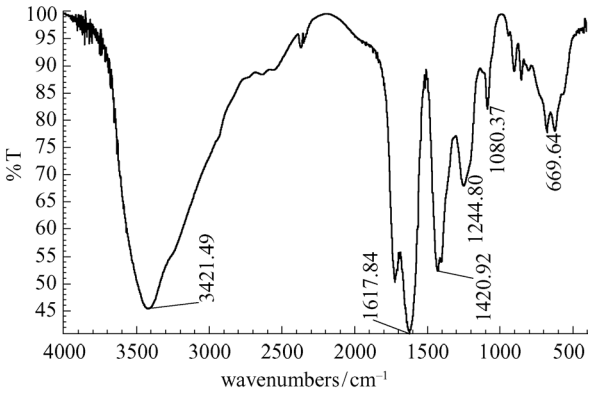

Fig. 1 FT-IR of magnesium citrate

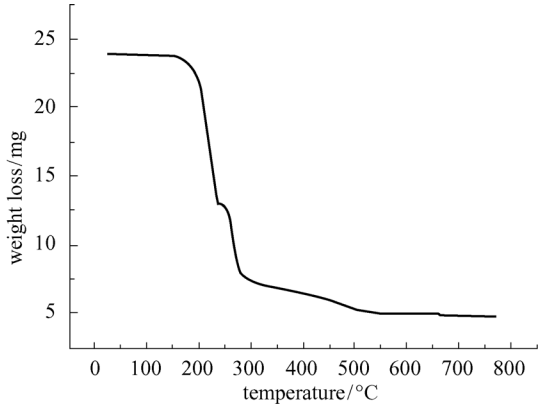

Fig. 2 TG curve of magnesium citrate without auto combustion

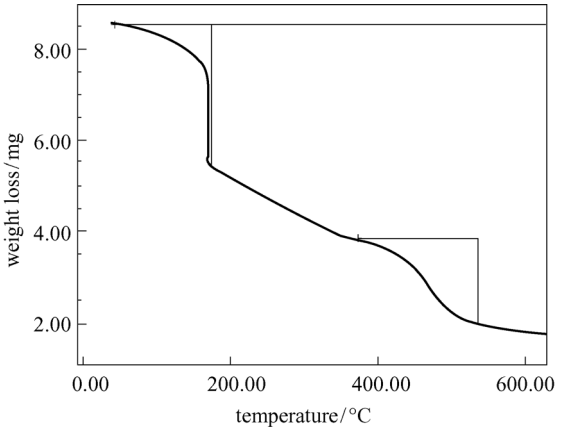

Fig. 3 TG curve of magnesium citrate with auto combustion

The decomposition of the dried gel precursor can be concluded as follows: According to Fig. 2, firstly, the weight loss that occurred from room temperature to 250°C was about 47%, which corresponded to the precursor dehydration, the decomposition of the citric acid residual in the dried gel, and the loss of adsorbed water. Secondly, the dehydrated precursor was decomposed as carbon, water, a few carbon monoxides and metal oxide accompanied with much heat. The temperature range was 250°C–300°C with a 24% weight loss. The third step was the burning of the remaining carbons with 7% weight loss occurring in the range of 300°C–550°C.

A comparison between the two TG curves indicates that there was a linear drop in Fig. 3 starting from 180°C, which did not appear in Fig. 2. It was proved that the combustion indeed occurred and rapidly propagated at about 180°C, the oxidation-reduction reaction took place and NO_3^- acted as oxidant, and when the dried gel was ignited at that point, the combustion rapidly propagated forward until all the gels were completely burnt out to form fluffy powders with yellowish-brown color. Now the nanometer MgO particles were already formed and enwrapped by the organic compound, which was not decomposed completely. The second decomposition lasted to about 350°C, and the third weight loss took place in the range of 350°C–550°C. In our experiment, an appropriate way of heat treatment was selected according to the TG curves as follows: the dried gel was precalcined at 350°C for 1.5 h, and then calcined at 600°C for 3 h to remove carbon.

4.3 Factors influencing the particle size of MgO

4.3.1 Heat treatment

It was observed in a prior experiment that the product calcined directly at high temperature was impure and agglomerated with a mottled appearance. The appropriate way of heat treatment was selected according to the TG curves. The dried gel was firstly pre-calcined at 350°C for 1.5 h, during which the carbon powders would mingle with some residual organics, then the temperature was raised to 600°C and the powders heated for 3 h. The pores formed by the combustion of the carbons had a positive effect in controlling agglomeration. The magnesia sample prepared by this heat-treatment method was white, fluffy and porous. Compared with the gel precursor, the product exhibited obvious expansion and high specific surface.

4.3.2 The influences of pH value and the molar ratio of citric acid to nitrate

In the study on the influence of the molar ratio of citric acid/nitrate, the product was agglomerated as the molar ratio of citric acid to nitrate was smaller than 3, while fluffy and porous powders were obtained when the molar ratio was 4. When pH value was higher than 4, a crystalline phase identified to be NH_4NO_3 appeared from the XRD patterns [6]. So we inferred that the effect of ammonia was not only to adjust the pH value but also to form NH_4NO_3, which can liberate gases such as NO, NO_2, and O_2. The more gases liberated, the greater the removal of the thermal energy which can accelerate the growth of particles. It was helpful to reduce the particle size [7]. In conclusion, the pH was chosen to be 4, and the molar ratio of citric acid to nitrate was 4.

4.3.3 Grain size and specific area

Figure 4 and Fig. 5 show the TEM micrographs of the MgO samples. The sample shown in Fig. 5 was prepared by the traditional sol-gel technique; the sample shown in Fig. 4 was prepared by sol-gel auto combustion. It can be observed from Fig. 4 that the sample prepared by sol-gel auto combustion is uniform in size and the average size is smaller than 10 nm with a narrow size distribution, whereas the product obtained via the conventional sol-gel technique exhibits relatively large and varied grain sizes.

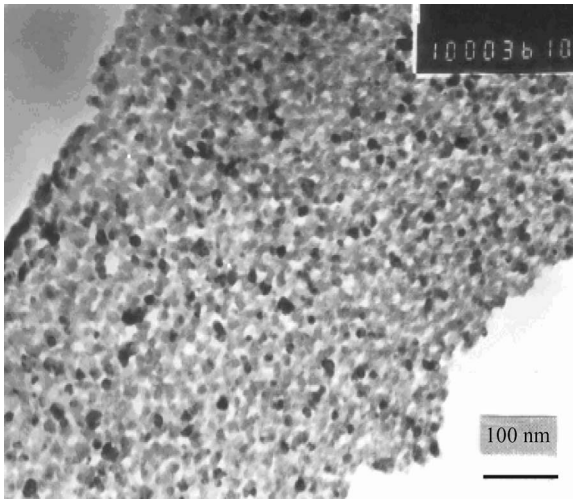

Fig. 4 TEM images of MgO from sol-gel auto-combustion

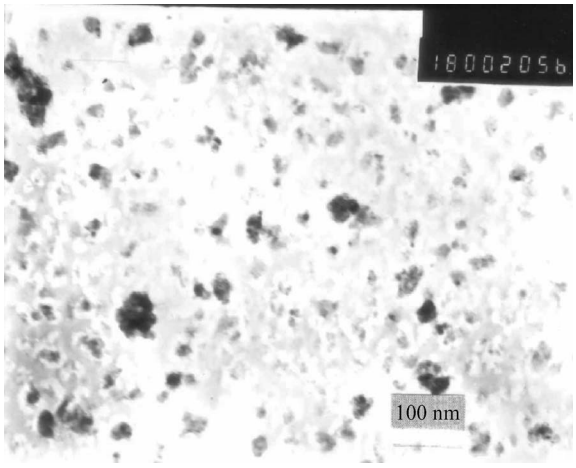

Fig. 5 TEM images of MgO from sol-gel

Figure 6 shows the XRD pattern of the sample prepared by sol-gel auto combustion. The crystallite size of as-burnt powders was measured as 8.9 nm via the well-known Scherrer equation, and the strong and sharp peaks indicate the high degree of crystallization. The nitrogen adsorption-desorption isotherm and the corresponding BJH pore size distribution curve are shown in Fig. 7, from which the specific area of the sample is determined to be 26.34 m^2/g.

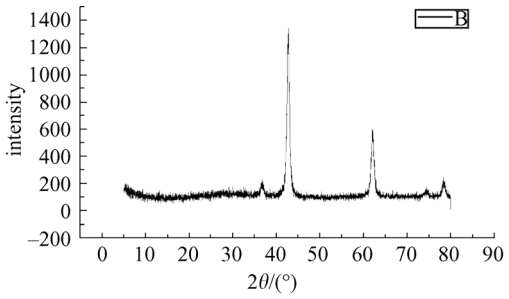

Fig. 6 XRD pattern of magnesia from sol-gel auto-combustion

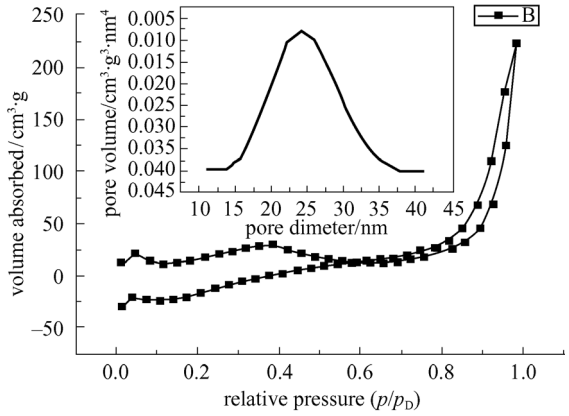

Fig. 7 Nitrogen adsorption-desorption isotherms for MgO Inset: Corresponding Barret-Joyner-Halenda(BJH) pore size distribution curve determined from the N_2 desorption isotherm

4.4 Frothing process

After being dried in a vacuum oven at 120°C, the gel is crisp, poriferous and has obvious expansion character due to the water and carbon dioxide decomposed from citric acid. This is identified as a frothing process [8]. The pores obtained in this process play a role in preventing the close approach of the particles.

The formation of hard agglomerates was attributed to non-bridging hydroxyl groups which could bond to metal ion on the particle surface. When calcined, further dehydration led to the formation of an actual Mg–O–Mg chemical bond between the close contacting powder particles yielding hard agglomeration [9]. The frothing process can effectively prevent the formation of chemical bonds between colloidal particles.

$$Mg-OH+HO-Mg \rightarrow Mg-O-Mg+H_2O$$

Otherwise, the synchronous decomposition of a great deal of reactant will destroy the network structure of the gel. Low temperature and complete dehydration caused by the frothing process can reduce this risk and an intermediate of the gel can be obtained with high conversion. It has been reported that the auto-combustion temperature of gel prepared without the frothing process is higher than that of the dried gel prepared with the frothing process, and the higher combustion temperature could result in harder agglomerates [10].

In the frothing process, the formation of the chemical bond Mg–O–Mg was prevented, network structure was preserved, and auto-combustion temperature was lower. All of these could effectively control agglomeration.

Some chemists have emphasized the connection between the frothing process and auto-combustion. In this paper, the chelation between magnesia and citric acid was not an oxidation-reduction reaction and no auto-combustion took place, but the frothing process still occurred when the gel was dried. Therefore, the frothing process is not a characteristic of auto-combustion.

5 Conclusions

By comparing the different TG curves of the MgO samples obtained from two different ways, we can confirm that auto-combustion indeed occurs and NO_3^- ions act as oxidants. Highly dispersed MgO nanoparticles formed during auto-combustion are enwrapped by the organic compounds, which are not decomposed completely. Crystallites with small grain size and homogeneous morphology can be obtained after appropriate heat treating.

Sufficient expansion of the gels at 120°C removes non-bridging hydroxyl groups and breaks down the chemical bonds between particles, so the formation of hard agglomerates can be avoided.

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