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Microwave assisted "coffee effect" synthesis of spherical and porous spherical nano aluminum hydroxide

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Abstract: $AlNH_4(SO_4)_2 \cdot 12H_2O$ was dissolved in the mixture of ethanol and glycol, then spherical and porous $Al(OH)_3$ nanoparticles were synthesized by microwave heating at different temperatures. The products were characterized by XRD and SEM, and the formation process was analyzed by coffee effect.

Key words: microwave heating; coffee effect; controlled synthesis

1. Introduction

Aluminum hydroxide is a kind of inorganic material with small solubility product and difficult to dissolve. In the medical field, it can be used as an antacid [1] and a vaccine adjuvant [2] with excellent application effect, as well as a flame retardant and water purification agent with excellent performance [3,4]. In 1997, physicists Sidney Nagel and Thomas Witten of the University of Chicago published a paper in nature, describing the phenomenon of "coffee effect" formally for the first time [5]. On August 18, 2011, physicists Peter Yunke and yodh of the University of Pennsylvania in the United States thoroughly solved the mystery of "coffee effect". The research paper "looking for the killer of coffee effect, how to suppress coffee effect" published became the cover story of the current Nature magazine [6]. These studies have promoted people's thinking about this effect. In fact, many solutions with solid and small particles will appear similar situation after liquid evaporation [7-9]. In recent years, research on the preparation of nano materials by using coffee effect has begun [10,11]. In this experiment, $AlNH_4(SO_4)_2 \cdot 12H_2O$ was dissolved in ethanol and glycol, and spherical and porous $Al(OH)_3$nanoparticles were synthesized by microwave heating at different temperatures. The products were characterized by XRD and SEM, and the formation process was analyzed by coffee effect.

2 Experiment section

2.1 Reagents

Aluminum ammonium sulfate ($AlNH_4(SO_4)_2 \cdot 12H_2O$, Tianjin yongda chemical reagent development center), ethanol, glycol ($HOCH_2CH_2OH$, Tianjin Fuyu Fine Chemical LTD.), the above reagents are pure.

2.2 Main instruments

Field emission scanning electron microscopy (JEOL JSM-6701F), X - ray diffractometer (Rigaku height III, the Japan's neo-confucianism), electronic balance (JA5003N, Shanghai Fine family), high-speed centrifuge (TG16K - II, east popular instrument), electric blast drying oven (hg101-2a, Nanjing Yingxin Experimental Instrument Co., Ltd.).

2.3 Experimental process

2.3.1 Preparation of Nano-$Al(OH)_3$

Using $AlNH_4(SO_4)_2 \cdot 12H_2O$ to prepare a solution with a concentration of 0.1mol/l, the solution is divided into six parts, each 25ml is placed in a microwave oven, and the temperature is respectively 80 ℃, 100 ℃, 120 ℃, 140 ℃, 160 ℃, 180 ℃ for 3 minutes. It was found that the samples above 120 ℃ produced milky white precipitates, which were dripped on the quartz substrate and dried naturally.

2.3.2 Characterization of specimens

Electron microscope (SEM) characterization: take the emulsion sample from the capillary tube and prepare the sample on the silicon wafer, dry it in the drying oven for 15 hours, spray gold treatment, and then use the scanning electron microscope FESEM (JEOL jsm-6701f) to observe and analyze the size and morphology of the powder particles under the voltage of 5 kV. X-ray diffractometer characterization: the samples were centrifuged and dried. The phase composition of the powder samples was determined by RIGAKU Ultima III type X-ray diffractometer (CuKα as Ray source, Experimental conditions: tube voltage 40 kV, tube current 40 MA), Scanning speed 8 °/ min, scanning range 20-80°.

3. Results and discussions

3.1 Composition of the product

Fig. 1 is the X-ray powder diffraction pattern of the synthesized product. From Fig. 1, it can be seen that the diffraction peaks at 2θ are 18.4 °, 20.5 °, 26.5 °, 36.6 °, 37.5 °, 44.3 °, 50.6 °, 52.2 °, 54.4 ° are consistent with the standard pattern, and the PDF number is 70-2038, which proves that the synthesized material is aluminum hydroxide.

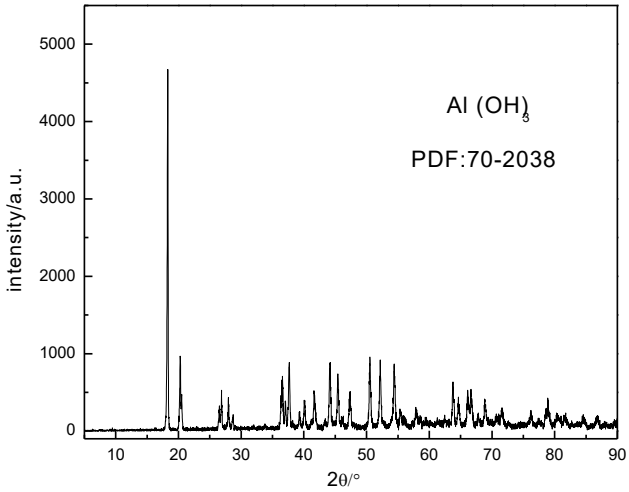

Fig.1 XRD Pattern of the produt

3.2 Thermogravimetric analysis of the product

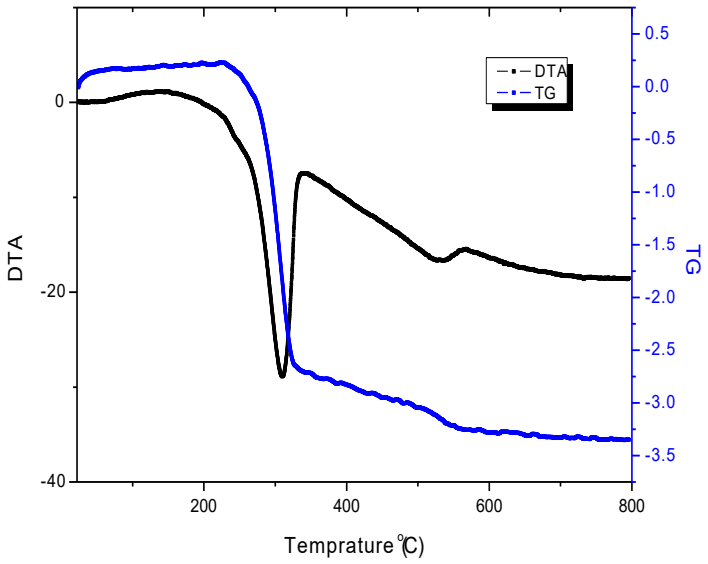

Fig.2 TG-DSC curves of the product

In order to study the decomposition of $Al(OH)_3$ when heated, we have carried out thermogravimetric

analysis with a thermobalance. Fig. 2 is the thermogravimetry differential thermal analysis diagram of the product. It can be seen from the figure that in the TG curve, when the temperature rises to 300 ℃, the curve drops sharply, indicating that the weight loss rate of the sample is 36%, corresponding to the decomposition of $Al(OH)_3$ to generate AlOOH, and when the temperature rises to 520 ℃, the curve decreases, and the weight loss of the sample is obvious. Therefore, it can be concluded that the change of crystal form of the tested sample may occur, that is, the transformation of AlOOH to γ - Al2O3. There are obvious endothermic Valley at about 300 ℃ and 520 ℃ in DTA curve, which indicates that endothermic reaction occurs in this stage. The overall response is as follows:

$$Al(OH)_3 \longrightarrow AlOOH \longrightarrow \gamma\text{-}Al_2O_3$$

3.3 Electron microscope image analysis

Fig. 3 is a scanning electron microscope picture of reaction of 0.15m aluminum ammonium sulfate heated by microwave at 120 ℃. It can be seen from the figure that spherical particles with a diameter of about 60 nm and a relatively uniform size gather together.

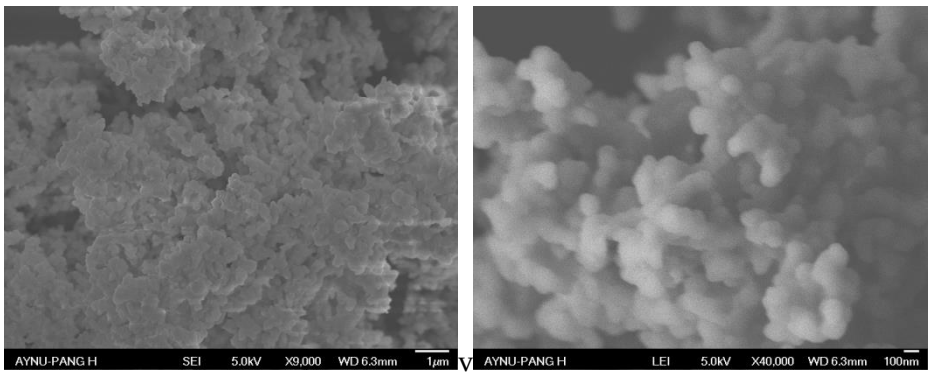

Fig.3 SEM images of the product heated under 120℃

(a：amplified 9000 times, b: amplified 40000 times)

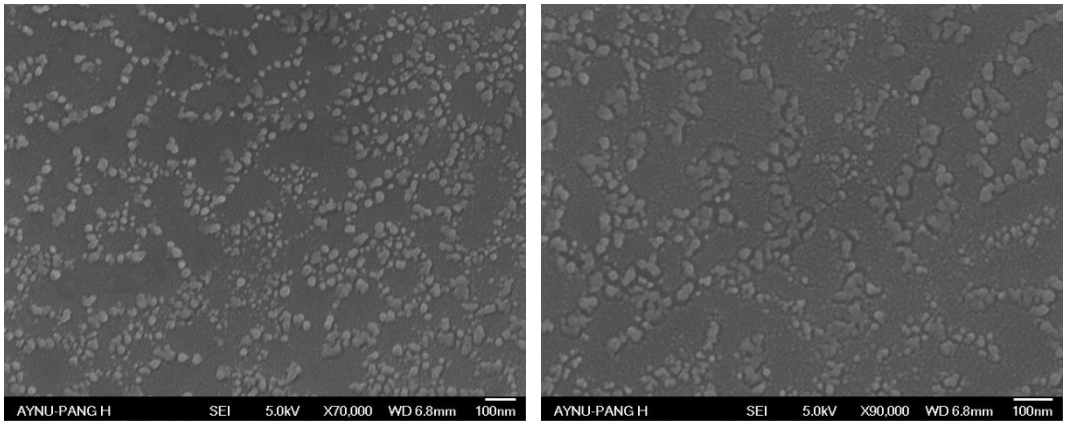

Fig.4 SEM images of the product heated under 140℃

(a：amplified 70000 times, b: amplified 90000 times)

Fig. 4 is the SEM picture of 0.15m aluminum ammonium sulfate after being microwave heated at 140 ℃ and dropped on the quartz substrate for natural drying. It can be seen from the figure that the particles are composed of spherical particles with a diameter of about 20 nm, uniform size, orderly arrangement and a tendency to form a ring. This is a kind of structure formed by coffee effect, that is, because the movement rate of some particles at the edge of the droplet is greater than that of the central particles during the drying process, the nano ring structure is formed.

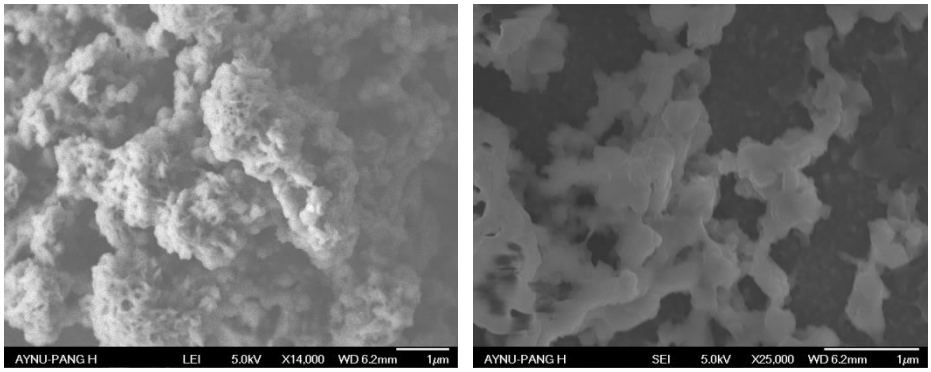

Fig.5 SEM images of the product heated under 160℃

(a：amplified 14000 times, b: amplified 25000 times)

Fig. 5 is a scanning electron microscope picture of reaction of 0.15m aluminum ammonium sulfate heated by microwave at 160 ℃. It can be seen from the figure that the further aggregation of nanoparticles are no longer spherical.

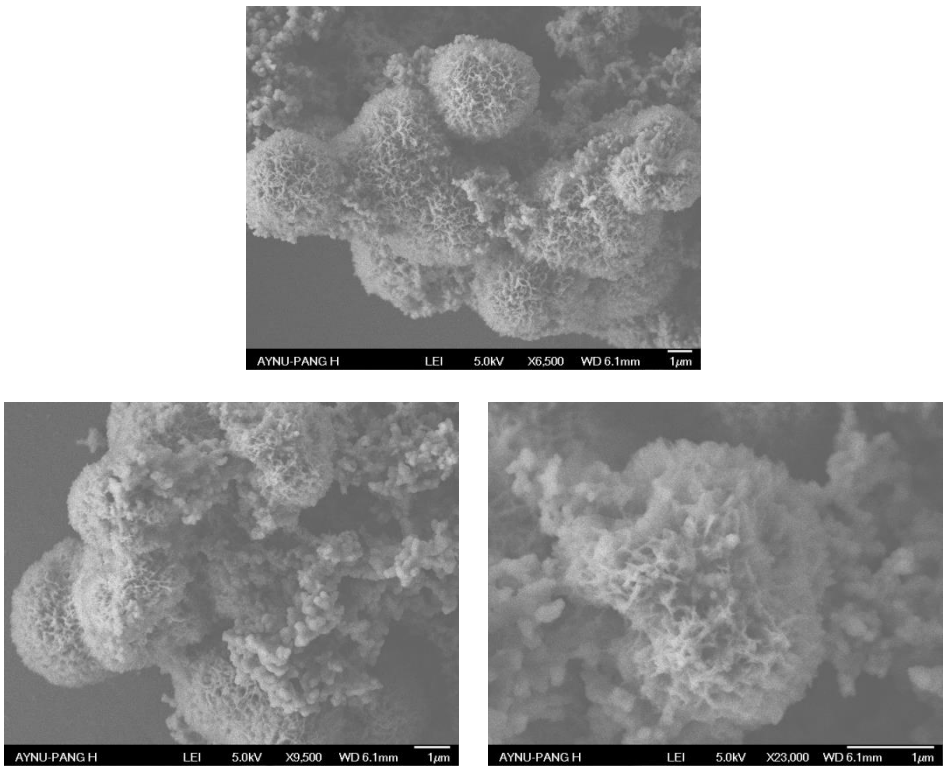

Fig.6 SEM images of the product heated under 180℃

(a：amplified 6500 times, b: amplified 9500 times, c: amplified 23000 times)

Fig. 6 is the scanning electron micrograph of the product after microwave heating at 180 ℃. At low magnification, the particles still look spherical with a diameter of about 2 to 3 microns. It can be concluded that compared with the smooth sphere, the surface area of the particles is significantly increased, and the adsorption capacity is greatly enhanced. It can be seen from the above electron microscopic analysis that the reaction temperature is an important factor influencing the morphology of the products under the condition of a certain concentration of reactants. In the whole process, glycol plays the role of cap reagent.

4 Conclusion

In this experiment, spherical and porous spherical nano-aluminum hydroxide were prepared from ammonium aluminum sulfate by microwave heating combined with coffee effect. The products were spherical or porous, with small particle size, uniform distribution and orderly arrangement. Especially with the coffee effect this natural, low energy consumption and green environmental protection method, is worth promoting the use.

References:

[1] M.Z.Huang. Clinical analysis of domperidone combined with compound aluminum hydroxide in the treatment of bile refluxing gastritis. *J. Gannan Medical College*, 2017，37(06):927-928.

[2] N.Ogasawara,M.Misaki,M.Adachi. Method for the determination of residual formaldehyde in an inactivated Zika vaccine formulated with aluminum hydroxide gel. Biologicals : *J. Intern Association Biological Standardization*, 2019, 58.

[3] Y.Zhang, X. Zhang , Y.J. Liu, et al. The influence of $Al(OH)_3$ on the flame retardant performance of high-speed train compartment laminates. *Sci Techn Innovation Appl*, 2017 (16): 88-90

[4] H.Z.Sun. Flame retardant: the God of fire safety. *China Mining daily*, 2020-01-15(007).

[5] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel , T. A. Witten. Capillary flow as the cause of ring stains from dried liquid drops. *Nature 1997, 389*, 827-829

[6] P.J. Yunker, T. Still, M. A. Lohr , A. G. Yodh. Suppression of the coffee-ring effect by shape-dependent capillary interactions. *Nature 2011, 476*, 308-311

[7] R. Henning, R.M.Sarhan, C.Prietzel, M. Bargheer ,J. Koetz. A new route to gold nanoflowers. *Nanotechnology 2018, 29*,1361 - 6528

[8] G.Hu, J.Kang, L.W. T. Ng, et al. Functional inks and printing of two-dimensional materials. *Chem. Soc. Rev.*, 2018, 9，3007-3382

[9] J. R. Trantum, D. W. Wright, F.R. Haselton. Biomarker-mediated disruption of coffee-ring formation as a low resource diagnostic indicator. *Langmuir* 2012, 28, 2187−2193

[10] O-G Eric, R-R Maricarmen, R-S Jesús Carlos. Leveraging the coffee ring effect for a defect-free electroformation of giant unilamellar vesicles. *Langmuir*，2019, 35，50.

[11] J.Subhavna, B.Jaydeep. Coffee ring effect assisted improved S. aureus screening on a physically restrained gold nanoflower enriched SERS substrate. *Colloids and surfaces. B,* 2019, 182. 110349