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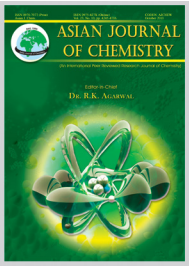

Synthesis and Surface Modification of a Rod Shaped Nanometer γ-Al_2O_3

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A simple co-precipitation method was adopted to synthesize nanometer γ-Al_2O_3 and then surface modification was implemented by coupling agent KH-550. The structure and morphology of the modified and unmodified γ-Al_2O_3 were characterized by XRD, IR and TEM. The results show that the particles were 30 nm rod shape and homodisperse. The lipophilic groups were endowed onto the surface of modified γ-Al_2O_3.

Key Words: Precipitation, γ-Al_2O_3, KH-550, PEG.

INTRODUCTION

Alumina is a low cost material most widely used as a catalyst and catalyst support[1]. γ-Al_2O_3 have a cubic close packing of oxygen ions resulting in high surface area, mesoporosity and surface acidity. As a result of these important properties, γ-Al_2O_3 is extensively used as an adsorbent[2]. Solid acid catalysts *e.g.* γ-Al_2O_3 are widely used as excellent catalysts for the dehydration of methanol to DME[3]. However nano-γ-Al_2O_3 has the potential physical and chemical properties different from the conventional materials, therefore the preparation of nano-γ-Al_2O_3 powders become a hot research[4]. To date, there are different synthesis methods such as: micro-emulsion, sol-gel method, hydrolysis, precipitation and many other chemical synthesis techniques. Compared with other methods, the precipitation process is simple, low cost and the powders from it have excellent performance[5]. It is the most practical one promising approach. But, a serious agglomeration may form at every stage such as: precursor nucleation, nuclei growth, washing, drying and calcination. So, to obtain uniform, fine, narrow distribution powder, the whole process of the powder preparation must be strictly controlled. Try to mixing the reaction partners as much as possible at the molecular, ionic level to promote Al_2O_3 precursor precipitates of homogeneous nucleation, so that the nucleus growth and agglomeration of particles to be effectively controlled. The unique ultrasonic cavitation can increase nuclei formation rate several orders of magnitude. Increase of nuclei production rate can reduce the size of precipitation particles, inhibiting the aggregation and growth of nuclei, but also prevent the formation of hard agglomerates of nanoparticles, helping control the size, shape of nanoparticles. Inexpensive aluminum nitrate, ammonium bicarbonate were used as raw materials in this paper. The ultrasonic technology was introduced in chemical precipitation to prepare nano-γ-Al_2O_3.

EXPERIMENTAL

Synthesis: A.R. of Al $(NO_3)_3.9H_2O$ and NH_4HCO_3 were dissolved respectively in 50 mL deionized water to a certain concentration. The molar ratio of NH_4HCO_3/Al $(NO_3)_3.9H_2O$ was 7 and 7 % (mass) of PEG4000 was dissolved in $Al(NO_3)_3$ solution. The two aqueous solutions were ultrasonic agitated respectively in an ultrasonic cleaner for 2 min and then poured the NH_4HCO_3 solution into the $Al(NO_3)_3$ solution and ultrasonic stirring for 15 min. After filtration and washing with absolute ethanol twice, the precursor was dried for 24 h at 100 ºC and calcined in flow of air at 900 ºC for 2.5 h with a heating rate of 2 ºC/min to obtain γ-Al_2O_3.

2 mL silane couple agent (KH550) were dissolved in 10 mL water/ethanol solution, then added 1.5g γ-Al_2O_3 after ultrasonic dispersion for 10 min. Heated while stirring to 70 ºC and keeping thermostatically for 24 h. Filtered and washed with absolute alcohol several times, then vacuum drying at 60 ºC for 8 h.

Powder X-ray diffraction patterns were recorded on a Rigaku D/MAX-3B diffractometer with Ni-filtered CuK_α radiation at a scanning rate of 5º min, a tension of 40 kV and a current of 30 mA, the angle 2θ being covered between 10º and 80º. Transmission electron microscopy images was taken in a JEOL-2010 system. FTIR spectra were measured in the range of 400-4500 cm^{-1} with a Perkin-Elmer 1710 FT-IR spectrometer using a KBr pellet containing the corresponding sample.

RESULTS AND DISCUSSION

Effect of reactants ratio to particles size

From the chemical equation:

$$Al(NO_3)_3 + 4NH_4HCO_3 == NH_4Al(OH)_2CO_3\downarrow + 3NH_4NO_3 + 3CO_2\uparrow + H_2O$$

The molar ratio of $NH_4HCO_3/Al(NO_3)_3$ was 4. Because aluminum nitrate solution presents a strong acidic, while ammonium bicarbonate solution shows some alkaline, the hydrogen ions (H^+) were neutralizing first in the reaction, until the pH value reached to form a stable $NH_4Al(OH)_2CO_3$ precursor. Therefore, when the molar ratio is small, that content of NH_4HCO_3 is small, few and little nuclei formed. Low concentrations and high solubility of precipitates leading to the supersaturation is low. According to Weimarn theory, the nucleation rate and growth rate are low, but the overall result is the growth rate of nuclei is greater than the nucleation rate and the particle size is relatively large. However, with the increase of molar ratio, NH_4HCO_3 content increasing in unit volume, part of H^+ were neutralizing, there is more precipitation ions promote the reaction to the positive direction rapidly and a large number of nuclei formed instantly, then the concentration of precipitation improving, supersaturation of the solution also increased rapidly. In the present investigation, the molar ratio of $NH_4HCO_3/Al(NO_3)_3$ was 7.

Preparation and characterization of γ-Al_2O_3 from precursor: The γ-Al_2O_3 powder was obtained from the thermal decomposition of $NH_4Al(OH)_2CO_3$ precursor. The reaction as follows:

$$2NH_4Al(OH)_2CO_3 \rightarrow Al_2O_3 + 2NH_3 + 3H_2O + 2CO_2$$

Fig. 1 show the XRD pattern of calcined $NH_4Al(OH)_2CO_3$ precursor at 900 ºC for 2.5 h in air. The characteristics peaks of γ-Al_2O_3 phase at 2θ = 45.78º for (111) reflection and 2θ = 66.76º for (211) reflection, in addition, 2θ = 37.6º for (110) reflection and 2θ = 60.89º for (211) reflection are all seen in pattern.

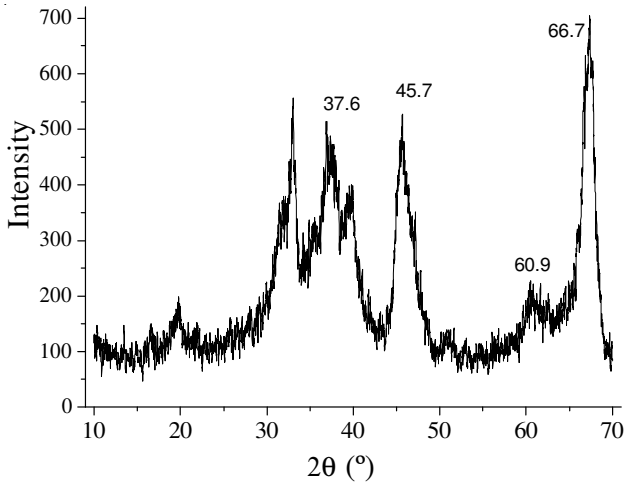

Fig. 1. XRD pattern of γ-Al_2O_3

The FT-IR spectrum shown in Fig. 2(A) clearly, indicate the presence of primary amine group of KH550 on the surface of γ-alumina. Compares A with B, there are significant differences at bands between 2700 cm^{-1} and 3500 cm^{-1}, 500 cm^{-1} and 1500 cm^{-1}. The characteristic absorption peaks (Fig. 2A) in the region 3500-3400 cm^{-1} are assigned to the stretching mode of N-H of KH550 and a shoulder observed at 2900 cm^{-1} is thought to be due to the stretching mode of C-H. The absorption bands corresponding to Si-O-C and Si-C at 1100-900 cm^{-1} and 900-650 cm^{-1} can be found in Fig. 2A. These confirm γ-alumina can be modified successfully by KH550.

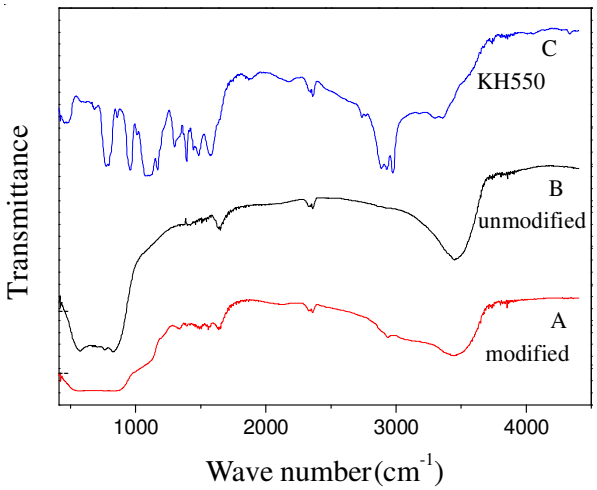

Fig. 2. FT-IR spectra of modified (A), unmodified γ-Al_2O_3 (B) and coupling agent KH550 (C)

TEM studies have been undertaken to understand the effects of poly(ethylene glycol) on the morphology of γ-Al_2O_3 powder. Fig.3 gives the TEM image of γ-Al_2O_3, which is prepared without adding PEG4000. The particles agglomerate seriously. However, when add PEG4000 in the preparation, the particles uniformly dispersed after been calcined, as can be seen from Fig. 4 that shows the rod shaped particles with different lengths (30-60 nm) having a diameter of 15-20 nm. In the calcination process, the gases generated from the decomposition of macromolecular polymer PEG4000 and deposition precursor, increasing the distance between Al_2O_3 powder particles when the gases releasing, volatilizing. This, to a certain extent, plays the role of dispersed particles, avoiding reunion due to enhance of mass transfer capabilities in the high temperature.

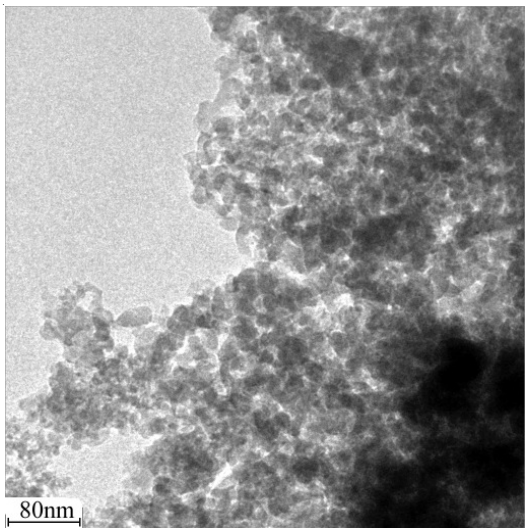

Fig. 3. TEM image of γ-Al_2O_3 (without PEG4000)

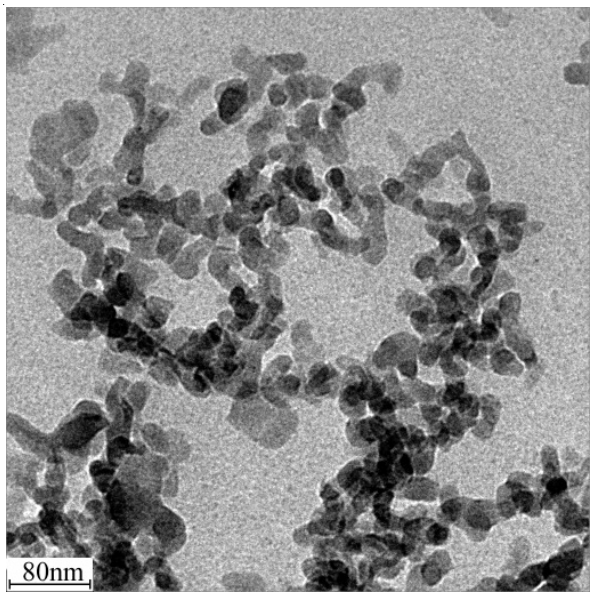

Fig. 4. TEM image of γ-Al_2O_3 (with PEG4000)

Conclusion

Nano-sized γ-Al_2O_3 can be prepared by adopting chemical precipitation method, during which suitable ratios of NH_4HCO_3/Al $(NO_3)_3$ is required. Addition of macromolecular polymer PEG4000 helped to obtain nanometer particles without seriously agglomeration. Ultrasonic cavitation can also help to control size of particles. Couple agent KH550 can react with the hydroxyl (HO^-) of inorganic particle surface, thus enhance the lipophilicity of the inorganic particles.

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