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Hydrothermal synthesis of high surface area mesoporous lithium aluminate

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Abstract

Mesoporous α-$LiAlO_2$ powders have been successfully prepared by a hydrothermal route based on using the surfactant CTAB as the template. The structure and morphology of the products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The crystallization transition process of the precursor after hydrothermal reaction was investigated by thermal gravity analysis. The prepared lithium aluminate had a morphology of two-dimensionally mesoporous nanoflakes with single crystal structure. A high specific surface area up to 124 m^2/g was obtained by this method.

Keywords: Mesoporous; Lithium aluminate; Hydrothermal; Specific surface area

1. Introduction

Lithium aluminate ($LiAlO_2$), presents three different crystalline phases: α-, β- and γ-$LiAlO_2$, which are hexagonal, monoclinic and tetragonal, respectively. Wherein, γ-$LiAlO_2$ is the stable phase at high temperature, and α- or β-$LiAlO_2$ phases transform to γ-$LiAlO_2$ at an elevated temperature [1]. γ-$LiAlO_2$ exhibits excellent thermo-chemical stability and favorable irradiation behavior. It is widely used as a matrix material in molten carbonate fuel cells (MCFC) and as a tritium-breeding material in nuclear fusion reactor [2,3]. α-$LiAlO_2$ can be utilized as a better matrix support material in MCFC [4]. Furthermore, 3 wt.% 10 μm γ-$LiAlO_2$ particle is added into polymeric electrolyte of lithium secondary battery to enhance the ionic conductivity [5].

Previously, γ-$LiAlO_2$ was prepared by conventional solid state methods, combustion synthesis or sol-gel methods [6–8]. High temperature and long time reaction were required in the solid state reactions, and the sol-gel method had a disadvantage in controlling the morphology of particles. Recently, γ-$LiAlO_2$ particles with a high surface area of 45 m^2/g have been prepared by an ultrasonic spray pyrolysis from an aqueous solution of aluminum nitrate and lithium salt [9]. Sokolov synthesized γ-$LiAlO_2$ with three-dimensional periodic arrays of interconnected macropores by a colloidal crystal templating (PMMA) wet chemical process [10]. The diameter of the macropores was 275–375 nm and the surface area was 48–56 m^2/g. However, the synthesis process was a little complicated, and a large excess of the lithium precursor was required. There are a few papers about the preparation of α-$LiAlO_2$. α-$LiAlO_2$ with a pore in the range of 0.9–0.2 μm was prepared by the technique of tape casting [11].

In this paper, we applied a simple hydrothermal route to synthesize mesoporous α-$LiAlO_2$ powders with single crystal structure using cationic surfactant CTAB as the template. The products showed high hydrothermal stability. The specific surface area of the hydrothermal product was much higher than the reported results.

2. Experiment

The starting materials selected were $LiOH \cdot H_2O$ (A.R.), aluminum iso-propoxide (AIP) (A.R.), hex-adecyltrimethyl ammonium bromide (CTAB) (A.R.). The synthesis procedure was indicated as follows: distilled water (50 mmol) was added slowly to the

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mixture of $LiOH{\cdot}H_2O$ (100 mmol), CTAB (100 mmol) and AIP (100 mmol). Furthermore, 50 ml ethylalcohol was added to enhance the solution ability of AIP. The mixture was stirred with ultrasonic irradiation for at least 10 min to obtain the homogeneous gel. Then the well-mixed gel was put into a Teflon autoclave vessel. The hydrothermal reaction was followed at 120 °C under autogenous pressure for 24 h–48 h. The precursor was washed several times by ethanol, dried at 80 °C for 10 h, and then calcined at 500 °C for 4 h in air. The products were denoted as MLA-24 (mesoporous lithium aluminate) and MLA-48 for hydrothermal reaction time of 24 h and 48 h, respectively.

The phase structure of the as-produced sample was characterized by a Bruker D8 advance X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å). A JEM-2010 transmission electron microscopy (TEM) with an acceleration voltage of 200 kV, $L = 1$ m was used to observe the morphology of the samples. Samples for TEM observation were prepared by air-drying a drop of a sonicated suspension of the dried powder in ethanol onto carbon-coated copper electron microscope grids. TG-DTA analysis was taken on Setaran 92-16.18 thermal analyzer in air with a heating rate of 20 °C/min. The special-surface area was estimated by the Brunauer–Emmett–Teller (BET) four points method, on the basis of the nitrogen gas adsorption isotherm (77.4 K) with a NOVA4000 high gas sorption analyzer. The pore size distribution was also analyzed with the same apparatus.

3. Results and discussion

$LiAlO_2$ phase was not found in the precursor without heat treatment in Fig. 1(a). The products after calcination at 500 °C can be characterized as a hexagonal ($R\bar{3}m$) α-$LiAlO_2$ phase (Fig. 1(b)), with lattice constants $a = 2.800$ Å and $c = 14.21$ Å (JCPDS No.74-2232). It demonstrated that mesophases containing surfactants were transformed into α-$LiAlO_2$ phase during the heat-treatment process. The well-crystalline α-$LiAlO_2$ phase could be kept when the calcining temperature was increased up to 1200 °C (Fig. 1(c, d)). However, cubic $Li_2Al_2O_4$ phase (JCPDS No.01-1306) with $a = b = c = 7.90$ Å, exhibited as the minor phase when the calcining temperature reached above 1000 °C. There were no significant differences in the XRD patterns between the samples MLA-24 and MLA-48.

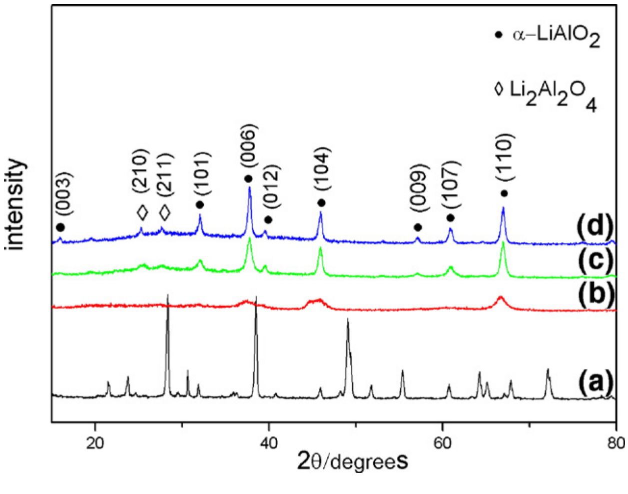

Fig. 1. XRD patterns of the precursor (a) and the products calcined at different temperature: (b) 500 °C, (c) 1000 °C and (d) 1200 °C.

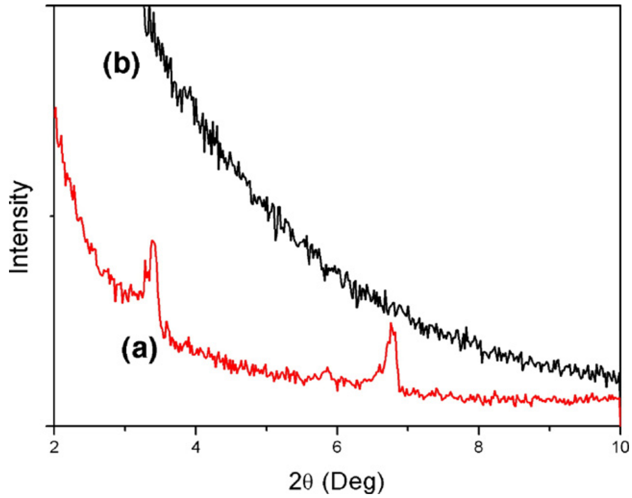

Fig. 2. Small-angle diffraction patterns for (a) the precursor, and (b) the as-prepared sample MLA-48.

Fig. 2 showed the small-angle diffraction patterns for the precursor and the as-prepared sample for MLA-48. The clear diffraction peaks at around 3.5° and 7° could be observed from the XRD patterns of the precursor, showing the uniform ordering of the pore structure. However, the XRD patterns of the sample MLA-48 did not show any resolved diffraction peak, which implied the absence of a mesostructure order in the pore arrangement. This results showed that the uniformly mesostructured precursor has been obtained under the hydrothermal conditions because of the existence of the surfactant template. However, the ordering mesostructure was completely lost during the calcination process.

The decomposition of the precursor can be seen from the TG-DTA curves in Fig. 3. Several reactions occurred when the precursor was heated. The endothermic peak at 252 °C was originated from the loss of the water absorbed in the particle surface. The exothermic peak at 293 °C was attributed to the crystallization transition process of the precursor to α-$LiAlO_2$ phase, corresponding to the X-ray patterns in Fig. 1. There was an endothermic peak at 334 °C, which was due to the elimination of the water molecules in the pore channels. The exothermic

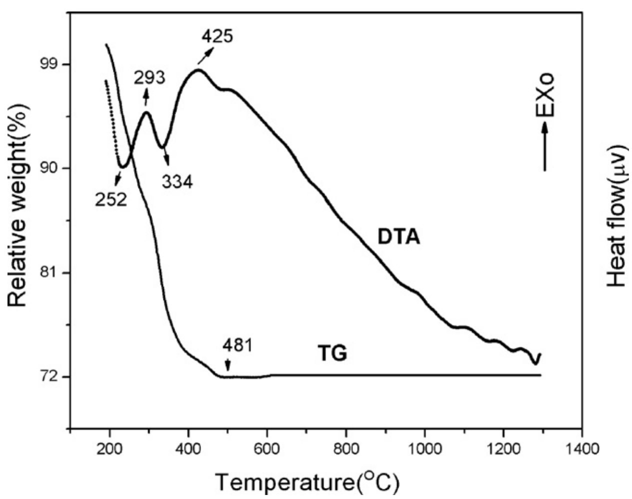

Fig. 3. TG-DTA curves of the precursor for MLA-48.