

Structural and thermal stability of mesoporous alumina synthesized by Al-based coordination polymer

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ABSTRACT

Mesoporous alumina with a narrow pore size distribution is synthesized by direct thermolysis of Al-based coordination polymer. By applying the appropriate thermolysis temperature, both high surface area and large pore volume are obtained with the collapses and elimination of the 1,4-benzenedicarboxylate linkers of Al-based coordination polymer. This new class of mesoporous alumina display better adsorption properties and higher thermal stability, which retain mesoporous properties and high surface area after calcination in 900 °C. This thermolysis method provides a new approach to synthesize mesoporous alumina with high thermal stability by using coordination polymers.

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1. Introduction

Aluminum oxide is a subject of significant interest in part due to its utility in a vast number of applications (e.g., gas sensors, chemiresistors, adsorbents, catalysts for the degradation of pollutants and catalyst supports) [1–3]. In particular, mesoporous alumina with high surface area, large mesopores, narrow pore-size distributions are highly desirable for many of the aforementioned applications [4,5].

To obtain mesoporous alumina, ionic and non-ionic surfactants have been used as structure-directing agents. Among various synthesis routes, the materials synthesized through evaporation induced self-assembly (EISA) in the presence of the poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO)_x(PO)_x(–EO)_x] triblock copolymer attract a lot of attention, however, this pathway required a strict control of experimental conditions and all afforded products that collapsed upon surfactant removal [6].

Porous coordination polymers (PCPs) or metal organic frameworks (MOFs) constructed from transition-metal ions and organic ligands have received much attention over the past few years because of their promising applications, such as in gas storage, separation, catalysis and conductivity [7–10]. Owing to their open channels, permanent cavities, and ordered crystalline lattice, MOFs will provide great potential as hosts to prepare microporous oxides [11]. Metal oxide clusters with the size in order of angstrom in MOFs can be converted into nanostructural metal oxides, which are of great importance in many applications [12].

In the literature [13], we first develop a novel and simple MOFs route for preparing mesoporous alumina, which involves the processes of converting metal oxide subunits in MOF into mesoporous alumina under heated conditions. We choose to use the aluminum compounds $[Al(\mu_2-OH)(1,4-bdc)]_n$, which have pore dimensions of about 8 Å. In the experiments, MIL-53(Al) has been hydrothermally synthesized by heating a mixture of aluminum nitrate, 1,4-benzenedicarboxylic acid, and water, for three days at 220 °C. Then MIL-53(Al) is transformed into mesoporous alumina by heating at 650 °C for 10 h in air. In this work, we mainly discuss the thermal stability of mesoporous alumina and the forming process of the crystalline mesoporous alumina. The results show that this synthesis afforded mesoporous alumina with better adsorption properties and higher thermal stability, which remain mesoporous properties and high surface area after calcination in 900 °C for 5 h.

2. Experimental

Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 99%) was supplied by Tianjin Kermel Chemical Reagent Co., Ltd. 1,4-benzenedicarboxylic acid ($C_{12}H_8O_4 \geq 99\%$) was supplied by Aladdin. All chemicals were analytical grades and used as received.

A mixture of $Al(NO_3)_3 \cdot 9H_2O$ (1.965 g), 1,4-benzenedicarboxylic acid (0.435 g) and deionized water (10 ml) was placed in a 30 ml Teflon autoclave and heated at 220 °C for three day. After filtering and washing with distilled water, a white powder was obtained. The excess terephthalic acid molecules in the pores were removed upon heating at 330 °C for three days in the air. A earth yellow powder was obtained, which was denoted as MIL-53(Al) with

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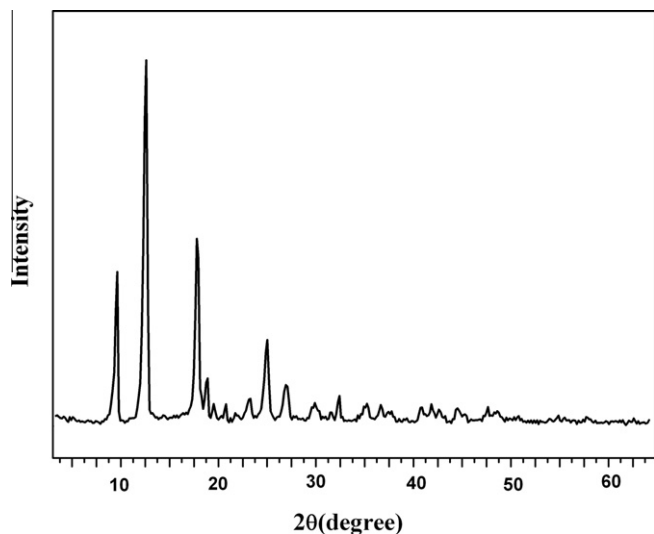


Fig. 1. XRPD patterns of MIL-53(Al).

empty pores. Finally, mesoporous alumina which was denoted as MA-650 was synthesized by heating MIL-53(Al) powder at 650 °C for 10 h in air. MA-900 was gained by calcining MA-650 in 900 °C for 5 h.

The structural and morphological properties of MIL-53(Al) and mesoporous alumina (MA-650 and MA-900) were characterized by several techniques. X-ray diffraction (XRD) data of samples were collected by using X-ray diffractometer (D/max-2200) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm, scan rate: $3^\circ/\text{min}$, accelerating voltage: 40 kV, emission current: 30 mA) at room temperature. Transmission electron microscopic (TEM) investigations were carried out using an instrument (JEOLJEM-2000FXII) operated at 160 kV accelerating voltage. Energy dispersive spectra were observed by using a spectrometer (EDX, Link ISIS). Thermogravimetric (TG) analyses were done on a NETZSCH 449C instrument in the temperature range of 40–750 °C (heating rate 4 °C/min in N_2 flow). Nitrogen adsorption/desorption isotherms were measured at 77 K using surface area and pore size analyzer (3H-2000PS4) and the sample was outgassed under vacuum at 200 °C for 2 h prior to measurement.

3. Results and discussion

The powder XRD pattern of MIL-53(Al) (Fig. 1) is consistent with the literature [14], and structural order and crystallinity are well. Crystal data for MIL-53(Al) are as follows: monoclinic system, Cc (No. 9), $a = 19.513(2)$, $b = 7.612(1)$, $c = 6.576(1)$ Å, $\beta = 104.24(1)^\circ$. The structures of sample comprised an infinite number of chains of corner-sharing $\text{AlO}_4(\mu_2\text{-OH})_2$ interconnected by the dicarboxylate ligand, resulting in a 3D framework containing 1D channel. This compound shows the property of a rigid framework, which consists of two kinds of rectangular channel with dimensions of 7.7×7.7 and 3.0×3.0 Å² running along the c axis [9].

Fig. 2 shows the powder X-ray diffraction pattern of mesoporous alumina MA-650 and MA-900. In the case of the MA-650, there is no obvious peak observed, revealing the amorphous state of mesoporous alumina. In comparison, there are three broad diffraction peaks that have appeared for the MA-900, which are attributed to $\gamma\text{-Al}_2\text{O}_3$ phase. This appearance indicates the crystallization of alumina during the transformation from powdery alumina to monolithic alumina [15]. It is mainly due to that the prolonged calcination duration at 900 °C results in the realization of the crystallization of alumina.

The thermal behavior of MIL-53 (Al) is characterized by two weight losses (Fig. 3). The first (40–70 °C) is assigned to the removal of water molecules (~5.0%) and the dehydrated structure is stable up to 530 °C. The second weight loss, above 530 °C, corresponds to the collapses and elimination of the 1,4-benzenedicarboxylate linkers from the framework. It accounts for 55% weight loss corresponding to this process. Between 530 and 630 °C, MIL-53(Al) is gradually transformed into amorphous Al_2O_3 . From 630 to 900 °C, the weight loss of sample is very small, indicating the thermal stability of obtained alumina. As further discussed within the text, a comparison of PXRD, nitrogen adsorption isotherms, and TEM images shows that this process correspond to crystallization of the channel walls upon heating to higher temperatures.

The morphology of the MIL-53(Al) and mesoporous alumina is observed by TEM. Fig. 4a shows TEM image of the MIL-53(Al), it is flake and hasn't mesoporous channels. Heat treatment of MIL-53(Al) results in 1,4-benzenedicarboxylate ligands vaporized rapidly from framework, forcing apart adjacent layer and, thus, forming mesoporous channels (Fig. 4b). The obtained MA-650

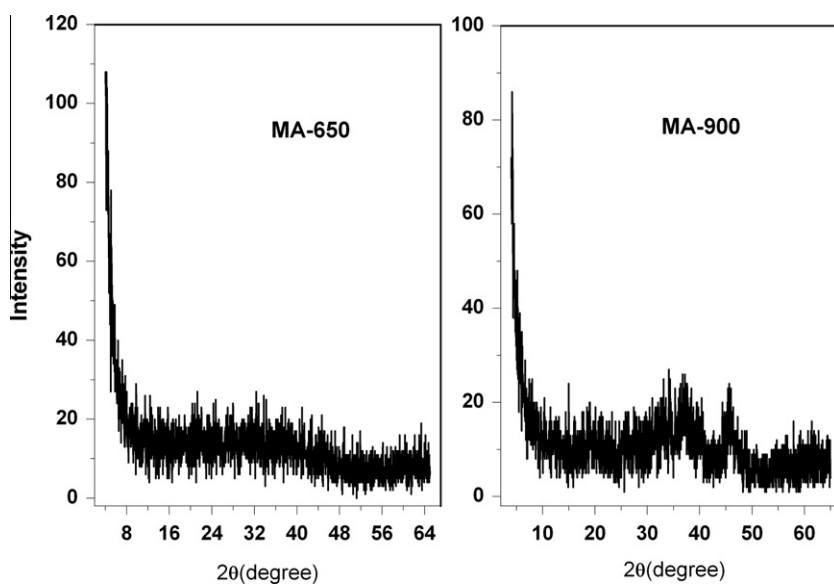


Fig. 2. XRPD patterns of MA-650 (left) and MA-900 (right).

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