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The structure-directed effect of Al-based metal–organic frameworks on fabrication of alumina by thermal treatment

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ABSTRACT

In this work, the block-shaped Al-based metal–organic frameworks (Al-MOFs) MIL-53 have been synthesized by hydrothermal method. To detect the correlation between the structure of Al-MOFs and the formation of alumina, the ligands are eliminated by thermal treatment. MIL-53 and the calcination products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), transmission electron microscopy (TEM), nitrogen adsorption–desorption and solid-state ^{27}Al nuclear magnetic resonance (^{27}Al NMR). It was found that after calcination, the block-shaped Al-MOFs precursor turns into high-crystallinity mesoporous alumina nanosheets, and the thermal treatment product γ-alumina possesses a dual pore system and a large surface area (146 m^2/g), with five-fold aluminum. During the thermal treatment process, the structure of MIL-53 and its secondary building units have structure-directed effect in the formation of alumina.

1. Introduction

In the past decades, the metal–organic frameworks (MOFs) have become one of the most promising porous materials [1–3]. These materials exhibit huge porosity, novel structures, open channels, and crystalline organized pore systems, which can find a wide variety of potential applications, including gas adsorption [4,5] and storage [6], chemical separation [7], heterogeneous catalysis [8], drug delivery [9], and so on [10,11]. Recently, most interests are focused on the control and application of the pore properties in MOFs, however, its various structures, especially the novel secondary building units (SBUs), are sometimes not fully studied. SBUs consist of metal and coordinate atoms in the form of clusters or polymeric metal oxide (or nitride and sulfide) subunits [12,13], which can convert into metal oxide with great importance in many applications [14].

Aluminum-based MOFs (Al-MOFs) have shown to be materials with highly desirable properties, such as lightweight, nontoxic, high thermal and chemical stabilities, stable against hydrolysis, as well as the cost-effective availability of its usually nontoxic starting materials [15]. In addition, due to the structure variability of Al^{3+} in aqueous solutions [16,17], various inorganic building units are formed in different reaction conditions [18–27], which are also very attractive. Those reported inorganic building units, such as one-dimensional infinite chains of corner- or edge-sharing $AlO_4(OH)_2$-octahedra in MIL-53 [21] and MIL-120/121 [26,28], trimeric clusters in MIL-100 [27] and MIL-101 [25], octameric clusters in MIL-110 [29], and wheel-shaped 8-ring unit [30] and 12-ring unit [31] (Fig. 1), are all novel inorganic aluminum clusters. If these Al-MOFs with diverse structures could be exploited, this would be very meaningful to improve the performance of alumina materials.

We all know that alumina with different morphology and nature keeps great importance in the industry. To detect whether the novel structure of Al-MOFs has new directing effects on the properties of metal oxide, in this paper, the aluminum-based MOFs were calcined to eliminate the organic ligands in order to get the alumina subunits. This method has been used successfully to prepare some other functional metal oxides materials with high performance [32], such as MOF-derived cobalt oxide nanoparticles as electrode material of lithium ion battery [33], zinc oxide nanoparticles as catalyst support [34], iron oxide with outstanding electron capacity [35], and some other metal oxides with various morphologies, while using Al-MOFs as the precursor is rarely

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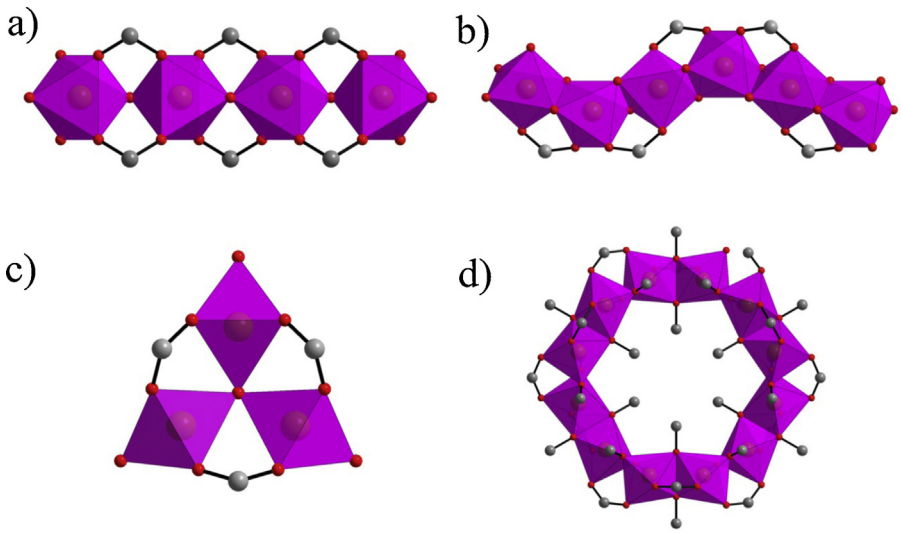

Fig. 1. Different inorganic building units in Al-based MOFs (a) corner-sharing AlO_6-octahedra; (b) edge-sharing AlO_6-octahedra; (c) trinuclear cluster; (d) wheel-shaped 12-ring unit.

reported. MIL-53 is one of the most representative Al-MOFs, which is built up by the interconnection of infinite 1D *trans* chains of corner-sharing $AlO_4(OH)_2$ polyhedra by terephthalic acid linkers, forming one-dimensional rhombic channel. Many researchers concentrated their attention on it mainly due to its high thermal stability, chemical stability, big specific surface area and large breathing effect [21]. Moreover this kind of 1D inorganic building units and topology structure has many isoreticular products, like MIL-69 [36], MIL-253 [37], CYCU-3 [38] and so on. Parast and Morsali [39] and Liu and He [40] are the only two representatives reporting the synthesis of nano-alumina and mesoporous alumina by thermal treatment using MIL-110 and MIL-53 as precursor respectively. Here, for the propose of investigating the effect of precursor structure on the formation of alumina, we detect the relationship between precursor structure and alumina. Based on the detection results, the performance of alumina product can be controlled in the future, and the alumina structure can be modulated by using different Al-MOFs with novel aluminum building units. The precursor and calcination products were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption–desorption, Fourier-transform infrared (FT-IR) and solid ^{27}Al NMR, to discover the difference of structure and performance between the precursor and calcination product, as well as the influence of precursor structure on the formation of alumina. In the end, the formation mechanism of alumina and the origin of its properties were discussed.

2. Experimental

2.1. Synthesis

Aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) and 1,4-benzenedicarboxylic acid ($C_8H_6O_4$) were all purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purification.

Aluminum-terephthalate MIL-53 was hydrothermally synthesized based on the typical synthesis, and in order to synthesis more efficiently, MIL-53 was scale up synthesized. A mixture of Al $(NO_3)_3{\cdot}9H_2O$ (5.20 g), 1,4-benzenedicarboxylic acid (1.152 g) and deionized water (20 mL) were added in a 100 mL teflon-lined steel autoclave at 210 °C under autogenous pressure for 72 h. The resulting white products (MIL-53) were filtered off, washed with deionized water and dried at 60 °C overnight. Based on the TG curves of MIL-53 (Fig. S1), alumina was prepared by heating the as-synthesized products (MIL-53) at 650 °C for 1 h at a heating rate of 5 °C/min.

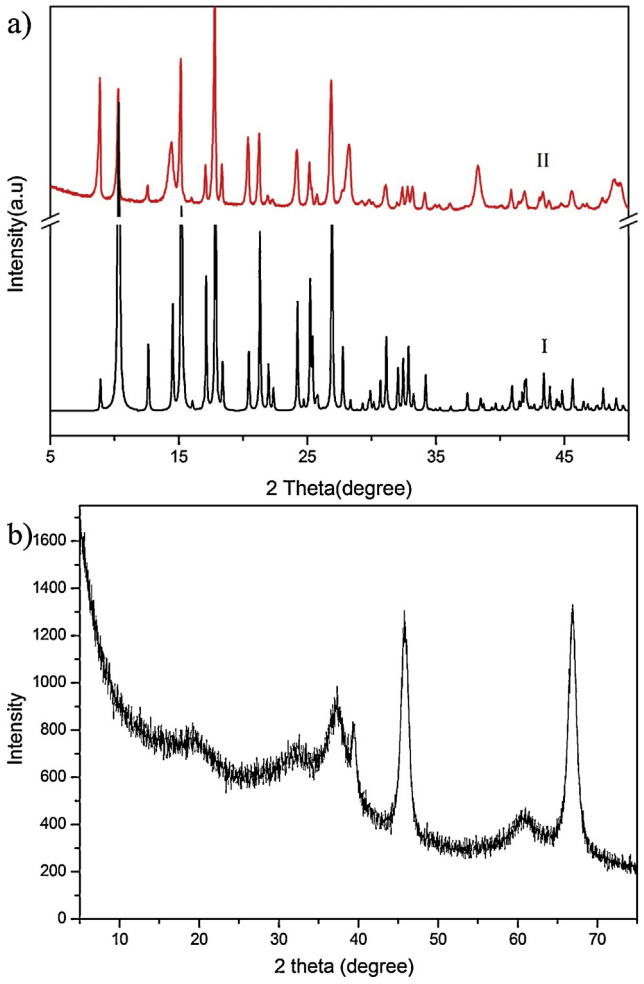

Fig. 2. XRD patterns of (a) MIL-53: I–simulated pattern and II–pattern of as-synthesized sample; (b) alumina after calcined.