The Transformation of Al-based MOFs to Mesoporous Al_2O_3 with Pre-defined Morphology and Modulated Microstructure

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Abstract. Hexagonal spindle-shaped mesoporous alumina was prepared using Al-based metal-organic frameworks (MOFs) MIL-96 as precursor through thermal treatment method. The MIL-96 and alumina products were characterized by XRD, SEM, BET and 27Al-NMR. Results from these characterizations showed that alumina products keep the morphology of their precursor, and the thermal treatment time has large effect on the alumina microstructures. In addition, the aluminium environment and the ratio of Al (IV)/Al (V)/Al (VI) could also be modulated by the treatment time.

1. Introduction

Alumina is a kind of material widely used in industries as adsorbent [1], ceramic [2], membrane [3] and catalyst support [4] due to its unique physical and chemical properties. The properties of alumina are mainly determined by the crystal phase, composition, pore structure and morphology. Therefore, the performance of alumina could be optimized by adjusting the surface area, pore structure and morphology. [5] As a result, the synthesis of nanostructured alumina with controllable structure and morphology has attracted attention in recent years.

Alumina with various controlled morphologies has been reported [6], and its synthetic methods are multiple [7], but these methods always need organic solvents, surfactants as structure directing agents, or seed crystal, which made them less attractive. Recent years, metal-organic frameworks, as one kind of inorganic-organic hybrid species, have developed rapidly [8]. Metal-organic frameworks (MOFs) are built from metal ions or metal-oxo-clusters and organic bridging ligands, and can easily transform into oxides via thermal treatment at high temperature in air, which is an effective way to synthesize metal oxide with controlled size, morphologies, structures and properties [9]. Alumina, as a kind of typical metal oxide, can also be obtained by solid state transformation of Al-based MOFs.

MIL-96 [10], as a kind of porous Al-based MOFs, is crystallized from aluminum nitrate and trimesic acid. Furthermore, since the reaction conditions of MIL-96 are different from others, the construction of MIL-96 exhibits novel aluminum arrangement and structure. Herein we utilize this kind of Al-MOFs as precursor for the preparation of alumina particles with novel morphology and different controllable pore structures.

2. Experimental Section

2.1 Synthesis of MIL-96 and alumina.

The following chemicals used for Al-based MOFs in this work are commercially available. MIL-96 was hydrothermally synthesized from a mixture of aluminum nitrate (1.31 g), 1,3,5-benzenetricarboxylic acid (H_3btc, 0.11 g) and 5 mL deionized water. The starting mixture was placed in a 25 mL Teflon cell, which was heated in a steel Parr autoclave for 24 h at 210 °C under autogenous pressure. The resulting powdered white product was filtered off, washed with deionized water and dried in an oven at 60 °C for 8 h.

MIL-96 was heated to 650 °C at a heating rate of 5 °C/min for 4 h and 8 h in muffle furnace (Nabertherm, Germany), and then got the alumina product after cooling to room temperature. The two alumina products were named Al_2O_3-4h and Al_2O_3-8h, respectively.

2.2 Characterization.

Powder XRD patterns were recorded on a Panalytical X'Pert Pro MPD diffractometer (Netherlands) equipped with Cu Kα radiation (λ=1.5406 Å) with a scan speed of 0.257 $°s^{-1}$ in 2θ. SEM images were taken using an S-4800 field emission scanning electron microscopy (FE-SEM, Hitachi, Japan) with an acceleration voltage of 1.5 kV. Solid-State ^{27}Al-NMR studies were performed on a Bruker Avance 300 spectrometer. Nitrogen physisorption isothermals were measured at 77K on Micromeritics TRISTAR 3020 volumetric adsorption apparatus. The samples were pretreated before measurement, MIL-96 was outgassed under vacuum at a temperature of 423 K for 12h, and the alumina was outgassed at 573 K for 6 h.

3. Results and Discussions

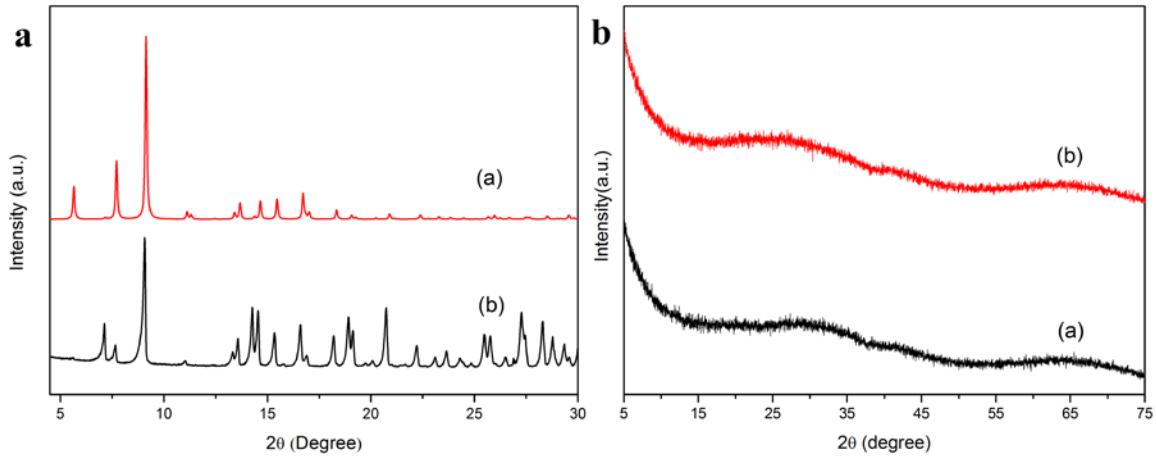

Fig. 1 XRD pattern of: a MIL-96 precursor (a) simulated MIL-96 (b) as-synthesized MIL-96 and b Al2O3 (a) Al2O3-4h, (b) Al2O3-8h.

Fig. 1 shows the X-ray diffraction patterns of the simulated and as-synthesized MIL-96, as well as the resulting alumina products, respectively. The XRD pattern of MIL-96 (Fig. 1a) shows the high-crystallinity of the product, and all of the observed peaks agree well with the simulated one, representing the purity of the phase. While after the thermal treatment, the powder X-ray diffraction spectra of the resulting calcination products (Fig. 1b) show an amorphous alumina phase, indicating the decomposition of the original MIL-96 frameworks.

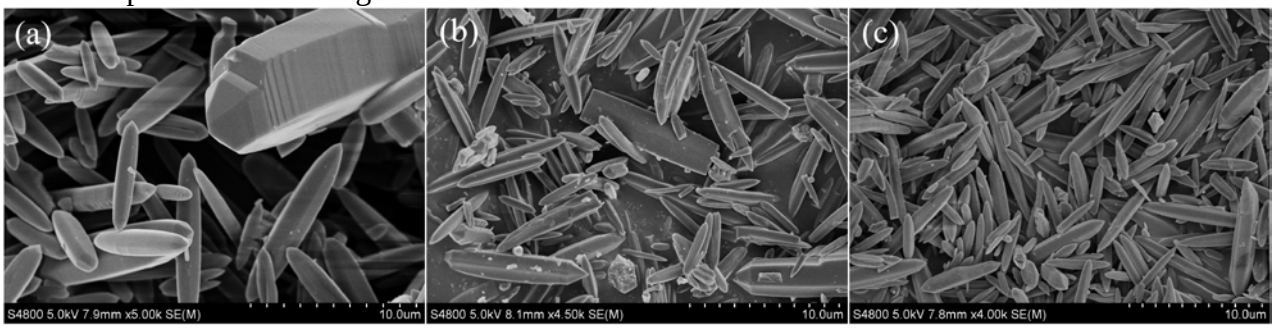

Fig. 2 SEM images of (a) MIL-96 precursor, (b) Al2O3-4h and (c) Al2O3-8h after treatment.

The size and morphology of MIL-96, as well as the resulting alumina particles using MIL-96 as precursor were then characterized by FE-SEM. As shown in Fig. 2a, the MIL-96 consists of regular hexagonal spindle-like crystals with smooth surface. After thermal treatment, the morphology of resulting Al_2O_3-4h was retained from the original morphology of the MIL-96 precursor, while the overall size of the hexagonal spindle-shaped Al_2O_3-4h is decreased compared with that of the precursor, accompanied by the collapse of frameworks in the treatment. With the extending of time for the thermal treatment to 8 h, the morphology of precursor was still remained in Al_2O_3-8h, and the

size was even smaller than the previous one. The continuous decrease of particle size is attributed from the sintering of alumina crystallite during the thermal treatment.

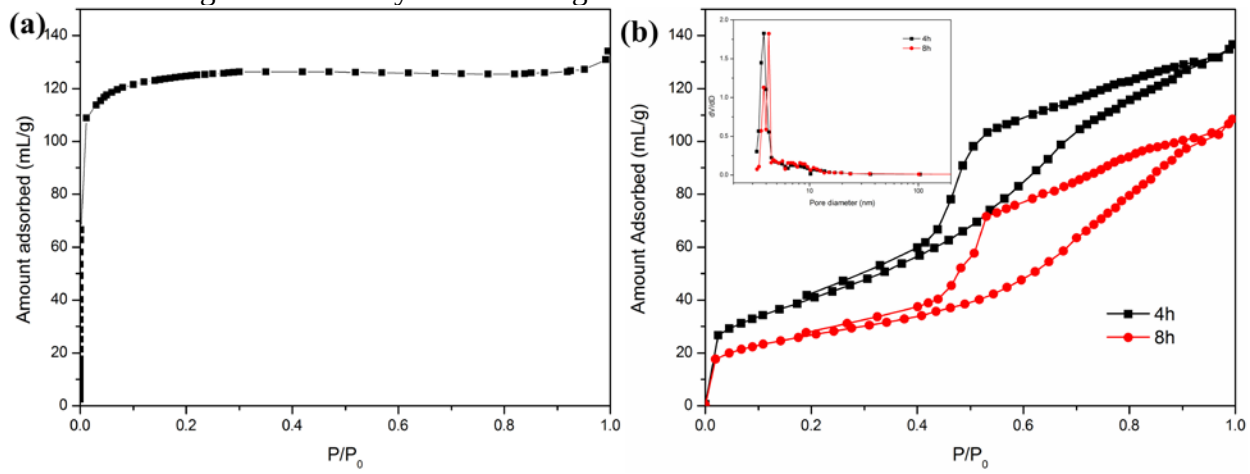

Fig. 3 Nitrogen sorption isotherms at 77K for (a) MIL-96 and (b) Al2O3-4h, Al2O3-8h, inset is the pore size distribution of Al2O3-4h and Al2O3-8h.

The evolution of pore properties of MIL-96 precursor and alumina products were characterized by N_2 sorption measurements. The nitrogen sorption isothermals of MIL-96 reveals a type I isotherm without hysteresis on desorption (Fig. 3a), which is a characteristic of microporous material. The BET surface area of MIL-96 is 467 m^2g^{-1}, with a micropore volume of 0.20 cm^3g^{-1}. After treatment, the N_2 sorption isotherms of Al_2O_3 changed into IV isotherms with a combined H2-H4-type hysteresis loop, which demonstrates the formation of ink-bottle like pores in the solid. The BET surface area of Al_2O_3-4h and Al_2O_3-8h are 148 m^2 g^{-1} and 96 m^2 g^{-1}, respectively, indicating that the permanent porosity of the MIL-96 precursor completely disappears after formation of Al_2O_3 (Fig. 3b). The pore size distribution of the two mesoporous alumina was concentrated, furthermore after increasing the treatment time to 8 h, the most probable pore size distribution of alumina increased from 3.8 nm to 4.2 nm, and the later one presents dual distribution. The difference on texture may come from the sintering of alumina crystallite leading to the growth of crystallite size and the reduce of porosity, and this may result in the decrease of surface area and increase of pore size.

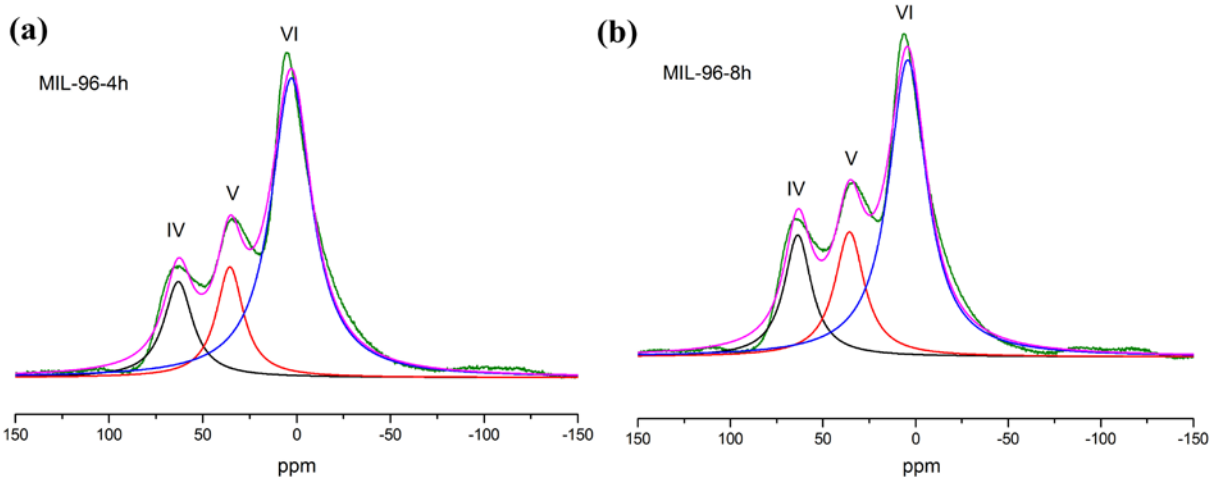

Fig. 4 27Al NMR spectrum of a) Al2O3-4h and b) Al2O3-8h (green line), including its simulation (pink line) with its individual components (red line for the Al(IV) site , blue line for the Al(V) site and black line for the Al(VI) site).

The obtained two alumina are further subjected to ^{27}Al-NMR measurements, and the spectra are displayed in Fig. 4. Fig. 4a shows the ^{27}Al-NMR spectrum of Al_2O_3-4h, and three distinct resonance peaks are observed, which are assigned to four-fold coordinated aluminum (50-80 ppm), six-fold coordinated aluminum (-10-20 ppm) and five-fold coordinated aluminum (30-40 ppm), according to

the reported results [11]. The ratio of the three kinds of aluminum is 1: 1: 4.4 for Al (IV)/Al (V)/Al (VI). In the ^{27}Al-NMR spectrum of Al_2O_3-8h (Fig. 4b), there are also three distinct resonance peaks, but the ratio of the three kinds of aluminum changed into 1: 1.1: 3.4 for Al (IV)/Al (V)/Al (VI). By comparing the spectra of two alumina, we can know that, after the extending the thermal treatment, more hexacoordinated aluminum in alumina dehydrate and convert into four-fold or five-fold coordinated aluminum. In addition, the high ratio of five-coordinated aluminum is also relevant with the low crystallinity of the alumina product.

4. Summary

In this paper, we have synthesized alumina particles with novel hexagonal spindle-shaped morphology using Al-MOFs as precursor, and modulate the microstructure by changing the thermal treatment time. The original morphology of MIL-96 was retained in the resulting Al_2O_3 products, so we can get alumina with pre-defined novel morphology in this way. We have also suggested that the thermal decomposition time of Al-MOFs is important in determining the microstructure and porosity of Al_2O_3 product. By changing the thermal treatment time, mesoporous alumina with different pore size could be obtained. Besides, ratio of the three kinds of aluminum (Al(IV)/Al(V)/Al(VI)) in NMR spectra could be modulated with the treatment time. Because this work presents a method to produce alumina with tailored morphology and microstructure by modulating the thermal treatment time, the control of properties of alumina and other metal oxide materials may become possible.

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