The synthesis and characterization of mixed ligand AlF(bdc) Metal-Organic Framework

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Abstract

Mixed ligand aluminum fluoride 1, 4-benzeneducarboxylate (AlF(bdc)) and aluminum fluoride 2-amino-1, 4-benzeneducarboxylate (AlF(bdc-NH$_2$)) has been successfully synthesized via solvothermal route. Several techniques such as powder X-ray diffraction, Fourier-transform infrared spectroscopy, field emission scanning electron microscopy and thermogravimetric analysis have been employed to characterize the as-made materials. Mixed ligand AlF(bdc) includes AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$) and AlF(25%bdc)(75%bdc-NH$_2$) and complete ligand substitution of bdc by bdc-NH$_2$ yields AlF(bdc-NH$_2$). All of them are isostructural to AlF(bdc) but poorer in crystallinity. The crystal morphology of each synthesized materials was observed and found to be similar. AlF(bdc) crystal has a shape of prism with random diameter. Substitution of bdc-NH$_2$ into the AlF(bdc) framework promotes needle like crystals which become the majority of crystal form when the amount of bdc-NH$_2$ is increased. AlF(bdc-NH$_2$) crystal is similar in shape with AlF(bdc) except that the crystals are shorter in length and present together with random shaped aggregates. Decomposition temperatures of each as-made materials were observed. They show a variation of weight loss profile. However, it is evident that the incorporation of bdc-NH$_2$ deprives the thermal stability of the structure. Increasing amount of bdc-NH$_2$ lowers the decomposition temperature of the materials and the complete substitution of bdc-NH$_2$ leads to a hundred temperature degree lower of decomposition temperature when compared to that of AlF(bdc).

Keywords: Metal-Organic Framework, porous materials, MIL-53, breathing effect

Introduction

Metal-Organic Framework, so called MOF, is a category of porous material that has attracted considerable attention from researchers all over the world for nearly two decades. This is owing to its fascinating properties such as large surface area and pore volume, high framework rigidity upon guest molecule removal, high degree of structure versatility and easily tailored and tunable pore structure [1]. Their properties has paved the way for them to be used in various applications such as gas storage and separation [2,3] gas sensing [4] catalysis [5] and drug delivery [6]. MOFs are crystalline materials that comprise of metal ions bound covalently to functional groups of organic ligands, generally –COOH group. The connection leads to the formation of metal oxide node which is commonly called secondary building unit. These secondary building units are linked by the organic moieties forming one-dimension, two-dimension or three-dimension pore structure [7]. The specific combination of metal and organic ligand has led to a vast number of different types of MOFs that possess unique physical and chemical properties.

One of the prototypical MOF materials is M^{III}(X)(bdc), known as MIL-53, where M = Al, Cr, V, Sc, Fe, In, Ga; X = OH, F. They are renowned for their unprecedented framework flexibility toward external stimuli such as water and heat. This phenomenon is termed breathing effect.[8] As shown in Figure 1 a), MIL-53 is constructed by the connection between corner sharing chains of metal oxide octahedral and terephthalate anions. This leads to three dimensional network with

one-dimension lozenge shaped tunnels. The characteristic of metal cluster elaborately control the framework flexibility and properties. For instance, from all of the 8 analogous structures, there are only VO(bdc) and AlF(bdc) that show no breathing effect while the other 6 materials exhibit reversible structure transition upon heating and inserting of guest molecules [9,10]. Intensive research on this unusual behavior has been done both experimentally and theoretically and meets the concrete conclusion that the structure flexibility depends deeply on both structure and energy of the materials. In term of structure, the inorganic cluster, the ligand and its conformation and the connection between them define the degree of freedom of the framework. In term of energy, various interactions such as host-host, guest-guest and host-guest interaction play a key role in driving to structure flexibility [11].

As mentioned above, the organic ligand plays important role on controlling the chemistry of the materials. Moreover, variation of organic ligand can also improve the chemical and physical properties of such material. For instance, $Al(OH)(bdc-X)$, X = -Cl, -Br, -CH_3, NO_2, -$(OH)_2$ were successfully synthesized. All of them show breathing effect with slightly different unit cell volume when comparing to the pristine $Al(OH)(bdc)$. Changing from bdc ligand to bdc-X ligand was found to slightly lower the amount of N_2 and CO_2 adsorbed by the framework.[12] Mixing of organic ligand can also be used for tailoring the properties of MOF. For example, mixed ligand $Al(OH)(bdc-OH)_x(bdc-NH_2)_{1-x}$ materials were recently reported. The accessibility of water molecules into these materials can be pragmatically controlled by the mole ratio between the two ligands [13].

In this work, the successful synthesis and characterization of mixed ligand $AlF(100-X\%bdc)(Xbdc-NH_2)$, X = percent mole ratio, are reported and discussed.

Materials and Methods

All chemicals used in the synthesis were purchased from commercial venders and used without further purification. Powder X-ray diffraction data were obtained using X' Pert MPD PHILIPS diffractometer with Cu K_α radiation (λ = 1.5418 Å) with the step size of 0.02°. FT-IR spectrum were collected using Perkin Elmer Spectrum GX spectrometer between 400 and 4000 cm^{-1} using the KBr pallet method. Scanning electron micrographs were captured using Zeiss GeminiSEM Field emission scanning electron microscopy. Thermogravimetric analysis was performed using a Perkin Elmer thermogravimetric analyzer with heating rate of 10 °C per minute from room temperature to 1200 °C.

AlF(bdc) was synthesized via solvothermal route with a slight modification from the literature. A mixture of 16.78 mg of AlF_3 and 0.9968 g of 1,4-benzenedicarboxylic acid (bdc) was dissolved in 20 mL of N,N-diethylformamide (DEF). The mixture was then transferred into 45 mL Teflon-liner stainless steel autoclave and heated to 220 °C for 5 days. The reaction was then let to cool down to room temperature slowly. White powder product was recovered by a simple filtration where the product was washed by 20 mL of fresh DEF twice. The as-synthesized material was dried overnight at 70 °C.

Mixed ligand $AlF(100-X\%bdc)(X\%bdc-NH_2)$ materials were synthesized by using similar procedure as described above. A slight adjustment was made by an addition of 2-amino-1,4-benzenedicarboxylic acid (bdc-NH_2). The amount of bdc-NH_2 and bdc was varied from 25, 50 and 75 percent mole ratio respectively. For example, $AlF(75\%bdc)(25\%bdc-NH_2)$ was synthesized by dissolved 16.78 mg of AlF_3, 0.7476 g of bdc and 0.2717 g of bdc-NH_2 in 20 mL of DEF.

Results and Discussion

The success of the synthesis of mixed ligand AlF(100-X%bdc)(X%bdc-NH$_2$) materials was confirmed by several characterization techniques. Powder X-ray diffraction patterns (PXRD) of as-made materials including AlF(bdc), AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$), AlF(25%bdc)(75%bdc-NH$_2$) and AlF(bdc-NH$_2$) were collected. The PXRD patterns of AlF(bdc) were indexed using unit cell parameter from the literature (Orthorhombic, *Imma*, *a* = 6.5502(7) Å, *b* = 16.250(4) Å, *c* = 13.378(2) Å). It was found that PXRD pattern of as-made AlF(bdc) was in good agreement with the simulated one which confirmed the success of the synthesis of AlF(bdc). The PXRD pattern of as-made AlF(bdc) was then plotted against AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$), AlF(25%bdc)(75%bdc-NH$_2$) and AlF(bdc-NH$_2$) as shown in Figure 1 b). It is evident that in all mixed ligand AlF(bdc) and AlF(bdc-NH$_2$) are isostructural to AlF(bdc). There is diffraction peak at 2θ = 26.03°, marked by black asterisk, was indexed to be an excess AlF$_3$ which appears in PXRD patterns of AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$), AlF(25%bdc)(75%bdc-NH$_2$) and AlF(bdc-NH$_2$). For AlF(75%bdc)(25%bdc-NH$_2$), a phase of unreacted bdc is also present and is indicated by purple asterisks. Broad diffraction peaks with low intensities imply poor crystallinity of materials as can be seen in AlF(50%bdc)(50%bdc-NH$_2$) and AlF(bdc-NH$_2$).
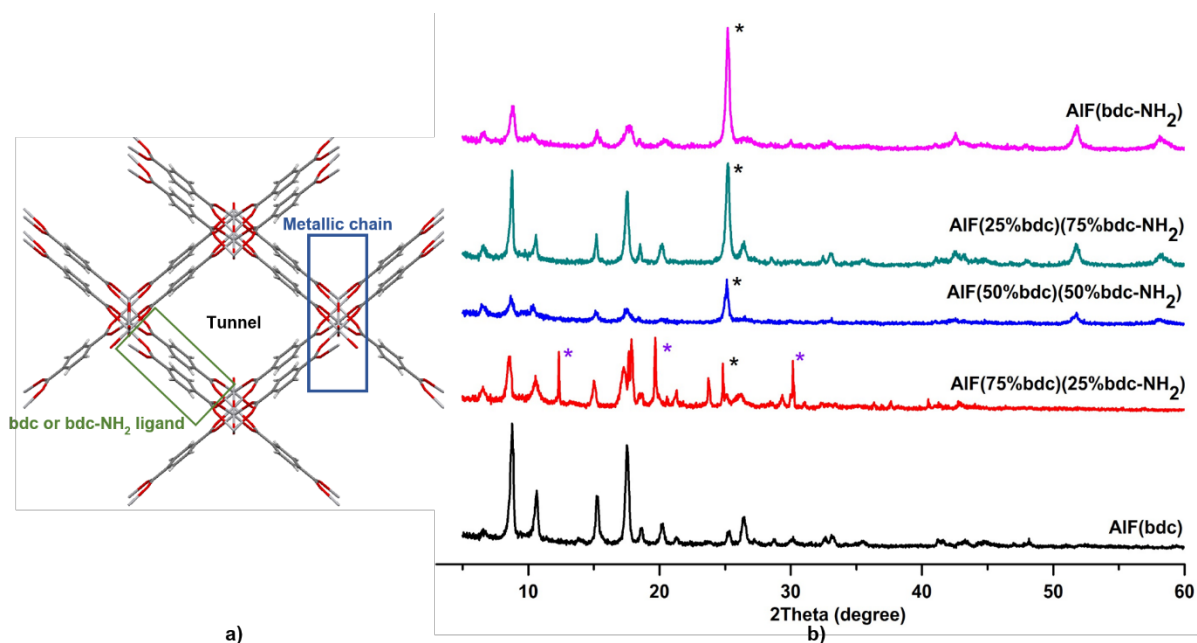
Figure 1 a) MIL-53 Framework viewed along the [100] direction b) PXRD patterns of all as-made materials.

To confirm the presence of bdc-NH$_2$ linker in the framework of mixed ligand AlF(bdc), FT-IR spectra of the as-made materials were collected and were shown in Figure 2.
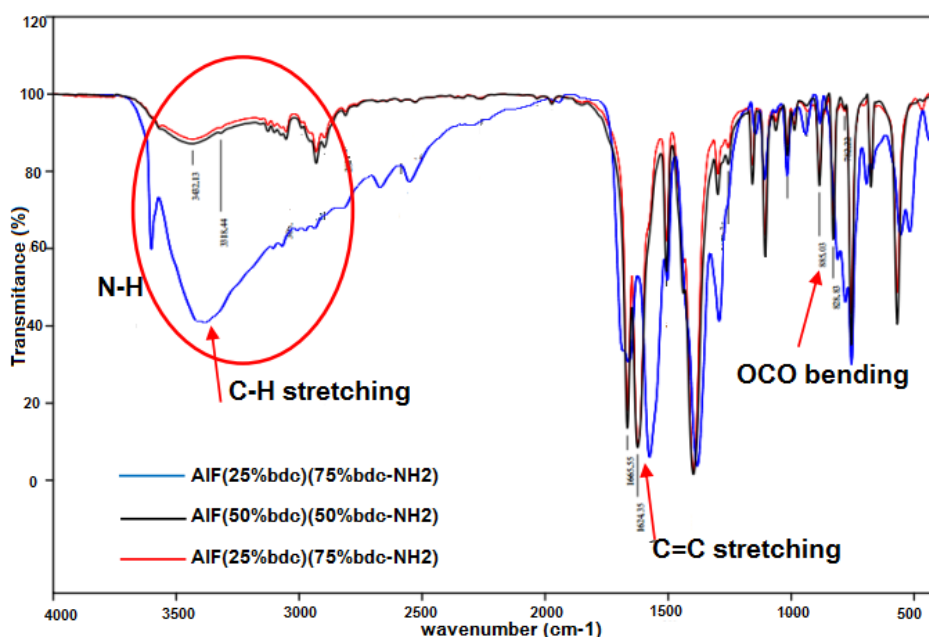
Figure 2 FT-IR spectra of AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$), AlF(25%bdc)(75%bdc-NH$_2$).

The characteristic peak at 3300 - 3400 cm^{-1} indicates N-H stretching of primary amine functional group which means bdc-NH$_2$ was incorporated into the framework of AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$) and AlF(25%bdc)(75%bdc-NH$_2$). In AlF(25%bdc)(75%bdc-NH$_2$), a broad and strong peak at 3000 - 3500 cm^{-1} indicates the presence of bound O-H stretching which suggests that there are water guest molecules in the framework tunnel.

SEM micrographs of AlF(bdc), AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$), AlF(25%bdc)(75%bdc-NH$_2$) and AlF(bdc-NH$_2$) were shown in Figure 3 a) – e) respectively. Overall, their morphology is similar where random sized prism crystals aggregates with needle-like crystals as a cluster. It is also noticeable that needle-like crystals become the majority when more amount of bdc-NH$_2$ is incorporated into the framework. In case of AlF(bdc-NH$_2$), needle-like crystals are disappeared and only short prism crystals are present with random shaped aggregates.
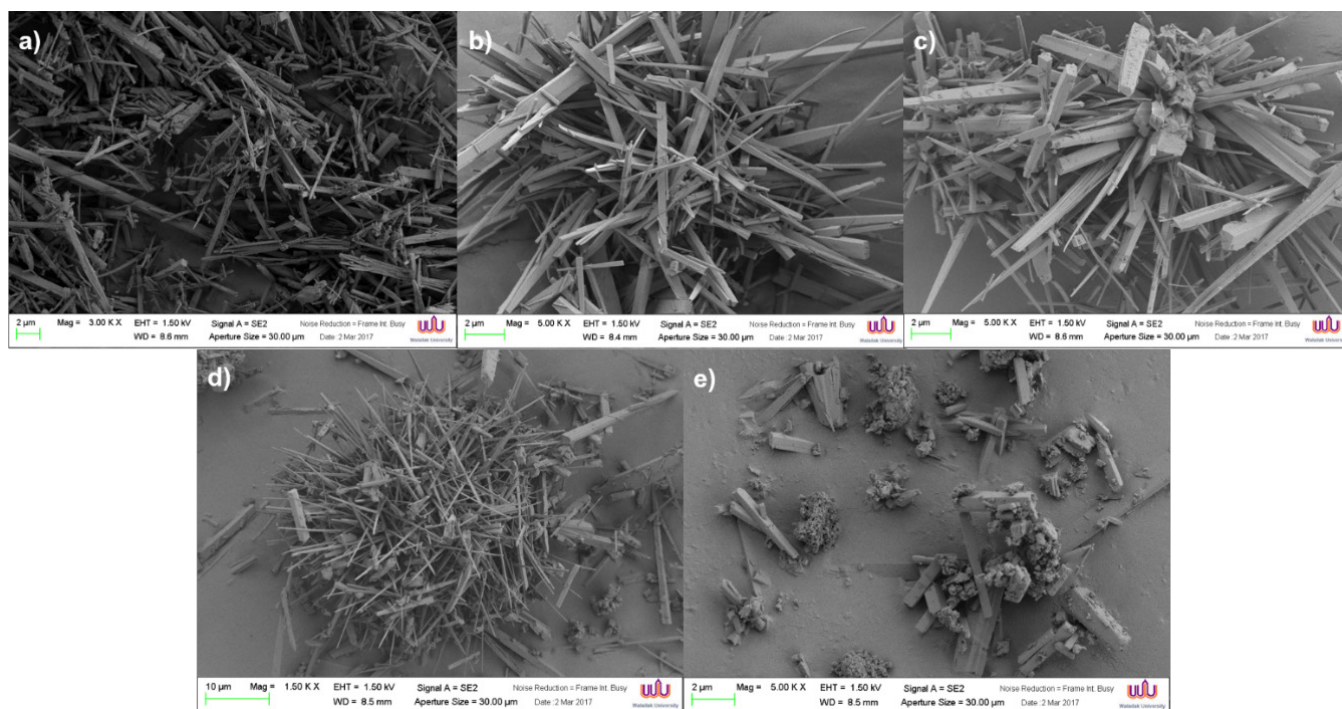
Figure 3 SEM micrographs of a) AlF(bdc), b) AlF(75%bdc)(25%bdc-NH$_2$), c) AlF(50%bdc)(50%bdc-NH$_2$), d) AlF(25%bdc)(75%bdc-NH$_2$) and e) AlF(bdc-NH$_2$).

The stability of as-made materials toward heat was investigated by means of thermogravimetric analysis (TGA). From TGA thermogram of AlF(bdc), there is a continuous loss of guest molecules such as water, DEF and unreacted ligand from a temperature range of 50 – 320 °C. The decomposition temperature of the framework is at about 500 °C which is corresponding well with the literature.[14] For AlF(75%bdc)(25%bdc-NH$_2$) and AlF(50%bdc)(50%bdc-NH$_2$), similar trend of TGA thermograms with AlF(bdc) was observed. However, decomposition temperature of the framework is lower than that of AlF(bdc) by 20 °C in case of AlF(75%bdc)(25%bdc-NH$_2$) and by 30 °C in case of AlF(50%bdc)(50%bdc-NH$_2$). It is noteworthy that gradual weight loss of AlF(50%bdc)(50%bdc-NH$_2$) over the temperature range of 150 – 300 °C is observed and only 3 percent weight of material was decomposed. While in AlF(75%bdc)(25%bdc-NH$_2$), the weight loss over this temperature range is 10 %. TGA thermogram of AlF(25%bdc)(75%bdc-NH$_2$) shows gradual weight loss over the whole observed temperature range. The unreacted bdc and bdc-NH$_2$ decompose over the temperature range of 200 – 300 °C which overlaps to the decomposition temperature of the framework at about 350 °C. In case of AlF(bdc-NH$_2$), large amount of water bound to the crystal surface left the framework over the temperature range of 30 – 100 °C. Gradual weight loss of 2 percent is observed before bdc-NH$_2$ linkage starting to depart at 325 °C. From the results, although the weight loss trend of each as-made materials is different, it is clear that adding bdc-NH$_2$ to the AlF(bdc) framework lowers the thermal stability of the materials. This implies that the linkage between metallic chain and bdc-NH$_2$ ligand is weaker that the one with bdc ligand. Similar phenomenon was found in case of Al(OH)(bdc) and Al(OH)(bdc-NH$_2$) where the decomposition temperature of Al(OH)(bdc-NH$_2$) is lower by 100 °C.[15]
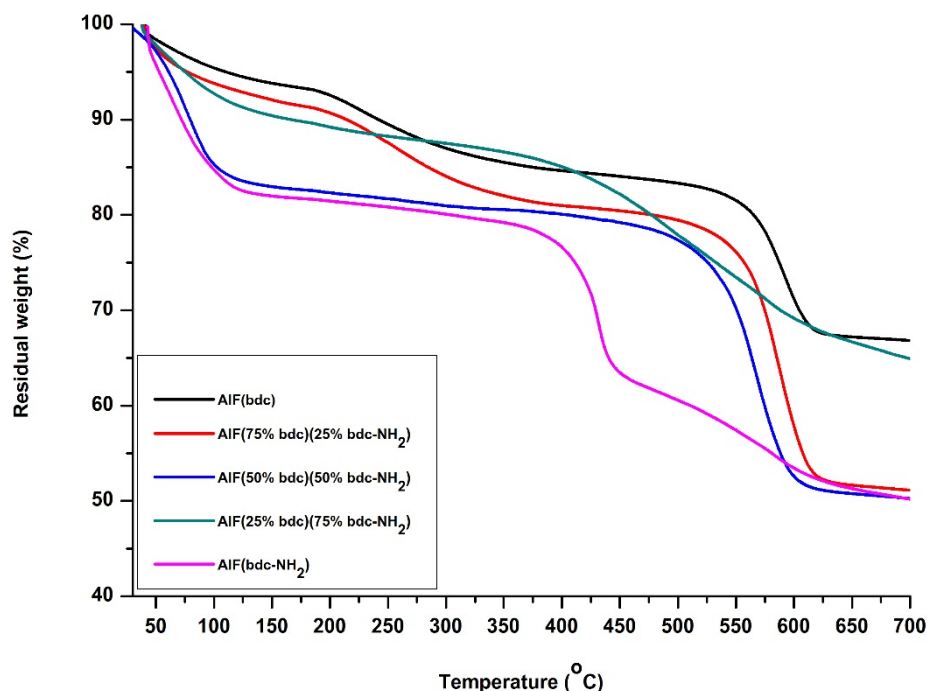
Figure 4 TGA thermograms of all as-made materials.

Conclusions

Partial and complete ligand substitution of bdc by bdc-NH$_2$ into the AlF(bdc) framework have been successfully conducted. The four materials including AlF(75%bdc)(25%bdc-NH$_2$), AlF(50%bdc)(50%bdc-NH$_2$), AlF(25%bdc)(75%bdc-NH$_2$) and AlF(bdc-NH$_2$) was successfully characterized. The morphology of mixed ligand materials shows two distinct crystal forms of prism and needle like crystals. Increasing amount of bdc-NH$_2$ substituted into the AlF(bdc) framework promotes needle like crystal form. While, complete substitution of bdc by bdc-NH$_2$ decreases the length of prism like crystal and inhibit needle like crystal morphology. In addition, the presence of bdc-NH$_2$ lowers the thermal stability of the framework. The more amount of bdc-NH$_2$ incorporated into the AlF(bdc) framework, the lower the decomposition temperature of the framework gets. It is interesting to conduct further investigation on the structure transition of mixed ligand AlF(bdc) in order to observe whether they show breathing effect or not. Moreover, the effect of bdc-NH$_2$ ligand on the gas adsorption property of these materials is still unknown and needs to be fulfilled.

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