HYDROTHERMAL STABILITY AS AN IMPORTANT CHARACTERISTICS OF METAL-ORGANIC FRAMEWORK MATERIALS

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ABSTRACT

We have studied the hydrothermal stability of three aluminium (MIL-96, MIL-100, MIL-110) and one zinc carboxylates. Among aluminium-based MOFs, MIL-96(Al) and MIL-100(Al) show higher stability in water as the MIL-110(Al) material, which is stable only when water is present in traces. Hydrothermal stabiliy of ZnBTC structure is a rarity for Zn-based MOFs and the reason lay in the presence of hydrogen bonds between adsorbed water and the framework and due to the π-π interactions beetween benzene rings. However, high water resistance even at elevated temperatures together with promising water sorption properties (0.7 g of water per g of material) implies that only MIL-100(Al) material is a potential candidate for water sorption based energy applications.

Keywords: metal-organic frameworks, zinc carboxylates, aluminium carboxylates, hydrothermal stability.

INTRODUCTION

Metal organic framework (MOF) materials are promising for a variety of applications including gas and heat storage, separation, sensing, catalysis and drug delivery due to their high surface areas, porosity and tuneable structures [1]. However, sensitivity or instability in the presence of moisture turns out to be a decisive factor and major limitation for their industrial scale development [2, 3]. Since MOF materials have been considered as potential candidates for low temperature heat storage applications based on the adsorption/desorption of vapours, the evaluation of its hydrothermal stability is not just required but mandatory. [4]

It has been known that MOFs with imidazolates and other N-containing ligands are more stable in water then carboxylate based MOF materials. [5] Beside the strength of metal-ligand interaction, the hydrothermal stability of metal-organic framework materials also depends on the coordination number and/or oxidation state of the metal, dimensionality of the framework and other structural characterististics. [2] Among porous carboxylates chromium, alumnium and iron based MOFs show the highest stability in water. On the other hand zinc carboxylates (MOF-5, MOF-177, DUT-30, UMCM-1, DMOF-1) are in general unstable in humid conditions. [6] In this work we have focused on the investigation of the hydrothermal stability of three aluminium (MIL-96, MIL-100, MIL-110) [7-9] and one zinc trimesates [10] (benzene-1,3,5-tricarboxylates = BTC) in order to determine the role of geometry of secondary building units, strength of metal-ligand interaction and/or other weaker interaction on their resistance in humid conditions.

EXPERIMENTAL

All investigated metal-organic framework materials were hydrothermally or solvothermally synthesised under autogenous pressure in Teflon-lined stainless-steel 23 ml autoclaves. Aluminium MOF materials were synthesised in accordance with literature data [7-

9]. Zinc trimesate was prepared under solvothermal conditions, while it was previously synthesised hydrothermally [10]. An X-ray analysis was used to identify the obtained products. The measured powder XRD patterns were compared with simulated patterns of corresponding known MOFs.

The size and morphology of the crystals in the products were studied by using scanning electron microscope Zeiss Supra™ 3VP. Structural changes and hydrothermal stability of all materials were monitored by powder X-ray diffraction measurements on a PANalytical X'Pert PRO high-resolution diffractometer with Alpha1 configuration (CuKα1 λ = 1.5406 Å radiation) using continuous scanning mode in 2θ range from 5 to 35° using step of 0.016° per 100 s. Thermogravimetric (TG/DTG) analysis was performed on a SDT 2960 Thermal Analysis System (TA Instruments, Inc.). The measurement was carried out in static air with the heating rate of 10 ^{o}C min^{-1}. Thermal stability was studied by a high-temperature X-Ray diffraction and NMR spectroscopy. The XRD measurements were performed in vacuum employing a PANalytical X'Pert PRO diffractometer from 2 to 60^{o} 2θ using step of 0.016^{o} per 100 s in the temperature range between 25 and 700 °C, while ^{1}H and ^{1}H-^{13}C CPMAS NMR spectra were recorded on a 600 MHz Varian NMR system equipped with a 3.2 mm Varian probehead.

Water sorption characteristics were determined by an IGA-100 gravimetric analyzer (Hiden Isochema Ltd). Water sorption isotherms were obtained by setting equal pressure intervals of 1.6 mbar between vacuum and saturation vapour pressure at selected temperature with an equilibrium time of 80 s. Before adsorption measurements, the sample was outgassed to a constant weight under ultra high vacuum at high temperatures (150 or 200 °C). The hydrothermal stability of the material was additionally evaluated with cycle test measurements consisting of 40 cycles between designated temperatures of 40 and 140 °C in a helium gas flow with 75 % relative humidity. The adsorption and desorption of water on zinc carboxylate was monitored also by *in situ* IR spectroscopy. A Nicolet 6700 IR spectrometer equipped with a MCT detector and an extended-KBr beam splitter was used for the acquisition of spectra recorded in the 400-5500 cm^{-1} range.

RESULTS AND DISCUSSION

The framework of ZnBTC material is built up from infinite chains of Zn-containing tetrahedral and octahedral building units which are connected through BTC linkers to the 3-D structure. Parallel channels are occupied with water molecules. MIL-100(Al) is assembled from trimers of μ_3-O-bridged Al(III) octahedra, which are connected by BTC linkers into a large pore framework structure. MIL-96(Al) and MIL-110(Al) also exhibit a three-dimensional framework: the structure of MIL-96(Al) contains isolated trinuclear μ_3-O-bridged aluminum clusters and infinite chains of aluminium octahedra forming a honeycomb lattice with 18-membered rings. In the MIL-110(Al) structure octanuclear aluminium-carboxylate clusters are linked through BTC ligand forming hexagonal channels.

Water sorption measurements (Figure 1) revealed that the highest capacity is reached in MIL-100(Al) which has also the largest specific area. The shape of the water sorption isotherm showed the presence of micro- and meso-porous cages, while the isotherms of all other materials are characteristic for microporous solids.

Hydrothermal stability was studied by the hydrothermal cycling from 40 to 140 ^{o}C at 75 % humidity. MIL-96(Al) and MIL-100(Al) withstood 40 cycle-hydrothermal stability tests (Figure 2). Taking into account literature data [2] it was expected that MIL-110(Al) is stable in water. However, this study showed that its structure decomposes at selected conditions. From the obtained results we conluded that MIL-110(Al) is only kinetically stable in water, since the immersion of material in water causes its structure to collapse. On the other hand

MIL-96(Al) and MIL-100(Al) materials exhibit also termodinamical beside kinetical stabilty in humid conditions. From the obtained results and known structural properties of investigated aluminium carboxylates we attributed the hydrothermal stability of MIL-96(Al) to the presence of corner sharing AlO_6 octahedra in inorganic chains that are additionally stabilized through a hydrogen bond network. The instability of MIL-110(Al) in water in comparison with MIL-100(Al) material may lay in the fact that the octameric clusters are more susceptible to reaction with water and consequently the ligand displacement. Test of hydrothermal stability also revealed that ZnBTC material retained its structure after hydrothermal testing (Figure 2) which is a rarity for Zn-based MOFs. By using NMR and *in situ* IR spectroscopy we determined that the high chemical stability towards water is a consequence of the presence of π-π interactions between aromatic ligands and hydrogen bonds between coordinated water and free water molecules located between the vertices of octahedra.

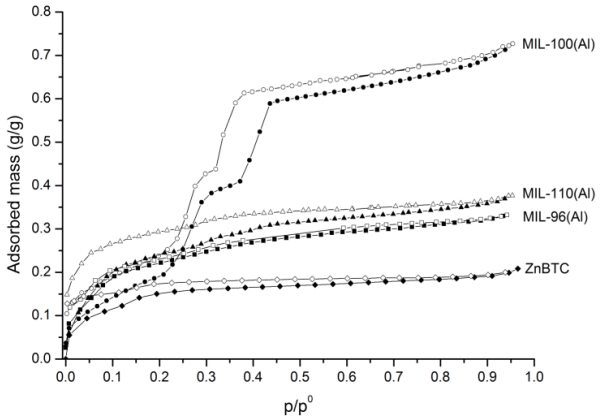

Figure 1. Water sorption isotherms of MIL-96(Al), MIL-100(Al), MIL-110(Al) and ZnBTC materials.

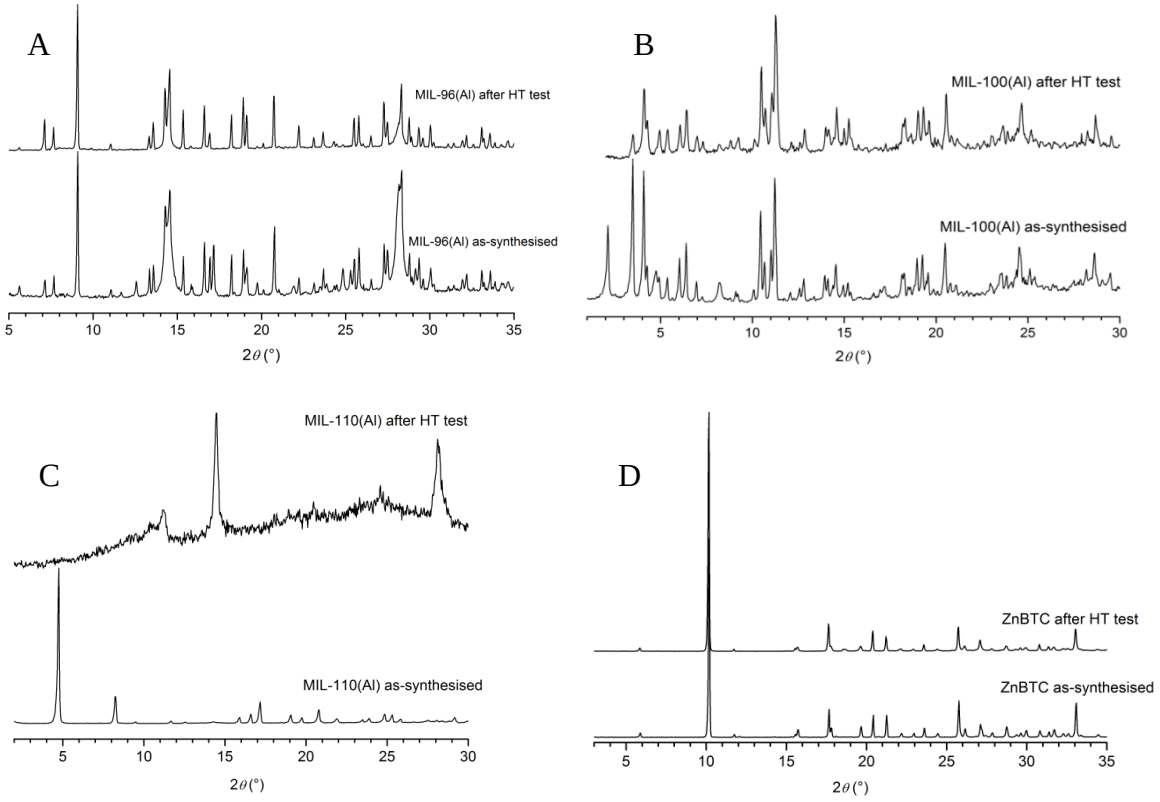

Figure 2. X-ray diffraction patterns of as-synthesised materials and after hydrothermal treatment (40 cycles) of (A) MIL-96(Al), (B) MIL-100(Al), (C) MIL-110(Al), (D) ZnBTC material.

CONCLUSION

MIL-96(Al), MIL-100(Al) and ZnBTC materials were found to exhibit good hydrothermal stability, while the MIL-110(Al) did not retain its strucutre after cycling test in water. The hydrothermal stability of metal organic frameworks depends on the type of inorganic secondary building units and that different type of intramolecular interactions such as hydrogen bonds or/and π-π interactions have significant contribution to the MOFs stability in water.

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