



## Systematic study of the chemical and hydrothermal stability of selected “stable” Metal Organic Frameworks



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### ABSTRACT

In this work, the hydrothermal and chemical stability towards acids, bases, air, water, and peroxides of Metal Organic Frameworks, that are commonly considered to be stable, is presented. As a proof of stability both the crystallinity and porosity are measured before and after exposure to the stress test. The major part of the MOFs examined in this study show a good hydrothermal stability except for UiO-67, NH<sub>2</sub>-MIL-101 (Al) and CuBTC. The chemical stabilities towards acids and bases show a similar tendency and an ordering can be proposed as: MIL-101(Cr) > NH<sub>2</sub>-UiO-66 > UiO-66 > UiO-67 > NH<sub>2</sub>-MIL-53 > MIL-53(Al) > ZIF-8 > CuBTC > NH<sub>2</sub>-MIL-101(Al). In the tests with H<sub>2</sub>O<sub>2</sub> most materials behaved poorly, only the UiO-66 and NH<sub>2</sub>-UiO-66 frameworks show a good stability.

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### 1. Introduction

Metal Organic frameworks (MOFs) are a class of inorganic-organic hybrid materials that have received great interest over the past decades. While the initial research on MOFs was focused on the synthesis and structural characterization, an increasing number of MOFs are now being examined for their interesting properties, including optical, magnetic and electronic properties as well as for their various potential applications such as in catalysis, ion exchange, gas storage and separation, sensing, polymerization and drug delivery [1–3]. However, one of the major problems that limits the use of MOFs is their relatively poor stability. Besides their low thermal stability (limited to 350–400 °C), few MOFs are known to be stable in the presence of water. This is due to the hydrophilic properties of the metal nodes which results in a strong interaction with water molecules and therefore leads to the cleavage of

coordination bonds, hence, destroying the framework [4]. Since the pioneering study of Low et al. many other studies have been carried out on the water sensitivity of MOFs [5–7]. Very few MOFs showed no structural integrity loss in the presence of water. Within this context, the pyrazolate based frameworks showed a remarkable stability after exposure to boiling water and other solvents which was attributed to the high pK<sub>a</sub> value of the imidazole ligands [8]. Besides the pyrazolate based frameworks, the hydrothermally synthesized MIL series constructed from octahedrally coordinated aluminium or chromium metal clusters (MIL-53 or MIL-101 type) and zeolitic imidazolate frameworks (ZIFs) have been reported to be stable in water [9,10]. In particular, the ZIF-8 material, in which the zinc atoms are coordinated to methylimidazolate ligands via Zn–N bonds possess a very high stability, not only under mechanical pressure but also in aqueous solutions [11,12]. The higher basicity of the imidazolate linker, in comparison to the carboxylate linkers, results in stronger metal-ligands bonds and therefore in an enhanced stability towards water [8]. Interesting work on the water-stability of MIL-101(Cr) was performed in a study on dehumidification over hierarchically porous MOFs and the use as advanced water adsorbents, by Chang et al. [13]. Furthermore, MOFs constructed from Zr<sub>6</sub> based nodes also show a remarkable

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high stability (mechanical, hydrolytical, and chemical stability). The high stability of these Zr-based MOFs, of which UiO-66 is a prototypical example, is due to the Coulombic interaction of the highly oxophilic Zr<sup>IV</sup> metal sites with the negatively charged termini of the carboxylate linkers [14].

Nevertheless, for the evaluation of MOFs towards processes in industry, the chemical, thermal, and hydrothermal stability are important factors as many processes are performed in the presence of acids or bases (for reactions in the liquid phase) or at elevated temperature (for gas phase reactions). Furthermore, the stability of MOFs towards commonly used oxidants is also very crucial in oxidative processes. Although there have already been studies on the chemical, thermal, and hydrothermal stability of MOFs, to the best of our knowledge no systematic and no long-term stability tests have been carried out [15].

Here, we present for the first time a systematic comparative study of reportedly “stable” Metal Organic Frameworks which will be denoted in the following as MIL-101(Cr), NH<sub>2</sub>-MIL-101(Al), MIL-53(Al), NH<sub>2</sub>-MIL-53, UiO-66, NH<sub>2</sub>-UiO-66, UiO-67, ZIF-8 and CuBTC. More specifically, their hydrothermal and chemical stability to aqueous acids (pH = 0 or pH = 4), -bases (pH = 12), and oxidative environment (5 wt. % H<sub>2</sub>O<sub>2</sub>) is studied on short-term (3 days) and long-term (60 days). Additionally, their short and long-term exposure to water and air has been evaluated.

## 2. Materials and methods

### 2.1. General procedures

All chemicals were purchased from Sigma Aldrich or TCI Europe and used without further purification. Nitrogen adsorption experiments were carried out at –196 °C using a Belsorp-mini II gas analyzer. Prior to analysis, the samples were dried under vacuum at 120 °C to remove adsorbed water. X-Ray powder diffraction (XRPD) patterns were collected on an ARL X'TRA X-ray diffractometer with Cu K $\alpha$  radiation of 0.15418 nm wavelength and a solid state detector. Thermogravimetric Analysis (TGA) was performed on an SDT 2960 from TA Instruments.

### 2.2. Synthesis of the MOF materials

#### 2.2.1. MIL-101 (Cr)

MIL-101(Cr) was synthesized according to an adapted recipe from Edler et al. [16]. In a typical experiment, 0.665 g terephthalic acid (4 mmol) and 1.608 g Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (4 mmol) were added to 20 mL deionised water. The resulting suspension was placed in a Teflon-lined autoclave at 210 °C during 8 h under autogenous pressure (2 h warm-up). After cooling down to room temperature, the mixture was filtered and the green solid was collected and washed thoroughly with dimethylformamide (DMF) and water in order to purify the material by removing any unreacted reagents. The material was not subjected to additional activation steps.

#### 2.2.2. NH<sub>2</sub>-MIL-101(Al)

The NH<sub>2</sub>-MIL-101(Al) material was prepared in a few smaller batches as proposed by Fischer et al. [17] 270 mg (1.49 mmol) of 2-aminoterephthalic acid was dissolved in 60 mL of DMF. This solution was heated to 110 °C and 730 mg (3.0 mmol) AlCl<sub>3</sub>·6H<sub>2</sub>O was added in 6 equal portions, one each 15 min. The solid material began to form after approximately 30 min of reaction. After adding the last portion, the mixture was stirred for an additional 3 h. In a final step the mixture was placed under heating without stirring for 16 h. Afterwards, the solid was filtered off and washed several times with DMF after which a soxhlet extraction with acetone was performed for 6 h in order to remove any free linkers and AlCl<sub>3</sub>.

#### 2.2.3. CuBTC

For the synthesis of CuBTC, 2 g (9.52 mmol) of benzene-1,3,5-tricarboxylic acid was added to 50 mL of a 1:1:1 mixture of DMF/EtOH/H<sub>2</sub>O. 3.4 g (17.24 mmol) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O was added with 50 mL of the same solvent mixture and both mixtures were combined under stirring. Finally triethylamine (2 mL) was added, after which the resulting mixture was stirred for 23 h at room temperature. The product was collected by filtration and washed 2 times with 25 mL of DMF [18].

#### 2.2.4. UiO-66-X (X = H, NH<sub>2</sub>)

The UiO-66-X materials were synthesized according to a slightly modified procedure of Van Der Voort et al. [19] Typically 0.3 g (0.89 mmol) ZrO<sub>2</sub>Cl<sub>2</sub>·8H<sub>2</sub>O and 0.1545 g (0.93 mmol) terephthalic acid or 0.168 g (0.93 mmol) 2-aminoterephthalic acid were added to 3.6 mL formic acid and 9 mL dimethyl acetamide. After 20 min of sonication, the solution was transferred to a Teflon-lined autoclave and placed in an oven at 150 °C for 12 h. When cooled down, the solid was filtered off and subsequently stirred in DMF (12 h) and methanol (24 h) to remove respectively free linker and DMF from the pores. The resulting materials were dried under dynamic vacuum at 65° (X = H) and 220° (X = NH<sub>2</sub>) for 24 h.

#### 2.2.5. UiO-67

The synthesis procedure of UiO-67 was based on the recipe of Farha et al. [20]. 0.27 mmol ZrCl<sub>4</sub> and 0.38 mmol 4,4'-diphenyldicarboxylic acid (BPDC) was dissolved in 15 mL DMF and 0.5 mL concentrated HCl. The resulting solution was sonicated for 20 min and transferred afterwards in a thermoblock at 80° for 12 h. After filtration and washing with DMF and ethanol, the samples were dried under a dynamic vacuum at 90 °C and activated at 150 °C (3 h).

#### 2.2.6. MIL-53 (Al)

MIL-53 (Al) was synthesized according to a slightly modified procedure of Ferey et al. [21]. A mixture of AlCl<sub>3</sub>·6H<sub>2</sub>O (2.90 g, 12.0 mmol), terephthalic acid (2.00 g, 12.0 mmol), and deionised water (60 mL) is placed in a Teflon-lined autoclave at 210 °C for 24 h. Afterwards the MIL-53 (Al) as is collected by filtration and washed with acetone, followed by a calcination at 300 °C for 72 h to obtain MIL-53 (Al).

#### 2.2.7. NH<sub>2</sub>-MIL-53

The NH<sub>2</sub>-MIL-53 was synthesized following the recipe of Stock et al. [22]. 1.48 g (6.13 mmol) of AlCl<sub>3</sub>·6H<sub>2</sub>O was mixed with 1.13 g (6.24 mmol) of 2-aminoterephthalic acid in 15 mL of deionised water. The resulting solution was placed in a Teflon-lined autoclave at 150 °C (heating rate: 1 h) for 5 h. Afterwards the solid material was filtered off and placed with DMF in an autoclave for an additional 15 h at 150 °C to remove unreacted linker. The DMF molecules were removed by a thermal treatment in air at 130 °C in a muffle furnace.

#### 2.2.8. ZIF-8

For the synthesis of ZIF-8, 0.733 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.46 mmol) was dissolved in 50 mL deionised water. A second solution of 1.622 g HMe-Im (19.75 mmol) and 2.00 g TEA (19.76 mmol) in 50 mL deionised water was prepared. The Zn solution was added to the second solution under stirring which resulted immediately in an opaque white solution. After stirring for an additional 10 min at room temperature, the solid was separated through centrifugation and placed in water for 12 h. This procedure was repeated 2 times. Hereafter the solid was collected and dried in air at 110 °C. Finally, the sample was dried under vacuum at 150 °C for 1 h [23].

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