



Microwave-assisted synthesis of zirconium-based metal organic frameworks (MOFs): Optimization and gas adsorption

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ABSTRACT

Microwave-assisted synthesis of zirconium (Zr) based metal organic frameworks (MOFs) were performed and the yield and porous property of UiO-67 was optimized by varying the quantity of the modulator (benzoic acid, BenAc and hydrochloric acid, HCl), reaction time and temperature. It was found that (i) an increase in the amount of modulator enhanced the specific surface area and pore volume of UiO-67 due to the promotion of linker deficiency; and (ii) the presence of modulators influenced the number of nuclei (and hence the crystal size) and nucleation time (and hence the yield). Optimum amounts of BenAc and HCl for synthesizing UiO-67 under microwave irradiation were determined as 40 mol equivalent and 185 mol equivalent (to Zr salt), respectively. In comparison to conventional solvothermal synthesis, which normally takes 24 h, microwave methods promoted faster syntheses with a reaction time of 2–2.5 h (at similar temperatures of 120 °C and 80 °C for BenAc and HCl, respectively). The thermal effect of microwave is believed to contribute to the fast synthesis of UiO-67 in the microwave-assisted synthesis. The reaction mass efficiency and space-time yield show that microwave heating promoted the simple yet highly efficient preparation of Zr-based MOFs. In addition, UiO-67 MOFs from different synthesis methods (*i.e.* the microwave-assisted and solvothermal method) were evaluated using single-component (CO₂ and CH₄) adsorption, showing comparable gas uptakes.

1. Introduction

Research on metal organic frameworks (MOFs) has experienced a tremendous growth over the past two decades due to their well-known features of large surface areas, high micropore volumes and the tunability of pore chemistry and shape [1,2]. These intriguing porous crystalline materials have been studied as promising candidates for various applications including energy storage [3–5], separation [6–8], catalysis [9–12], chemical sensing [13] and drug delivery [14]. However, the application of MOFs has often been questioned since most well-known MOFs suffer from poor thermal and chemical stabilities [15]. For example, HKUST-1 (or CuBTC, a copper-based MOF) has been manufactured at large scale [16] and recognized as a good candidate for gas adsorption. However, its instability in the presence of moisture has impeded practical applications of HKUST-1 [17–19]. To address this problem, numerous efforts have been made to improve the stability of MOFs by design such as (i) the use of high oxidation state metals (*e.g.* Zr⁴⁺, Fe³⁺, Al³⁺) to reinforce the bonds between metal sites and linkers [20,21]; and (ii) the post-synthetic modification of organic linkers and/or metal sites by hydrophobic groups [22] or functional dopants

[6].

In 2008, a class of zirconium (Zr)-based MOFs, *i.e.* UiO MOFs (UiO for Universitetet i Oslo), was designed with remarkable stability that was not typically found in other MOFs [23]. UiO-66/-67 MOFs are by far the most widely studied UiO MOFs, in which Zr₆O₄(OH)₄ clusters are joined by organic linkers of 1,4-benzenedicarboxylate acids (BDC, for UiO-66) and 4,4-biphenyldicarboxylate acids (BPDC, for UiO-67). Zr⁴⁺ ions in the Zr Clusters have strong interactions with the carboxylate ligands and are theoretically fully coordinated to other clusters by 12 organic linkers, forming a highly connected framework [24,25]. Thanks to this strong interaction between the organic and inorganic regions, UiO MOFs are thermally stable up to 450 °C and chemically stable in various organic solvents. The existence of small tetrahedral cages (7.5 Å for UiO-66 and 12 Å for UiO-67) and large octahedral cages (12 Å for UiO-66 and 16 Å for UiO-67) in their frameworks make them good candidates for adsorption and catalysis, respectively [23,26,27].

Laboratory syntheses of UiO MOFs were first achieved under solvothermal conditions by Lillerud's group [23]. However, the original synthetic method was inefficient and often led to the production of

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intergrown crystals with poor crystallinity due to the formation of zirconia gel (amorphous precursors) at the beginning of reaction [28,29]. In 2011, Behrens and co-workers [27] investigated the effect of monocarboxylic acids on the modulated synthesis of Zr-based MOFs and found that modulating agents are key elements to promote the self-assembly of UiO MOFs. According to the proposed modulation mechanism, during the synthesis, modulators (e.g. benzoic acid and acetic acid) firstly compete with bidentate ligands to coordinate with Zr cations, then ligand exchange (between bidentate linkers and coordinated modulators) follows to render the framework. As a result, the formation of amorphous precursors is prevented by the modulated synthesis. In addition, the reproducibility and crystallinity of resulting MOFs are enhanced. Monocarboxylic acids of formic, trifluoroacetic and benzoic acids as well as hydrochloric acid have been commonly used as modulators for synthesizing UiO MOFs [29–32].

It has also been found that size and morphology of UiO MOFs are tunable from micro-sized aggregates of intergrown crystals to individual octahedral crystals (up to 2 μm), depending on the amount and type of the modulator used in the synthesis [27,33]. Despite modulators being necessary, recent studies using thermogravimetric analysis (TGA) and neutron diffraction have revealed the formation of structural defects in UiO MOFs as a result of their presence during the synthesis [31,34–37]. Structural defects in UiO MOFs are created mainly by the partial ligand-exchange between dicarboxylic ligands (linkers) and monocarboxylic ligands (modulators), which lead to the presence of modulators (acting as defect-compensating ligand [25]) in the final structure of MOFs, i.e. the defective framework [34]. These defects corresponds to either missing linkers [25] or missing clusters [38], benefiting the porosity and specific surface area of resulting MOFs, and hence their adsorption capacity (e.g. 50% increase in CO_2 uptake of UiO-66 at 35 bar) [25] and reactivity (e.g. up to 96% conversion in aldol condensation of acetaldehyde on UiO-66-Cr and UiO-67-Cr catalysts) [34].

To date, MOFs have been mostly synthesized using solvothermal methods which require lengthy reaction time and high energy input [39]. Consequently, the development of alternative synthetic routes that are more economical and sustainable is of great interest to the research community. For Zr-based MOFs, an electrochemical method was developed for the synthesis of UiO-66, in which modulators (acetic acid) were used to control the cathodic and anodic film deposition of UiO-66 on zirconium foils with a fast reaction time (30 min) and mild reaction temperature (100 $^\circ\text{C}$) [40]. Microwave-assisted synthesis is another alternative for preparing MOFs [41]. In microwave synthesis, heat is generated internally within reaction media by dielectric heating as opposed to the conventional heating in which heat is conducted to the media from external heating sources [41,42]. Hence, a uniform and intensive heating can be initiated under microwave irradiation facilitating the nucleation and crystal growth in the synthesis of MOFs [43]. The effect of microwave irradiation on reactions can be classified into (i) the thermal effect and (ii) the non-thermal effect (i.e. specific microwave effects such as the direct interaction of the electric field with specific molecules in the reaction medium which is not linked to macroscopic temperature change [44–46]). It is generally agreed that enhancements (in terms of yield, product purity and efficiency) observed in microwave-assisted syntheses are mostly a consequence of thermal/kinetic effects (i.e. high local temperatures promote fast reaction rates). In contrast, the non-thermal effect of microwave-assisted synthesis is controversial leading to debate in the scientific community. It is noteworthy that the combination of both effects makes the investigation of the effect of microwave irradiation on the synthesis a relatively complex task.

Recently, UiO-66 MOF was prepared using a short reaction time of 120 min with a high yield of ca. 90% (based on ZrCl_4) in a microwave-assisted method, the product showed good capacity for liquid phase dye adsorption (98% removal efficiency for acid chrome blue K) [47]. In addition, Taddei et al. optimized the synthesis condition of UiO-66

under microwave irradiation with high productivity, energy efficiency and crystallinity of materials [48]. Furthermore, it was also found that the microwave irradiation usually decreased the size of crystals as a result of the accelerated nucleation, i.e. increased number of nuclei produced that grew into small crystals [47,49]. For instance, the crystal size of UiO-66 from the microwave synthesis (< 100 nm) was four times smaller than that by conventional heating (ca. 400 nm) [47]. Small crystal size at submicron and nano scales can be beneficial in applications such as non-equilibrium adsorption and catalysis since interparticle diffusion limitation can be greatly reduced [50] or the nano-crystallites can be used in the formation of thin film membranes for molecular separations [51]. Conversely, MOFs with large crystals may be of interest for equilibrium adsorption where a big pore volume is needed. Therefore, the development of a fast and energy-efficient synthesis route for UiO MOFs, which are able to simultaneously reduce reaction time and control crystal size, could boost their application in a wide range of fields where different specifications are required.

Herein, we report the development and optimization of the microwave-assisted modulated synthesis of UiO-67 MOF, in which the benefit of focused microwave-induced heating is combined with modulation for controlling the properties of materials (e.g. morphological and porous features). To the best of our knowledge, it is the first time that UiO-67 MOF has been prepared by the microwave-assisted method. UiO-67 was synthesized with benzoic acid (BenAc) and HCl as modulators. A systematic and comparative approach, taking into account the yield and properties of resulting materials, was employed to optimize the synthesis condition in terms of the reaction time, temperature and the amount/type of modulators. The resulting materials were carefully characterized and evaluated by single-component gas adsorption (using CO_2 and CH_4) and compared to UiO-67 prepared by the conventional solvothermal method.

2. Experimental

2.1. Chemicals and synthesis of materials

Terephthalic acid (BDC), ZrCl_4 and 4,4'-biphenyldicarboxylic acid (BPDC) were purchased from Arcos. Benzoic acid (BenAc), hydrochloric acid (HCl) and acetic acid (AC) were purchased from Sigma-Aldrich. *N,N'*-dimethylformamide (DMF) was obtained from Fischer Scientific. All chemicals were used as received, with no further purification.

UiO-66/-67 MOFs (UiO-66 was prepared as the secondary material in this work) were synthesized solvothermally using different modulating agents according to methods reported by Schaate et al. [26] and Katz et al. [29]. The synthesis mixture was prepared by dissolving ZrCl_4 and modulators (HCl or AC for UiO-66; HCl or BenAc for UiO-67) in 20 ml of dimethylformamide (DMF) under sonication, followed by the addition of organic linkers (BDC for UiO-66; BPDC for UiO-67) to the solution. The opaque white solution was then transferred to a 50 ml Teflon-lined autoclave reactor and heated at 120 $^\circ\text{C}$ under hydrostatic conditions. After 24 h, the reactor was cooled down to room temperature and precipitates were centrifuged. Full details of the synthesis, washing and activation procedures have been provided in the Supporting Information (SI).

A CEM Discover SP microwave system was used to prepare UiO MOFs under microwave irradiation, where the synthesis solution (SI) was kept in a Pyrex vial (35 ml) and irradiated under constant power (150 W, 2.5 GHz). After synthesis, the resulting materials were washed and activated using the same procedure as that in the solvothermal synthesis (SI).

2.2. Characterization of materials

Powder X-ray diffraction (PXRD) was carried out on a Rigaku Miniflex diffractometer using $\text{CuK}\alpha_1$ radiation (30 kV, 15 mA, $\lambda = 0.15406$ nm). Measurements were made over a range of

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