



Binary supercritical CO₂ solvent mixtures for the synthesis of 3D metal-organic frameworks



Ana López-Periago, Pedro López-Domínguez, Jorge Pérez Barrio, Gerard Tobias^{**}, Concepción Domingo^{*}

Institute of Materials Science of Barcelona (ICMAB-CSIC), Campus de la UAB s/n, Bellaterra, 08193, Spain

ARTICLE INFO

Article history:

Received 8 April 2016

Received in revised form

15 June 2016

Accepted 10 July 2016

Available online 14 July 2016

Keywords:

MOFs

Supercritical CO₂

Ionic liquid

Green chemistry

ABSTRACT

Efficient and sustainable synthesis of MOFs, as nano or microcrystalline powder, is crucial for the development of new applications for these compounds. For this purpose, the synthesis of Zn²⁺, Cu²⁺ and Fe³⁺-based MOFs was attempted in this study by using a binary medium consisting of supercritical CO₂ mixed with an ionic liquid (emimBF₄ or emimBr). In comparison with conventional solvothermal and ionothermal synthesis, MOFs were herein obtained under mild reaction conditions, *i.e.* 200 bar and 65 °C, after relatively short reaction periods (<10 h). To explore the described synthesis method as a generic procedure for the preparation of three-dimensional MOFs, different linkers of the imidazole and carboxylic acid families were tested. Widely investigated MOFs, such as ZIF-8 and HKUST-1, were prepared along with the complex mesoporous MIL-100(Fe). The structure and composition of the synthesized materials were determined by X-ray powder diffraction and elemental analysis. N₂ adsorption at low temperature was used to assess the textural properties.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Metal-organic frameworks (MOFs) are an emerging class of porous materials, built up by the assembly of metal ions with organic linkers through coordination bonds. These compounds are crystalline solids with a well-defined microporosity, regular pore structure and high surface area. These characteristics allow their use for the manipulation of atoms and molecules in important applications, which include heterogeneous catalysis, adsorption, gas separation, gas/liquid storage, molecular sensing, luminescence or drug delivery, among others [1].

The controllable synthesis of MOF products in a cost-effective and environmentally friendly manner is crucial for their large-scale application. However, the synthesis of MOFs is a complex process, since starting from a specific reaction mixture, but using diverse synthetic methods, or even solvents, different MOFs can be obtained. Moreover, alternative routes can lead to similar structural compounds, but with different particle size and morphology and, thus, to different physicochemical and textural properties.

Currently, several solvent methods have been well-established to synthesize MOFs, most of them in basic organic solvents, such as N,N-dimethylformamide (DMF), but also in water or water/ethanol mixtures. Direct precipitation of MOFs at high temperature in organic solvents under either ambient or autogenous pressure (solvothermal synthesis) is the most studied procedure. The energy needed for the synthesis is given either by conventional heating or microwave irradiation. Sonochemistry, electrochemistry and mechanochemistry are also widely used approaches for the production of MOFs [2,3]. Recently, ionothermal synthesis has attracted much attention for the crystallization of MOFs, since with the right choice of the ionic liquid (IL) both the organic and inorganic reagents can be simultaneously dissolved in it [4,5]. The IL can behave as a solvent, reactant, structure directing agent, charge-compensation template and/or inclusion [6]. Moreover, there is a vast range of possibilities to control the synthesis of MOFs and to prepare new structures by tuning the properties of the IL, mainly adjusting the cation or anion [7–11]. However, in most of the described results, the cation of the IL is incorporated into the structure of the MOF, either by itself [12–19] or together with the anion [5,20,21].

The use of supercritical carbon dioxide (scCO₂) in the field of MOFs has been mainly limited to post-synthesis treatment, either for pore activation [22,23], removing entrapped undesired by-

* Corresponding author.

** Corresponding author.

E-mail address: conchi@icmab.es (C. Domingo).

products or solvents, or pore modification [24], with only one example found on the reactive precipitation of one-dimensional MOFs in $scCO_2$ media [25]. For specific applications related to microporous systems, $scCO_2$ has the advantage of having gas-like diffusivity and zero surface tension, allowing an easy penetration of this fluid into small pores [26,27]. Nevertheless, $scCO_2$ is a poor solvent for high-molecular weight or polar molecules, which, in principle, would rule out many possibilities in the synthesis of MOFs. An effective way to solve this problem is to create mixtures of solvents that own the capacity of solubilizing both polar and apolar substances. Most examples are based on mixtures involving $scCO_2$ and organic solvents [28]. These binary solvents are widely used for polymer processing and for the precipitation of fine particles. The preparation of a Cu-MOF in $scCO_2$ expanded DMF has also been described [29].

Mixtures comprising ILs and $scCO_2$ are known as green “designer solvents”, due to the possibility of tuning their specific properties for a particular need, either by changing the anion or cation in ILs or by varying the operating pressure and temperature in $scCO_2$ [30,31]. ILs are highly polar, while CO_2 only has a quadrupolar moment. ILs dissolve small amounts of CO_2 and, therefore, expand only moderately. As a result, some properties of the IL such as viscosity change significantly, while others such as polarity do not. Literature on the use of $scCO_2$ /IL mixtures for the synthesis of MOFs is scarce, reporting the formation of complex porous superstructures by using an unusual IL, a guanidinium salt, and fluorinated surfactants [32–34]. The addition of gas or liquid CO_2 has been described to increase the kinetics of MOF formation in a more conventional imidazolium IL [35].

The main objective of this work is to establish the basis of a generic method for developing different structures of MOFs in a $scCO_2$ /imidazolium IL solvent mixture. Synthesis protocols are extended to the two most important families of organic linkers in MOFs design, i.e., imidazolate and carboxylate. Divalent Zn^{2+} and Cu^{2+} and trivalent Fe^{3+} transition metals were chosen as metal centers. The structure and composition of the resulting crystalline precipitates were determined by X-ray diffraction and elemental analysis, respectively. The thermal stability, textural properties and morphological appearance of precipitated products were also analyzed.

2. Experimental

2.1. Materials

Zinc acetylacetonate building block ($Zn(acac)_2 \cdot xH_2O$) and copper and iron nitrate metal salts ($Cu(NO_3)_2 \cdot 3H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$) were chosen as metal sources. 2-methylimidazole (Hmim) and benzene-1,3,5-tricarboxylic acid (H_3BTC) were used as the organic linkers. The synthesis of the different MOFs was carried out in the presence of compressed CO_2 (99.995%, Carburos Metálicos S.A.) mixed with either 1-ethyl-3-methylimidazolium tetrafluoroborate (emimBF₄) or 1-ethyl-3-methylimidazolium bromide (emimBr). Reagents and solvents were all purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis method

Sample preparation under $scCO_2$ was carried out in a 100 mL high pressure reactor (TharDesign) described elsewhere [26]. In the different batches, ca. 100–150 mg of ligand and the stoichiometric molar amount (or a small excess) of metal complex or salt calculated as a function of the targeted structure (Table 1), were used. Weighted reagents were placed in a Pyrex vial to which the ionic liquid was added (ca. 200–300 mg). The vial was introduced into a

stainless steel autoclave, which was heated using resistances and pressurized with a syringe pump (Teledyne Isco 260D). Supercritical experiments were carried out under stirring at 200 bar and 65 °C during a reaction time of ca. ~10 h. At the end of each experiment, the system was slowly depressurized and allowed to cool down to room temperature. Products recovered from the $scCO_2$ /IL system were subjected to three times centrifuge cleaning by consecutively washing them first with 10 mL of ethanol (EtOH) and then twice with methanol (MeOH). Finally, they were dried at 40 °C under vacuum for 24 h. For comparative purposes, blank synthesis tests were independently performed under similar experimental conditions, but in the absence of CO_2 , i.e., under ambient pressure.

2.3. Characterization

The obtained products were characterized by powder X-ray diffraction (XRD) in a Siemens D-5000 diffractometer with Cu K $_{\alpha}$ radiation. Recorded powder XRD patterns were compared with published simulated patterns derived from X-ray single crystal data. The weight percentages of C, H and N in the samples were determined by elemental analysis using a Flash EA2000 Thermo Fisher Scientific analyzer. The thermal stability of the synthesized products was assessed by thermogravimetric analysis (TGA) in air using a PerkinElmer 7 TGA instrument. Textural properties were determined by N_2 adsorption at –196 °C using an BET ASAP 2000 Micromeritics INC. Samples were previously degassed at 120 °C for 24 h. Specific surface area (S_{aBET}) was determined by the BET method. Micropore surface area (S_{amp}) and volume (V_{mp}) were estimated by the t-curve method. Obtained results were compared with reported textural data for similar compounds. Experimental values from materials synthesized following conventional solvent methods and published values obtained by analyzing the simulated N_2 adsorption isotherms on perfect crystal structures were used [36]. Morphological features were examined by scanning electron microscopy (SEM) with a SEM Quanta FEI 200-FEG microscope.

3. Discussion

In the last few years, the ionothermal approach has been used to prepare 3D MOFs based on diverse metals, such as Cu [5], Cd [17,19,20], Co [11,13], Zn [12], Ni [13], Mn [13,16], Mg [14,15] and few lanthanides [18]. To date, bmimBF₄/Br and emimBF₄/Br have been the most used ILs for the synthesis of MOFs, in a weight ratio of ca. 2–3(IL):1(reagents). Ionothermal synthesis must be performed in sealed Teflon-lined autoclaves at temperatures between 150 and 180 °C for long periods of time, ranging from 48 to 360 h. The slow growth kinetics usually attained in the highly viscous ILs are not always appropriate for the formation of MOFs at a reasonable rate. The present study relies on the idea that the use of $scCO_2$ would increase the efficiency of the ionothermal method for the synthesis of MOFs by increasing the kinetics of the process [37].

The preparation of three different MOFs of Zn^{2+} , Cu^{2+} and Fe^{3+} was explored, choosing the organic linker from the imidazolate and carboxylate families. Targeted structures were ZIF-8, HKUST-1 and MIL-100 phases. Composition and important textural properties described for these phases are shown in Table 1.

Some physical properties of ILs such as melting point, density and viscosity are related to the mechanical and engineering components associated with the precipitation process taking place in these fluids. Compared to conventional organic solutions, ILs have a viscosity one to three orders of magnitude higher [38]. In this work, some trial experiments were performed using either emimBF₄ or emimBr as the IL. EmimBF₄ has a melting point of 14 °C and, thus, it is liquid at room temperature and has a relatively low viscosity

Download English Version:

<https://daneshyari.com/en/article/71923>

Download Persian Version:

<https://daneshyari.com/article/71923>

[Daneshyari.com](https://daneshyari.com)