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

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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.

Key words: MOFs, supercritical CO₂, ionic liquid, green chemistry

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-products or solvents, or pore modification [24], with only one example found on the reactive precipitation of one-dimensional MOFs in scCO₂ media [25]. For specific applications related to microporous systems, scCO₂ 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, scCO₂ 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 scCO₂ 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 scCO₂ expanded DMF has also been described [29].

Mixtures comprising ILs and scCO₂ 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 scCO₂ [30,31]. ILs are highly polar, while CO₂ only has a quadrupolar moment. ILs dissolve small amounts of CO₂ 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 scCO₂/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 CO₂ 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 scCO₂/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 Zn²⁺ and Cu²⁺ and trivalent Fe³⁺ 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·xH₂O) and copper and iron nitrate metal salts (Cu(NO₃)₂·3H₂O and Fe(NO₃)₃·9H₂O) were chosen as metal sources. 2-methylimidazole (Hmim) and benzene-1,3,5-tricarboxylic acid (H₃BTC) were used as the organic linkers. The synthesis of the different MOFs was carried out in the presence of compressed CO₂ (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 scCO₂ 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 scCO₂/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 CO₂, 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_α 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 N₂ 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_{BET}) was determined by the BET method. Micropore surface area (S_{mp}) 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 N₂ 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 scCO₂ 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 (36.9 mPa·s at 25 °C) [39]. Contrarily, emimBr is a solid at room temperature with a melting point of *ca.* 75 °C. This solid melts in the presence of scCO₂ at the working temperature (65 °C), which allows the dissolution of reagents and further end-product precipitation. CO₂ solubility depends on the choice of the anion, being higher in ILs involving fluoroalkyl groups [40].

X-ray analysis indicated that attempts to obtain similar products in blank experiments performed in emimBF₄ under similar experimental conditions of solvent, temperature and reaction time, but without scCO₂, failed to yield the desired product. In these tests, an amorphous material was predominantly recovered, which was formed together with a small amount of unidentifiable crystalline solid. In the absence of scCO₂, ZIF-8 and HKUST-1 targeted products could only be obtained under ionothermal conditions, i.e., by performing the reaction in sealed vessels involving a large amount of IL, at significantly higher temperature and extending the reaction time to minimum 48 h.

3.1. Imidazole-based MOFs: ZIF-8

Imidazole and its derivatives have been widely used as linkers to generate zeolite-like metal-organic frameworks (ZIFs), particularly with Zn^{2+} cations [41,42]. The conventional synthesis of ZIFs relies on solvothermal techniques, which involve the use of large amounts of expensive and environmentally unfriendly imidazole ligands and organic solvents [43]. Initially, the reaction of $\text{Zn}(\text{acac})_2 \cdot x\text{H}_2\text{O}$ and Hmim to obtain ZIF-8 in a supercritical medium with emimBF₄ was evaluated. The XRD pattern of the sample synthesized in scCO_2/IL medium matches the profile simulated from ZIF-8 single crystal structure [42] (Fig. 1a). Moreover, the C, H and N weight values determined by elemental analysis of the precipitated sample (Table 2) were compatible with the theoretically calculated values for stoichiometric ZIF-8 (Table 1), involving only a small amount of methanol (*ca.* 0.5 MeOH per ZIF-8 unit). Methanol molecules could only be incorporated into the product during the cleaning step. The considerable good match between the N values in the stoichiometric molecule and the precipitated product indicates that the ionic liquid was not significantly incorporated into the sample, since pore impregnation with this fluid would largely affect the N content.

BET characterization by N₂ adsorption indicated the precipitation of a microporous product (Fig. 1b) with a micropore surface area of 1090 m²g⁻¹ and a micropore volume of 0.39 m³g⁻¹ (Table 2). These values are comparable to reported textural data for ZIF-8 micrometric particles precipitated following different methodologies (Table 1) [44] and slightly lower than those reported for the commercial Basolite Z1200 product, constituted by micrometric ZIF-8 particles produced by BASF following an electrochemical procedure, reporting surface areas in the order of 1300-1800 m²g⁻¹. The TGA revealed structural stability in air up to temperatures of 300 °C (Fig. 1c), a common value obtained

for Zn imidazolate derivatives. SEM analysis indicated that well crystallized particles, with sizes comprised between 0.3 and 1 μm , were precipitated (Fig. 1d). Several of the typical morphologies of ZIF-8 crystals, from cubes to rhombic dodecahedra [45], can be observed in the SEM micrograph, although the stable equilibrium shape, involving the rhombic form, was clearly predominant.

A second set of experiments aiming at synthesizing ZIF-8 was performed under similar experimental conditions, but varying the IL anion from BF_4 to Br. The use of $\text{scCO}_2/\text{emimBr}$ mixtures allows the preparation of ZIF-8 with similar structural and textural characteristics to those described for the sample obtained using $\text{scCO}_2/\text{emimBF}_4$. The XRD displayed only the peaks of ZIF-8. A BET surface area value of $1257 \text{ m}^2\text{g}^{-1}$ was measured for this compound, with a micropore volume of $0.40 \text{ m}^3\text{g}^{-1}$. Taking into account that similar results were obtained by using both studied ILs, emimBF_4 was chosen to perform further experiments. The main reason is related to the extremely high hygroscopic character of emimBr , which is reduced by exchanging the Br anion in the IL for the fluorinated BF_4 . Hence, for the experimental procedure, emimBF_4 was more easily stored in dry conditions. Moreover, the hydrophobic scCO_2 fluid was more readily dissolved in emimBF_4 than in emimBr , thus leading to less viscous solutions with enhanced precipitation kinetics.

3.2. Carboxylate-based MOFs

Carboxylate-based compounds are widely studied within the family of MOFs, since by a judicious choice of the linker, a large amount of stable and truly porous compounds can be prepared [1]. One of the main drawbacks is their instability against moisture [46]. Cu^{2+} materials were first considered, since this family includes some of the earliest and most studied MOFs. Next, trials were performed with Fe^{3+} by taking advantage of its

Lewis acidity that results in strong coordinating bonds with carboxylates. The use of a rigid ligand (H₃BTC) was assayed in this work

3.2.1. HKUST-1

To obtain HKUST-1, Cu(NO₃)₂ and H₃BTC were allowed to react in the scCO₂/emimBF₄ binary solvent. Due to the high instability of carboxylate MOFs against moisture, the highly hygroscopic emimBr was not used for HKUST-1 synthesis. The XRD pattern of the precipitated product was in complete accordance with the single crystal simulated profile obtained for HKUST-1 [47] (Fig. 2a). As well, the determined C and H contents from elemental analysis (Table 2) matched the theoretically calculated values for HKUST-1 (Table 1), involving some adsorbed methanol and water molecules (*ca.* 3MeOH and 1H₂O per HKUST-1 unit). Moreover, the elemental analysis showed that N was not present in the sample, which is a clear indication of the absence of ionic liquid impregnated into the pores. The sample precipitated in this work was microporous (Fig. 2b), with surface area and micropore volume values (Table 2) in good agreement with published textural data for HKUST-1 (Table 1) [48]. The decomposition of the crystallized sample in air occurs at *ca.* 300 °C (Fig. 2c), indicating similar thermal behavior than the solvothermally synthesized HKUST-1 phase. SEM analysis of precipitated particles showed the habitual cube-shaped morphology of HKUST-1 (Fig. 2d). However, crystal size was one order of magnitude smaller (0.2-2.0 μm) than the hydrothermally precipitated particles (5-20 μm) [49].

3.2.2. MIL-100(Fe)

The objective of this trial was to obtain a MIL-100(Fe) structure by reacting Fe(NO₃)₃ and H₃BTC in scCO₂/emimBF₄. MOFs with the MIL-100 structure of Cr³⁺ and of Fe³⁺ have been hydrothermally crystallized, but with the aid of hydrofluoric acid. Compounds

formulated as $[(M^{3+})_3O(H_2O)_2F(BTC)_2] \cdot nH_2O$ are thus formed [50]. Currently, BASF and STREM commercialize MIL-100(Fe) products free of F with formula $[Fe_3O(H_2O)_2OH(BTC)_2] \cdot nH_2O$ ($n > 12$) (Table 1) and certain, although low, crystallinity [51]. The precipitated sample obtained following the supercritical approach also presents some degree of crystallinity, as illustrated in the XRD pattern (Fig. 3a), which is comparable to the one published for the commercial F-free product. Based on C and H elemental analysis (Table 2), the chemical formula of this product was estimated as $[Fe_3O(H_2O)_2OH(BTC)_2] \cdot 6H_2O$. However, this analysis also gave a significant amount of N, despite this element does not form part of the atomic composition of MIL-100. The N was first attributed to unreacted iron nitrate trapped into the pores (*ca.* 0.15 molecules of $Fe(NO_3)_3$ per each Fe in the structure). However, the presence of N in the elemental analysis could also indicate that some residual ionic liquid was forming part of the sample. The recorded BET adsorption isotherm was characteristic of microporous solids (Fig. 3b), as described for the hydrothermally synthesized MIL-100 products, even if these materials are described to have small mesopores connected by micropore windows. The BET surface area value measured for the precipitated sample was in the order of $650 \text{ m}^2\text{g}^{-1}$, which is approximately two-third of that reported for the BASF MIL-100(Fe) Basolite F300 commercial product ($S_{\text{BET}}=950 \text{ m}^2\text{g}^{-1}$). Reasons for the obtained low values of surface area can be related to different outgassing temperatures, lack of sufficient crystallization and the small crystal size found for the $scCO_2$ /IL precipitated particles with a significant amount of surface defects producing micropore blocking [36]. The precipitated compound showed high thermal stability, with three noticeable steps of weight loss in the TGA curve (Fig. 3c), attributed to loss of adsorbed and coordinated water (100-300 °C), followed by the decomposition of BTC in several consecutive steps

taking place between 300 and 465 °C. SEM micrographs revealed a nanometric system constituted by isometric particles of *ca.* 0.1-0.2 μm forming large agglomerates (Fig. 3d).

4. Conclusions

A novel route for promoting the crystallization of different MOFs in a highly sustainable solvent, constituted by scCO_2 and emimBF_4 , has been developed in this work. scCO_2 dissolution in ILs reduces the viscosity of the mixture, thus, enhancing mass transfer and allowing reactions to occur at lower temperatures (*ca.* 65 °C) and in shorter period of time (*ca.* 10 h) than in ionothermal conventional processes (150-180 °C and 24-48 h). One of the main advantages of using ILs together with scCO_2 is the ability of the mixture to dissolve a large variety of metal centers and organic linkers, thus allowing the formation of different MOF structures. Moreover, the needed amount of expensive ionic liquid is very small, similar in weight to the amount of reagents used. Some of the traditionally most studied 3D microporous MOFs, ZIF-8 and HKUST-1, were synthesized with yields in the order of 95 and 60 %, respectively, avoiding the incorporation of the ionic liquid in the structure or pores. Further, the MIL-100(Fe) phase was also prepared following this route with a yield of *ca.* 50%. The precipitated material has similar characteristics to those of the commercial F-free BASF product. On the basis of the above results and discussion, we believe that additional MOFs can be prepared by this scCO_2 /IL route using other metal ions and ligands.

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Table 1. Target structures and experimental compositions used for MOFs synthesis. C, H and N values correspond to the calculated values for the stoichiometric target structure. The depicted micropore surface area values (S_{mp}) are reported data calculated from the perfect crystal structure. For comparison, the range of BET surface area (S_{BET}) values reported for materials synthesized following conventional procedures are also shown.

Target structure	Reagents	C, H, N [wt%]	S_{mp} [m^2g^{-1}]	S_{BET} [m^2g^{-1}]
ZIF-8	$\text{Zn}(\text{acac})_2:2\text{Hmim}$	42.2, 4.4, 24.6	1950 [42]	1000-1600 [43,44]
HKUST-1	$3\text{Cu}(\text{NO}_3)_2:2\text{H}_3\text{BTC}$	35.7, 1.0, 0	2000 [52]	850-1500 [48]
MIL-100(Fe)	$\text{Fe}(\text{NO}_3)_3:1.5\text{H}_3\text{BTC}$	24.9, 4.0, 0	2800 [50]	1000-2000 [51,53]

Table 2. Structure, composition (C, H and N from elemental analysis), textural properties (S_{ABET} , S_{amp} and V_{mp}), thermal stability in air and crystal size of precipitated samples in $\text{scCO}_2/\text{emimBF}_4$ mixtures.

Target estructure	C, H, N [wt%]	S_{ABET} [m^2g^{-1}]	S_{amp} [m^2g^{-1}]	V_{mp} [cm^3g^{-1}]	Thermal stability [°C]	Crystal size [μm]
ZIF-8	41.7, 4.5, 22.8	1156	1090	0.39	290	0.3-0.8
HKUST-1	34.9, 2.8, 0	1290	1200	0.47	290	0.2-2
MIL-100(Fe)	26.7, 2.5, 0.6	640	559	0.21	350	0.1-0.2

Figure captions

Figure 1. ZIF-8 crystals prepared in $\text{scCO}_2/\text{emimBF}_4$: (a) experimental XRD pattern (top) and simulated from ZIF-8 crystal structure [42] (bottom), (b) N_2 adsorption isotherm (the inset corresponds to a zoom of the 0-0.2 P/P_0 range), (c) TGA profile, and (d) SEM micrograph.

Figure 2. HKUST-1 crystals prepared in $\text{scCO}_2/\text{emimBF}_4$: (a) experimental XRD pattern (top) and simulated from HKUST-1 crystal structure [52] (bottom), (b) N_2 adsorption isotherm (the inset corresponds to a zoom of the 0-0.2 P/P_0 range), (c) TGA profile, and (d) SEM micrograph.

Figure 3. MIL-100(Fe) crystals prepared in $\text{scCO}_2/\text{emimBF}_4$: (a) experimental XRD pattern (top) and simulated from data corresponding to F-free MIL-100 [50], (b) N_2 adsorption isotherm (the inset corresponds to a zoom of the 0-0.2 P/P_0 range), (c) TGA profile, and (d) SEM micrograph.

Figure 1

Figure 2

Figure 3