



Supercritical CO₂ utilization for the crystallization of 2D metal-organic frameworks using *tert*-butylpyridine additive

Núria Portolés-Gil^a, Sarah Gowing^a, Oriol Vallcorba^b, Concepción Domingo^{a,*}, Ana M. López-Periago^{a,*}, José A. Ayllón^{c,*}

^a Instituto de Ciencia de Materiales de Barcelona (CSIC), Campus UAB, 08193, Bellaterra, Spain

^b ALBA Synchrotron Light Source, Cerdanyola del Vallés, Barcelona, Spain

^c Universidad Autónoma de Barcelona, Campus UAB, Bellaterra, Spain



ARTICLE INFO

Keywords:

Metal-organic frameworks
Supercritical CO₂
Tert-butylpyridine additive
Surface grafting

ABSTRACT

Recently, the study of the synthesis of metal-organic frameworks (MOFs) in the presence of supercritical CO₂ (scCO₂) has become a burgeoning direction in materials science. MOFs crystallization in scCO₂ is often carried out in the presence of other solvents, such as ionic or organic liquids, to increase reagents solubility in the reaction media. In this work, a totally new and cleaner way is followed, utilizing small amounts of an ancillary ligand to increase metal solubility, which result in a more efficient use of scCO₂. The precipitation of 2D MOFs, based in the combination of different trifluoroacetates of transition metals (M(tfa)₂, M^{II} = Cu^{II} or Zn^{II}), and a bidentate pyridine derivative (dpy), was studied. MOFs of the type [M(tfa)₂(dpy)_x]_n were precipitated using scCO₂ as the solvent medium and the ligand *tert*-butylpyridine (*t*-bpy) as additive. The targeted 2D MOFs were precipitated after a short reaction time (ca. 3 h) operating under relatively soft supercritical conditions (20 MPa and 333 K). This new synthetic approach is thought as a generic method that can be used to modify metal precursors in systems in which the reaction is too slow or incomplete in neat scCO₂. Moreover, the increase of metal centre solubility allowed the in situ deposition of MOF crystals grafted on modified substrates.

1. Introduction

Clean fluid technologies have become an important field of research due to the incremental societal demand towards creating new products in a more eco-efficient way, importantly avoiding the use of volatile organic compounds [1]. In this sense, over the past decade, coordination polymers or metal-organic frameworks (MOFs) have emerged as enabling materials for a wide variety of sustainable technologies, leading to their recent commercialization in a natural gas car prototype [2], and having a large fraction of their potential applications in the direction of roles of green materials, such as gas separation and gas storage [3]. MOFs are a class of crystalline materials produced by the coordination of transition-metal cation complexes with multidentate organic linkers, forming extended frameworks that often are highly porous [4]. Nowadays, it is mandatory to associate sustainability with the development of emerging materials for environment, health, and safety reasons. Hence, the development of valuable MOFs is dependent on the availability of synthetic and manufacturing procedures mindful of environmental impact. However, developed synthetic methods for MOFs are based on the use of large amounts of organic solvents, such as

the solvothermal approach. BASF fabricates several of these compounds in large scale by using a more efficient electrochemical synthetic procedure. Alternatively, ball milling mechanochemistry has emerged as a generic approach in solvent-free synthesis, which in addition allows targeting previously elusive MOF structures [5]. The main drawback of this method is the formation of poor quality crystals. New developed methods are focused on the use of unconventional solvents, including supercritical fluids, ionic liquids and fluorinated solvents. The low surface tension and viscosity of supercritical solvents make them suitable fluids to process porous systems, particularly the green supercritical carbon dioxide (scCO₂) [6]. scCO₂ is a poor solvent for high-molecular weight and polar molecules, which, in principle, would rule out many possibilities in MOFs synthesis. An effective way to solve this problem is to create mixtures of scCO₂ with other solvents that own the capacity of solubilizing both polar and apolar building units needed for MOFs synthesis. One example is the use of combinations of scCO₂ and organic solvents (e.g., dimethylformamide), known as expanded switchable solvents [7]. Another explored option has been the ionothermal synthesis carried out in mixtures of scCO₂ and an ionic liquid [8,9].

* Corresponding authors.

E-mail addresses: conchi@icmab.es (C. Domingo), amlopez@icmab.es (A.M. López-Periago), joseantonio.ayllon@uab.es (J.A. Ayllón).

The use of neat scCO₂ in the field of MOFs has been mainly limited to post-synthesis activation by cleansing entrapped undesired by-products or solvents to obtain ultra-high surface area MOFs [10]. A generic method for the crystallization of MOFs in scCO₂ is being developed in our research group, with focus on the synthesis of one- (1D) [11], two- (2D) [12] and three-dimensional (3D) [13] MOFs. In this ongoing research, the purpose is to perform a comprehensive analysis of different approaches that can be used to crystallize MOFs in scCO₂. The research focuses on tuning and controlling building unit's solubility in scCO₂ by the modification of the experimental parameters and/or the use of additives. Herein, main factors influencing MOFs crystallization in scCO₂ are rationalized taking as a model the reaction of a metal trifluoroacetate (M(tfa)₂) complex, having null solubility in scCO₂, with a bidentate pyridine linker highly soluble in scCO₂ [14]. Aside of studying the influence of the running time in the different reactions, the addition of additives is the main experimental parameter scrutinized in this work. To increase the solubility of the metal precursor, the use of either ethanol as a co-solvent or *tert*-butylpyridine (*t*-bpy) as ancillary ligand for the metal complex is assayed [15]. Two previously described and four new 2D MOFs were precipitated using this procedure. The thus achieved solubility enhancement in scCO₂ of the metal precursor allowed the use of the supercritical fluid reactive deposition technique for the preparation of thin films of the synthesized MOFs by exposing the supercritical solution to a modified substrate [16]. Preliminary results on the deposition of one of the studied products on silicon wafer are also presented and discussed, showing the potential of the developed solubility enhancement protocol for the preparation of thin films of a wide variety of organometallic and hybrid compounds.

2. Materials and methods

2.1. Materials

The structures of the used organic reagents and additives are schematized in Fig. 1. Copper(II) trifluoroacetate hydrate (Cu(tfa)₂), zinc(II) trifluoroacetate hydrate (Zn(tfa)₂), 4,4'-dipyridine (bpy), 1,2-bis(4-pyridyl)ethylene (bpe), 1,3-bis(4-pyridyl)propane (bpp), *tert*-butylpyridine (*t*-bpy) were of commercial grade and used as received (Sigma Aldrich). Ethanol (EtOH) was purchased from Panreac. Compressed CO₂ (99.95 v%) was supplied by Carbueros Metálicos S.A. (Spain).

2.2. Equipment and synthesis

MOFs preparation in scCO₂ was carried out in a high pressure 100 mL Thar Design autoclave, equipped with two opposite sapphire windows (Fig. 2). In each experiment, the autoclave was charged with ca. 200 mg of M(tfa)₂ and a weighted amount of each studied dipyridin (dpy), calculated slightly in excess of the quantity needed to achieve the molar ratio 1:2 for M^{II}:dpy. The reagents were added into a 10 mL Pyrex vial together with a small magnetic stir bar. The vial was capped with filter paper. The reactor was sealed at ambient temperature and filled with liquid CO₂ at 6 MPa, while stirring at 500 rpm. In a typical experiment, the system was then heated at 333 K using resistances and the

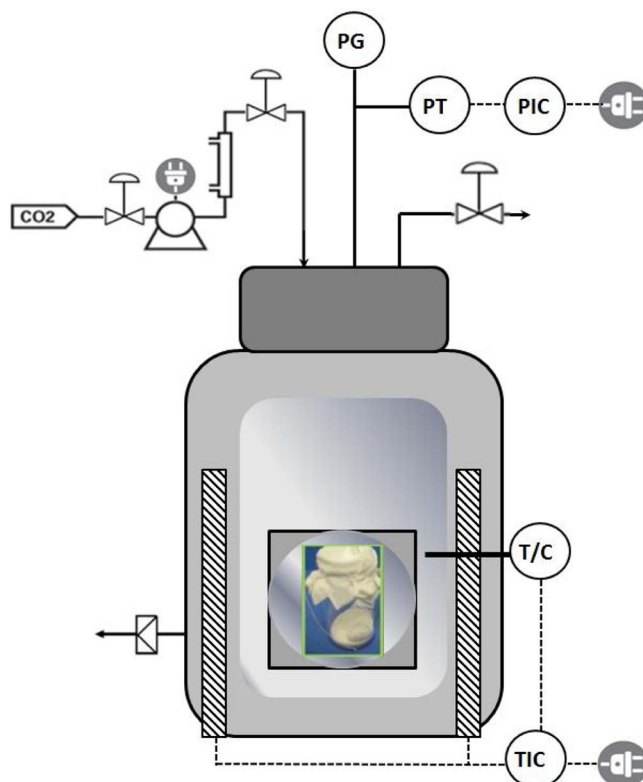


Fig. 2. Schematic representation of the high pressure equipment used in the MOFs crystallization experiments.

pressure was increased up to 20 MPa with a syringe pump (Teledyne Isco 260D). These working conditions were maintained for a period of 3 h. Finally, the reactor was depressurized to atmospheric pressure and cooled to room temperature. Four different methods were used to obtain the desired end-product, which are described following.

Method A. The reaction time was increased from 3 h in the standard protocol to 60 h.

Method B. 2 mL of EtOH were added as a co-solvent to the Pyrex vial together with the MOF reagents.

Method C. A metal complex intermediate containing the *t*-bpy unit, with formulae M(tfa)₂(*t*-bpy)_x, was prepared by reacting M(tfa)₂ with an excess of liquid *t*-bpy. After partial evaporation of the *t*-bpy excess, the composition of the recovered intermediate complexes was determined by EA as $x = 2.3$ and 2.5 for Zn^{II} and Cu^{II}, respectively. In the MOF synthesis experiments, the intermediate was added to the Pyrex vial instead of the corresponding M(tfa)₂ hydrate.

Method D. The *t*-bpy was added to the Pyrex vial as free ligand, thus avoiding the necessity of synthesizing the intermediate. Different ratios of M^{II}:*t*-bpy were experimentally tested (Table 1).

[Cu(tfa)₂(bpy)₂]_∞ complex was immobilized onto different silicon wafer surfaces using scCO₂. The substrate was first activated by cleaning with freshly prepared “piranha” solution (H₂SO₄:H₂O₂ 3:1 v/v

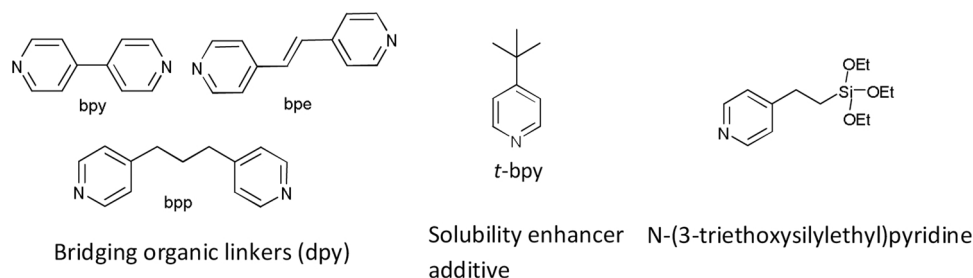


Fig. 1. Structures of the used reagents and additives.

Download English Version:

<https://daneshyari.com/en/article/6528874>

Download Persian Version:

<https://daneshyari.com/article/6528874>

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