

Supercritical CO₂ for the synthesis of nanometric ZIF-8 and loading with hyperbranched aminopolymers. Applications in CO₂ capture



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ABSTRACT

ZIF-8 nanometric particles are prepared *via* an environmentally friendly supercritical method aimed to minimize the environmental impact of current developed technologies for the synthesis of metal organic frameworks. In this synthetic process, CO₂ and ZIF-8 precursors are exclusively employed, avoiding the use of organic liquids, difficult to recover additives or large amounts of expensive ligand excess. The straight and high yield precipitation of empty-pore ZIF-8 nanopowder with tunable morphology was achieved. The powder was fully characterized in regard to the composition, structure, stability, morphology and textural properties. This work also focuses in the development of an eco-efficient method for the *in situ* polymerization of ethyleneimine inside the synthesized ZIF-8 pores, by using supercritical CO₂ as a solvent, reaction medium and catalyst for the aziridine ring-opening. The use of the prepared materials in CO₂ capture is assessed by analyzing CO₂ adsorption isotherms.

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1. Introduction

During the last few years, microporous coordination polymers, or three-dimensional metal-organic frameworks (3D MOFs), with zeolitic topologies have become a major focus of research in advanced functional materials. These novel materials have relevance in diverse sorption applications, such as CO₂ capture or gas separation, heterogeneous catalysis and sustained drug release, to name some [1–3]. Nevertheless, the time-consuming and expensive solvothermal and hydrothermal procedures, frequently needed for the synthesis of MOFs, represent the most important drawbacks for the development of industrial applications.

ZIF-8, with formula [Zn(2-methylimidazole)₂] and sodalite topology, is currently one of the most extensively investigated zeolitic imidazole frameworks (ZIFs), a subclass of MOFs [4]. The conventional solvothermal procedure described to synthesize ZIF-8 requires the use of dimethylformamide (DMF) and a heating period of 24 h at 140 °C [5]. Micrometric particles are thus precipitated, but DMF molecules remain trapped inside the pore space and must be removed by solvent exchange in methanol,

followed by vacuum drying; the whole preparation method lasting several days. The use of microwave irradiation and sonochemical treatments have been explored to reduce the crystallization time in the solvothermal procedure [6]. Using a more sustainable approach, nanometric ZIF-8 crystals have been prepared at room temperature in methanol or water [7,8], but these are processes reporting low yields and requiring either the aid of a deprotonating additive [6] or the addition of a large excess of organic ligand [9]. High ZIF-8 yields have been achieved by mechanochemistry, but this process again requires the use of additives and results in particles with a poorly defined morphology [10]. ZIF-8 have also been synthesized using a solvent-free approach at high pressures, in the order of 0.3 GPa, but this process gives low yields below 10 wt.% [11]. A ionothermal method assisted by compressed CO₂ has recently been reported as a plausible procedure for the preparation of ZIF-8 nanoparticles [12]. ZIF-8 micrometric powder is produced by BASF (Basolite Z1200) using an electrochemical procedure.

For practical applications and a feasible scale-up, the development of environmentally friendly, one-pot synthetic methods of fine particles of ZIF-8 is desirable. The process should afford the formation of ZIF-8 as a dry and empty-pore powder in a high yield, with the use of minimal amounts of expensive imidazole, whilst avoiding the need of additives or organic solvents [13,14]. All these requirements have been successfully fulfilled in this work by using exclusively a green solvent, supercritical CO₂ (scCO₂), as the

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reaction medium for ZIF-8 synthesis. The use of compressed or scCO₂ as a solvent in organic and coordination chemistry has been deeply explored during the last 30 years, since this fluid can dissolve many organic and some organometallic compounds [15–17]. To date, it is only one reported example on the synthesis of coordination polymers by using scCO₂, which is referred to one-dimensional phases [18]. Indeed, the use of compressed CO₂ in the field of MOFs has been mainly limited to the post-synthesis activation by cleansing entrapped undesired by-products or solvents, performed either by batch solvent exchange/scCO₂ treatment or, directly, from the solvated crystals by flowing scCO₂ [19]. In any case, the use of scCO₂ in the activation step has demonstrated to have a significant impact in enhancing the specific surface area, at the same time avoiding the pore collapse for MOFs that are unstable upon guest removal [20]. The present work documents that not only the activation, but also the synthesis of 3D MOFs can be carried out in scCO₂, leading straightforwardly to an empty pore end product with near theoretical specific surface area values.

The chemical and thermal stability of ZIFs permit many applications, such as in the capture of CO₂ and its selective separation from industrially relevant gas mixtures [21]. These porous adsorbents only have physisorption contribution to CO₂ adsorption, however they show an exceptionally high capacity for CO₂ capture in comparison with other porous adsorbents operating also by physisorption [22]. The present work also addresses the application of synthesized ZIF-8 products for CO₂ capture at low temperatures. A significant CO₂ chemisorption contribution is expected by adding aminopolymers to the pores, f.i., polyethyleneimine (PEI) with a high density of amine groups that can efficiently bind with CO₂ forming carbamates [23,24]. Again, current developed methods to prepare hyperbranched polyamines grafted onto micro and mesoporous substrates need the use of organic solvents, catalysts, temperature and/or long reaction times [25,26]. A new method has been developed for polymerizing ethyleneimine straight into the microporous synthesized ZIF-8 by using the scCO₂ technology [27,28]. The CO₂ adsorption efficiency of prepared ZIF-8 samples, either as-synthesized or loaded with the aminopolymer, was evaluated by analyzing the adsorption isotherms at low temperature.

2. Materials and methods

2.1. Materials

Zinc acetylacetonate hydrate (Zn(acac)₂·xH₂O) and 2-methylimidazole (Hmim) (Sigma Aldrich) were used as the ZIF-8 precursors. The 3-membered ring ethyleneimine, also referred as aziridine, was kindly provided by Menadiona S.A. Compressed CO₂ (99.995 wt%) was supplied by Carburos Metálicos S.A.

2.2. Equipment and procedure

Sample preparation under scCO₂ was carried out in the high pressure equipment schematized in Fig. 1. A stainless steel reactor of 100 mL volume (Thar process), equipped with two opposite sapphire windows, was used for the synthesis of ZIF-8 and its further impregnation with PEI. The autoclave was charged with ca. 125 mg of Zn(acac)₂ and the corresponding amount of Hmim to obtain 1:1, 1:2 and 1:2.25 Zn(acac)₂:Hmim molar ratios. The reagents and a small magnetic stir bar were added to a 10 mL Pyrex vial capped with filter paper and placed within the reactor. The autoclave was then sealed. The system was heated and pressurized to 38 °C and 20 MPa, respectively. The vessel was operated in the batch mode under stirring at 150 rpm during 10 h, and finally slowly depressurized at a mean depressurization rate of ca. 0.1 MPa min⁻¹. Different activation methods were applied to the recovered samples, consisting in: (i) evacuating the samples under vacuum at 120 °C, (ii) rinsing with a continuous flow of scCO₂ at 20 MPa and 40 °C, or (iii) by alcohol cleaning after redispersing the powder first in EtOH and then in MeOH, followed by filtering and vacuum evacuation. The samples were referred with the subscripts *as* for as-synthesized, *va* for vacuum evacuation, *CO₂* for scCO₂ cleaning and *al* for alcohol cleaning.

For the polyethyleneimine (PEI) impregnation experiments, the 100 mL autoclave was charged with ca. 300 mg of synthesized ZIF-8 and 1 mL of aziridine, avoiding the physical contact between the two materials. The vessel was slowly pressurized with CO₂ at 10 MPa and heated at 45 °C. The experiment was run under stirring (120 rpm) during 20 min. The system was then depressurized and the recovered sample was used as-synthesized for further characterization.

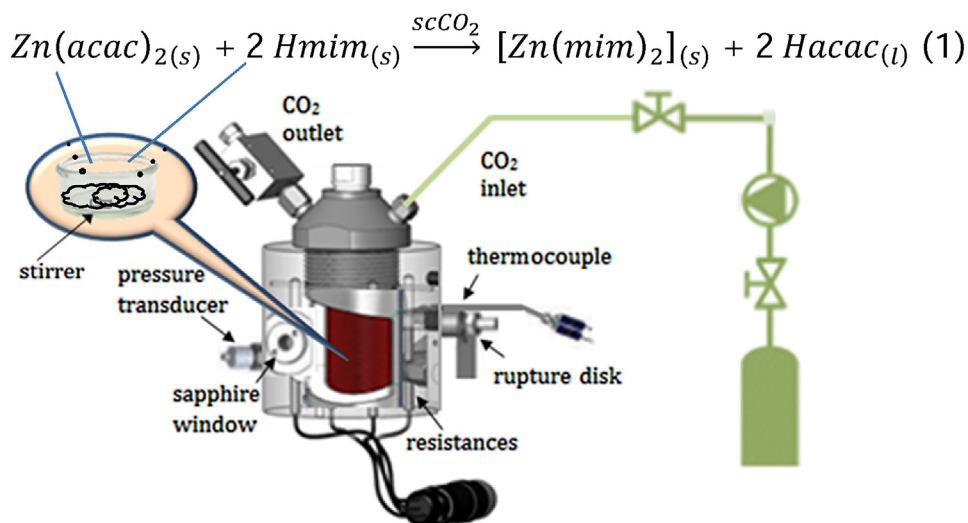


Fig. 1. Schematic representation of the high-pressure system used for the ZIF-8 reactive precipitation in scCO₂ and further ZIF-8 impregnation with aminopolymers.

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