

# **N<sub>2</sub> and CO<sub>2</sub> Adsorption Isotherms of micro and mesoporous materials crystallized in scCO<sub>2</sub>**

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## **ABSTRACT**

For a long time, our research team has intensively been working in the synthesis, processing and functionalization/impregnation of different micro and mesoporous materials using supercritical fluids. Moreover, hierarchical nanostructures, involving micro and mesoporosity, can be obtained using the scCO<sub>2</sub> procedure [1]. In this kind of products, the specific surface area, as well as the pore size and pore interconnectivity, is often the most important parameters used to ascertain their most useful characteristics in different applications (adsorption, drug delivery, insulators, etc). Proper characterization of these compounds is carried out using gas adsorption. This work analyses the Ar, N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms recorded for supercritically obtained micro- (metal-organic frameworks, MOFs) and meso- (graphene aerogels) porous materials. The Ar and N<sub>2</sub> adsorption was treated by the Brunauer-Emmett-Teller (BET) theory and the t-method, while the adsorption of CO<sub>2</sub> was estimated by the Dubinin-Radushkevich model. For microporous MOFs, different pathways are found in the adsorption and desorption steps due to flexibility in the polymeric structure. For light mesoporous aerogels of graphene, a calibration curve, make as a function of weight, is necessary to give reliable values.

## **INTRODUCTION**

Metal organic frameworks (MOFs) 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]. A green method for the synthesis of these compounds is highly desirable. Mixtures comprising ILs and scCO<sub>2</sub> 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<sub>2</sub>. Moreover, scCO<sub>2</sub> itself is considered a green solvent. The main objective of this on-going work is to establish the basis of a method for developing different structures of MOFs in pure scCO<sub>2</sub>, and to study their capacity for gas adsorption. Synthesis protocols are extended to the imidazolate ZIF-8 [2,3], a material proposed in the literature for CO<sub>2</sub> adsorption.

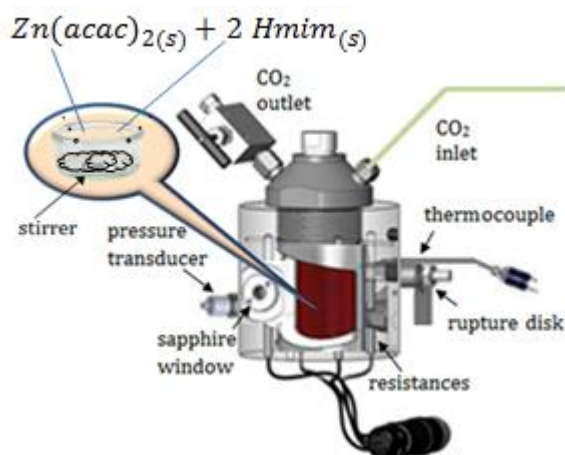
The chemical and thermal stability of ZIFs permit many applications, such as in the capture of CO<sub>2</sub> and its selective separation from industrially relevant gas mixtures. These porous adsorbents only have physisorption contribution to CO<sub>2</sub> adsorption, however they show an exceptionally high capacity for CO<sub>2</sub> capture in comparison with other porous adsorbents

operating also by physisorption [4]. The present work also addresses the application of synthesized ZIF-8 products for CO<sub>2</sub> capture at low temperatures. A significant CO<sub>2</sub> chemisorption contribution is expected by adding aminopolymers to the pores, f.i., polyethylenimine (PEI) with a high density of amine groups that can efficiently bind with CO<sub>2</sub> forming carbamates. 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. A new method has been developed for polymerizing ethyleneimine straight into the microporous synthesized ZIF-8 by using the scCO<sub>2</sub> technology [5]. The CO<sub>2</sub> adsorption efficiency of prepared ZIF-8 samples, either as-synthesized or loaded with the aminopolymer, was evaluated by analyzing the CO<sub>2</sub> adsorption isotherms at low temperature.

## MATERIALS AND METHODS

Zinc acetylacetonate hydrate ( $Zn(acac)_2 \cdot xH_2O$ ) and 2-methylimidazole (Hmim) (Sigma Aldrich) were used as the ZIF-8 precursors in scCO<sub>2</sub>. Compressed CO<sub>2</sub> (99.995 wt%) was supplied by Carbueros Metálicos S.A.

Sample preparation under scCO<sub>2</sub> 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 the MOFs. The autoclave was charged with *ca.* 125 mg of metal reagent and the corresponding amount of organic linker to obtain the stoichiometric product. The reagents, the ionic liquid if necessary, 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 40-60 °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 MPamin<sup>-1</sup>. 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 scCO<sub>2</sub> 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.



**Figure 1.** Schematic representation of the high-pressure system used for the ZIF-8 reactive precipitation in scCO<sub>2</sub>.

For the polyethylenimine (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 CO<sub>2</sub>

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.

MOF products were first study by powder X-ray diffraction (XRD) in a Siemens D5000 using the Cu K $\alpha$  incident radiation. The textural properties were determined by N<sub>2</sub> adsorption at -196 °C using an ASAP 2000 Micromeritics Inc. The BET surface area (Sa) was calculated applying the BET equation, while the micropore surface area (Sa<sub>mp</sub>) was estimated by the t-method. Samples were first degassed at 120 °C for 24 h. Sorption isotherms of CO<sub>2</sub> were obtained in the interval 0–100 kPa at 0 °C using a Quantacrome Nova Win2 analyzer. Prior to the measurements, samples were outgassed under reduced pressure following the same procedure than for N<sub>2</sub> adsorption.

## RESULTS

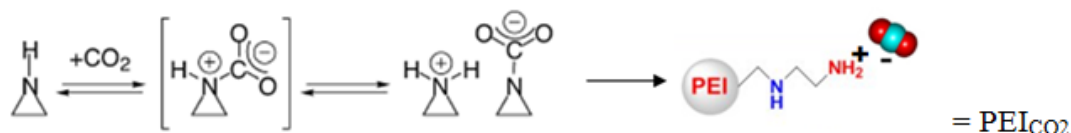
The main experimental parameters influencing the supercritical synthetic procedure were pressure, temperature and Zn(acac)<sub>2</sub>:Hmim molar ratio. Initial tests indicated that optimal working pressure and temperature were 20 MPa and 38 °C, respectively. Under further similar experimental conditions, by increasing the pressure beyond this value similar results were obtained, while a temperature increase to 45 °C resulted in the precipitation of a less pure ZIF-8 phase. The stoichiometric ZIF-8 ratio, corresponding to a 1:2 Zn(acac)<sub>2</sub>:Hmim molar ratio, was assayed. The main advantage of working under stoichiometric conditions was the straightforward synthesis of a product free of organic contaminants. The as-synthesized sample only requires short thermal treatment at 120 °C to eliminate adsorbed impurities, thus easing the materials evacuation regime, while streamlining potential bulk production in industry. The recorded X-ray diffraction (XRD) profile of the synthesized sample is shown in Fig. 2, together with the simulated pattern of ZIF-8 determined from the X-ray single crystal structure [6]. The as-synthesized product give patterns that perfectly match with the simulated ZIF-8 profile. BET characterization indicates in all the cases the precipitation of a microporous product, with textural values in the range of the ZIF-8 Basolite Z1200 product (1300-1800 m<sup>2</sup>g<sup>-1</sup>). The micropore surface area and micropore volume of the as-synthesized and alcohol-washed samples are comparable to the values found in the literature for ZIF-8 fine particles precipitated following different methodologies (Table 1), but not yet reaching the calculated values obtained by analyzing the simulated N<sub>2</sub> adsorption isotherm on the ZIF-8 single crystal structure of 1950 m<sup>2</sup>g<sup>-1</sup>. By treating this sample with a continuous flow of scCO<sub>2</sub> at 20 MPa and 40 °C, the textural values increased to 1200 m<sup>2</sup>g<sup>-1</sup> and 0.46 cm<sup>3</sup>g<sup>-1</sup>. Still, these values were easily raised to 1600 m<sup>2</sup>g<sup>-1</sup> and 0.58 cm<sup>3</sup>g<sup>-1</sup> just by washing the as-synthesized material with MeOH/EtOH. The alcohol-cleaned sample has a BET surface area of 1702 m<sup>2</sup>g<sup>-1</sup>, which is in the range of the highest reported values for ZIF-8. Indeed, a deviation of only 15 % was estimated for the micropore specific surface area with respect to the simulated value in a perfect crystal.

**Table 1.** BET and micropore surface areas (BET Sa and Sa<sub>mp</sub>) and micropore volume (V<sub>mp</sub>) determined by N<sub>2</sub> adsorption.

| Sample          | BET Sa<br>[m <sup>2</sup> g <sup>-1</sup> ] | Sa <sub>mp</sub><br>[m <sup>2</sup> g <sup>-1</sup> ] | V <sub>mp</sub><br>[cm <sup>3</sup> g <sup>-1</sup> ] |
|-----------------|---|---|---|
| ZIF-8*          | ---   | 1950  | 0.66  |
| as syntetized   | 1050  | 980   | 0.41  |
| scCO2 cleaned   | 1261  | 1128  | 0.42  |
| alcohol cleaned | 1702  | 1600  | 0.58  |

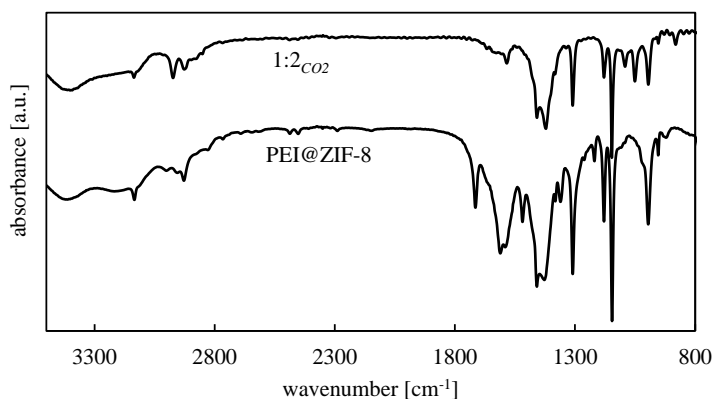
\*Single crystal data

Previous studies performed in our laboratory have demonstrated that compressed CO<sub>2</sub> can be used as an efficient catalyst for the ring opening polymerization of aziridine, giving place to hyperbranched PEI [7], which does not incorporate CO<sub>2</sub> to the polymer chain. By using the scCO<sub>2</sub> route, the PEI can be directly formed in the interior of porous substrates. PEI@porous substrate systems are considered highly efficient Class III adsorbents for CO<sub>2</sub> capture [8]. In the present work, the process of ring-opening polymerization of aziridine aided by scCO<sub>2</sub>, previously developed for the modification of the MCM-41 mesoporous silica, was extended to the impregnation of synthesized ZIF-8 synthesized under stoichiometric conditions. It was described, that aziridine polymerization in compressed CO<sub>2</sub> results in a violent exothermic reaction, which vaporizes monomers and just-formed short-chain aminopolymers (Fig. 2). This enables the impregnation of the porous support with PEI [9].



**Figure 2.** Schematic representation of aziridine polymerization into PEI.

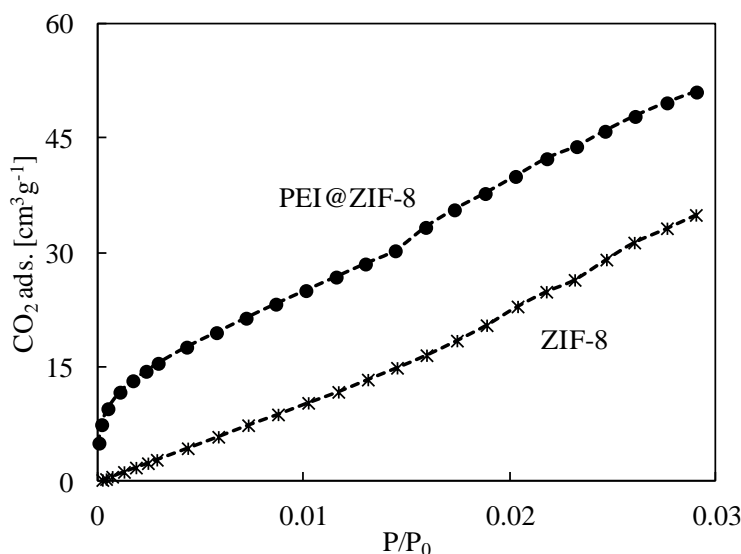
The composition of the obtained end-product could not be characterized by elemental analysis, since both ZIF-8 and PEI hold C, H and N atoms in the structure. The presence of PEI in the sample was confirmed by FTIR analysis in the as-synthesized stoichiometric sample (Fig. 3). The spectrum of the impregnated PEI exhibits the characteristic absorption peaks of polyamines, involving N–C and –NH vibration bands between 1500 and 1600 cm<sup>-1</sup>. Moreover, carbamate formation during synthesis in the CO<sub>2</sub> rich atmosphere by reaction with the formed PEI was evidenced by the presence of the band corresponding to C=O stretching at *ca.* 1715 cm<sup>-1</sup>. After PEI loading, the value of the micropore surface area in the ZIF-8 was reduced from *ca.* 1100 to 300 m<sup>2</sup>g<sup>-1</sup>, suggesting the successful incorporation of the PEI inside the pores.



**Figure 3.** FTIR spectra of as-synthesized stoichiometric sample 1:2CO<sub>2</sub> and impregnated PEI@ZIF-8 product.

CO<sub>2</sub> adsorption isotherms were used as the primary metric to evaluate the performance of synthesized hybrid samples in CO<sub>2</sub> capture (Fig. 4). At the studied temperature of 0 °C, CO<sub>2</sub> adsorption isotherms for pristine ZIF-8 support showed insignificant adsorption at very low pressures, and increased physisorption capacity up to 100 kPa. The equilibrium CO<sub>2</sub> adsorption values found for the ZIF-8 products prepared in this work were in line with the values found in the literature. Contrarily, the PEI@ZIF-8 samples had a high initial CO<sub>2</sub> adsorption at very low pressures, which corresponds to the contribution of the chemical reaction, and then physisorption at higher pressures. CO<sub>2</sub> adsorption occurs by a chemical reaction with primary and secondary amines in the PEI polymer, forming a carbamate through an exothermic acid-base reaction. As a consequence, in the PEI loaded samples the specific volumetric adsorption at 100 kPa increases in *ca.* 30 wt% with respect to the pristine product. The reaction of CO<sub>2</sub>

with PEI is reversible, allowing for the adsorbent to be regenerated by thermal, vacuum or pressure swing adsorption cycles.



**Figure 4.** CO<sub>2</sub> adsorption isotherms at 0 °C for the synthesized ZIF-8 product under stoichiometric conditions and the further supercritically prepared composite PEI@ZIF-8.

## CONCLUSIONS

A straightforward one-pot synthesis of ZIF-8 in supercritical CO<sub>2</sub>, which does not require the use of additives or organic solvents, is reported. These process characteristics would enable the scaling-up, while promoting their industrial use. By using a stoichiometric molar ratio of reagents, a post-synthesis washing step was not necessary and yields of *ca.* 95 wt.% were achieved. The results presented in this work open the way to synthesize additional MOFs by the described scCO<sub>2</sub> route, involving other metal ions and/or ligands. The ZIF-8 sample can be further modified with polyethylenediamine by using a scCO<sub>2</sub> post-synthetic method to enhance its adsorption performance towards CO<sub>2</sub>. The CO<sub>2</sub> adsorption capacity was increased in a 30 v/wt. % for the PEI loaded substrate with respect to pristine ZIF-8.

## ACKNOWLEDGEMENTS

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