

# Hydrogen Adsorption on Isorecticular Metal-Organic Framework

S. Loera-Serna\*, E Ortiz\*

\*Departamento de Ciencias Básicas, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana Unidad Azcapotzalco, Av. San Pablo 180, Col. Reynosa Tamaulipas, Azcapotzalco, Ciudad de México, 02200, Mexico, sls@azc.aum.mx

## ABSTRACT

Implement the use of hydrogen as an alternative energy source would reduce the use of fossil fuels, therefore it seeks to challenge any difficulty, mainly storage; an alternative of great interest is the use of metal organic networks (MOFs) and which implement different experimental strategies of synthesis due to its high chemical and structural versatility, allowing design their properties to increase its affinity for hydrogen.

In this work we present the results of hydrogen uptake at 77 K and 12 bar using the isorecticular MOF: MOF-5, MOF-5-NH<sub>2</sub> and MOF-199, synthesized by stirring at room temperature. The cubic structure and pore size make these materials excellent candidates for the hydrogen adsorption, the maximum adsorption was obtained for MOF-199.

**Keywords:** isorecticular metal organic-frameworks, adsorption, hydrogen.

## 1 INTRODUCTION

The MOFs, represent a new class of inorganic-organic hybrid compounds, whose porous crystalline structure has attracted increasing interest in recent years, both in the research field and in the industrial sector, thanks to its properties derived from the combination between the components of its structure, which is constructed by a trained center metal oxides, an example of these are: Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup> and Fe<sup>3+</sup>, in coordination with various organic linkers (L) through strong links that provide mechanical and thermal stability also it allows acquire a structure with well-defined geometry of crystalline nature type of binders containing these compounds can be mono-, di-, tri-, and tetravalent, among these are the neutral ligands, such as piperazine, 4,4-bipyridine or the anionic, as polycarboxylates [1-3].

Applications that can be highlighted from these porous materials are storing gases, heterogeneous catalysis, medicine, adsorption, separation, microelectronics photoluminescence and nonlinear optics [4-9].

Several of these hybrid compounds have been highlighted by its high adsorption capacities, particularly MOF-5 MOF-199. These microporous MOFs generally show good thermal stabilities (decompose at temperatures higher than 623.15 K) however, its disadvantage is the low hydrolytic stability, it is for this reason that its use is limited in catalytic oxygenation reactions where water is a product

of important reaction, because the decomposition of frame occurs rapidly if the phase gaseous or liquid contains certain percentages of water.

The difference of the taunts compared to other materials (zeolites, carbons) is the variety of factors that may influence its adsorption capacity of this gas; within these factors we can see the synthesis and activation of the material, surface area and pore volume, and structure of the organic ligand functionalization, geometry and pore size, accessibility of the metal centers and the post-synthesis treatment.

The material obtained was characterized by powder X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), thermogravimetric analyses (TGA), scanning electron microscope (SEM) and ultraviolet-visible spectroscopy (UV-Vis).

## 2 EXPERIMENTAL SECTION

### 2.1 MOF-5

1.48 mol of zinc nitrate hexahydrate was added to 10 mL of dimethylformamide (DMF), once dissolved. The solution was mixed with 1.12 mmol of terephthalic acid (H<sub>2</sub>BDC), droplets of deionized water (0.18mL) were added and stirring for 10 minutes. The molar ratio of components was Zn(NO<sub>3</sub>)<sub>2</sub>:H<sub>2</sub>BDC:DMF:H<sub>2</sub>O= 1: 0.76: 175: 8.12. Once past the stirring time of the reagents, subjected to heating in an oven for 48 hours at 120 ° C and then allowed to cool to room temperature. Colorless cubic crystals were washed three times with DMF, then dry in the oven at 150 ° C for 12 hours. The solid obtained was stored in a desiccator with silica gel [2].

### 2.2 MOF-5-NH<sub>2</sub>

1.48 mol of zinc nitrate hexahydrate in 10 mL of dimethylformamide pre- mixed with distilled terephthalic 1.12 mmol amino acid (H<sub>2</sub>BDC-NH<sub>2</sub>) was added, droplets of deionized water (0.18mL) were added and kept under stirring for 10 minutes. Molar ratio of the components will be Zn(NO<sub>3</sub>)<sub>2</sub>:H<sub>2</sub>BDC-NH<sub>2</sub>:DMF:H<sub>2</sub>O = 1:0.76:175:8.12. Once past the stirring time of the reagents, subjected to heating in a reflux system for 12 hours, then allowed to cool to room temperature. Colorless cubic crystals were washed three times with DMF, then dry in the oven at 150 ° C for 12 hours. The formed solid was separated by centrifugation and the liquid was allowed to dry at room temperature.

## 2.3 MOF-199

The MOF-199 was prepared with a solution of 2 moles of tricarboxylic acid 1,3,5-biphenyl in 120 mL of deionized water, then a solution of 3 moles of copper nitrate trihydrate in 40 mL of absolute ethanol and the mixture is allowed to stir be added for 12 hours. The solid formed is separated from the liquid by centrifugation and allowed to dry at room temperature [4].

## 2.4 Characterization

Materials were characterized by X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) and N<sub>2</sub> adsorption. XRD patterns were collected on a powder diffractometer (Philips X'PERT PRO) coupled to a copper anode X-ray tube was used to identify the crystalline structure of each sample by XRD. The Cu K $\alpha$  radiation (45 kV, 40 mA,  $k = 1.5406 \text{ \AA}$ ) was selected with a diffracted beam monochromator and with a step size of  $0.01^\circ$  and a time per step of 0.9 s. The FT-IR spectra ( $4000\text{--}400 \text{ cm}^{-1}$ ) were obtained with a resolution of  $2 \text{ cm}^{-1}$  at room temperature on a Bruker Tensor-27 spectrometer, fitted with a DTGS detector. The FT-IR spectra were recorded through the ATR technique. The micrographs were acquired in a scanning electron microscope model Supra 55VP, with field emission cathode, in high vacuum. All adsorption measurements were conducted using a BELSORP-max (BELL Japan Inc.) system at  $-196 \text{ }^\circ\text{C}$ . Samples were degassed under dynamic conditions (extra-dry air flow) over 24 h at  $100 \text{ }^\circ\text{C}$  prior to N<sub>2</sub> or H<sub>2</sub> adsorption measurements. BET specific surface areas were calculated from the N<sub>2</sub> adsorption isotherms.

## 3 RESULTS AND DISCUSSION

Figure 1, shows a comparison of the diffractograms obtained experimentally through synthesis of MOF-5, MOF-5-NH<sub>2</sub> and MOF-199, with the simulated diffractogram obtained from database "Cambridge Crystallographic Data Base "(CSD). Figure 1a) correspond to diffractograms of MOF-5, which clearly shows that all the experimental peaks coincide with the simulated diffractogram. Figure 1b) the corresponding diffraction patterns are shown on the MOF-5-NH<sub>2</sub>, and Figure 1c) belongs to the diffractogram of MOF-199.

Table 1 summarizes the physicochemical characteristics of the synthesized MOF. All MOF have a cubic structure with space group Fm-3m, this feature makes isorecticular MOF (same structure, different organic linker). Other properties such as the cell parameter, cell angles, crystal density, free diameter and porosity are reported. The cell parameter of the MOF-5 and MOF-5-NH<sub>2</sub>, were calculated using standard peak at  $26.603^\circ$  ( $2\theta$ ) corresponding to graphite and the peak at  $22.64^\circ$  ( $2\theta$ ) attributed to the MOF. The experimental cell parameter of MOF-5 is similar to the

theoretical one. A greater difference however exists in the cell parameter of the MOF-5-NH<sub>2</sub>, it is important to note that the parameters in Table 1 were from an article where a procedure for the synthesis of MOF-5-NH<sub>2</sub> was different. In this work hydrothermal conditions were used to synthesize, indeed it is possible to change the cell parameter by changing the synthesis condition due to the number of molecules solvent occluded in the structure [4, 10].

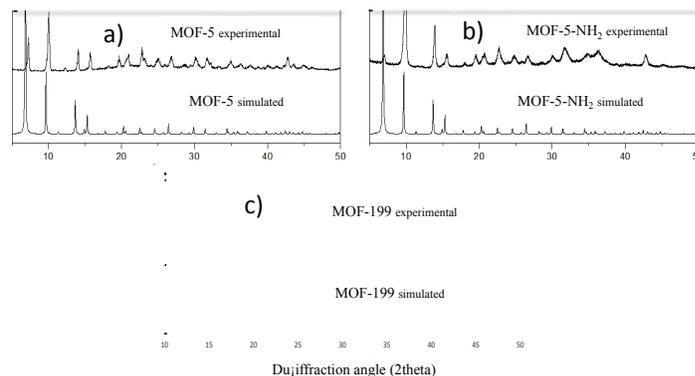


Figure 1: Diffractograms of synthesized samples.

Property	MOF-5	MOF-5-NH <sub>2</sub>	MOF-199
Chemical formula	C <sub>8</sub> H <sub>12</sub> N <sub>4</sub> Zn	C <sub>8</sub> H <sub>14</sub> N <sub>5</sub> Zn	C <sub>18</sub> H <sub>12</sub> O <sub>15</sub> Cu <sub>3</sub>
Pore type	cubic	cubic	cubic
Space group	Fm-3m	Fm-3m	Fm-3m
Cell parameter theoretical (Å)	a=b=c=25.83	a=b=c=25.75	a=b=c=26.95
Cell parameter experimental (Å)	a=b=c=25.82	a=b=c=25.81	a=b=c=25.34
Cell angles (°)	$\alpha=\beta=\gamma=90$	$\alpha=\beta=\gamma=90$	$\alpha=\beta=\gamma=90$
Crystal density (g·cm <sup>-3</sup> )	0.61	0.63	0.96
Free diameter (Å)	11.2	9.6	9.0
Porosity (%)	79.2	78.9	40.7

Table 1: Physicochemical properties of MOF-5, MOF-5-NH<sub>2</sub> and MOF-199.

Figure 2 shows the IR spectra of the synthesized samples. Spectrum 2a) corresponds to the MOF-5 in the wavenumber  $1659 \text{ cm}^{-1}$  is seen in the corresponding amides, this is because the dimethylformamide embedded in pores MOF due to the condition synthesis. In the wavenumber  $1660, 1570, 1500, 1250, 1150, 1100, 960, 800, 770, 700$  and  $600, 400 \text{ cm}^{-1}$  approximately, several bands are observed, which are corresponding to aromatic rings in position disubstituted. Also, between the wave numbers of  $3600$  and  $3200 \text{ cm}^{-1}$  the band correspond to  $-\text{OH}$  groups. Spectrum 2b) bands

corresponding to the MOF-5-NH<sub>2</sub> observed. Wavenumbers at 3125, 1623, 1550, 1499, 1236, 1028, 950, 900, 849, 815, 770, and 726 cm<sup>-1</sup> approximately presenting bands corresponding to trisubstituted aromatic rings. Spectrum 2c) corresponds to the MOF-199. Bands corresponding to trisubstituted aromatic rings, are observed at 1660, 1570, 1500, 1250, 1150, 1100, 960, 800, 770, 700 and 600 cm<sup>-1</sup>. Also, between 3600 and 3200 cm<sup>-1</sup>, a characteristic band can be observed attributed to -OH group, this can be explained due to the presence of ethanol and water molecules inside the structure.

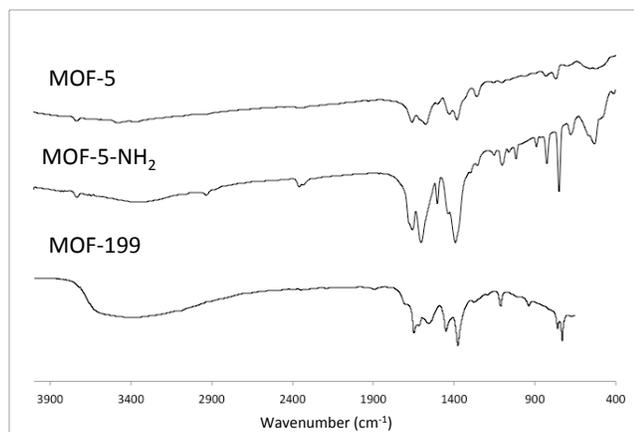


Figure 2: FT-IR spectra of synthesized samples.

The details of the morphological and structural features of the as-synthesized MOF crystal were studied using Scanning Electron Microscopy (SEM). SEM micrographs of the synthesized samples are presented in Figure 3. Irregular particles with size less than 0.5 μm is present for MOF-5. Cubic particles with size of 15 μm are observed for MOF-5-NH<sub>2</sub>. Figure of MOF-199 shows the SEM micrograph of MOF-199, rods (> 40 μm) surrounded by typical polyhedral morphology (10 μm) with a uneven surface are present.

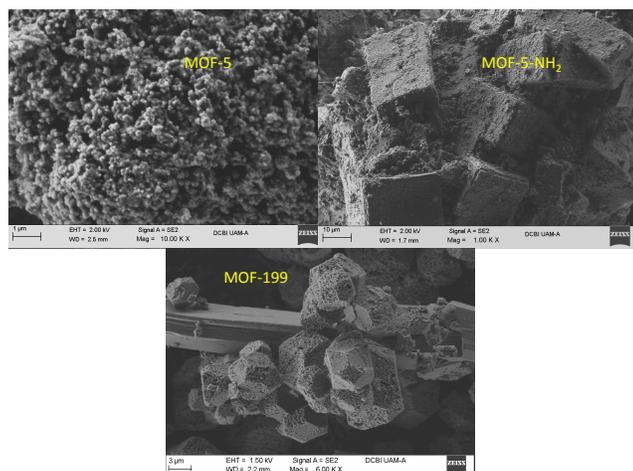


Figure 3: SEM micrographs of synthesized samples.

Figure 4 compares the nitrogen adsorption isotherms of the synthesized MOF. All isotherms correspond to Type, which relates to microporous solid. All isotherms are concave relative to the axis of relative pressure, indicating that all these solid synthesized show increased adsorption capacity at low pressures. The MOF-5-NH<sub>2</sub> low adsorption compared with the rest. The BET surface areas were calculated for the MOF: 1645.98, 528.90 and 1732.05 and m<sup>2</sup>/g for MOF-5, MOF-5-NH<sub>2</sub> and MOF-199, respectively.

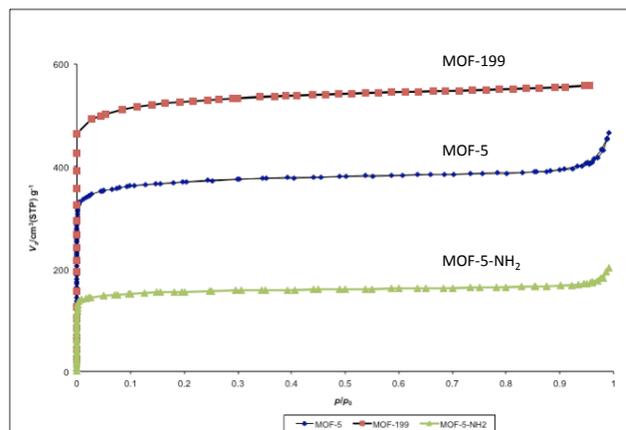


Figure 4: N<sub>2</sub> adsorption of synthesized samples.

Figure 5 present hydrogen adsorption isotherms at 77K. The MOF-199 has a higher H<sub>2</sub> adsorption capacity of 5% wt. up to 109 bar. While the MOF-5-NH<sub>2</sub> have the lowest capacity with only 2.8% wt. up to 103 bar.

The difference in hydrogen adsorption of MOFs is determined by the physicochemical properties as: type of linker, structure, surface area, free diameter and porosity. The adsorption capacity has the same trend as the surface area, indeed the greater the surface area has the greater hydrogen adsorption capacity.

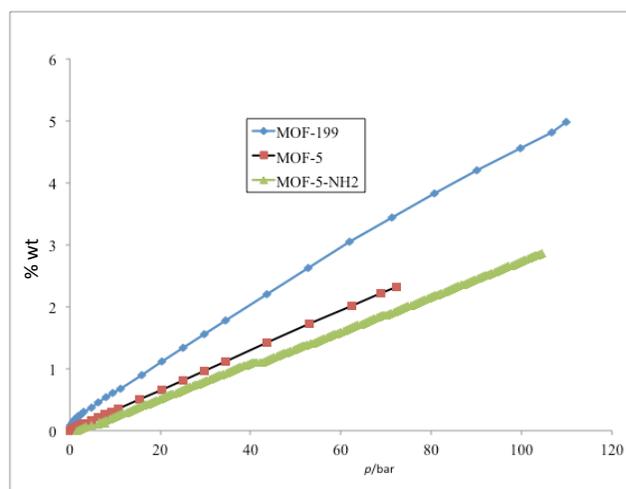


Figure 5: H<sub>2</sub> adsorption of synthesized samples..

## 4 CONCLUSIONS

They were able to synthesize three isoreticular MOF with cubic structure and surface area of 1645.98, and 528.90, 1732.05 m<sup>2</sup>/g for MOF-5, MOF-5-NH<sub>2</sub> and MOF-199, respectively. It was possible to remove the solvent molecules could be trapped in the pores of the network, by washing with solvent and heat treatment. Morphology was well defined for MOF-5-NH<sub>2</sub> and MOF-199, while the MOF-5 presents an irregular morphology.

All MOF able to adsorb hydrogen, being the MOF-199 higher capacity (3.4%), followed by MOF-5 (2.3%) and finally the MOF-5-NH<sub>2</sub> (1.9%) at 70 bar, this trend is the same as was observed in the area surface, so one can conclude that a greater surface area greater hydrogen storage capacity.

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