

Feature Article

Evaluation of basic sites of ZIFs metal organic frameworks in the Knoevenagel condensation reaction



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ABSTRACT

Metal-organic frameworks represent a new class of hybrid inorganic-organic materials which are characterized by high stability, high porosity and well-defined crystalline structures. One of their applications is in Catalysis, where bifunctional catalysts may be developed, with both acidic and basic sites. Zeolitic imidazole framework (ZIF) is a subfamily of MOFs which combines the advantages of MOFs with high thermal and chemical stability of zeolites. The objective of this work is to evaluate the basic character of synthesized ZIFs (ZIF-8 and ZIF-67). Samples were characterized by N₂ adsorption, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA). The Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate was chosen as model reaction to evaluate the basic sites. The reaction was conducted at 40 °C and aniline was used as homogeneous catalyst for comparison. Characterization has shown high crystallinity, the presence of functional groups typical of ZIFs structures and high thermal stability. Both ZIF catalysts have shown good catalytic activity (around 90% at 8 h of reaction), similar to the activity of aniline, a homogeneous catalyst. So the presence of basic sites of ZIF-8 and ZIF-67 and their activity were proven in this work.

1. Introduction

Metal-organic frameworks (MOFs) are a class of hybrid inorganic-organic materials with bi or tridimensional structures [1]. Also called coordination polymers or coordination frameworks, they are formed by self-assembly of metallic ions or clusters and organic ligands, with repeated unit cells that form tridimensional structures [2]. A material can be considered a MOF if the unit cell are spatially organized to form crystalline porous structures with channels and cavities with regular form and size, also presenting high stability and strong metal-ligand bond [1,3]. Besides Catalysis, MOFs are applied in several fields, like gas storage and separation, selective adsorption, biomedicine, chemical sensors, ion exchange, etc. [4].

MOFs synthesis usually involves the addition of two solutions, one containing the metal precursor and the other the organic component. A self-assembly process occurs, where metal or clusters form the nodes

and the organic molecule the rods, acting as ligands and electron donor in the coordinate bond with the metallic center. Guest molecules may be present in the structure. It is possible to modulate both the porous structure and the electronic properties of the active site, by the choice of the organic ligand or by post-synthesis treatment [4]. As the zeolites, MOFs are formed by unit cells resulted from the assembly of secondary building units (SBUs), forming a tridimensional structure with high porosity and crystallinity. Geometric and chemical characteristics of the SBUs make possible the prediction of the network topology [5].

MOFs can be designed to act as bifunctional catalysts, possessing both acid and basic sites. Acidity may be present in moieties of the original MOF or can be introduced by post-synthesis treatment, like sulfonation. Basicity may also be present in the original structure, by the presence of moieties like pyridine, pyrrolidine, amine and guanidine. They have some advantages compared to traditional acid and basic catalysts reported in the literature, like CaO-ZrO₂ [6], like higher

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crystallinity and surface area (up to $6000 \text{ m}^2 \text{ g}^{-1}$) and better control of Lewis and Brønsted acid and basic sites. The ZIF-8 MOF, having zinc as the metal and 2-methylimidazole as the organic ligand, has been applied in the rapeseed oil transesterification reaction with several alcohols and showed a yield higher than 90% with methanol with two hours of reaction [7]. Authors have claimed the existence of strong Lewis sites (Zn_{II} species), as well as strong Brønsted acid sites (NH groups), together with basic sites (OH groups and N^- moieties). The choice of the organic ligand is crucial for the properties of the MOFs [8].

Zeolite imidazolate frameworks (ZIFs) is one of the most studied subfamily of the MOFs because it merges all the advantages cited before of the MOFs with high thermal and chemical stability and zeolitic topologies. Zinc (ZIF-8) or cobalt (ZIF-67) are linked to nitrogen atoms from imidazole (Im) organic groups, forming a structure with 6, 8 or 12-member rings that generates nanometric porous, that is, T-O-T (T = Si, Al, P) bonds of zeolites are replaced by M-Im-M (M = Zn, Co) bonds, with similar bond angles, around 145° [9,10]. They can be applied in guest sorption, exchange, storage and catalysis [11].

ZIF-8 ($\text{Zn}(\text{mim})_2 \cdot 2\text{H}_2\text{O}$, mim = 2-methylimidazole) is a ZIF MOF that exhibits a high surface area (around $1400 \text{ m}^2 \text{ g}^{-1}$), thermal stability up to 420°C and large porous diameter (around 11 \AA) [11,12]. ZIF-67 ($\text{Co}(\text{mim})_2 \cdot 2\text{H}_2\text{O}$, mim = 2-methylimidazole) is an isostructure of ZIF-8, with a smaller porous diameter (around 3.4 \AA) [10].

The Knoevenagel condensation reaction has been used as a model reaction to check the activity of basic sites [13–15]. It can be represented in Fig. 1. It is an Aldolic-type condensation of an organic compound with active methylene group (e.g. benzaldehyde) with an aldehyde or ketone (e.g. ethyl cyanoacetate). The basic sites are necessary for the direct abstraction of proton from active methylene compounds in order to form the carbanion or for the interaction of amine sites (or similar base strength groups) with benzaldehyde to form an imine intermediate [16].

ZIF-8 and ZIF-67 have been studied in several applications, including catalysis, but, to the best of our knowledge, any work was reported in Knoevenagel condensation reaction using ZIF-67 as catalyst. Tran et al. [15] have applied ZIF-8 in the Knoevenagel reaction, but using mainly toluene as solvent (in this work, we used ethanol). It is a good point to compare these isostructural materials directly, in the same experimental apparatus, in the same reaction conditions, in one of the most potential applications, that is based-catalyzed reactions, exploring their basic sites (OH groups and N-moieties). Additionally we have also used two traditional basic catalysts for comparison, a homogeneous (aniline) and a heterogeneous (hydrotalcite) one.

So the main objectives of this work were to synthesize and test the basic activity of ZIF-8 and ZIF-67 MOFs in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, aiming applications that need bifunctional catalysts with basic and acid sites, like the biodiesel synthesis.

2. Material and methods

2.1. Catalysts synthesis

ZIF-8 MOF was synthesized according to the methodology proposed by Cravillon et al. [17]. A methanolic solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (9.87 mmol, Aldrich, reactant grade) was rapidly poured into a

methanolic solution of 2-methyl imidazole – Hmin (79.04 mmol, Aldrich, 99%). The mixture was kept under agitation at room temperature for 1 h and after that the crystals were separated from the milky dispersion by centrifugation (3000 rpm), washed with methanol and dried at 40°C in air. ZIF-67 MOF was prepared through a similar methodology proposed by Li et al. [18], from methanolic solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10.01 mmol) and Hmin (79.04 mmol). The mixture was kept under agitation at room temperature for 8 h and after that the crystals were separated by centrifugation (4000 rpm), washed with methanol and dried at 80°C in an oven. In order to compare the catalytic performance with traditional basic catalysts, aniline (SIAL, 99.5+ %) and Mg-Al hydrotalcite ($\text{Al}/(\text{Mg} + \text{Al}) = 0.20$) prepared according to methodology proposed by Silva et al. [19] was used as homogeneous and heterogeneous basic catalysts, respectively.

2.2. Catalyst characterization

The catalysts total specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The nitrogen physisorption measurement was performed on a Micromeritics ASAP 2000 instrument. The sample was dried prior to the measurement at 200°C for 24 h. Next, the sample was cooled down to 77 K and nitrogen isotherms were collected from $P/P_0 = 10^{-6}$ to $P/P_0 = 1$.

X-ray powder diffraction patterns were recorded on a bench Shimadzu XRD-6000 diffractometer using $\text{Cu K}\alpha$ (40 KV and 30 mA) radiation in the range of $5-60^\circ$ at $2^\circ/\text{min}$. Infrared spectra ($4000-400 \text{ cm}^{-1}$, resol. 4 cm^{-1} , 16 scans) were recorded on a Perkin Elmer Spectrum BX spectrometer. Thermogravimetric analysis (TGA) was performed with a Netzsch STA 449 F1 Jupiter in the temperature range of $25-1000^\circ \text{C}$ under N_2 atmosphere at a heating rate of $10^\circ \text{C min}^{-1}$, using $\alpha\text{-Al}_2\text{O}_3$ as the reference sample.

2.3. Knoevenagel condensation reaction

The Knoevenagel condensation of benzaldehyde (Aldrich, 99.5%) with ethyl cyanoacetate (Aldrich, 98+ %) was performed in a glass Erlenmeyer in a heating plate with a micro processed temperature controller according to the methodology adapted from Gascon et al. [19]. An ethanolic solution of benzaldehyde (8 mmol) was prepared and also an ethanolic solution of ethyl cyanoacetate (7 mmol). The catalyst mass (3% w/w in relation to benzaldehyde) was added to the ethyl cyanoacetate solution (5 mL). The mass of aniline used as homogeneous catalyst for comparison was calculated based on the same number of nitrogen atoms of the MOFs. After the stabilization of the temperature (40°C), the reaction started with the addition of the benzaldehyde solution and the system was kept under agitation. Samples of $50 \mu\text{L}$ were withdrawn periodically (0, 20 e 40 min, 1, 2, 3, 5, 8 and 24 h) to construct the kinetic curves, filtered, diluted in 1 mL of dichloromethane and immediately injected in a GC-qMS instrument (QP2010 plus, Shimadzu) equipped with an AOC20i auto-injector (split/splitless mode). A capillary column (ZB-5MS, 5% phenyl/95% dimethylpolysiloxane, $60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was used. Conversion was calculated based on the decrease of the area of the limitant reactant (ethyl cyanoacetate). The main product was ethyl (E)- α -cyanoacrylate (see Fig. 1). The existence of by-products was checked but the selectivity towards them was always less than 0.2%.

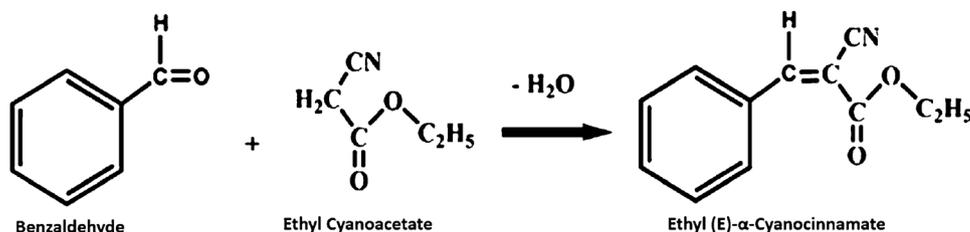


Fig. 1. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

Table 1
Textural properties of MOFs used in this work.

Property	ZIF-8	ZIF-67
Specific BET surface area ($\text{m}^2 \text{g}^{-1}$)	1229	1881
Pore radius (Å)	17	15
Mesopore volume ($\text{cm}^3 \text{g}^{-1}$)	0.26	0.34
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.90	1.25

3. Results and discussion

3.1. Catalyst characterization

Table 1 presents the data obtained from the N_2 adsorption isotherms, using the BET method to calculate the total specific surface area and the BJH method to calculate the pore volumes and pore diameters. Samples have shown a Type II isotherm, according to IUPAC classification, characteristic of materials with meso and macropores.

ZIF-67 has shown a higher surface area than ZIF-8. BET surface areas are in accordance to the ones reported in the literature. Cravillon et al. [17] has claimed a ZIF-8 surface area of $962 \text{ m}^2 \text{ g}^{-1}$, while Li et al. [17] has showed a ZIF-67 surface area of $2380 \text{ m}^2 \text{ g}^{-1}$. Differences can be attributed to different degree of removal of molecules (methanol, hmim) inside the structure.

The XRD spectra of ZIF-8 and ZIF-67 can be observed in Figs. 2 and 3. The peaks are very intense, which indicates a high crystallinity, and the patterns are in accordance with the data obtained from single crystals available in the database Cambridge Crystallographic Data Centre [20], with the inscriptions CCDC 602542 and CCDC 671073, respectively, and the XRD spectra of ZIF-8 reported by Tran et al. [15], proving that the synthesis was well succeeded.

The crystallite size was estimated using the Scherrer equation applied to the most intense peak (around 7.6°) and the results were reported in Table 2. Sizes are very similar, which is expected since they are isostructural materials. ZIF-67 has a higher crystal size which can be attributed to the higher atomic radius of cobalt (169 pm) compared to zinc (142 pm).

The FTIR spectra of ZIF-8 and ZIF-67 can be seen in Figs. 4 and 5, respectively. The main bands are properly identified. In ZIF-8 the bands at 3138 and 2933 cm^{-1} can be assigned to stretching vibrations of C–H bonds in the methyl group and the imidazole ring, while the band at 1595 cm^{-1} can be attributed to the C=C bond, the ones in the 1400 – 1100 cm^{-1} range to the C–N bond and the one at 421 cm^{-1} to the Zn–N stretching vibration [15,22]. Similar bands can be found in the ZIF-68 spectrum, with an additional band at 3450 cm^{-1} attributed to the N–H bond [21].

Figs. 6 and 7 present TGA and DTA curves of ZIF-8 and ZIF-67, respectively. Both TGA profiles are very similar. A small mass loss

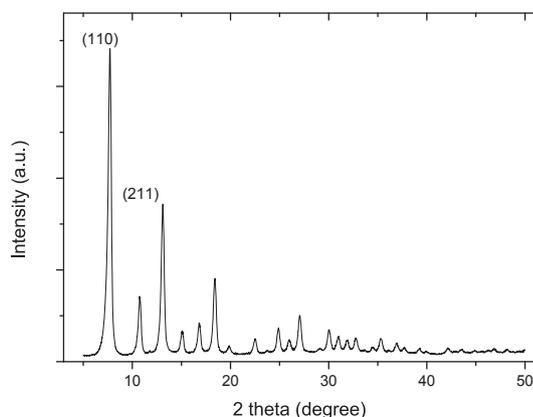


Fig. 2. XRD pattern of ZIF-8.

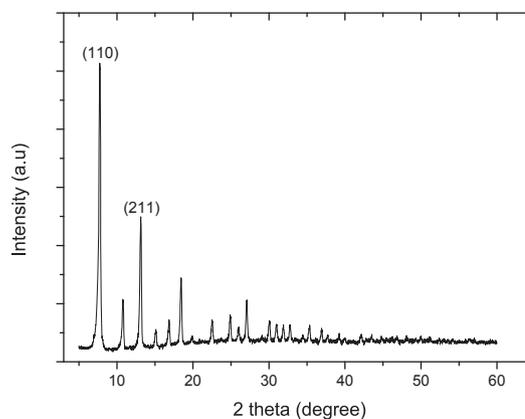


Fig. 3. XRD pattern of ZIF-67.

Table 2
Crystal sizes according to the Scherrer equation.

MOF	Crystal Size (Å)
ZIF-8	206.9
ZIF-67	296.7

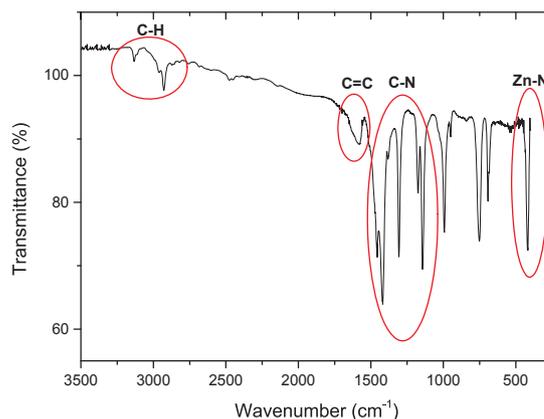


Fig. 4. FTIR spectra of ZIF-8.

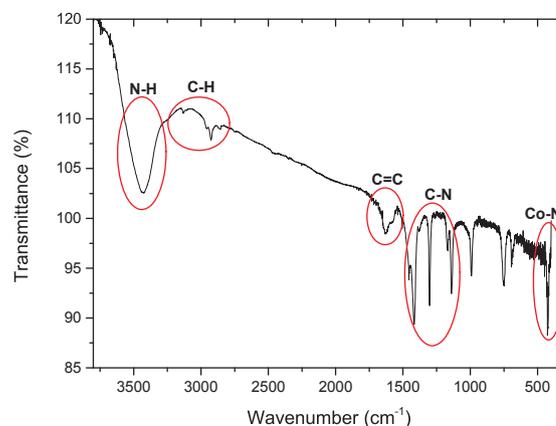


Fig. 5. FTIR spectra of ZIF-67.

(around 1%) was observed at temperatures up to 200°C , which can be attributed to the removal of guest molecules (e.g., methanol) from the cavities and some species (e.g. Hmin) from the surfaces of the crystals [17]. After that, a small mass loss occurs at temperatures up to 582°C (ZIF-8) and 490°C (ZIF-68) can be assigned to the removal of coordinated guest molecules. Then the organic linker molecules starts to

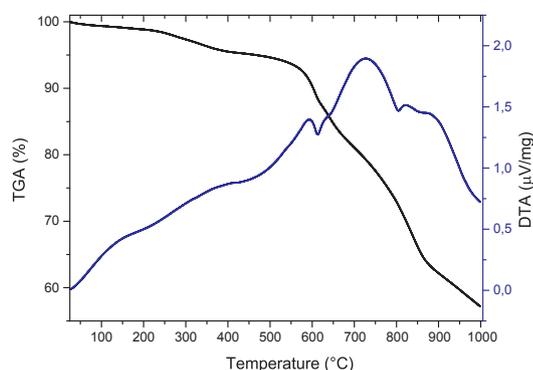


Fig. 6. TGA analysis of ZIF-8.

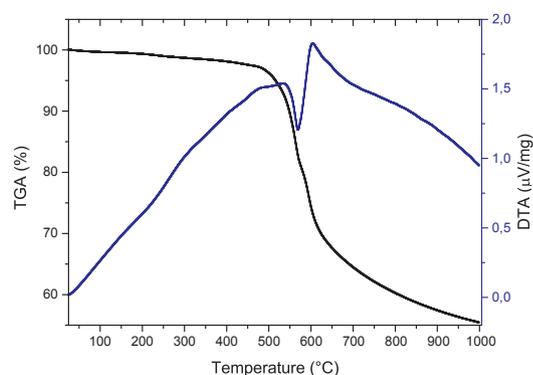


Fig. 7. TGA analysis of ZIF-67.

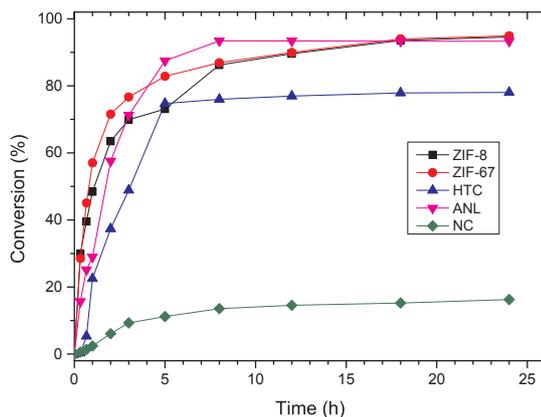


Fig. 8. Kinetic curves in the Knoevenagel condensation of ethyl cyanoacetate and benzaldehyde. $T = 40\text{ }^{\circ}\text{C}$, $\text{MR} = 1:1.14$, 3% w/w catalyst. HTC = hydrotalcite; ANL = aniline; NC = non-catalytic reaction.

Table 3

Conversion in the Knoevenagel condensation of ethyl cyanoacetate and benzaldehyde^a.

Catalyst	Conversion (%)
Non catalytic	6.08
ZIF-8	63.5
ZIF-67	71.6
Aniline	57.6
Hydrotalcite	37.4

^a Reaction conditions: $t = 2\text{ h}$, $T = 40\text{ }^{\circ}\text{C}$, $\text{MR} = 1:1.14$, 3% w/w catalyst.

decompose and the final residues are the oxides (ZnO and CoO). ZIF-8 has presented a higher thermal stability, since the decomposition started at higher temperatures. In general both materials present high

thermal stability and ZIF-8 has showed the highest one. Concerning thermal stability, both materials can be applied safely at temperatures below $400\text{ }^{\circ}\text{C}$.

3.2. Knoevenagel condensation reaction

The reaction was performed at $40\text{ }^{\circ}\text{C}$, where the MOFs are very stable. All the catalysts were compared at the same reaction conditions. Fig. 8 presents the kinetic curves of all the catalysts used in the reaction, where Table 3 presents the conversions with 2 h of reaction. All the catalysts employed have shown catalytic activity since conversions were higher than the non-catalytic run. ZIFs had the best performance at the beginning of the reaction (up to 2 h), with conversions higher than aniline, a homogeneous catalyst. Their conversions were much higher than hydrotalcite, a conventional basic heterogeneous catalyst. Tran et al. [15] have applied ZIF-8 in the Knoevenagel reaction, but using mainly toluene as solvent. The conversions reported are very similar to the ones reported in this present work, between 60 and 80% with 2 h of reaction. To the best of our knowledge any work was reported in this reaction using ZIF-67 as catalyst.

According to Chizallet et al. [7], ZIFs present strong Lewis sites (ZnII species), as well as strong Brønsted acid sites (NH groups), together with basic sites (OH groups and N- moieties). These basic sites are responsible for the activity of these materials in this reaction. Among the ZIFs, ZIF-67 containing Co atoms, was more active than ZIF-8, containing Zn atoms. Since they are isostructural and the main basic sites are in the organic part of the MOF, it was not expected differences in activity. The higher activity of ZIF-67 may be explained by its higher specific surface area ($1881 \times 1229\text{ m}^2\text{ g}^{-1}$), providing greater contact area.

4. Conclusions

Zeolite imidazolate frameworks (ZIFs) MOFs using 2-methyl imidazole as organic ligand were prepared in this study: ZIF-8 containing zinc as metal atom and ZIF-67 containing Co as metal atom. Both catalysts were compared in their characteristics and catalytic performance.

ZIF-67 has shown a higher surface area than ZIF-8, but a lower thermal stability, although both have presented a good thermal stability, been thermally stable at least $400\text{ }^{\circ}\text{C}$. All the properties showed are similar to the ones reported in the literature, proving the successful of the synthesis.

The ZIFs have showed excellent catalytic performances (conversions around 65% at 2 h of reaction), superior to traditional homogeneous (aniline) and heterogeneous (hydrotalcite) catalysts, making them promising for reactions that needs basic sites, in special acid/base reactions like the synthesis of biodiesel. The direct comparison between ZIF-8 and ZIF-67, differing only in the metal of the framework (Zn or Co, respectively), has shown a higher activity for ZIF-67, probably due its higher surface area, providing greater contact area.

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