



Influence of divalent metal ions on CO₂ valorization at room temperature by isostructural MOF-74 materials

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ABSTRACT

At present, the concentration of carbon dioxide (CO₂) has increased to unprecedented levels. The valorization of CO₂ into high value-added chemicals can be a very interesting alternative to stabilize the concentration of this atmospheric pollutant while the current energy transition takes place. The well-known M-MOF-74 family (M = Mg, Co, Ni, Cu and Zn) have been evaluated as heterogeneous catalysts to carry out several cycloaddition reactions at room temperature with several epoxides (epichlorohydrin; 1,2-epoxyhexane and styrene oxide) as substrate, to evaluate the influence of the metal in this reaction. Zn-MOF-74 showed the highest catalytic activity, always with conversion and selectivity values above 93% regardless of the epoxides studied and the carbonates obtained, due to the higher acid character of the Zn²⁺ ion. Therefore, it is confirmed that the influence of the metal is key in this reaction, despite the fact that Cu-MOF-74 with an adsorption capacity of 5 mmol/g of CO₂ (45 °C, 5 bar) converts 26% of styrene oxide under the conditions evaluated compared to Zn-MOF-74, which is the material with the lowest adsorption capacity (3 mmol/g of CO₂) and shows a conversion of 93%.

1. Introduction

At present, the excessive consumption of fossil fuels, due to economic and social advances, has increased the concentration of greenhouse gases (GHG) in the atmosphere, favoring the global warming. The urgency in taking measures that contribute to achieving a decarbonized economy by 2050 are indicated in the United Nations Sustainable Development Goal (SDG) number 13 [<https://sdgs.un.org/es/goals>]. One of these gases is carbon dioxide (CO₂) which, although naturally occurring in the atmosphere, its concentration has risen to unprecedented levels. To stabilize the concentration of CO₂ while the current energy transition to renewable solutions is being carried out, different technologies must be implemented, including the valorization of CO₂ to obtain high added-value chemical products, giving it a second life, thus fulfilling the objectives of the circular economy [1,2]. In industrial processes CO₂ is commonly generated and emitted together with other gases. To transform the CO₂ into other high-value compounds, it should be first separated from the other gases and impurities in exhaust streams. This industrial separation is usually carried out using aqueous amine

solutions, which are highly selective towards carbon dioxide. However, this technology has numerous disadvantages, including partial amine degradation, corrosion issues and high energy consumption [3]. To overcome these limitations, carbon dioxide capture processes by adsorption on porous solids have also been extensively investigated. For this purpose, different types of materials have been tested such as zeolites, activated carbons or mesostructured aluminosilicates [4]. However, all these types of materials have a very low CO₂ adsorption capacity/selectivity under the conditions that are generally found in exhaust gas streams of power plants after the desulphurization units.

Additionally, once CO₂ is captured, a solution for its utilization is also needed, so valorizing it by chemical transformations leading to new compounds with higher added value is an attractive option [5]. These transformations are not always easy, mainly due to the high stability of the carbon dioxide molecule, so extreme conditions of pressure and temperature are required to boost the reaction. One alternative to achieve the activation of the CO₂ molecule and facilitate its transformation is the use of catalysts that can reduce the energy requirement, allowing more sustainable processes as well [6]. One of the most interesting CO₂

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valorization routes is to obtain cyclic carbonates by means of the cycloaddition reaction from epoxides, as it is a promising reaction due to its 100% atom economy [7]. Cyclic carbonates have important applications, such as solvents in chemical processes, electrolytes in lithium-ion batteries, monomers for polymers and lubricants in industrial processes [8–12]. For all the above mentioned reasons, emerging combined CO₂ capture and utilization processes is a useful, profitable and sustainable solution for CO₂ emissions [13].

In this context, the use of metal-organic frameworks (MOFs) as adsorbents and heterogeneous catalysts for CO₂ capture and subsequently synthesis of cyclic carbonates has recently gained much attention [14–17]. MOFs offer a promising platform for addressing the dual challenge of CO₂ capture and transformation owing to the designable and tunable structures and high internal surface area that can expedite selective CO₂ binding [18]. Moreover, the easily accessible and uniformly distributed high density active sites throughout the framework facilitate the transfer of substrates and products [19]. A key structural advantages of MOF materials over other heterogeneous materials, is that they can have Lewis basic groups in their organic linkers that can increase the CO₂ reactivity, getting higher reaction yields than in common heterogeneous catalyst. Besides, MOF materials present intrinsic Lewis acid groups which are the metal ions in their inorganic clusters that can play an important role in cycloaddition reaction between CO₂ and epoxides, since they can interact with the oxygen atom of the epoxide molecule, favoring the opening of the epoxide's ring. So, the synergic effect achieved with Lewis basic and acid groups coexisting in the same structure can lead good reaction yields [20]. The acidity of metal ion is an important parameter to consider over the opening of epoxide's ring and hence the reaction yield [21]. The MOF-74 structure present infinite rod units contain a high density of open metal sites serving as Lewis acid sites and the 2-oxidobenzoate anions acting as basic sites, which have been demonstrated as highly active nodes capable of gas adsorption [22, 23] and catalytic processes [24,25]. So, the well-known MOF-74 family constituted by 2,5-dihydroxyterephthalic acid as organic ligand and with hexagonal channels that can favor the diffusion of substrates is an interesting family series to assess to study in this reaction [26].

In this work, we have selected five MOF-74 materials with different divalent metal ions (M= Mg²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺), to evaluate the influence of the metal on CO₂ valorization at room temperature to obtain cyclic carbonates from epoxides. In addition, the influence of the epoxide substituent on the cycloaddition reaction has also been evaluated to obtain different cyclic carbonates.

2. Experimental

2.1. Catalysts preparation

Family of MOF-74 was synthesized from 2,5-dihydroxyterephthalic acid (H₂dhtp) as organic ligand and different metal salts. Mg, Co, Ni [27], Cu [28] and Zn-MOF-74 [29] were synthesized by solvothermal methods published elsewhere, which are also detailed in the Supporting Information. In a beaker, a joint solution of the corresponding metal source and 2,5-dihydroxyterephthalic acid (H₂-dhtp), used as organic ligand, was prepared in a previously prepared mixture of solvents. Once these reagents have been dissolved, they are transferred to an ISO bottle, which is placed in a preheated oven and subjected to certain conditions of temperature and time. Then, the ISO canister is removed and allowed to cool to room temperature so that the solid formed can be separated by vacuum filtration. Subsequently, the materials obtained are immersed in methanol in order to exchange the molecules of the synthesis solvents. For this purpose, the solid is washed with methanol for three days, replacing the methanol every 24 h. After washing, the material is separated from the methanol by vacuum filtration and dried in an oven at 70 °C for 30 min. Finally, materials are activated under vacuum (10⁻³ bar) and a temperature of 130 °C for 18 h using a Schlenk flask.

2.2. Catalyst characterization

X-Ray powder diffraction (XRD) patterns were acquired on a PHILIPS XPERT PRO diffractometer using CuK α radiation (1.542 Å). The data were recorded from 5 to 50 (2 θ) with a resolution of 0.01°. Nitrogen adsorption-desorption isotherms were measured at 77 K using an AutoSorb equipment. Samples were degassed at 130 °C and high vacuum during 12 h. The specific surface area was calculated by using the Brunauer-Emmett-Teller (BET) model. The pore volume was estimated by using the Dubinin-Radskevich equations. The pore size distribution was estimated using non-local DFT calculations, assuming a kernel model of split pore, N₂-carbon at 77 K. External surface was estimated by *t*-plot method and Harkins Jura equation. Simultaneous thermogravimetry and derivative thermogravimetric analyses (TGA/DTG) were carried out under a nitrogen atmosphere with an N₂ flow of 100 mL·min⁻¹ at a heating rate of 5 °C/min up to 800 °C, using a SDT 2860 apparatus. Adsorption/desorption isotherms of pure CO₂ were obtained in a volumetric analyzer type VTI HPVA-100 Scientific Instrument. Metal content in the filtered solution after reaction was measured by ICP-OES analysis collected in a Varian VISTA AX system. ¹H NMR spectra were collected with a Varian Mercury Plus spectrometer at 400 MHz using trimethyl silane as an internal standard. FID files were processed using MestRe-C software version 4.9.9.6. The chemical shifts (δ) for ¹H spectra, given in ppm, are referenced to the residual proton signal of the deuterated chloroform.

2.3. Reaction procedure

In a model experiment, 1 mmol of epoxide, 1.5 mol% (active metal sites to epoxide ratio) of degassed MOF catalyst and 0.05 mmol of tetrabutylammonium bromide (TBAB) were added in a 100 mL stainless-steel autoclave [17]. The system was evacuated with CO₂ three times before being pressurized. Then, the reaction was carried out at room temperature under moderate stirring. Once the reaction time was completed, the residual carbon dioxide was slowly discharged, and the catalyst was separated by centrifugation. To determine the reaction conversion and selectivity, the products were analyzed by ¹H NMR using CDCl₃ as solvent and 1, 2, 4, 5-tetrachloro-3-nitrobenzene as internal standard.

3. Results and discussion

3.1. Catalyst characterization

MOF-74 materials were physicochemically characterized to confirm the successful synthesis of all materials M-MOF-74 (M=Mg, Co, Ni, Cu, Zn). Firstly, by powder XRD (Fig. 1), the main diffraction peaks characteristic of the MOF-74 structure (6.8° and 11.8°) were observed in all cases, confirming the presence of the desired crystalline phase in the bulk samples.

To study thermal stability of these materials, TGA in nitrogen atmosphere were collected from 40° to 800°C (Fig. 2). In all samples it was observed two weight loss steps, the first between 100 and 150 °C, corresponding to the removal of guest MeOH molecules in from the porous system. The second weight loss was observed between 350 and 450 °C, relating to the organic linker degradation and structure collapse. This difference in the thermal stability of the different M-MOF-74 materials is related to the strength of the metal-oxygen bond between the metal ions in the structure and the oxygen atoms from the carboxylic and hydroxyl groups of the organic ligand. Based on TGA results, MOF-74 materials were activated at 130 °C under vacuum (10⁻³ bar) for 18 h before gas adsorption and reaction tests.

To evaluate textural properties of MOF-74 materials, nitrogen adsorption/desorption isotherms were carried out (Fig. 3). In Table 1 BET surface area, pore volume and pore diameter are summarized, observing the highest and lowest surface area were 1230 and 995 m²/g

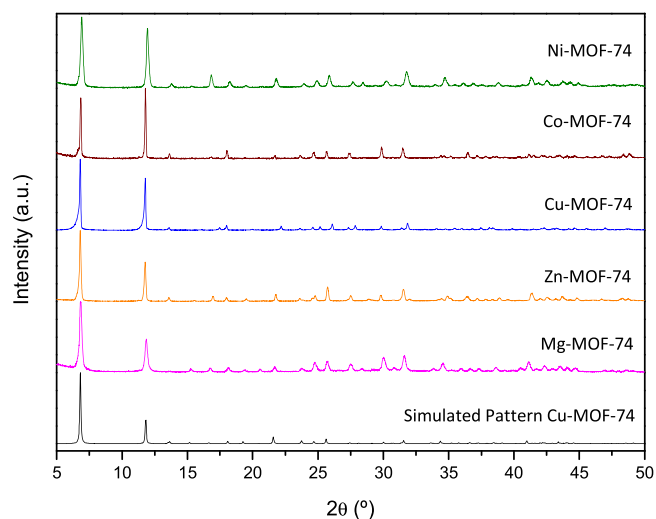


Fig. 1. XRD diffractograms of MOF-74 series and the simulated pattern of Cu-MOF-74.

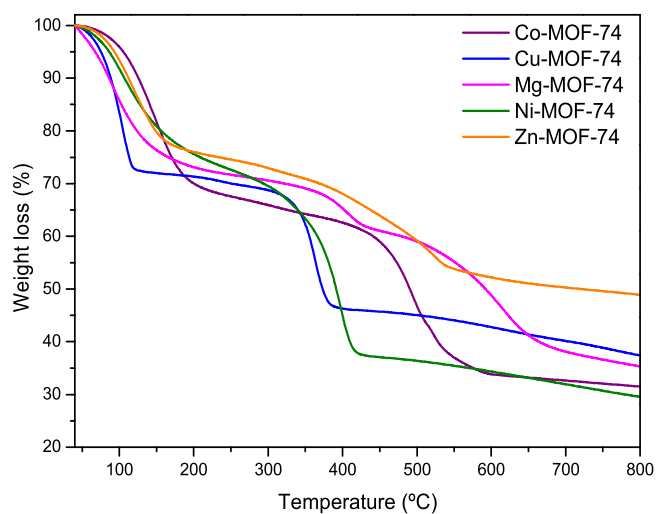


Fig. 2. Nitrogen TGA of M-MOF-74.

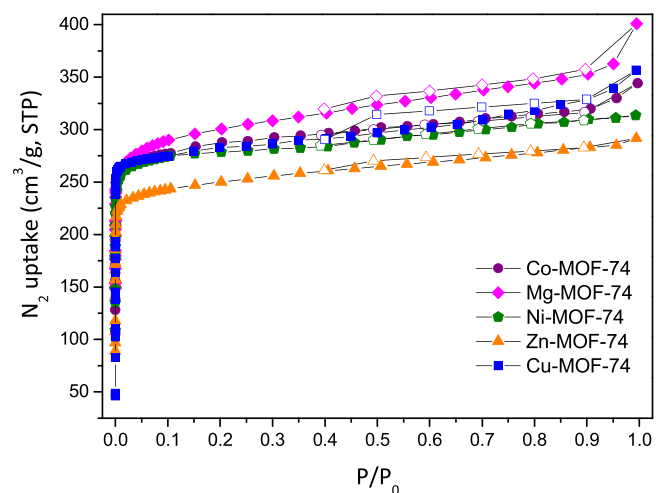


Fig. 3. N_2 adsorption/desorption isotherms of MOF-74 family.

Table 1
Textural properties of MOF-74 family.

Material	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_{Pore} (\AA)
Co-MOF-74	1127	0.54	12
Cu-MOF-74	1126	0.55	
Ni-MOF-74	1121	0.49	
Zn-MOF-74	995	0.44	
Mg-MOF-74	1230	0.43	

for Mg-MOF-74 and Zn-MOF-74, respectively. The specific surface area values calculated for all materials are as described in the literature, except for the material Mg-MOF-74, which is somewhat lower than in some literature references [29–33]. To corroborate that this difference in the specific surface area of the Mg-MOF-74 material is not due to the degassing process, a TGA analysis (Figure S1) was performed on all the materials to confirm the absence of solvents in the pores of the catalysts.

3.2. CO_2 adsorption/desorption isotherms

MOF-74 materials were evaluated in carbon dioxide adsorption test at 45 °C and up to 5 bar, to bring the conditions closer to the ones found in exhaust streams of power plants (Fig. 4). In all cases, the isotherms show a large contribution of physical adsorption, with a high adsorption capacity dependence on the operation pressure, especially in the case of the Cu-MOF-74 material. It is very important to note that metal plays a fundamental role in the CO_2 adsorption properties of the MOF-74 family of materials, due to the strong interaction between the carbon dioxide molecules, through one of their oxygen atoms, and the metal ions of the MOF-74 materials structure [34,35]. These metal centres are the main adsorption centres at low partial pressure of the adsorbate (under surface coating), while as the pressure of adsorbed CO_2 increases, these molecules start to localize in the centre of the porous channels of the material, leading to the filling of the channels [34,36]. According to the literature, unlike what happens with the adsorption of molecules such as N_2 or CO that present a bond angle with the metal ion of the structure close to 180°, in the case of carbon dioxide molecules, they present a bond angle with the metal ion of approximately 129°, due to the lateral interactions existing between the CO_2 molecules and the oxygen atoms corresponding to the carboxylic group of the organic ligand [34,35]. The CO_2 adsorbed amount is summarized in Table 2, where it can be observed that Cu-MOF-74 is the material with the best properties for CO_2 adsorption at higher pressures and Zn-MOF-74 with the lowest one.

Nonetheless, at low pressure (up to 1 bar) the results are different,

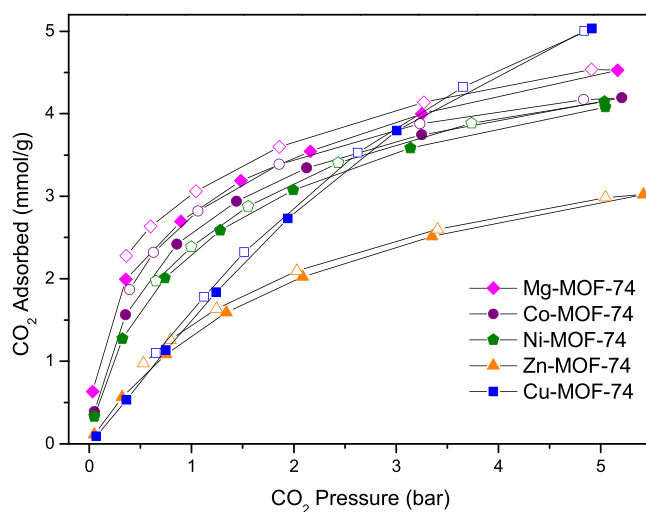


Fig. 4. CO_2 adsorption/desorption isotherms of MOF-74 materials at 45 °C and 5 bar of CO_2 .

Table 2
CO₂ adsorption capacities of MOF-74 materials at 45 °C.

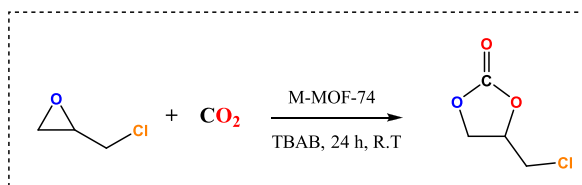
Material	CO ₂ Uptake (mmol/g) at 1 bar	CO ₂ Uptake (mmol/g) at 5 bar
Co-MOF-74	2.45	4.19
Cu-MOF-74	1.83	5.03
Ni-MOF-74	2.08	4.14
Zn-MOF-74	1.59	3.02
Mg-MOF-74	2.78	4.52

being Mg-MOF-74 and Co-MOF-74 the materials with highest amount of CO₂ uptake with values of 2.78 and 2.45 mmol/g, respectively. The higher interaction between the Mg²⁺ ions of the MOF and the carbon dioxide molecules has been related to the higher ionic character of the Mg-O bond, and consequently the higher positive partial charge compared to the metal oxygen coordination bond in the rest of the materials of the MOF-74 family materials synthesized with transition metals [27,37]. Hou et al. also indicate that in the case of the Mg-MOF-74 material there are lower electronic repulsions between the magnesium metal centers and the carbon dioxide molecules, compared to the rest of the MOF-74 materials, synthesized with transition metals, with electrons in *d* orbitals [34]. As one moves to the right in the first series of transition metals, a progressive decrease in adsorption capacity can be observed. This is due to an increase in the electronic repulsions between the metal ions of the MOF-74 structure and the carbon dioxide molecules, so that the interaction between the CO₂ molecules and the metal centers becomes weaker. However, in the specific case of copper, the value obtained is lower than expected, possibly due to the Jahn-Teller effect of distortion of the octahedron of Cu²⁺ ions [38]. The consequence of this effect is that, for an octahedral coordination of the copper atom, there is an elongation of the bond length in the axial coordination positions, leading to a lower binding energy in these positions between the metal ion and the organic ligands [39,40]. It is precisely at these axial positions that the interaction between the CO₂ molecules and the metal centers of the structure takes place. This behavior of Cu-MOF-74 changes as the adsorption pressure increases, since the metal centers become saturated and, therefore, the CO₂ adsorption capacity no longer depends only on the interaction of the gas with the metal centers, but also on the space available in the porous cavities of the material as the porous channels of the structure are progressively filled. The high adsorption capacity of these materials makes them suitable as carbon dioxide adsorbents in the conditions of CO₂ emissions in chimneys [22].

3.3. Catalytic studies of M-MOF-74 in Cycloaddition of CO₂ and epoxides

Due to the good carbon dioxide adsorption properties of this family series, the high surface area and high density of Lewis acid sites (metal sites), they were tested as heterogeneous catalysts in cycloaddition reaction between CO₂ and epoxides. The aim of this part of the work is to assess the influence of the metal ions nature over the performance of the CO₂ reaction conversion, using isostructural materials with the same organic ligand and similar textural properties.

The reaction conditions were selected from a previous work of our researcher group for a Zn based MOF material [17]: 1.5% of catalyst, 5% of co-catalyst, 12 bar of CO₂ pressure, 24 h and room temperature. For



Scheme 1. Cycloaddition reaction between CO₂ and epichlorohydrin using M-MOF-74 catalysts.

these first experiments, epichlorohydrin was selected as substrate due to it is a small molecule and relatively high boiling point (Scheme 1) [17].

In general terms, M-MOF-74 materials exhibited high epichlorohydrin conversion (> 79%) and selectivity to carbonate formation (> 99%) (Table 3). Zn-MOF-74 showed the best catalytic performance with an epichlorohydrin conversion of 98% and a selectivity to chloropropene carbonate of > 99% (Entry 5, Table 3), meanwhile the worst results were found for Ni-MOF-74 with 79% of epichlorohydrin conversion. At the end of each of the reactions, the presence of metal in the liquid phase of the reaction (measured by ICP-OES analysis) was checked and the absence of homogeneous active species was confirmed, therefore it can be confirmed that all the catalytic activity is due to the heterogeneous catalyst. The high epichlorohydrin conversion of Zn-MOF-74 was attributed to the stronger Lewis acidity of Zn²⁺ compared with other metals (Mg²⁺, Co²⁺, Ni²⁺ and Cu²⁺) [41–44]. This higher Lewis acidity of Zn²⁺ is due to the smaller ionic radius of this metal ion. The Lewis acidity of metal ions increases with smaller ionic radius size and higher charge, but in this case all the metal ions evaluated have the same charge, so the ionic radius size is the main factor affecting the Lewis acidity [45–47]. Although there are other important factors that facilitate CO₂ catalysis when using MOFs, such as accessible functional groups and even the presence of defects in the crystal lattice, none of them apply in this study [48]. On this way, Zn-MOF-74 favors, in a stronger manner, the opening of the epoxide ring because of the higher interaction between Zn²⁺ ions and the oxygen atom of the epoxide, allowing to an effective nucleophilic attack of the bromide ion, from TBAB, to the less substituted carbon atom [49].

Besides, to check the influence of the epoxide length, 1,2-epoxihexane was used as a substrate in the cycloaddition reaction (Scheme 2). In Table 4, the catalytic results are summarized for the different M-MOF-74.

When 1,2-epoxihexane was used as substrate, the best results of epoxide conversion were achieved for Co-MOF-74 and Zn-MOF-74 with 92% and 98% (Entries 7 and 10, Table 4). These results agreed with the nature of the metal ions due to Co²⁺ and Zn²⁺ show the higher Lewis acidity increasing the epoxide activation, as it was mentioned before [41–44]. Similar behavior was observed for the selectivity, obtaining the highest for Zn-MOF-74 and Co-MOF-74 (93% and 76%, respectively), being more selective to cyclic carbonate the Zn-MOF-74 material, obtaining as 2,5-dibutyl-1,4-dioxane as byproduct. This molecule can be formed thought cyclodimerization reaction of epoxide without CO₂ [50].

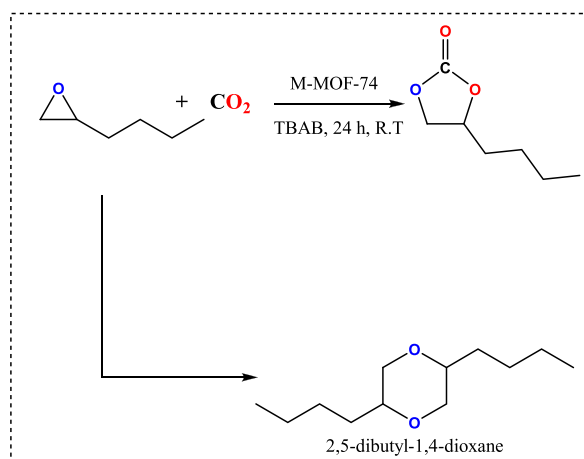
The conversion results with 1,2-epoxihexane were slight lower than with epichlorohydrin, because the length of alkyl chain can raise the steric hindrance inside the porous system of M-MOF-74 structure.

Styrene oxide was also used as substrate in the cycloaddition reaction (Scheme 3) under the same tested conditions to study the influence of bulkier substituent groups in the epoxide molecule (Table 5). In this reaction, phenylene group reduce the epoxide conversion significantly when Mg-MOF-74, Co-MOF-74, Ni-MOF-74 and Cu-MOF-74 were used as catalyst, showing an epoxide conversion of only 21%, 38%, 27% and 26%, respectively (Entries 11–14, Table 5). Besides, the selectivity to cyclic carbonate was lower for styrene oxide than for epichlorohydrin and 1,2-epoxihexane showing values of 57%, 64%, 55% and 61% for

Table 3
Cycloaddition reaction results between CO₂ and epichlorohydrin.

Entry	Material	Conversion (%) ^a	Selectivity (%) ^b	TON ^c	TOF ^d
1	Mg-MOF-74	87		58	2.4
2	Co-MOF-74	90		60	2.5
3	Ni-MOF-74	79	> 99	53	2.2
4	Cu-MOF-74	86		57	2.3
5	Zn-MOF-74	98		65	2.7

^{a-b} The epichlorohydrin conversion and selectivity to carbonate was determined by ¹H NMR analysis. ^cTON = (moles of product)/(moles of metal in the catalyst). ^dTOF = TON/reaction time.

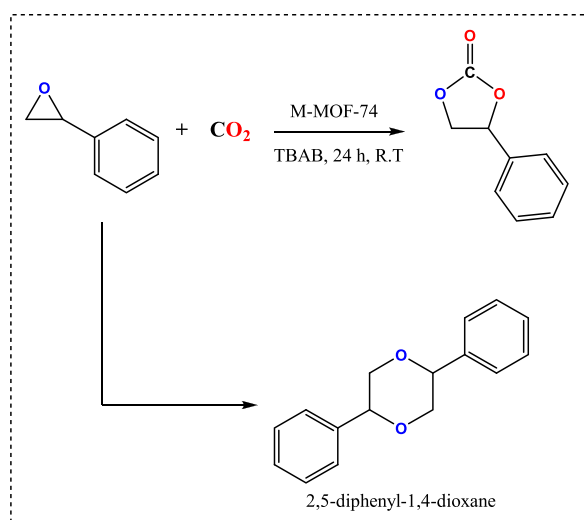


Scheme 2. Cycloaddition reaction between CO₂ and 1,2-epoxihexane.

Table 4
Cycloaddition reaction results between CO₂ and 1,2-epoxihexane.

Entry	Material	Conversion (%) ^a	Selectivity (%) ^b	TON ^c	TOF ^d
6	Mg-MOF-74	79	66	33	1.4
7	Co-MOF-74	92	76	46	1.9
8	Ni-MOF-74	68	63	28	1.1
9	Cu-MOF-74	76	68	35	1.5
10	Zn-MOF-74	98	93	60	2.5

^{a-b} The epichlorohydrin conversion and selectivity to carbonate was determined by ¹H NMR analysis. ^cTON= (moles of product)/(moles of metal in the catalyst). ^dTOF= TON/reaction time.



Scheme 3. Cycloaddition reaction between CO₂ and styrene oxide.

Table 5
Cycloaddition reaction results between CO₂ and styrene oxide.

Entry	Material	Conversion (%) ^a	Selectivity (%) ^b	TON ^c	TOF ^d
11	Mg-MOF-74	21	57	8	0.3
12	Co-MOF-74	38	64	16	0.6
13	Ni-MOF-74	27	55	9	0.3
14	Cu-MOF-74	26	61	10	0.4
15	Zn-MOF-74	93	> 99	62	2.6

^{a-b} The epichlorohydrin conversion and selectivity to carbonate was determined by ¹H NMR analysis. ^cTON= (moles of product)/(moles of metal in the catalyst). ^dTOF= TON/reaction time.

Mg-MOF-74, Co-MOF-74, Ni-MOF-74 and Cu-MOF-74, respectively (Scheme 3), as referenced in literature for other MOFs like Zn-URJC-8 [17], which is attributed to the formation of 2,5-diphenyl-1,4-dioxane byproduct [50,51] that come from the ring opening of epoxide and its intramolecular nucleophilic attack.

Remarkably, Zn-MOF-74 showed the best results in cycloaddition reaction between CO₂ and styrene oxide with a 93% of epoxide conversion and total selectivity to styrene carbonate being more selective than the other isostructural MOF-74 materials (Entry 15, Table 5). This greater performance as heterogeneous catalyst is due to the higher Lewis acid character of the Zn ion, as discussed above. In addition, the conversion slightly decreases compared to epichlorohydrin due to the higher steric hindrance generated by the aromatic ring inside the MOF cavities. However, the epoxide conversions of styrene oxide were also lower those for 1,2-epoxihexane, because the alkyl chain may accommodate within the M-MOF-74 cavities since its the sp³ hybridization, reducing diffusional restraints, favoring the catalytic process, and hence giving rise to higher reaction yields.

In addition, to check the chemical stability of these materials under reaction conditions, they were characterized by XRD after cycloaddition reaction between CO₂ and epichlorohydrin. The XRD pattern of all samples showed the typical pattern of MOF-74 phase, identifying the characteristic diffraction peaks, such as the most intense at 6.8 and 11.8 ° of 2θ (Figure S2). So, that the good catalytic performance as well as the high stability of these MOF make them potential catalysts for cycloaddition reaction of CO₂ and epoxides, and particularly in the case of Zn-MOF-74 material.

3.4. Mechanism of cycloaddition reaction catalyzed by Zn-MOF-74

The proposed catalytic cycle of Zn-MOF-74 in the cycloaddition reaction between carbon dioxide and epoxides is based on the mechanism described in literature for Zn-URJC-8 and Cu-URJC-8 materials [17, 52–57] (Fig. 5). In Step I, epoxide enters inside the cavities of Zn-MOF-74 and interacts, by means of oxygen atom, with unsaturated metal sites favoring the nucleophilic attack of bromide ion from TBAB to the less hindered carbon of epoxide (Step II). The oxygen atom of open epoxide ring can then attack the carbon atom of CO₂ promoting the nucleophilic attack of one oxygen atom of CO₂ to the carbon atom of epichlorohydrin bonded to bromide ion, forming the cyclic carbonate (Step III). Finally, in Step IV the oxygen atom of cyclic carbonate broke the interaction with unsaturated metal center releasing the product of reaction.

4. Conclusions

M-MOF-74 material series was systematically studied in CO₂ adsorption and conversion by means of cycloaddition reaction. Under power plant exhaust gases conditions, Mg-MOF-74 resulted the best adsorbent because of the basic character its structural magnesium ions meanwhile for CO₂ conversion in cycloaddition with epoxides at soft conditions the Zn-MOF-74 was the outstanding catalyst since the more acidic metal (Zn) among the others that favors the course of the reaction. Studied M-MOF-74 materials exhibited complete selectivity to the chloropropene carbonate, and the best conversion reaction was achieved by Zn-MOF-74 with 98%. When other epoxides with bulkier substituents like 1,2-epoxihexane and styrene oxide were used, the conversion reaction decreased due to the steric hindrance of those molecules inside the cavities of M-MOF-74 materials, especially in the case of styrene oxide. In these cases, the best catalytic performance was also achieved by Zn-MOF-74, showing a conversion of 98% and 93% and selectivities of 93 and > 99% for 1,2-epoxihexane and styrene oxide, respectively. All materials showed high stability under reaction conditions. Since the remarkable performance of this family series, they are suitable candidates to be used for the combined purpose of CO₂ capture and conversion via cycloaddition reaction with epoxides.

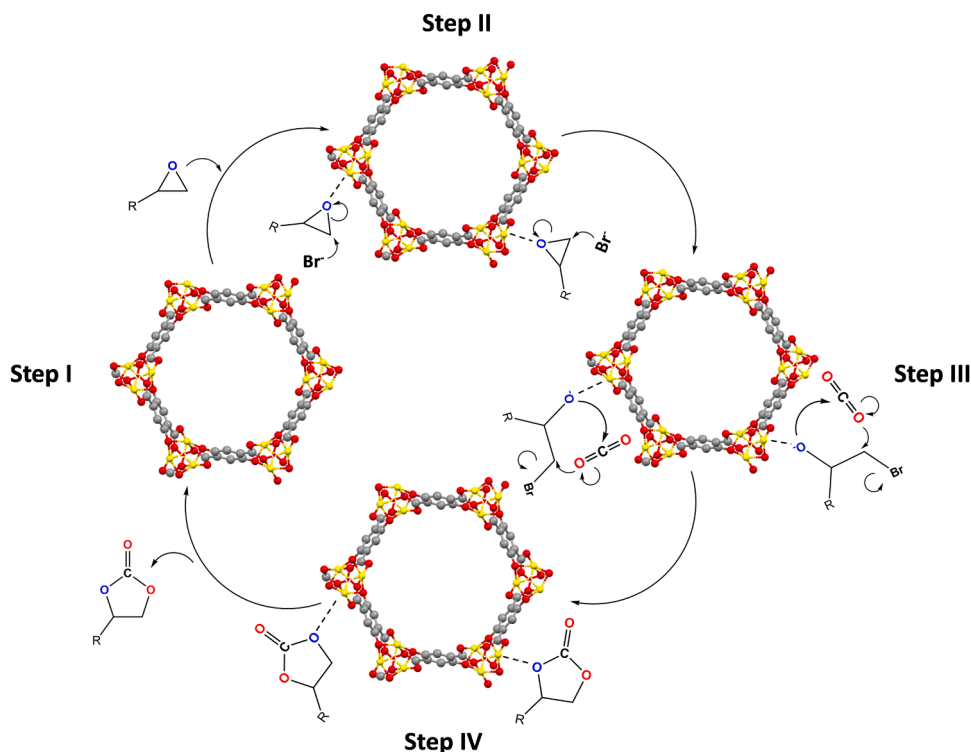


Fig. 5. Catalytic cycle of cycloaddition reaction among CO₂ and epoxides catalyzed by Zn-MOF-74.

CRedit authorship contribution statement

J. Tapiador: Conceptualization, Methodology, Investigation, Writing – original draft. **E. García-Rojas:** Methodology, Investigation, Writing – original draft. **P. López-Patón:** Investigation. **G. Calleja:** Supervision, Funding acquisition. **G. Orcajo:** Validation, Writing – review & editing, Supervision. **C. Martos:** Validation, Writing – review & editing, Supervision. **P. Leo:** Conceptualization, Validation, Writing – original draft, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.109497](https://doi.org/10.1016/j.jece.2023.109497).

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