



Copper MOFs performance in the cycloaddition reaction of CO₂ and epoxides

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ABSTRACT

The research in advanced materials for effective CO₂ capture and conversion is an imperative duty for the next years. In this sense MOF materials are being intensively tested for this purpose. Herein, seven different copper-based MOF materials with different functional organic groups in their linkers have been assessed to comprehend some structural features that influence the CO₂ transformation via cycloaddition reaction with epoxides: Cu-URJC-1 (tetrazole group), Cu-URJC-8 (primary amine group), Cu-MOF-74 (hydroxyl group), JUC-62 (azo group), PCN-16 (triple bond group), HNUST-1 (amide group) and HKUST-1. When epichlorohydrin was used as a substrate, Cu-URJC-8 produced the best epoxide conversion (90%) and selectivity to cyclic carbonate (>99%), despite showing a modest surface area. This result can be explained by the higher basicity of primary amines than other basic functional organic groups of the MOFs. However, when styrene oxide was used as substrate, Cu-URJC-1 led to the best reaction results with a conversion and selectivity toward cyclic carbonate of 60 and 86%, respectively. This result was achieved because this material presents the synergic effect of having in its flexible structure 12 Å channels, that favors the styrene oxide diffusion, and a great number of basic nitrogen atoms, which can increase the reactivity of carbon dioxide. In summary, the presence of nitrogen atoms in the organic linker increases the CO₂ conversion by promoting the reactivity of this molecule.

1. Introduction

The anthropogenic activity has increased the carbon dioxide concentration in the atmosphere from 280 ppm in the pre-industrial era to 418 ppm in 2021 [1]. This increase in the concentration has created different environmental problems such as global warming, acidification of seas and polar ice melting, among others [2]. For these reasons, considerable research efforts are being developed in finding sustainable solutions for human society development, such as CO₂ capture, sequestration, and transformation into high value-added chemicals [3, 4].

One way to valorize the CO₂ is through cycloaddition reactions with epoxides to obtain cyclic carbonates [5–7]. This type of reaction is a 100% atom-economic reaction, that can be effectively carried out by using active catalysts that boost the epoxide ring opening and leave the CO₂ labile to react [8,9]. Different catalysts have been tested in this reaction, although some of them present some important disadvantages. Thus, homogeneous catalysts such as metal complexes, ionic liquids

generate high reaction yields but then the separation from the reaction medium is an expensive process [10,11]. On the other hand, heterogeneous catalysts require too high temperatures and CO₂ pressures to obtain a good reaction yield [12–15]. So, it is still a challenge to develop new heterogeneous catalysts able to operate in milder convenient conditions.

Metal-organic frameworks (MOFs) have emerged as porous, crystalline, and versatile materials, formed by metal ions or cluster nodes and functional organic ligands, connected through coordination bonds [16]. Due to their high porosity and chemical tunability, they are attractive for CH₄, CO₂, and H₂ adsorption [17,18], but also their use as catalysts is being extensively explored [19–21]. In this sense, MOFs are potential catalysts for the cycloaddition reaction between carbon dioxide and epoxides since they can have acid and basic Lewis sites forming part of their crystalline structure. Thus, metal ions act as acid Lewis sites and they can interact with the oxygen atom of the epoxide favoring the opening of the three-member ring [22,23]. At the same time, the Lewis acidity of metal ions is able to increase the yield of the reaction. This is

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the case of Zr^{4+} , Hf^{4+} , Al^{3+} and In^{3+} , which show a high Lewis acidity because their small size; other metal ions like Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} , with a moderate Lewis acidity, achieve great epoxide activation [24]. In turns, organic ligands can present functional groups with free electron pairs that perform as Lewis bases, so that they can also interact with CO_2 molecules, increasing their reactivity [25]. So, the complementary effect between acid and basic Lewis sites can improve the reaction yield of cycloaddition reaction, so the use of MOF materials containing both functionalities in their structure is an interesting feature to study as well as the structural stability given by the coordination number of the metal and the hydrophobic character of the catalyst that would also increase the selectivity of cycloaddition reaction [23].

In this way, Liping et al. tested the catalytic activity of NH_2 -UiO-66 in the cycloaddition reaction between CO_2 and different epoxides [25]. The multimetallic cluster of Zr present in NH_2 -UiO-66 could activate the epoxide and amine groups could activate the carbon dioxide molecule, obtaining 91% of yield and 100% of selectivity with styrene oxide as substrate under 100 °C, 1.0 bar of CO_2 for 8 h and using tetrabutylammonium bromide (TBAB) as cocatalyst. When other substrates were used, like epoxypropyl phenyl ether, 1,2-epoxyhexane, 1,2-epoxyoctane and cyclohexene oxide, the reaction yield was 92, 99, 99 and 28%, respectively, indicating that the higher volume of the epoxide's substituent the worse the reaction performance due to steric hindrances inside the MOF porous system. Qiuxia et al. synthesized a polyoxometalate-based homochiral MOF, called Zn-PYIs, constituted by Zn^{2+} as metal ion, $TBA_4W_{10}O_{32}$ as polyoxometalate and L-N-tert-butoxy-carbonyl-2-(imidazole)-1-pyrrolidine and 3-amine-4,4'-bipyridyl as organic linkers [26]. This material showed a good performance as catalyst achieving a 99% of reaction yield for styrene oxide under 50 °C, 5 bar of CO_2 for 48 h, using TBAB as co-catalyst. This good result was presumably due to the contribution of metallic centers that interacted with the oxygen atoms of the epoxide and the NH_2 - groups which boost the activation of the carbon dioxide molecule. Cherian Kathalikkattil et al. synthesized a Zn-based MOF material using L-glutamic acid as ligand and they tested this new MOF as catalyst in the cycloaddition reaction [27]. They obtained a yield of 92% at room temperature, 10 bar of CO_2 for 24 h when using propylene oxide as substrate, TBAB as co-catalyst and water as solvent. Lescouet et al. tested the materials MIL-68(In) and MIL-68(In)- NH_2 as catalyst in the reaction of styrene oxide with CO_2 [28]. They proved the important role played by the amine group in the cycloaddition reaction, since the reaction yield, when MIL-68(In) was used as catalyst, increased from 36% to 74%, at 150 °C, 8 bar of CO_2 for 8 h using DMF as solvent. In most cases, the basic Lewis sites were constituted by nitrogen atoms from primary, secondary or tertiary amines, but also by other functional groups that can act as Lewis basic sites, such as triazole, imidazole, tetrazole and hydroxyl.

In this work copper was selected as the structural metal ion for the new MOF phase because it can easily assemble an stable MOF and its Lewis acidity can increase the yield of cycloaddition reaction between CO_2 and epoxides [29–32]. Besides, copper is a non-expensive metal compared to others frequently used in MOFs. For these reasons, several copper-based MOFs with different organic functionalities were tested in the CO_2 conversion by reacting with epoxides to produce cyclic carbonates: Cu-URJC-1, Cu-URJC-8, Cu-MOF-74, HKUST-1, HNUST-1, JUC-62 and PCN-16, being some of them developed in our research group for the first time. All catalytic tests were carried out using epichlorohydrin and styrene oxide as substrates, under mild conditions. The structural stability of the materials was also studied after each experiment.

2. Experimental section

Materials and Measurements. All starting materials and solvents were purchased from Cymit Química S.L. and used without further purification.

Synthesis of organic ligands. 2-Aminoterephthalic acid, 4,4'-bipyridyl and 2,5-dihydroxyterephthalic acid were purchased commercially. The organic ligand of Cu-URJC-1, 1H-imidazole-4,5-tetrazole (HIT), was prepared in according to the synthetic procedure described by Leo et al. [33]. The organic ligand of HNUST-1, Bis(3,5-dicarboxyphenyl) terephthalamide, was synthesized following the procedure described by Zheng et al [34]. The organic ligand of JUC-62, 3,3',5,5'-azobenzene tetracarboxylic acid, was prepared according to the procedure described by Montes-Andrés [35]. And finally, the organic linker of PCN-16, 5,5'-(Etine-1,2-diyl) diisophthalic acid, was synthesized following the procedure described by Montes-Andrés [36].

Synthesis of different MOF materials. All MOF materials were synthesized by the solvothermal method previously published for Cu-URJC-1 [33], Cu-URJC-8 [37], Cu-MOF-74 [38], HNUST-1 [34], JUC-62 [39] and PCN-16 [40]. HKUST-1 material was purchased to Sigma Aldrich company.

Physicochemical characterization techniques. 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. Powder X-ray diffraction (PXRD) patterns were obtained in a Philips XPERT PRO using $CuK\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation with a 0.01 step, 10 s of accumulation time between steps. In all the cases, the sample were grounded to avoid the effects of preferred crystal orientation. Fourier transform-infrared spectra (FT-IR) were recorded for powder samples in a Varian 3100 Excalibur Series spectrometer with a resolution of 4 cm^{-1} . Argon adsorption-desorption isotherms were measured at 87 K on an AutoSorb equipment (Quantachrome Instrument). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation [41]. Scanning electron microscopy (SEM) images were obtained on a TM1000-Hitachi operated at 15 kV.

Catalytic Studies for the cycloaddition of CO_2 and epoxides at mild conditions. Before catalytic measurements all Cu-MOF materials were degassed at 110 °C for 12 h. In a model experiment, 1 mmol of epoxide, 1.0 mol % (active metal sites to epoxide ratio) of degassed MOFs catalyst and 0.04 mmol of tetrabutylammonium bromide (TBAB), were added in a 100 mL stainless-steel autoclave. The system was purged with CO_2 three times before being pressurized at 12 bar. 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 $CDCl_3$ as solvent and 1, 2, 4, 5-tetrachloro-3-nitrobenzene as internal standard, with high accuracy of 0,1 ppm.

3. Results and discussion

3.1. MOF characterization

Different ditopic, tritopic and tetratopic organic ligands were used for the synthesis of seven copper-based MOF materials (Fig. 1). The organic ligands of Cu-URJC-1, JUC-62, PCN-16 and HNUST-1 were synthesized in our laboratory by following the organic routes mentioned in the Experimental section; meanwhile the organic ligands of Cu-URJC-8, Cu-MOF-74 and HKUST-1 were purchased.

The different organic nature of these linkers provides them several ways to coordinate to copper ions. The organic ligand of HKUST-1, JUC-62, PCN-16 and HNUST-1 are monodentate-coordinated to Cu^{2+} ions by means of oxygen atoms of the acid groups, forming a plane-square geometry (Fig. 2a). In Cu-MOF-74 there are two different copper ions, one of them is monodentate-coordinated to one oxygen atom of the acid group, while the second one is coordinated in bidentate chelate form to one oxygen atom from another acid group and one oxygen atom from a hydroxyl group (Fig. 2b). The geometry of copper ions present in Cu-MOF-74 is a square-base pyramid once the solvent molecules are

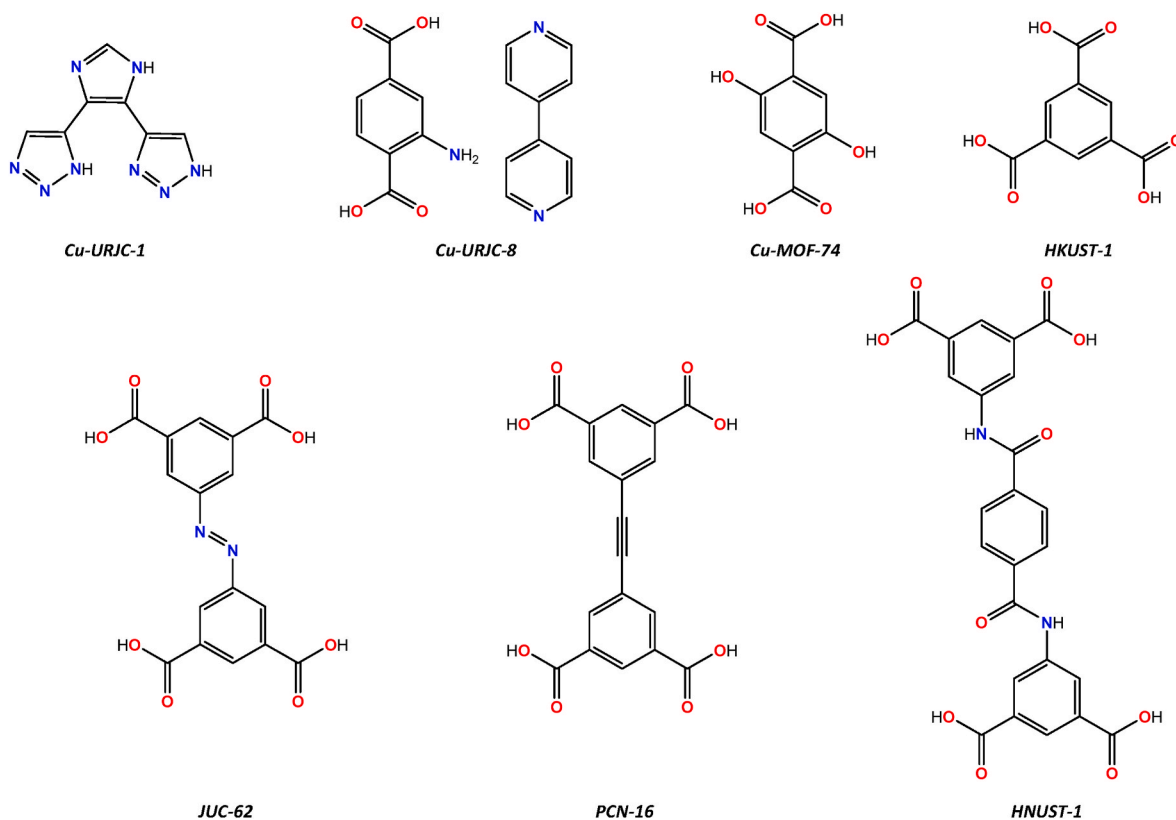


Fig. 1. Organic ligands of selected Cu-based MOF materials.

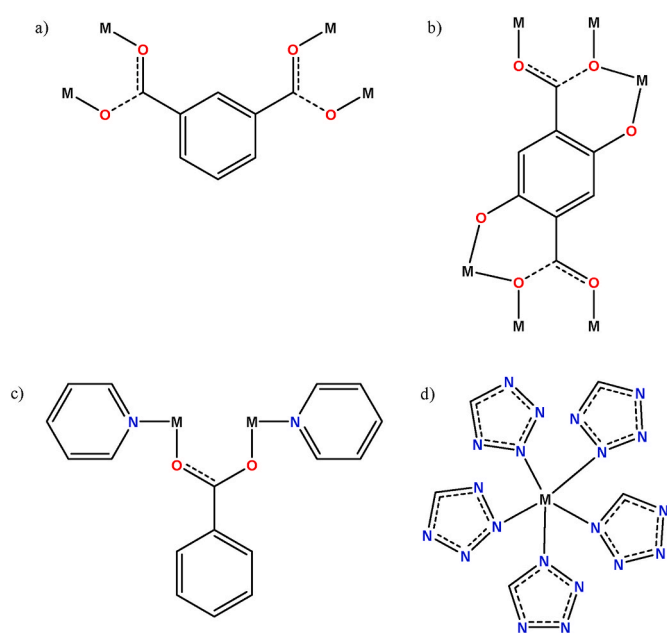


Fig. 2. Coordination mode of organic linkers in a) JUC-62, PCN-16, HNUST-1 and HKUST-1, b) Cu-MOF-74, c) Cu-URJC-8, d) Cu-URJC-1.

evacuated, leaving the metal accessible and unsaturated to interact with the guest molecules/substrates. The coordination of Cu ions in Cu-URJC-8 is based on four oxygen atoms of four acid groups and one nitrogen atom of one 4,4'-bipyridine. The oxygen and nitrogen atoms are monodentate-coordinated to copper ions forming a square-base pyramid (Fig. 2c). And finally, the copper ion is monodentate-coordinated by means of the nitrogen atoms of HIT organic ligand presents in the Cu-

URJC-1 material, generating a square-based pyramid geometry (Fig. 2d).

Besides, not only copper coordination mode is important in these structures but also the functional organic groups belonging to the linkers. Nitrogen atoms are present in the structure of four of these ligands forming part of tetrazole, primary amine, azo and amide groups in Cu-URJC-1, Cu-URJC-8, JUC-62 and HNUST-1, respectively. These nitrogen atoms have different basicity, which is an important factor in cycloaddition reaction. The triple bond in the organic ligand of PCN-16 material gives a rigidity that could provide structural stability, and therefore a better diffusion of epoxides and carbon dioxide molecules. The hydroxyl groups in the linker of Cu-MOF-74 can act as Lewis basic groups as well, despite of participating in the coordination to the metal; and the 1,3,5-benzenetricarboxylic acid does not have any functional organic group in the HKUST-1 material that can act as a Lewis basic group, so it is considered as a reference material.

In the case of non-commercial MOFs, once the organic ligands were successfully synthesized and then used to crystallize the MOF structures, checking by powder X-Ray diffraction the presence of exclusively each copper MOF phase. This was also carried out for the materials with commercial ligands. In the Supporting Information (Section S1-S7), the XRD patterns of the seven Cu-MOF materials compared to their corresponding simulated XRD patterns from single crystal XRD are shown. In all cases, the purity of the desired MOF phase was confirmed in the bulk samples, since the most important diffraction peaks were shown in the experimental patterns.

The seven copper-based MOFs were studied by thermogravimetric analyses (TGA) under air atmosphere to determine their thermal stability and to know the appropriate outgassing temperature of each material (Section S1-S7). Regarding the TGA profiles, 110 °C was the activation temperature for JUC-62 and PCN-16 materials, 120 °C for Cu-URJC-8, HKUST-1 and HNUST-1 materials and 150 °C for Cu-URJC-1 and Cu-MOF-74 materials. Once these materials were subjected to those temperatures and high vacuum, the porosity of MOFs was

Table 1
Structural and textural properties of Cu-MOF materials.

Material	Coordination number of Cu ²⁺ ^a	S _{BET} ^b (m ² /g)	V _p ^c (cm ³ ·g ⁻¹)	Pore diameter ^d (Å)
Cu-URJC-1	5	408	0.24	12.0
Cu-URJC-8	6	93	0.171	11.2
Cu-MOF-74	5	1126	0.55	14.8
HKUST-1	4	1455	0.55	11.3
JUC-62	4	2037	0.873	12.9
PCN-16	4	2056	1.20	17.0
HNUST-1	4	232	0.153	8.2

^a Cu²⁺ coordination number of activated MOF materials.

^b Specific surface area using the BET equation.

^c Total pore volume at P/P₀ = 0.98.

^d Estimated from crystal data of each material.

Table 2
CO₂ adsorption capacities and Q_{st} value of selected Cu-MOF materials.

Material	CO ₂ adsorbed (mmol/g) ^a	Q _{st} (kJ/mol)	Ref
Cu-URJC-1	2.17	32.7	This work
Cu-URJC-8	0.60	29.2	[37]
Cu-MOF-74	2.51	24.0	[38]
HKUST-1	4.40	25.5	[42]
JUC-62	2.05	29.0	[43]
PCN-16	4.60	22.5	[44]
HNUST-1	4.15	31.2	[34]

^a CO₂ pressure 1 bar, 25 °C.

measured by Ar adsorption/desorption at 87 K (Section S1-S7). BET surface area and pore volume are summarized in Table 1. Besides, FT-IR analyses and SEM images of crystals have been included in the characterization set of all studied materials. In all cases, the FT-IR molecular fingerprint correspond to each structure, regarding those published in literature, as well as the morphology described for those MOFs. So, all characterization results for each Cu-MOF unequivocally demonstrate the presence of the desired crystalline material.

Another relevant parameter to consider for heterogeneous catalysts to be used in CO₂ conversion, is their CO₂ adsorption capacity as well as the interaction strength between the CO₂ molecules and the MOF surface, evaluated from the isosteric heat of adsorption. The results are summarized in Table 2, being PCN-16 the material with the highest CO₂ adsorption capacity at 1 bar and 25 °C (4.60 mmol/g), because this material presents the highest specific surface area, due to the high accessibility to the unsaturated copper sites in the degassed structure, as mentioned above. In turns, the highest Q_{st} values correspond to those materials that contain basic Lewis centers like tetrazole, amide, primary amine and azo groups in Cu-URJC-1, HNUST-1, Cu-URJC-8 and JUC-62, respectively. So, these functionalities may enhance the interaction between the CO₂ and MOF structure probably because of the electronic effect provided by the free electron pairs in those groups.

3.2. Catalytic studies for the cycloaddition reaction of CO₂ and epichlorohydrin/styrene oxide

Cu-MOFs were tested as heterogeneous catalyst in the cycloaddition reactions between carbon dioxide and epoxides. For this study, two

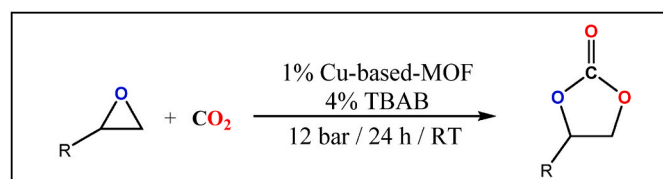


Fig. 3. General chemical transformation scheme for cycloaddition reaction of CO₂ and epoxides using Cu-MOFs.

epoxides were used as substrate: epichlorohydrin and styrene oxide. The initial conditions selected for this comparative study correspond to the best ones found for the Cu-URJC-8 material in our previous work (Fig. 3) [37].

Table 3 summarizes the reaction results, observing important differences in epoxide conversion among copper materials, but the same maximum selectivity to cyclic carbonates for all cases. In addition, TOF values were calculated as moles of product/moles of metal in the catalyst per hour.

Firstly, the blank experiment with no catalyst, but with 4.0% of co-catalyst (TBAB) showed a moderate conversion, less than 40%. The highest epoxide conversion was obtained for Cu-URJC-8, Cu-URJC-1, JUC-62 and HNUST-1 materials, being 90, 84, 83 and 78%, respectively. These four catalysts have nitrogen heteroatoms in their organic ligands, whose basicity may play an important role. The higher the Lewis basicity, the higher the CO₂ reactivity, as it has been described by other authors [25,28], where UiO-66-NH₂ and MIL-68(In)-NH₂ improved their catalytic activity due to the presence of amine groups. In general speaking, these results lead to the following order of active functional groups in CO₂ cycloaddition reaction with epichlorohydrin: primary amines > azo > amides > hydroxyl > triple bond).

Among the nitrogen-based functionalities found in the mentioned four MOFs, the NH₂-group of 2-aminoterephthalic acid contained in Cu-URJC-8 is presumably the most basic functional group, so that it enhances the reactivity of carbon dioxide molecule to produce the highest reaction yield. In turn, Cu-URJC-1 presents a high number of nitrogen atoms in its organic ligand, but some of them are coordinated to copper ion reducing their basicity, and the other free nitrogen atoms reduce their basicity since the inductive effect generated to compensate the electron deficiency of the nitrogen atoms coordinated to the metal centers. The organic linker of JUC-62 is the azo group with the two nitrogen atoms generating a mutual electronegative effect reducing the availability of the electron pair to interact with the CO₂ molecules. Amide group in HNUST-1 structure has near-zero basicity due to its resonant forms, but carbonyl group can interact with carbon dioxide molecule increasing its reactivity (Fig. 4). Finally, the organic ligand without free electron pairs (PCN-16, HKUST-1 and Cu-MOF-74) achieved the lowest epoxide conversion because they cannot increase the

Table 3
Reaction results for cycloaddition between CO₂ and epichlorohydrin^a.

Material	Conversion (%)	Selectivity (%)	Yield (%)	TOF (h ⁻¹)
Cu-URJC-8	90	>99	89	0,291
Cu-URJC-1	84		83	0,174
JUC-62	83		82	0,138
HNUST-1	78		77	0,164
HKUST-1	70		69	0,092
Cu-MOF-74	67		66	0,096
PCN-16	52		51	0,087
Blank	39		38	-

^a 4.0% TBAB, 1.0% Catalyst, 12 bar CO₂, 24 h, R.T.

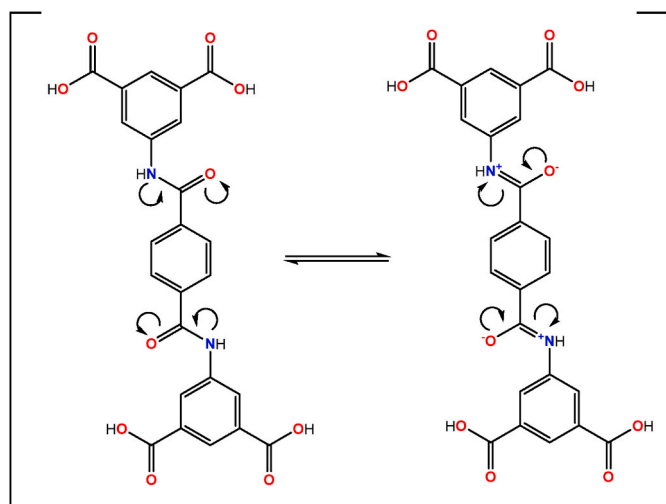


Fig. 4. Resonant forms of amide group in organic ligand of HNUST-1.

reactivity of CO_2 [45].

On the other hand, the epoxide conversion agrees with the TOF value, that is the cyclic carbonate moles produced as a function of the copper active sites per hour, which is reasonable since the amount of catalyst (amount of copper moles) is the same for all experiments. However, the catalytic system is not as simple as considering just copper sites since, the basic sites from the organic ligands and the textural properties are also influencing the reaction behavior.

In addition, to check the chemical stability of these catalysts under reaction conditions, a comparison of the XRD simulated and experimental patterns after reaction between CO_2 and epichlorohydrin was

made. In all cases, both patterns were coincident for the most important diffraction peaks of each MOF phase (Section 12 in SI), confirming their structural stability.

To check the influence of the MOF porosity on the reaction, a bulky molecule such as styrene oxide was assessed as epoxide substrate, knowing that epichlorohydrin is a small molecule that can enter easily in the microporous system of all MOF catalysts of this study. The epoxide conversion, selectivity, yield to styrene carbonate and TOF are summarized in Table 4.

When styrene oxide is used as a substrate, the pore size of the MOF catalysts is playing an important role. Thus, Cu-URJC-1 achieved the best epoxide conversion (60%) because its average pore size of 12 Å (Table 1), that can favor the diffusion of the styrene oxide molecules. Additionally, the organic linker of this substrate contains nitrogen atoms with high basicity that can increase the reactivity of CO_2 molecule. Besides, it has been observed that Cu-URJC-1 structure is flexible [46], so that it can accommodate the styrene oxide molecules avoiding the repulsion forces inside the pores [47]. It can be mentioned that again epoxide conversion is in line with the TOF values, indicating the full

Table 4

Reaction results for cycloaddition between CO_2 and styrene oxide.^a

Material	Conversion (%)	Selectivity (%)	Yield (%)	TOF (h^{-1})
Cu-URJC-1	60	86	52	0,106
JUC-62	53	86	46	0,077
Cu-URJC-8	49	54	26	0,086
HNUST-1	46	74	34	0,072
Cu-MOF-74	41	78	32	0,046
HKUST-1	32	83	27	0,035
PCN-16	23	85	19	0,033

^a 4.0% TBAB, 1.0% Catalyst, 12 bar CO_2 , 24 h, R.T.

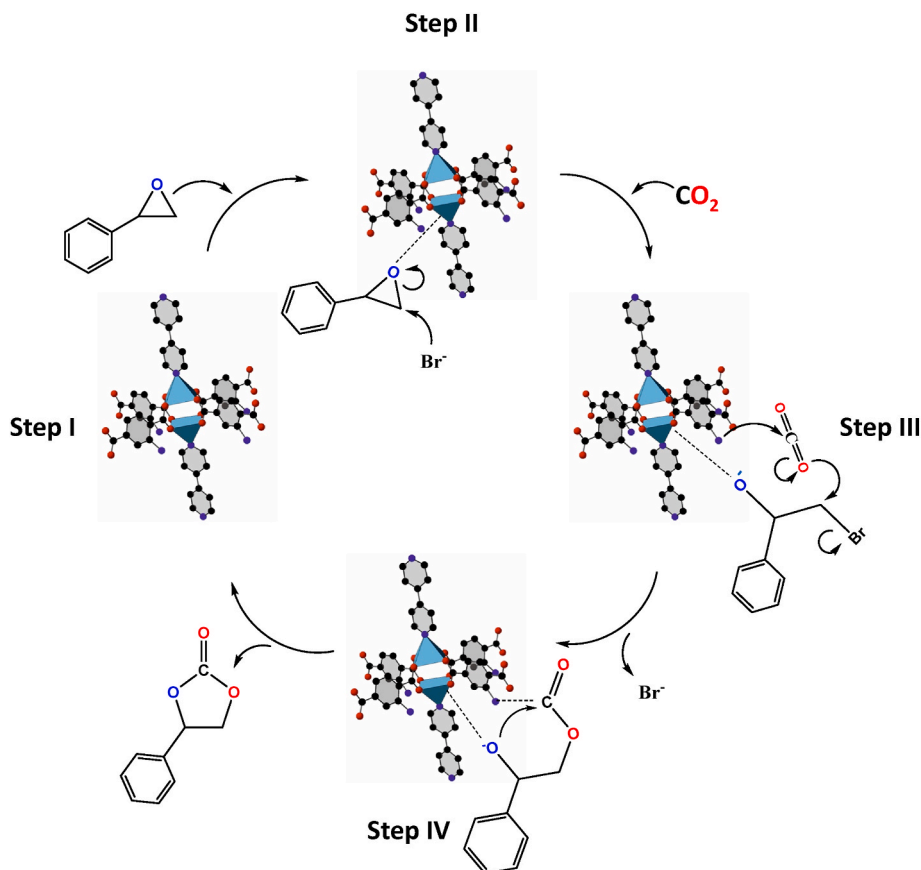


Fig. 5. Scheme of the cycloaddition reaction mechanism between CO_2 and styrene oxide when using Cu-URJC-8 as a catalyst.

availability of the catalytic sites. JUC-62 and Cu-URJC-8 catalysts showed a good epoxide conversion as well (53 and 49%, respectively), since their pore size (Table 1) enable the diffusion of epoxide and carbonate molecules facilitating the interaction with the metal centers [37]. The slight differences in the reaction performance using both catalysts could come from the larger pore of JUC-62 structure compared to Cu-URJC-8, even though the functional group of the latter is more basic. The following material was the HNUST-1, reaching a conversion of 46%, partially due to the low basicity of the amide group in its linker. Then, MOF materials without free electron pairs, like Cu-MOF-74, HKUST-1 and PCN-16, in spite of their larger pore size (14.8, 11.3 and 17 Å, respectively), they showed the lowest reaction yields because the absence of Lewis basic functional groups.

Since Cu-URJC-1 showed the best catalytic results with the bulky epoxide -styrene oxide-, it is relevant to know the kinetic behavior of the reaction. On the contrary of those results showed by the system Cu-URJC-8 with epichlorohydrin published in other work [37] with a linear trend of the conversion, herein, for the system Cu-URJC-1 with styrene oxide (Figure S10.8), it is evidenced a lower conversion rate at earlier times below 6 h and faster rate from that time, which could be attributed to diffusional limitations in the beginning of the reaction.

The possible mechanism of the cycloaddition reaction between CO₂ and epichlorohydrin was proposed in a previous work for Cu-URJC-8 as catalyst [37], herein adapted mechanism for styrene oxide as substrate is shown in Fig. 5. At a first step, the styrene oxide molecule interacts with the acid Lewis groups -structural copper ions- of the Cu-URJC-8 framework. Through this interaction, the bond among oxygen atom and the less substituted carbon atom of the styrene oxide is polarized making this carbon atom susceptible to be nucleophilic attacked by the bromide ion (Step II). Then, the carbon dioxide molecule can be activated by -NH₂ groups from the 2-aminoterephthalic acid. The activated CO₂ molecule can attack the carbon-bromide bond producing the output of the bromide ion, generating a reaction intermediate (Step III). Finally, the reaction intermediate suffers an intramolecular attack from oxygen

atom-of styrene oxide-to the carbon atom of CO₂. This attack produces the formation of the cyclic carbonate compound and the catalyst regeneration (Step IV).

When using styrene oxide as substrate instead of epichlorohydrin, the selectivity to cyclic carbonate reduces in all cases, due to a secondary reaction taking place [48–51]. The selectivity is also depending on the pore size, as shown by Cu-URJC-1, JUC-62 and PCN-16 catalysts. The highest selectivity towards cyclic carbonate of these three materials was 86, 86 and 85%, respectively, showing that as the pore size increases the selectivity to cyclic carbonates also increases when Lewis basic sites are present. Therefore, the byproduct 2,5-diphenyl-1,4-dioxane is favored by lower pore size catalysts, such as Cu-URJC-8 and HNUST-1 with pores of 11.2 and 8.2 Å, respectively, which means a reduction in selectivity to styrene carbonate. The possible mechanism of the formation of 2,5-diphenyl-1,4-dioxane is showed in Fig. 6. As shown, the molecule of styrene oxide interacts with the metal center favoring the nucleophilic attack of bromide ion of TBAB, over the least substituted carbon atom, producing the opening of the epoxide (Step II). Then, the intermediate obtained in step II suffers a new nucleophilic attack of an oxygen atom from another epoxide molecule producing the elimination of the bromide ion (Step III). Finally, the intermediate formed in step III undergoes an intramolecular attack of the oxygen atom over the carbon atom closing the six-member cycle releasing the 2,5-diphenyl-1,4-dioxane (Step IV).

To expand the epoxide size study, the best catalyst Cu-URJC-1 and Cu-URJC-8 materials (both synthesized for the first time in our research group) were selected to be compared when using allyl 2,3-epoxypropyl ether as a substrate, since their most basic active groups, the difference between their textural properties, being the S_{BET}, pore volume and diameter of 408 m²/g, 0.24 cm³/g and 12.0 Å for the Cu-URJC-1 material and 93 m²/g, 0.171 cm³/g and 11.2 Å for the Cu-URJC-8 material, and also because of the flexibility of Cu-URJC-1 [46].

The CO₂ cycloaddition results found are shown in Figure S11.1, where it can be observed that the Cu-URJC-1 material achieved a higher

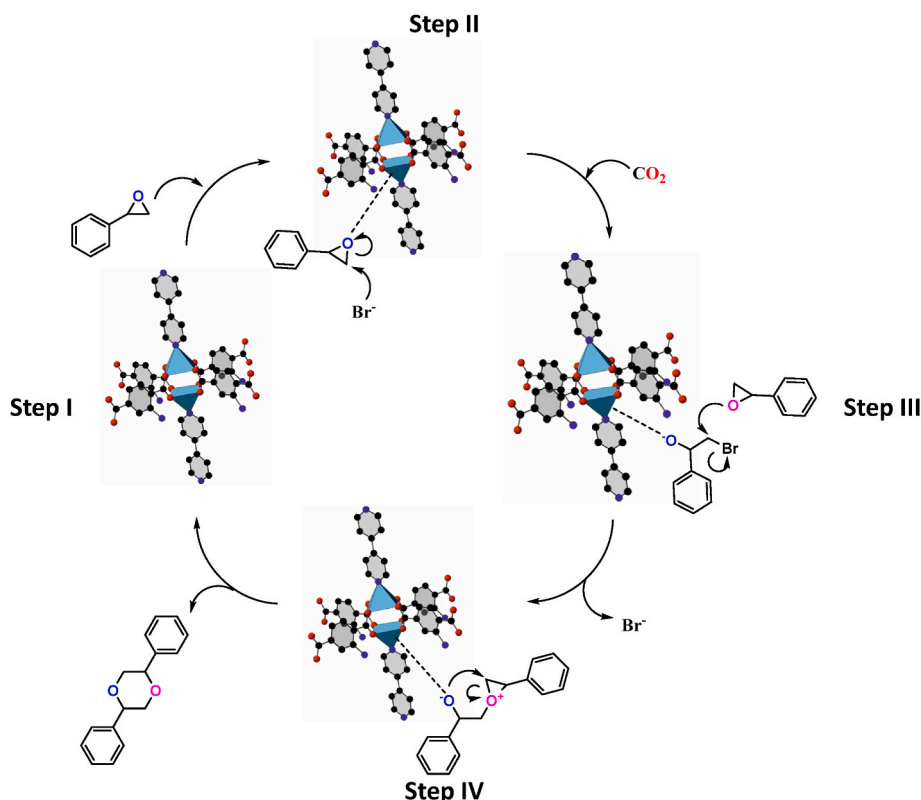


Fig. 6. Scheme of the reaction mechanism of styrene oxide cyclodimerization.

epoxide conversion than the Cu-URJC-8 material, despite the latter having the more basic functional groups. Again, it is evidenced that the higher porosity and the flexibility in the case of Cu-URJC-1 play a fundamental role in the cycloaddition reaction with epoxides with bulky substituents, as it happened when styrene oxide was used as a substrate. Therefore, it can be concluded that in the case of epoxides with bulky and long-chain substituents, in addition to the presence of functional groups with free electron pairs, a suitable porosity and flexible framework of the MOF is decisive, reducing the steric hindrance produced by the epoxide during the reaction.

4. Conclusions

Seven copper-based MOF materials (Cu-URJC-1, Cu-URJC-8, Cu-MOF-74, HKUST-1, JUC-62, PCN-16 and HNUST-1) have been studied in CO₂ adsorption and cycloaddition reactions of CO₂ with epoxides. They have been successfully synthesized and characterized by different physico-chemical techniques confirming the presence of the clean desired phases. The seven MOFs having additional functional groups in their respective linkers, such as primary amine group (URJC-8), azo group (URJC-1, JUC-62), amide group (HNUST-1), hydroxyl groups (Cu-MOF-74), triple bond (PCN-16), as well as the MOF without additional functionality (HKUST-1), showed good adsorption properties. PCN-16 showed the highest CO₂ adsorption capacity, 4.6 mmol/g, according to the easier accessibility of CO₂ molecules to the unsaturated copper sites. However, the interaction strength of CO₂ evaluated from the isosteric heat of adsorption was higher for with MOFs with nitrogen atoms in their structure, being this interaction decreasing in the order Cu-URJC-1, HNUST-1, Cu-URJC-8 and JUC-62. All MOFs were also tested as catalysts in the cycloaddition reaction between carbon dioxide and epichlorohydrin or styrene oxide. For epichlorohydrin, a smaller molecule, Cu-URJC-8 catalyst showed the highest epoxide conversion (90%) with a selectivity of 99%, which is due to the Lewis basicity of the primary amine group existing in the linker molecule. The reaction yields obtained for these microporous materials are in agreement with the Lewis basicity degree of the functionalities contained in those copper-based MOFs: primary amines the best functional organic group. For the styrene oxide, a larger molecule than epichlorohydrin, the best result was obtained with Cu-URJC-1 (60% conversion and 86% selectivity to styrene carbonate) due to the good balance between a suitable pore size, structure flexibility and the presence of nitrogen atoms with free electron pairs in the organic ligand. Therefore, it is concluded that the cycloaddition reaction between CO₂ and small epoxide molecules is favored by the presence of Lewis basic groups in the organic linker, but for larger bulky epoxide molecules, the pore size of the catalyst is also important regarding the selectivity to cyclic carbonates. After this study, Cu-URJC-1 and Cu-URJC-8 appear as efficient and robust catalysts for cycloaddition reaction of CO₂ and should be further studied using other substrates of industrial interest.

CRedit authorship contribution statement

Jesús Tapiador: Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Elena García-Rojas:** Writing – original draft, Investigation. **Pedro Leo:** Visualization, Validation, Supervision, Methodology. **Carmen Martos:** Writing – review & editing, Visualization, Supervision, Project administration. **Guillermo Calleja:** Conceptualization, Funding acquisition, Writing – review & editing. **Gisela Orcajo:** Writing – review & editing, Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, 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

The data described in the article is not confidential

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Appendix A. Supplementary data

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