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# Robust Cu-URJC-8 with mixed ligands for mild CO<sub>2</sub> cycloaddition reaction

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## ABSTRACT

The synthesis of the new MOF Cu-URJC-8, containing two different organic ligands, 2-aminoterephthalic acid and 4,4'-bipyridyl, is reported in this work. Cu-URJC-8 shows a pillared-layer structure consisting of [Cu<sub>2</sub>(-CO<sub>2</sub>)<sub>4</sub>(-N)<sub>2</sub>] paddlewheel secondary building units, with the 4,4'-bipyridyl linkers acting as pillars in the two-fold interpenetrated networks, which provides a robust structure to the material. Cu-URJC-8 presents Lewis acid and basic sites, constituted by Cu<sup>2+</sup> and -NH<sub>2</sub> groups, respectively, and it is chemically stable in different commonly used organic solvents. This new material shows a CO<sub>2</sub> uptake of 1.59 and 1.07 mmol/g at 25 and 45 °C, respectively, and a Q<sub>st</sub> value of 27 kJ/mol, higher than those observed for other reported MOFs with higher textural properties, possibly due to the presence of amino groups in the MOF structure. Its catalytic activity in the cycloaddition reaction of epichlorohydrin and CO<sub>2</sub> was evaluated under various conditions and the best performance (90 conversion and 99% selectivity) was achieved when using 1% mol of catalyst, 4% mol of co-catalyst, 12 bar of carbon dioxide pressure, and room temperature. When different epoxides with bulkier radical groups are used as substrates, the epoxide conversion decreases, evidencing steric hindrances for diffusion inside cavities of Cu-URJC-8. Finally, Cu-URJC-8 has a high stability, keeping its structural integrity and catalytic activity after successive CO<sub>2</sub> cycloaddition reaction cycles. These results show that Cu-URJC-8 is a promising catalyst for CO<sub>2</sub> revalorization.

## 1. Introduction

Metal-organic frameworks (MOFs) have received increasing attention over the past few years owing to their functional and structural diversity [1]. Their high porosity, adjustable composition and decorative pore surface make them versatile materials for wide applications, including the adsorption and separation of small molecules such as H<sub>2</sub> and CO<sub>2</sub>, heterogeneous catalyst, luminescent properties, magnetism and others [2,3]. They can be formed by different metal ions, divalent, trivalent and tetravalent and organic ligands with diverse functionalities that confer to the framework specific properties [4]. Considerable MOFs based on copper have been reported in the literature due to its CO<sub>2</sub> adsorption properties. Chui et al. synthesized a Cu-based MOF, the well-known HKUST-1, with coordinatively unsaturated metal sites when guest water molecules are removed [5]. For this reason, HKUST-1 has been used in a wide variety of applications. Bordiga et al. demonstrated the high H<sub>2</sub> adsorption capacity of this material with 11.16 mmol/g at 1 bar and 18 mmol/g at 10 bar (both at 77 K) [6] and Deniz et al. achieved

a CO<sub>2</sub> adsorption of 1.39 mmol/g at 1 bar and 298 K [7]. Other MOF materials based on Cu<sup>2+</sup> reached great CO<sub>2</sub> adsorption values at low CO<sub>2</sub> pressure and 298 K, such as CuTATB-60, SNU-50, MOF-505, UMCM-150 and UMCM-150(N)<sub>2</sub>, retaining 3.9, 3.6, 3.3, 2.37 and 2.51 mmol/g, respectively [8–11]. This shows that the copper ion is a suitable metal for carbon dioxide capture.

Nowadays, the progressive increasing of CO<sub>2</sub> emissions to the atmosphere has led the current global warming scenario [12]. Carbon dioxide capture is a technique that allows for CO<sub>2</sub> emissions reduction but its efficient transformation into value chemicals still remains a strong scientific challenge. Cyclic organic carbonates are molecules used in many applications such as pharmaceutical and plastic production [13]. Five-member cyclic carbonates can be obtained by cycloaddition reaction between epoxides and carbon dioxide by means of a ring-opening-mechanism. Common heterogeneous catalysts have been tested in the CO<sub>2</sub> conversion to cyclic carbonates, but it is still required to overcome some difficulties like the low values of reaction yield and selectivity, poor recyclability and short lifetime and, being necessary to

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use high temperatures and pressures to reach acceptable yields, which increase the costs of the chemical process [14–19]. Some Cu-based MOFs reported in the literature have been tested in the cycloaddition reaction using several epoxides and carbon dioxide. Wen-Yang et al. synthesized a new MOF, MMCF-2, which can achieve 95.4 % of conversion in cycloaddition reaction of propylene oxide using *n*Bu<sub>4</sub>NBr as co-catalyst, after 48 h reaction at room temperature and 1 bar of CO<sub>2</sub> [20]. Zhou and coworkers prepared a new Cu-MOF using a large octatopic carboxylate bridging ligand. With this MOF a 96 % yield is obtained in the cycloaddition reaction between propylene oxide and CO<sub>2</sub> employing 0.65 g of TBAB under 1 bar of CO<sub>2</sub> at room temperature for 48 h [1]. Cu<sub>4</sub>MTTP, TMOF-1 and MMPF-9 were tested in propylene oxide cycloaddition reaction under 1 bar of CO<sub>2</sub>, room temperature and 48 h reaction, obtaining 96%, 99 % and 87 % yield, respectively. In the three cases, TBAB was used as cocatalyst [1,21,22]. Dinesh et al. prepared a new Cu-based MOF, L<sub>Cu</sub>, which was tested in the reaction of styrene oxide and carbon dioxide to obtain the corresponding carbonate, by using TBAB as co-catalyst. With this material 50 % yield was achieved under 20 bar of CO<sub>2</sub> and 120 °C for 12 h [23].

So, it is proved that the copper ion is suitable for cycloaddition reaction, being several Cu<sup>2+</sup>-based MOF able to produce a great yield of product; however, in some cases a high amount of co-catalyst is required, as well as large reaction times and high CO<sub>2</sub> pressures and temperatures [24].

Based on these results, we have developed a new MOF based on copper with a mixed architecture, called Cu-URJC-8 (URJC stands for “Universidad Rey Juan Carlos”). It is formed by two different organic ligands: 2-aminoterephthalic acid and 4,4'-bipyridyl with Lewis basic groups (amine) that can enhance the carbon dioxide reactivity and hydrophobic groups (pyridyl) to favor the formation of cyclic carbonates. Cu-URJC-8 had been evaluated in CO<sub>2</sub> adsorption at 25 and 45 °C and tested in the catalytic CO<sub>2</sub> cycloaddition reaction using various epoxides with different radical groups, under mild conditions. Structural stability of this material was also experimentally checked.

## 2. Experimental section

### 2.1. Materials and measurements

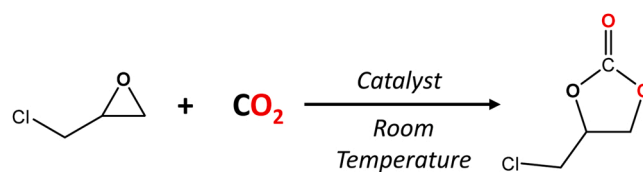
All starting materials and solvents were purchased from Cymit Química S.L. and used without further purification.

### 2.2. Synthesis of Cu-URJC-8

0.2 mmol (0.036 g) of 2-aminoterephthalic acid, 0.1 mmol (0.016 g) of 4,4'-bipyridyl and 0.1 mmol (0.024 g) of Cu(NO<sub>3</sub>)<sub>2</sub> were mixed in 10 ml of DMF and 2 ml of H<sub>2</sub>O. The green solution was sonicated for 15 min and then heated at 90 °C for 72 h. Green crystals were separated by filtration, washed three times with DMF and dried in air. Yield: 73 % based on linker 4,4'-bipyridyl. FT-IR: 3468 (w), 3358 (w), 3062 (w), 2929 (w), 2860 (w), 1662 (m), 1606 (sh), 1579 (s), 1492 (m), 1415 (s), 1375 (s), 1334 (m), 1255 (s), 1217 (m), 1153 (w), 1095 (w), 1068 (w), 1043 (w), 1008 (w), 962 (w), 898 (w), 831 (m), 810 (m), 763 (s), 704 (w), 659 (w) and 630 (m) cm<sup>-1</sup>.

### 2.3. Physicochemical characterization techniques

Powder X-ray diffraction (PXRD) patterns were obtained in a Philips XPERT PRO (URJC, Móstoles, Spain), and with a Bruker d8 equipped with a position sensitive detector (X-ray diffraction facility, ICMM), using CuK $\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ) radiation. In all the cases the sample were grounded to reduce the effects of preferred crystal orientation. Structural analysis including Rietveld refinement was completed with BIOVIA Materials Studio 2021 software package. Additional crystal data are shown in Table S1. Copies of the data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/products/csd/request>. High Temperature



**Scheme 1.** Cycloaddition reaction of epichlorohydrin and carbon dioxide.

PXRD in situ analysis was carried out under a dynamic air atmosphere of 1 ml/min with a heating ramp of 10 °C/min up to 350 °C. <sup>1</sup>H 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 ( $\delta$ ) for <sup>1</sup>H spectra, given in ppm, are referenced to the residual proton signal of the deuterated solvent. Fourier transform-infrared spectra (FT-IR) were recorded for powder samples in a Varian 3100 Excalibur Series spectrometer (URJC, Móstoles, Spain) with a resolution of 4 cm<sup>-1</sup>. Thermogravimetric analyses (TGA) were carried out under an air atmosphere with a Mettler-Toledo DSC-TGA Star System device. Scanning electron microscopy (SEM) images and EDS analysis were obtained on a TM1000-Hitachi operated at 15 kV. Argon adsorption-desorption isotherms were measured at 87 K on an AutoSorb equipment (Quantachrome Instrument, URJC, Móstoles, Spain). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation [25].

### 2.4. Adsorption/desorption isotherms of pure CO<sub>2</sub> and isosteric heat of adsorption

Adsorption/desorption isotherms of pure CO<sub>2</sub> were obtained in a volumetric analyzer type VTI HPVA-100 Scientific Instrument. Approximately 150 mg of Cu-URJC-8 were previously evacuated in-situ under vacuum (9·10<sup>-3</sup> bar) at 110 °C for 12 h, and then cooled down up to the analysis temperature using a thermostatic polyethylene glycol bath. Isotherm equilibrium points were collected considering the following two equilibrium criteria: i) a pressure drop below 0.2 mbar in 3 min or ii) a maximum equilibrium time of 60 min. CO<sub>2</sub> adsorption equilibrium points at 25 and 45 °C were fitting to Sips equation (Sips, 1948). The Clausius-Clapeyron equation was used to determine the isosteric heat of adsorption from the slope of the best linear fit of ln(P) versus (1/T) at each CO<sub>2</sub> loading (additional details are included in SI).

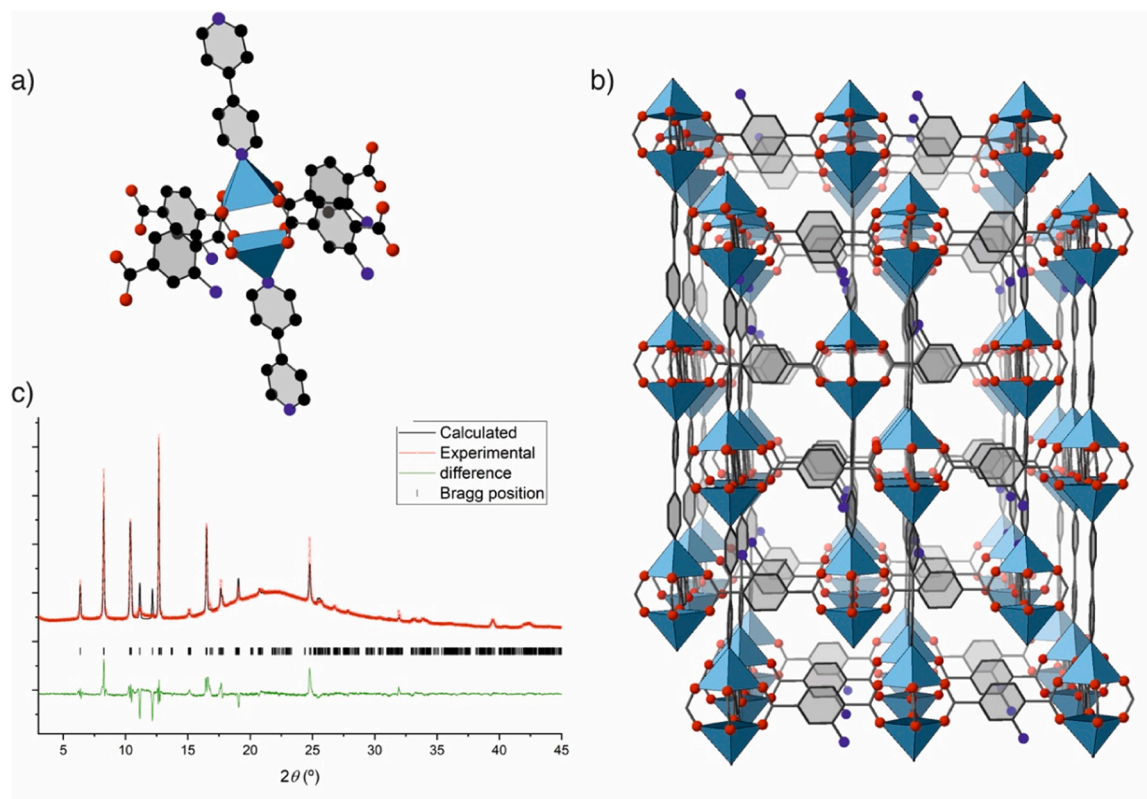
### 2.5. Catalytic studies of Cu-URJC-8 for the cycloaddition of CO<sub>2</sub> and epoxides

In a model experiment, 1 mmol of epoxide, 0.5–2.0 mol% of degassed MOF catalyst (Cu to epoxide ratio) and 1–5 mol% of co-catalyst (tetrabutylammonium bromide, TBAB) (to epoxide ratio) were added in a 100 ml stainless-steel autoclave. The system was evacuated with CO<sub>2</sub> three times before being pressurized (Scheme 1). 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 conversion of epoxide and selectivity to cyclic carbonate, the products were analyzed by <sup>1</sup>H NMR using CDCl<sub>3</sub> as solvent and 1, 2, 4, 5-tetrachloro-3-nitrobenzene as internal standard.

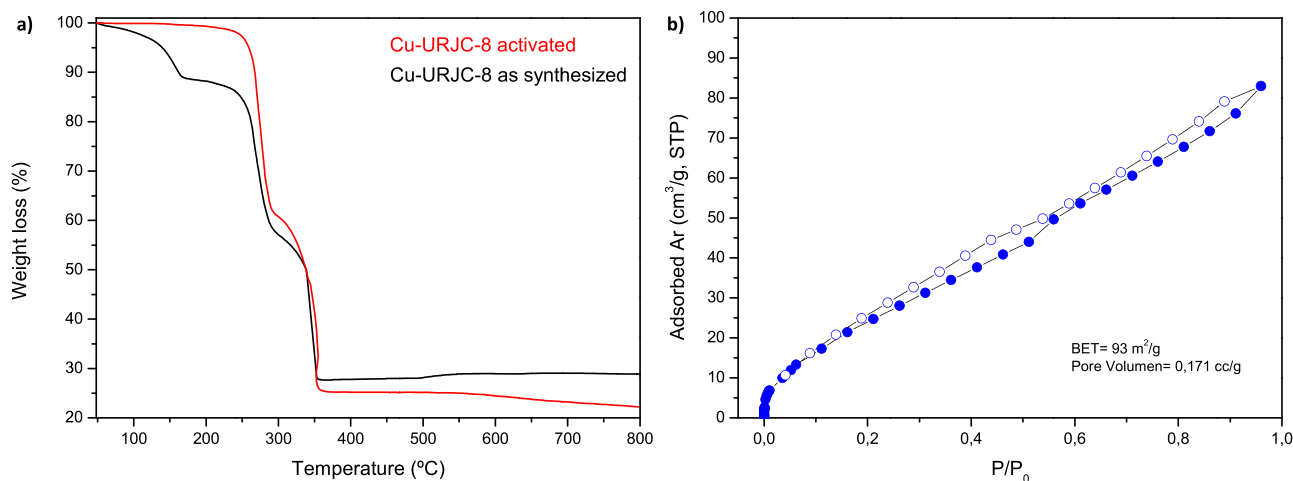
## 3. Results and discussion

### 3.1. Catalyst characterization

Analysis of PXRD indicated that the pattern of Cu-URJC-8 was isotreticular to the [Cu<sub>2</sub>(bdc)<sub>2</sub>(bpy)] MOF reported by Kitagawa et al. [26], (*P*-1,  $a = 10.8141(6) \text{ \AA}$ ,  $b = 10.8480(9) \text{ \AA}$ ,  $c = 14.0353(5) \text{ \AA}$ ,  $\alpha = 89.860(3)^\circ$ ,  $\beta = 89.323(6)^\circ$ ,  $\gamma = 85.020(5)^\circ$ ), with a pillared-layer structure consisting of [Cu<sub>2</sub>(-CO<sub>2</sub>)<sub>4</sub>(-N)<sub>2</sub>] paddlewheel secondary building units



**Fig. 1.** 2-aminoterephthalic acid and 4,4'-bipyridyl linkers coordinate to copper atoms forming paddlewheel SBUs (a), resulting in two-fold interpenetrated pillared-layer structure of Cu-URJC-8 (b). For sake of clarity, hydrogen atoms and solvent molecules are omitted, and the amino nitrogen atoms are displayed in only one of the four equivalent positions. Copper atoms are represented as blue polyhedra, and carbon, oxygen and nitrogen atoms are black, red, and blue spheres, respectively. The plot of the Rietveld refinement ( $R_{wp} = 8.00\%$ ,  $R_p = 4.73\%$ ) is shown in c).



**Fig. 2.** a) TGA curves of Cu-URJC-8. b) Ar adsorption/desorption isotherms at 87 K of Cu-URJC-8.

(SBUs), with the 4,4'-bipyridyl linkers acting as pillars in the two-fold interpenetrated networks. The amino group of the 2-aminoterephthalic acid linkers were statistically disordered over the four possible positions of the phenyl ring, and oriented towards the pore of the MOF, where solvent molecules are occluded. Crystallographic data for the reported structure have been deposited in the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2177910 (Fig. 1).

Temperature-dependence PXRD of Cu-URJC-8 was carried out among 30–300 °C. The structure was stable up to 200 °C observing the complete structural degradation at 250 °C (Fig. S2.1a). Besides, the chemical stability of this new material was examined by dispersing the

solid sample in different organic solvents (hexane, toluene, acetone, methanol, acetonitrile) during 24 h at room temperature (Fig. S2.1b). The solvents were selected for a wide range of polarity, (from 0 polarity index of hexane to 5.8 of acetonitrile). The crystalline structure remained intact after the chemical stability tests in all solvents, evidencing a strong coordination between copper and 2-aminoterephthalic acid/4,4'-bipyridyl organic ligands, becoming this material suitable for catalytic applications.

The thermal stability of Cu-URJC-8 was also studied by means of TGA analysis in air atmosphere (Fig. 2a). The first weight loss of 11.8 % corresponds to the molecules of guest DMF hosted inside the pores. After

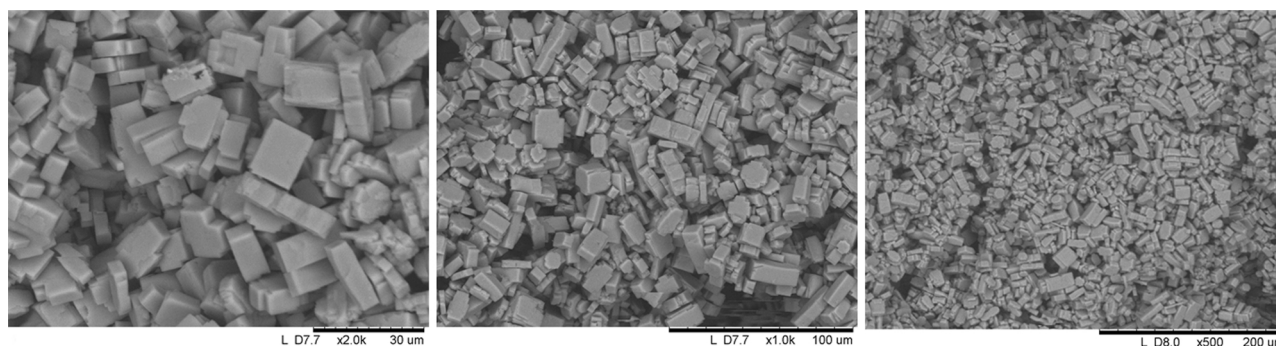


Fig. 3. SEM micrographs of the as-synthesized Cu-URJC-8 sample.

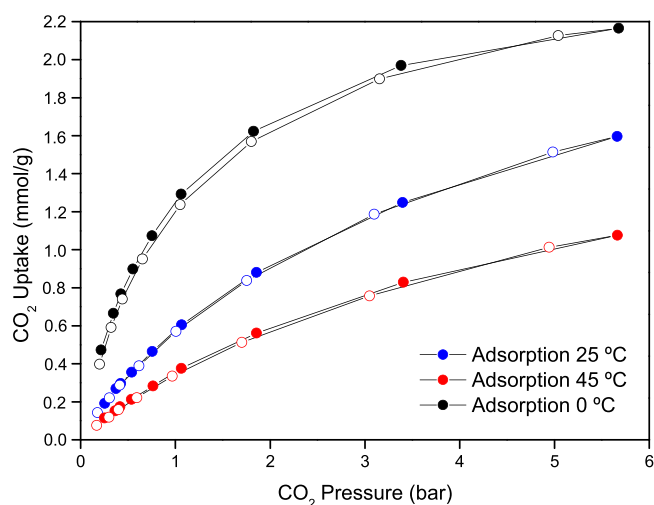


Fig. 4. CO<sub>2</sub> adsorption/desorption isotherms for Cu-URJC-8.

MOF activation at 110 °C for 12 h, the first weight loss disappears thus verifying the correct MOF activation, and the second fall was found at 250 °C, corresponding to the organic linker degradation, confirming the results derived from the PXRD analysis at the temperature at which the framework collapsed. In addition, PXRD of degassed material was carried out to confirm the structural integrity after heating at 110 °C for 12 h (Fig. S2.2).

Through FT-IR analysis of Cu-URJC-8 material, the characteristic vibration bands of the constituent organic ligands were detected. At 3468 and 3361 cm<sup>-1</sup> appeared the vibration band of amine group and at 1662 cm<sup>-1</sup> the one corresponding to carbonyl group of 2-aminoterephthalate ligand; meanwhile at 1560 cm<sup>-1</sup> showed the vibration band (N=C) of 4,4'-bipyridyl ligand.

The porosity of degassed Cu-URJC-8 was measured by argon adsorption/desorption isotherms at 87 K, which show an initial sharp increase due to a certain contribution of microporosity, but then, the slope of the adsorption got lower, like Type II isotherms corresponding to macroporous materials, regarding the IUPAC classification. This macroporosity could come from in the space generated between the crystals [27]. The BET surface area was found to be 93 m<sup>2</sup>/g and a pore volume of 0.171 cc/g at  $P/P_0$  of 0.986 (Fig. 2b). This result agrees with the single crystal data, where it was found a bulky structure with low accessible volume. SEM images of this new material were obtained at different magnifications, and it was observed a homogeneous cuboid morphology with an average crystal size of 15 μm (Fig. 3). Besides, the same polyhedral shape morphology was confirmed by optical microscopy (Fig. S2.4).

Table 1

Heat of CO<sub>2</sub> adsorption for different reported MOFs.

Material	Q <sub>st</sub> (kJ/mol)	Reference
MIL-47	25	[28]
IRMOF-3	19	[29]
MOF-253	23	[30]
Zn(dobdc)(datz)	22	[31]
UMCM-1	12	[32]
CuBTtri	21	[33]
Zn <sub>2</sub> (BDC) <sub>2</sub> (4,4'-bpy)	19	[34]
HKUST-1	23	[11]
Cu-URJC-8	27	This work

### 3.2. CO<sub>2</sub> adsorption studies

After MOF activation at 110 °C under vacuum (9·10<sup>-3</sup> bar) for 12 h, carbon dioxide adsorption on the new material Cu-URJC-8 was studied at 0, 25 and 45 °C and 6 bar. As shown in Fig. 4, CO<sub>2</sub> adsorption isotherms show an uptake value of 2.16, 1.59 and 1.07 mmol/g at 0, 25 and 45 °C, respectively, at near 6 bar. This important increase with the temperature reduction indicates that, despite the limited porosity of Cu-URJC-8, CO<sub>2</sub> molecules can enter in its porous system since the high quadrupole moment of CO<sub>2</sub> molecules that favors their diffusion and interaction to the structure, and ii) at low temperature, the molecules have low thermal vibration, so higher amount of CO<sub>2</sub> is adsorbed in the material. The interaction between carbon dioxide molecules and Cu-URJC-8 was estimated by calculating the heat of CO<sub>2</sub> adsorption, using the Clausius-Clapeyron equation, obtaining a value of 27 kJ/mol. Despite the low porosity of this material, the CO<sub>2</sub> adsorption capacity is higher than expected, which could be related to its remarkable affinity to CO<sub>2</sub> molecules, reflected in the higher Q<sub>st</sub> value compared to other well-known MOFs (Table 1). In fact, this value is slightly higher than the corresponding to HKUST-1, so the presence of amino groups (Cu-URJC-8) enhances the interaction to CO<sub>2</sub> molecules more effectively than open copper sites (HKUST-1) [11].

### 3.3. Cycloaddition reaction with epichlorohydrin and carbon dioxide

Since Cu-URJC-8 possesses an excellent affinity to CO<sub>2</sub>, a high density of Lewis acid sites coming from copper ions and basic sites that come from amino and pyridyl groups, it could be an excellent catalytic material for the cycloaddition of CO<sub>2</sub> with epoxides to produce cyclic carbonates. As shown in Table 2, different experiments were carried out varying different reaction conditions such as catalyst concentration (0.5–2 mol%), co-catalyst concentration (1–5 mol%), CO<sub>2</sub> pressure (1–12 bar) and reaction time (3–24 h), using epichlorohydrin epoxide (ECH).

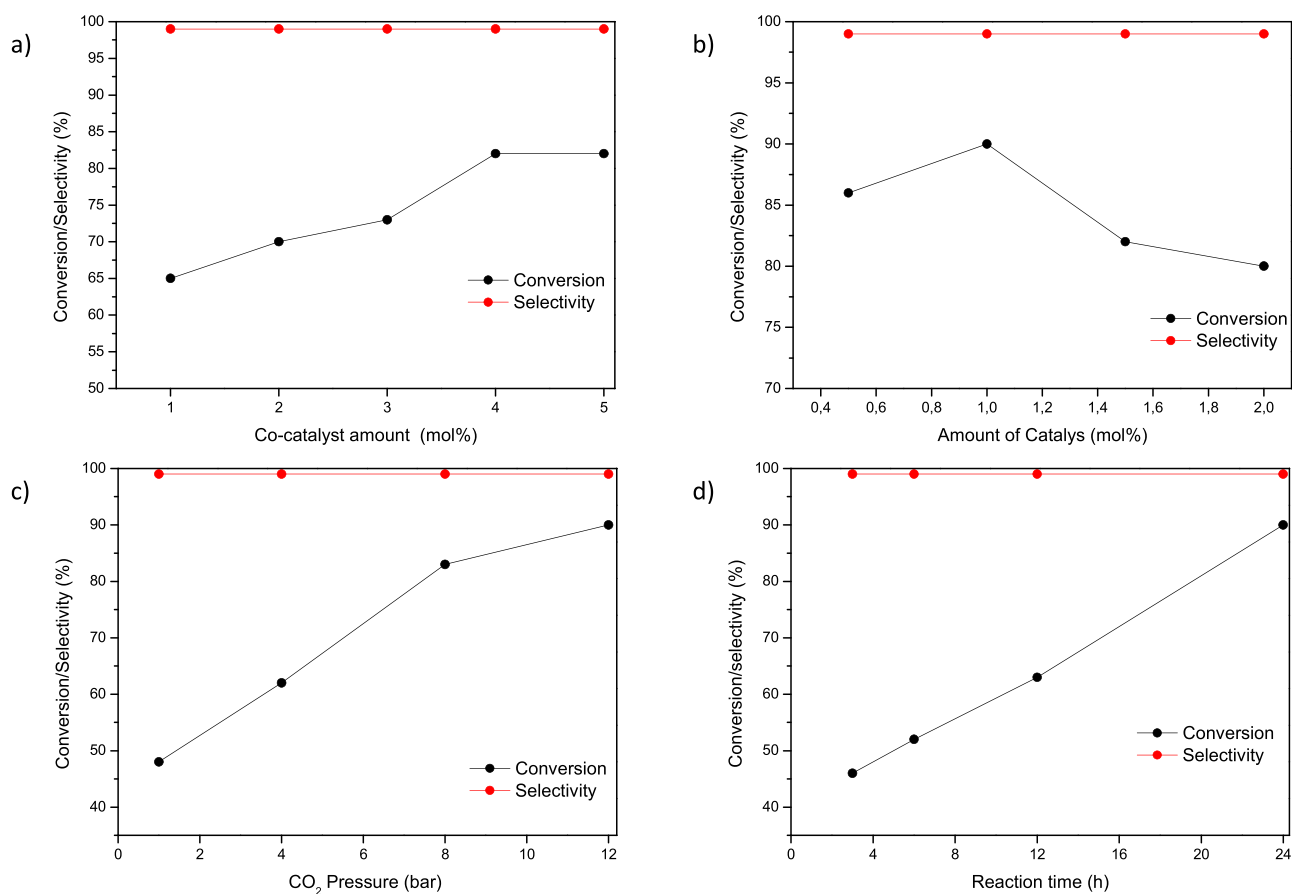
Cu-URJC-8 showed in general a high catalytic activity in the cycloaddition of epichlorohydrin with CO<sub>2</sub> at room temperature (Table 2, Fig. 5). The co-catalyst concentration was studied first (entries 1–9,

**Table 2**  
Different reaction conditions for converting CO<sub>2</sub> into cyclic carbonates<sup>a</sup>.

Entry	Catalyst (mol%)	Co-catalyst (mol%)	Pressure (bar)	Time (h)	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>
1	1.5	0-TBAB	12	24	3	> 99
2	1.5	1-TBAB	12	24	65	> 99
3	1.5	2-TBAB	12	24	70	> 99
4	1.5	3-TBAB	12	24	73	> 99
5	1.5	4-TBAB	12	24	82	> 99
6	1.5	5-TBAB	12	24	82	> 99
7	1.5	4-TBACl	12	24	77	90
8	1.5	4-TBAI	12	24	77	95
9	1.5	4-TBAOH	12	24	80	91
10	0.5	4-TBAB	12	24	86	> 99
11	1	4-TBAB	12	24	90	> 99
12	2	4-TBAB	12	24	80	> 99
13	1	4-TBAB	8	24	83	> 99
14	1	4-TBAB	4	24	62	> 99
15	1	4-TBAB	1	24	48	> 99
16	1	4-TBAB	12	12	63	> 99
17	1	4-TBAB	12	6	52	> 99
18	1	4-TBAB	12	3	46	> 99

<sup>a</sup> Reaction conditions: ECH 1 mmol, RT (25 °C).

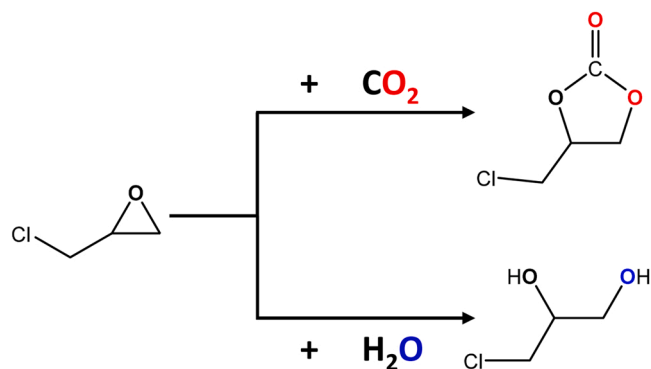
<sup>b</sup> The epichlorohydrin conversion and selectivity to carbonate was determined by <sup>1</sup>H NMR analysis.



**Fig. 5.** Conversion and selectivity of different parameters tested in the cycloaddition reaction. a) Co-catalyst amount, b) Amount of catalyst, c) Carbon dioxide pressure and d) Reaction time.

Fig. 5.a), since it plays an important role in this reaction by opening the epoxide ring, thus favoring the reaction with the carbon dioxide (entry 1) [35]. When tetrabutylammonium bromide (TBAB) concentration increases from 1 to 4 mol% the epoxide conversion also increases from 65 % to 82 %, but no improvement was observed at higher concentrations (entry 6). To evaluate the nature of ammonium salt anion, different salts (TBAX, X = Cl, Br, I and OH, 4 % mol) were tested (entries 7–9). The best result was achieved for TBAB, that could be associated to its lower

amount of moisture than in the rest salts, observed in their TGAs (Fig. S4.19). The presence of moisture can favor the formation of diol, a sub-product from the reaction among epoxide and water (Scheme 2). The amount of MOF catalyst was also assessed from 2.0 to 0.5 mol% (entries 5, 10–12, Fig. 5.b), observing better results for lower MOF concentrations. The epoxide conversion raised from 82 % to 90% when increasing concentration from 1.0 to 0.5 mol%, probably due to the easier diffusion of the substrate in a less concentrated media [36].



**Scheme 2.** Reaction between epichlorohydrin, carbon dioxide and water.

**Table 3**  
Comparison of catalytic results among different copper-based catalyst.

Material	Conversion (%)	Selectivity (%)
Cu(NO <sub>3</sub> ) <sub>2</sub>	77	> 99
HKUST-1	70	> 99
CuO	61	> 99
Cu-URJC-8	90	> 99

However, the reaction carried out without catalyst showed a conversion of just 39 % (not shown in the table), indicating the essential role of Cu-URJC-8 material in the mechanism of this reaction. CO<sub>2</sub> pressure is also a critical parameter (entries 5, 13–15, Fig. 5.c), being the epoxide conversion at 1 bar 48 % and 90 % at 12 bar. The reaction time is also important, observing that conversion increased from 46 % at 3 h of reaction to 90 % at 24 h (entries 5, 16–18, Fig. 5.d). So, it can be summarized that the best reaction conditions using Cu-URJC-8, were 1 % mol of catalyst, 4 % mol of co-catalyst, 12 bar of carbon dioxide pressure, 24 h of reaction time and room temperature, getting an epoxide conversion of 90 % with a 100 % selectivity to cyclic carbonates.

The catalytic performance of Cu-URJC-8 material was also compared to other homogeneous and heterogeneous copper-based catalyst, in the best reaction conditions found for Cu-URJC-8 (12 bar of CO<sub>2</sub>, 1 % mol of catalyst, 4 % mol of TBAB, room temperature, 24 h reaction) (Table 3). When an homogeneous copper catalyst (Cu(NO<sub>3</sub>)<sub>2</sub>) was used, the epoxide conversion was 77 %, significantly lower than the 90 % obtained for Cu-URJC-8, which demonstrates that the MOF crystalline structure is playing an important role in the catalytic reaction. For the well-known HKUST-1 material, the conversion was 70 %, despite exhibiting around 10 times higher specific surface area [5], a result that can be explained by the absence of organic group with free electron pairs that can activate the carbon dioxide molecule. This is similar for the heterogeneous material CuO (61 % conversion), which is not porous and has no organic species with electron pairs.

**Table 4**  
Cycloaddition reaction of various epoxides and CO<sub>2</sub> using Cu-URJC-8 catalyst.

Entry	Epoxide	Product	Conversion (%)	Selectivity (%)
1			90	> 99
2			> 99	> 99
3			70	> 99
4			54	> 99
5			47	> 99

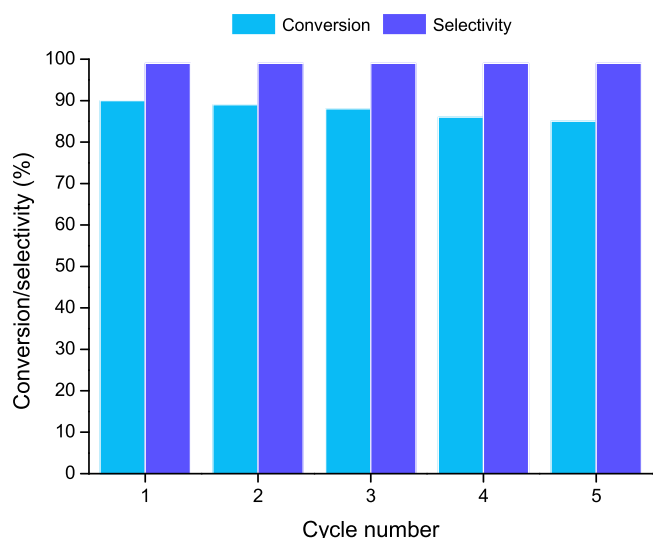


Fig. 6. Recyclability of Cu-URJC-8 in epichlorohydrin cycloaddition with CO<sub>2</sub>.

### 3.4. Catalytic activity with different epoxides

After the good results of the catalyst Cu-URJC-8 in the cycloaddition reaction, the influence of different radical groups in the epoxide molecule was considered of interest to explore (Table 4). For this reason, various epoxides (propylene oxide, glycidol, allyl 2,3-epoxypropyl ether and styrene oxide) were tested under the best reaction conditions for epichlorohydrin: 1% mol catalyst, 4% mol co-catalyst, 12 bar of CO<sub>2</sub>, at room temperature for 24 h.

As observed, the conversion of propylene oxide (entry 2) was found to be the highest, 99%, due to smaller -CH<sub>3</sub> group compared to the chlorine radical, which favors the diffusion of the epoxide inside the pores. In the case of substituting a hydrogen atom of -CH<sub>3</sub> radical for a hydroxide group, the conversion reaction reduces to 70% (entry 3), which can be related again to the more voluminous dimension of the group as well as its higher electronegativity, even higher than chlorine in epichlorohydrin. A larger chain group (entry 4) or an aromatic ring

(entry 5) in the epoxide molecule led to a decrease in conversion to 54 % and 47 % respectively, due to a higher steric hindrance of these substrates to diffuse into the Cu-URJC-8 porous structure [37,38]. The conclusion is that the steric hindrance is a determining factor in the cycloaddition reaction process, significantly reducing the conversion, although it does not affect the selectivity.

### 3.5. Recyclability test of Cu-URJC-8

Cu-URJC-8 material was evaluated in five consecutive reaction cycles under the best conditions previously found (Fig. 6). For each cycle, the mixture was centrifugated after reaction to separate the solid phase catalyst from the liquid phase, being the catalyst three times washed with acetone and then activated under vacuum (10<sup>-3</sup> bar). The epoxide conversion obtained was practically the same in the five reaction cycles, just slightly decreasing along the process from 90 % to 85 %. The structural stability was checked by XRD after the fifth cycle observing that the crystalline structure of Cu-URJC-8 was maintained practically intact (Fig. S6.1).

### 3.6. Mechanism of cycloaddition reaction

A possible mechanism of cycloaddition reaction catalyzed by Cu-URJC-8 is proposed (Fig. 7) based on Liang et al. findings [38]. Ring-opening of the epoxide involves a Cu(II) Lewis acid site of the catalyst and a bromide anion of TBAB cocatalyst. The oxygen atom of the epoxide interacts with the structural copper ions, making the epoxide molecule more susceptible to nucleophilic attack on a less hindered carbon atom by a bromide ion from TBAB (step II). The interaction of carbon dioxide with the amine groups of 2-aminoterephthalic acid produces the polarization of CO<sub>2</sub> molecule forming carbamate species. Then, there is a nucleophilic attack of the carbamate species to the carbon atom, binding to bromide ion which produces its removal, forming an intermediate species (step III). Finally, the intermediate species undergoes an intramolecular nucleophilic substitution to give the cyclic carbonate (step IV) and the catalyst is liberated.

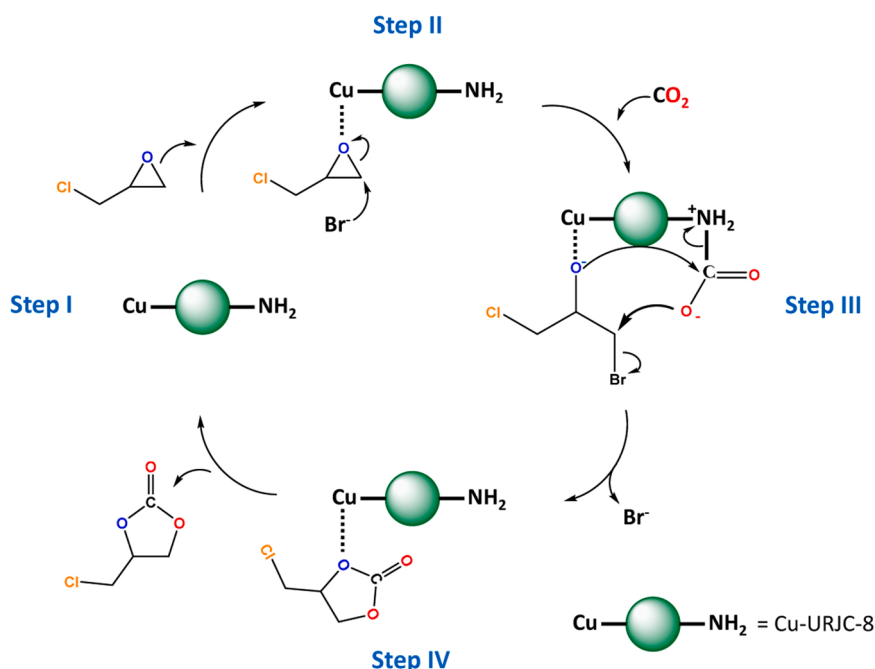


Fig. 7. Possible mechanism of cycloaddition reaction using Cu-URJC-8 as catalyst.

#### 4. Conclusions

The synthesis and characterization of a novel Cu-based MOF named Cu-URJC-8 has been reported. The new MOF contains two different organic ligands: 2-aminoterephthalic acid and 4,4'-bipyridyl with Lewis basic groups, showing a pillared-layer structure consisting of [Cu<sub>2</sub>(-CO<sub>2</sub>)<sub>4</sub>(-N)<sub>2</sub>] paddlewheel secondary building units, with the 4,4'-bipyridyl linkers acting as pillars in the two-fold interpenetrated networks. This MOF has Lewis acid and basic sites, provided by Cu<sup>2+</sup> and -NH<sub>2</sub> groups, respectively. This new Cu-MOF material is stable until 200 °C, according to powder x-ray diffraction and thermogravimetric analysis, and is chemically stable in different commonly used organic solvents (methanol, acetone, acetonitrile, hexane, toluene). This new material showed a CO<sub>2</sub> uptake of 1.59 and 1.07 mmol/g at 25 and 45 °C, respectively, and a Q<sub>st</sub> value of 27 kJ/mol, higher than those reported for other MOFs with more apparently advantageous textural properties. The catalytic activity in the cycloaddition reaction between epichlorohydrin and CO<sub>2</sub> was evaluated, obtaining 90 % conversion and 99 % selectivity in the best reaction conditions: 1 % mol of catalyst, 4 % mol of co-catalyst, 12 bar of carbon dioxide pressure, 24 h reaction and room temperature. When different epoxides with bulkier radical groups were used as substrates, the epoxide conversion decreased, evidencing a steric hindrance for diffusion into the catalytic sites of Cu-URJC-8. Finally, Cu-URJC-8 was tested in successive catalytic reaction cycles, confirming a high stability in terms of structural integrity and catalytic activity. As a result of this study, Cu-URJC-8 is considered a very promising catalyst for cycloaddition reactions and should be also tested in other copper-catalyzed reactions.

#### CRedit authorship contribution statement

**Jesús Tapiador:** Investigation, Writing – original draft. **Pedro Leo:** Conceptualization, Methodology. **Felipe Gándara:** Investigation. **Guillermo Calleja:** Supervision, Funding acquisition. **Gisela Orcajo:** Supervision, Writing – review & editing, Conceptualization, Methodology.

#### 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.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2022.102166](https://doi.org/10.1016/j.jcou.2022.102166).

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