

Formation of bio-based cyclic carbonates from CO₂ and renewable feedstocks via porous poly(azomethine) -based heterogeneous catalysts approach

Marcelo Echeverri^a, Eva M. Maya^b, Dulce M. Muñoz^{a,*}

^a *Fundación Tecnológica Advantx (FUNDITEC), C/ Faraday 7, Edificio CLAUD, Cantoblanco, Madrid 28049, Spain*

^b *Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Sor Juana Inés de la Cruz, 3, Cantoblanco, Madrid 28049, Spain*

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ABSTRACT

Two families of heterogeneous porous catalysts based on iron or cobalt poly(azomethine) (PAM) networks were reported to synthesize cyclic carbonates from bio-based aliphatic oxides epoxides and carbon dioxide (CO₂). The different PAM supports were prepared by reacting 2,6-pyridine dicarboxaldehyde with 1,3,5 tris(4 aminophenyl) benzene (PAM-1) or with melamine (PAM-2) by microwave activation. Both supports exhibited high thermal stability and similar CO₂ uptake (1.3 mmol/g) but PAM-2 showed higher specific surface area (779 m²/g vs 401 m²/g), more crystallinity and less capacity for anchoring metals than PAM-1. The novel catalysts were used in the cycloaddition of CO₂ to renewable feedstocks. Thus, using epoxidized methyl oleate (MOE) the corresponding cyclic carbonates were obtained with excellent yields (78–96 %) using a CO₂ pressure of 7 bars, 120 °C and 16 h of reaction. The best catalysts of the series, Fe@PAMs were also evaluated in the cycloaddition of CO₂ to epoxidized soybean oil (ESBO) in the same condition reaction obtaining excellent performance, epoxide conversions and cyclic carbonate yields greater than 90 %.

1. Introduction

Chemical fixation of carbon dioxide (CO₂) has aroused a lot of interest because CO₂ can be considered an ideal building block in the development of sustainable processes for the production of useful organic chemicals and a renewable feedstock since it is a waste product of many industrial processes, inexpensive and widely available [1]. However, the use of CO₂ as a starting material and reagent requires overcoming some limitations such as the high thermodynamic and kinetic stability which has been saved thanks to the use of highly reactive substrates and high CO₂ pressures and temperatures to activate it [2]. Thus, the activation of CO₂ represents a great challenge, which has led to the development of many catalytic strategies to favor its conversion. One of the most promising methodologies in this area is the synthesis of five-membered cyclic carbonates via the coupling of CO₂ to epoxides. This reaction is of great interest since transforms CO₂ into high-added value chemicals such as cyclic carbonates, which are appreciated as precursors for polymeric materials such as polycarbonates, as aprotic polar solvents, are used also as pharmaceutical and fine chemical intermediates, and in many biomedical applications [3]. Among the

different cyclic carbonates, those derived from bio-based aliphatic oxides epoxides, are becoming very important because they can be used as plasticizers, electrolytes and recently, as monomers for non-isocyanate polyurethanes which makes them have promising applications in industrial coating, foams and adhesives and biomedicine [4–6].

Among the bio-based model epoxides, epoxidized methyl oleate (Fig. 1a) has been the most studied. Thus, a great variety of homogeneous catalysts have been developed to obtain this cyclic carbonate, being the catalytic systems based on metals such as V, Co, Al, Mo, W, Cr or Fe and tetrabutylammonium salts as co-catalyst, the most employed [6–12]. The use of heterogeneous catalysts to activate this reaction presents great advantages compared with the homogeneous catalysts, due to its easy separation from the reaction products, recyclability, and high thermal stability. A great variety of heterogeneous catalysts have been successfully used in the cycloaddition of CO₂ to non-bio-based epoxides such as styrene oxide, epichlorohydrin, propylene oxide etc [13–15]. Among all of them, it is worth highlighting porous materials such as Zeolites and mesoporous silica-based materials, metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and porous organic polymers (POPs) as excellent heterogeneous catalysts due to their larger

* Corresponding author.

E-mail address: dmunoz@funditec.es (D.M. Muñoz).

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contact surface area, the presence of active sites capable of interact with the substrates and the existence of pores which implies space to accommodate the captured CO₂ and serve as a nanoreactor [16–20]. In addition, works are also being reported where the formation of cyclic carbonates is carried out in the absence of solvents [20–23].

Within POPs, porous poly(azomethine)s (PAMs) have emerged as very promising heterogeneous catalysts due to their possibility to anchor metals through the nitrogen atoms of the imine bonds. Moreover, due to the extensive cross-linking degree, these networks stabilized the anchored metal centers, reducing the possibility of leaching of the metal under reaction conditions, and imparting great insolubility which makes them very interesting as heterogeneous catalysts. Thus, porous PAMs containing metals such as Fe, Co, Cr, Al or Ru have been used as efficient heterogeneous catalysts in the cycloaddition of CO₂ to some epoxides such as styrene oxide, epichlorohydrin and cyclohexene oxide [24–26]. Moreover, porous PAMs can be easily prepared by microwave irradiation [24,25] which besides allowing obtaining the polymeric supports at gram scale and short the reaction time is a more environmentally friendly procedure than a conventional synthesis of PAMs that involves between 1 and 3 days of reaction time [27,28].

However, surprisingly, the use of heterogeneous catalysts, has been little investigated in the cycloaddition of CO₂ to bio-based epoxides [29]. Specifically, only four works have been found on the cycloaddition of CO₂ to methyl oleate epoxide (MOE) to obtain the corresponding methyl oleate cyclic carbonate (MOC) [30–33]. In all works (Fig. 1a) high CO₂ pressure was used (30 bars), cyclic carbonate yields of less than 75 % were obtained, and in most of the works, no study of the recyclability of catalysts is reported. Regarding the synthesis of cyclic carbonates from epoxidized vegetable oils, published examples are even rarer. From epoxidized soybean oil (ESBO) (Fig. 1a) using

heterogeneous catalysts, two works have been reported [34,35] yielding the soybean oil cyclic carbonate (SBOC) with excellent yields using moderate CO₂ pressure (10 bars). Finally, the synthesis of cyclic carbonates from epoxidized linseed oil was achieved with heterogenous catalysts using CO₂ pressures ranging from 10 to 50 bars [35].

Considering the moderate yields that have been achieved so far, the high pressures that are needed, and the few recyclability studies reported, it is necessary to continue the research in the development of recyclable heterogeneous catalysts in a more efficient cycloaddition of CO₂ to bio-based epoxides using softer conditions.

Thus, in this work, we present a series of 4 heterogeneous porous catalysts based on poly(azomethine)s (PAMs) (Fig. 1b) as very efficient catalysts in the cycloaddition of CO₂ to methyl oleate epoxide (MOE) to obtain the corresponding methyl oleate cyclic carbonate (MOC) using low CO₂ pressure (7 bars) in absence of solvents. The best catalysts of this series have been used also in the cycloaddition of CO₂ to a vegetable oil, epoxidized soybean oil (ESBO) in similar conditions to obtain the soybean oil cyclic carbonate (SBOC) in excellent yield.

2. Experimental

2.1. Materials and methods

2,6-pyridine dicarboxaldehyde (98 %) and cobalt (II) chloride anhydrous (CoCl₂, 99 %) were supplied by Cymit. 1,3,5-Tris(4-aminophenyl)benzene (TAPB, 93 %) was supplied by VWR. Melamine (4,4',4''-(1,3,5-Triazine-2,4,6-triyl) trianiline) (TTA, 95 %), iron(II) tetrafluoroborate hexahydrate (Fe(BF₄)₂·6 H₂O, 97 %) and Soybean oil were provided by Sigma Aldrich. Tetrabutylammonium bromide (TBAB, 98 %) and epoxidized methyl oleate (MOE) (>60 %) were supplied by

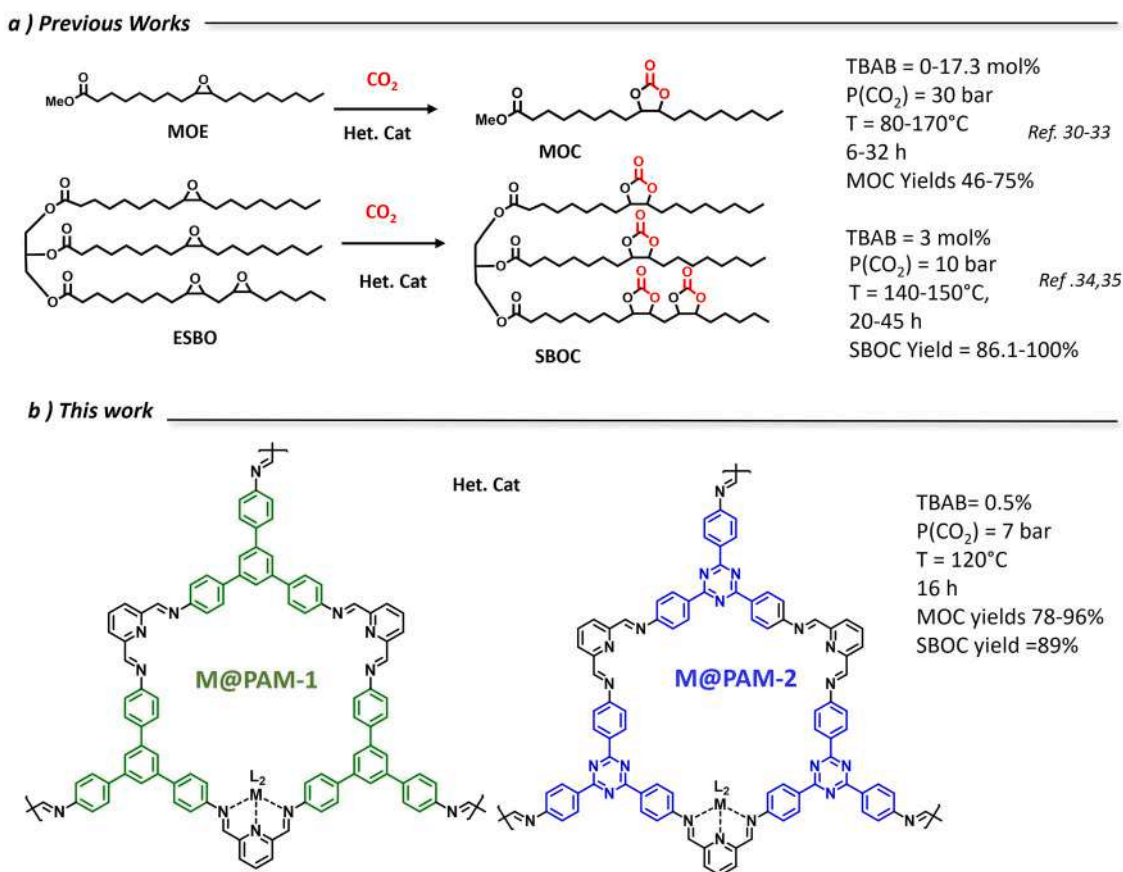


Fig. 1. a) Synthesis conditions of bio-based cyclic carbonates reported b) Synthesis conditions of bio-based cyclic carbonates of this work (TBAB: tetrabutylammonium bromide (co-catalyst)).

TCI Chemicals.

The solvents and other chemicals were of commercial grade purity and used without previous purification.

2.2. Synthesis of epoxidized soybean oil (ESBO)

In a 50 mL round-bottom flask, soybean oil (5 g, 0.0057 mol) was solved in dichloromethane (DCM) (34 mL) and the resulting solution was cooled to 0°C for 10 minutes followed by slowly addition of 3-chloroperbenzoic acid (MCPBA, 7.8 g, 0.045 mol) in portions. The solution was left stirring for 16 h at room temperature. The resulting suspension was washed with Na₂SO₃, NaHCO₃ and NaCl saturated aqueous solution. The organic phase was dried over MgSO₄ anhydrous. Then, the solvent was evaporated, and the residual oil was further used without additional purification. ¹H NMR (300 MHz, CDCl₃) δ 5.26 (p, *J* = 5.2 Hz, 1 H), 4.29 (dd, *J* = 11.9, 4.4 Hz, 2 H), 4.14 (dd, *J* = 11.9, 5.9 Hz, 2 H), 3.29 – 2.85 (m, 8 H), 2.31 (t, *J* = 7.5 Hz, 6 H), 1.88 – 1.22 (m, 74 H), 0.89 (t, *J* = 6.9 Hz, 9 H). Yield: 80 %.

2.3. Synthesis of poly(azomethine) supports

2.3.1. General procedure

In a 30 mL microwave vial were added: 2,6-pyridine dicarboxaldehyde (100 mg, 0.49 mmol), the corresponding amine: 1,3,5-Tris(4-aminophenyl)benzene (TAPB) (173 mg, 0.74 mmol) for the synthesis of PAM-1 support and 4,4',4''-(1,3,5-Triazine-2,4,6-triyl)trianiline (TTA) (175 mg, 0.74 mmol) for PAM-2, 6 mL of 1,4 dioxane and 0.6 mL of acetic acid 6 M. The vial was introduced in a Microwave and it was heated to 115 °C at 150 W. This temperature was kept for 90 min and then the vial was cooled down to 55°C. The resulting yellow-brown precipitate was collected by filtration and successively washed with water (H₂O), methanol (MeOH), tetrahydrofuran (THF), dichloromethane (DCM) and acetone. The final solid was dried at 150 °C under vacuum overnight.

PAM-1: Elemental analysis calculated C₃₄H₂₂N₄: C = 83.93 %, H = 4.56 %, N = 11.51 %; Found C = 79.27 %, H = 4.90, N = 11.91 %. Yield 92 %. ¹³C NMR (100.32 MHz) δ 155 ppm (imine carbon, Cg), 150–115 ppm (aromatic carbons, Ca-f and Ch-j).

PAM-2: Elemental analysis calculated for C₃₁H₁₈N₇: C = 76.22 %, H = 3.71 %, N = 20.07 %; Found C = 71.93 %, H = 4.34, N = 19.94 %. Yield 93 %. ¹³C NMR (100.32 MHz) δ 170 ppm (triazine carbon, Ca), 155 ppm (imine carbon, Cf), 150–115 ppm (aromatic carbons, Cb-Ce and Cg-i).

2.4. Synthesis of metal catalysts

2.4.1. General procedure

In a 50 mL round bottomed flash provided with magnetic stirring and a reflux condenser, the metallic salts Fe(BF₄)₂·6H₂O or CoCl₂ were stirred in 20 mL of THF for 10 min. Then 100 mg (0.2 mmol) of the corresponding polymer (**PAM-1** or **PAM-2**) was added and heated under reflux for 24 h. The yellow-brown solid was filtered, successively washed with H₂O, THF, DCM and acetone, and the catalyst was dried at 150°C under vacuum overnight.

Fe@PAM-1: Metal salt: Fe(BF₄)₂·6H₂O (21 mg, 0.06 mmol). Elemental analysis calculated for [C₃₄H₂₂N₄]₆[C₃₄H₂₂N₄Fe(BF₄)₂]₁: C = 78.42 %, H = 4.31 %, N = 10.90 %; Fe = 1.55 %; Found C = 66.00 %, H = 4.49 %, N = 9.26 %, Fe = 1.52 % (determined by ICP-OES). Yield: 79 %.

Co@PAM-1: Metal salt: CoCl₂ (8 mg, 0.06 mmol). Elemental analysis calculated for [C₃₄H₂₂N₄]₆[C₃₄H₂₂N₄CoCl₂]₁: C = 80.85 %, H = 4.39 %, N = 11.09 %, Co = 1.67 %; Found C = 64.68 %, H = 4.38 %, N = 9.45 %. Co = 1.18 % (determined by ICP-OES). Yield: 75 %.

Fe@PAM-2: Metal salt: Fe(BF₄)₂·6H₂O (60.5 mg, 0.18 mmol). Elemental analysis calculated for [C₃₁H₁₈N₇]₂₀[C₃₁H₁₈N₇Fe(BF₄)₂]₁: C = 74.55 %, H = 3.63 %, N = 19.63 %, Fe = 0.52 %; Found C = 71.17 %, H = 4.38 %, N = 19.60 %.

Fe = 0.42 % (determined by ICP-OES). Yield: 60 %.

Co@PAM-2: Metal salt: CoCl₂ (38 mg, 0.18 mmol). Elemental analysis calculated for: [C₃₁H₁₈N₇]₁₂[C₃₁H₁₈N₇CoCl₂]₁: C = 69.94 %, H = 3.45 %, N = 19.42 %; Found C = 62.594 %, H = 4.32 %, N = 16.65 %. Co = 0.93 % (determined by ICP-OES). Yield: 75 %.

2.5. Catalytic activity

2.5.1. Cycloaddition of CO₂ to bio-based epoxides MOE and ESBO

2.5.1.1. General procedure. MOE or ESBO (1 mL), TBAB (5 % mol) and the corresponding catalyst in a ratio epoxide:metal 1500:1 (Fe@PAM-1: 6.9 mg; Co@PAM-1: 4.7 mg; Fe@PAM-2: 35.0 mg; Co@PAM-2: 3.6 mg) were added to a 10 mL Tinyclave Büchi glass reactor. The reactor was purged three times with CO₂ and then charged with 7 bar of CO₂ and heated in a silicone bath at 120 °C for 7–16 hours (depending on the experiment described in Results and Discussion section). The mixture was centrifuged and 10 μL of supernatant were dissolved in CDCl₃ (0,5 mL) and analysed by ¹H-NMR spectroscopy.

The conversion of the epoxides and the yields of the corresponding cyclic carbonates were determined by ¹H-NMR spectroscopy (see Figure S1 and Figure S2). The integration of the proton of the epoxides and carbonates was used to calculate the conversion, yield and selectivity using the next equations:

$$\text{Conversion} = \frac{H_c \text{ signal of consumed Epoxide}}{H_c \text{ signal of initial Epoxide}}$$

$$\text{Yield} = \frac{H_c \text{ signal of obtained Cyclic Carbonate}}{H_c \text{ signal of initial Epoxide}}$$

$$\text{Selectivity} = \frac{H_c \text{ signal of Obtained Cyclic Carbonate}}{H_c \text{ signal of consumed Epoxide}}$$

2.5.1.2. Recycling test. Methyl oleate epoxide (2 mL), TBAB (90.8 mg, 5 %mol) and Fe@PAM-2: (70 mg) were added to a 10 mL Tinyclave Büchi glass reactor. The reactor was then purged three times with CO₂ and charged with 7 bar CO₂ and heated in a silicone bath at 120 °C for 16 h. The mixture was centrifuged and 10 μL of the liquid phase was dissolved in CDCl₃ (0,5 mL) and analysed by ¹H-NMR spectroscopy. The precipitate was washed and centrifuged 3 times with MeOH (10 mL). The solid was then filtered and dried at 150 °C under vacuum overnight for next cycle.

2.6. Characterization techniques

Fourier Transform Infrared with attenuated total reflectance (FTIR-ATR) spectra were recorded in a Perkin-Elmer RX-1 instrument Spectrum 65. The spectra were registered with a resolution of 2 cm⁻¹ and performed in a spectral range of 600–4000 cm⁻¹; Elemental Analysis (EA) were recorded on Elemental Analyzer LECO CHNS-932; Nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Bruker Avance III-HD Nanobay 300 MHz and on a Bruker AV 400 WB spectrometers using CDCl₃ as solvent. The solid-state ¹³C NMR spectra were recorded in a Bruker AV-400-WB at room temperature and 100.32 MHz using a 4 mm triple channel probe with ZrO rotors and Kel-F plug with a rotation speed of 10 KHz in all cases. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 409/C instrument. The experiments were carried out under an air atmosphere at the heating rate of 10 °C min⁻¹ to a final temperature of 800 °C; Nitrogen adsorption/desorption isotherms were recorded in Monosorb Surface Area Analyser MS-13 Quantachrome. Previously, the samples were degassed for 12 h at 120 °C. Specific surface areas were determined by BET technique and the pore size average by DFT methods; CO₂ adsorption isotherms were obtained in a Autosorb IQ (Quantachrome Instruments) using ~150 mg

of powder sample. Before adsorption experiments, samples were out-gassed at 120 °C for 10 h under turbo-molecular high vacuum. Scanning electron microscopy (SEM) micrographs were obtained with a Hitachi SU-8000 microscope operating at 0.8 and 1 kV for PC and MMMs, respectively. The catalysts were directly dispersed on a double-sided adhesive and the membranes were fractured under liquid nitrogen and the cross-section was observed with a magnification that varied from 2k to 90 K.

3. Results and discussion

3.1. Synthesis and characterization of poly(azomethine) supports (PAM-1 and PAM-2)

The synthesis of the polyazomethine supports was carried out using microwave irradiation by reacting 2,6-pyridine dicarboxaldehyde with two amines having C_{3v} symmetry, 1,3,5-tris(4-aminophenyl)benzene (TAPB) or 4,4',4''-(1,3,5-triazine-2,4,6-triyl)aniline (TTA) also known as melamine (Fig. 2). 2,6-pyridine dicarboxaldehyde was selected as monomer since it forms bis(imino)pyridine units in the network which can act as pincers for effective metal anchoring [26] On the other hand the C_{3v} symmetry of triamines has been shown that they are suitable monomers to build 2D porous materials, and also in the case of the triazine-based triamine, to incorporate more nitrogen atoms into the network to tune other properties [36–40].

Thus, the synthesis of the supports, **PAM-1** and **PAM-2** was carried out by microwave irradiation, heating the corresponding monomers at 115 °C using a mixture of 1,4 dioxane and acetic acid 6 M as solvent. An irradiation time of 90 min was maintained after which **PAM-1** and **PAM-2** were obtained with excellent yields of 92 % and 93 %, respectively.

The chemical structure of both supports was first confirmed by elemental analysis, Fourier transform infrared spectroscopy (FT-IR), and solid state ¹³C nuclear magnetic resonance (¹³C-NMR) (Fig. 3). The percentages of C, N, and H agreed with the proposed structures, with more N content in the case of **PAM-2** as it was expected (see experimental section).

Both FT-IR spectra (Fig. 3a) show a vibration at 1711 cm⁻¹ attributed to traces of unreacted or terminal aldehyde groups and an intense band at 1502 cm⁻¹ attributed to the vibrations of conjugated C=C bonds. The band attributed to the vibration of the imine stretching bonds (C=N) appeared at 1593 cm⁻¹. It appears displaced respecting to the characteristic band of imines (1610–1627 cm⁻¹) [24–26] as it was previously reported for imine-linked COFs [38]. Additionally, the FT-IR spectrum of **PAM-2** shows two bands at 1578 and 1361 cm⁻¹ attributed to the triazine rings [41]. Obtaining **PAM-2** by microwave in an acidic

medium is an exciting contribution since polycondensation reactions of melamine and 2,6-pyridine dicarboxaldehyde under microwave irradiation in dimethyl sulfoxide yielded polyaminals (PAs) instead of polyazomethines (PAMs) [41].

¹³C-NMR spectra (Fig. 3b) showed the signals corresponding to the expected structures. Both spectra showed an intense signal at 155 ppm attributed to the imine carbons of **PAM-1** and **PAM-2**, (carbons g and f respectively). The signals corresponding to the aromatic carbons appear in the range from 115 ppm to 150 ppm. Additionally, in the spectrum of **PAM-2**, the presence of the carbons of the triazine moiety are observed by the appearance of a signal around 170 ppm (carbons a).

The thermal stability was evaluated in an air atmosphere (Fig. 3c). Both polymers showed high thermal stability with a decomposition pattern in one step and with starting decomposition temperatures of 445 and 470 °C respectively. The macro-structure was investigated by X-ray diffraction experiments (Fig. 3d). Both polymers show intense peaks around 2θ = 5° corresponding to the (110) plane and another one around 2θ = 25° from the (003) plane resulting from the 2D sheet stacking. The crystallinity and stacking in **PAM-2** is higher than **PAM-1**. This result indicates the high tendency of these structures to organize and stack, which is favorable for large π-conjugated systems.

The porosity properties were evaluated by N₂ adsorption/desorption experiments (Fig. 4a, Table S1). Both polymers exhibited some N₂ uptake at low pressures which is characteristic of microporous polymers and the adsorption increased when the pressure was increased as is attributed to porous materials. **PAM-2** shows a significantly higher specific surface area (779 m²/g) than **PAM-1** (401 m²/g), which could be produced for a better stacking observed in the X-ray experiments.

Despite the different structure of both supports, the CO₂ uptake (Fig. 4b) was similar in both polymers (1.31 and 1.29 mmol/g, respectively) which are lower values than the few CO₂ absorption values published for polyazomethines [42,43].

Finally, the scanning electron microscopy images were recorded to see the morphology of the obtained polymers. In both cases, the morphology is characterized by the formation of agglomerates of small globular-shaped particles (Fig. 4c), this is a common morphology displayed by porous polymers.

3.2. Synthesis and characterization of poly(azomethines) metal complexes (M@PAM1 and M@PAM-2)

The PAM supports have an azomethine-pyridine structure which acts as a chelating ligand for metal ions to facilitate the incorporation of metals into the polymeric networks to obtain heterogeneous catalysts. In this context, Fe and Co salts have been used to obtain metal complexes

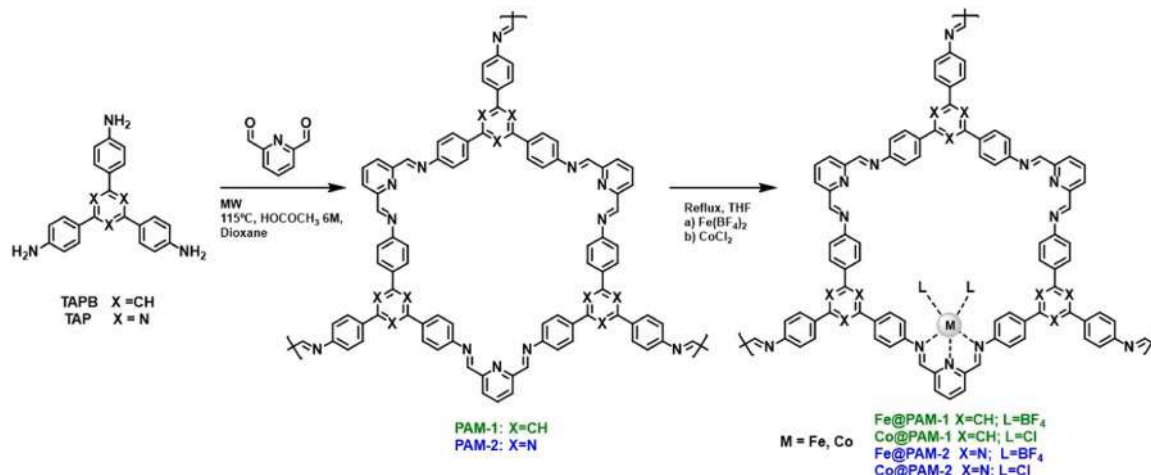


Fig. 2. Synthesis of **PAM-1** and **PAM-2** supports and the corresponding metal complexes.

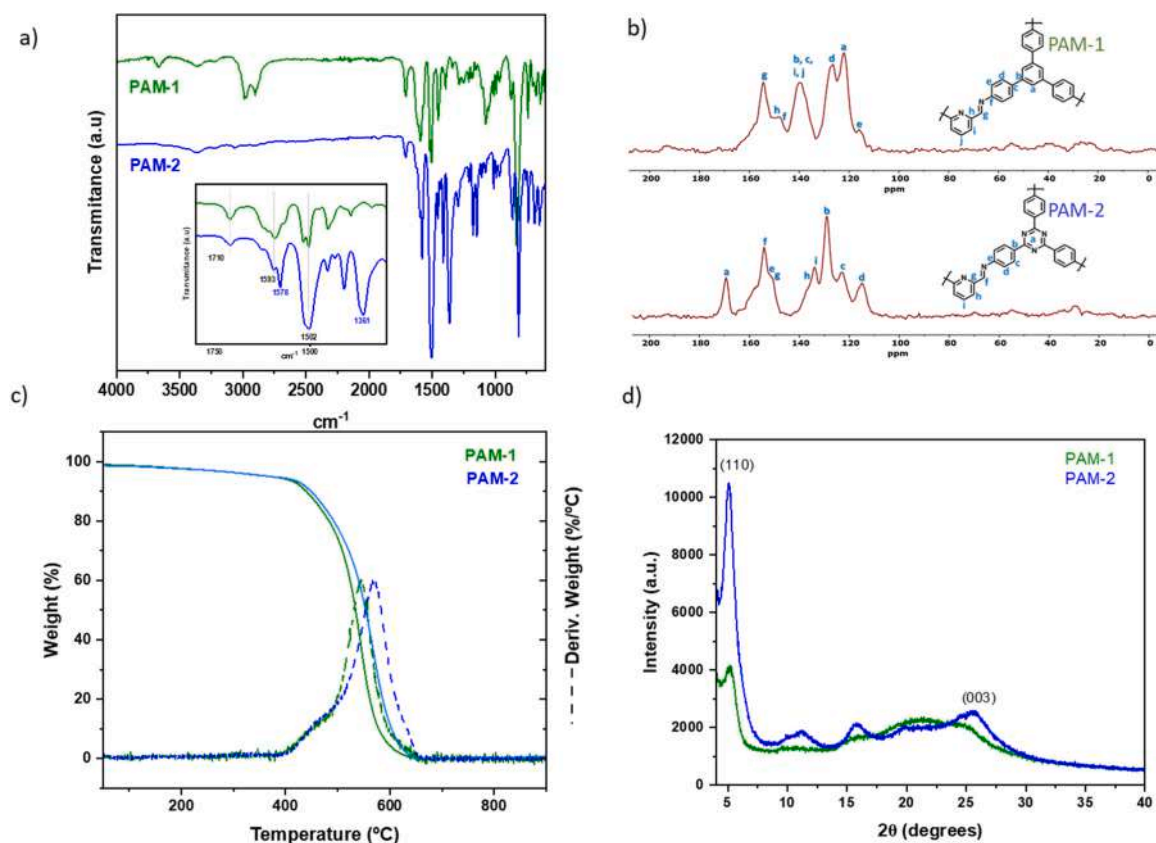


Fig. 3. a) FT-IR spectra; b) ¹³C-NMR spectra; c) TGAs and d) X-Ray diffraction patterns of PAM-1 and PAM-2.

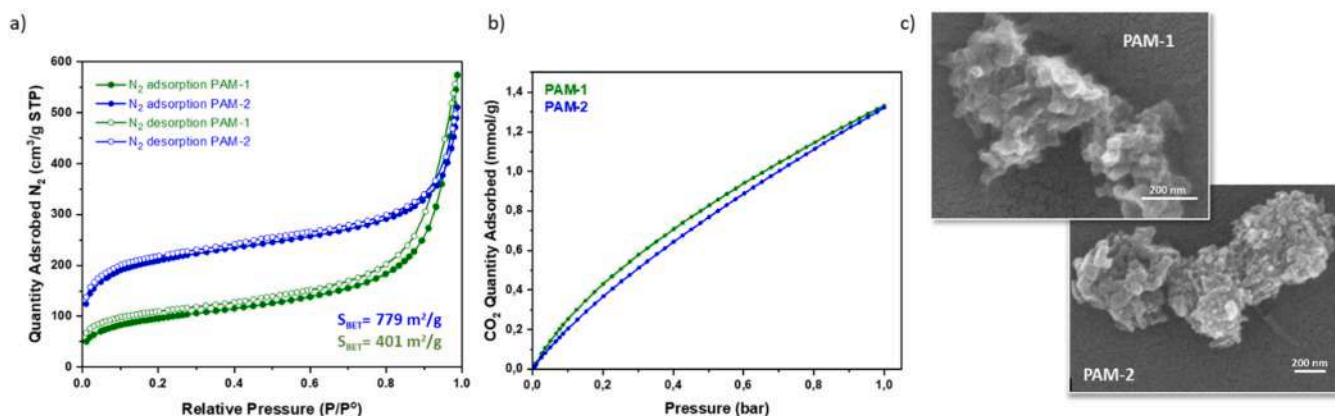


Fig. 4. a) N₂ adsorption/ desorption isotherms; b) CO₂ uptake and c) SEM images of PAM-1 and PAM-2.

and polymers for use as catalysts, particularly in the conversion of CO₂ [20,24,25].

The M@PAM catalysts were initially prepared by heating 0.2 mmol of the corresponding support, PAM-1 or PAM-2 with 0.06 mmol of the corresponding metal salts, Fe(BF₄)₂ and CoCl₂, in anhydrous THF under reflux overnight. The metal contents were determined by inductively coupled plasma spectroscopy (ICP). PAM-1 showed 1.52 % of iron and 1.18 % of Co. These metal contents and the elemental analyses obtained (see experimental part) showed that metal was incorporated in one of every six repetitive units.

In contrast, PAM-2 does not present appreciable percentages of any of the metals. The amount of salt was increased to 0.18 mmol, obtaining low metal contents (0.42 % of Fe and 0.93 % of Co). These results and the elemental analyses obtained indicated that in the case of Fe@PAM-

2, the metal was incorporated in one of every twenty repetitive units whereas for Co@PAM-2, one of every twelve repetitive units coordinated cobalt. These results revealed a low metal coordination capacity of the PAM-2 support. Even after further increasing the amount of metal salt, the incorporation of higher metal percentages was not achieved.

The FT-IR analyses (Figure S3) do not show a significant shift of the bands assigned to the vibration of the imine bonds (C=N) as a consequence of the low metal coordination, although a slight signals widening is observed respecting the metal-free support.

Thermal stability of Metal@PAMs was evaluated in air atmosphere. All metal-containing poly(azomethine)s showed very high thermal stability with decomposition temperatures above 380 °C although the incorporation of metal decreases the thermal stability with respect to the support (Fig. 5). This effect has already been observed previously in the

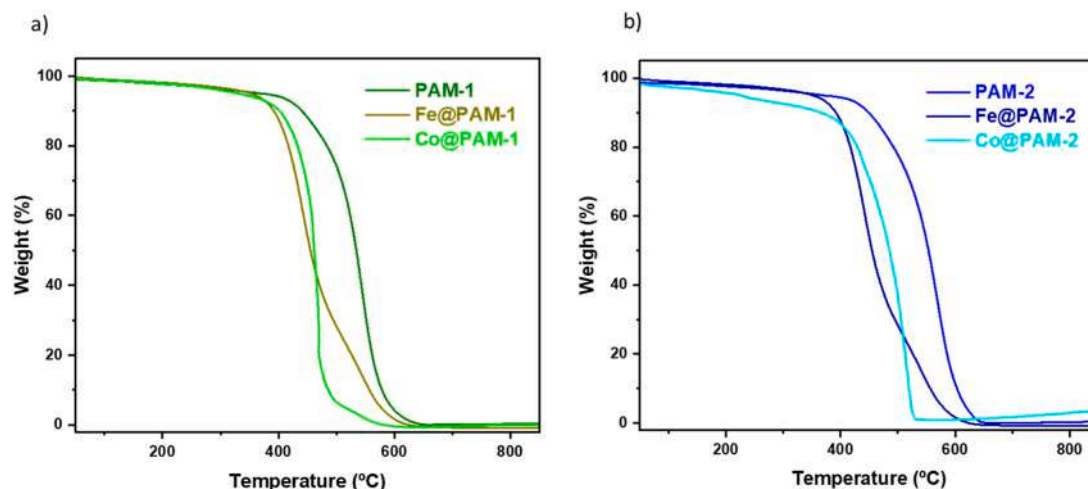


Fig. 5. a) TGA of M@PAM-1 compared with PAM-1 and d) TGA of M@PAM-2 compared with PAM-2.

incorporation of metals into polyazomethines [24–26].

Additional studies were performed by SEM (Fig. 6a) and EDX (Fig. 6b) analysis to prove the metal distribution inside the porous polymers. In Fig. 6b can be observed the homogenous distribution of Fe or Co in all polymers confirming also the molecular coordination of the metal in the polymeric networks.

3.3. Catalytic activity

Initially, the four metal complexes were tested as heterogeneous catalysts in the CO₂ conversion of methyl oleate epoxide (MOE) to methyl oleate cyclic carbonate (MOC) (Table 1). The experiments were performed in a Tinyclave steel Büchi glass reactor which was coupled to a specially designed pressure-tight tank to operate at high temperatures and stable pressure. The reactions were done at 120 °C and initially, at a CO₂ pressure of 7 bars, without solvent, and using a 5 % weight (concerning to the epoxide) of tetrabutylammonium bromide (TBAB) as a co-catalyst. In these conditions, after 7 hours of reaction, the iron-based catalysts (entries 1 and 3) yielded the cyclic carbonates with moderated yields (>60 %) and good epoxide conversions (>70 %), while with the cobalt complexes, neither epoxide conversions nor cyclic carbonate yields above 40 % were achieved (entries 2 and 4). Increasing the time to 16 h, excellent catalytic performance was achieved for the four catalysts (entries 5–8), notably the iron complexes, with epoxy conversions and cyclic carbonates yield above 95 % (entries 5 and 7). In addition, after this reaction time, 99 % selectivity is achieved for the cyclic carbonates.

To evaluate the role of the co-catalyst, TBAB, in this conversion, an experiment control was done without adding any PAM-based catalysts (entry 9). The use of TBAB produced 47 % of MOC with 51 % of MOE conversion confirming the positive effect of this co-catalyst to the CO₂ cycloaddition to bio-based epoxides as it was previously observed in the CO₂ cycloaddition on non-bio-based epoxides [13–18]. Due to the low metal content of these complexes, two more control experiments were carried out, directly using the supports PAM-1 and PAM-2 as catalysts (entries 10 and 11). As can be observed with both polymers good epoxide conversions were achieved (92 and 82 respectively), but the yields and selectivity towards the cyclic carbonates were lower than using the iron complexes which confirms that iron plays a crucial role in the catalytic performance of these catalysts.

Given the results obtained, the CO₂ cycloaddition was carried out over epoxidized vegetable oils, such as epoxidized soybean oil (ESBO) using the iron-based complexes Fe@PAM-1 and Fe@PAM-2 (entries 12 and 13). As can be observed, both catalysts showed very good catalytic performance using a substrate that contains four epoxides.

As examples, Figures S4, S5 and S6 show the ¹H-NMR spectra of the experiments of entries 7, 9 and 13.

Recyclability of a heterogeneous catalyst is an essential property to assure its real application. Thus,

the recyclability of Fe@PAM-2 was evaluated. After the first run, methanol was added, and the catalyst was separated from the solution by centrifugation. The catalyst was washed three times with methanol and after dry it was used in a fresh reaction. This procedure was repeated until the five cycles were completed.

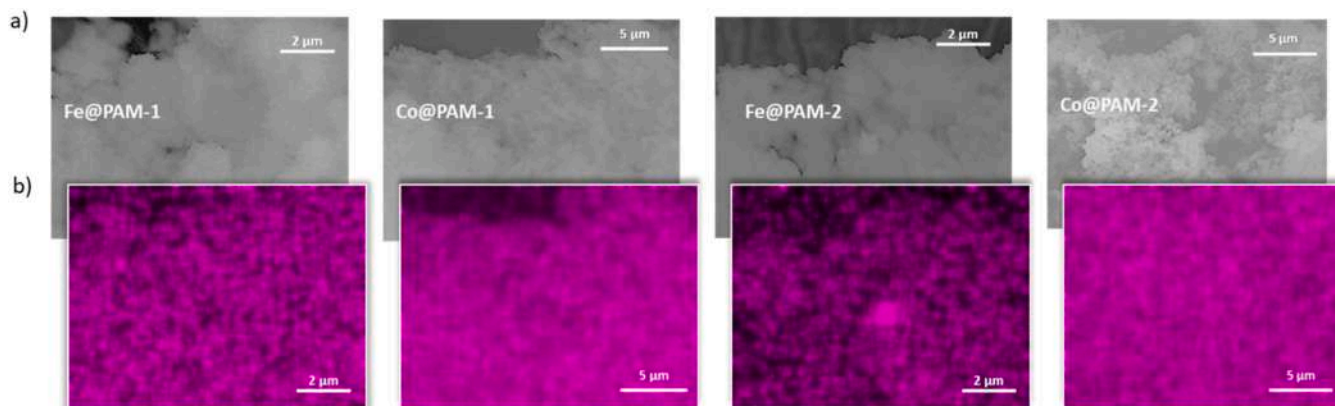


Fig. 6. a) SEM images and b) EDX mapping of Fe and Co distribution in the support PAM-1 and PAM-2.

Table 1
Cycloaddition of CO₂ to bio-based epoxides, MOE and ESBO^[a].

Entry	Catalyst ^[b]	t (h)	Conv. (%)	Yield (%)	Selec. (%)
1	Fe@PAM-1	7	71	63	89
2	Co@PAM-1	7	36	34	94
3	Fe@PAM-2	7	76	62	81
4	Co@PAM-2	7	38	38	>99
5	Fe@PAM-1	16	97	96	>99
6	Co@PAM-1	16	78	78	>99
7	Fe@PAM-2	16	97	96	>99
8	Co@PAM-2	16	92	76	83
9	None	16	51	47	92
10	PAM-1	16	92	77	84
11	PAM-2	16	82	70	86
12	Fe@PAM-1	16	95	93	98
13	Fe@PAM-2	16	98	94	96

All reactions were performed without solvent at 120°C, 16 h, 7 bar CO₂. Molar Proportion Metal: TBAB (1:75) (5 % mol TBAB with respect to epoxide); Molar Proportion Metal: Epoxide (1:1500), (0.07 % mol of metal with respect to epoxide)

As can be observed in Fig. 7, the results show good recyclability with MOE conversion of up to 82 % after 5 cycles and MOC yields of up to 90 % which confirm the excellent recyclability of this catalyst. The TON and TOF values for this catalyst was around 1420 and 88.8 respectively.

We have analysed the structure of the recycled catalyst by FT-IR (Figure S7) noting that the structure remains unchanged after the five cycles.

Based on previously reported mechanisms for the cycloaddition of CO₂ to epoxides using metal-based catalysts and TBAB as co-catalysts [44,45], a possible mechanism for this reaction is proposed in Fig. 8. Initially, the oxygen of the epoxide coordinates with the metal center of the catalyst (M@PAM), activating the epoxide. This is followed by the nucleophilic attack of the bromide anion (Br⁻) from TBAB on the less sterically hindered carbon atom of the epoxide, resulting in ring opening (step 1). In the next step (step 2), CO₂ is inserted into the metal-oxygen bond of the ring-opened alkoxide intermediate. Finally, a cyclic

carbonate is formed through a ring-closing step (step 3), regenerating both M@PAM and Br⁻ for the next catalytic cycle.

To evaluate the catalytic performance of the novel catalysts, they were compared with the fourth heterogeneous catalysts reported in the literature for the cycloaddition of CO₂ to MOE (Table 2).

Thus, 0.5 mol% of the catalyst Z-3 which is a Zn(II) complex (entry 1) promoted the conversion of MOE into MOC with a yield of 46 % using a small amount of tetrabutylammonium bromide (TBAB) as a co-catalyst. The reaction was carried out at 80°C but at high CO₂ pressure (30 bars). The catalyst was recycled up to 5 times [30]. The 4-pyrrolidine pyridine iodide supported in a mesoporous silica Zn/SBA-15 catalyst (Zn/SBA-15 (0.12)-4PPI, entry 2) worked in absence of TBAB at 140°C and also at 30 bars of CO₂ during 32 h to produce MOE in 75 % yield. However, only 1 recycling cycle was reported for this catalyst [31]. The acid-base MOF (UiO-66-NH₂, entry 3) was used to promote this reaction operating at 120 °C, 30 bars of CO₂ in the presence of big amount of co-catalysts during 12 h obtaining MOC with 69 % yield [32]. Finally, the use of a carboxymethylcellulose-supported ionic liquid system (HBimCl-NbCl 5 /HCMC, entry 4) as catalyst at a temperature of 170 °C and 30 bares of CO₂ converts 68.45 % of MOE into cyclic carbonate in 6 h of reaction [33]. No recyclability experiments have been reported for these last two catalysts.

Thus, as can be observed the catalysts here presented work at lower CO₂ pressures than all reported. Specifically, those of iron presented higher yields towards the bio-based cyclic carbonate formation since besides a small amount of catalyst used, they were more selective than those reported.

Concerning the synthesis of SBOC from ESBO (Table 3), the Pt-doped H₃PW₁₂O₄₀/ZrO₂ catalyst (entry 1) worked at moderated reaction conditions (150°C and 10 bars of CO₂) but needed 30 h of reaction to achieve epoxide conversions up to 80 %. Moreover, the catalyst had to be calcined to be reused [34]. The silica-supported 4-pyrrolidinopyridinium iodide (SiO₂-I) catalyst (entry 2) produced the cyclic carbonate quantitatively with full conversion of epoxide but using a CO₂

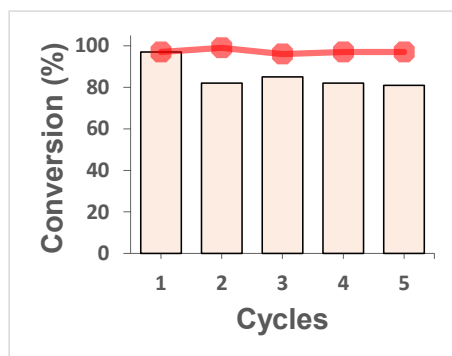


Fig. 7. : Recycling experiments of Fe@PAM-2 in the cycloaddition of CO₂ to MOE. Selectivity towards the cyclic carbonate (MOC) is represented by red line and dots.

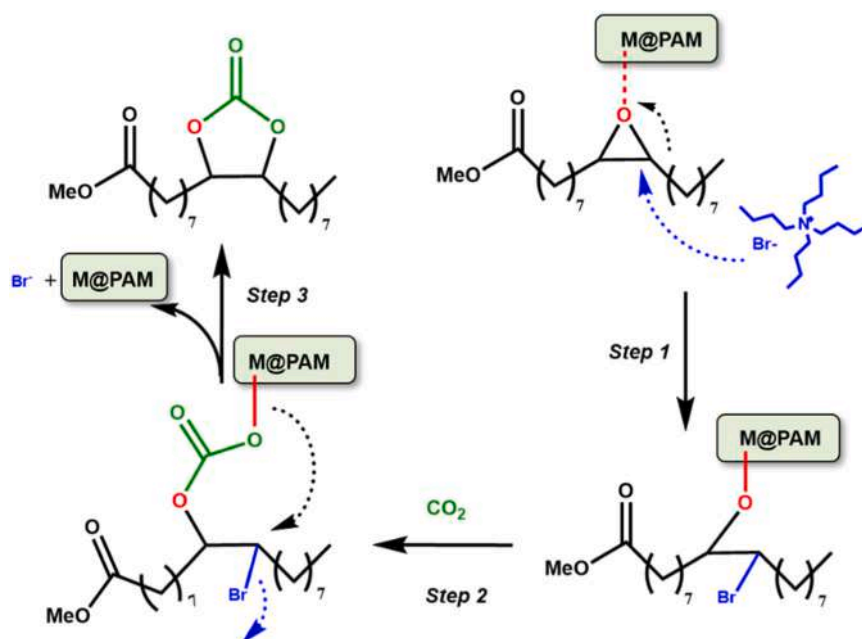


Fig. 8. Proposed mechanism for CO₂ cycloaddition to MOE catalyzed by M@PAM/TBAB.

Table 2

Catalytic comparison of cycloaddition of CO₂ to MOE to obtain MOC.

Entry	Catalyst	Cat.	TBAB (mol%)	T (°C)	P (bar)	t (h)	Conv. (%)	Yield (%)	Select. (%)	Ref.
1	Zn-3	0.5 mol%	0.1	80	30	16	nr	46	nr	[30]
2	Zn/SBA-15(0.12)-4PPI	7.4 mol%	-	140	30	32	nr	75	91	[31]
3	UiO-66-NH ₂	10 ^{a)}	17.3	120	30	12	94	69	65	[32]
4	HBimCl-NbCl ₅ /HCMC	0.042 ^{b)}	-	170	30	6	68.45	nr	nr	[33]
5	Fe@PAM-1	0.07	5	120	7	16	97	97	>99	This work
6	Co@PAM-1	0.07	5	120	7	16	78	78	>99	
7	Fe@PAM-2	0.07	5	120	7	16	97	95	98	
8	Co@PAM-2	0.07	5	120	7	16	92	76	83	

a) wt%

b) mL/g; nr: not reported

Table 3

Catalytic comparison of cycloaddition of CO₂ to ESBO to obtain SBOC.

Entry	Catalyst	Cat.	TBAB (mol%)	T (°C)	P (bar)	t (h)	Conv. (%)	Yield (%)	Select. (%)	Ref.
1	Pt H ₃ PW ₁₂ O ₄₀ /ZrO ₂	5 ^{a)}	-	150	10	30	83.2	nr	nr	[34]
2	SiO ₂ (I)	3	-	140	30	45	100	100	nr	[35]
3	Fe@PAM-1	0.07	5	120	7	16	95	93	98	This work
4	Fe@PAM-2	0.07	5	120	7	16	98	94	96	

a) wt%; nr: not reported

pressure of 30 bars, and 45 hours of reaction [35]. Our iron-based catalysts were more competitive since were able to convert ESBO into SBOC with excellent performance (conversion, yields, and selectivity up to 90 %) in much less time using much lower CO₂ pressures.

4. Conclusions

The synthesis of bio-based cyclic carbonates was carried out in excellent yield (up to 90 %) from two interesting feedstocks, bio-based epoxides (methyl oleate epoxide, MOE and epoxidized soybean oil, ESBO) and CO₂, using heterogeneous catalytic systems formed by iron-based poly(azomethine)s and tetrabutylammonium bromide as a co-catalyst. Despite the low iron content of the catalysts, it seems that

iron plays a crucial role in the catalytic performance since in its absence worse performance and selectivity are obtained. Moreover, the catalysts can be recycled up to five runs and the conversions were done at 120 °C, 7 bars of CO₂ and, 16 h of reaction which represents the mildest conditions reported to date for this type of biomass-derived aliphatic epoxides. Thus, the iron-based poly(azomethine) catalysts here reported are excellent alternatives for the production of bio-based cyclic carbonates.

CRedit authorship contribution statement

Dulce M. Muñoz: Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Marcelo Echeverri:** Methodology,

Investigation. **Eva M Maya**: Writing – review & editing, Writing – original draft.

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.

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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.2024.102977](https://doi.org/10.1016/j.jcou.2024.102977).

Data availability

Data will be made available on request.

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