

Valuable chemicals from CO₂ and renewable feedstocks, a polyimine-based heterogeneous catalysts approach

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Introduction

Carbon dioxide (CO₂) can be considered an ideal renewable feedstock in the development of sustainable processes for production of useful chemicals, since it is a waste product of many industrial processes, it is thus inexpensive and widely available.¹ Moreover, the cycloaddition of this CO₂ to epoxides is a valuable method for the production of cyclic carbonates, which are interesting organic intermediates in the synthesis of polymers. Additionally, biomass of vegetable origin offers a wide range of molecules to be used as bio-based monomers to create sustainable polymeric materials that could fulfil the requirements of circular economy.

The use of CO₂ as a starting material and reagent however requires overcoming some limitations such as the high thermodynamic stability. Although homogeneous catalysts are somewhat more efficient than the heterogeneous counterparts, their separation from the final products remains troublesome and catalyst reutilization is difficult. The use of heterogeneous catalysts is preferred due to its easy separation from the reaction products, recyclability and high thermal stability. One class of interesting heterogeneous catalysts as those based on porous organic polymers (POPs). Due to their tunable pore structure, and wide range of chemical functional groups that can be introduced, show a strong potential for tuning their catalytic properties.

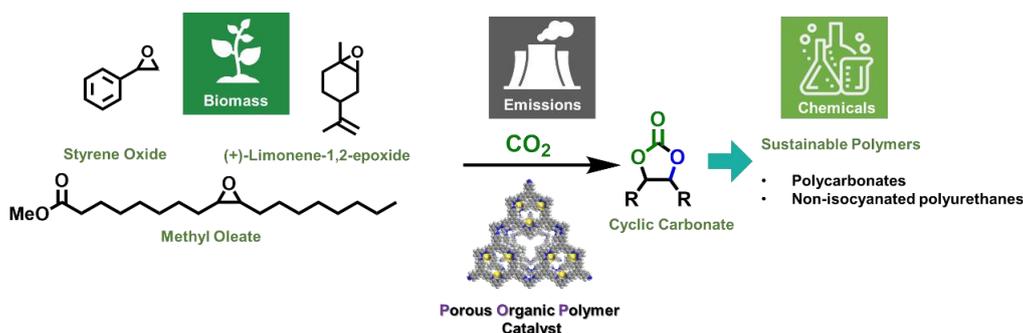


Figure 1. Conversion approach for biomass and CO₂ valorization towards sustainable chemicals and polymers

In this work we report the study carried out on the utilization of polyimine-based heterogeneous catalysts for the carbonation of epoxidized molecules derived from renewable feedstocks, such as vegetable oils. These polymeric networks with imine functionalities not only are able to absorb and activate CO₂, but also are very interesting materials to be used as heterogeneous catalysts due to their possibility to anchor metals through the nitrogen atoms of the imine bond and also due to the insolubility given by the high degree of cross-linking of these porous networks.

Results

In the first part of the work, we carried out the synthesis of the polymeric structures (polyimines), coupling 2,6-pyridine dicarboxyaldehyde (DA-Py) and different aromatic diamines (di- and triamines). The reaction was carried out in dimethylsulfoxide (DMSO) using microwave irradiation as heating method (180°C for 1,5h) to obtain porous polymers in relatively short times and yields above 80%. In a second step we prepared in a simple way the metal containing PIs from different metallic salts (FeBF₄ and CoCl₂). The structure of all polymers was confirmed by spectroscopic techniques as solid state ¹³C-NMR, FT-IR, elemental analyses.

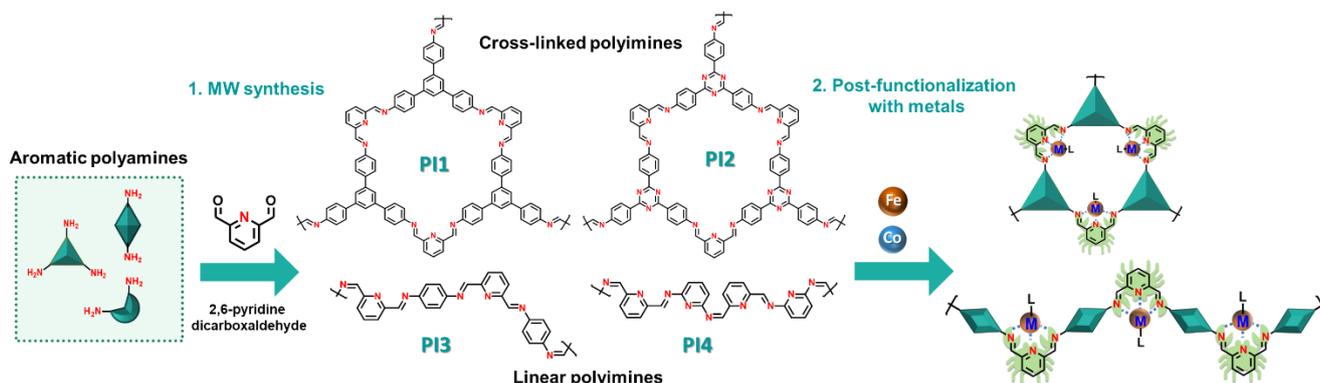


Figure 2. Synthesis of heterogeneous catalysts based on polyimine metal complexes

All polymers have excellent thermal stability with decomposition temperature ($T_{d_{onset}}$) above 400°C. X-Ray diffraction spectra of **PI1** and **PI2** present typical COFs x-ray pattern with intense peaks around $2\theta = 5^\circ$ corresponding to the (110) plane and a d-spacing of 18.4 Å and 18.0 Å. The reflection from the (003) plane arises from the 2D sheet stacking corresponding to the peak at $2\theta = 25.0^\circ$ and 24.7° (3.6 Å). Regarding the porosity properties, the polymer structure (branched vs linear) seems to have great influence in the overall porosity of the polymers as show the good surface obtained (Table 1) for **PI1** and **PI2** (259 m²/g and 502 m²/g respectively) compared to **PI3** and **PI4** (153 m²/g and 197 m²/g, respectively).

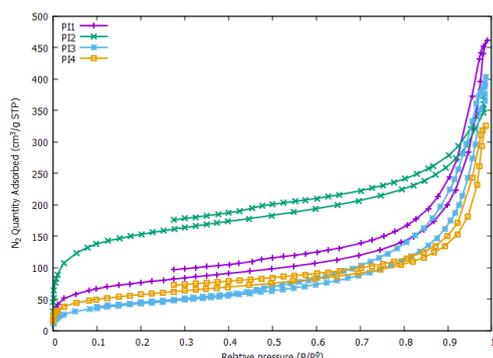


Figure 3. Nitrogen adsorption isotherms of PIs

Table 1. Porous properties of PIs

	S_{BET} (m ² /g)	Δ Pore Size (nm)	Pore Vol. (cm ³ /g)
PI1	259	11,0	0,71
PI2	502	4,6	0,58
PI3	153	16,3	0,62
PI4	197	10,2	0,50

The metal (Fe and Co) complexes from polyimines (**PI1**, **PI2**, **PI3** and **PI4**) were tested as catalysts in the cycloaddition reaction of CO₂ to epoxides such as styrene oxide, epoxy methyl oleate and limonene oxide.

Typically, the synthesis of organic cyclic carbonates from large molecules needs high carbon dioxide pressures (10-50 atm) and temperatures from 80 to 140°C.² Here we report the conversion of CO₂ to cyclic carbonates from steric hindered substrates like MOE and LO using novel heterogeneous catalysts at milder conditions than the previously reported ones: 5-7bar and 100-120°C, without solvent, with relationships epoxide/metal of 1500 and in the presence of TBAB as base.

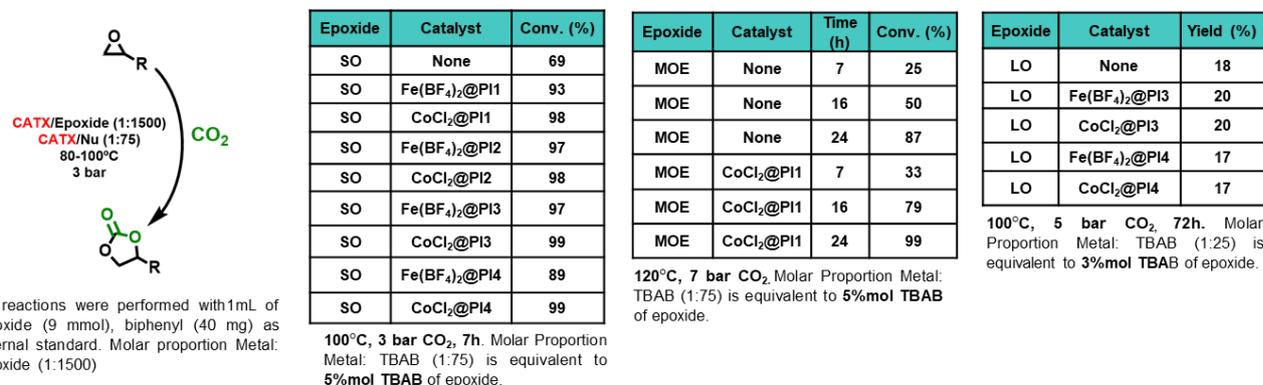


Figure 4. Cycloaddition of CO₂ to styrene oxide (SO), methyl oleate epoxide (MOE) and limonene oxide (LO)

We found that following the above-described protocol, the developed polyimine metal complexes resulted very efficient catalysts with conversions between 89% and 99% in only 7h and 3bar PCO₂ for SO, with the formation of the cyclic carbonates as unique products. All polymers showed good recyclability up to 5 cycles, with turnover numbers (TON) higher than 1400.

Moreover, some of these catalysts showed also conversions between 79% and 99% at only 7bar PCO₂, 120°C after 16-24h, for the more sterically hindered epoxide MOE, with the formation of the cyclic carbonates as unique products.

These catalysts are currently being tested in the conversion of LO to the corresponding cyclic carbonates, where the yields obtained are still very modest under the conditions tested so far.

References

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