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Activation of carbon dioxide mediated by organometallic complexes derived from earth-abundant metals.

Activación de dióxido de carbono mediada por complejos organometálicos derivados de metales abundantes en la tierra.

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January 2024

UNIVERSITAT DE BARCELONA
B:KC Barcelona Knowledge Campus
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Me gustaría agradecer a mi tutor, José Luis Núñez. Por la gran paciencia que ha tenido y todo el tiempo que ha dedicado a este trabajo.

Agradecer a mi madre por sus consejos y apoyo en cada decisión a lo largo de esta etapa.

Para Arnau y Mireia.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

The sustainable development goals are a well-established objectives to achieve sustainability and health at all levels from the earth biosphere to the local community. The primary objective is to guarantee that all of us are able to enjoy peace and prosperity not only now but also in the future.

On 2015 a crucial reflection was made at the United Nations organisation (UN) referring the degree of achievement of these objectives and their maintaining. This resulted in the creation of the 2030 Agenda for Humanity and that included the 17 Substantiable Development Goals (SDG) – https://sdgs.un.org/goals – which encompass the social, economic and environmental challenges that guide the development of human beings under the laws of sustainability.

The research on the catalytic conversion of carbon dioxide has allowed not only to take advantage on a waste resource that exists in large quantities on our planet, but also has provided an alternative and sustainable source of raw materials that can replace, for example, the crude oil that is widely used in the chemical industry.

Furthermore, the use of earth-abundant metals catalysts instead of the noble-metal ones is the key-enabling condition for solving the environmental concerned problems. The noble metals are currently considered as Critical Raw Materials by the European Union due to their low abundance, high market value and also the geostrategic dependence they create on those countries where the deposits of these metals are located.

This report can help achieve the SDG by providing understanding and useful knowledge applicable to four SDG: 7. Affordable and clean energy; 9. Industry, Innovation and infrastructure; 11. Sustainable cities and communities and 13. Climate action.


7
AFFORDABLE AND
CLEAN ENERGY


9
INDUSTRY, INNOVATION
AND INFRASTRUCTURE


11
SUSTAINABLE CITIES
AND COMMUNITIES


13
CLIMATE
ACTION

CONTENTS

1. SUMMARY

The formation of carbonates through the reaction between carbon dioxide and an epoxide is a process that has attracted special attention because it allows the use of a gas that is present in moderate concentrations in the atmosphere to transform it into useful raw materials for the industry. However, under standard conditions, this reaction does not take place and requires the presence of a catalyst.

Until today, this catalytic process has been carried out using catalysts based on noble metals as the metallic centre. In the last decade, the need to replace these metals due to their toxicity and the environmental impact they generate has led to the search for more sustainable alternatives with promising results comparable to the noble metal catalysts.

The optimal reaction conditions, such as time, temperature, CO_2 pressure and the potential need for a co-catalyst to improve the catalyst's activity will be studied for eight 3-d metals from the first-raw. Additionally, the type of catalyst and ligand nature involved in this transformation will be evaluated for each metal to determine which shows best results.

Keywords: Catalysis, earth-abundant metals, catalyst, epoxide ring-opening, CO_2 activation.

2. RESUM

La formació de carbonats mitjançant la reacció entre diòxid de carboni i un epòxid és un procés que ha despertat especial atenció ja que permet aprofitar un gas que esta en concentracions massa elevades a l'atmosfera i transformar-lo en productes de partida útils en l'industria. Però en condicions estàndards aquesta reacció no té lloc i requereix de la presència d'un catalitzador.

Fins a dia d'avui, aquest procés catalític s'ha dut a terme mitjançant catalitzadors basats en metalls nobles com a centre metàl·lic. En aquesta ultima dècada, la necessitat de substituir aquests metalls degut a la seva toxicitat i l'impacte mediambiental que generen, ha portat a la recerca d'alternatives més sostenibles i amb resultats prometedors equiparables als catalitzadors amb metalls nobles.

S'estudiarà, per a vuit metalls 3-d de la primera fila, les condicions òptimes de reacció com ara el temps, la temperatura, la pressió de CO2 i si es requereix la presència d'un co-catalitzador per a millorar l'activitat del catalitzador. També s'avaluarà quin es el lligand i tipus de catalitzador que presenta millors resultats per a cada metall.

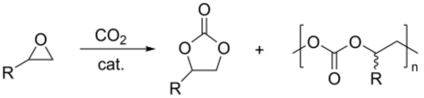
Paraules clau: Catàlisi, metalls abundants, catalitzadors, obertura d'epòxid, activació de CO_2.

3. INTRODUCTION

Over the last century, the concentration of carbon dioxide on the planet has been rising and has reached the point where it has become a problem. Today CO_2 is the major contributor for many environmental problems such as the global warming or the greenhouse effect.

Driven by the idea of reducing this greenhouse-gas emissions through a chemical process, the catalytic conversion of carbon dioxide has awoken interest within the scientific community and specially in those seeking to provide a sustainable alternative source of raw materials that can replace the costly petrochemical feedstocks currently used in industry for the production of polycarbonates, electrolytes for batteries, aprotic polar solvents or fuel additives.

The reaction between carbon dioxide and an epoxide (Scheme 1) is particularly interesting due to the nature of this gas. Apart from being a 100% atom economical reaction, CO_2 is non-flammable and harmless which makes it easy to store and its consideration of a waste effluent resource available in almost an infinite amount in the atmosphere is turning it into a promising prospect. With this reaction, two products are obtained: cyclic carbonates which is the thermodynamic product and polycarbonates which is the kinetic one (Scheme 1). Cyclic carbonates are of a broad application in nowadays industry. The application of these cyclic carbonates encompasses the use as electrolytes in Li-ion batteries because of their high dielectric constant. Additionally, they function as aprotic solvents, replacing traditional solvents such as DMSO, DMF, DMAP, and acetonitrile since they violate European REACH regulations[1]. These materials hold significant importance in engineering applications as plastic precursors in the plastic industry and polymer products, cosmetics, adhesives, fuel additives and fine chemicals.[2]



Scheme 1: Catalytic reaction between an epoxide and carbon dioxide.

However, the fact that carbon dioxide is the most oxidated form of carbon results in an inertness that makes it impossible to reduce the kinetic barrier of breaking the C=O bonds under mild conditions and here is where catalysis becomes the cornerstone for the formation of this carbonates.

CO_2 exists as lineal molecule in its lowest energy state. In this state, the carbon atom exhibits electrophilic characteristics while the oxygen atom is nucleophilic. Carbon dioxide is highly regarded as an efficient C-1 building block due to its abundance, low cost, non-flammability, accessibility, and non-toxic nature. Despite being inert from a thermodynamic and kinetic standpoint, CO_2 demands a high-energy source, either in the form of energy-rich reactants/substrates or through heat, light, or electricity, for activation and meaningful utilisation. Numerous catalytic technologies (biocatalysis, electrocatalysis or photocatalysis) are known for effectively utilising CO_2 to generate value-added products. But some of these catalytic processes face challenges such as the high cost of catalysts requiring frequent modifications, less efficiency in yield, and decreased catalytic performance in practical applications.

Regardless of the extensive research conducted in this field, there is still incertitude when it comes to production cost and the development of greener reaction conditions that persist, prompting further investigations. The cycloaddition of CO_2 and epoxides has been explored in the presence of some well-established catalysts, including polymers, metal-organic frameworks, ionic liquids, metal-based catalysts, Schiff-bases and metal oxides. The catalytic activity of these catalysts has been studied and reviewed under the influence of various reaction parameters.

Catalytic reactions involving CO_2 with Earth-abundant metals hold a prominent position in catalysis due to their reported high catalytic performance and product selectivity under mild reaction conditions and compared to other metals.[3] This catalytic reaction has experienced significant and continuous expansion since ground-breaking work by Inoue in 1969 using diethylzinc and water to yield CO_2 copolymer. Earth-abundant metals, for example Aluminium, Zinc, Cobalt, Copper, and other transition metals, have been extensively researched due to their environmental compatibility[4]. These metals are more cost-effective and readily available compared to noble metals, as they can be easily extracted from the Earth's crust.[4] Certain Earth-abundant first-row transition metals exhibit noteworthy catalytic activities in organic transformations due to their adjustable properties and distinctive d-electron configuration[5].

3.1. PLATINUM, PALLADIUM AND RHODIUM AS CATALYSTS

Despite the environmental footprint Platinum, Palladium and Rhodium leave on our planet, at present they still are the most widely used in almost all fine organic synthesis. Five decades of research in precious metal catalysis have established a consistent chemistry, typically relying on two-electron changes between diamagnetic oxidation states. This significant influence of noble metals in catalysis is exemplified, for example, by the extensive application of palladium in catalysis regarding the production of pharmaceuticals and electronic materials, a recognition underscored by the Nobel Prize in 2010.[4]

On the one hand, one of the principal problems is the toxicity of these metals when they come in contact with the human organism.[6] It is true that whereas the metallic state of these elements is inert, some salts of these three metals are highly irritating and a health hazard, promoting the developing of several chronical diseases.

On the other hand, the high cost of these noble metals is an important consideration that is hard to deny.[4] The inflated price of these precious metals is a direct result of the low abundance we find in the earth's crust natural deposits (Figure 1).

3.2. EARTH-ABUNDANT METALS ALTERNATIVE

Recently there has been a revived focus in the challenging task of replacing the widely recognised noble metals catalysts with some 3d metals analogues that are able to achieve or surpass the activity and selectivity demonstrated by the precious metals.

The implementation of earth-abundant metals as catalyst has raised significant results combining abundance, low toxicity, and cost with extremely high activity obtaining surprising reaction rates, selectivities and yields. However, it is worth noting that 3d metals are known for undergoing facile one electron oxidation state changes frequently associated to spin state complexity, uncontrolled reactions with dioxygen, and facile ligand redistribution.[4]

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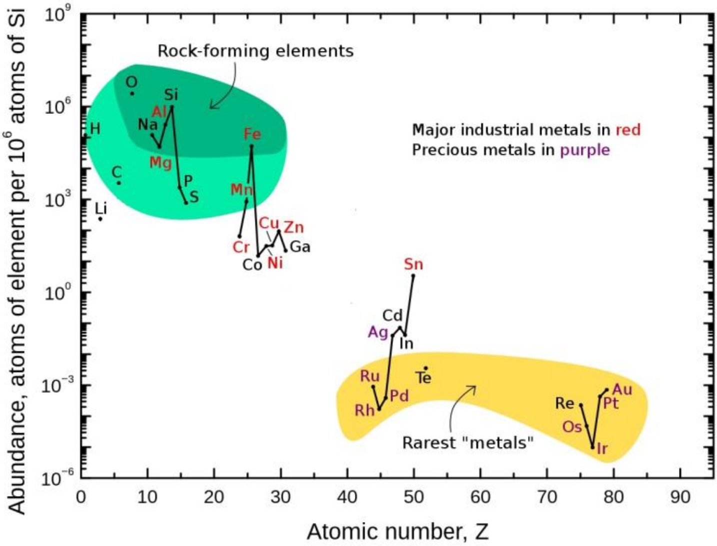


Figure 1: Abundace of elements in Earth's crust

4. OBJECTIVES

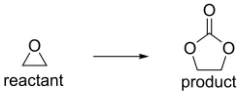
The main objective of this work is, through bibliographic research, to compile the most recent state of the art about the catalytic conversion and activation of carbon dioxide. To this end, the research will be focused on the reaction between carbon dioxide and an epoxide with a number of earth-abundant metal-based catalysts.

A total of eight metals (i.e. Aluminium, Zinc, Copper, Nickel, Cobalt, Iron, Manganese and Chromium) will be studied. For all of them, emphasis will be put on the variety of ligands that have been used for this conversion over the years and whether the type of ligand, the reaction conditions (temperature, time, CO_2 pressure, etc.) and the stereochemistry are determining factors to enhance the overall performance.

5. METHODS

The bibliographic information in this work has been compiled using the databased SciFinder^n.

The research started with a first general search of the reaction between the ethylene oxide and carbon dioxide to form ethylene carbonate (Scheme 2) in order to obtain the volume of articles published within this reaction.



Scheme 2: Reaction between ethylene oxide and carbon dioxide.

There was a total of 641 articles published between 1999 and now, including articles that used labelled ^{13}C and also stereoselective transformations due to the use of the appropriate combination of ligand and substrate.

Next, the “Advanced Search” allowed to accurate the search by adding two “Advanced Search Field”, both of them categorised as “Abstract/Keyword”:

- The name of the metal, for example “Zinc”.
- The word “catalysis”.

On the left side of the webpage, the "Structure Match" default field was changed to "Substructure". This change allowed to include in the research all articles that use both ethylene epoxide and other terminal epoxides.

The procedure is followed equally for each metal.

Finally, the articles that are of interest were stored in EndNote, a management software package that is used to manage bibliographies and references when writing essays, reports, and articles. A total of 129 articles were compiled, published from 1999 until nowadays (Figure 2). Some articles focused exclusively on one metal whether others presented more than one metal (Figure 3).

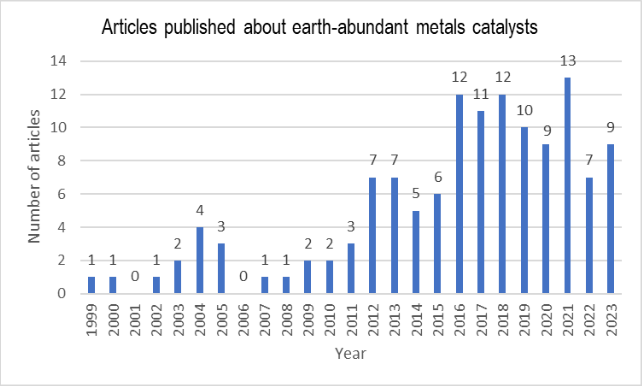


Figure 2: Compilation of articles published about earth-abundant metals catalysts.

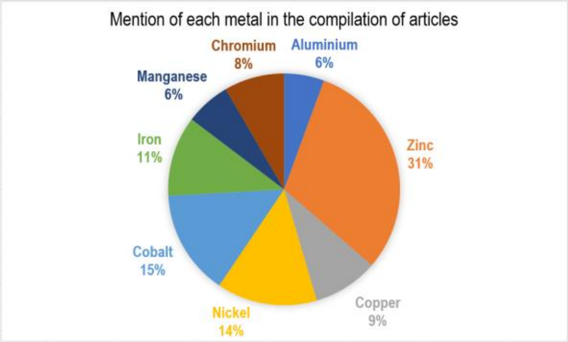


Figure 3: Mention of each metal on the compilation of articles published about earth-abundant metals.

6. RESULTS AND DISCUSSION

6.1. Aluminum

Aluminium stands out as one of the most abundant metals found in the Earth's crust.[1] Its cost-effectiveness is an advantage worth considering that makes aluminium-based catalysts suitable for a diverse range of applications.

Researchers have extensively explored the cycloaddition reaction of epoxides and carbon dioxide that leads the formation of carbonates. Notably, aluminium complexes have demonstrated remarkable catalytic activities at mild conditions whether it comes to the fixation of CO_2. This section broadly categorises and brings into focus the aluminium-based metal complexes, examining the incorporation of various ligand systems with the aluminium as the metal centre.

Xiao Wu *et al.*[7] reported the use of a bimetallic aluminium(salphen) complex (Figure 4) which was synthesised using the commercial product 1,2,4,5-benzenetetramine tetrahydrochloride making it react with 3,5-di-*tert*-butylsalicylaldehyde and a first salphen ligand was obtained. Next, it was treated with diethylaluminium chloride (under reflux conditions) and the bimetallic aluminium(salphen) was obtained. This bimetallic catalyst was used in the reaction of carbon dioxide and styrene oxide which was performed at 25 ºC and 1 bar CO_2 pressure (Table 1, entries 1 and 2). Additionally, tetrabutylammonium bromide (TBAB) was used as a co-catalyst to improve the activity of the aluminium complex. Under these conditions, a 96% of conversion of the initial styrene oxide was achieved despite the complex initially was not fully dissolved in the reaction mixture. To further, the reaction was carried out with an internal epoxide, the 1-phenylpropylene oxide was reacted at 50 ºC and 10 bar CO_2 pressure with a 77% of conversion and 54% yield (Table 1, entries 1 and 2).

In 2016 Castro-Osma *et al.*[8] reported the synthesis of aluminium salphen complexes (Figure 5) that exhibited impressive catalytic efficacy in synthesising cyclic carbonates from various epoxides and carbon dioxide. To obtain this complex, aluminium triethoxide was reacted with 4-(diethylamino)salicylaldehyde. The aluminium complex was studied within the reaction of dodecane oxide as the substrate at 25 ºC and 1 bar CO_2 pressure. For the purpose of evaluating the influence of the reaction time in the activity of the catalyst the reaction was made in three reaction times (Table 1, entry 3) and it was observed that, while the yield remained the same, as longer the reaction time was, higher conversions were obtained.

Table 1: Conditions for the synthesis of cyclic carbonates using aluminium salphen complexes.

Entry	Catalyst	Substrate	Co-cat.	Conv. (%)	Yield(%)
1	Figure 4	Styrene oxide	TBAB	96	–
2	Figure 4	1-phenylpropylene oxide	TBAB	77	54
3	Figure 5	Dodecene oxide	TBAB	45,85,100[a]	90

(a) Determined after 3, 6 and 24h.

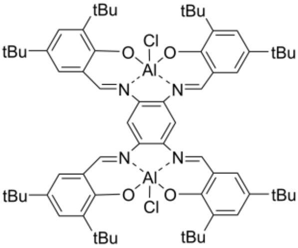


Figure 4: Bimetallic aluminium(salphen) complex

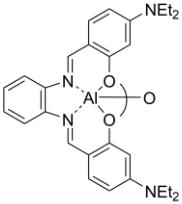
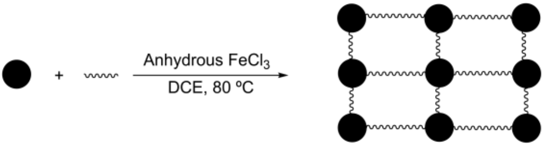
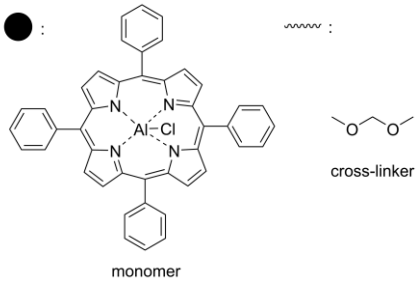


Figure 5: Aluminium-based salphen complex

Through a Friedel-Crafts alkylation, Yaju Chen *et al.* [9] were able to synthesise a metalloporphyrin-based hyper-crosslinked polymers (M-HCPs) using a commercial metalloporphyrin as raw material (Scheme 3). Al-HCP exhibited remarkable catalytic activity in a solvent-free synthesis of cyclic carbonates from carbon dioxide and epoxides. The conditions this reaction took place in were 40 ºC and 1 MPa CO_2 pressure. A co-catalyst (TBAB) was also needed to ensure the catalyst efficiency. Terminal and internal epoxides were examined to evaluate the substrate's influence on the catalyst activity and it was observed that the catalytic performance is strongly dependent on the structure of the epoxide. For the terminal epoxide, a 99% yield was obtained and quite the opposite for the internal that an 85% yield was obtained.





Scheme 3: Synthesis of the Al metalloporphyrin-based hyper-crosslinked polymer.

Another phenolate complex was studied by Whiteoak *et at.*[10] to improve the ring-opening reaction. The catalyst was obtained by slowly adding $AlMe_3$ to a solution of a ligand precursor, which is the resultant product of reacting 2,4-dichlorophenol and hexamethylene tetramine. Uniquely, tetra-n-butylammonium iodine was used as a co-catalyst. It was reported that under the same conditions, the co-catalyst alone was ineffective and so no conversion of the epoxide was detected. The aluminium phenolate attached to a methyl (Figure 6) showed least effective, in terms of conversion, than the same catalyst attached to a chlorine (Figure 7, compare entries 1 and 2 in Table 2). Also, it was studied the effect of the temperature on the activity of the catalyst, and it was observed that even with lower concentration of catalyst and co-catalyst but higher temperatures a higher conversion rate was obtained (Table 2).

Fiorani *et al*.[11] described an amino-tris(phenolate) (Figure 8) complex and its coupling activity in the carbon dioxide and acyclic terpene oxides reaction. For this synthesis the substrate was 1-methylcyclohexene oxide. The optimal reported conditions for this reaction were 85 ºC and 10 bar CO_2 pressure. Bis(triphenylphosphine)iminium chloride (PPNCl) was used as a nucleophile additive that has shown to improve the overall kinetics of the reaction. Was found that as the reaction time increases the yield increases as well, despite the selectivity decreased (Table 3).

Table 2: Comparison of the catalyst activity of Al phenolate catalysts at various temperatures.

Entry	Catalyst	Substrate	Co-cat.	Conv.(a) (%)	Select.(%)
1	Figure 6	Hexene oxide	Bu_4NI	74	>99
2	Figure 7	Hexene oxide	Bu_4NI	91	>99
3	Figure 7	Hexene oxide	Bu_4NI	96(b)	>99

(a) Determined at 30 ºC; (b) Determined at 90 ºC.

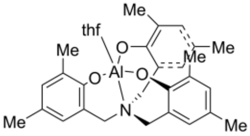


Figure 6: Al(III) amino-phenlate ligand (attached to Me) complex

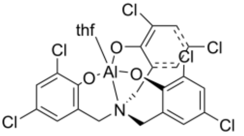


Figure 7: Al(III) amino-phenlate ligand (attached to Cl) complex

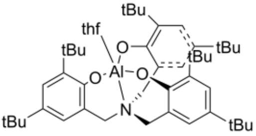


Figure 8: Al(III) amino-phenlate ligand (attached to tBu) complex

Table 3: Comparison of the catalyst activity of Al phenolate catalysts at various reaction times.

Entry	**Catalyst**	**Substrate**	**Co-cat.**	**Yield[a] (%)**	**Select.(%)**	**Time**
1	Figure 8	1-methylcyclohexene oxide	PPNCl	26	>99	24h
2	Figure 8	1-methylcyclohexene oxide	PPNCl	40	>99	48h
3	Figure 8	1-methylcyclohexene oxide	PPNCl	49	>75	66h

Bimetallic aluminium(heteroscorpionate) complexes were synthesised in very high yields by Javier Martínez *et al.*[12] were evaluated as catalysts for the activation of carbon dioxide. The catalyst (Figure 9) was synthesised through an alkene elimination route that involved a reaction of a previously alcohol containing heteroscorpionate precursors. The reaction showed satisfactory results carried out at 50 ºC and 1 bar CO_2 pressure and for this catalyst it was also needed the presence of the co-catalyst TBAB. The epoxide used in this case was styrene oxide and it was observed that maintaining the same conditions but increasing the pressure of CO_2 from 1 bar to 10 bar the conversion increased significantly (Table 4).

Lastly, Ryan E. Baker *et al.*[13] developed a silica-supported unsymmetrical salphen aluminium complex (Figure 10). The metal catalyst was synthesised starting from a suspension of silica-supported amines that were added a salicylaldehyde to afford a salicylaldehyde solution. Afterwards, Et_2AlCl was added in order to obtain the final product. The aluminium catalyst was used to enable the reaction between carbon dioxide and 2-(phenoxymethyl)oxirane that was performed at 50 ºC and 1 bar CO_2. It was also used TBAB as a co-catalyst to improve the activity of the salphen. It was found that doubling the concentration of the catalyst, the reaction conversion barely increased (from 43 to 44%).

Table 4: Comparison of the catalyst activity of a bimetallic Al heteroscorpionate catalyst at various CO_2 pressures.

Entry	Catalyst	Substrate	Co-cat.	Conv. (%)	Yield(%)	CO_2 pressure
1	Figure 9	Styrene oxide	TBAB	96	74	1 Bar
2	Figure 9	Styrene oxide	TBAB	100	85	10 Bar

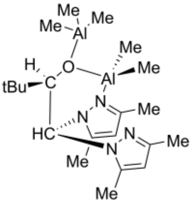


Figure 9: Bimetallic aluminium(heteroscorpionate) complex

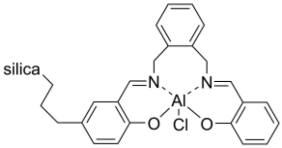


Figure 10: Silica-supported unsymmetrical salphen aluminium complex.

6.2. Zinc

Zinc metal, in general, exhibits qualities of being non-toxic, cost-effective, and resistant to oxidation. Recently, there has been significant interest in zinc-based complexes among catalytic systems for CO_2 fixation reactions. This interest is attributed to the abundance, Lewis acidic nature, and structurally tunable properties of zinc. [14] These metal-based catalysts offer advantages such as easy synthesis, the ability to coordinate with a wide range of ligand skeletons, and thermal stability.

Zinc-based catalysts have demonstrated catalytic activity in the CO_2 fixation reaction with relatively low catalyst loading, albeit under moderately elevated pressure and temperature conditions. Some noteworthy reports highlight catalysts containing both Lewis acidic and nucleophilic groups, eliminating the need for an external co-catalyst to achieve quantitative yields.

As an example, Chihiro Maeda *et al.*[15] reported bifunctional metalloporphyrin catalyst which the metal centre and Br^- ion act as a Lewis acid and nucleophile respectively (Figure 11).

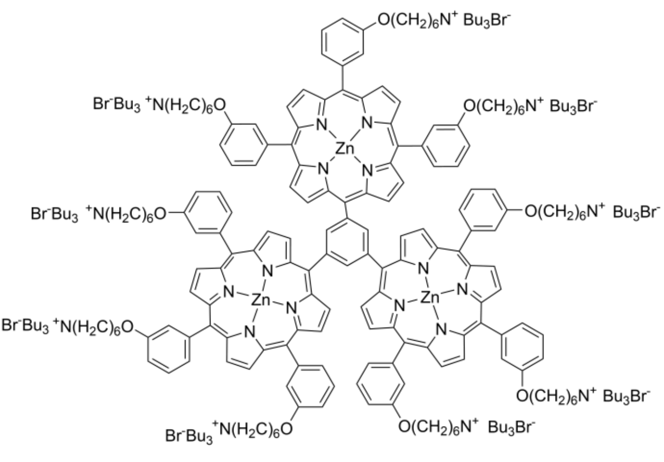


Figure 11: Bifunctional Zn metalloporphyrin catalyst

The catalyst was synthesised by way of a treatment of a porphyrin previously synthesised with 1,3,5-*tris*(trimethylstannly) benzene and afterwards a zinc (II) metalation was performed in order to obtain the final product. The epoxide used was hexene oxide and the reaction was made at 120 ºC and the CO_2 pressure was 1.7 MPa. A second reaction was made maintaining the same conditions but increasing the CO_2 pressure up to 2.5 MPa and it was observed a reduced performance reflected in the isolated yield of the product.

In another attempt by the same group,[15] they reported another bifunctional metalloporphyrin but with quaternary ammonium bromides (that behave as nucleophiles) at the *meta* position of *meso*-phenyl groups (Figure 12). The substrate used for the activation of carbon dioxide was hexene oxide. Reactions performed at 120 ºC and 0.1 MPa CO_2 pressure required only 24 h to achieve the same yield of reactions performed at 1.7 MPa for 120 h, thus confirming the great dependence of the activity of the catalyst with the CO_2 pressure.

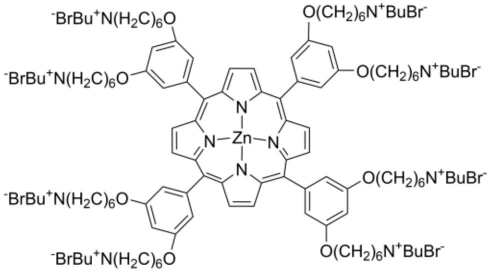


Figure 12: bifunctional metalloporphyrin but with quaternary ammonium bromides at the meta position of meso-phenyl groups.

A novel inorganic material was synthesised and studied by Wei-Dong Yu *et al.*[16] in order to evaluate it in the activation of carbon dioxide. Anderson-type polyoxometalates (POMs) will be the catalysts used in the reaction between epichlorohydrin and carbon dioxide at 70 ºC and 1 atm CO_2 pressure. These catalysts, $\{ZnMo_6(tris\text{-}NH_2)\}$ and $\{ZnMo_6(tris\text{-}CH_3)_2\}$, are synthesised by using a microwave-driven method. Two complexes that differed in one of the substituents were analysed for this reaction. Surprisingly, it was obtained the same yield for both catalysts (99.9%).

A linear tetradentate aminopyridine (N4) ligand composed of diamine and pyridine motifs (Figure 13) was synthesised by Bingyang Wand *et al.*[17] and applied to the coupling of CO_2 with epoxides. Zn-N4 complexes with a halogen anion are suitable for this reaction in absence of a co-catalyst. Also, the synergy between the Lewis acidic centre and the nucleophilic site of the halogen anion provides excellent results under mild and solvent-free conditions. The reaction took place at 80 ºC and the time reaction was 6 hours. A variation in the CO_2 pressure and the epoxide reagent was made in order to evaluate their influence over the catalyst's activity (Table 5).

Table 5: Comparison of the catalyst activity of a tetradentate aminopyridine Al catalyst at various CO_2 pressures and epoxides .

Entry	Catalyst	Substrate	Yield (%)	Select. (%)	CO_2 pressure
1	Figure 13	Epichlorohydrin	98	98	10 Bar
2	Figure 13	Epichlorohydrin	96	94	8 Bar
3	Figure 13	Styrene oxide	95	95	10 Bar

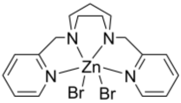


Figure 13: Tetradentate aminopyridine Zn complex

Yanwei Ren *et al.*[18] developed a new type of Lewis-acid bifunctional Zn(salphen) complex with two N-methylhomopiperazine groups as nucleophiles (Figure 14). The structure of the catalyst which includes tertiary amine moiety as the Lewis base and the Zinc in the centre as the Lewis acids stabilises the catalyst and strengthens the recycling performance, allowing the catalyst to be recycled and recovered up to five times without significant loss of the performance. The reaction conditions were 100 ºC and 2 MPa CO_2 pressure. Propylene oxide and epichlorohydrin were used as substrates and there was an increase in the yield when epichlorohydrin was used as reactant. A 92% and 99% yield were obtained respectively.

In 2005, Sik Kim *et al.*[19] published the study of a phosphane adduct of zinc(II) halide, $ZnBr_2(PMe_2Ph)_2$, that demonstrated promising results for the coupling reaction of carbon dioxide and ethylene oxide. This catalyst was synthesised by the reaction of $ZnBr_2$ with two equivalents of the phosphane. The reaction time was 1 hour at 100 ºC and 3.4 MPa CO_2 pressure. An 82% yield was obtained for this synthesis.

A series of Zn_8 metal complexes based on a bis-nucleating salen ligand scaffold (Figure 15) were synthesised by Robert M. Haak *et al.*[20] in order to implement them on the reaction between propylene oxide and carbon dioxide to form cyclic carbonates. The complex $(L1Zn_2)_4$ was synthesised by reacting the ligand L1 with 2 equivalents of $Zn(OAc)_2{\cdot}2H_2O$. The reaction was at 45 ºC, 10 bar CO_2 pressure, and NBu_4I was needed as a co-catalyst. It took 68 hours to achieve 87% yield.

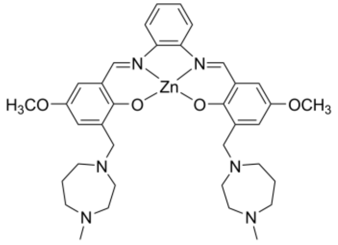


Figure 14: Lewis-acid bifunctional Zn(salphen) complex with two N-methylhomopiperazine groups as nucleophiles.

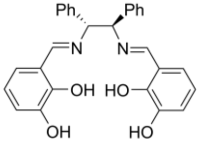


Figure 15: Bis-nucleating salen ligand scaffold (L1).

Ting-Yi Chen *et al.*[21] developed an imine-benzotriazole phenol ligands to afterwards synthesise an air-tolerant, monomeric and homoleptic zinc complex (Figure 16) by reacting two equivalents of the ligand with $ZnEt_2$. This catalyst was used in the reaction between propylene oxide and carbon dioxide. The reaction conditions were 50 ºC, 150 psi CO_2 pressure and a co-catalyst was needed to enhance the catalyst performance, in this case TBAB was used and a 98% conversion rate was obtained.

Metal clusters based on Schiff bases were synthesised by Nicola Kielland *et al.*[22] for the interesting properties they present regarding the cyclo-addition of carbon dioxide to propylene oxide. The reaction was studied at 45 ºC and 10 bar CO_2 pressure. It was observed that the catalyst (Figure 17) studied with electron-donating groups showed promising results (in this case, 100% yield and a selectivity >99% was achieved) due to a higher susceptibility towards exchange of ligated H_2O for the epoxide which has shown to be a vital reaction for the substrate activation process.

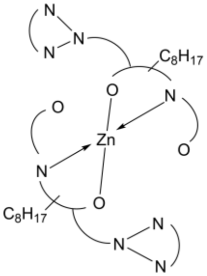


Figure 16: Air-tolerant, monomeric and homoleptic zinc complex.

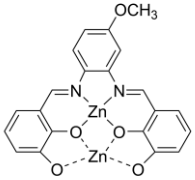


Figure 17: Metal cluster based on Schiff base Zn catalyst

Al-Qaisi *et al.*[23] reported the synthesis of a zinc curcumin (Zn-Cur) complex (Figure 18) for the cyclic carbonate synthesis from CO_2 and epoxides. The catalyst was obtained via one-step synthesis by reacting Zn-Br_2 and Cur/DMSO and afterwards obtained the product by precipitation in chloroform. The reaction was performed at 60 ºC and 1 bar CO_2 pressure. Two different epoxides (epichlorohydrin and styrene oxide) were used to evaluate the activity of the catalyst regarding the substrate. For both epoxides a >99% conversion was obtained.

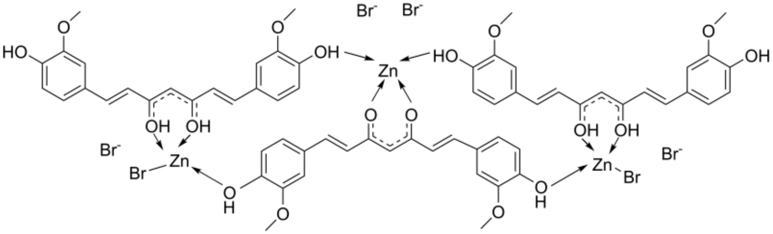


Figure 18: Zinc curcumin complex.

A bifunctional Zn-salen complex with multiple hydrogen bonding donors and protic ammonium (Figure 19) was developed by Lang *et al.*[24] as an efficient catalyst for the formation of cyclic carbonates from carbon dioxide and styrene oxide. The reaction was performed at 120 ºC and 0.1 MPa CO_2 pressure. The multiple hydrogen bonding donors (protoned tertiary ammonium and phenolic hydroxyl group) interact with the epoxide via hydrogen boning interaction facilitating the ring opening of the epoxide by bromide anion. A 98% yield was observed after 24 hours when styrene oxide was used as reactant.

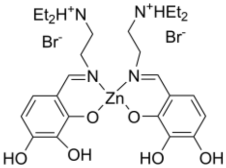


Figure 19: Bifunctional Zn-salen complex with multiple hydrogen bonding donors and protic ammonium.

Jiawei Li *et al.*[25] reported a metal-organic framework (MOF) with high thermal stability and strongly active catalytic properties. The reaction was performed at 50 ºC and 1 atm CO_2 pressure. The best conversions were obtained when epichlorohydrin and the 2-ethenyloxirane were used as substrates. This is due to the presence of electron-withdrawing substituents on both epoxides. These substituents contribute to an enhanced nucleophilic attack by Br^- during the ring opening of the epoxides. However, a slight decrease on the selectivity is observed when 2-vinyloxirane is used as substrate.

Following the same catalyst type, Tran *et al.*[26] also reported an isostructural metal-organic framework (MOF). The crystal structure of this catalyst is a rod-shaped metal clusters ($Zn_3[(-O)_3(-CO_2)_3]$) joined with Zn_2(4,4'-(ethylene-1,2-diyl)bis(2-oxidobenzoate)). This catalyst showed good potential in the reaction between styrene oxide and carbon dioxide. The reaction took place at 80 ºC and 1 atm CO_2 pressure obtaining a 96% conversion, 82% yield and a selectivity of 85%.

Patel *et al.*[27] prepared a zinc metal-organic framework (MOF) (Figure 20). This catalyst, {[Zn(benzene-1,4-dicarboxylic acid)(4-pyridylcarboxaldehyde)]·*x*G}$_n$ (G= lattice guests), was stable, efficient, and reusable in the conversion of epoxide into carbonate. The recycling performance suggests that it can undergo multiples cycles without experiencing reduction in its catalytic activity. The epoxide studied was propylene oxide and the reaction was carried out at 40 ºC and 10 Bar CO_2 pressure. Initially the reaction time was 4.5 h and it was observed that a reduction in the time of reaction did not affect the conversion and neither the selectivity of the reaction.

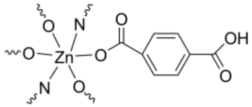


Figure 20: Zinc metal-organic framework

Wolfgang Kleist *et al.*[28] developed a mixed-linked metal-organic framework (MIXMOF) with the general formula Zn_4O(benzene-1,4-dicarboxylate)$_x$(2-aminobenzene-1,4-dicarboxylate)$_{3-x}$. The catalytic reaction between propylene oxide and carbon dioxide took place at 140 ºC and the use of NEt_4Br as a co-catalyst was needed. A 63% yield of propylene carbonate was obtained.

Another interesting approach was the study of Han-Ung Kim *et al.*[29] where two types of metal azolate frameworks (MAFs) were synthesised. These catalysts have uncoordinated nitrogen atoms (N donors) that show high adsorption affinity for carbon dioxide. The two catalysts were used in the reaction of epichlorohydrin with carbon dioxide and the reaction conditions were 80 ºC and 1.2 MPa CO_2 pressure. For both catalyst the selectivity obtained was >99%.

Yi Liu *et al.*[30] developed a zinc bromide-based deep eutectic ionic liquid (DEIL) efficient and stable, for the use the formation of cyclic carbonates from carbon dioxide. To prepare the catalyst ($ZnBr_2 \cdot 2Bu_4PBr$), a one-step heating method was used by mixing $ZnBr_2$ and tetralkylphosphonium bromide (Bu_4PBr) until a homogeneous liquid is formed. To study the efficiency of this ionic liquid it was reacted with two epoxides, ethylene and propylene oxide at 130 ºC and 3 MPa CO_2 pressure. The catalyst showed a higher yield and conversion for the less branched-chain epoxide (Table 6, entries 1 and 2).

Several authors have reported the successful use of ionic liquids to perform this catalytic reaction, Weihua Shen *et al.*[31] prepared an amino-functionalised halide ionic liquid with halogen anions to catalyse the cycloaddition of CO_2 to propylene oxide in absence of solvent. The catalyst, [aminopropyl-3-butyl-imidazolium]Cl/ZnX_2 ([Apbim]Br/$ZnBr_2$) was prepared by reacting N-butyl imidazole and 3-chloropropylammonium chloride and afterwards, $ZnBr_2$ was added. The reaction conditions were 120 ºC and 2 MPa CO_2 pressure and it was obtained a conversion of 99.2% and 99.7% selectivity.

Additionally, Mengshuai Liu *et al.*[32] developed an eutectic-based ionic liquid (IL) catalyst that showed exceptional activity without the need of a co-catalyst and solvent for the conversion of epoxides into cyclic carbonates. The catalyst is synthesised by mixing urea and ZnI_2 to form [urea-Zn]I_2. The reaction took place under the conditions of 120 ºC and 1 MPa CO_2 pressure and both the time of reaction and the epoxide used as substrate were tested for any variation on the catalyst overall performance (Table 6, entries 3 and 4).

Table 6: Comparison of the catalyst activity of Zn catalysts at various CO2 pressures, temperatures, and epoxides.

Entry	Catalyst	Substrate	Conv. (%)	Yield (%)	Select. (%)	CO_2 pressure (MPa)
1(a)	$ZnBr_2·2Bu_4PBr$	Ethylene oxide	98.5	97.5	–	3
2(a)	$ZnBr_2·2Bu_4PBr$	Propylene oxide	95.8	94.8	–	3
3(b)	[urea-Zn]I_2	Propylene oxide	–	95	98	1
4(b)	[urea-Zn]I_2	Epichlorohydrin	–	97	98	1

(a) Reaction temperature = 130 ºC.
(b) Reaction temperature = 120 ºC

Dongwoo Kim *et al.*[33] synthetised a metal-containing ionic liquid (MIL) for the chemical fixation of CO_2 into epoxides. Two polymer-supported Zn-containing imidazolium salts were synthetised, (1-(2-hydroxyethyl)imidazole)$_2$ZnX_2 (X = I or Br) (Figure 21). The reaction with both catalysts was done under the same conditions, 60 ºC and 10 bar CO_2 pressure. For both catalysts the same selectivity was obtained (>99%) but a higher conversion rate (99.9% for the I^- and 62% for the Br^-) is observed with the presence of I^- anions. This is due to the halide ion nucleophilicity ($Br^- < I^-$).

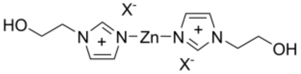


Figure 21: Zn-containing imidazolium salts

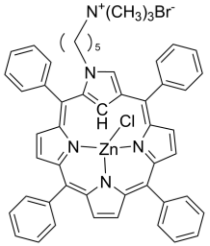


Figure 22: N-confused tetraphenylporphyrin (NCTPP)

Recently, dela Cruz *et al.*[34] reported a zinc N-confused tetraphenylporphyrin (NCTPP) [*sic*] in which the nitrogen was substituted with trimethylammonium bromide (Figure 22). The reaction was performed at 120 ºC, 1 MPa CO_2 pressure, and the presence of TBAB was required to enhance the catalytic efficiency. Epichlorohydrin and glycidol (Figure 23) were used as substrates, and excellent yield were obtained, 96% and 90% respectively. The outstanding synergy between the catalyst and the epichlorohydrin is due to the presence of Cl (electron-withdrawing substituent) that allows the epoxide ring-opening easier and for the glycidol was found to play a double role as a substrate and a catalyst in this reaction due to the presence of the hydroxyl group.

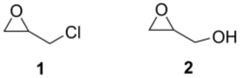


Figure 23: Epichlorohydrin (1) and Glycidol (2).

Another group, Lina Liu *et al.*[35] studied the synthesis of a bifunctional polymer co-incorporated with porphyrin-Zn (PP) for the cycloaddition of dilute CO_2 with epoxides (Figure 24). The reaction was performed at 100 ºC and 1.5 MPa CO_2 pressure. The reaction was studied for two epoxides, propylene oxide and hexene oxide. For the propylene oxide for both yield and selectivity it was obtained a 99%. However, for the hexene oxide it was observed a decrease in the conversion of the epoxide due to the steric hindrance of the substituent that signifies a key factor for affecting the attack of the nucleophile to the epoxide ring.

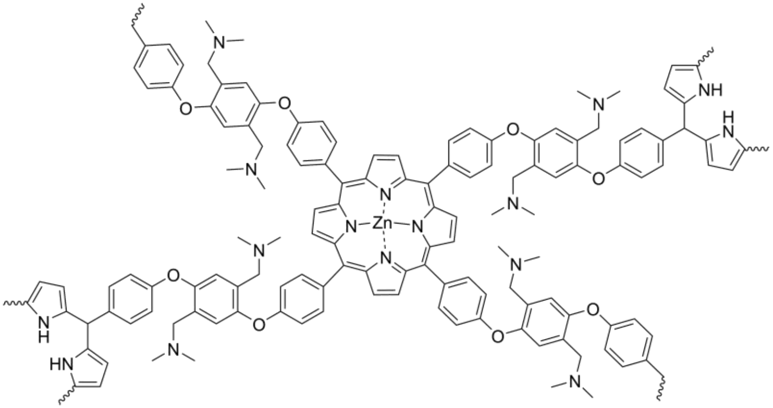


Figure 24: Bifunctional polymer co-incorporated with porphyrin-Zn (PP)

Lastly, for the conversion of CO_2 into cyclic carbonates, Gang Wang *et al.*[36] designed a heterometallic 3d/4d-4f coordination polymer catalyst featuring $[Dy_2Zn_2L_4(OAc)_2(MeOH)_5(H_2O)]$. In this case, reaction was also studied for the two anterior epoxides at 120 ºC, 1 MPa CO2 pressure, propylene oxide and hexene oxide. Also, TBAB was needed as a co-catalyst. The results obtained followed the same trend, for the hexene oxide it was observed a lower yield which was ascribed to the steric effect.

6.3. Copper

Copper, owing to its unique redox properties and versatility, serves as effective catalyst in the transformation of carbon dioxide into valuable cyclic carbonates.

A key advantage of employing copper in this reaction include their abundance, cost-effectiveness, and compatibility with various epoxide substrates. The tunable nature of copper complexes allows for the optimisation of reaction conditions, including temperature, pressure, and solvent, to achieve higher yields and selectivity. Additionally, copper catalysts exhibit promising catalytic activity under mild reaction conditions, minimising consumption and enhancing the overall sustainability of the process.

Research efforts are directed toward the development of novel copper catalysts. This area of study not only contributes to the advancement of green chemistry but also aligns with the broader goal of utilising renewable sources for chemical synthesis, thereby reducing the environmental footprint of industrial processes.

For instance, Bo Zou *et al.*[37] reported a copper-containing coordination polymer, CuL_n (L = (Z)-2-(5-chlorin-2-hydroxybenzylideneamino) acetic acid) (Figure 25) that showed an outstanding catalytic activity for the conversion of atmospheric CO_2 into cyclic carbonates. Hexene oxide was reacted, using TBAB as a co-catalyst, at two different temperatures (35 and 60 ºC) in order to see if the catalytic activity was modified. It was observed that by increasing the temperature, it required less reaction time to achieve a higher yield (92 and 99% respectively).

Another example of polymer-based catalyst is the coordination polymer done by Bhaskaran *et al.*[38] A three-dimensional motif with fused hexagonal rings ($[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]$) was synthesised by reacting copper cyanide to a solution of CH_3OH containing NH_3 and hexamethyleneamine. This catalyst was used in the reaction between propylene oxide and carbon dioxide at room temperature and 1 atm CO_2 pressure and a 95% yield was obtained. The activity of the catalyst was also tested during the first four cycles of reaction and did not show a decline in the catalyst's activity.

Ravishankar G. Kadam *et al.*[39] studied a copper-based intermetallic electride catalyst ($LaCu_{0.67}Si_{1.33}$) in which the copper sites are activated by anionic electrons uniformly dispersed and with low-work function. The reaction took place at 25 ºC, 1 atm CO_2 pressure, and with the presence of TBAB as a co-catalyst to enhance the catalyst activity. Two epoxides (propylene oxide and bromoethylene oxide) were used as reactants to evaluate if the activity of the catalyst depends on the type of substrate. For the propylene oxide a 99% conversion was obtained and, surprisingly, for the bromoethylene oxide only a 65% conversion was obtained.

Yanwei Ren *et al.*[18] developed a new type of Lewis-acid bifunctional Cu(salphen) complex with two N-methylhomopiperazine groups as nucleophiles (Figure 26). This catalyst (in the absence of any co-catalyst) was used to catalyse the reaction of propylene oxide and carbon dioxide at 100 ºC and 1 MPa CO_2 pressure, obtaining a yield of 70%.

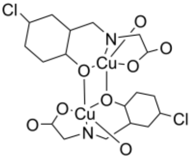


Figure 25: Copper-containing coordination polymer (CuLn)

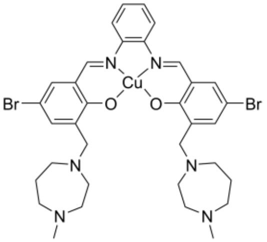


Figure 26: Bifunctional Cu(salphen) complex with two N-methylhomopiperazine groups

In 2020, Zhiying Fan *et al.*[40] published the research on a series of new defect-engineered metal-organic frameworks (DEMOFs) with truncated linkers. L_{Py} (5-(5-carboxypyridin-3-yl)isophtalate) bearing a weaker interacting ligator site is incorporated into the framework of Cu_2(biphenyl-3,3',5,5'-tetracarboxylates) to obtain the catalyst. The reaction was performed with propylene oxide as the substrate at 55 ºC, 2 bar CO_2 pressure and with TBAB as a co-catalyst, obtaining 96% conversion. The catalytic activity of this catalyst comes from a structural characteristic: L_{Py} has defects that are mainly generated since the pyridyl N has a weak ligand-metal interactions.

6.4. Nickel

Nickel catalysts stand out as indispensable tools in catalysis, offering a myriad of advantages across diverse industrial applications. Their versatility allows them to catalyse a broad range of reactions, showcasing adaptability in various chemical transformations. Moreover, nickel's abundance on the Earth crust makes it an economically viable choice for large-scale processes, contributing to overall economic feasibility.

As an environmentally sustainable choice, nickel catalysts often exhibit the capacity for regeneration, prolonging their useful lifespan, aligning with the principles of green chemistry.

The efficient metal-ligand cooperation observed in nickel catalysts enhances the catalytic efficiency and selectivity of these catalysts, positioning them as pivotal contributors to advancing both academic research and industrial processes across a spectrum of chemical reactions and applications.

Guan-Lin Liu *et al.*[41] published a study of Ni(II) species containing hexadentate BiIBTP (benzotriazole iminophenolate) ligand and two phenolate coligands (Figure 27). An internal epoxide (cyclohexene oxide) was used to react with carbon dioxide at 140 ºC and 300 psi CO_2 pressure. It was observed that increasing the reaction time (from 4 to 6 hours) increased the reactant conversion but the selectivity remained the same (>99%) (Table 7, entry 1).

Another approach to phenolates is the research done by Li-Shin Huang *et al.*[42] about a nickel carboxylate complex based on the ^{R}BiIBTP derivatives (bis(benzotriazole iminophenolate)) (Figure 28). For this reaction it was also used the same internal epoxide at 130 ºC and 300 psi CO_2 pressure. The same tendency that the last 2 reports is observed here, as the reaction time increases (from 16 to 24 hours), the conversion also increases while the selectivity remains constant (Table 7, entry 2).

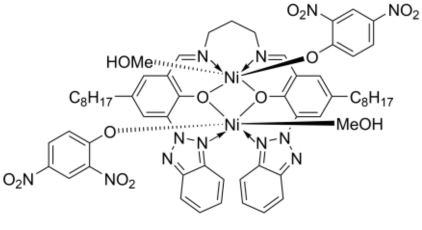


Figure 27: Ni(II) catalyst containing hexadentate benzotriazole iminophenolate ligand and two phenolate coligands.

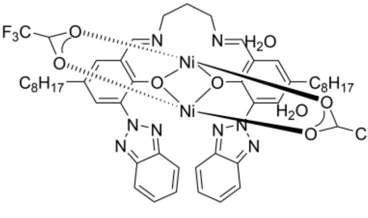


Figure 28: Nickel carboxylate complex based on bis(benzotriazole iminophenolate) derivates.

Also, Tsai *et al.*[43] reported a bimetallic bis(benzotriazole iminophenolate) (BiIBTP) nickel complex containing biocompatible mandelate or *tert*-butoxycarbonyl (Boc)-protected glycinate co-ligands (Figure 29). The same internal epoxide mentioned before was used for this reaction at 130 ºC and 20.7 bar CO_2 pressure. In this case, the reaction time was not evaluated and the reaction time was 6h (Table 7, entry 3).

Yu-Chia Su *et al.*[44] also developed a nickel complex bearing a new type of pyrazolyl based diamine-bisphenolate ligand (Figure 30). In this report, like the ones mentioned before, the same research steps are followed. The internal epoxide reacted at 140 ºC for 6 h. A variation in the CO_2 pressure is made in order to evaluate if the activity of the catalyst depends on the pressure. It is observed that an increase of the CO_2 pressure causes an increase in the conversion with no changes in the selectivity (Table 7, entry 4).

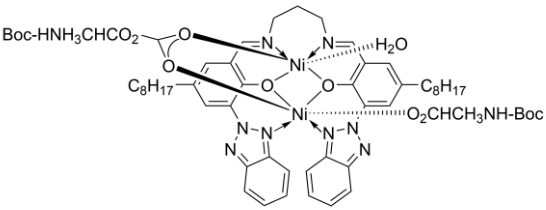


Figure 29: Bimetallic bis(benzotriazole iminophenolate) nickel complex

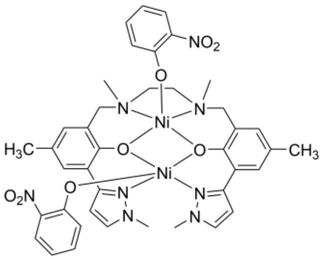


Figure 30: Ni complex bearing a pyrazolyl based diamine bisphenolate ligand

Table 7: Comparison of the activity of different Ni catalyst.

Entry	Catalyst	Substrate	Conv. (%)	Select.(%)
1	Figure 27	Cyclohexene oxide	58, 71 (4 and 6h)	>99
2	Figure 28	Cyclohexene oxide	81, 91 (16 and 24h)	>99
3	Figure 29	Cyclohexene oxide	81 (6h)	>99
4	Figure 30	Cyclohexene oxide	77(6h)	>99

Previously mentioned, dela Cruz *et al.*[34] also reported a nickel N-confused tetraphenylporphyrin (NCTPP) in which the nitrogen was substituted with trimethylammonium bromide (Figure 31). The reaction was performed with epichlorohydrin at 110 ºC, 1.5 MPa CO_2 pressure, and TBAB as a co-catalyst. Two catalysts were evaluated in order to determine the optimum catalyst under these conditions.

Tran *et al.*[26] referred previously in this work for the synthesis of metal-organic frameworks using various metals as the metal centre. The nickel catalyst was used for the reaction between styrene oxide and carbon dioxide at 80 ºC and 1 atm CO_2 pressure. It showed that when the time of reaction was increased (from 4 to 6 hours), the conversion rate also increased (from 35 to 61%).

In 2016, Zhen Zhou *et al.*[45] published a study of a Ni(II)-based coordinated framework having large pores that can accommodate organic molecules and absorb gas, and incorporate a tetraphenylethylene moiety as the four-point connected node. Two catalyst (Ni-1 and Ni-2) (Figure 32) were used in the reaction of propylene oxide and carbon dioxide at 35 ºC, 1 atm CO_2 and TBAB as a co-catalyst. Both catalysts have the same number of catalytic sites, Ni-2 showed a higher activity than Ni-1, displaying size-selective catalytic performance.

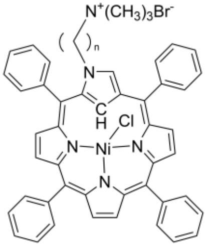


Figure 31: N-confused tetraphenylporphyrin (NCTPP)

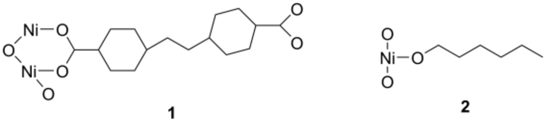


Figure 32: Ni(II)-based coordinated framework Ni-1 (1) and Ni-2 (2).

Recently, Xiuling Zhang *et al.*[46] reported a new type of coordinated polymer formed by organic ligands connecting metal nodes. The catalyst, $[Ni(Htzbt)(bpy)]_n$(Htzbt = 2-(1H-1,2,4triazol-1-yl)benzene-1,3,5-tricarboxylic acid and bpy = 4,4’- Bipyridine), has been used for the synthesis of cyclic carbonates from butylene oxide. The reaction took place at 60 ºC, 1 atm CO_2 pressure and using TBAB as the co-catalyst. A 65.5% yield was obtained.

Ting-Yu Lee et al.[47] studied the epoxide coupling of nickel acetates based on carbazolide-bis(NHC) (NHC = N-heterocyclic carbene) (Figure 33). Two catalysts were studied for the reaction between an internal epoxide (cyclohexene oxide) and carbon dioxide at 170 ºC and 500 psi CO_2 pressure. A 99% conversion was obtained and a selectivity of >99%.

Lastly, Muthuramalingam *et al.*[48] reported a novel nickel(II) complex (Figure 34) for the conversion of atmospheric CO_2 into organic cyclic carbonates. Propylene oxide was used as substrate in the presence of a co-catalyst (TBAB) at 25 ºC and 1 atm CO_2 pressure. Under these conditions, in general poor yields were obtained (<90%).

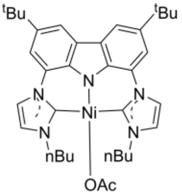


Figure 33: Carbazolide-bis(NHC) complex.

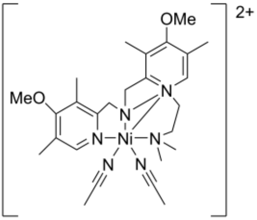


Figure 34: Novel Nickel(II) catalyst.

6.5. Cobalt

Many industries prefer non-cytotoxic metals with minimal environmental impact, such as cobalt. Metals like cobalt exhibit multiple valances, states, and ferromagnetic properties which have gained significant attention for their enhanced efficiency in CO_2 fixation. Consequently, there is a high demand for cobalt in metal-based catalysis due to its economic and environmental advantages.

Cobalt, as a first-row transition metal, readily facilitates ligand-localised reduction owing to its multiple oxidation states. Moreover, cobalt complexes exhibit a range of cobalt metal states from 0 to +3, and the attached auxiliary ligand enhances the chemical stability of the resulting complex, making gram-scale synthesis relatively straightforward. Notably, diverse array of cobalt complexes has been employed as catalysts for the cycloaddition of epoxides and CO_2, forming cyclic carbonates under both harsh and mild reaction conditions.

Ahmet Kilic *et al.* [49] reported the synthesis of a cobaloxime (1) (Figure 35) and organocobaloxime (2) (Figure 36) complexes used in the synthesis of epichlorohydrin to form cyclic carbonates. The reaction took place at 100 ºC and 1.6 MPa CO_2 pressure. For both catalysts it was observed a high catalytic efficiency due to the high catalytic solubility of them in the epoxide.

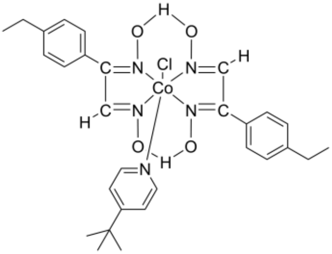


Figure 35: Cobaloxime (1)

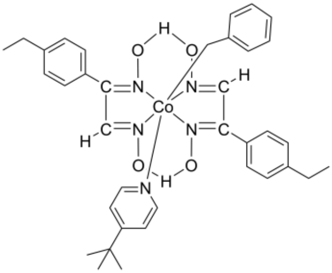


Figure 36: Organocobaloxime (2)

Previously referred in, Xiuling Zhang *et al.*[46] also studied the catalyst with cobalt as the metallic centre. The reaction took place at 60 ºC, 1 atm CO_2 pressure and using TBAB as the co-catalyst. A higher yield was obtained compared to the Ni-catalyst (79.1%).

A series of metalloporphyrin-based polymers were prepared by Yaju Cen *et al.*[50] for diverse metals. For the Cobalt-based catalyst, the epoxide used as reactant was propylene oxide and a worst yield and conversion were obtained compared to the Al-based catalyst. A 24% conversion and 23% yield were obtained.

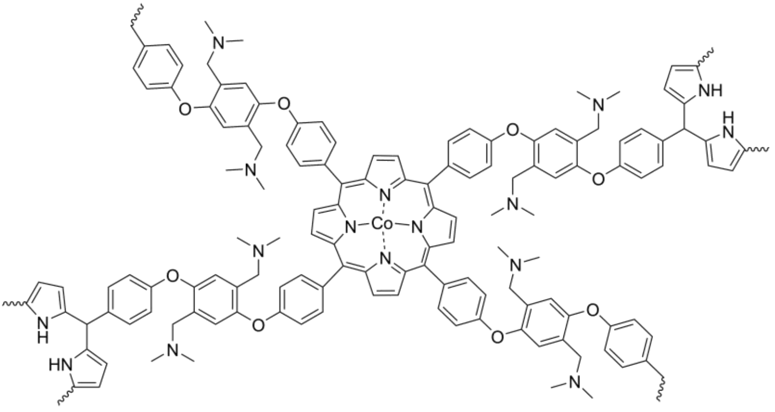


Figure 37: Bifunctional polymer co-incorporated with porphyrin-Co (PP)

Another catalysts synthetised by Lina Liu *et al.*[35] was studied incorporating the Zinc and the Cobalt as the metallic centres. When it comes to the Co-based catalyst (Figure 37), the reaction was at 140 ºC and 3 MPa CO_2 pressure. A yield of 79% was obtained (99% selectivity).

Also, Xu Jiang *et al.*[51] reported a bisimidazole-functionalised porphyrin cobalt(III) complex (Figure 38) that were applied to the activation of carbon dioxide without the need for a co-catalyst. The reaction conditions were 140 ºC and 1 atm CO_2 pressure.

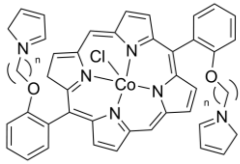


Figure 38: Bismidazole-functionalised porphyrin cobalt(III) complex

Table 8: Comparison of the activity of a bismidazole porphyrin Co(III) complex with different ligands.

Entry	Catalyst	Ligand	Substrate	Yield (%)	Select.(%)
1	Figure 38	n = 4	Propylene oxide	99.1	>99
2	Figure 38	n = 6	Propylene oxide	99.9	>99
3	Figure 38	n = 8	Propylene oxide	99.9	>99

Tsai et al.[43] developed a series of bimetallic nickel and cobalt complexes. The cobalt-based catalyst was used in the synthesis of cyclic carbonates from epoxides. The epoxide used for this synthesis was propylene oxide and a variation on the co-catalyst (n-Bu4NX; X = Cl, Br, I) were made in order to evaluate the performance of the catalyst. It was observed that TBAI is the most effective one due to the better nucleophilicity and leaving group ability of the I^-.

In 2020, a bimetal mixed MOF catalysts study was published by Yuanfeng Wu *et al.*[52] to evaluate the activity of these catalysts under solvothermal conditions as an accelerant for the activation of carbon dioxide reaction. The reaction conditions were 100 ºC and 3 MPa CO_2 pressure. High conversion and yield were obtained (95.4 and 93.3% respectively).

Tran et al.[26] has previously been referred in this work for synthesising a series of metal-organic frameworks (MOFs) with various metals. The cobalt MOF was used in the reaction between styrene oxide and carbon dioxide at 80 ºC and 1 atm. The conversion obtained was a 72% with a selectivity >82%.

Another catalysts are the Co-salen grafted cellulose nanocrystals (Figure 39), developed by Lingling Hu *et al.*[53] in order to use them in the catalytic synthesis of cyclic carbonates. This catalyst (CNC-Co(III)-Salen) was used in the reaction between propylene oxide and carbon dioxide at 25 ºC, 1 MPa and using TBAB as a co-catalyst. The results observed were satisfactory by obtaining a >99% yield. The catalyst's reusability was also tested obtaining surprising results (>99 reusability).

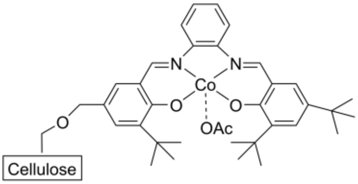


Figure 39: Bifunctional polymer co-incorporated with porphyrin-Co (PP)

6.6. Iron

Iron is the second most abundant metal, following aluminium. There is a significant demand for utilising iron as preferred metal in the synthesis of various materials for diverse applications. Its ability to exhibit multiple valence states and facilitate electron transfer makes it particularly suitable for coupling reactions, showcasing high catalytic activity in synthetic and modern chemistry applications. The oxidation and spin states of iron enable to interact with incoming ligands in iron complexes.

Extensive efforts have been made to chemically fix CO_2 into epoxides using iron as an active metal centre leading to the development of iron-based catalysts. Recognising the advantage of iron, the ongoing research agenda emphasises the creation of new cost-effective environmentally friendly, and reusable catalysts.

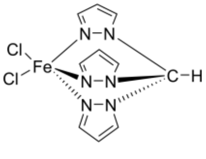


Figure 40: C-scorpionate iron(II) complex

For instance, Ribeiro *et al.*[54] synthetised a C-scorpionate iron(II) complex in a tailor-made ionic liquid (IL) (Figure 40) as a catalyst for the reaction between an epoxide and carbon dioxide. For the same reaction conditions (80 ºC and 8 bar CO_2 pressure). The reaction took place in different ionic liquids and it was observed that the activity of the catalyst improved with the viscosity of the IL since the viscosity affects the mass transfer of the reaction (Table 9).

Table 9: Comparison of the performance of the catalyst in different ionic liquids.

Entry	Ionic liquid	Complex	Substrate	Yield (%)	Select.(%)
1	[emim][N(CN)$_2$]	Figure 40	Propylene oxide	96.7	100
2	[emim]Cl	Figure 40	Propylene oxide	81.6	100
3	[emim][NTf$_2$]	Figure 40	Propylene oxide	72.8	100

A favourable monometallic ionic iron(II) (Figure 41) and iron(III)-n-N_2O_2-ligand (Figure 42) systems were developed by Fuchs *et al.*[55] for the conversion of carbon dioxide into cyclic carbonates. Propylene oxide was used as the substrate at 80 ºC, 50 bar CO_2 pressure and TBAB as a co-catalyst. It was observed that for the iron(III) catalyst, a lower concentration of the catalyst was needed to achieve a grater yield compared to the iron(II) catalyst.

In 2019, Kamphuis *et al.*[56] published the study of a new families of single-component catalysts based on earth-abundant metals. The catalyst studied was a anionic mono(formazanate) iron(III) complex (Figure 43) bearing labile halide ligands. The reaction was performed with propylene and styrene oxides to evaluate the activity of the catalysts within the substrate. A lower conversion for the styrene oxide was observed due to the steric hindrance of the aromatic group.

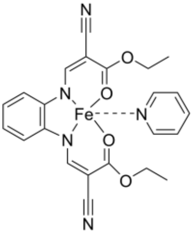


Figure 41: Monometallic iònic iron(II) catalyst.

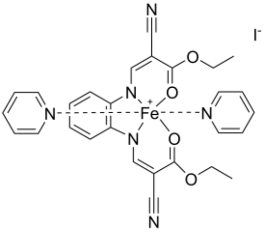


Figure 42: Monometallic iònic iron(III) catalyst.

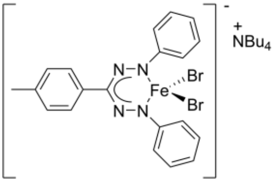


Figure 43: Anionic mono(formazanate) iron(III) complex.

Chandan Kumar Karan and Manish Bhattacharjee[57] synthesised a bimetallic iron-alkali metal complexes of amino acid (serine)-based reduced Schiff base ligand and the heterogeneous version of this catalysts by immobilising it with an anion-exchange resin (Figure 44). The conditions of the reaction for both catalysts were 27 ºC and 1 bar CO_2 pressure. For both catalysts was obtained almost the same conversion.

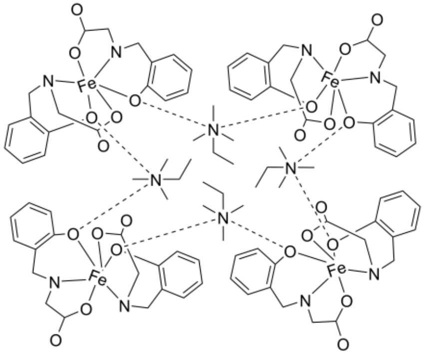


Figure 44: Bimetallic iron-alkali metal complex immobilised with an anion-exchange resin.

Fe(III) carbamates were employed by Giulio Bresciani *et al.*[58] in solvent-free conditions to activate carbon dioxide and form cyclic carbonates. The catalyst, $Fe(O_2CNEt_2)_3$, was used under mild conditions (25 ºC and 1 bar CO_2 pressure). When propylene oxide was used as a catalyst, remarkable results were obtained: >99% conversion, 90% yield and >99% selectivity.

Through a Friedel-Crafts reaction between lignin and metalloporphyrin, Kunpeng Song *et al.*[59] developed a lignin-based porous organic polymer (P-(L-FeTPP)). This catalyst was used when propylene and butylene oxide were used as substrates and it was obtained a 99.6 and 99% yield respectively.

6.7. Manganese

The use of manganese catalysts is emerging as practical substitute for noble-metal catalysts, primarily due to the abundance of this metal and the environmental concerns associated with precious metals and manganese offers an alternative for catalytic applications. Its widespread availability makes it a cost-effective and environmentally friendly choice compared to noble metals. Additionally, it is less toxic and contributes to the development of greener and more sustainable catalytic processes.

The advantages of using manganese catalysts in this ring-opening reaction include their cost-effectiveness, the reduction of the environmental impact compared to noble metals. In short, the development of manganese-based catalysts for this application aligns with the broader goal of designing sustainable processes for chemical synthesis, especially those involving the utilisation of carbon dioxide as a feedstock.

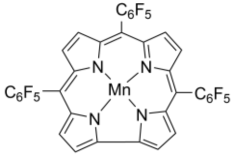


Figure 45: Manganese corrole complex

Maximilian Tiffer *et al.*[60] studied the cooperative catalytic activity a metal corrole complex (Figure 45) for the activation of carbon dioxide. Three epoxides, propylene oxide, styrene oxide and epichlorohydrin, were reacted with carbon dioxide to evaluate the performance of the catalyst when changing the substrate (Table 10).

Table 10: Comparison of the activity of a catalyst with various substates.

Entry	**Catalyst**	**Substrate**	**Conv. (%)**	**Yield (%)**
1	Figure 45	Styrene oxide	>95%	94%
2	Figure 45	Propylene oxide	>95%	88%
3	Figure 45	Epichlorohydrin	>89%	88%

A manganese metalloporphyrin was synthesised by Lucas D. Dias *et al.*[61] to catalyse the reaction between styrene oxide and carbon dioxide. The reaction was performed at 80 ºC and 10 bar CO_2 pressure. Two catalysts (Figure 46 and Figure 47) were used to determine if the activity of the catalyst changes by changing its substituents. When Cl was used as substituent instead of F, an higher conversion of the epoxide is observed.

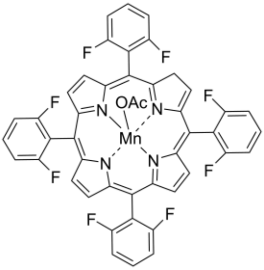


Figure 46: Manganese metalloporphyrin catalyst with F as the substituent.

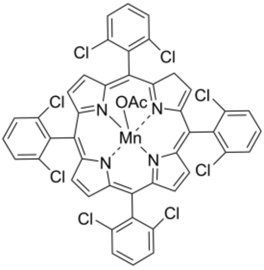


Figure 47: Manganese metalloporphyrin catalyst with Cl as the substituent.

In 2008, Fabian Jutz *et al.*[62] developed a homogeneous and immobilised manganese-salen complex (Figure 48) to test as catalysts in the formation of carbonates. Styrene oxide was used as epoxide at 140 ºC. It was observed that when the immobilised catalyst was used, a higher yield was obtained.

Figure 48: Immobilised manganese-salen complex

Lastly, Shan Cheng *et al.*[63] published the study of a three-dimensional porous Mn(II)-based metal-organic framework (MOF), [Mn4(2,6-di(2’,5’-dicarboxylphenyl)pyridine)]. This catalyst was implemented in the reaction between an epoxide and carbon dioxide. Two epoxides were used, propylene oxide and epichlorohydrin, at 80 ºC and using TBAB as a co-catalyst. It was observed that a higher yield was obtained when using epichlorohydrin.

6.8. Chromium

Chromium-based catalysts play a pivotal role in catalysis, finding extensive use in the industrial synthesis of cyclic carbonates.

Despite the industrial efficacy of these catalysts, ongoing discussions in the academic sphere revolve around issues such as the precise configuration of chromium species, the oxidation states of the chromium centre, the influence of the co-catalyst and ligands, and the fundamental catalytic mechanisms. Over the past few decades, significant progress has been made in unravelling all these concerns through extensive and successive investigations into these Cr-based catalyst for this ring-opening reaction.

This evolving knowledge not only contributes to refining existing catalysts but also explores alternative green catalysts in the pursuit of sustainable and environmentally friendly cyclic carbonates production.

Castro-Osma *et al.*[8] reported the study of a salphen complexes (Figure 49) for aluminium and chromium to catalyse the reaction between carbon dioxide and an epoxide to form cyclic carbonates. The reaction took place at 25 ºC, 1 bar CO2 pressure, and styrene oxide was used as the substrate. For evaluating the influence of the reaction time in the activity of the catalyst the reaction was made in three reaction times and it was observed that the yield remained the same but as longer the reaction time was, higher conversions were obtained (Table 11).

Table 11: Comparison of the activity of a Cr-catalyst increasing the reaction time

Entry	Catalyst	Substrate	Time	Conv. (%)	Yield (%)
1	Figure 49	Styrene oxide	1h	33	84
2	Figure 49	Styrene oxide	6h	55	84
3	Figure 49	Styrene oxide	24h	100	84

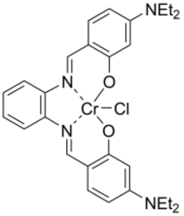


Figure 49: Chromium salphen complex.

Lucas D. Dias *et al.*[61] synthetised a chromium metalloporphyrin, also synthetised the same catalyst for another metal (6.7. Manganese). The reaction was performed under the same conditions, at 80 ºC and 10 bar CO_2 pressure. Two catalysts (Figure 50 and Figure 51) were used to determine if the activity of the catalyst changes by changing its substituents. Surprisingly, same conversion was obtained for both catalysts.

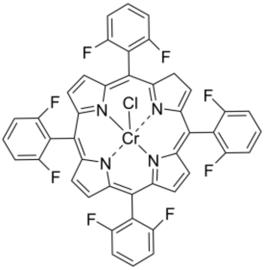


Figure 50: Chromium metalloporphyrin catalyst with F as the substituent.

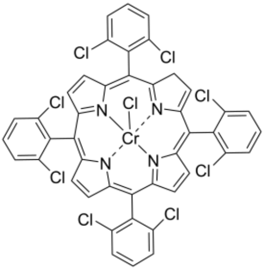


Figure 51: Chromium metalloporphyrin catalyst with Cl as the substituent.

In 2013, Olga V. Zalomaeva *et al.*[64] published the study of a metal-organic framework (Cr-MIL-101). This catalyst was used in the reaction between an epoxide and carbon dioxide. The reaction took place at 25 ºC and 8 atm CO_2 pressure. Propylene and styrene oxide were used as reactants and a higher yield for styrene oxide was obtained.

Another metal organic framework, MIL-101-ImEtOH, is reported by Yi Liu *et al.*[65] in which 2-(1-imidazol-1-yl) ethanol is immobilised on MIL-101 (Cr) (Figure 52). This catalyst was used in the reaction between butylene oxide and epichlorohydrin at 90 ºC and 0.5 MPa CO2 pressure. Almost the same yield was obtained for both epoxides (98.2 and 98.1% respectively).

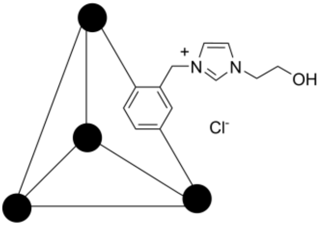


Figure 52: Imobilised Metal organic framework MIL-101-ImEtOH

7. CONCLUSIONS

In this report we compiled the progression of publications and the state-of-the-art research done in the field of CO_2 activation towards the production of carbonates through the ring opening of epoxides, underscoring its broad applicability within the research community.

The formation of cyclic carbonates is highly dependent on the electrophilic nature of the catalyst metal centre and the nucleophilicity of the attacking group of the co-catalyst. The consideration of the metal centre relies on its Lewis acidity, which is directly linked to the activation ability of the epoxide substrate. This Lewis acidity facilitates the ring-opening and is influenced, and depends not only on the nature of the metal element but also on the electronic properties of the framework. It is observed that the same catalyst but with different metal centres (Al and Co) show disparate yields ascribed to the weaker Lewis acidity of Cobalt.[50]

The reactivity and characteristics of these complexes can be easily adjusted by selecting the metal and organic ligand substitutions, leading to a range of structural variations. After reviewing the available literature, it can be concluded that the performance of these catalysts in the ring opening of epoxides is strongly dependent on the structure of the epoxide, being the internal epoxides less reactive than the terminal ones, as expected. Also, less branched-chain epoxides show more favourable results due to a lower steric hindrance of the substituents. Moreover, epoxides with electron-withdrawing substituents exhibit grater results. .

All the authors have been able to optimise the catalytic performance of their catalysts in terms of conversion and selectivity by variation of the temperature, reaction type, and CO_2 pressure. In general, it is observed that an increase in the CO_2 pressure causes a higher activity of the catalyst and thus higher selectivities, conversions, and yielding.

Since the pioneering work by Inoue in 1969 and specially these latter two decades, the utilisation of earth-abundant metals and various connecting ligand frameworks to construct metal complexes as catalysts has rapidly emerged as a robust approach to the CO_2 utilisation in order to eventually replace the use of precious metals catalysts as a viable cost-reducing alternative, less toxic, and achieving imposing catalysts' activities and selectivities certainly comparable to the ones exhibit by the catalysts based on noble metals.

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12. ACRONYMS

DMSO: Dimethyl sulfoxide

DMF: Dimethylformamide

DMAP: 4-Dimethylaminopyridine

REACH: Registration, Evaluation, Authorisation and restriction of chemicals

TBAB: Tetrabutylammonium bromide

M-HCP: Metalloporphyrin-based hyper-crosslinked polymer

PPNCl: Bis(triphenylphosphine)iminium

POM: Polyoxometalate

MOF: Metal-organic framework

DEMOF: Defect-engineered metal-organic framework

DEIL: Deep eutectic ionic liquid

MIL: Metal-containing ionic liquid

NCTPP: N-confused tetraphenylporphyrin

BiIBTP: Benzotriazole iminophenolate.