



TESIS DOCTORAL:

Tailor-made heterogeneous catalysts for the synthesis of high value-added compounds from CO₂

MEMORIA PARA OPTAR AL TITULO DE DOCTORA EN QUÍMICA
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“Nos estamos yendo por los cerros de Úbeda”

Dra. Marta Iglesias

“¿Puedes venir un momentito, porfa?”

Dra. Eva Maya

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List of abbreviations

ACN	Acetonitrile
BCMA	<i>Bis</i> (chloromethyl) anthracene
BCMBP	<i>Bis</i> (chloromethyl)biphenyl
BDD	Boron-doped diamond
BET	Brunauer-Emmett-Teller
BmimBF ₄	1-butyl-3-methylimidazolium tetrafluoroborate
CBM	Cement-based materials
CMP	Conjugated microporous polymers
CNTs	Carbon nanotubes
CTF	Covalent triazine frameworks
COF	Covalent organic frameworks
COK	Centre for Research Chemistry and Catalysis
DBU	8-diazabicyclo [5.4.0] undec-7-ene
DCM	Dichloromethane
DCX	Dichloroxylene
DEC	Diethyl carbonate
DME	Dimethyl ether
DMF	N,N-Dimethylformamide
DMSO	Dimethylsulfoxide
FA	Furfural
FC	Friedel-Craft
FDA	Formaldehyde dimethyl acetal
FDCA	2,5-dicarboxylic acid
FDME	2,5-Furan dicarboxylic methyl ester
FTIR	Fourier transform infrared
HAP	hydroxyapatite
HCP	Hyper crosslinked polymer
HER	hydrogen evolution reaction
HMM	Hiroshima Mesoporous Material

HMF	Hydroxymethyl furfural
ILHCPS	Hyper crosslinked ionic polymer
ILS	Ionic Liquids
IUPAC	International Union of Pure and Applied Chemistry
MCM	Mobil Crystalline Materials
MF	2-Methyl furoate
MSNs	mesoporous silica nanoparticles
MOF	Metal-Organic Framework
NBS	N-bromosuccinimide
NHC	N-Heterocyclic carbene
NMP	N-methylpyrrolidone
NMR	Nuclear magnetic resonance
PAF	Porous aromatic framework
PEF	Polyethylene furan-2,5-dicarboxylate
PET	Polyethylene terephthalate
PIM	polymers of intrinsic microporosity
POP	Porous organic polymer
PXRD	powder X-ray diffraction
RWGS	Reverse Water-Gas Shift reaction
SBA	Santa barbara
SEM	Scanning electron microscopy
TBAB	Tetrabutylammonium bromide
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TUD	Technical Delft University
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
XPS	X-ray photoelectron spectroscopy

Summary

Summary

Catalysis represents an essential component of sustainable chemistry, which is defined as the development of chemical products and processes that minimize or eliminate the use and generation of harmful substances. The creation and implementation of innovative catalysts and advanced catalytic systems enable the simultaneous achievement of two key goals: environmental preservation and economic optimization.

In the industry, heterogeneous catalysts are the most widely used due to their numerous advantages, such as their easy recovery from the reaction medium, high stability, and reusability over several cycles. An additional advantage of solid catalysts is the possibility of fixing different functional groups on the same support, which helps prevent deactivation by keeping them separated from each other. Therefore, heterogeneous catalysts are considered promising options for performing multifunctional catalytic roles.

Hyper-crosslinked polymers (HCPs) are a class of porous polymeric materials mainly composed of light elements such as C, H, O, and N. They have been proven useful in a wide range of applications, including gas adsorption, catalysis and drug delivery. These materials typically have large surface areas, easy synthesis routes from aromatic monomers that do not require functionalization, and well-defined chemical-physical stability. Besides, these aromatic rings can integrate various catalytic centres, both inorganic and organic, generally through post-functionalization, which positions HCPs as ideal catalytic supports.

Carbon dioxide chemistry has recently attracted considerable attention due to growing concerns about the greenhouse effect it causes. Furthermore, CO₂ is an easily available, abundant, cheap, non-toxic, non-flammable, and renewable gas. Although it is a thermodynamically very stable molecule and therefore less reactive. Thus, converting it into value-added compounds continues to be of

interest both in the scientific community and at social level. Currently, CO₂ can be transformed into numerous important chemicals.

Thus, in this thesis, we have carried out the synthesis, functionalization, and characterization of different HCPs based on various core structures, with or without metals, which have been used as catalysts in different reactions to transform CO₂ into high-value-added products. The work is organized into three chapters, according to the type of HCP functionalization and the CO₂ conversion performed.

Chapter 1. Imidazolium chloride-based hyper-crosslinked polymer catalysts for the synthesis of formamides from amines and CO₂

Ionic liquids (ILs) have been widely investigated as homogeneous catalysts for CO₂ transformations, due to the strong Van der Waals and electrostatic interactions generated between ILs and CO₂, as well as the counter-anions of ILs acting as nucleophiles that can accelerate reactions. However, the high viscosity and hydrophilic properties of ILs create separation and circulation issues, hindering their industrial application. To overcome these challenges, they can be inserted into hyper-crosslinked polymers, combining the characteristics of polymers and ILs. The design and preparation of hyper-crosslinked ionic liquid polymers with high ionic density for CO₂ conversion is an important challenge in materials science. Through Friedel-Crafts alkylation, we have developed new ionic liquid based catalysts, namely based on imidazolium chloride supported on hyper-crosslinked polymers, HCP-BzmimCl and HCP-*Bis*(BzmimCl), prepared in a single step directly from the corresponding monomers (Figure S.1)

Summary

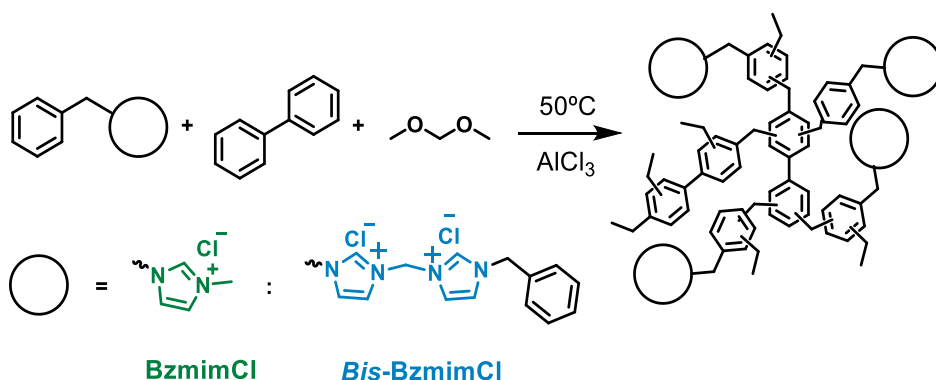


Figure S.1 Synthesis of heterogeneous imidazolium chloride-based hypercrosslinked polymers.

Once synthesized and characterized, these materials were evaluated as heterogeneous catalysts in the synthesis of formamides from secondary amines and CO₂ as the carbon source using phenylsilane as the hydrogen donor and dimethylformamide (DMF) as a crucial polar additive. (Figure S.2)

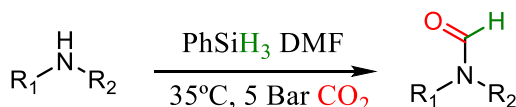


Figure S.2 *N*-Formylation reaction of secondary amines.

The reactions took place in the absence of solvent, at moderate pressures of CO₂ (5 bar), mild temperatures (35°C) and DMF as a key polar additive which activates the N-H and Si-H bonds, shortening reaction times. Obtaining 100% conversions were achieved using dipentylamine as a reagent, and the catalysts could be recycled for 10 consecutive cycles. A reaction scope analysis was carried out with different amines, achieving conversions between 65-100%.

The results of this chapter are reported in:

DMF-assisted synthesis of formamides from amines using CO₂ catalyzed by heterogeneous metal-free imidazolium-hypercrosslinked.

B. Fuerte-Díez, E. Rangel-Rangel, M. Iglesias, and E. M. Maya. Journal of CO₂ Utilization, 2024. 80, 102679.

Chapter 2. Heterogenized metal-N-heterocyclic carbene hypercrosslinked polymer catalysts for the synthesis of carbamates and carbonates.

Asymmetric carbonates are highly relevant compounds in various sectors, used in the production of fuel additives, lithium battery solvents, lubricants, plasticizers, automotive materials, and herbicides.

Cyclic carbamates also known as 2-oxazolidinones, on the other hand, are part of antibiotics used to treat serious infections, such as linezolid and eperzolid. Additionally, this core is present in natural products with various biological activities, such as enzyme inhibitors and antimicrobial agents. In recent research has shown that CO₂ can be transformed into cyclic carbamates and asymmetric linear carbonates through three-component reactions with CO₂, propargylic alcohols and primary amines or alcohols using *N*-heterocyclic carbenes-metal complexes (NHC-M)

In this chapter we have transformed the imidazolium-hypercrosslinked polymers of the previous chapter into hypercrosslinked N-heterocyclic carbene polymers with Ag₂O and CuI, (HCP-NHC-M, HCP-*Bis*NHC-M; M = Ag, Cu) (Figure S.3).

Summary

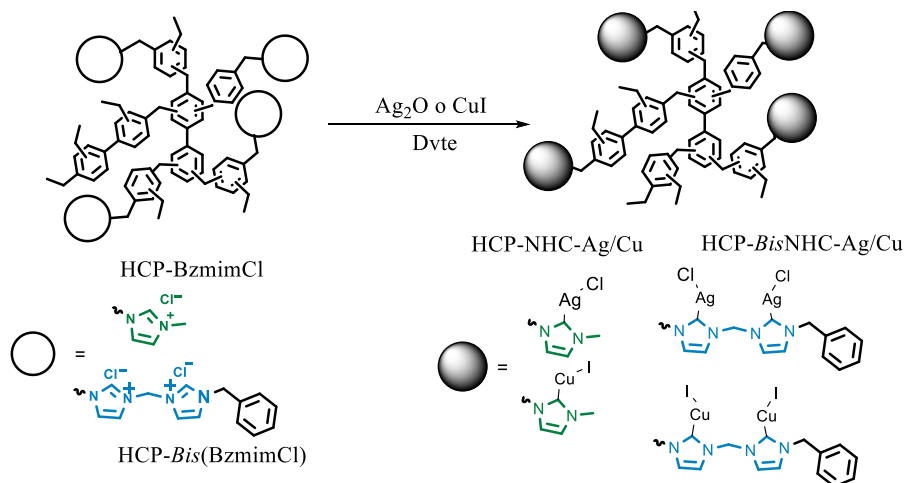


Figure S.3 Synthesis of the heterogenized HCP-NHC-M complexes.

These versatile catalysts facilitate the three-component coupling of CO_2 , propargylic alcohols, and primary amines to produce cyclic carbamates (2-oxazolidinones), as well as CO_2 , propargylic alcohols, and primary alcohols to produce asymmetric linear carbonates. (Figure S.4)

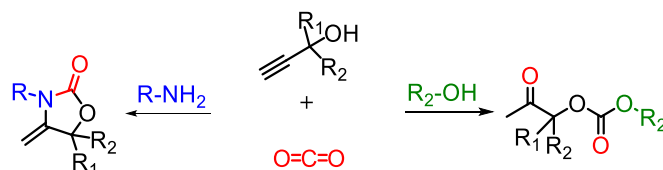


Figure S.4 Synthesis of cyclic carbamates (2-oxazolidinones) and asymmetrical organic carbonates.

We have found that they work under moderate conditions $P(\text{CO}_2) = 5$ bar, $T = 120^\circ\text{C}$, reaction times between 4 and 12 hours, yielding the desired products with complete propargyl alcohol conversion and high selectivity and yields (90–100%) and can be reused at least five cycles.

The results of this chapter are reported in:

Three-Component Coupling of CO₂ for the Synthesis of Carbamates and Carbonates using Metal-Supported Hypercrosslinked N-Heterocyclic Carbene Polymer (HCP-NHC) Catalysts. B. Fuerte-Díez, M. Iglesias, and E. M. Maya. 2025 *Under preparation*.

Chapter 3. Functionalized hyper-crosslinked polymer catalysts to produce 2,5-furan dicarboxylic methyl ester (FDME).

Interest in polymers derived from renewable resources has continued to increase both in academia and industry. One class of polymers derived from renewable resources is furan-based polymers. The growing interest in these materials is mainly due to two key factors: sustainability and their unique chemical properties. From a sustainability perspective, furan monomers can be easily synthesized from renewable raw materials.

2,5-furan dicarboxylic methyl ester (FDME) is a bio-based molecule very persecuted as a monomer in the synthesis of polyethylene furanoate (PEF), a polyester with excellent properties such as high glass transition temperature, low melting temperature, good processability, and good gas barrier properties, making it a promising material for high-performance fibres and packaging applications. PEF is thus positioning itself as a promising candidate to replace polyethylene terephthalate (PET), the most common petroleum-derived thermoplastic polymer.

This chapter mainly focuses on the synthesis of FDME from furfural and CO₂ through a three-step reaction process. The first step involves the synthesis of 2-methyl furoate by furfural oxidative esterification, followed by carboxylation using CO₂ as feedstock and an acid esterification step to obtain the desired product. To achieve this, two types of HCP-based catalysts were used: one

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containing imidazole chlorides as active centres, described in Chapter 1 to accomplish step 1, and the other based on *N,N'*-Bis(salicylidene)-1,2-phenylenediamine (“Salphen”) structures endowed with cobalt for the second step. Their catalytic activity in each reaction was evaluated to determine the optimal reaction conditions (Figure S.5).

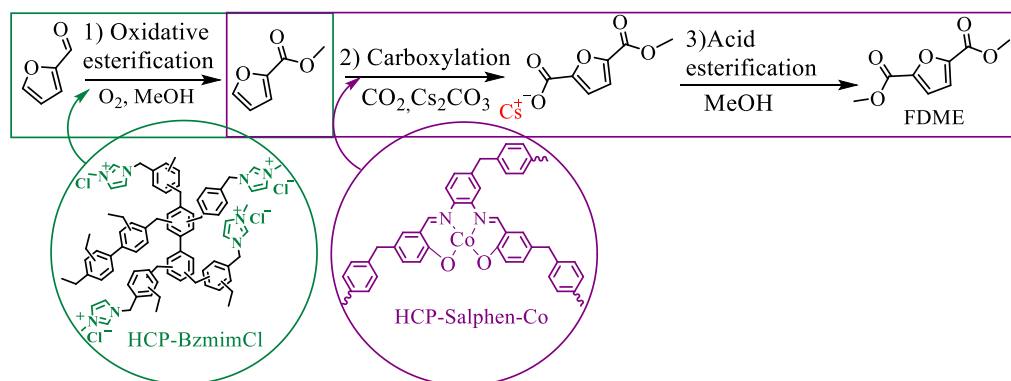


Figure S.5 Synthetic scheme of 2,5-furan dicarboxylic methyl ester from Furfural and CO₂.

In the case of step one, the imidazolium-based catalyst operates under 5 bar of oxygen pressure and 60°C, achieving conversions above 95% in 6 h. The cobalt-salphen catalyst operates under 10 bar of CO₂ pressure, 200°C and 7 h of reaction. We have found that both catalysts were reused at least five consecutive cycles in the corresponding reactions, maintaining their catalytic activity and structure.

The results of this chapter are reported in two publications:

Metal-free catalytic systems based on imidazolium chloride and strong bases for selective oxidative esterification of furfural to methyl furoate. B. Fuerte-Díez, E. Rangel-Rangel, M. Iglesias, and E. M. Maya *Applied Catalysis A: General*, 2023. 654, 119088.

Insertion of CO₂ to 2-methyl furoate promoted by a cobalt hypercrosslinked polymer catalyst to obtain a monomer of CO₂-based biopolyesters. E, Rangel-Rangel, B. Fuerte-Díez, M. Iglesias, and E. M. Maya. RSC Sustainability, 2024. 2(10), 2896-2902.

To summarize the main aspects developed in this thesis, the following outline is presented below.

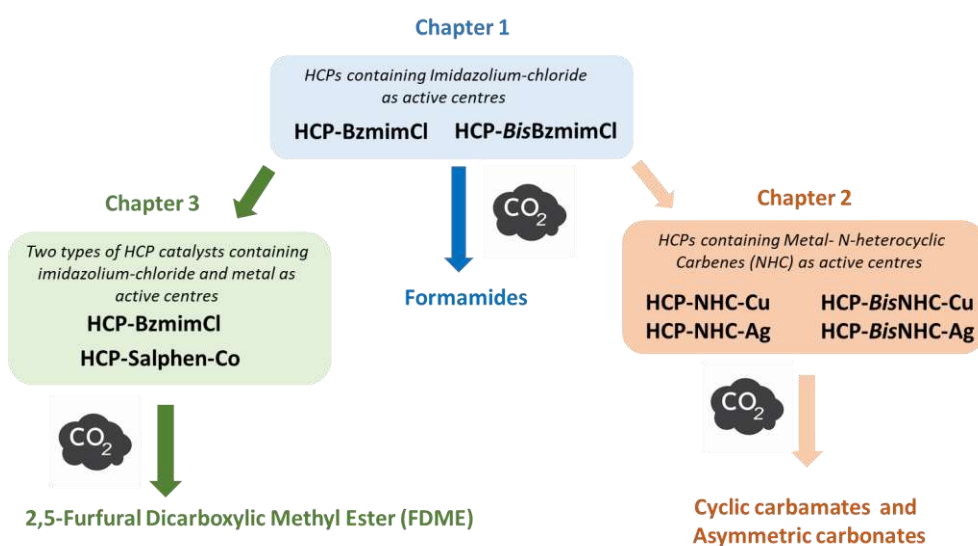


Figure S.6 Schematic representation of the general goals of this doctoral thesis.

Resumen

La catálisis representa un componente esencial de la química sostenible, la cual se define como el desarrollo de productos y procesos químicos que minimizan o eliminan la utilización y generación de sustancias nocivas. La creación e implementación de catalizadores innovadores y sistemas catalíticos avanzados están permitiendo alcanzar simultáneamente dos metas clave: la preservación del medio ambiente y la optimización de los beneficios económicos.

En la industria, los catalizadores heterogéneos son los más utilizados debido a sus numerosas ventajas, como su fácil recuperación del medio de reacción, su alta estabilidad y su capacidad de reutilización a lo largo de varios ciclos. Una ventaja adicional de los catalizadores sólidos es la posibilidad de fijar distintos grupos funcionales en un mismo soporte, lo que ayuda a prevenir su desactivación al mantenerlos separados entre sí. Por ello, los catalizadores heterogéneos se consideran opciones prometedoras para desempeñar funciones catalíticas multifuncionales.

Los polímeros hiper-reticulados (HCPs por sus siglas en inglés *Hyper-crosslinked polymers*) son un tipo de materiales poliméricos porosos compuestos principalmente por elementos ligeros como C, H, O y N. Se ha demostrado que son útiles en una amplia gama de aplicaciones, incluyendo la adsorción de gases, catálisis y liberación de fármacos. Estos materiales suelen presentar grandes áreas superficiales, rutas de síntesis sencillas a partir de monómeros aromáticos que no requieren funcionalización y una estabilidad químico-física bien definida. Además, estos anillos aromáticos pueden integrar diversos centros catalíticos, tanto inorgánicos como orgánicos, generalmente a través de funcionalización, lo que posiciona a los HCPs como soportes ideales de catalizadores homogéneos.

La química del dióxido de carbono ha atraído recientemente una gran atención debido a la creciente preocupación por el efecto invernadero que causa. Además, el CO₂ es un gas fácilmente disponible, abundante, barato, no tóxico, no

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inflamable y renovable. Aunque es una molécula termodinámicamente muy estable y, por lo tanto, menos reactiva, su conversión en compuestos de valor añadido sigue siendo de interés tanto en la comunidad científica como a nivel social. Actualmente, el CO₂ puede transformarse en numerosos productos químicos importantes.

En esta tesis, hemos llevado a cabo la síntesis, funcionalización y caracterización de diferentes HCPs basados en varias estructuras que incorporan o no metales, los cuales han sido utilizados como catalizadores en diferentes procesos de transformación de CO₂ en productos de alto valor añadido. El trabajo se ha organizado en 3 capítulos, en función del tipo de funcionalización del HCP y sus aplicaciones en reacciones de conversión de CO₂.

Capítulo 1. Catalizadores poliméricos hiper-reticulados basados en cloruro de imidazolio para la síntesis de formamidas a partir de aminas y CO₂.

Los líquidos iónicos (LIs por sus siglas en inglés *ionics liquids*) han sido ampliamente investigados como catalizadores homogéneos para transformaciones de CO₂, debido a las fuertes interacciones de Van der Waals y electrostáticas generadas entre los LIs y el CO₂, así como a los contra-aniones de los LIs como agentes nucleófilos que pueden acelerar la reacciones. Sin embargo, la alta viscosidad y las propiedades hidrófilas de las LIs provocan problemas de separación y utilización, lo que dificulta su aplicación industrial. Para superar estos problemas, se introducen en polímeros hiperreticulados combinando las características de los polímeros y de los LIs. El diseño y la preparación de polímeros iónicos hiperreticulados con alta densidad iónica para la conversión de CO₂ es un reto importante en la ciencia de los materiales. Por ello mediante una reacción de alquilación Friedel-Crafts hemos desarrollado nuevos catalizadores mediante la síntesis de polímeros heterogéneos basados en líquidos iónicos de

cloruro de imidazolio, (HCP-BzmimCl y HCP-*Bis*-BzmimCl). preparados en un solo paso, directamente a partir de los correspondientes monómeros (Figura R.1)

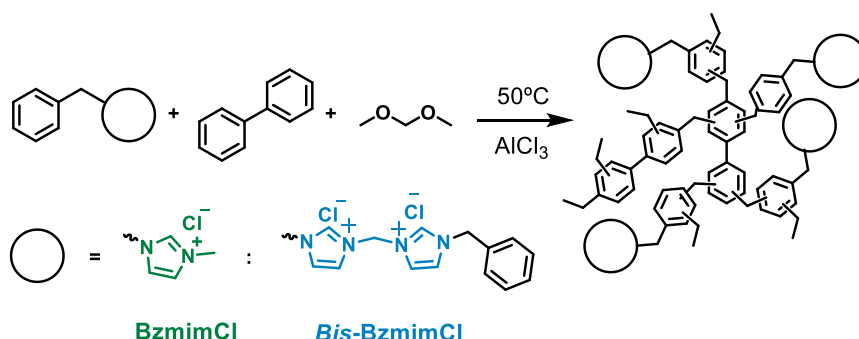


Figura R.1 Síntesis de polímeros hiper-reticulados basado en líquidos iónicos de cloruro de imidazolio.

Una vez sintetizados y caracterizados, estos materiales fueron probados como catalizadores heterogéneos en la síntesis de formamidas a partir de aminas secundarias utilizando CO₂ como fuente de carbono, fenilsilano como dador de hidrógeno y dimetilformamida como aditivo polar indispensable (Figura R.2)

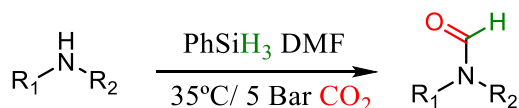


Figura R.2 Síntesis de *N*-formamidas a partir de aminas secundarias.

Las reacciones tuvieron lugar en ausencia de disolvente, a presiones moderadas de CO₂ (5 bar), temperaturas suaves (35°C) y DMF como aditivo polar clave que activa los enlaces N-H y Si-H, acortando los tiempos de reacción. Se obtuvieron conversiones del 100% utilizando dipentilamina como reactivo, y además los catalizadores se pudieron reciclar hasta en 10 reacciones consecutivas. Se realizó un estudio con diferentes aminas, obteniendo conversiones entre el 65% y el 100%.

Los resultados de este capítulo se han recogido en la siguiente publicación:

DMF-assisted synthesis of formamides from amines using CO₂ catalyzed by heterogeneous metal-free imidazolium-hypercrosslinked. B. Fuerte-Díez, E. Rangel-Rangel, M. Iglesias, and E. M. Maya. Journal of CO₂ Utilization, 2024. 80, 102679.

Capítulo 2. Catalizadores poliméricos metal-carbeno-N-heterociclos hiperreticulados para la síntesis de carbamatos y carbonatos.

Los carbonatos asimétricos son compuestos de gran relevancia en diversos sectores, que se utilizan en la producción de aditivos para combustibles, disolventes para baterías de litio, lubricantes, plastificantes, materiales para la industria automovilística y herbicidas. Por otro lado, los carbamatos cíclicos (2-oxazolidinonas), son partes fundamentales de antibióticos utilizados para tratar infecciones graves, como el linezolid y el eperzolid. Además, este núcleo está presente en productos naturales con diversas actividades biológicas, como inhibidores enzimáticos y agentes antimicrobianos.

Investigaciones recientes han demostrado que el CO₂ puede transformarse en carbamatos cíclicos y carbonatos lineales asimétricos mediante reacciones de tres componentes, utilizando alcoholes propargílicos y aminas o alcoholes primarios, y catalizadores basados en complejos de carbenos N-heterocíclicos con metales (NHC-M).

En este capítulo, hemos transformado los polímeros de cloruro de imidazolio hiper-reticulados del capítulo anterior en polímeros hiper-reticulados de carbeno N-heterocíclico con Ag₂O y CuI (HCP-NHC-M, HCP-BisNHC-M; M = Ag, Cu) (Figura R.3).

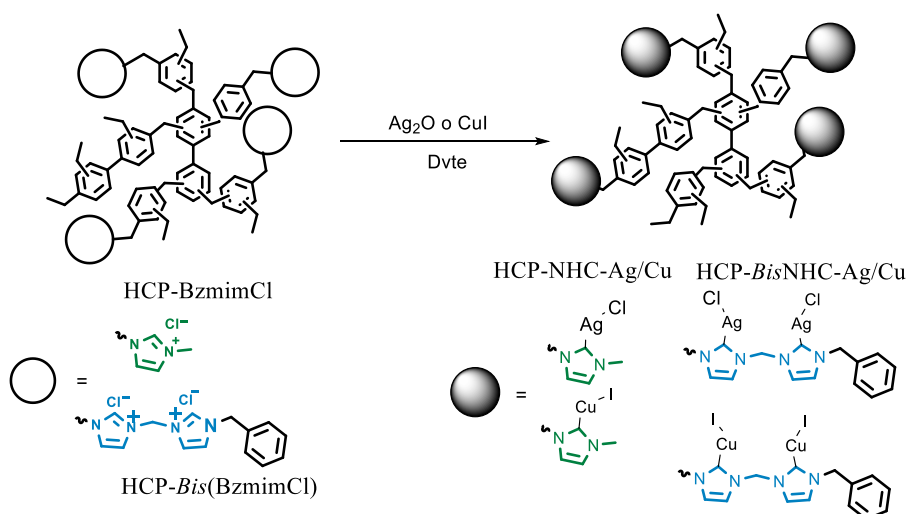


Figura R.3 Síntesis de los HCP-NHC.

Estos catalizadores versátiles catalizaron la reacción multicomponente entre CO_2 , alcoholes propargílicos y aminas primarias para producir carbamatos cíclicos (2-oxazolidinonas), y CO_2 , alcoholes propargílicos y alcoholes primarios para producir carbonatos asimétricos (Figura R.4).

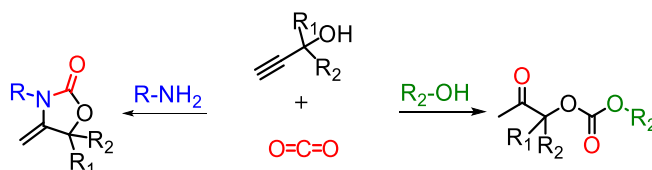


Figura R.4 Síntesis de los carbamatos cíclicos (2-oxazolidinonas) y de los carbonatos asimétricos.

Estos catalizadores funcionaron bajo condiciones moderadas ($\text{P}(\text{CO}_2) = 5$ bar, $T = 120$ °C, tiempos de reacción entre 4 y 12 horas), obteniéndose los productos deseados con conversión completa del alcohol propargílico y alta selectividad (90–100%). Además, fueron reciclables al menos durante cinco ciclos consecutivos.

Los resultados de este capítulo se han recogido en la siguiente publicación:

Three-Component Coupling of CO₂ for the Synthesis of Carbamates and Carbonates using Metal-Supported Hypercrosslinked N-Heterocyclic Carbene Polymer (HCP-NHC) Catalysts. B. Fuerte-Díez, M. Iglesias, and E. M. Maya. 2025. *Bajo preparación*.

Capítulo 3: Catalizadores polimericos hiper-reticulados para producir éster metílico del éster metílico dicarboxílico de 2,5-furfural (FDME).

El interés por los polímeros derivados de recursos renovables no ha dejado de aumentar tanto en el ámbito académico como en el industrial. Esta gran de actividad abarca una gama cada vez más amplia de fuentes y metodologías a escala mundial. Una clase de polímeros derivados de recursos renovables son los basados en furanos. El creciente interés por estos materiales se debe principalmente a dos factores clave: la sostenibilidad y sus propiedades químicas únicas. Desde el punto de vista de la sostenibilidad, los monómeros de furano pueden sintetizarse fácilmente a partir de materias primas renovables ampliamente disponibles.

El éster metílico del ácido 2,5-furfural (FDME) es una molécula de origen biológico, muy perseguida como monómero, que se utiliza en la síntesis del furanoato de polietileno (PEF), un poliéster con excelentes propiedades como una alta temperatura de transición vítrea, baja temperatura de fusión y procesado y buenas propiedades de barrera a los gases lo que hace que tenga aplicaciones muy prometedoras como fibras de alto rendimiento y como materiales de envasado. Así, el PEF se está posicionando como un prometedor candidato para sustituir al tereftalato de polietileno (PET), el polímero termoplástico más común, derivado del petróleo.

Por ello este capítulo trata de la síntesis de FDME a partir de furfural y CO_2 mediante un proceso de reacción en tres etapas. La primera etapa consiste en la síntesis de furoato de metilo por oxidación esterificativa de furfural, seguida de una etapa de carboxilación usando CO_2 como materia prima y por último, una esterificación ácida para obtener el producto deseado. Para lograrlo, es necesario usar dos tipos de catalizadores HCPs, uno que contiene cloruros de imidazolio como centros activos, descrito en el capítulo 1 y el otro basado en complejo de cobalto con el ligando de *N,N'*-Bis(salicilideno)-1,2-fenilendiamina (“salphen”). Se evaluó la actividad catalítica en cada reacción, para obtener las condiciones más favorables de cada reacción (Figura R.5)

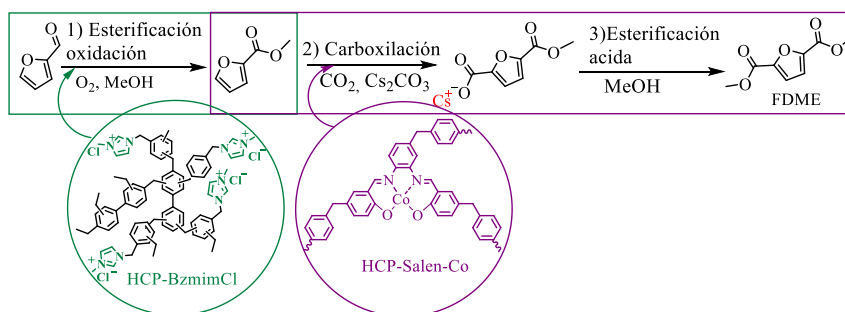


Figura R.5 Esquema de las síntesis de furfural dicarboxylic methyl ester.

En el caso de la primera etapa, el catalizador basado en cloruro de imidazolio operó en condiciones de 5 bares de presión de oxígeno y 60°C , logrando conversiones superiores al 95% en 6 horas de reacción. Mientras que catalizador de cobalto funcionó a 10 bares de presión de CO_2 y 200°C y en 7 horas de reacción. Se comprobó que ambos catalizadores fueron reciclables en al menos cinco ciclos de las reacciones correspondientes, manteniendo su actividad catalítica y estructura.

Los resultados de este capítulo se han recogido en las siguientes publicaciones:

Metal-free catalytic systems based on imidazolium chloride and strong bases for selective oxidative esterification of furfural to methyl furoate. B. Fuerte-Díez, E. Rangel-Rangel, M. Iglesias, and E. M. Maya *Applied Catalysis A: General*, 2023. 654, 119088.

Insertion of CO₂ to 2-methyl furoate promoted by a cobalt hypercrosslinked polymer catalyst to obtain a monomer of CO₂-based biopolyesters. E, Rangel-Rangel, B. Fuerte-Díez, M. Iglesias, and E. M. Maya. *RSC Sustainability*, 2024. 2(10), 2896-2902.

Para resumir los principales aspectos desarrollados en esta tesis, se presenta a continuación el siguiente esquema.

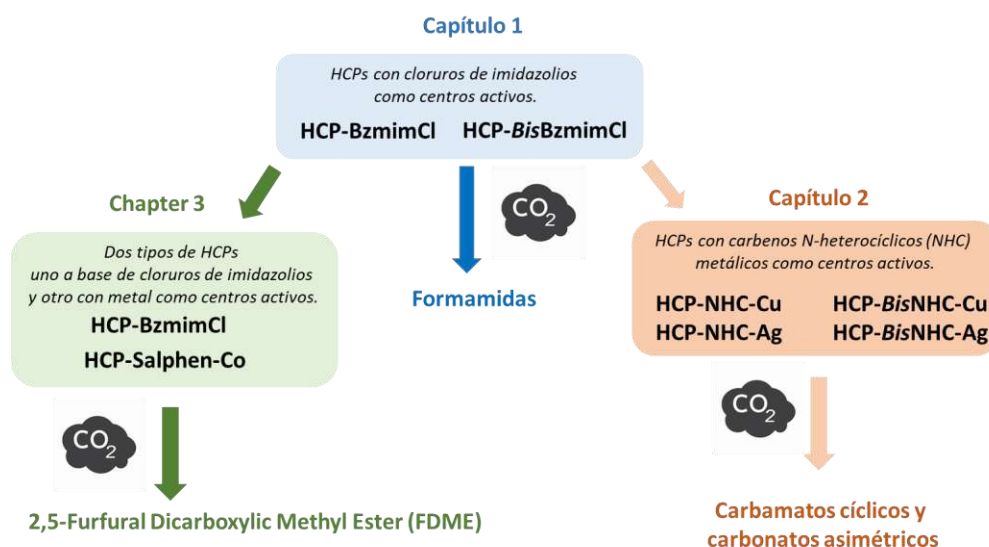


Figura R.6 Representación esquemática de los objetivos generales de esta tesis doctoral.

Introduction

This doctoral thesis is situated within the field of sustainable chemistry, as it focuses on the development of innovative porous materials designed to enable significant CO₂ conversion into value-added products, therefore, will be the three key points discussed in this introduction: sustainable chemistry, porous materials, and CO₂ conversions.

1.1 Sustainable chemistry

Chemistry is a continuously evolving science that plays a significant role today since it greatly contributes to increasing our life expectancy by providing solutions to infectious diseases, agricultural pests, and food resource shortages among many others^[1], but it should be safe, sustainable, and environmentally friendly. Since the 1940s, environmental issues began to emerge in connection with the growth of industrial activities, as the increasing production and use of synthetic chemicals led to pollution, resource depletion, and ecological imbalances.^[2] The production, use, and management of synthetic chemicals and the waste generated caused problems for human health and the environment. This, along with social, political, and legal pressure, led to the emergence of a movement known as sustainable chemistry at the end of the last century.^[3]

Green Chemistry is defined as the “design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances”. and whose pillars are contained in the “Twelve Principles of Green Chemistry” formulated by Paul Anastas and John Warner in 1998.^[4] This discipline not only seeks to minimize the environmental impact of the chemical industry but also fosters innovation in the development of safer and more efficient materials, promoting a circular and sustainable economy (Figure 1.1).

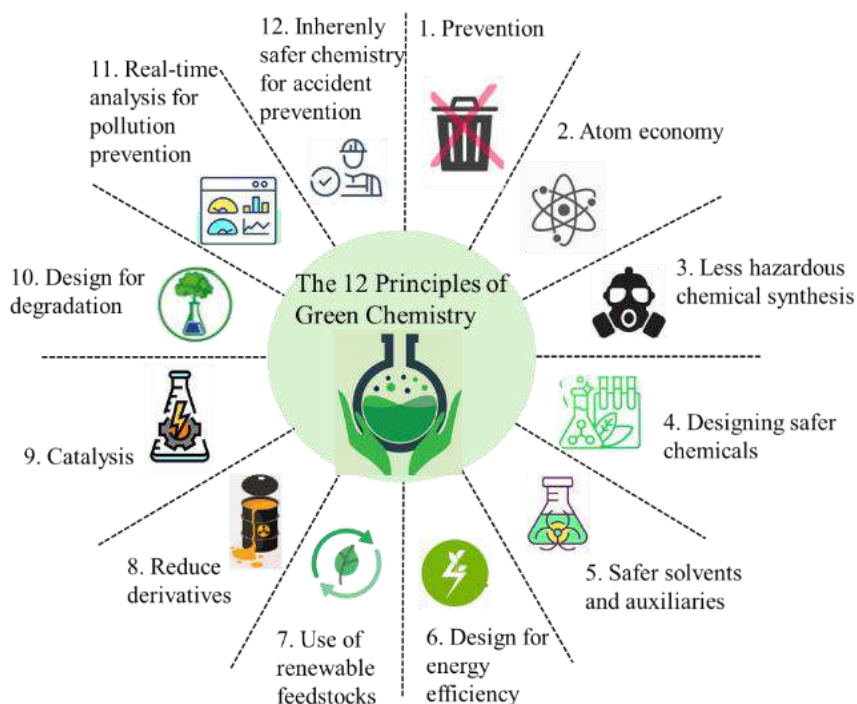


Figure 1.1 The twelve principles of Green Chemistry.

Catalysis is one of the fundamental pillars of Green Chemistry, as it involves using reactants in small (catalytic) amounts instead of stoichiometric quantities. The design and application of new catalysts and catalytic systems simultaneously achieve the dual objectives of environmental protection and economic benefit. Additionally, they can reduce energy consumption by decreasing the number of reactants and synthesis steps, and they help minimize or eliminate the generation of hazardous substances as by-products.^[5] The more active and selective a catalyst is, the fewer by-products are generated.

1.1.1 Catalysis

In 1836, J. J. Berzelius used the term “catalysis” to describe the increase in speed of same reactions when another substance is added to the reaction vessel

without being consumed during the reaction. Later, in 1880, the German chemist W. Ostwald began a systematic investigation of reactions catalysed by the presence of acids and bases, thus expanding the concept of a catalyst. It therefore needs to be present only in catalytic amounts and can nevertheless transform large quantities.^[6] As mentioned earlier, catalysis involves the increase in the rate of a chemical reaction through the interaction of the reactants with a substance (catalyst) that provides an alternative reaction pathway with lower activation energy thereby facilitating the formation of products without the catalyst appearing among the reactants or products^[7]. Thus currently, most chemical processes in the industry are catalytic processes, as they involve a catalyst in one of the production stages. Catalytic reactions play a fundamental role in the development of environmentally sustainable chemical processes, as they contribute to economic efficiency by enabling the efficient use of resources, preventing spills caused by reactions with stoichiometric reagents, improving energy efficiency, and reducing derivatization-recovering processes. This is possible because catalysts lower the activation energy of chemical transformations, increasing reaction rates, facilitating high selectivity, and being crucial in minimizing the number of process steps.^[8] They also play a role in the production of numerous healthcare, pharmaceutical, and agrochemical products. For all these reasons, catalysis is a key technology that enhances our quality of life.

1.1.1.1 Type of catalysis

There are several ways to classify types of catalysis, depending on the criteria used for classification. A basic classification can be made based on whether the catalysts are in the same phase as the reaction medium or not. Thus, catalysis can be categorized into three types: homogeneous catalysis, heterogeneous catalysis, and enzymatic catalysis.

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In homogeneous catalysis, the catalyst, reactants, and products are in the same phase, forming a homogeneous medium. In heterogeneous catalysis, the catalyst, reactants, and products are in different phases, usually solid-liquid or solid-gas, resulting in a heterogeneous reaction medium. Sometimes, a combination of these two types occurs, leading to what is known as heterogenized catalysis. This approach involves the use of catalysts that are not initially in the same phase but can generate compounds that dissolve and participate in a homogeneous catalysis cycle.^[9, 10] Finally, enzymatic catalysis involves the use of enzymes, biological catalysts found in nature, which are typically protein-based.^[11]

We will delve deeper into heterogeneous catalysis and its catalysts since in this thesis, we will focus mainly on heterogeneous catalysis, although some homogeneous catalysis tests will be conducted in specific reactions. The economic importance of heterogeneous catalysis is such that nearly 80% of industrial processes involve a solid-catalysed reaction at some stage. The products synthesized through heterogeneous catalytic processes are highly diverse, both in terms of their chemical nature and the quantity produced, as well as their cost per unit weight.^[12] These range from liquid fuels and sulfuric acid, which are substances with simple chemical structures and are produced in large quantities at relatively low prices, to various types of pharmaceuticals, fragrances, agrochemicals, and polymers, some of which have highly complex chemical structures.^[13, 14]

In heterogeneous catalysis, the catalytic phenomenon is related to the chemical properties of the surface of the solid chosen as the catalyst. For the reaction to occur, one or more of the reactants must diffuse to the surface of the catalyst and adsorb on it, forming a substrate-catalyst surface complex. After the reaction, the products must desorb from the surface and diffuse away from the

solid surface. Often, this transport of reactants and products between phases plays a dominant role in limiting the reaction rate.^[12, 13, 15] The most used solid heterogeneous catalysts are metal oxides, which are combinations of oxygen and metal and constitute an important class of catalytically active materials, capable of developing acid-base and redox properties. For example, aluminas are aluminium oxides (Al_2O_3), silicas are weak Brønsted acid oxides, with amorphous silica being the most used in catalysis, magnesium oxide, or transition metal oxides (Fe, Co, Ni, Pd, Pt, Cr, W, Ag, Cu), as they have partially occupied d orbitals that can participate in the bond formation of chemisorbed species. These oxides have their main field of application in oxidation reactions.^[16, 17]

Currently, porous polymers are being used as supports for the catalytically active centre, facilitating the dispersion and stability of the active catalytic phase. These porous polymers are a very good alternative to classical supports (metal oxides or silicas) as they are characterized by having a high surface area, a suitable pore size distribution, and good thermal and chemical stability. Initially, supports were considered inert, but it has been proven that they can also play a role in the catalytic process.^[18, 19]

Since this thesis describes heterogeneous synthetic catalysts, such as porous materials, their introduction and analysis will be carried out.

1.2 Porous Materials

A porous material is a continuous solid network containing pores or spaces that enable the diffusion of molecules throughout its structure. The characteristics and structure of the pores determine how porous materials are utilized. Therefore, the basic parameters of porous materials are the porosity, the pore size distribution and the surface area.^[20] Due to these characteristics and properties, these porous

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materials are of interest in a wide range of applications, from catalysis, adsorption, detection, and separation to biotechnology.^[21-24]

According to the definitions and recommendations of the International Union of Pure and Applied Chemistry IUPAC,^[25] porous materials are classified into three categories based on pore size: microporous materials, which have pore sizes smaller than 2 nm; mesoporous materials, with pore sizes ranging from 2 to 50 nm; and macroporous materials, which feature pore sizes greater than 50 nm. Furthermore (Figure 1.2), within each porous material, two types of pores can be distinguished: open pores, which have continuous pathways connected to the external surface of the porous structure, and closed pores, which are isolated from each other.

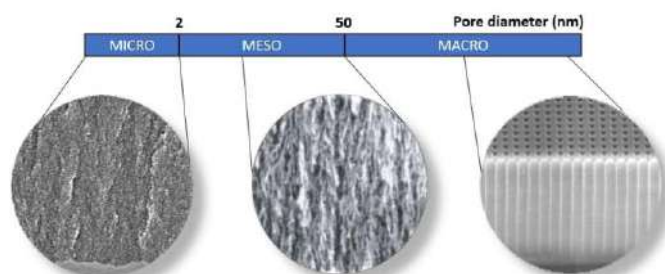


Figure 1.2 IUPAC classification of pores according to their size.

Porous materials can also be classified based on their structural composition and are divided into three major groups: inorganic materials (such as zeolites and mesoporous silicas), inorganic-organic hybrid materials like MOFs (Metal-Organic Frameworks), and organic materials, specifically POPs (Porous Organic Polymers). Within these groups, various materials can be identified based on their structural organization, which will be briefly discussed (Figure 1.3)^[26]

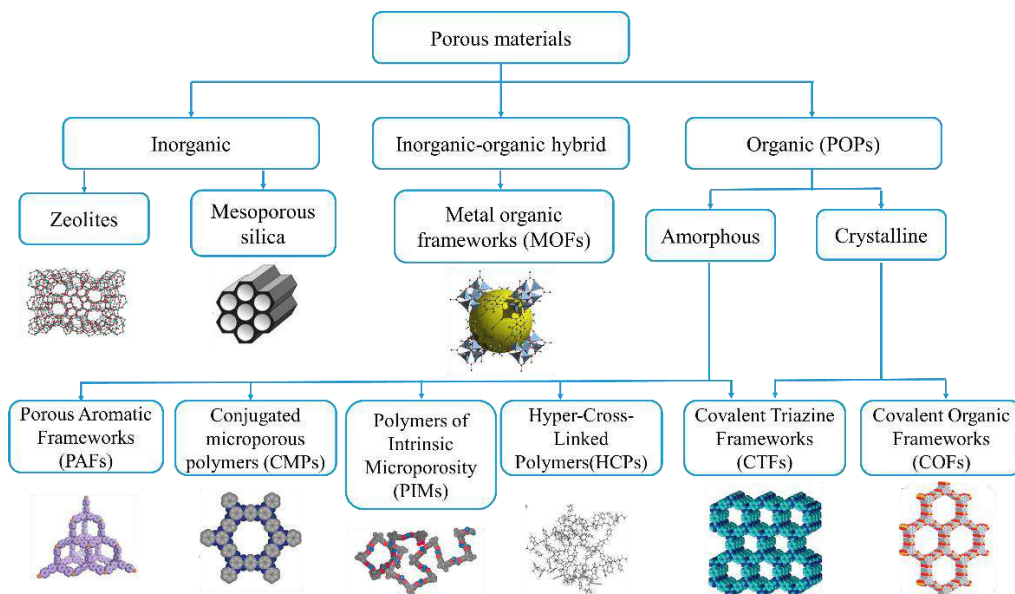


Figure 1.3 Classification of porous materials based on its composition and structure.

1.2.1 Inorganic Materials

1.2.1.1 Zeolites

They are crystalline materials with a porous structure formed by regular networks of corner-sharing tetrahedral alumina and silica units, connected through oxygen atoms whose first syntheses are documented in Barrer's reports in 1948.^[27] They have high surface area, molecular-sized pores, high adsorption capacity, selective distribution of reactants and products, the ability to modulate the electronic properties of active sites, and the potential to preactivated molecules within the pores through strong electric fields and molecular confinement.^[28] In addition to these characteristics, their robustness has not yet been surpassed, which is why today, zeolites continue to be the most widely used material in the industry.

Crystalline structures of the zeolite type but with coordinated Si, Al, or P as well as transition metals and many group elements such as B, Ga, Fe, Cr, Ge, Ti, V, Mn, Co, Zn, Be, Cu are collectively known as zeotypes.^[29, 30] These three-dimensional networks of micropores can serve as reaction channels, with enhanced activity and selectivity through the addition of active sites. The strong electric fields and controllable adsorption properties within the pores create a unique catalyst, functioning as a catalytic microreactor.^[28, 31]

1.2.1.2 Mesoporous silica nanoparticles (MSNs)

These materials are a type of inorganic porous material formed by the condensation of sodium silicate or silicon alkoxides around an ordered surfactant used as a template. Although the synthesis of mesoporous materials dates back to the 1970s,^[32] Mobil Research and Development Corporation was the first to synthesize mesoporous solids using the liquid crystal templating mechanism in 1992. They called it MCM-41 (Mobil Crystalline Materials or Mobil Composition of Matter).^[33, 34] The pore size in mesoporous materials can be adjusted depending on the surfactants used. For example, MCM-41 has a hexagonal structure and is used in drug delivery. In addition to MCM-41, other mesoporous materials have been synthesized, such as MCM-48 with a cubic structure and MCM-50 with a lamellar structure.^[35]

Non-ionic triblock copolymers like alkyl poly(ethylene oxide) (PEO) oligomeric surfactants and poly(alkylene oxide) block copolymers have also been used as a template which has been designated as SBA-11 (cubic), SBA-12 (hexagonal) but with a different arrangement compared to SBA-15, SBA-15 (hexagonal) and SBA-16 (cubic cage-structured). SBA-15, with larger pores and thicker silica walls than MCM, is used in biomedical applications.^[36] Other mesoporous materials, such as FSM-16, are synthesized using a quaternary ammonium surfactant as a template and layered kanemite

polysilicate.^[37] Additionally, other mesoporous silica nanoparticles (MSNs) have been synthesized, including Technical Delft University (TUD-1), Hiroshima Mesoporous Material-33 (HMM-33), Korea Advanced Institute of Science and Technology, (KIT-5) and Fairleigh Dickinson University (FDU-2), which vary in symmetry and pore shape. ^[38-40] some examples are shown in the Figure 1.4.

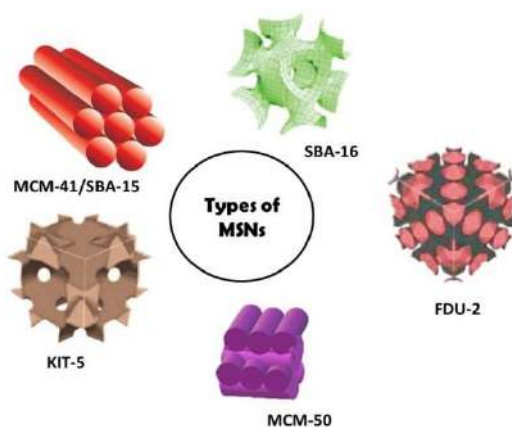


Figure 1.4 Representation of different types of mesoporous silica nanoparticles (MSNs).^[40]

1.2.2 Porous inorganic-organic hybrid materials

A hybrid material can generally be defined as one that is composed of at least two types of units of different nature, typically one inorganic and one organic, which are interconnected at the nanometric scale.^[41]

The Metal-Organic Frameworks, (MOFs), are the more representative porous hybrid materials. They are extended, typically crystalline structures built with metal ions or clusters (nodes) that provide directional bonds to the organic ligand through the metal's preferential geometry and coordination number, forming voids within the structure that give rise to porosity. In other words, they are fabricated by linking inorganic and organic units through strong bonds (reticular synthesis). The nodes are generally based on transition metals or

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polynuclear metal clusters with different coordination numbers and geometries, while the organic ligands or spacers are typically of the carboxylate, sulfonate, β -diketonate, α -aminocarboxylate, or phosphonate type.^[42] They combine the flexibility and functionality provided by the organic component, which is often aromatic, with the mechanical, thermal, and structural stability, as well as the rigidity, conferred by the inorganic component. The ability to vary constituent elements, such as geometry, size, functionality, and thus flexibility has led to more than 20,000 different MOFs being reported and studied within the past decade.^[43] The synthesis of MOFs is predominantly carried out through solution-based routes that use either a pure solvent or an appropriate mixture of solvents. The most used method is solvothermal crystallization, which involves combining an organic ligand and a metal precursor in a coordination solvent (such as water, DMF, THF, etc.) at a specific temperature, typically ranging from 353 to 533 K, for a certain period. Under these conditions, MOF crystallization occurs through the self-assembly of organic and metal units via coordination bonds.^[44] A representative hybrid material within this group is MOF-5 (Figure 1.5), which is composed of zinc clusters (formed by four ZnO_4 tetrahedra) connected by 1,4-benzenedicarboxylate molecules in a three-dimensional structure.^[45] There are alternative synthesis techniques that introduce energy into the reaction through microwave irradiation,^[46] mechanical force (mechanochemistry),^[47] electric potential (electrochemistry),^[48] and ultrasound-assisted synthesis (sonochemistry).^[49] These methods can have several advantages compared to conventional electric heating, for example shorter reaction times, smaller particle sizes, lower amounts of solvents and safer conditions. All of them have a wide range of applications, for example, in biomedicine,^[50] catalysis,^[51] water splitting,^[52] photochemistry,^[53] as well as separation, storage,^[54] and gas capture,^[55] adsorption,^[56] and liquid storage.^[57]

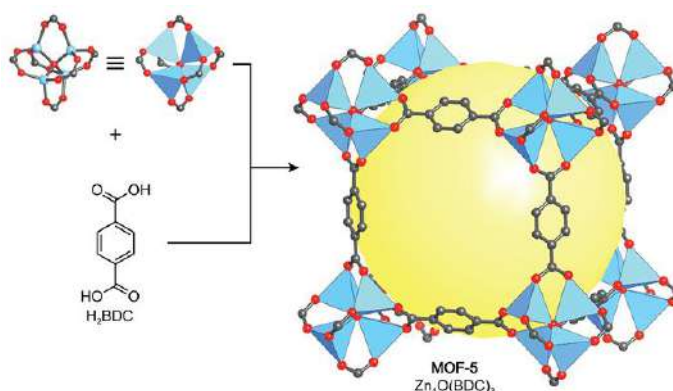


Figure 1.5 General scheme of MOF-5 synthesis.^[45]

1.2.3 Porous organic polymers (POPs)

The Porous organic polymers are highly reticulated organic networks considered emerging materials due to their high specific surface area, adjustable porosity, low density, high chemical and thermal stability, variable composition, convenient post-functionalization, extended π -conjugation, and high content of carbon, nitrogen, oxygen, and other non-metallic atoms.^[58] These materials have potential applications in catalysis, photocatalysis,^[59] CO_2 uptake,^[60] energy storage,^[61] detection and removal of water contaminants,^[62] sensing,^[63] sustained drug release, and many other applications. Depending on the type of link that is generated between the monomers to build the network, POPs could be divided into different types:

1.2.3.1 Porous aromatic frameworks (PAFs)

The first reference of this type of porous network was in 2008, when Arne Thomas synthesized the porous aromatic framework PAF-1 (Figure 1.6).^[64] PAFs are a class of highly stable organic materials composed of stable organic building blocks connected by carbon-carbon bonds through irreversible cross-coupling reactions using Suzuki-Miyaura,^[65] Yamamoto^[66] or Ullman^[67] coupling

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reactions. Since they primarily consist of periodic 2D/3D aromatic frameworks, this structure imparts a high specific surface area, adjustable porosity, open architectures, robust skeletons, and excellent thermal and chemical stability.^[65, 68, 69] Their strong carbon-carbon bonds enable PAFs to withstand harsh conditions and their aromatic rings are easily functionalized through aggressive chemical treatments, such as chlorosulfonic acid to introduce sulfonic acid groups into the network.^[70, 71] Thanks to their modular design, PAFs can be customized for various applications, such as gas storage and separation,^[72, 73] catalysis,^[74] ion extraction,^[75] energy storage^[76] and other domains.

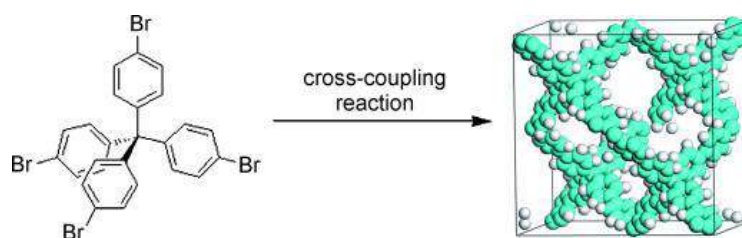


Figure 1.6 Synthesis of PAF-1.

1.2.3.2 Conjugated microporous polymers (CMPs)

In 2007, were reported the first examples of CMPs, with BET surface areas of up to $834 \text{ m}^2 \text{ g}^{-1}$.^[77] and, subsequently, in 2008,^[78] exceeding $1000 \text{ m}^2 \text{ g}^{-1}$. CMPs are three-dimensional semiconductor materials in which rigid aromatic groups are linked through double or triple bonds, resulting in π -conjugated microporous networks.^[79] This conjugation, formed by alternating single and multiple bonds in the extended network, provides valuable electronic properties. In most cases, covalent bonds in CMPs are irreversibly formed through a kinetic pathway, resulting in amorphous structures. The variety of molecular building blocks allows precise control over the functionality and structure of CMPs.^[80, 81] These materials can be synthesized by numerous procedures such as the Suzuki

cross-coupling reaction,^[82] the Yamamoto reaction,^[83] the Sonogashira-Hagihara reaction (Figure 1.7),^[84] and the Friedel-Crafts arylation,^[85] among others.

Since its discovery, they have been established as an important subclass of porous materials. When they were first discovered, CMPs were the only porous materials that possessed π -conjugation throughout the entire three-dimensional porous network.^[86, 87] CMPs hold promise for a wide variety of applications due to their extensive conjugation, significant porosity, adjustable chemistry, and frequently outstanding chemical and thermal stability, are used in gas storage and separations,^[77] encapsulation of chemicals,^[88] heterogeneous and photoredox catalysts,^[89-91] energy storage,^[92] biological,^[93] and photocatalytic H_2 evolution.^[94]

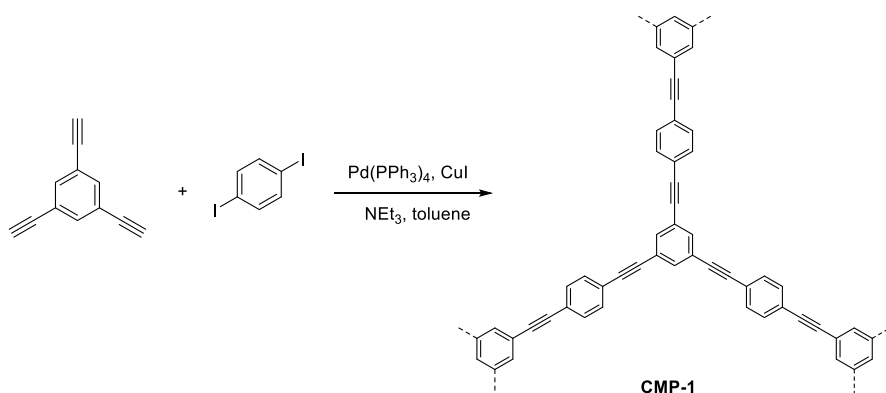


Figure 1.7 Synthesis of poly(aryleneethynylene) network, CMP-1 by Sonogashira-Hagihara coupling reaction.

1.2.3.3 Polymers of Intrinsic Microporosity (PIMs)

In 2002, McKeown and colleagues introduced a new class of POPs, synthesized through a polymerization reaction involving aromatic double nucleophilic substitution to form the dibenzodioxin linkage.^[95, 96] This reaction efficiently forms two covalent bonds simultaneously, enabling the creation of

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ladder-type polymers with a high average molecular mass. (Figure 1.8). They are characterized by their rigid and contorted structure, which prevents the efficient packing of polymer chains, thereby creating a permanent network of micropores with diameters smaller than 2 nm. This unique structure provides them with high porosity, typically ranging from 300 to 2000 m² g⁻¹, and excellent permeability.^[97] The great importance of these PIMs lies in the fact that, unlike conventional microporous materials, they are soluble and can be easily processed using solvent-based techniques.^[98] Thus they can be transformed into thin films to be used as highly selective gas separation membranes^[97, 99] or for organic nanofiltration.^[100] Other applications are also described, such as in heterogeneous catalysis,^[101] hydrogen storage,^[97] and sensors.^[102]

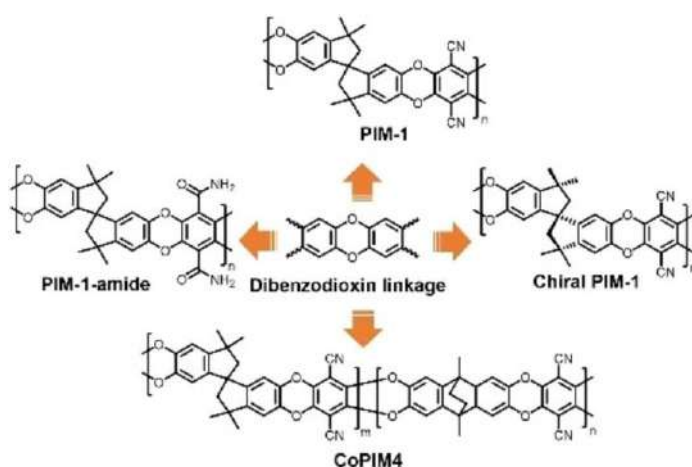


Figure 1.8 Scheme for the synthesis of PIMs.

1.2.3.4 Covalent Triazine Frameworks (CTFs)

In 2008, Thomas et al. synthesized a series of polymers containing triazine units through the cyclotrimerization of nitrile groups under ionothermal conditions, using molten zinc chloride (ZnCl₂) as a strong Lewis acid at 400 °C.^[103] These polymers can be partially crystalline and amorphous, with

conjugated and layered structures which are composed of ultra-strong aromatic C=N bonds (triazine units),^[104] providing them with excellent chemical and thermal stability.^[105] Additionally, they possess a high specific surface area, a large pore volume,^[106] They can have good resistance to strong acids and bases and exhibit flexibility in their design.^[107] CTFs can be prepared using different strategies (Figure 1.9), such as the ionothermal synthesis of nitrile groups,^[103] phosphorus pentoxide (P₂O₅)-catalyzed condensation of aromatic amides,^[108] superacid-catalyzed trimerization, typically using microwaves and CF₃SO₃H,^[109] Friedel-Crafts reactions,^[110] or Suzuki,^[111] Ni-catalyzed Yamamoto,^[112] and Pd-based Sonogashira couplings.^[113]

Recently, CTFs have attracted significant attention due to their remarkable heteroatom effect and unique applications in energy storage,^[107] heterogeneous catalysis,^[114] photocatalysis,^[115] gas separation and storage,^[116] and for activation of CO₂.^[117]

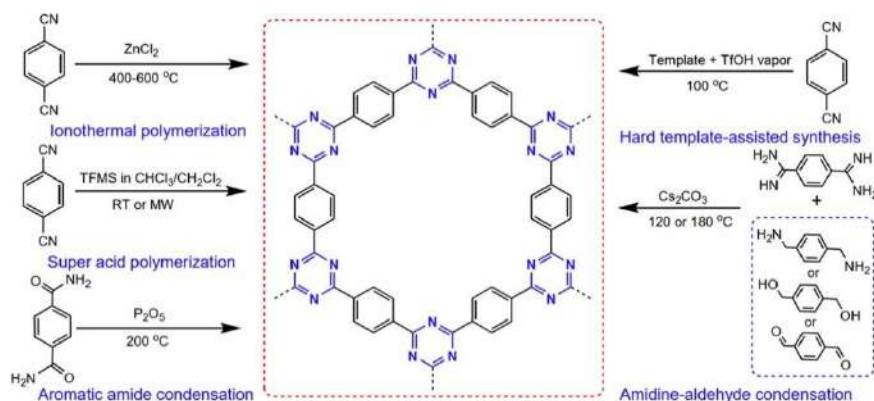


Figure 1.9 Synthesis of CTFs. ^[118]

1.2.3.5 Covalent Organic Frameworks (COFs)

It was Yaghi's research group that first introduced this type of porous solid in 2005, synthesized through condensation reaction of phenyl diboronic acid and

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hexahydroxytriphenylene.(Figure 1.10)^[119] They are a class of crystalline porous polymers that enable the integration of organic units into extended structures with periodic skeletons and ordered nanopores through strong covalent bonds. The formation of these strong bonds provides well-defined and predictable 2D or 3D crystalline structures. ^[120]An important feature of COFs is that they are designable; that is, the geometry and dimensions of the building blocks can be controlled to direct the topological evolution of structural periodicity. COF materials offer advantages such as low density, large surface area, adjustable pore size and structure, easily adaptable functionality, and a versatile covalent combination of building units.^[121] The well-defined crystalline porous structures, along with tailor-made functionalities, have provided COF materials with superior potential in various applications, such as gas storage,^[122] adsorption,^[123] optoelectronics,^[124] catalysis^[125] and electrochemical sensors.^[126]

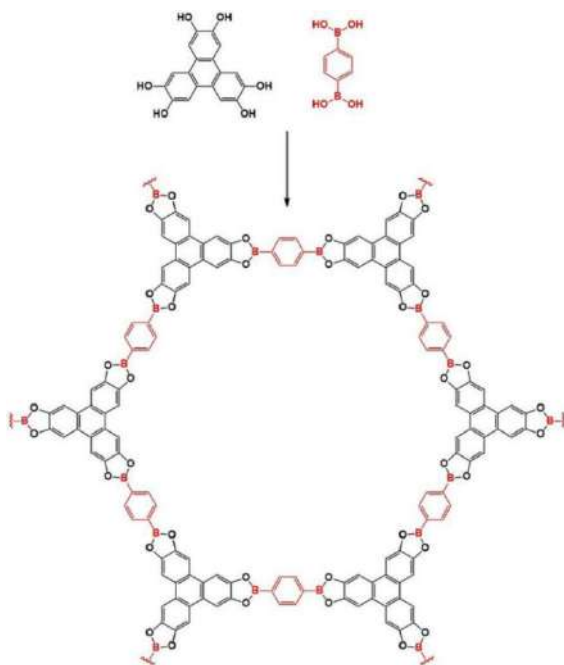


Figure 1.10 Synthesis of COF with diboronic acid and hexahydroxytriphenylene.

The last type of porous polymers, the hyper-crosslinked polymers, are the focus of this doctoral thesis, which is why they are described in greater detail in the following section.

1.2.3.6 Hyper-Cross-Linked Polymers (HCPs)

These materials were first introduced in the late 1960s by Davankov and collaborators, ^[127-133] who carried out a Friedel Craft reactions on polystyrene-type precursors in their swollen state, using spacers such as divinylbenzene chloride. The hyper-crosslinked polymers described by Davankow were known for being highly crosslinked structures, which gave them remarkable mechanical, thermal and chemical resistance, but their porous properties were not considered. However, it was not until 2011 that these materials really began to be known as a new class of porous polymers, thanks to the group of Prof. B. Tan.^[134] They produced HCPs through the direct polycondensation of aromatic molecule monomers, without the need of functionalization. Thus, the innovative approach proposed by Tan and collaborators, is known as the "knitting solvent strategy," in which formaldehyde dimethyl acetal (FDA), a highly reactive external crosslinker, is used to combine various simple aromatic compounds, such as benzene or biphenyl, through rigid methylene bridges via the anhydrous FeCl_3 catalyzed Friedel–Crafts reaction to form highly porous networks.

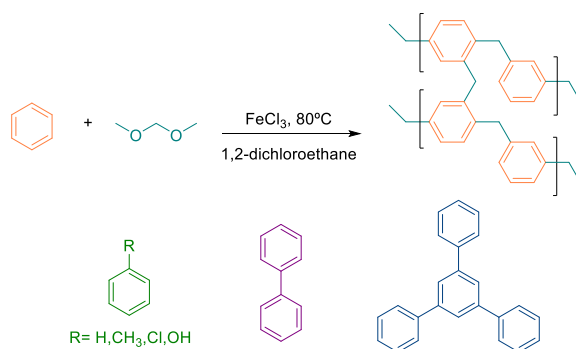


Figure 1.11 Synthetic pathway to obtain HCPs reported by Prof. B. Tan.^[134]

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This method avoids the need for monomers with specific polymerizable groups and eliminates using precious metal coupling catalysts. By adjusting the ratio of the external crosslinker, both the surface area and pore volume can be controlled. Additionally, various functional groups can easily be introduced into the porous structures by simply selecting the appropriate monomers.^[135] In addition to the use of an external crosslinking agent, it is possible to obtain HCPs using the solvent of the reaction CH_2Cl_2 or CHCl_3 as crosslinking agent as proposed N. McKeown and coworkers.^[136]

Recently mechanochemical synthesis,^[137] has become a more environmentally friendly and faster method for synthesizing HCPs, as it consumes less energy during the reaction and avoid the use of solvents.^[138] Thus, Lee and collaborators prepared the first HCPs using a simple ball milling method chose benzene, pyrrole, aniline, biphenyl, triphenylbenzene, and tetramethylbenzene as monomers.^[139] As mentioned earlier, hypercrosslinked polymers have several key characteristics, such as their microporous and highly crosslinked structure, which provides them with very high surface areas, often exceeding $1000 \text{ m}^2/\text{g}$, and a large pore volume. HCPs are chemically stable under a variety of conditions and can maintain their structure at relatively high temperatures. Their chemical stability and flexibility vary depending on the functional groups present in the material. They also have a high density of crosslinks, which enhances their structural rigidity and resistance to deformation, making them more durable than other porous materials. All these characteristics make them key materials for various industrial and environmental applications.^[140, 141]

Due to synthetic versatility and ease of preparation, hypercrosslinked polymers have undergone rapid development in both synthetic strategy and morphology control. These materials with adjustable physical and chemical properties are promising candidates for potential applications in gas capture and

storage, removal of pollutants, energy storage, catalysis, (Figure 1.12) among others.

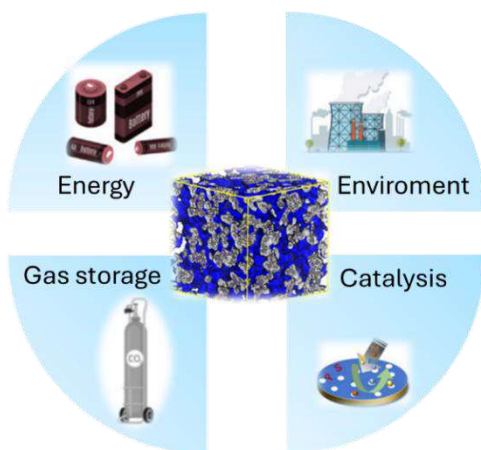


Figure 1.12 Applications of multifunctional hyper-cross-linked polymers.

Gas capture and storage was the first application published for these materials, being able of storing hydrogen, methane, and CO₂. due to the large surface areas and a high pore volume, they have.^[142] The adsorption capacity is comparable to many other microporous systems, but it does not reach the materials with higher micropore volumes, such as MOFs. but with high surface area, good thermal stability, and ease of functionalization, HCPs are promising candidates for CO₂ capture.^[143]

In **removal of micropollutants** HCPs have been used as solid absorbents in solid-phase extraction,^[144] treatment of waste waters,^[145] adsorption of organic vapours,^[146] and chromatographic analysis.^[147] Due to their abundant narrow micropores, the adsorbed molecules are transferred from the surface to the inner micropores through the channels, enhancing both the adsorption capacity and the adsorption rate. Additionally, HCP materials with a hydrophobic skeleton have a

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greater affinity for organic molecules, showing promising potential in water treatment.^[148]

HCPs not only have high specific surface area and excellent electrical conductivity, but they also exhibit remarkable cycle stability and long lifespan in **energy storage** devices. The dense HCP network allows favours energy absorption and release, especially in applications such as supercapacitors and batteries. Furthermore, their resistance to chemical and thermal degradation ensures a long service life, which is crucial for long-term energy storage devices. Their ability to rapidly store and release charges makes them ideal for systems requiring high efficiency and rapid charge-discharge cycles.^[149-151]

Finally, these materials can be used as **heterogeneous catalysts** in thermocatalysis, photocatalysis and electrocatalysis.^[152, 153] HCPs are considered one of the most efficient materials in catalysis for various reasons derived from their unique properties and structural characteristics, which facilitate their use as heterogeneous catalysts. These materials exhibit a high surface area and pore volume, which increases the number of active sites available for catalytic reactions, thereby improving the efficiency of the process. Furthermore, the high pore volume enhances the availability of reactants and products within the material structure.^[141] Their porous structure is adjustable, allowing the selection of different monomers and reaction conditions to create materials with specific pore characteristics. Some of these materials are characterized by two main pore size distributions: micropores and mesopores; this structure with mixed-sized pores has proven to be beneficial for improving substrate and product mass transfer, enhancing their diffusion, and optimizing reaction speed.^[154]

The high chemical and thermal stability of HCPs allows them to be used in catalytic reactions under demanding conditions, such as acidic, or basic conditions, or even in aqueous solvents. This stability also facilitates their

application in a wide range of industrial processes without losing effectiveness over time.^[155] Additionally, these materials allow the introduction of different functional groups, such as coordination sites for catalytic metal species, making it easier to adapt the material to specific catalytic needs. Acidic, basic, or even metal-coordinated sites can be added, allowing the structural integrity of HCPs to be easily adjusted by varying the selection of monomers and reaction conditions. This adaptability facilitates their use in a variety of catalytic reactions. Finally, these materials can be synthesized on a large scale and at a low cost.^[156]

There are numerous examples describing the synthesis of HCPs functionalized with basic groups or acids. For example for the case of basic hcp, Turner et al.^[157] developed series of amine-containing HCPs-based CO₂ adsorbents, divinylbenzene-maleic anhydride (DVB-MAH) copolymer. Recently, Liu et al.^[158] also reported one type of amine-functionalized HCPs (XAD-4-pc) through two steps including the reaction of Friedel-Crafts, and the impregnation with polyethyleneimine(PEI). While sulfonation is the most common strategy for acidic HCPs. Dong et al. synthesized sulfonated hypercrosslinked benzene networks containing up to 2 mmol g⁻¹ of SO₃H for the selective dehydration of D-(-)-fructose to 5-hydromethylfurfural,^[159] Sulfonated carbazole-based HCPs with impressive SO₃H densities were developed for the esterification of a number of fatty acids to produce biofuels.^[160]

Tan and co-workers reported the synthesis of organometallic catalysts by incorporating Pd(II) ions into three HCP networks containing PPh₃ as small molecular ligands. After incorporation of Pd(II) ions, the resulting KAPs(Ph-PPh₃)-Pd material showed the highest specific surface area (1036 m²/g), obtaining excellent performance in the Suzuki-Miyaura coupling reaction of aryl chlorides even under milder reaction conditions and in aqueous media.^[161] Other examples of these are polymers based on N-heterocyclic carbenes were also developed to

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incorporate metals such as palladium and copper. Pd-Catalysts facilitated reactions in aqueous media, while those with copper showed exceptional performance in organic synthesis, such as oxidative condensation reactions and Ullmann and Glaser-type couplings.^[162, 163] KAPs were also successfully synthesized by Ding and co-workers from the copolymerization of TPP and aryl compounds and were directly used as a support platform for Rh catalysts.^[164]

In summary, HCPs can be post-functionalized with different active centres including metals, which makes them very versatile catalysts. Figure 1.13 shows an analysis of the articles published in the Scopus database on HCPs used in catalysis, showing a remarkable increase in the number of publications since 2018. Thus, these materials may be promising heterogeneous catalysts.

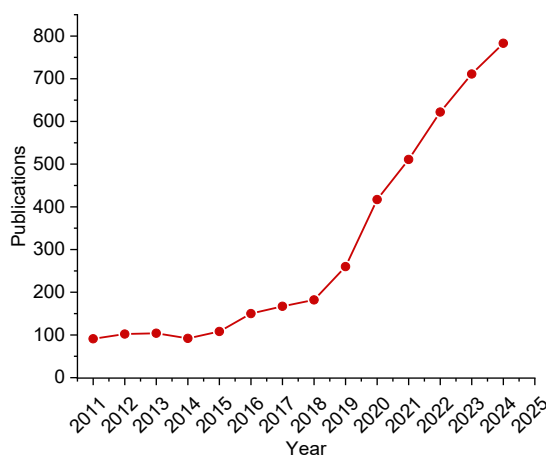


Figure 1.13 Publications per year registered recorded in Scopus regarding the use of HCPs as heterogeneous catalysts with HCPs catalyst and KAPs words.

1.3 Carbon dioxide utilization

The increase in CO₂ concentration in the atmosphere is a key factor in global warming, which can trigger extreme events, accelerated polar ice melt, and unpredictable natural disasters. Therefore, it is essential to mitigate the impact of

greenhouse gases and efficiently manage CO₂, to achieve a balance that is both environmentally sustainable and economically viable.^[165]

It is essential to avoid the generation of CO₂ from fossil sources and control its origin, as civilization largely depends on carbon-based products and services. The increase in CO₂ derived from fossil resources should be reduced, and CO₂, even from renewable sources, should be considered a valuable raw material rather than a waste product.^[166] To tackle this challenge, it is crucial to develop strategies for capturing, storing, and converting CO₂ in ways that allow its levels to be reduced and utilized effectively.^[167] However, there is a reactivity issue with CO₂, which can largely be directed using catalysts. These catalysts can activate the CO₂ molecule, as CO₂ in its molecular form is very stable and has limited reactivity. Catalysts reduce energy activation, helping to decrease the energy required to initiate a reaction. They are also used to generate highly reactive intermediates so that the reactions can proceed effectively.^[168, 169] CO₂ can be converted into numerous compounds. Here, we will discuss the main ones shown in the Figure 1.14: carbonaceous derivatives, alcohols and ethers, sugars and starches, aldehydes and ketones, acids, esters and acetates, and carbonates.

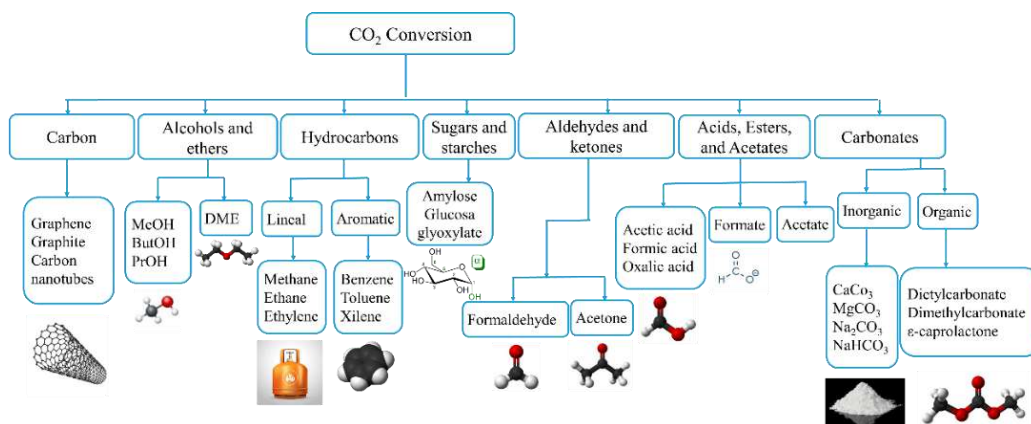


Figure 1.14 Compounds obtained from CO₂.

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The conversion of carbon dioxide into **carbonaceous materials**, such as graphene^[170], graphite^[171], carbon nanotubes^[172], or diamonds^[173], requires the transfer of four electrons per carbon atom. To facilitate this electron transfer, reducing agents such as alkaline metals, alkaline earth metals,^[174] or NaBH₄^[175] are used, typically at high temperatures and pressures, which also allows for the attainment of the supercritical state of CO₂. The main pathways for CO₂ reduction into carbonaceous materials involve combustion^[176] or electrolysis processes.^[177]

Alcohols, including methanol,^[178] ethanol,^[179] butanol,^[180] and propanol,^[181] as well as **ethers** such as dimethyl ether (DME), methyl tert-butyl ether,^[182] among others, are formed from the reduction of CO₂ with enough equivalents of H₂ through electrocatalytic,^[183] photocatalytic,^[184] and thermocatalytic reduction.^[185] Alcohols and ethers can serve as additives or replacements for fuels or act as chemical intermediates to produce polycarbonates.^[186] Traditional methanol production uses syngas and the Reverse Water-Gas Shift reaction (RWGS), as well as direct hydrogenation of CO₂ to methanol.^[187] Ethanol can be effectively produced as an intermediate after direct hydrogenation to methanol in the synthesis of butanol. A wide range of catalytic materials is used for these types of reactions, including Al, Co, Cu, In, Cr, La, Rh, Si, Ti, Zr, Pd, and Zn.^[188-190] DME serves as a crucial precursor for methylation agents, a fuel substitute for diesel engines and gas turbines, and is obtained through methanol dehydration. This process relies on hybrid/bifunctional catalysts that incorporate metal sites for CO₂ hydrogenation to methanol and Brønsted acid sites for the dehydration of methanol to produce DME.^[191, 192]

The **hydrocarbons** obtained from CO₂ include methane, ethane, ethylene, and aromatic compounds such as benzene, toluene, and xylene,^[193] can be obtained through electrochemical,^[194] photocatalysis,^[195] and plasmonic catalysis.^[196]

Methane is the simplest (C_1) hydrocarbon, constituting more than 90% of natural gas, which represents over 20% of the world's primary energy, thus being a key advancement in obtaining methane by CO_2 conversion.^[197, 198] Ethane (C_2), can be obtained electrochemically using copper-doped palladium^[194] or Fe_2O_3 catalysts.^[199] Additionally, the use of Cu_2O as a working electrode has shown the production of ethylene and ethane.^[194] Efforts to directly convert CO_2 into ethylene are primarily based on electrocatalytic methods, where copper-based materials are almost exclusively used.^[200] Direct conversion of CO_2 into benzene, toluene, and other aromatic compounds has been achieved using Zn/ZrO -zeolite,^[201] or $Zn/AlOx$ Zeolite.^[202]

Sugars and starches are a class of molecules used in the surfactant, textile and plastics industries. Most CO_2 -to-sugar routes involve CO , formaldehyde, or methanol as intermediates prior to thermal or electrochemical conversion to sugars. For example, B doped diamond electrode is used for formaldehyde synthesis,^[203] and divalent cations (typically calcium) are used for its conversion to sugars, that it's the Formose reaction.^[204] Studies using stereospecific ligands to increase the yield of D-glucose in the Formose reaction have also been reported.^[205] In addition, these studies have been extended beyond simple sugars to include amyloid, amylopectin, and glycoxylate as larger sugar polymers.^[206]

Ketones and aldehydes are widely used in industry due to the benefit of having carbonyl groups ($C=O$). The conversion of CO_2 into these compounds is being studied through thermal hydrogenation,^[207] photocatalysis,^[208] biochemical transformations,^[209] and electrocatalysis.^[210] It has been demonstrated that electrochemical reduction can only be carried out using copper as a monometallic electrode.^[211] Formaldehyde, used as a preservative in plastics, is obtained with boron-doped diamond (BDD) electrodes, however, these electrodes are expensive and are manufactured under extreme conditions. Therefore, it has been shown that

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the use of a Cu electrode improves the forming efficiency.^[212] There are new avenues of research that instead of using electrochemistry explore the use of thermo-, biochemical and catalytic systems. These processes tend to incorporate semiconductor co-catalysts based on cobalt nanomaterials on photoactive titania supports.^[213] To convert CO₂ to ketones such as acetone, more energetically costly C-C bond couplings must occur. Recent researchers employed a Cu electrode together with a KHCO₃ electrolyte^[214] or single atom Cu catalysts dispersed on N-doped carbon substrates to obtain acetone as the main product.^[215]

The conversion of CO₂ into **acids, esters and acetates** is one of its most extensively researched transformations. In addition to being integrated into larger molecules like salicylic acid, CO₂ can be directly transformed into compounds such as acetate, acetic acid, and formate.^[216-218] Formic acid is the most prevalent and is produced by reducing CO₂ to formate through electrochemical,^[219] thermal,^[220] or photochemical.^[221] Subsequently, formate undergoes protonation to yield formic acid or is esterified into alkyl formates. Recently, the production of formic acid from CO₂ in flow gas catalyzed by a mixed covalent triazine triazine framework (CTF) of Ru-doped bipyridine has been reported.^[222] Oxalic acid can also be synthesized from CO₂ via three pathways: direct electrochemical reduction ^[223] or two indirect methods, involving formate conversion using superbases as catalysts^[224] or oxidative carbonylation of CO catalyzed by palladium in the presence of alkyl nitrites.^[225]

Inorganic and organic carbonates are essential in industry and carbon capture. Inorganic carbonates such as CaCO₃, MgCO₃, and Na₂CO₃ ^[226-228] are obtained through mineral carbonation, precipitation, or geological injection with metal oxides or hydroxides.^[229-231] An example is their use in cement-based materials (CBM).^[232] Na₂CO₃, which is key in glass and detergent manufacturing, is produced via the Solvay process,^[233] while NaHCO₃ is obtained by reacting

Na_2CO_3 with additional CO_2 , and is used in antacids and water treatment.^[229] Other metallic carbonates (K, Li, Ba) are used in fertilizers, batteries, and pharmaceuticals.^[234-236] Organic carbonates are primarily generated by oxidative carbonylation. Key examples include dichloromethane (DMC) and dichloroethane (DEC), which are used as solvents or methylation agents. They are synthesized from CO_2 and alcohols using alkaline or metal oxide catalysts such as CeO_2 .^[237, 238] They can also be obtained through redox-neutral electrochemical conversion with Pd/C catalysts and NaBr electrolytes.^[239] Cyclic carbonates result from the cycloaddition of epoxides with CO_2 in the presence of catalysts, such as in the production of ϵ -caprolactone for biomedical applications.^[240] Di(aryl) carbonates are synthesized through oxidative carbonylation of phenols with CO or CO_2 .^[241] Additionally, the reaction of epoxides with CO_2 leads to polymeric carbonates, with applications in plastics and advanced polymers.^[242]

1.3.1 HCPs in CO_2 conversion

As it was previously mentioned HCPs, serve as highly effective catalysts and as expected can also provide a robust platform for converting CO_2 into various products. This process can be further enhanced through simple functionalization of HCPs. Thus, in recent years, numerous studies have focused on the conversion of captured CO_2 using HCPs as catalysts, with particular emphasis on factors such as stability, efficiency, and recoverability.^[243] They have been used as catalysts to convert CO_2 into series of important chemical products such as linear and cyclic carbonates, polycarbonates,^[244, 245] urethanes, polyurethane,^[246] oxazolidinones,^[247, 248] formamides,^[249] and others.^[250] In particular, the conversion of CO_2 into carbonates has been the most studied reaction over the past decade, leading to the design of various types of HCPs. Thus, for example, amino based on tetraphenyl porphyrin of Al, Fe, Mn or Co.^[251]

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Have demonstrated a high affinity for CO₂ and efficient catalytic performance under moderate temperature and pressure conditions. Li et al. reported that N,N'-*Bis*(salicylidene)-ethylenediamine (Salphen) and fluoranthene could be used as monomers to generate hollow spherical HCPs obtaining outstanding performance, achieving a remarkable 94% CO₂ conversion.^[252] However, many of these catalysts exhibit low efficiency as they require harsh reaction conditions and/or rely on the presence of additives, or solvents to achieve optimal performance. For this reason, ionic liquids have proven to be excellent activators of CO₂ for its conversion into valuable products, with imidazolium salts being particularly noteworthy.^[253] Regarding porphyrins, a series of HCP based on aluminum porphyrin and ionic liquids has been developed. The incorporation of imidazolium-based ILs as flexible side chains into the porphyrin backbone enhances the stability of the active metal species, optimizing their catalytic performance.^[254] Other examples based on ionic liquids include the work of Huang et al. who synthesized benzimidazole-functionalized HCPs for efficient CO₂ capture and conversion ^[255] to obtain cyclic carbonates with high CO₂ conversion. Additionally, Wang et al. modified HCPs with imidazolium salts as functionalized active sites for the conversion of CO₂ into propylene carbonate^[256]. Ding et al. reported that HCPs grafted with ionic liquids could convert up to 96% of propylene oxide into propylene carbonate.^[257] Seo et al. successfully loaded various imidazolium-based ionic liquids into polymers for CO₂ cycloaddition,^[258] while Li et al. prepared mesoporous PILs with a high charge density for the same reaction.^[259] The porous structure of these polymers is crucial for CO₂ capture, while anionic halides such as bromide (Br⁻), iodide (I⁻), and chloride (Cl⁻) in the polymer backbone can act as ring-opening agents in the CO₂ cycloaddition reaction.^[260]

1.4 References

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Objectives

The main goal of this thesis is the synthesis of porous organic materials based on hyper-crosslinked polymers for their application as heterogeneous catalyst to obtain high-value-added products understudied from CO₂. For this purpose, three chapters have been developed where different CO₂ conversions are carried out using catalysts tailored for each transformation.

Chapter 1:

This chapter aims at the synthesis and characterization of monomers containing ionic liquids based on imidazolium chloride moieties. Subsequently, they will be polymerized by Friedel-Crafts reactions to obtain the corresponding hyper-crosslinked polymers, which will also be characterized by standard solid-state techniques.

Finally, the catalytic activity of these materials for the synthesis of formamides from amines and CO₂ will be studied, including an analysis of their recovery and a proposal of the reaction mechanism.

Chapter 2:

In this chapter, four metallic catalysts will be prepared and characterized using the HCPs synthesized in the previous chapter to obtain metal-N-heterocyclic carbenes by incorporating Ag (I) and Cu (I) (HCP-NHC-Cu, HCP-NHC-Ag, HCP-*Bis*NHC-Cu and HCP-*Bis*NHC-Ag).

Study of their catalytic performance in multicomponent reactions to obtain cyclic carbamates using propargylic alcohol, CO₂, and primary amines or asymmetric carbonates from a primary alcohol as a third component. This study will include recycling studies and reaction mechanism proposals.

Chapter 3:

This chapter will address the synthesis of a specific molecule, 2,5-furan dicarboxylic methyl ester (FDME) from furfural and CO₂ by a three-step reaction. The first step will involve an oxidative esterification catalyzed by HCP-BzmimCl (Chapter 1). For the second step, the carboxylation reaction, a new HCP catalyst based on cobalt (II), (HCP-Salphen-Co) will be synthesized. In this case as a novelty the HCP support will be prepared by a mechanochemically activated Friedel-Crafts reaction. The last step will consist of a conventional acid esterification.

The catalytic activity and recyclability of the corresponding catalysts will be evaluated and mechanisms for the oxidative esterification and carboxylation reactions will be proposed.

Chapter 1. Imidazolium chloride-based hyper-crosslinked polymers catalysts for the synthesis of formamides from amines and CO₂

3.1 Introduction

Formamides are highly versatile industrial chemicals since are integral in the production of various pharmaceuticals, agrochemicals, and nitrogen-based heterocycles serving as key intermediates in the synthesis of a wide array of bioactive molecules, including antibiotics, anti-cancer agents, and herbicides, thus playing a pivotal role in enhancing agricultural productivity and healthcare outcomes.^[1] Formamides can be prepared from CO₂ and amines (Figure 3.1) by a *N*-formylation process that involves the addition of carbon dioxide to the amine usually in the presence of a reducing agent that also acts as proton donor (silanes or boranes) and a catalyst.

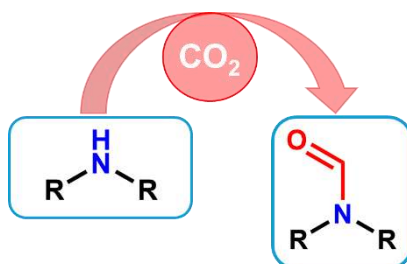


Figure 3.1 Synthesis of formamides from CO₂.

A range of noble metals, including Ir, Pt, Pd, Ru or Rh or non-noble metals such as Fe, Ni, Co, Cu, Mb or Zn, have been identified as effective catalysts in the *N*-formylation of amines using CO₂ and reducing agents like hydrogen (H₂), silanes, or boranes. Despite the proven efficacy of these catalysts, most of the associated catalytic processes demand stringent operational conditions. High partial pressures of CO₂, (exceeding 10 bars), elevated reaction temperatures (above 100°C), and extended reaction times (typically between 16 and 24 hours) are generally required to achieve high yields of formamides.^[2] These stringent conditions demonstrate the complexity and challenges posed by the optimization of catalytic processes for the *N*-formylation of amines with CO₂. Moreover, the

energy requirements associated with these processes raise concerns regarding their overall sustainability and economic feasibility. Consequently, the research and development described are crucial to improving the efficiency and feasibility of these reactions, with the goal of simplifying the process, reducing energy consumption, and improving overall performance and scalability. Developing more efficient catalysts that operate under milder conditions could lead to a significant breakthrough in the sustainable and economically viable production of valuable chemicals from CO₂, contributing to both environmental protection and industrial innovation. [3-5] In this sense Ionic liquids have received increasing attention in the field of CO₂ capture due to their high CO₂ absorption capacity, stability, and low saturation vapor pressure.[6]

ILs are a class of materials composed of organic anions and cations, which are generally liquids at room temperature, initially developed as eco-friendly and sustainable solvents and later in other roles across various fields such as chemistry, chemical engineering energy,[7] environment,[8] medicine, and pharmaceuticals.[9] These materials have unique properties, such as being non-flammable, having high ionic conductivity, a wide electrochemical range, high thermal and chemical stability, extremely low vapor pressure, high solubilization capacity, and physicochemical properties that can be adjusted by modifying the structures of cations and anions.[6, 10]. Typical cations of ILs include imidazolium, pyridinium, quaternary ammonium, and quaternary phosphonium, among others, while typical anions include halides, carboxylates, phenolates, and azolates.[11] (Figure 3.2).

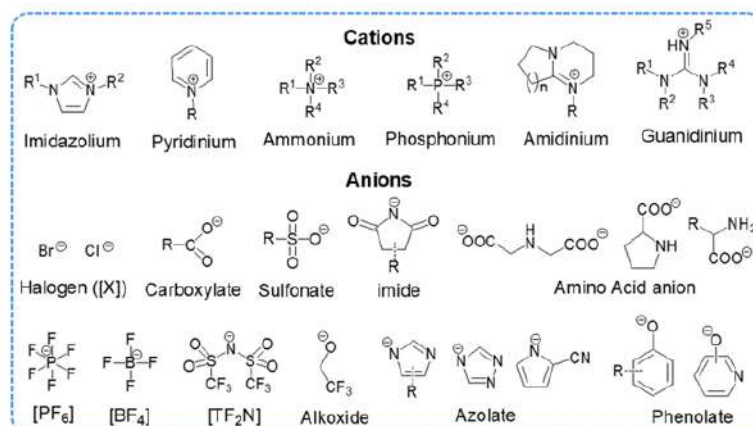


Figure 3.2 Structures of cations and anions of ILs.^[11]

Many types of ILs with functional anions, such as halides, alkoxides, carboxylates, imides, and carbanions, have been designed and synthesized, leading to a variety of CO₂ derived products.^[12-14]

In 2015, Liu et al. published a pioneering study demonstrating the efficacy of ionic liquids based on 1-alkyl-3-methylimidazolium salts as excellent catalysts for amine formylation. His method used 1 atmosphere of CO₂ and phenylsilane as proton donor at room temperature, resulting in the production of formamides with outstanding yields.^[15] This innovative method highlighted the potential of ionic liquids as metal-free catalysts for such reactions. The results aroused great interest in the scientific community due to the ability to carry out these reactions under mild conditions: room temperature and moderated CO₂ pressure (1-10 bar)^[16-19] The possibility of having a supported ionic liquid is a great opportunity since having a heterogeneous catalyst that can be recyclable would make the *N*-formylation much more sustainable. Many ionic liquids have been incorporated into (COFs)^[20, 21], (MOFs)^[22, 23] and (POPs)^[24, 25] mainly by post-functionalization techniques. These catalysts generally operate at room temperature and low CO₂ pressures (1-5 bar), requiring about 24 hours to achieve more than 85%

conversion of the respective amines. They also demonstrate good recyclability, retaining their efficiency for up to five cycles. Although hypercrosslinked polymers containing supported ionic liquids have been used as heterogeneous catalysts to produce cyclic carbonates from CO₂ [26, 27], there is only one example of such a polymer used to catalyze the synthesis of formamides from CO₂. This catalyst, known as PiP@QA (Figure 3.3) was synthesized by postfunctionalization of a preformed binaphthol-based porous polymeric network using a Williamson's ether reaction with quaternary ammonium bromide. This catalyst showed moderate catalytic performance, achieving a 58% yield for solvent-free *N*-formylation of *N*-methylaniline using CO₂ and phenylsilane as reducing agent at 35°C and 5 bar for 8 hours. Extending the reaction time to 16 hours resulted in a yield of 99%.^[28]

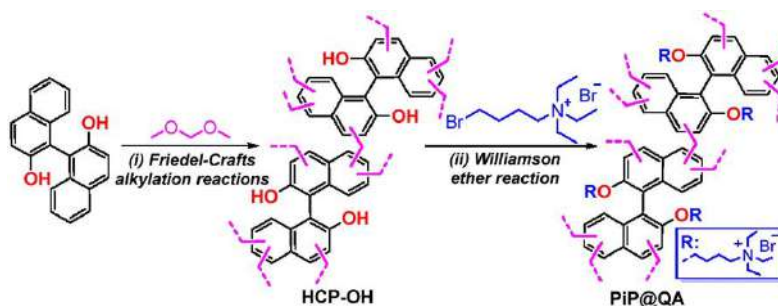


Figure 3.3 Synthesis of porous polymeric an ionic-liquid-based hyper-crosslinked polymer used as catalyst (PiP@QA).

Thus, in this chapter, the preparation of imidazolium chloride-based hyper crosslinked polymers, HCP-BzmimCl and HCP-Bis(BzmimCl), is reported in one step, directly from the polymerization of the corresponding imidazolium chloride-based monomers. Both heterogeneous catalysts were used in the *N*-formylation of different amines with CO₂ and phenylsilane as proton donor to obtain the corresponding formamides.

3.2 Objectives

Herein, we intend to use of imidazolium chloride-based hyper crosslinked polymers HCP-BzmimCl and HCP-*Bis*(BzmimCl) prepared in one step, directly from the corresponding ionic-liquid supported monomers, as heterogeneous catalysts in the formylation of different amines with CO₂ and phenylsilane to obtain the corresponding formamides.

- Synthesis and characterization of an imidazolium chloride-based monomer: *Bis*(BzmimCl), by a typical imidazole alkylation reaction using an excess of CH₂Cl₂ in the presence of DMSO as a key polar additive.
- Synthesis and characterization through standard solid-state techniques of two hyper crosslinked polymers using the above monomers and biphenyl as co-monomer (HCP-BzmimCl and HCP-*Bis*(BzmimCl))
- Study of the catalytic activity of the above catalysts in the synthesis of formamides from amines using CO₂ and phenylsilane as proton donor. This objective includes the study of recycling of the two catalysts, a mechanistic proposal of the reaction, and a comparison with other catalysts published for this same CO₂ conversion.

3.3 Results and discussion.

3.3.1 Synthesis and characterization of imidazolium chloride-based monomer *Bis*(BzmimCl)

The monomer *Bis*(BzmimCl) was prepared according to the literature from 1-benzylimidazole using excess of CH_2Cl_2 , in the presence of DMSO as a key polar additive.^[29] (Figure 3.4) for this type of imidazole alkylation reaction, DMSO is a key component because it stabilizes the key intermediate, phenyl-chloromethyl-imidazolium, formed with the alkylating agent, in this case dichloromethane, and also favors reaction rates and allows working at higher temperatures.

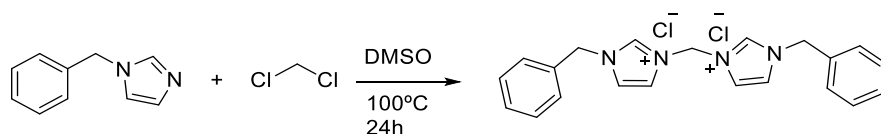


Figure 3.4 Reaction scheme for the synthesis of *Bis*(BzmimCl)

Bis(BzmimCl) was obtained in good yield (90%), and the structure was confirmed by NMR. In the ^1H -NMR spectrum it can be observed a signal at 9.61 ppm corresponding to the protons of the methylene bridge (b) which confirms the dimerization of 1-benzylimidazole. The signals corresponding to the protons of the imidazolium rings appear at 8.04, 7.85 and 6.66 ppm (a, c and d respectively) while those corresponding to the protons of the benzene rings appear between 7.44 and 7.85 ppm. Finally, the aliphatic proton (e) is showed at 5.46 ppm (Figure 3.5) In the ^{13}C -NMR, the signal corresponding to the carbon of the benzene ring that is attached to the aliphatic carbon is observed at 138 ppm (f). The signals corresponding to the carbons of the imidazolium ring appear at 134, 123 and 122 ppm (d, a and c, respectively), while the other carbons of the benzene ring are

around 128 ppm (C_{aromatic}). Finally, the two aliphatic carbons appear at 58 and 52 ppm (b and e, respectively). (Figure 3.6).

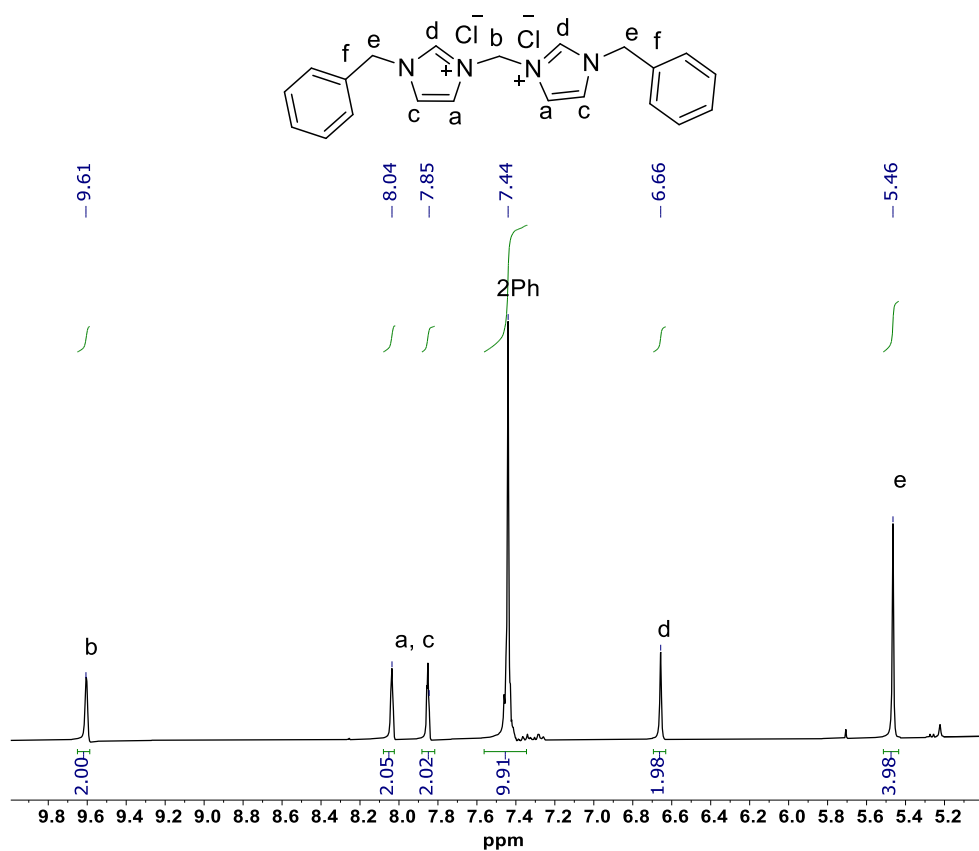


Figure 3.5 ^1H NMR spectrum of *Bis*(BzmimCl) (300 MHz, $\text{d}_6\text{-DMSO}$).

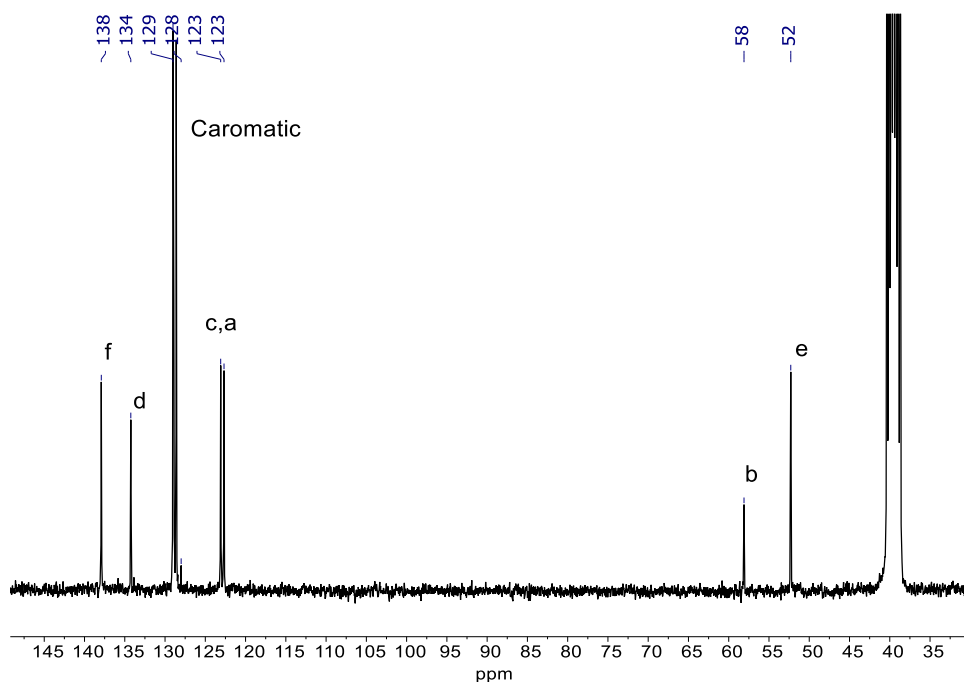


Figure 3.6 ^{13}C NMR spectrum of *Bis*(BzmimCl) (300 MHz, $\text{d}_6\text{-DMSO}$).

The elemental analysis was quite similar to the calculated one confirming the proposed structure (Table 3.1).

Table 3.1. Elemental analysis of *Bis*(BzmimCl)

Catalyst		C(%)	H(%)	N(%)	N/H
<i>Bis</i> (BzmimCl)	Calculated	62.85	5.53	12.96	2.34
	Experimental	58.74	5.15	12.82	2.48

The FTIR revealed the two characteristic bands of the imidazolium ring, located at 1550 cm^{-1} and 1160 cm^{-1} , which correspond to the C=N and C-N stretching vibrations, respectively. Furthermore, bands associated with the stretching vibrations of the aromatic biphenyl rings are observed in the range of $1400\text{-}1600\text{ cm}^{-1}$ (Figure 3.7).

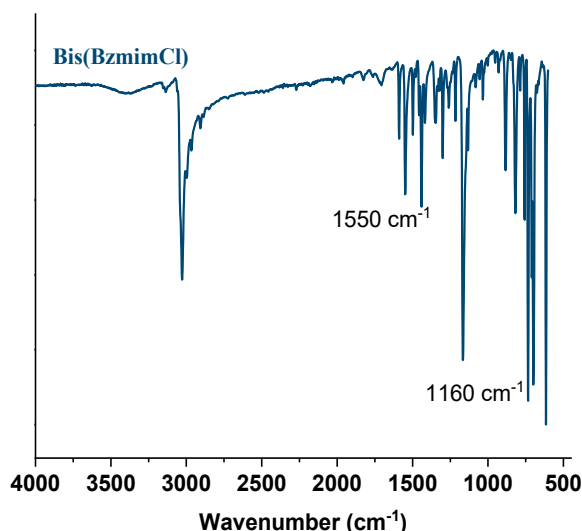
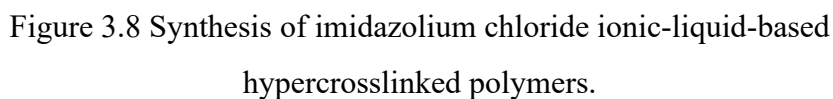


Figure 3.7 FTIR spectrum of *Bis*(BzmimCl).

3.3.2 Synthesis and characterization of imidazolium chloride-based hypercrosslinked polymer.

These polymers were synthesized in a one-step process from the corresponding monomers, a commercial monomer, BzmimCl, and the one synthesized above, *Bis*(BzmimCl), and biphenyl as comonomer. They reacted using AlCl_3 as a catalyst and dichloromethane as solvent and linker between the monomers. Due to the high reactivity of biphenyl in Friedel-Crafts coupling reactions, to ensure enough imidazolium chloride centers, the reaction was carried out with using an excess of BzmimCl and *Bis*(BzmimCl) monomers respect to biphenyl, as in the synthesis of other hypercrosslinked networks which biphenyl has been copolymerized.^[30-32]



66

Table 3.2 Elemental analysis of HCP-BzmimCl and of HCP-*Bis*(BzmimCl).

Catalyst		C(%)	H(%)	N(%)	N/H
HCP-BzmimCl	Calculated ⁽¹⁾	72.53	6.04	9.40	1.55
	Experimental	67.35	5.86	8.57	1.46
HCP- <i>Bis</i> (BzmimCl)	Calculated ⁽²⁾	72.11	6.72	9.34	1.39
	Experimental	58.2	5.6	9.4	1.67

(1) Two units of BzmimCl per biphenyl (Benzene / Imidazolium = 2)

(2) One unit of *Bis*(BzmimCl) per biphenyl (Benzene / imidazolium =2)

FTIR spectroscopy (Figure 3.9) showed the two characteristic bands of the imidazolium ring, located at 1550 cm^{-1} and 1150 cm^{-1} as it was also observed in the FTIR spectrum of the *Bis*(BzmimCl) monomer (Figure 3.7). These bands are indicative of the C=N and C-N stretching vibrations of the imidazolium ring, respectively, confirming the presence and correct incorporation of the imidazolium groups into the polymeric structure. In addition, the bands in the $1400\text{-}1600\text{ cm}^{-1}$ region are associated with the stretching vibrations of the aromatic biphenyl rings. The appearance of these signals in the FTIR spectra confirms the formation of the expected bonds between the monomers and biphenyl.^[33]

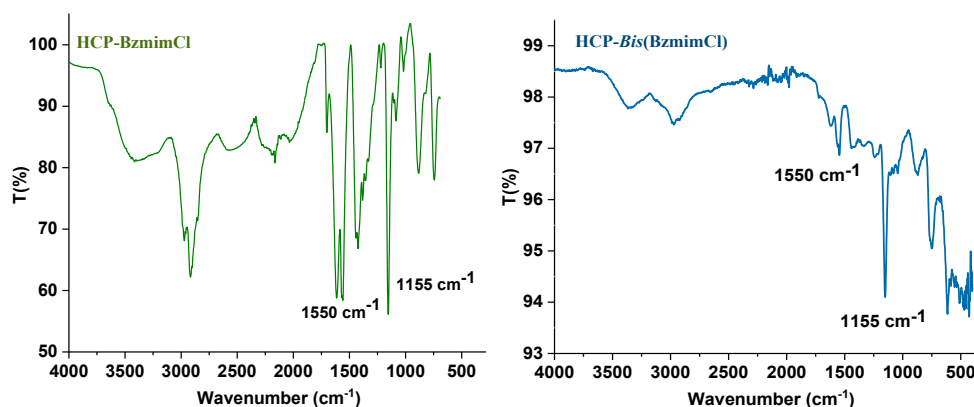


Figure 3.9 FTIR spectra of HCP-BzmimCl and HCP-Bis(BzmimCl).

The ¹³C NMR spectra (Figure 3.10) showed an intense and broad signal between 110 and 130 ppm attributed to the aromatic carbons of the benzene rings. This signal is accompanied by a shoulder around 140 ppm that was attributed to the aromatic carbons of the benzimidazolium rings. The characteristic signals of the methylene groups appeared between 35 and 50 ppm whereas the signal at 60 ppm was attributed to the methyl groups between the imidazolium moieties.^[34]

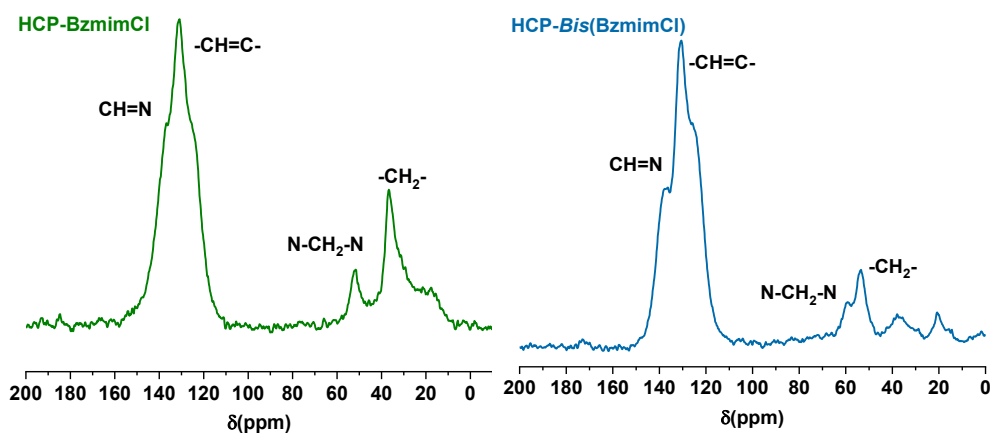


Figure 3.10 ¹³C NMR spectra HCP-BzmimCl and HCP-Bis(BzmimCl).

Thermogravimetric analyses (TGA) (Figure 3.11) indicated good thermal stability with a two-step degradation pattern. The first step starts at 280 °C with a weight loss between 12% and 17% attributed to the loss of the chlorine anions from the imidazolium units in both cases. The second step occurs at 500-540 °C, corresponding to the generalized degradation of the network. The absence of residue confirmed the complete elimination of the aluminum trichloride used during the polymer synthesis.

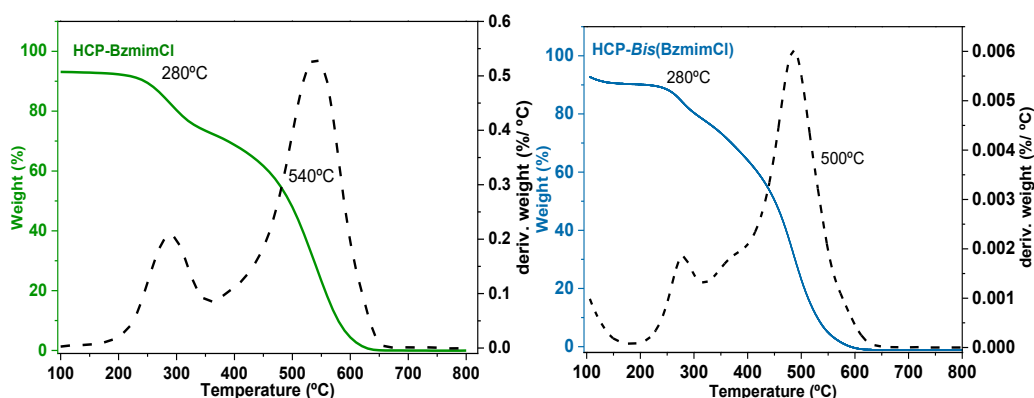


Figure 3.11 TGA of HCP-BzmimCl and HCP-Bis(BzmimCl).

The XPS survey spectra of both materials confirmed the presence of C, N, and Cl elements in the structures (Figure 3.12 and Figure 3.13). The C1s traces of both materials showed a predominant peak at 285eV, attributed to C-C bonds. Additionally, the C 1s XPS traces of HCP-BzmimCl displayed a second peak at a slightly higher energy of 287.2eV, corresponding to the binding energy of C-N bonds. The presence of an intense peak at 402eV in the N 1s traces confirmed the existence of quaternary nitrogen (N^+). Besides the peak at 394eV, which corresponds to the unprotonated nitrogen of the imidazole ring.^[35, 36] The characteristic Cl 2p^{3/2} peak was observed at 197eV and as expected, it was accompanied by a second peak at 199eV due to spin-orbit coupling^[37]. The Cl 2p

XPS traces of HCP-*Bis*(BzmimCl) revealed an additional peak at 200eV, indicative of covalent chlorine species^[38], which can be attributed to dichloromethane trapped within the network.

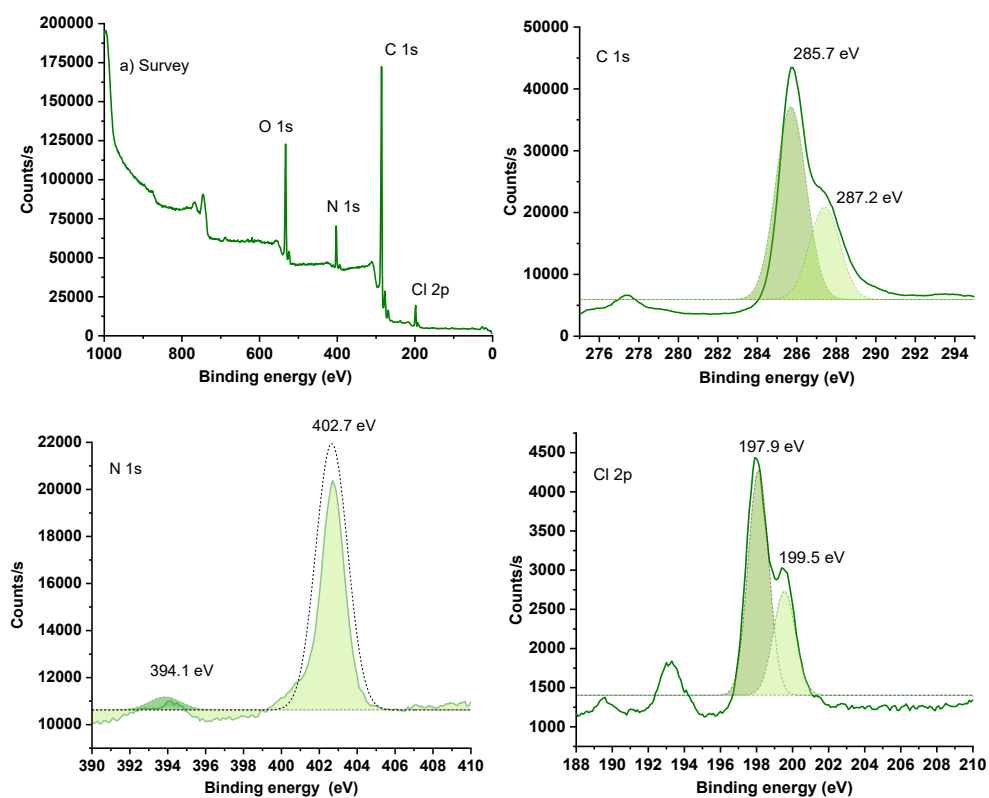


Figure 3.12 XPS a) survey spectra b) C 1s c) N 1s d) Cl 2p traces of HCP-*Bis*(BzmimCl).

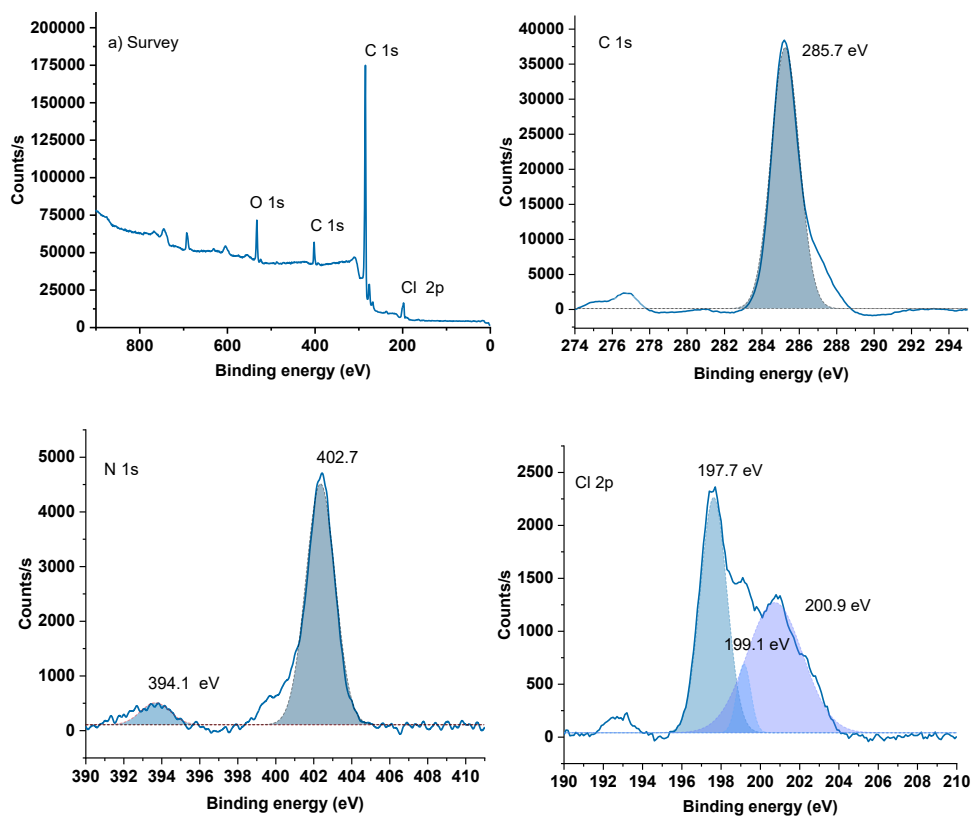


Figure 3.13 XPS a) survey spectra b) C 1s c) N 1s d) Cl 2p traces of of HCP-*Bis*(BzmimCl).

The porosity was investigated by N₂ adsorption/desorption isotherms (Figure 3.14). The specific surface areas of both polymers were low, 4.5 m²/g for HCP-BzmimCl and 16.9 m²/g for HCP-*Bis*(BzmimCl) which indicated low porosity for both catalysts.

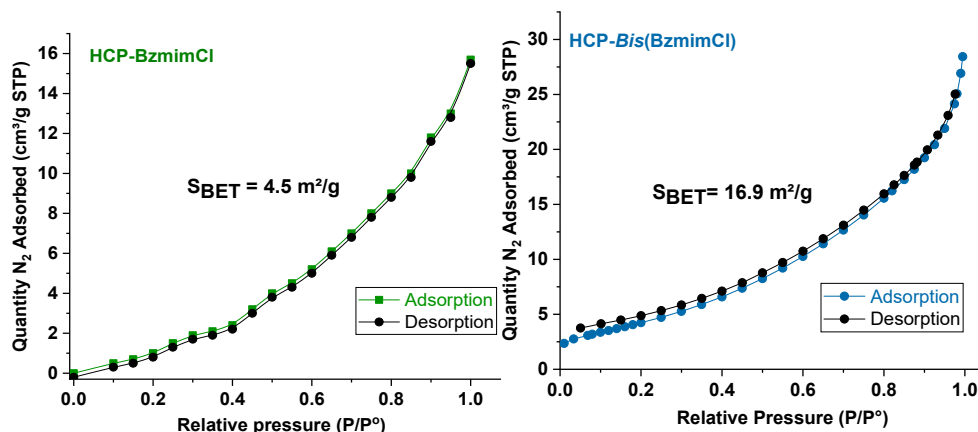


Figure 3.14 N_2 adsorption/desorption isotherms HCP-BzmimCl and HCP-Bis(BzmimCl).

The CO_2 isotherms (Figure 3.15) demonstrated a moderate CO_2 uptake capacity for both materials. Specifically, HCP-BzmimCl exhibited a CO_2 uptake of 0.8 mmol/g, while HCP-Bis(BzmimCl) showed a slightly lower uptake of 0.5 mmol/g. These uptake capacities correspond to moderate Langmuir surface areas of 147 m²/g for HCP-BzmimCl and 131 m²/g for HCP-Bis(BzmimCl). The relatively higher values observed in HCP-BzmimCl compared to HCP-Bis(BzmimCl) can be attributed to a more open structural configuration in HCP-BzmimCl. This openness likely enhances the accessibility of CO_2 molecules to the imidazolium rings embedded within the structure, thereby facilitating a greater adsorption capacity.

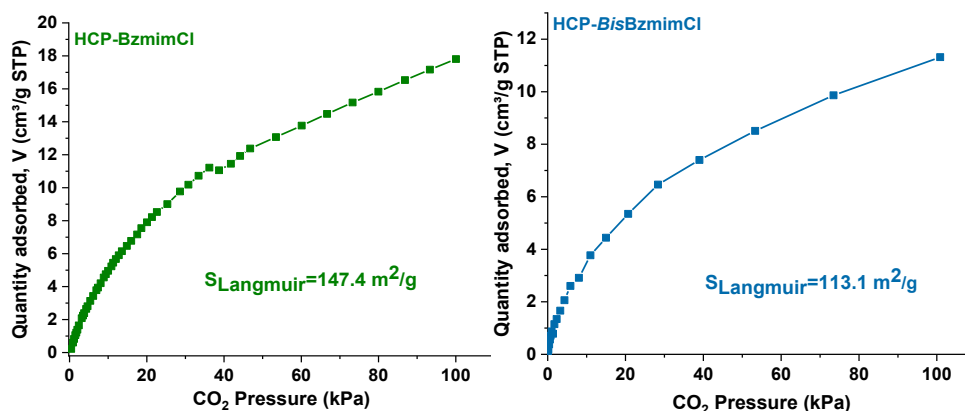


Figure 3.15 CO₂ isotherms HCP-BzmimCl (left) and HCP-Bis (BzmimCl) (right).

The SEM images (Figure 3.16) revealed that both polymers are formed by aggregates of irregularly shaped particles on the micrometer scale. The TEM images of both catalysts (Figure 3.17) also displayed a high degree of disorder, with some areas showing a certain level of microporosity in a similarly disordered manner.

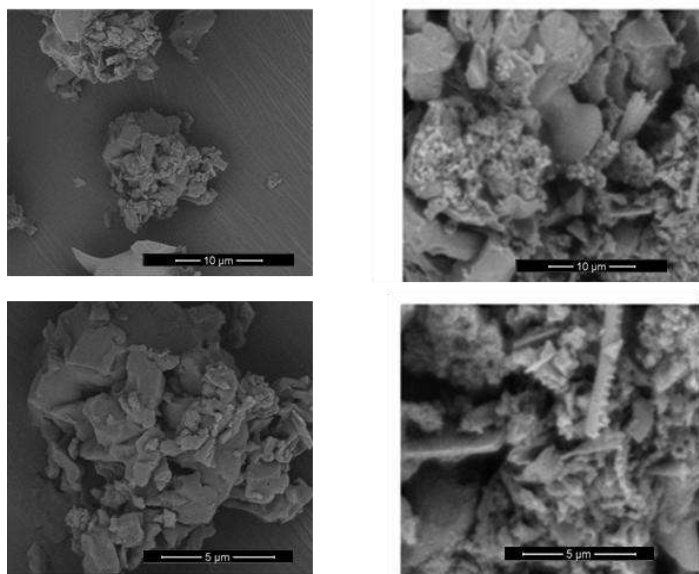


Figure 3.16 SEM images of HCP-BzmimCl (left), HCP-*Bis*(BzmimCl) (right).

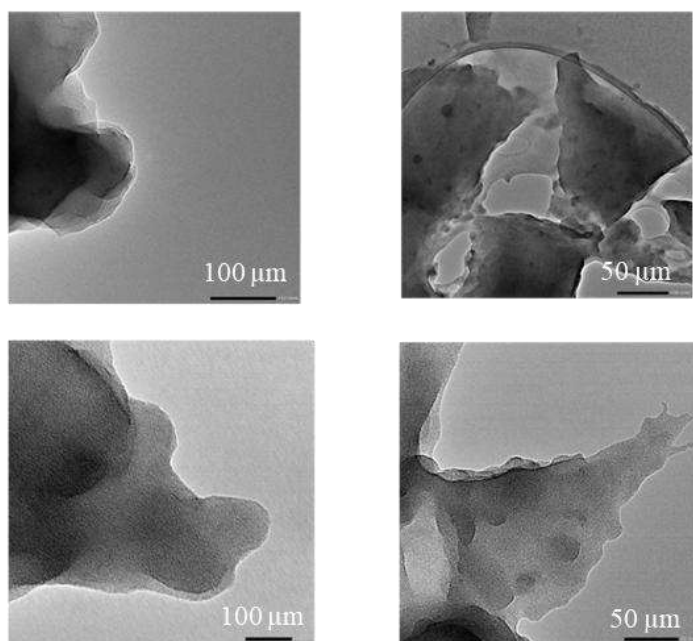


Figure 3.17 TEM images of HCP-BzmimCl (left) and HCP-*Bis*(BzmimCl) (right).

3.3.3 Catalytic activity

For the synthesis of formamides, optimization was first performed using dipentylamine as a model substrate and 10% of HCP-BzmimCl as a catalyst (based on N content) with respect to the amine (Table 3.3). Initially, a study was carried out with different pressures, temperatures and times. Starting at 5 bar of CO₂ pressure, room temperature and using phenylsilane as a reducing agent, a 60% amine conversion was obtained in 24 h of reaction (entry 1) and increasing the temperature to 35 °C, the complete conversion was achieved (entry 2). By decreasing the pressure (entry 3) or increasing the temperature and therefore reducing the reaction time, (entry 4) complete conversion was not achieved in no case, so a temperature of 35 °C, 5 bar of CO₂ and 24 h of reaction were established as the best initial conditions to carry out this reaction. Control experiments in the presence of different reducing agents such as Ph(CH₃)₂SiH, (Ph)₂SiH₂ or NaBH₄ (entries 5–7) yielded less amount of formamide which indicated the need for the phenylsilane to achieve good conversions in this reaction. In order to shorten the reaction time, a strong polar additive DMF was added to the reaction. It was reported that 2 equivalents of DMF promoted the *N*-formylation of amines in excellent yields and selectivity at room temperature playing an important role in the activation of the amines and PhSiH₃ favoring also the insertion of CO₂.^[39] Thus, in the presence of 2 equivalents of DMF (entry 8) the time of reaction was shortened to five hours obtaining excellent conversion and selectivity towards the formamide. As DMF has moderate toxicity, the amount of DMF was reduced to 1 mmol, however, the conversion of the amine was low (entry 9). The use of 1.5 mmol of DMF also did not lead to high amine conversion (entry 10). Thus, 2 mmol of DMF was established as the optimal amount to carry out this reaction. A control experiment in the absence of the catalyst and using only DMF was carried out (entry 11) leading to only 20% of the product confirming the necessity of both

components in the reaction mixture. Moreover, in absence of DMF gives low conversion confirming also the positive effect of DMF (entry 12).

Table 3.3. Optimization of the reaction conditions of N-Formylation of dipentylamine using HCP-BzmimCl as catalyst.^{a)}

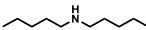
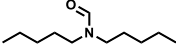
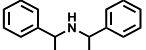
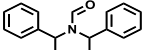
Entry	Red. agent	DMF (mmol)	T (°C)	P (bar)	t (h)	Conv (%)	Sel. (%)
1	PhSiH ₃	-	r.t	5	24	60	98
2	PhSiH ₃	-	35	5	24	100	99
3	PhSiH ₃	-	35	1	24	25	99
4	PhSiH ₃	-	90	5	5	50	99
5	Ph(CH ₃) ₂ SiH	-	35	5	24	4	99
6	(Ph) ₂ SiH ₂	-	35	5	24	10	98
7	NaBH ₄	-	35	5	24	50	98
8	PhSiH₃	2	35	5	5	100	99
9	PhSiH ₃	1	35	5	5	25	99
10	PhSiH ₃	1.5	35	5	5	60	99
11 ^{b)}	PhSiH ₃	2	35	5	5	20	99
12	PhSiH ₃	-	35	5	5	20	98

^{a)}Amine (1 mmol), reducing agent (1 mmol), catalyst (10% molar based on N content), ^{b)} without catalyst.

The use of the second catalyst under the most favorable conditions (entry 8, Table 3.3) yield also the expected formamide in 4 h with excellent conversion and selectivity (entry 1, Table 3.4). The reaction was extended to the synthesis of other formamides using both imidazolium chloride- catalysts (Table 3.4). By using an aliphatic-aromatic amine such as *N*-methylphenylamine (entries 4 and 5), more reaction time (10 h) was required with both catalysts, although the times used for

other catalysts based on liquid ions for this same substrate are higher (16–24 h).^[20, 21, 40] These results were attributed to the higher steric hindrance of this amine compared with the dipentylamine. When cyclic amines such as piperidine or morpholine were used (entries 6–9), the reaction times ranged from 9 to 16 h. Again, HCP-*Bis*(BzmimCl) was more effective, obtaining the corresponding formamides in less time, 14 and 9 h, respectively. These results could be attributed to the pK_a of the two amines: 9.73 for piperidine and 8.36 for morpholine. Thus, the lower pK_a of morpholine could facilitate the removal of the proton and therefore the reaction complete in less time. Finally, the use of *Bis*(1-phenylethyl)amine (entries 10 and 11) yielded the desired formamide with both catalysts although the amine conversion reached only 60% and 65%, respectively. This result was attributed to the high steric hindrance of this diamine which makes difficult the deprotonation as well as the insertion of CO₂ molecule. Selected ¹H NMR of these experiments are recorded in Figures A1-A5. To further evaluate the practicability of HCP-*Bis*(BzmimCl), the reaction was scale-up by using dipentylamine as substrate in higher amounts (10 times more). The corresponding formamide was quantitatively after 6 h (entry 2). This result showed the potential industrial application of the developed catalytic system.

Table 3.4. *N*-Formylation of amines with CO₂ using imidazolium-Chloride based hypercrosslinked polymers as catalysts^{a)}

$ \begin{array}{c} \text{R}_1\text{--}\text{N}\text{--}\text{H} \\ \text{R}_2 \end{array} \xrightarrow[35^\circ\text{C}/ 5 \text{ Bar CO}_2]{\text{PhSiH}_3 \text{ DMF}} \begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \diagup \\ \text{R}_1\text{--}\text{N}\text{--}\text{R}_2 \end{array} + \text{R}_1\text{--}\text{N}\text{--}\text{R}_2 $					
Entry	Amine	Catalyst	Product	t (h)	Conv. (%)
1		HCP- <i>Bis</i> (BzmimCl)		4	100
2 ^{b)}		HCP- <i>Bis</i> (BzmimCl)		6	100
3		HCP-BzmimCl		5	100
4		HCP- <i>Bis</i> (BzmimCl)		10	95
5		HCP-BzmimCl		10	90
6		HCP- <i>Bis</i> (BzmimCl)		14	98
7		HCP-BzmimCl		16	98
8		HCP- <i>Bis</i> (BzmimCl)		9	98
9		HCP-BzmimCl		10	98
10		HCP- <i>Bis</i> (BzmimCl)		24	65
11		HCP-BzmimCl		24	60

^{a)} Amine (1 mmol), PhSiH₃ (1 mmol), DMF (2 mmol), Catalyst (10 mol% based on N content), P (CO₂) = 5 bar, T = 35°C; ^{b)} 10 mmol of amine.

Once the generality of both catalysts was demonstrated in the *N*-formylation reaction, their heterogeneity was evaluated using dipentylamine as substrate. The recyclability of HCP-BzmimCl was limited to five cycles, observing a progressive decrease in the conversion of the diamine, although the selectivity towards the formation of the corresponding formamide was maintained (Figure 3.18). However, HCP-*Bis*(BzmimCl) showed excellent recyclability

maintaining the amine conversion and formamide selectivity at least 10 cycles (Figure 3.18). The better recyclability of HCP-*Bis*(BzmimCl) relative to HCP-BzmimCl can be attributed to higher stability of the imidazolium chloride groups within the HCP-*Bis*(BzmimCl) network, while the imidazolium chloride groups in HCP-BzmimCl are terminal groups of the network and are more exposed. We could attribute this fact to the starting monomer, *Bis*(BzmimCl) which maintains two imidazolium chloride groups linked to each other providing higher structural stability of these groups while the monomer BzmimCl disperses the imidazolium chloride groups in the network. Besides, a partial blocking of the micropores in this catalyst could contribute to the lack of recyclability of this catalyst.

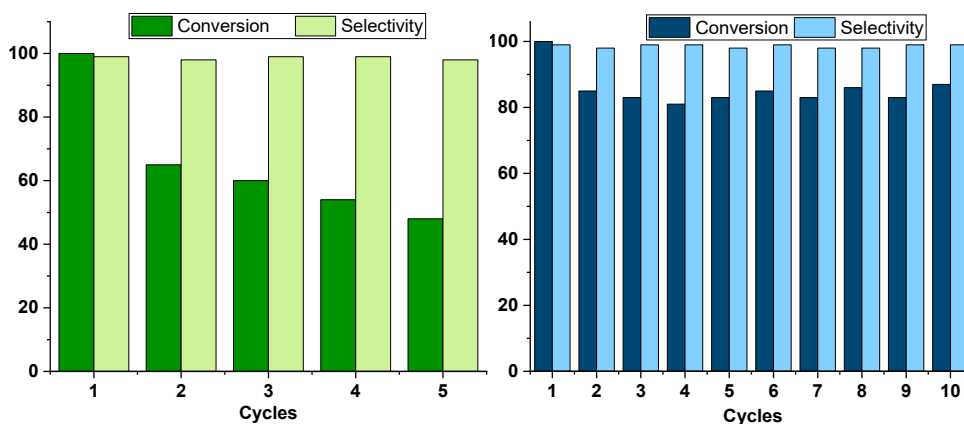


Figure 3.18 recycles with HCP-BzmimCl(left) and HCP-*Bis*BzmimCl (right).

The FTIR spectra and TGA after the corresponding reuses (Figure 3.19 and Figure 3.20) showed some structural changes in the recycled HCP-BzmimCl. The characteristic bands of the imidazolium ring at 1550 and 1150 cm^{-1} are maintained in the spectrum of HCP-*Bis*(BzmimCl), while in the case of HCP-BzmimCl, these bands have shifted and split. The TGA of the recycled HCP-

BzmimCl showed also lower thermal stability than HCP-*Bis*(BzmimCl) and some amount of solvent trapped within the network after the recycling experiments.

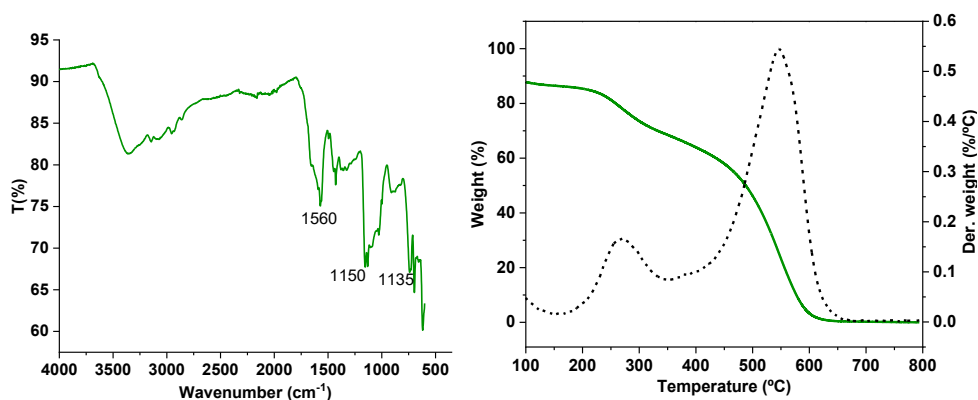


Figure 3.19 FTIR spectrum (left) and TGA (right) of HCP (BzmimCl) after five cycles.

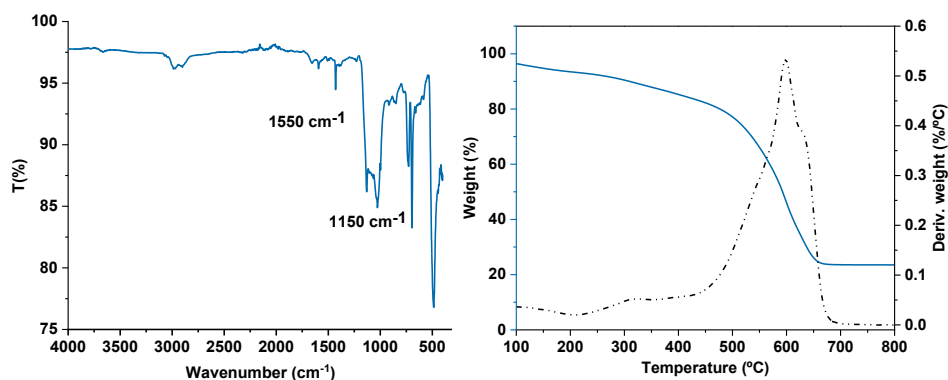


Figure 3.20 FTIR spectrum (left) and TGA (right) of HCP-*Bis*(BzmimCl) after five cycles.

To verify the heterogeneity of HCP-*Bis*BzmimCl, a hot filtration experiment was also carried out removing the catalyst after three hours of reaction. At this point, the conversion of dipentylamine was 51%, (Figure 3.21),

it does not increase significantly after 5 hours, which confirms that there is no release of catalytic species to the reaction medium.

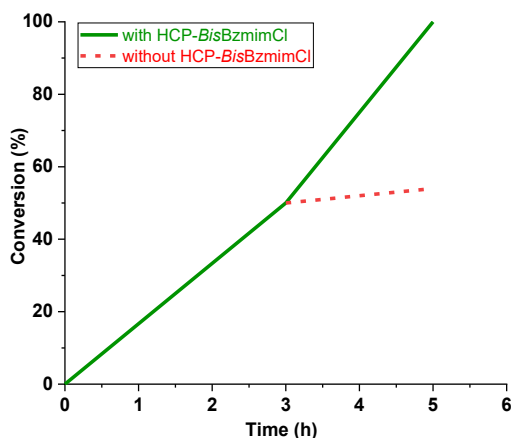


Figure 3.21 Leaching experiment with HCP-*Bis*(BzmimCl)

3.3.4 Mechanism proposal

The proposed reported mechanisms for the reaction of amines with CO₂ using PhSiH₃ as reducing agent are shown in Figure 3.22. The *route 1* (Figure A.6) is a direct reaction between the amine and PhSiH₃, generating H₂ and a silylamine, which can react with CO₂ to give silylcarbamate. In *route 2* the catalyst interacts with PhSiH₃ to form an active intermediate, which promotes CO₂ hydrosilylation leading to a silyl formate. Then the formamide was formed by the formylation of the amine with the formate. Finally, *route 3* (Figure A.8) yield the methylated products. This route involves the hydrosilylation of silyl formates to form silyl acetals follow by intermolecular hydrosilylation to form silylmethoxide species, and finally methylation of amines with silyl- methoxide to yield the methylated products. According to the results obtained in our experiments, *route 3* was the first to be ruled out because we did not detect *N*-methyldipentyl amine in any of our experiments. Despite this, we did a control experiment adding an excess of PhSiH₃ to force the formation of the tertiary

amine. The ^1H NMR spectrum (Figure A.9) shows a small signal characteristic of the methyl of the corresponding amine, therefore, even if phenylsilane is added in excess, the reaction is selective towards the corresponding formamide. To check if the mechanism develops through *route 1*, an experiment reacting PhSiH_3 with dipentylamine in absence of CO_2 was carried out to force the formation of the silyl formate intermediate. As can be observed ^1H NMR spectrum (Figure A.7) a mixture of the two reagents without signals from the *N,N*-dipentyl-1-phenylsilanamine was obtained, therefore this route was also discarded.

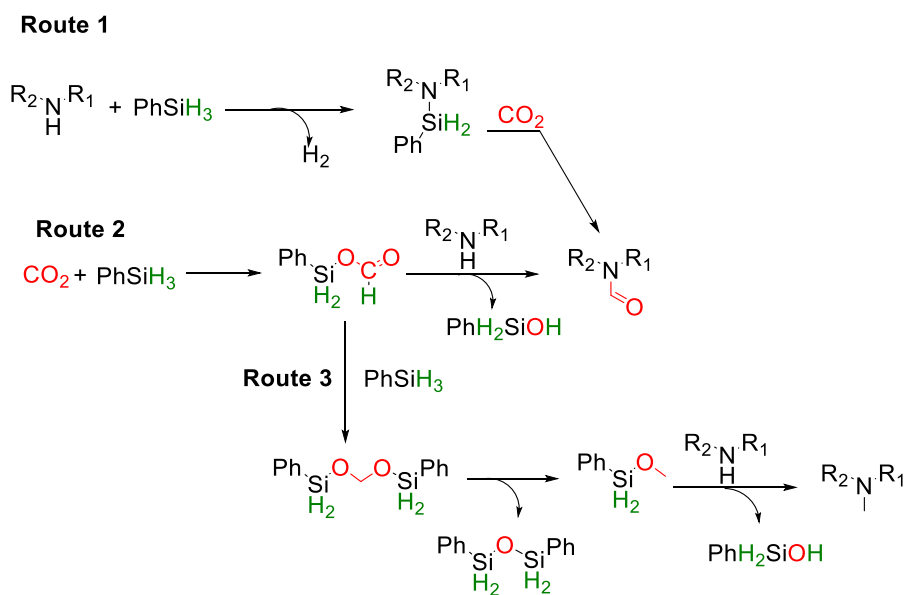


Figure 3.22 Proposed reported mechanistic routes in the reaction of amines with CO_2

Thus, based on the results obtained, the above control experiments and in combination with previous reported work,^[20, 21] the proposed reaction mechanism for the *N*-formylation of amine with CO_2 and PhSiH_3 over the chloride-based catalysts were deduced as described in Figure 3.23. The Si-H bond in PhSiH_3 was first activated by Cl^- of the catalyst and tuned by DMF which polarizes the Si-H

bond. The enriched CO₂ molecule was then inserted into the activated Si–H bond, affording a highly active pivotal silyl formate intermediate. Meanwhile, the coordination occurred between the Cl[−] of HCP and the H atom of the secondary amino group, which is also polarised by the DMF, through intermolecular hydrogen bonding to form an activated substrate containing a nucleophilic nitrogen atom. Subsequently, a new C–N bond formed through a nucleophilic attack of nitrogen atom on the electron- deficient carbon atom of silyl formate intermediate, thus producing the final targeted formamide.^[23, 24]

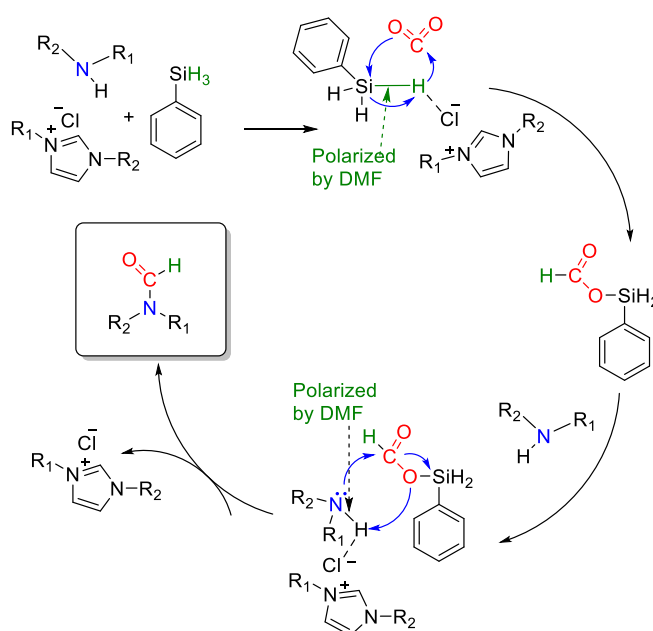


Figure 3.23 Proposed reaction mechanism for de N-formylation of amines with CO₂, PhSiH₃ assisted by DMF using an imidazolium chloride-based catalyst.

3.3.5 Catalytic performance

To establish the catalytic performance of the HCP-*Bis*(BzmimCl), a comparison has been carried out with the metal-free ionic liquid-based heterogeneous catalysts found in the literature that have been used in this reaction.

Specifically, the comparison has been made using N- methyl aniline as a common substrate to all the reported works. As can be observed in Table 3.5 all the reported catalysts need 16–24h to achieve a high conversion of the amine into the corresponding form amide, which is also necessary in most of the cases, a solvent to carry out the reaction. However, by using HCP-*Bis*(BzmimCl) as a catalyst in a solvent-free reaction assisted by DMF, a very high yield of the corresponding formamide was achieved in 10h. Besides, the recyclability of our catalyst was also higher than those reported. Thus, in terms of time and recyclability, our catalyst presents better catalytic performance than the reference catalysts mentioned.

Table 3.5 Metal-free ionic liquid based heterogeneous catalysts in the formylation of N-methylaniline with CO₂.^{a)}

$ \begin{array}{c} \text{H} \\ \\ \text{R}_1-\text{N}-\text{R}_2 \\ \xrightarrow[\text{CO}_2]{\text{PhSiH}_3} \\ \text{O}=\text{C}-\text{H} \\ \\ \text{R}_1-\text{N}-\text{R}_2 \end{array} $									
Catalyst	mol (%)	PhSiH ₃ (mmol)	Solvent	T (°C)	P _(CO₂) (bar)	t (h)	yield	Cycles	Ref
[Et4NBr]50%-Py-COF	5	2	DMF	30	1	24	94	4	[20]
[BE]X%-TD-COF	3.4	2	ACN	30	5	24	99	4	[21]
FIP-Im@QA	6	1	-	35	10	24	99	6	[24]
IPOP-3	10	4	ACN	r.t	AFG	24	71	5 ^{b)}	[40]
PiP@QA	5	1	-	35	5	16	99	6	[28]
HCP- <i>Bis</i> (Bzmim)Cl	10	1 ^{c)}	-	35	5	10	95	10 ^{d)}	This chapter

^{a)}N-methylaniline (1mmol),^{b)} p-methoxyaniline as substrate, ^{c)} with 2mmol of DMF, ^{d)} dipentylamine as substrate. AFG: CO₂ in anaerobic fermentation gas.

3.4 Conclusions

The hypercrosslinked polymers based on imidazolium chloride HCP-BzmimCl and HCP-*Bis*(BzmimCl), directly from imidazolium chloride-based monomers, are excellent heterogeneous catalysts for obtaining formamides from amines and CO₂ using PhSiH₃ as reducing agent and DMF as a key polar additive which activates the N-H and Si-H bonds in reaction times shorter than the published conversions for this reaction using other ionic-liquid-based heterogeneous catalysts.

Despite HCP-*Bis*(BzmimCl) showing less CO₂ capture capacity than HCP-BzmimCl, it has positioned itself as one of the most efficient metal-free catalysts, in terms of reaction time and recyclability because the reaction occurs between 4 and 16h, depending on the amine used, and the catalyst can be recycled up to 10 times. We attributed this excellent result to the fact that the imidazolium rings are very stabilized within this network, which affords a highly recyclable catalyst. However, in HCP-BzmimCl, although the imidazolium rings are more accessible to interact with CO₂, yielding higher CO₂ uptake capacity, at the same time more exposure increases its lability and therefore decreases the stability of this catalyst.

3.5 Experimental section

1-Benzyl-3-methylimidazolium chloride (BzmimCl, 97.0%) was supplied by Alfa Aesar. 1-Benzylimidazole was purchased by TCI with a purity $\geq 98\%$. Biphenyl was supplied by Fluka with a purity $> 98\%$; AlCl_3 and CH_2Cl_2 (anhydrous) (extra dry) were supplied by Acros Organics with purities $>98.5\%$ and $> 99.8\%$ respectively, and carbon dioxide (99.9% of purity) were supplied by Praxair. The other reagents and solvents were supplied by Aldrich with analytical grade and were used as received.

3.5.1 Synthesis of *Bis*(BzmimCl)

1-Benzylimidazole (474 mg, 3.0 mmol), CH_2Cl_2 (0.574 mL, 9.0 mmol), DMSO (0.170 mL, 2.4 mmol) was heated at $100\text{ }^\circ\text{C}$ for 24 hours, The resulting white heterogeneous mixture was allowed to cool to room temperature, anhydrous Et_2O (3 mL) was added, and the mixture was stirred at room temperature for 5 minutes. The resulting white suspension was filtered over Celite, washed with Et_2O (3 x 15 mL) to remove excess dichloromethane, remaining substrate and DMSO. The filtrate was discarded and washed with MeOH (3 x 25 mL) to dissolve the product. The resulting MeOH solution with the product was concentrated under vacuum affording the *Bis*(BzmimCl) as white solid (510 mg, 81% yield).

^1H NMR (400 MHz, DMSO- d_6) δ 9.61 (s, 2H), 8.04 (s, 2H), 7.85 (s, 2H), 7.44 (m, 10H), 6.66 (s, 2H), 5.46 (s, 4H).

^{13}C NMR (400 MHz, DMSO- d_6) δ 138, 134, 129, 128, 127, 126, 123, 58, 52.

Elemental analysis, ($\text{C}_{21}\text{H}_{22}\text{N}_4\text{Cl}_2$) calculated: C, 62.85; H, 5.53; N, 12.96. Found: C, 58.74; H, 5.15; N, 12.82.

3.5.2 Synthesis of Materials

3.5.2.1 Synthesis of HCP-BzmimCl

Biphenyl (62 mg, 0.4 mmol) and BzmimCl (334 mg, 1.60 mmol) were dissolved in dichloromethane (25 mL), and N₂ was bubbled for 20 min under stirring. Then, AlCl₃ (2 g, 15 mmol) was added, and the mixture was stirred at 50 °C for 48 h. The solid was isolated by filtration, washed with HCl 0.005 M, washed with water and then purified by Soxhlet extraction with methanol. The brown solid obtained was dried in a vacuum oven at 100°C for 12 h. yield (400 mg ,93%).

3.5.2.2 Synthesis of HCP-*Bis*(BzmimCl)

Biphenyl (62 mg, 0.4 mmol) and BzmimCl (642 mg, 1.60 mmol) were dissolved in dichloromethane (25 mL), and N₂ was bubbled for 20 min under stirring. Then, AlCl₃ (2g, 15 mmol) was added and the mixture was stirred at 50 °C for 72 h. The solid was isolated by filtration, washed with HCl 0.005 M, washed with water and then purified by Soxhlet extraction with methanol. The brown solid obtained was dried in a vacuum oven at 100°C for 12 h. yield (650 mg ,80%).

3.5.3 Synthesis of formamides

In a glass reactor, the corresponding amine substrate (0.1 mmol), the phenylsilane (1 mmol), dimethylformamide (2 mmol) and the catalyst (10% molar N) are added. The suspension is charged with 5 bar of CO₂ and heated at 35°C with magnetic stirring the time indicated in Tables 1 and 2. The reactor was cooled to room temperature, depressurized and opened. The catalyst was separated from the reaction by filtration and washing with CH₂Cl₂. The resulting mixture was subsequently washed with water (2 ×10 mL) and saturated NaCl aqueous solution

Chapter 1

(1 × 10 mL). The organic phase was dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. The reactions were monitored by ¹H NMR

3.5.4 Recycling experiment

After the reaction was completed, the polymer was separated from the reactions by filtration, washed with methanol and CH₂Cl₂ and dried in an oven at 100°C for 12h. Then it was used in a fresh run.

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Chapter 2: Heterogenized metal-N-heterocyclic carbene hypercrosslinked polymer catalysts for the synthesis of carbamates and carbonates

4.1 Introduction

The conversion of CO₂ into value added molecules is one of the most active areas of chemical research not only because of the usefulness of the molecules obtained, but also because it helps to close the carbon cycle, reducing dependence on fossil fuels by promoting the circular economy and sustainability by reusing a gas considered waste.

Five membered cyclic carbamates, also known as 2-oxazolidinones, are very interesting molecules with broad industrial applications in the fields of medicine, pesticides and insecticides due to their remarkable therapeutic and biological properties. In addition, they serve as very versatile building blocks in organic synthesis, and are of particular importance as chiral auxiliaries in asymmetric synthesis.^[1] The traditional approach to synthesizing cyclic carbamates typically relies on highly toxic phosgene or isocyanate derivatives as starting materials, posing significant risks to both environmental safety and human health.^[2] In recent years, the synthesis of these compounds by three-component coupling of primary amines, propargyl alcohols and CO₂ has gained much attention in the scientific landscape due to the accessibility and low cost of the starting materials, the nontoxic nature of the by-products and the simplicity of the reaction process (Figure 4.1, left).

By using primary alcohols instead of amines as third component of the reaction, it is possible to obtain asymmetrical organic carbonates (Figure 4.1, right). These molecules are also of great interest because it can be used as solvents in organic synthesis and electrolytes in lithium ion batteries.^[3] Moreover, they act as plasticizers and additives in polymers and serve as intermediates in the synthesis of various chemicals and, in pharmaceuticals, modifying drug solubility. Besides, these compounds also have applications in catalysis, carbon capture, and surface coatings. In the automotive industry, polycarbonates are used for

instrument panels, car bodies, and monomers for organic glass production^[4] and in agriculture, are employed in the production of herbicides, fungicides and seed disinfectants. ^[5]

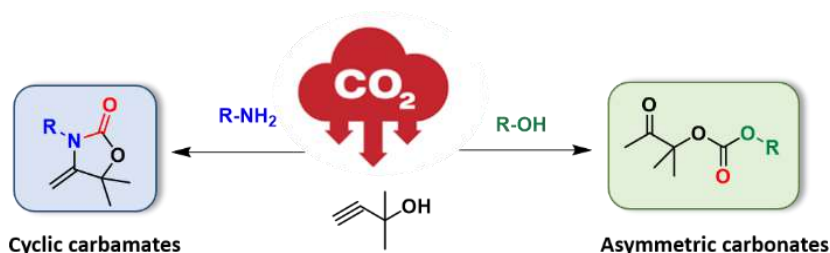


Figure 4.1 transformation of CO_2 into oxazolidinones and asymmetric carbonates.

Both process utilizes transition metal-based catalysts such as Cu ,^[6] Ru ,^[7] Pd ,^[8] Ag ,^[9] Au ,^[10] and Zn ,^[11] as well as metal-free catalysts, including protic ionic liquids,^[12] superbases,^[13-15] and N-heterocyclic carbenes.^[16] Recent advances have yielded numerous heterogeneous catalysts integrated with NHC structures for CO_2 conversions.^[17, 18] The NHC structure within a polymer can coordinate with metals to embed highly catalytic metal centers within the polymer and enhance the material's affinity for CO_2 through N atom interaction with CO_2 .^[18] These N-heterocyclic carbenes possess many favorable properties, such as a good coordination capacity at electron rich sites and the ability to adjust their structure. Their strong σ -donation ability significantly strengthens the NHC-metal bonds. As a result, their metal complexes exhibit good thermal stability and can be used as catalysts at high temperatures without decomposition^[19], although copper-based catalysts are the most investigated in the literature, silver(I) and gold(I) systems are emerging as efficient alternatives.^[20] In recent years these derivatives have also been successfully used as organocatalysts in the synthesis of cyclic carbamates and carbonates through the three-component coupling

of CO₂.^[21-25] However, to our knowledge, only one article has been reported on the synthesis of cyclic carbamates using heterogeneous NHC-complexes working at very high CO₂ pressures (30 bars) and 24h of reaction,^[26] and was used in the synthesis of asymmetric carbonates. Thus, the purpose of this chapter will be to explore these types of catalysts in these two reactions.

Chapter 2

4.2 Objectives

The general goal of Chapter 2 is to synthesize silver and copper N-heterocyclic carbene (NHC) hypercrosslinked polymer catalysts (HCP) to be used as heterogeneous catalysts in the synthesis of cyclic carbamates and linear asymmetric carbonates.

To achieve this general objective, this chapter has the following specific objectives:

- Synthesis and characterization of metal-N-heterocyclic carbene hypercrosslinked polymer catalysts: The HCP-BzmimCl and HCP-*Bis*-BzmimCl synthesized in Chapter 1 will be reacted with silver (I) and copper (I) complexes to obtain the corresponding metal N-heterocyclic carbene hypercrosslinked polymer catalysts: containing silver (HCP-NHC-Ag and HCP-*Bis*NHC-Ag) and copper (HCP-NHC-Cu and HCP-*Bis*NHC-Cu). Then, the four complexes will be characterized by standard solid-state techniques, such as FTIR, ^{13}C NMR, TGA, XPS, N_2 adsorption/desorption isotherms, CO_2 adsorption isotherms, and SEM and TEM microscopy.

- Evaluation of the catalytic activity in the formation of cyclic carbonates and asymmetric carbonates using CO_2 : The above catalysts will be evaluated as heterogeneous catalysts in the synthesis of cyclic carbamates through a three-component coupling reaction with CO_2 , propargylic alcohol, and primary amine, as well as in the synthesis of asymmetric carbonates using CO_2 , propargylic alcohol, and primary alcohol. Catalysts recycling will be studied and mechanisms for both transformations will be proposed.

4.3 Results and discussion

4.3.1 Synthesis and characterization of *N*-Heterocyclic Carbene hypercrosslinked polymer catalysts

The imidazolium-hypercrosslinked polymers, HCP-BzmimCl and HCP-*Bis*(BzmimCl) prepared in Chapter 1 were reacted with CuI in THF or with Ag₂O in DCM and the mixtures were stirred for 24 hours at room temperature to obtain the four HCPs containing metal-*N*-heterocyclic carbenes: HCP-NHC-Cu, HCP-*Bis*NHC-Cu and HCP-NHC-Ag, HCP-*Bis*NHC-Ag (Figure 4.2).

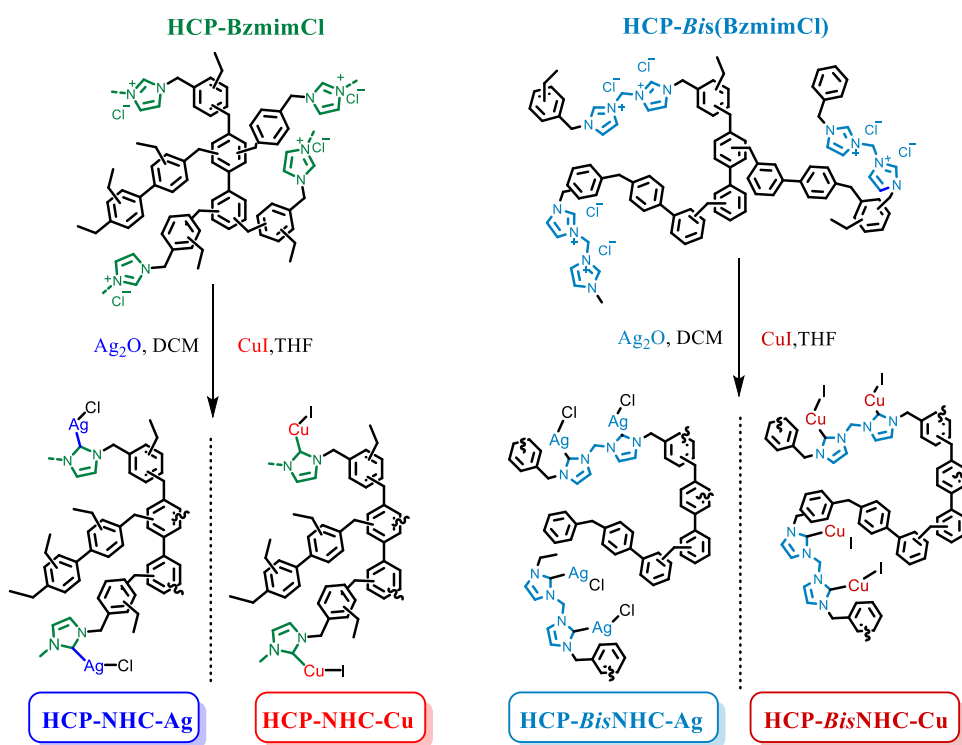


Figure 4.2 Synthesis of metal HCP-NHCs catalysts.

The elemental analysis (Table 4.1) showed a benzene to imidazolium ring ratio of 2:1 for HCP-NHC-M and 1:1 for HCP-*Bis*NHC-M. This indicates the successful incorporation of the intended functional groups during the synthesis

process. However, due to the difficulty associated with the complete combustion of cross-linked polymeric networks, the experimentally carbon percentages were slightly lower than the theoretical values.

Table 4.1 Elemental analyses of HCP-NHC-Ag/Cu and of HCP-*Bis*NHC-Ag/Cu.

Catalyst		C(%)	H(%)	N(%)
HCP-NHC-Ag	Calculated ⁽¹⁾	67.7	5.52	4.4
	Experimental	53.62	4.06	4.01
HCP-NHC-Cu	Calculated ⁽¹⁾	63.3	5.1	4.1
	Experimental	61.74	4.32	3.82
HCP- <i>Bis</i> NHC-Ag	Calculated ⁽²⁾	52.14	4.54	7.15
	Experimental	48.15	4.31	7.08
HCP- <i>Bis</i> NHC-Cu	Calculated ⁽²⁾	47.1	4.06	6.27
	Experimental	46.25	3.72	6.54

(1) Two benzene rings per imidazolium ring.

(2) One benzene ring per imidazolium ring.

The first evidence of the formation of the metal complexes was observed by FTIR spectra (Figure 4.3) since the peaks at 1555-1568 cm⁻¹, attributed to the stretching vibrations of C=N in the imidazole rings observed in the spectra of HCP-BzmimCl and HCP-*Bis*BzmimCl (Figure 3.9), while were not detected in that of HCP-NHC-M as consequence of the metal coordination. [27] The characteristic vibration bands of =C-N at 1150 cm⁻¹ and 1620 cm⁻¹, and the bending vibrations of the -CH₂- groups at 1445 cm⁻¹ which are present in all spectra, confirming the preservation of polymeric backbone of the solids.

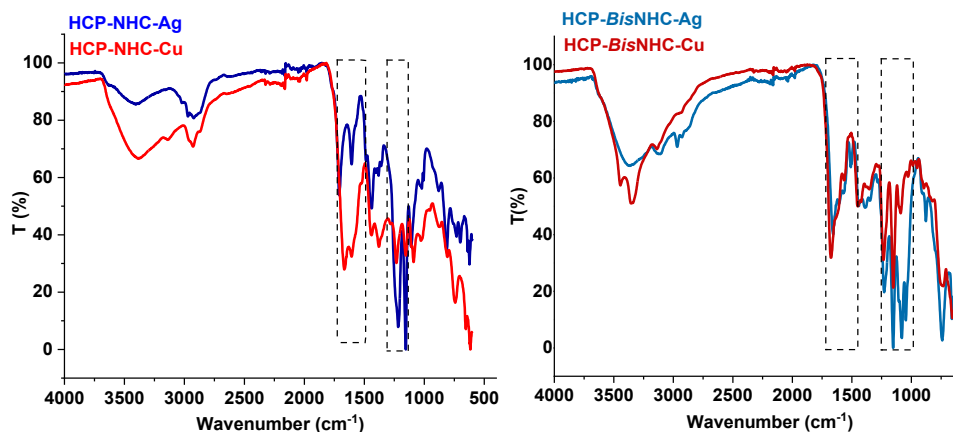


Figure 4.3 FTIR spectra of the metal-HCP-NHCs catalysts.

The solid-state ^{13}C -NMR spectra (Figure 4.4) did not provide any further information since all complexes showed the same groups of signals that are also present in the spectra of the precursor polymers. Thus, in all spectra were observed a broad chemical shift between 110 ppm and 130 ppm accompanied by a shoulder around 140 ppm attributed to the aromatic carbons of the benzene rings and to C-N atoms, respectively, together with the characteristic signals of the methylene and methyl groups at around 35 and 50 ppm, respectively.

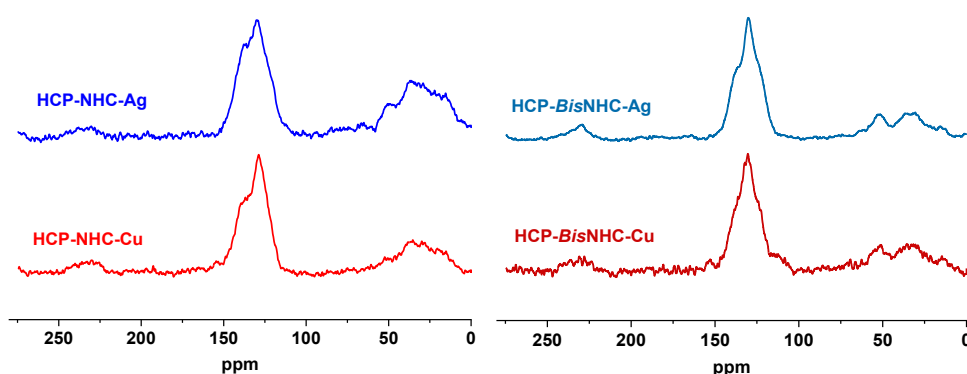


Figure 4.4 ^{13}C NMR spectra of the metal-HCP-NHCs catalysts.

The thermal stability of the four metal supported catalysts was evaluated using TGA analysis (Figure 4.5). All polymers exhibited good thermal stability with a degradation pattern in two steps. In the two copper ones, a large weight loss is observed between 275-280°C and a second one with little weight loss, close to 500°C. In contrast, the silver containing polymers show a small weight loss between 270-300°C and a big weight loss of around 500°C. The initial weight loss was attributed to the dissociation of the metal from the polymer network along with their partial degradation, as it was reported for other supported NCH–copper and silver complexes.^[28] The second weight loss is attributed to the generalized degradation of the polymeric network. The difference in counterions (I^- in Cu catalysts and Cl^- in Ag catalysts) could influence thermal stability and degradation behaviour. Iodide (I^-) in Cu-NHC complexes may contribute to a more pronounced weight loss in the first stage if it is released alongside the metal during thermal decomposition. In contrast, chloride (Cl^-) in Ag-NHC complexes might interact differently with the polymer network, potentially remaining more strongly bound and delaying significant mass loss until the second stage. This could explain why Ag-based catalysts show a higher weight loss at ~500°C, when the polymer undergoes complete degradation.^[29, 30]

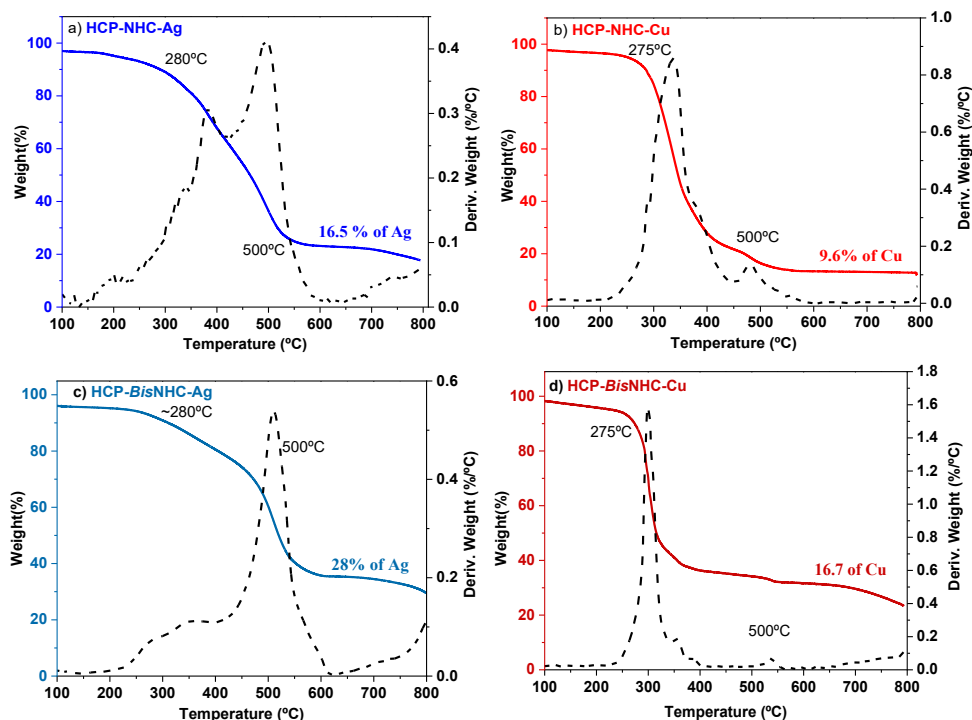


Figure 4.5 TGA analysis of the metal HCP-NHCs catalysts.

From the residue obtained, the percentage of metal in each case can be calculated, resulting in 9.6% and 16.7% for the copper-complexes, HCP-NHC-Cu and HCP-BisNHC-Cu, respectively, and 16.5% and 28% for the HCP-NHC-Ag and HCP-BisNHC-Ag, respectively. These experimental values were like those theoretically calculated (Table 4.2). The percentage of nitrogen and metal were determined in each case showing a good correlation between the experimental and theoretical values. Moreover, the nitrogen/metal ratio is also around 2 in all cases, which confirms the presence of one metal atom for every two nitrogen atoms and therefore the successful formation of the metallic carbene from the corresponding imidazolium units.

Table 4.2 Metal quantities and percentage composition of Nitrogen and Metal of the corresponding metal-HCP-NHCs catalysts.

Catalyst		M(%)	N(%)	N (%/g.mol ⁻¹)	M (%/g.mol ⁻¹)	N/M
HCP-NHC-Ag	Calculated	16.8	4.4	0.31	0.15	2.02
	Experimental	16.5	4.01	0.29	0.15	1.93
HCP-NHC-Cu	Calculated	9.3	4.1	0.29	0.14	2.01
	Experimental	9.6	3.82	0.28	0.15	1.86
HCP-BisNHC-Ag	Calculated	27	7.15	0.51	0.25	2.04
	Experimental	28	7.08	0.5	0.25	2.0
HCP-BisNHC-Cu	Calculated	15.2	6.27	0.45	0.23	1.95
	Experimental	16.7	6.54	0.47	0.25	1.88

X-ray photoelectron spectroscopy (XPS) analyses confirmed the formation of all metal-complexes since the four catalysts show the signal of nitrogen, chlorine or iodine, carbon and the corresponding metals are detected in the survey scans. (Figure 4.6)

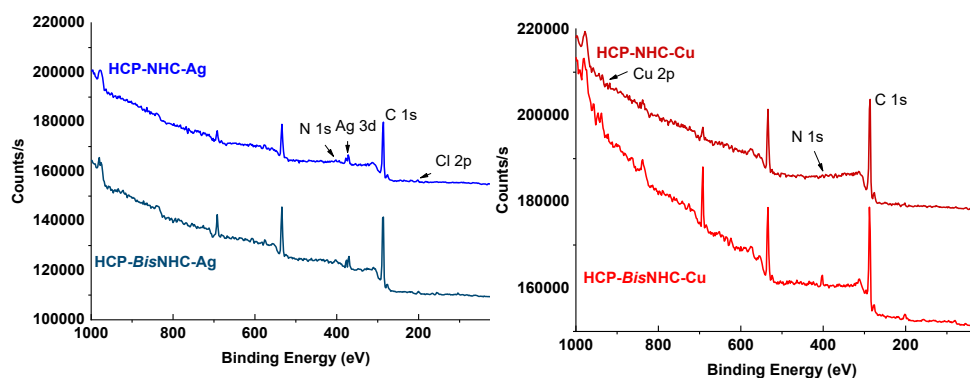


Figure 4.6 Survey scan of the metal-HCP-NHCs catalysts.

The XPS survey spectra of the four catalysts showed a dominant peak at 285 eV corresponding to C 1s (Figure A.10) which is associated with C-C bonds. A peak at 402 eV confirmed the presence of quaternary nitrogen (N^+) (Figure A.11).^[31, 32]

The XPS traces of the silver cations of HCP-NHC-Ag and HCP-*Bis* NHC-Ag (Figure 4.7) confirmed also the formation of NHC-Ag complexes as evidenced by the presence of two characteristic peaks of Ag 3d_{3/2} at 373 eV and Ag 3d_{5/2} at 367 eV. Besides, the two peaks at about 195 and 198 eV were observed in the Cl XPS traces (Figure A.12) which were assigned to Cl 2p_{1/2} and Cl 2p_{3/2}, respectively, confirming the presence of Cl⁻ ions in the silver-supported complexes.^[33, 34]

The XPS traces of the copper cations of HCP-NHC-Cu and HCP-*Bis* NHC-Cu (Figure 4.8), show the two peaks at 932 eV attributed to Cu 2p_{3/2} and at 952 eV due to Cu 2p_{1/2} characteristics of Cu(I) species.^[35, 36] In addition, the two peaks at about 630 eV and 619 eV were observed in the I XPS traces (Figure A.13), which were attributed to I 2p_{1/2} and I 2p_{3/2}, respectively, confirming the existence of I⁻ ions a counterions in the copper-supported hypercrosslinked N-Heterocyclic Carbene polymer complexes.

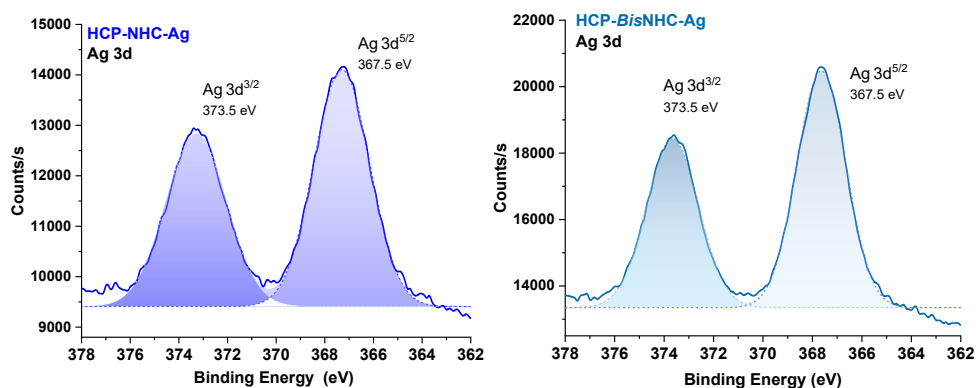


Figure 4.7 Ag 3d XPS traces of HCP-NHC-Ag and HCP-*Bis*NHC-Ag.

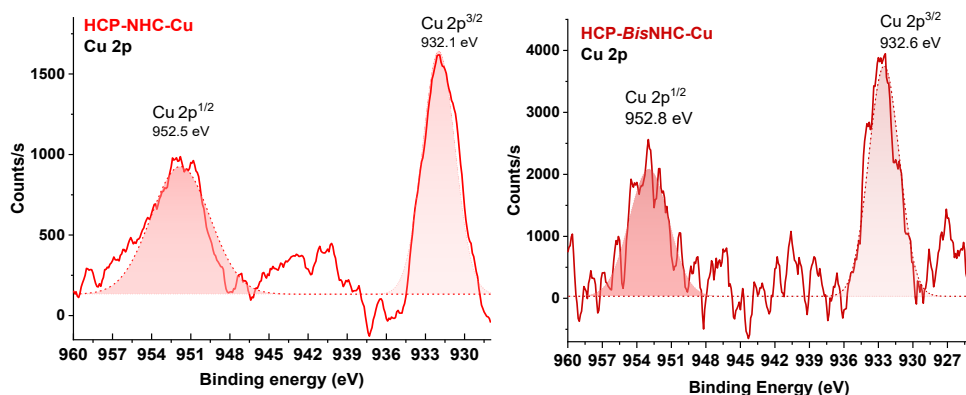


Figure 4.8 Cu 2p XPS traces of HCP-NHC-Cu and HCP-BisNHC-Cu.

The porous properties were evaluated by N₂ adsorption/desorption isotherms (Figure 4.9) showing low specific surface areas for all polymers, although they were larger than their respective precursors. Thus, HCP-NHC-Cu and HCP-NHC-Ag exhibited 21.1 m²g⁻¹ and 28.2 m²g⁻¹, respectively, while its precursor HCP-BzmimCl showed a very low value of 4.5 m²g⁻¹. (See in chapter 1) Likewise, the HCP-BisNHC-Cu and Ag complexes exhibited 68.8 m²g⁻¹ and 66.1 m²g⁻¹, while its precursor HCP-Bis(BzmimCl) showed a very low value of 16.9 m²g⁻¹. (See in chapter 1) These results suggest that, unlike typical cases where metal incorporation reduces the specific surface area due to the metal occupying space in this case, it appears to be expanding the structure. In general, the increase in surface area after metal incorporation can be explained by several factors, such as structural expansion induced by metal coordination that may generate additional accessible porosity, increased polymer rigidity due to Cu-NHC and Ag-NHC complexation that could prevent pore collapse, maintaining a more open structure, and possible creation of new internal microporous or cavities that might result from network reorganization or counterion effects. All these factors could suggest that metal incorporation expands rather than collapses the polymeric network. The pore size distribution indicated a pore diameter average of 2.6 nm

for HCP-NHC-Ag, 1.9 nm for HCP-NHC-Cu, 2.8 nm for HCP-*Bis*NHC-Ag, and 2.8 nm for HCP-*Bis*NHC-Cu (Figure A.15).

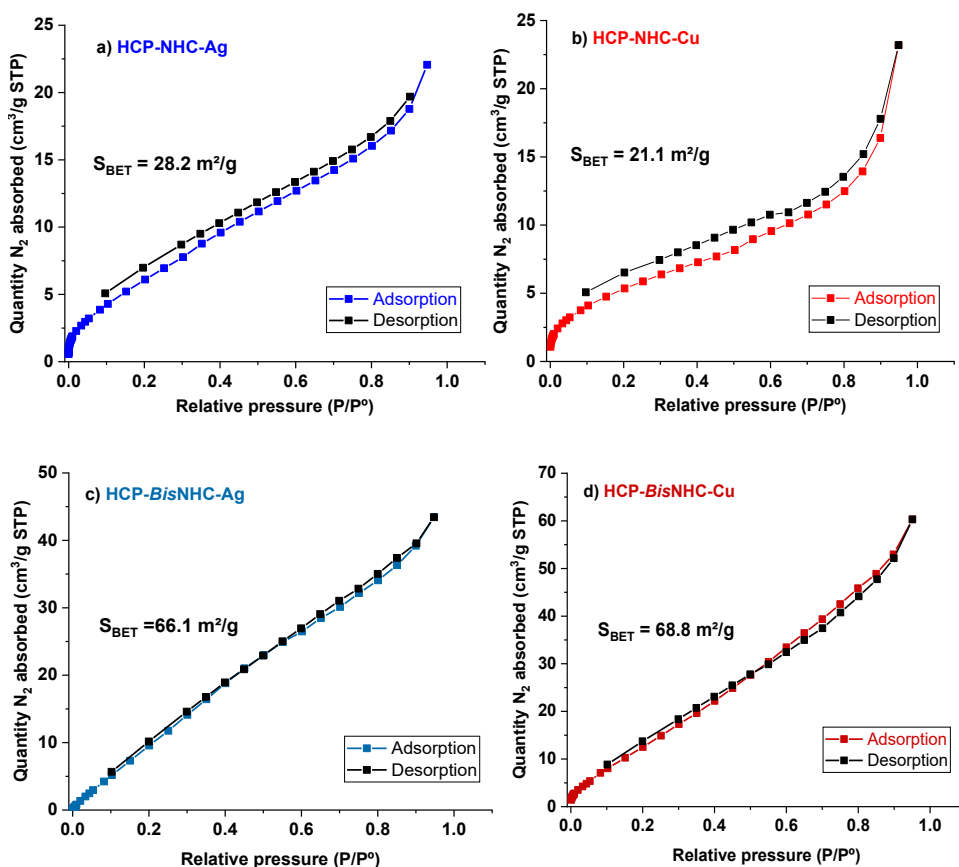


Figure 4.9 N₂-Adsorption/desorption isotherms of a) HCP-NHC-Ag, b) HCP-NHC-Cu, c) HCP-*Bis*NHC-Ag d) HCP-*Bis*NHC-Cu.

The CO₂ uptake was measured for the four complexes by CO₂ adsorption isotherms (Figure 4.10). The CO₂ uptake of the HCP-*Bis*NHC-Metal complexes were superior to those of the HCP-NHC-Metal complexes, most likely due to the larger Langmuir surface and higher N content of these complexes. Thus, HCP-*Bis*NHC-Cu showed the highest CO₂ uptake with an adsorption of 1.3 mmol.g⁻¹ followed by HCP-*Bis*NHC-Ag which exhibited 1.0 mmol.g⁻¹. HCP-NHC-Cu and

HCP-NCH-Ag exhibited adsorption of 0.7 and 0.8 mmol.g⁻¹ respectively. Although the CO₂ adsorption values appeared moderate, they were higher than those of the precursor polymers, indicating that the generation of metal carbenes positively enhanced CO₂ adsorption. In fact, the higher CO₂ adsorption observed in the HCP-*Bis*NHC-Metal series could be associated with higher nitrogen content present in these materials that provides more active sites for CO₂ interactions, enhancing adsorption capacity. Moreover, differences in pore distribution and accessibility may allow better diffusion of CO₂ in the *Bis*NHC structures. Overestimation of Langmuir surface area due to model assumptions could be observed, as Langmuir often gives higher values than BET without necessarily correlating with CO₂ uptake. In general, metal coordination effects may influence CO₂ interactions, but if the metal sites are not fully accessible, adsorption capacity remains moderate despite the high surface area.

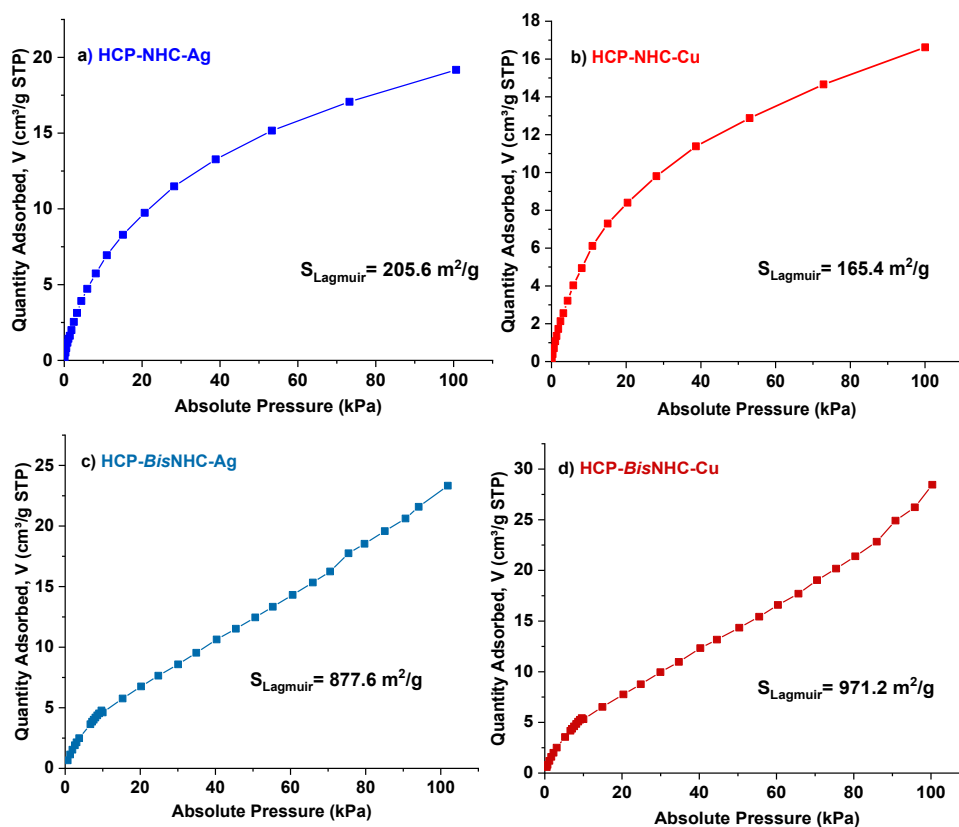


Figure 4.10 CO₂ uptake isotherms of a) HCP-NHC-Ag, b) HCP-NHC-Cu, c) HCP-BisNHC-Ag d) HCP-BisNHC-Cu.

Finally, the morphology of the complexes was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images (Figure 4.11) revealed the characteristic morphology of hypercrosslinked porous polymers, showing spherical aggregates of varying sizes, consistent with similar materials. The TEM images (Figure 4.12) provided further insight into the internal structure, revealing porous domains and an interconnected porous network. In all samples, the presence of dispersed electron dense-regions was observed, suggesting the formation of metal-containing species. While smaller and well-dispersed metallic nanoparticles were

predominant in HCP-NHC-Cu and HCP-NHC-Ag samples, larger nanoparticle-like structures were also identified, particularly in HCP-*Bis*NHC-Ag samples. However, XPS analysis did not show clear evidence of fully reduced metallic Cu or Ag species, indicating that these metal-containing domains may exist in an oxidized state or be strongly coordinated within the polymeric framework. These findings suggest that metal incorporation influences both the textural properties and the metal distribution in the polymeric network, which may have implications for catalytic performance.

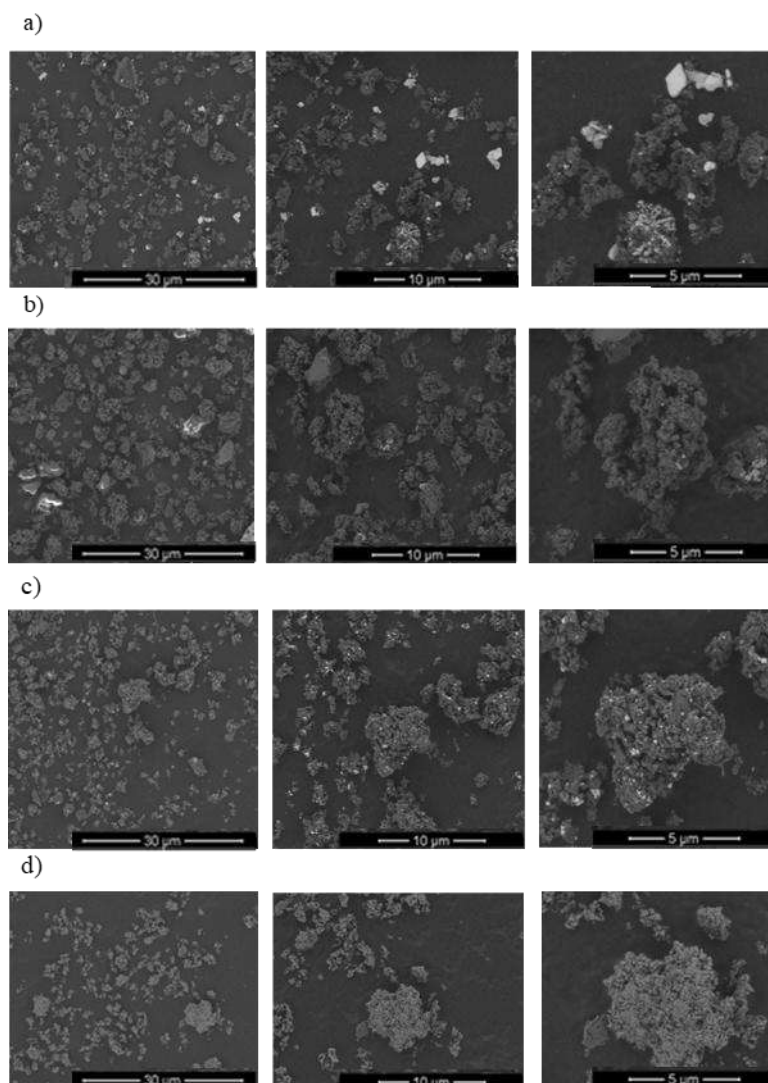


Figure 4.11 SEM images of a) HCP-NHC-Ag, b) HCP-NHC-Cu, c) HCP-BisNHC-Ag, d) HCP-BisNHC-Cu

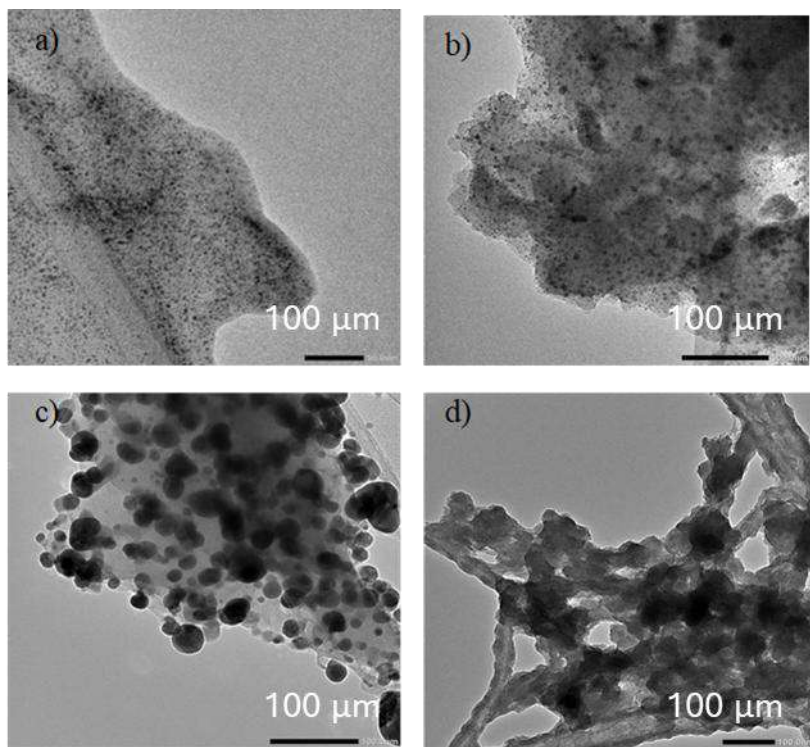


Figure 4.12 TEM images of a) HCP-NHC-Ag, b) HCP-NHC-Cu, c) HCP-*Bis*NHC-Ag, d) HCP-*Bis*NHC-Cu.

4.3.2 Catalytic activity

The synthesis of cyclic carbamates (2-oxazolidinones) via the three-component coupling reaction of CO₂ with 2-methylbut-3-yn-2-ol and a primary amine was optimized with n-butylamine as model substrate. (Figure 4.13).

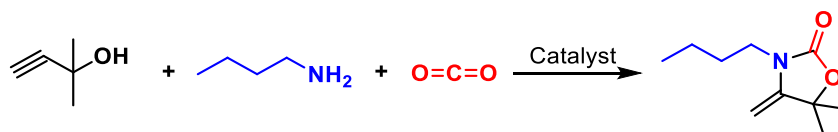


Figure 4.13 Scheme of synthesis of the model cyclic carbamate (3-butyl-5,5-dimethyl-4-methylene-2-oxazolidinone) used to optimize reaction conditions.

According to previously reported works the reactions were conducted under 120°C, 5 bar CO₂ pressure, 5 mol% catalyst (based on metal content), and acetonitrile as the solvent. (Table 4.3) Catalytic performance was evaluated for the four synthesized catalysts (entries 1–4) and their reaction kinetics profiles are recorded in Figure 4.14. The kinetic curves indicate notable differences in reaction rates among the catalysts. The copper-based catalysts (HCP-NHC-Cu and HCP-*Bis*NHC-Cu) exhibited faster conversion rates compared to their silver counterparts, suggesting a more efficient activation of the substrates, possibly due to stronger π -coordination between Cu and the propargyl alcohol. Among all catalysts, HCP-*Bis*NHC-Cu displayed the highest initial rate and reached full conversion in the shortest time and increased CO₂ adsorption capacity. In contrast, the silver-based catalysts required longer reaction times to achieve complete conversion, which may be attributed to differences in metal-ligand interactions affecting substrate activation. These trends highlight the key role of metal selection and polymer structure in determining catalytic efficiency.

All catalysts except HCP-NHC-Ag, yields quantitatively the carbamate with TOF values of 100 h^{-1} (HCP-NHC-Ag), 163 h^{-1} (HCP-NHC-Cu), 113 h^{-1} (HCP-*Bis*NHC-Ag) and 240 h^{-1} (HCP-*Bis*NHC-Cu).

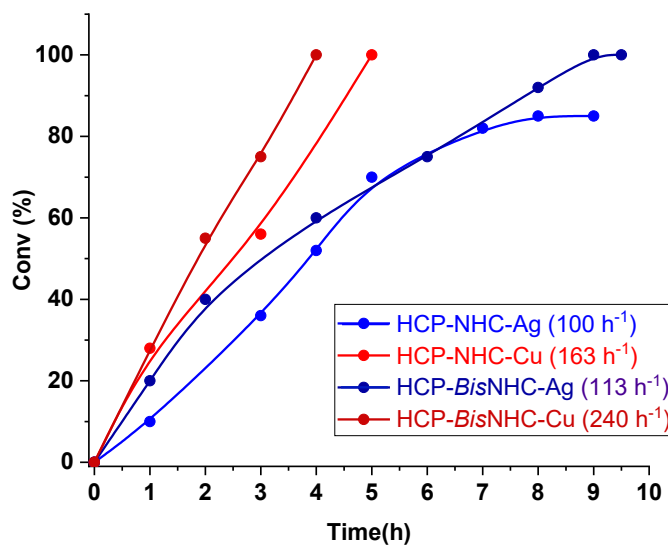


Figure 4.14 kinetic profile of four catalysts.

Table 4.3 Reaction conditions of the three-component coupling reaction using CO₂, propargyl alcohol (PA) and n-butylamine to obtain the cyclic carbamate (CC).

Entry	Catalyst	Dvte	T (°C)	P (bar)	t (h)	Conv (%)	CC Sel. (%)
1	HCP-NHC-Ag	ACN	120	5	9	85	99
2	HCP-NHC-Cu	ACN	120	5	5	100	99
3	HCP-BisNHC-Ag	ACN	120	5	9	100	98
4	HCP-BisNHC-Cu	ACN	120	5	4	100	99
5	CuI	ACN	120	5	16	10	99
6	Ag ₂ O	ACN	120	5	16	5	99
7	HCP-BisNHC-Cu	ACN	60	5	16	35	96
8	HCP-BisNHC-Cu	ACN	100	5	16	80	90
9	HCP-BisNHC-Cu	ACN	120	-	4	0	0
10	HCP-BisNHC-Cu	ACN	120	balloon	4	0	0
11	HCP-BisNHC-Cu	ACN	120	3	4	35	90
12	HCP-BisNHC-Cu	-	120	5	4	65	96
13	-	ACN	120	5	16	5	97
14 ^{a)}	HCP-BisNHC-Cu	ACN	120	5	10	100	99

Catalyst (5 mol% metal), 2-methylbut-3-yn-2-ol (0.5 mmol), Butylamine (1 mmol) and the ACN (0.5 mL) ^{a)} benzylamine as substrate.

Excepting HCP-NHC-Ag, with all catalysts, complete propargyl alcohol conversions were achieved, being copper derivatives faster, especially HCP-*Bis*NHC-Cu (entry 4, Table 4.3) which attained the best activity in 4 hours. Figure A.16 and Figure A.17 shows the ^1H -NMR and ^{13}C -NMR spectra of the cyclic carbamate (3-butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one) obtained in this reaction.

The control experiments conducted with the metal salts used process, CuI and Ag₂O as catalysts (entries 5 and 6) led to very low propargyl alcohol conversions of 10% and 5%, respectively, even with 16 h of reaction. These results confirmed the positive effect of supporting the metal in polymeric networks of this type. Once the optimal catalyst was identified, some additional experiments were carried out to assess the effects of varying pressure, temperature, and reaction time. Thus, by decreasing the temperature to 60°C or to 100°C even with long reaction time, complete conversion was not achieved (entries 7 and 8). As expected, the reaction does not take place in the absence of CO₂, but neither does it take place at atmospheric pressure (entries 9 and 10), and at a pressure of 3 bars the conversion of propargyl alcohol was very low 35% (entry 11), indicating that the optimal working pressure is 5 bar. The reaction in absence of solvent (entry 12) achieved a 65% of propargyl alcohol conversion. However, the reaction mixture became difficult to stir, suggesting that the solvent is crucial for the best dispersion of the reactants and catalyst. Finally, a control experiment without catalyst (entry 13) resulted in only 5% conversion after 16 hours, confirming the key role of the catalyst in driving the reaction. The reaction was also done using another more voluminous amine such as benzylamine (entry 14) also observing complete conversion and selective formation of the cyclic carbamate in 10 hours of reaction. Figure A.18 shows the ^1H -NMR and Figure A.19 the ^{13}C NMR of this cyclic carbamate.

In order to try to understand the lower reactivity of silver derivatives, X-ray powder diffraction spectra of all catalysts were recorded (Figure 4.15). The silver-complexes show the characteristic peaks of silver oxide, while the copper-complexes display an amorphous structure pattern. The probable presence of silver oxide could slow down the reaction, since in these complexes there would be fewer active species than in the copper ones.

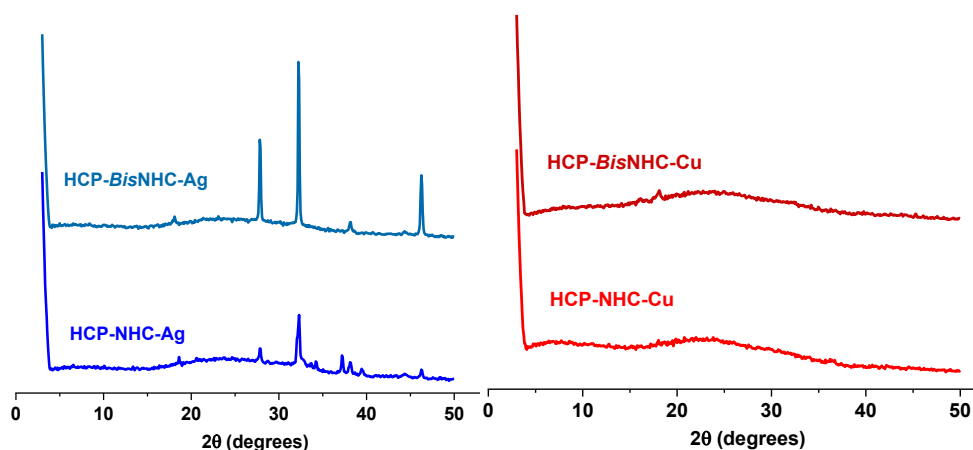
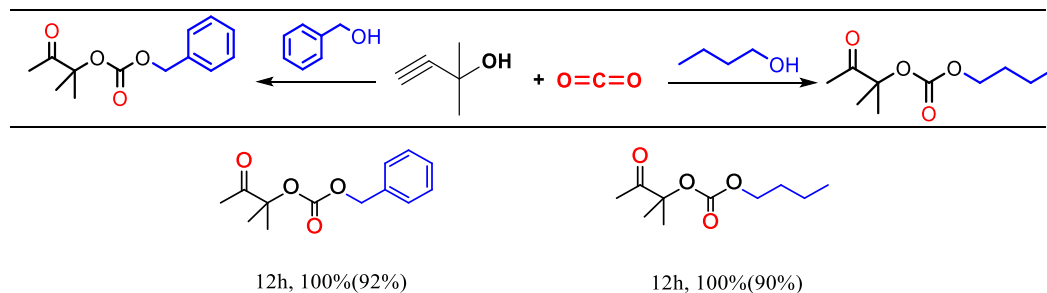


Figure 4.15 Powder X-ray diffraction of the catalysts.

To extend the study to other multicomponent reactions with CO_2 and propargyl alcohol, HCP-*Bis*NHC-Cu was evaluated in the synthesis of asymmetric carbonates, using *n*-butyl alcohol and benzyl alcohol as reagents (Table 4.4.). The reaction needs 12 hours for full conversion of propargyl alcohol and for the formation of the corresponding asymmetric carbonate with a selectivity between 90 and 95%. Figure A.20 and Figure A.22 show the ^1H -NMR spectra and Figure A.21 and Figure A.23 shows the ^{13}C NMR spectra of both asymmetric carbonates. In both cases a cyclic carbonate (4-dimethyl-5-methylene-1,3-dioxolan-2-one) was obtained as by-product. This by-product is formed in the first few hours of

the reaction. In fact, when the reaction is stopped after 3 hours, this derivative is obtained as the only product, as determined by ^1H - NMR (Figure A.24)

Table 4.4 Synthesis of asymmetrical carbonates using HCP-*Bis*NHC-Cu as catalyst.



Catalyst (5 mol% metal), 2-methylbut-3-yn-2-ol (0.5 mmol), alcohol (1 mmol), ACN (0.5 mL), $P(\text{CO}_2) = 5\text{bar}$, $T = 80^\circ\text{C}$.

Once the applicability of this catalyst was demonstrated in both reactions, its recyclability was evaluated. For the three-component coupling reaction to obtain 2-oxazolidinones, *n*-butylamine was used, while *n*-butyl alcohol was employed for the synthesis of asymmetrical organic carbonates. In both cases the recyclability was studied for seven cycles (Figure 4.16). In the case of the cyclic carbamate formation, the catalyst showed excellent activity, with propargyl alcohol conversions between 92% and 100% keeping the reaction over 5 h, and selectivity towards the cyclic carbamate close to 100%. In the synthesis of asymmetric carbonate, the conversion rate decreased with the use of recycles, though it stabilized at approximately 80%. Selectivity also experienced a slight reduction, but it remained consistent at around 85%.

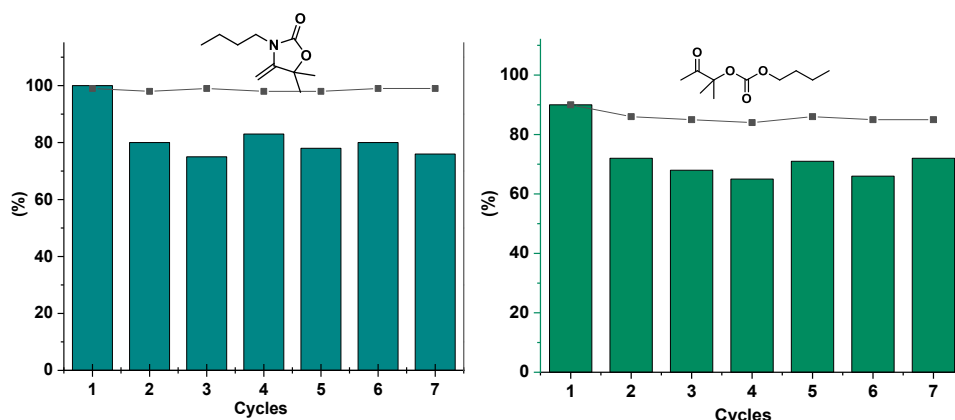


Figure 4.16 Recyclability of HCP-BisNHC-Cu in the two reactions.

To confirm the heterogeneity of HCP-BisNHC-Cu, a hot filtration experiment was also carried out removing the catalyst after two hours of reaction. At this time the conversion of propargyl alcohol was 55% as it shown in Figure 4.17. It does not increase significantly after four hours, only by 5%, which confirms that there is no significant release of catalytic species to the reaction medium.

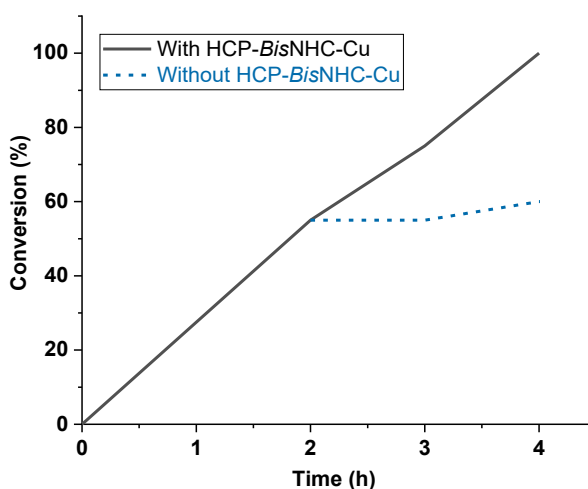


Figure 4.17 Hot filtration experiment.

The recovered catalyst was analyzed by TGA (Figure 4.18) showing small differences between before and after recycling, as the percentage of metal was 12.5%, like that of fresh catalyst.

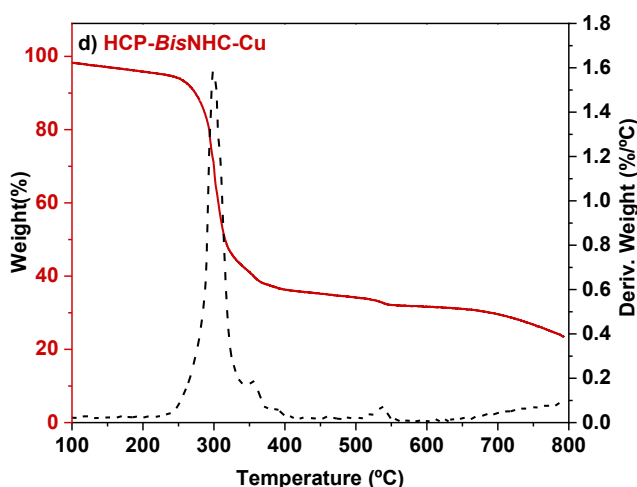


Figure 4.18 TGA of HCP-*Bis*NHC-Cu after seven cycles

4.3.3 Mechanism proposal

Based on some reported mechanisms,^[37, 38] a plausible mechanism for both reactions is depicted in Figure 4.19. The reaction starts with the coordination of the metal to the triple bond of propargyl alcohol to form the complex **(1)**. CO₂ is then inserted into this compound to obtain the CO₂-adduct **(2)**. Next, a ring-closing reaction occurs, leading to the formation of α -alkylidene carbonate **(3)**, regenerating the catalyst and allowing the catalytic cycle to continue. At this stage, the mechanism diverges into two pathways depending on whether a primary amine or alcohol is present.

If a primary amine is present, the reaction first undergoes aminolysis via the nucleophilic attack of the amine on the carbonyl, yielding the acyclic carbamate **(4)**. This intermediate can undergo cyclization through an

intramolecular attack of the amino group on the carbonyl. Finally, after dehydration, the corresponding cyclic carbamate (2-oxazolidinone) (**5**) is formed.

If a primary alcohol is present, a nucleophilic attack of this alcohol on the carbonyl of the cyclic carbonate (**3**) occurs, resulting in a ring-opening reaction to give intermediate (**6**) which after a subsequent tautomerization, yields the asymmetric carbonate (**7**).

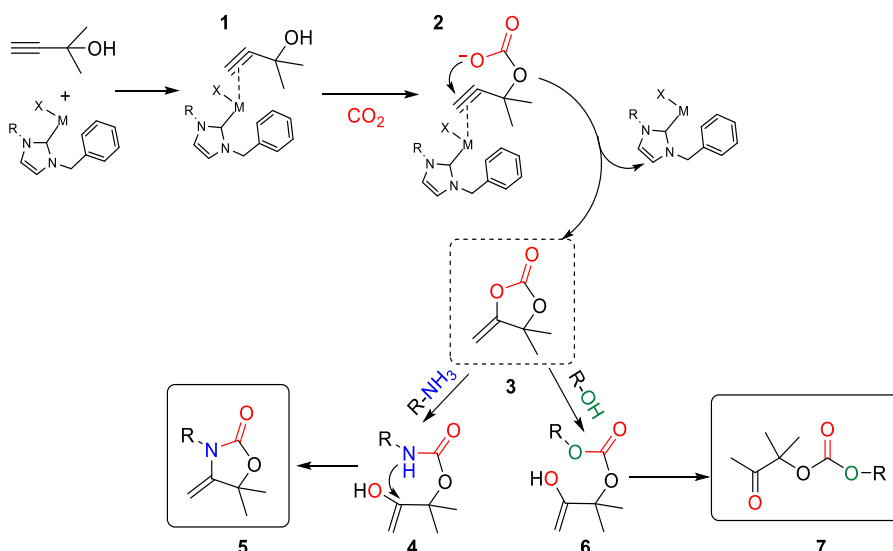


Figure 4.19 Mechanism proposal for the formation of cyclic carbamates (2-oxazolidinones) and asymmetrical carbonates using HCP-NHC-M as catalyst.

4.4 Conclusions

Heterogenized HCP-NHC-M-complexes (M= silver and copper) have been effectively obtained from HCPs-BzmimCl polymers and used as catalysts in the synthesis of cyclic carbamates (2-oxazolidinones) and asymmetric carbonates.

The developed catalysts demonstrated effective activity in obtaining cyclic carbamates from propargylic alcohol, CO₂ and primary amines. Particularly, the copper-based catalysts (HCP-NHC-Cu and HCP-*Bis*NHC-Cu) showed faster conversion rates compared to their silver counterparts, suggesting more efficient substrate activation, possibly due to stronger π -coordination between Cu and propargyl alcohol. In addition, the presence of silver oxide particles, which are not active in this conversion, was detected in the silver complexes, which could slow down the reactions with these catalysts.

The synthesis of asymmetric carbonates from propargylic alcohol, CO₂, and primary alcohols was slower than the synthesis of cyclic carbamates and less selective, since the formation of a cyclic carbonate (4-dimethyl-5-methylene-1,3-dioxolan-2-one) as secondary compound was detected. This by-product is formed from the first few hours of the reaction because it was the only product detected when the reaction was stopped after 3 hours.

4.5 Experimental section

2-methylbut-3-yn-2-ol purity 98% was supplied by Sigma Aldrich. Potassium tert-butoxide (98%) was supplied by thermos scientific, cuprous iodide (98%) and silver oxide (99.5%) were supplied by FluoroChem. The other reagents and solvents were supplied by Aldrich with analytical grade and were used as received.

4.5.1 Synthesis of Catalysts

4.5.1.1 Synthesis of HCP-NHC-Ag and HCP-*Bis*NHC-Ag

A flask (50 mL) was successively charged with HCP-BzmimCl or HCP-*Bis*BzmimCl (500 mg), a magnetic stirrer and degassed dichloromethane (DCM, 20 mL) under nitrogen atmosphere. After sonication of the mixture for 5 min, Ag₂O (90 mg, 0.39 mmol) was added to the vessel under nitrogen atmosphere. The resulting suspension was stirred vigorously for 24h at room temperature. Then, the mixture was filtered under vacuum and the resulting filter cake was washed thoroughly with DCM (50 mL × 3) methanol (50 mL × 3) and water (25 mL × 2). The solid was dried under vacuum for 12h at 110°C to obtain (520 mg, 96%).

4.5.1.2 Synthesis of HCP-NHC-Cu and HCP-*Bis*NHC-Cu

A flask (50 mL) was successively charged with HCP-BzmimCl or HCP-*Bis*(BzmimCl) (500 mg), a magnetic stirrer and degassed tetrahydrofuran (THF, 20 mL) under nitrogen atmosphere. After ultrasonication of the mixture for 5 min, CuI (140 mg, 0.39 mmol) and potassium tert-butoxide (44 mg, 0.39 mmol) were added to the vessel under nitrogen atmosphere. The resulting suspension was stirred vigorously for 24 h at room temperature. Then, the mixture was filtered under vacuum and the resulting filter cake was washed thoroughly with THF (50

mL $\times$ 3), Dichloromethane (50 mL $\times$ 3) and methanol (50 mL $\times$ 3). The solid was dried under vacuum for 12h at 110°C. (610 mg 92%).

4.5.2 Three-Component Coupling of CO₂ to Oxazolidinones:

General procedure: The catalyst (5 mol% metal), 2-methylbut-3-yn-2-ol (0.5 mmol), amine (1 mmol) and acetonitrile (0.5 mL) as solvent, were successively added into a steel autoclave reactor. After slowly purging the reactor with CO₂ (3.0 bar) three times, it was charged with CO₂ to a pressure of 5.0 bar. The reaction was maintained at 120 °C for 4 to 16 hours. Then, the reactor was cooled to room temperature, and the CO₂ pressure was slowly released. The reaction mixture was filtered under vacuum and thoroughly washed with DCM (3 $\times$ 10 mL). The resulting filtrate was collected and concentrated via rotary evaporation. The cyclic carbamate was purified by flash chromatography on a silica gel using hexane/ethyl acetate (1:1) as the eluent. The reaction was monitored by ¹H NMR spectroscopy.

4.5.3 Synthesis of asymmetrical carbonates

General procedure: The catalyst (5 mol% metal), 2-methylbut-3-yn-2-ol (0.5 mmol), alcohol (1 mmol), tetrabutyl ammonium bromide TBAB (0,05 mmol) and acetonitrile (0.5 mL) as solvent, were successively added into a steel autoclave reactor. After purging the reactor with CO₂ (3.0 bar) three times, it was charged with CO₂ to a pressure of 5.0 bar. The reaction was carried out at 80 °C for 10 to 16 hours. Upon completion, the reactor was cooled to room temperature, and the CO₂ pressure was slowly released. The reaction mixture was filtered under vacuum and thoroughly washed with DCM (3 $\times$ 10 mL). The resulting filtrate was collected and concentrated via rotary evaporation. The reaction was monitored by ¹H NMR spectroscopy.

4.5.4 Recycling experiment

After the reaction was completed, the polymer was separated from the reactions by filtration, washed with ACN and CH_2Cl_2 and dried at 100°C for 12h, then it was used in a fresh run.

4.6 References

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Chapter 3: Functionalized hypercrosslinked polymer catalysts to produce 2,5-furan dicarboxylic methyl ester (FDME)

5.1 Introduction

The incorporation of furan rings in polymers is having a great impact due to the excellent final properties it provides: high glass transition temperature, low melting and processing temperature and, excellent gas barrier properties which makes it have very up-and-coming applications such as high-performance fibers and as packaging materials.^[1, 2] 2,5-furan dicarboxylic methyl ester (FDME) is an interesting monomer widely used in the synthesis of furan-based polyesters which has been mainly prepared by oxidative-esterification of 5-hydroxymethylfurfural (HFM)^[2-5] or galactaric acid^[6, 7] using different homogeneous metal-based catalysts. The synthesis of FDME can also be achieved from 2-methyl furoate (MF) which is also a bio-based molecule very abundant in peanuts, cocoa, and coffee and offers a wide range of applications, for example in the synthesis of fuels or fuels additives, as an intermediate for the synthesis of compounds with medical applications or in the synthesis of renewable hydrophilic polyesters.^[8-10] However, as far as we have been able to investigate, one work has been published where the FDME has been prepared from MF (Figure 5.1). The procedure consists of a direct alkoxycarbonylation in a one-step reaction of three components, MF, methanol, and CHCl₃, using a copper catalyst. The reaction was conducted at 120°C for 12h to obtain FDME with good yield (80%).^[11]

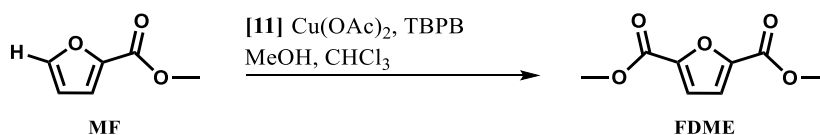


Figure 5.1 Reported syntheses of FDME from MF.

The synthesis of FDME from MF and CO₂ is an interesting alternative because besides obtaining this value monomer, it takes advantage of using CO₂

as feedstock. Thus, obtaining a monomer from CO₂ such as FDME that can be used to obtain a CO₂-based polymer is especially relevant.^[12]

Thus, in this chapter we reported the synthesis of FDME by the insertion of CO₂ to 2-methyl furoate catalyzed by a hypercrosslinked polymeric catalyst (HCP-Salphen-Co) which was prepared in one step, using a mechanochemical polymerization.

Although 2-methyl furoate is a bio-based molecule, it can be synthesized from furfural (FA), which is a very interesting renewable raw material as it is derived mainly from lignocellulosic biomass. Moreover, furfural is a versatile platform compound for the synthesis of other chemicals, biofuels and additives.^[13-16]

There have been many reports on the synthesis of MF from furfural via oxidative esterification with methanol. In most of these studies, mono- or bimetallic catalysts containing elements such as Au, Pd, Zr and Ce have been used. For instance, in the presence of oxygen, catalysts such as Au/ZrO₂ ^[17-20], Au/CeO₂ ^[21], Au-K₂CO₃ ^[22], Au/TiO₂ ^[17, 19, 23-25], Au-MgO ^[26], Au/CMK-3 ^[27] and AuPd/HAP-T^[28] have been used to obtain MF in high yield. Except for some examples that catalyzes the reaction at room temperature, such as Au/TiO₂ assisted by NaOCH₃.^[23] these processes rely completely on expensive chemical catalysts (precious metals) and high temperatures (100–120 °C), In 2013, Chiarotto et al. reported the oxidative esterification of furfural to obtain 2-ethyl furoate (EF) in moderated yield (25%) using an ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) as precatalyst in the presence of a mixture of 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) and cesium carbonate (Cs₂CO₃) and using MnO₂ as an oxidizing agent. The reaction was maintained at room temperature for 24 h^[29], In the same year, Kiran et al. reported a metal-free catalyst based on an ionic liquid (1,3-bis(2,4,6-trimethylphenyl)

imidazolium chloride) and the same strong base, DBU (Figure 5.2) using oxygen as a source of oxidation. The MF yield, in this case, was 63% and 24 h of reaction was necessary ^[30]. Recently, Song et. al proposed a two-step process which involves the use of the same ionic liquid in the first step and enzymes in the second to obtain MF in higher yield (83%) at 50 °C after 24 h of reaction ^[31] (Figure 5.2)

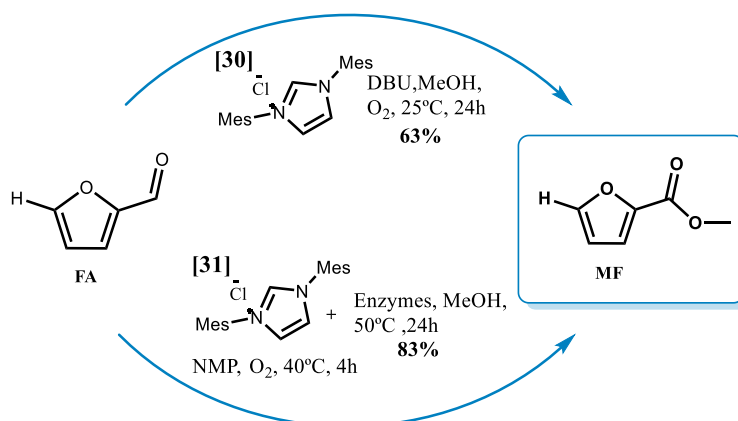


Figure 5.2 Ionic Liquid based systems reported for the oxidative esterification of furfural.

As discussed in the first chapter of this thesis, the possibility of having a supported ionic liquid is extremely interesting to have a heterogeneous catalyst that is reusable. Thus, considering that the synthesis of 2-methyl furoate MF has been carried out from Furfural with IL, we propose to carry out this synthesis using one of the polymers based on ionic liquid prepared in chapter 1

5.2 Objectives

The main objective of this chapter is the synthesis of 2,5-furan dicarboxylic methyl ester (FDME) from Furfural and CO₂ for which a three-steps strategy has been designed.

The first step involves the synthesis of 2-methyl furoate using Furfural as starting material, followed by a subsequent carboxylation using CO₂ and a final esterification step to obtain the desired product. To achieve this objective the next specific objectives will be carried out.

- Synthesis of 2-methyl furoate from Furfural using imidazolium chloride-based hypercrosslinked polymer catalyst. To obtain this intermediate, the catalyst HCP-BzmimCl prepared in Chapter 1 will be used as catalyst. Previously the condition reactions will be optimized using different bases and commercial ionic liquids.
- Synthesis and characterization of a cobalt-based hypercrosslinked polymeric catalyst (HCP-Salphen-Co). This catalyst will be prepared by mechanochemical polymerization and it will be characterized by standard solid-state techniques, such as FTIR, ¹³C NMR, TGA, XPS, N₂ adsorption/desorption isotherms, CO₂ adsorption isotherms, and SEM microscopy.
- Synthesis of FDME from MF using CO₂ To obtain the target molecule, FDME, the above catalyst, HCP-Salphen-Co, will be used as catalyst in the second step and an acid esterification in a last one. Previously, the condition reactions for the carboxylation step will be optimized using different metal salts.

5.3 Results and discussion

The synthesis of 2,5-furan dicarboxylic methyl ester (FMDE) was done in three steps (Figure 5.3). Furfural was first transformed into 2-methyl furoate (MF) by oxidative esterification, and then, this intermediate was carboxylate and esterification to obtain the target molecule

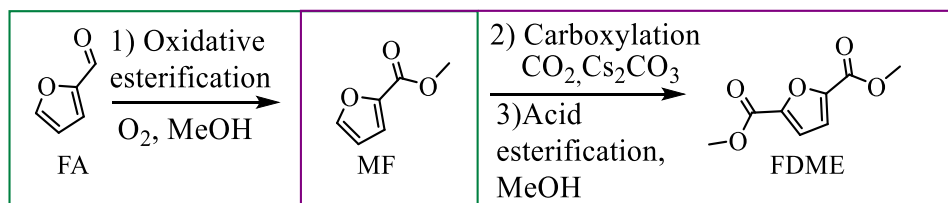


Figure 5.3 Scheme the synthesis of 2,5-Furan dicarboxylic methyl ester.

5.3.1 Synthesis of 2-methyl furoate from Furfural using imidazolium chloride-based hypercrosslinked polymer catalyst.

For the synthesis of 2-methyl furoate, the catalyst selected is the described in the chapter 1, HCP-BzmimCl. However, prior to its use, the reaction conditions were optimized using a commercial ionic liquid as a catalyst and two different bases, cesium carbonate (Cs_2CO_3) or 1,8-diazabicyclo[5.4.0]undeca-7-ene (1,8-Diazabicyclo[5.4.0]undec-7-ene) (DBU).

5.3.1.1 Catalytic activity assisted by Cs_2CO_3

Taking into account the conditions reported,^[28] our first attempt to obtain the desired compound involved using MnO_2 and O_2 as oxidants, Cs_2CO_3 as the base, and 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) as the catalyst (entry 1, Table 5.1). When the reaction was carried out at $80^\circ C$, no product was formed. This is likely since this temperature exceeds the melting point of $BmimBF_4$ ($70^\circ C$). However, by lowering the temperature to $60^\circ C$, a yield of 71% MF was achieved in 4 hours (entry 2) and increasing the amount of the ionic

catalyst (entry 3), a higher yield of 93% was obtained. By using 1-benzyl-3-methylimidazolium chloride (BzmimCl) in the same conditions (entry 4), the target compound was also obtained. When the reaction was done in absence of MnO_2 , increasing the amount of this IL, base and the reaction time (entry 5), the reaction also took place, although a decrease in the yield of MF was observed. This result pointed out that the reaction can take place using only O_2 as the oxidizing agent. Thus, some experiments free of MnO_2 were carried out to optimize the reaction, obtaining 82% of MF (entry 6) using half amount of Cs_2CO_3 that IL. Thus, in these conditions and using only O_2 as an oxidizing agent, it was possible to obtain MF in a higher yield than the ionic liquids catalysts previously reported. [30, 32]. Moreover, the reaction was scaled to 12 mmol of FA (entry 7) obtaining also a high yield of the target compound.

The catalytic activity of the hypercrosslinked ionic polymer, HCP-BzmimCl was studied in the same conditions of entry 6 that is using O_2 as the only oxidizing agent and half the amount of Cs_2CO_3 that polymeric catalyst, getting 50% yield of MF in 24 h (entry 8). Increasing the amount of base until equal to the amount of catalyst (1:1) it was possible to obtain MF also in excellent yield (entry 10). This result could be attributed to the less accessibility of the base to the imidazolium groups of HCP-BzmimCl compared with the BzmimCl molecule. In fact, some accessibility difficulties to imidazolium chloride groups in polymer networks have been previously reported. [33-35] In the absence of base (entry 11). The furfural was converted into 2-(dimethoxymethyl) furfural in 67% of yield. Figure A.28 shows the ^1H NMR spectrum of this reaction where the signal at 3.35 ppm indicates the formation of the mentioned acetal. When the reaction was carried out using only Cs_2CO_3 without catalyst (entry 12) no reaction took place since the ^1H NMR spectrum showed furfural as the main product. Some impurities were observed which did not correspond to possible intermediates as

furfuryl alcohol or furoic acid. Thus, the results in absence of imidazole chloride-based catalysts or Cs_2CO_3 (entries 11 and 12) demonstrate the synergic effect between the two components to obtain the target compound. To prove the O_2 activation in this reaction, a control experiment was run in absence of this oxidant (entry 13) which confirmed the role of oxygen in the reaction since no oxidized species was detected obtaining only the starting furfural.

Table 5.1. Study of oxidative esterification of furfural to obtain MF using BzmimCl/ Cs_2CO_3 or HCP BzmimCl/ Cs_2CO_3 as catalytic systems.

Entry	MnO_2 (mmol)	Ionic Catatys (mmol)	Cs_2CO_3 (mmol)	T (°C)	t (h)	Conv. (%)	Selec a. (%)
1	0.25	BmimBF ₄ (0.20)	0.25	80	4	-	-
2	0.25	BmimBF ₄ (0.20)	0.25	60	4	71	100
3	0.25	BmimBF ₄ (0.40)	0.25	60	4	93	100
4	0.25	BzmimCl (0.40)	0.25	60	4	85	100
5	-	BzmimCl (0.80)	0.50	60	24	68	100
6	-	BzmimCl (1.00)	0.50	60	24	82	100
7 ^{a)}	-	BzmimCl (12.0)	6.00	60	24	90	100
8	-	HCP-BzmimCl (1.0)	0.50	60	24	50	100
9	-	HCP-BzmimCl (1.0)	0.75	60	24	76	100
10	-	HCP-BzmimCl (1.0)	1.00	60	24	94	100
11	-	HCP-BzmimCl (1.0)	-	60	24	67	0
12	-	-	1.00	60	24	2	-
13 ^{b)}	-	HCP-BzmimCl (1.0)	1.00	60	24	0	-

Conditions: $\text{P}(\text{O}_2)$ = 5bar, MeOH = 2mL, FA (Furfural) = 1mmol, ^{a)} FA = 12mmol, ^{b)} $\text{P}(\text{N}_2)$ = 2bar.

An important aspect concerning the heterogeneous catalytic system is the possibility of being recycled. Thus, after the first run using the simple filtration, washed with methanol and dichloromethane, and finally dried in a vacuum oven

at 100 °C for 12 h. The polymer was then reused with a fresh reaction mixture, repeating the process to four more runs. The results showed good recyclability (Figure 5.4), even increasing the yield of the reaction in some cases.

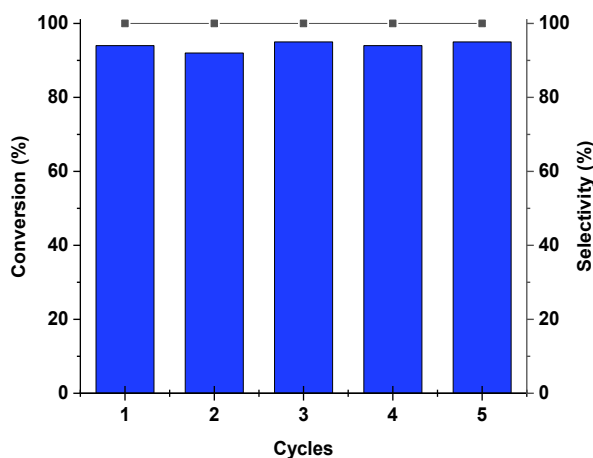


Figure 5.4 Recycling experiments of HCP-BzmimCl in the oxidative esterification using Cs_2CO_3 .

The recovered catalyst was analyzed by FTIR (Figure 5.5, left) and thermogravimetric analysis (Figure 5.5, right) observing differences between the materials before and after recycling although did not affect the catalytic activity.

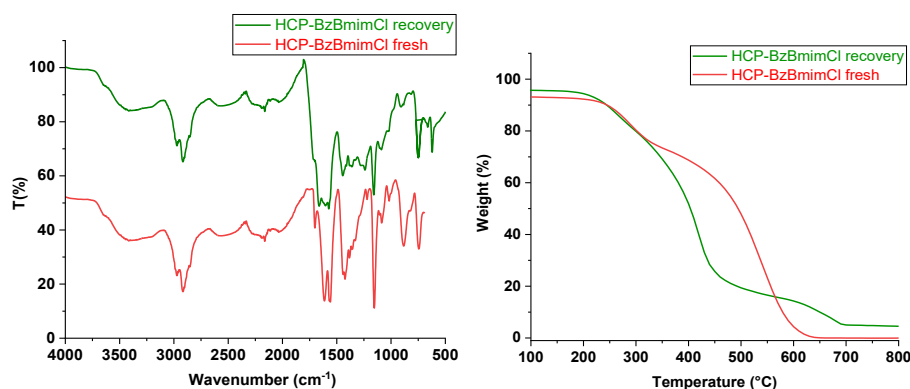


Figure 5.5 FTIR (left) and TGA (right) of recycled and Fresh HCP-BzmimCl.

5.3.1.2 Catalytic activity assisted by DBU

In order to explore an entirely organic catalytic system, the strong organic base DBU was used as an alternative to the Cs_2CO_3 , optimizing the reaction conditions with the hypercrosslinked ionic polymer (HCP-BzmimCl) due to the possibility of recycling that it offers. (Table 5.2) The use of the same ratio HCP-BzmimCl: base of the above study and the same reaction time, 24 h, MF was obtained with moderate yield (entry 1) but increasing the amount of this base led to the formation of MF with high yield and selectivity (entry 2). However, an attempt to reduce the amount of catalyst maintaining the amount of DBU caused the formation of a small amount of a secondary product, furan-2-carboxylic anhydride (FCA) (entry 3). The formation of this by-product was attributed to an excess base. In fact, when the amount of DBU increases a lot, this undesired FCA was obtained as the main product in 60% of the yield (entry 4). However, diminishing the reaction time to 4 h (entry 5), less amount of FCA was obtained (15%). Figure A.29 shows the ^1H NMR spectrum of this reaction in which the new signals can be observed at 6.70, 7.49 and 8.15 ppm attributed to the by-product. The chromatogram of this reaction (Figure A.30) shows the peaks of the three compounds detected, furfural (F), 2-methyl furoate (MF) and furan-2-carboxylic anhydride (FCA). As the best result was obtained using 1.2 mmol of DBU per mmol of HCP-BzmimCl (entry 2), the reaction was scaled using these conditions (entry 6), obtaining also excellent yield and selectivity towards the target compound.

Finally, BzmimCl was used as a homogeneous ionic catalyst assisted by DBU in the conditions of entry 5, observing worse catalytic performance than the heterogeneous catalyst since the target compound was obtained with a lower yield. By using more amount of the ionic catalyst and a longer reaction time, the MF was obtained with 81% of selectivity observing the formation of 19% of FCA

(entry 8). Only, by using half amount of base that ionic catalyst, as happened when Cs_2CO_3 was used as a base, a good selectivity towards the MF was obtained with complete furfural conversion (entry 9). By using DBU as unique component of the catalytic system (entry 10) no traces of 2-methyl furoate was observed. This result confirms again the synergic effect between the two components to obtain the target compound MF.

Table 5.2. Study of oxidative esterification of furfural (F) to obtain 2-methyl furoate (MF)

Entry	Ionic catalyst (mmol)	DBU (mmol)	t (h)	Conv. (%)	Selec a. (%)
1	HCP-BzmimCl (1.0)	0.5	24	50	100
2	HCP-BzmimCl (1.0)	1.2	24	98	100
3	HCP-BzmimCl (0.8)	1.2	24	95	94
4	HCP-BzmimCl (0.5)	1.2	24	100	40
5	HCP-BzmimCl (0.5)	1.2	4	100	85
6 ^{a)}	HCP-BzmimCl (6)	7.2	24	95	94
7	BzmimCl (0.5)	1.2	4	87	64
8	BzmimCl (1.0)	1.2	24	92	81
9	BzmimCl (1.0)	0.5	24	100	92
10	-	1.2	24	18	0

Conditions: $\text{P}(\text{O}_2) = 5\text{bar}$, $\text{MeOH} = 2\text{mL}$, FA (Furfural) = 1mmol . ^{a)} FA (6 mmol)

Just as in the previous catalytic system, the recyclability of the polymer HCP-BzmimCl was studied in conditions of run 2 (Figure 5.6). After the first run, HCP-BzmimCl was used in a fresh reaction observing a decrease in the catalytic activity. For this reason, the catalyst was treated with diluted HCl observing the

recovering of the activity. We attributed this result to a partial deactivation of the network during the reaction. Thus, a regeneration of the catalyst after each run was required by treatment of the recovered catalyst with diluted HCl. From the third run, a small amount of FCA was observed which indicated worse recyclability when DBU was used as a base.

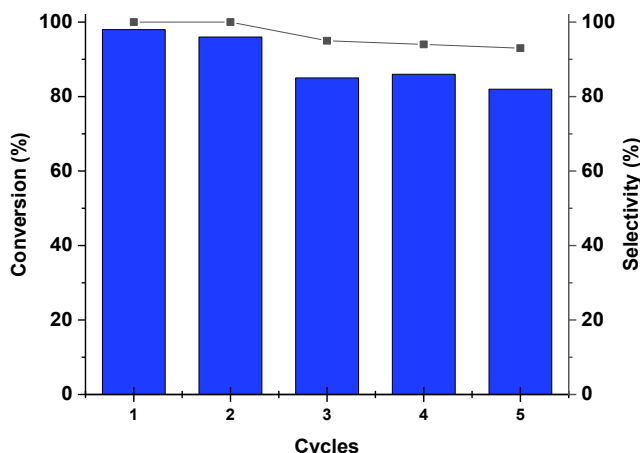


Figure 5.6 Recycling experiments of HCP-BzmimCl in the oxidative esterification of F using the HCP-BzmimCl and DBU as catalytic system.

5.3.1.3 Proposed mechanism

The reaction mechanism for oxidative esterification of furfural to obtain MF in the presence of strong bases and using O_2 as an oxidant was proposed in Figure 5.7, based on other previously reported oxidation mechanisms.^[36-39] First, a carbene intermediate can be formed from BzmimCl in the presence of the base **(2)**. Then, this carbene species reacts with furfural to form a highly reactive intermediate **(3)** which reacts with O_2 to form the peroxy anion **(4)** which upon decomposition results in the formation of the acyl intermediate **(5)**. Finally, the alkoxide ion formed from the alcohol reacts with **(5)** to give MF with the liberation of the carbene **(2)**. The formation of carbene species on the HCP-

BzmimCl catalyst is hindered, probably being the cause of the need to add more base to activate this catalyst and that the conversion of furfural was slightly lower than with the soluble catalyst, BzmimCl

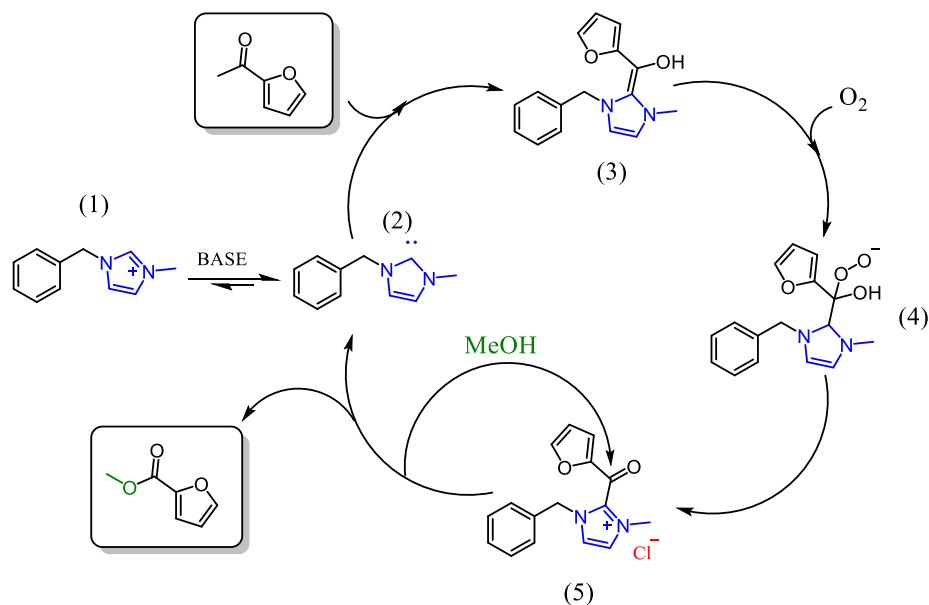


Figure 5.7 Proposed reaction pathway for the oxidative esterification of FA to obtain MF using the basic-ionic catalytic systems.

5.3.2 Synthesis of 2,5-furan dicarboxylic methyl ester (FDME) from 2-methyl furoate and CO₂ using a cobalt-based hypercrosslinked polymeric catalyst

5.3.2.1 Synthesis and Characterization of heterogenized Co-hypercrosslinked polymeric catalyst

The catalyst to carry out this transformation HCP-Salphen-Co was prepared according to the following scheme (Figure 5.8).



Figure 5.8 Functionalized hyper-crosslinked polymer catalysts to produce 2,5-furan dicarboxylic methyl ester (FDME).

The monomer *N,N'*-Bis(salicylidene)-1,2-phenylenediamine (Salphen) was prepared according to the literature.^[40] The synthesis was carried out reacting salicylic aldehyde and *o*-phenylenediamine and methanol as solvent, under reflux for 2 hours (Figure 5.9). The structure of the salphen monomer was confirmed by ¹H NMR (Figure 5.10) The characteristic signal of the hydroxyl group (-OH) can be observed around 13.09 ppm, whereas the signals corresponding to the imine protons appears at around 8.67 ppm, Finally, the signals of the aromatic protons are shown between 6.94 and 7.93 ppm.

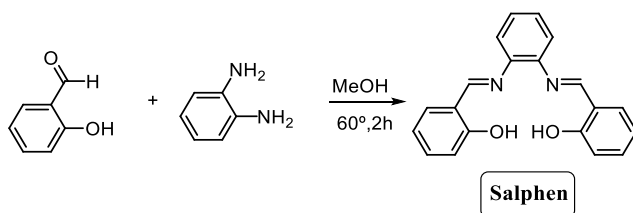
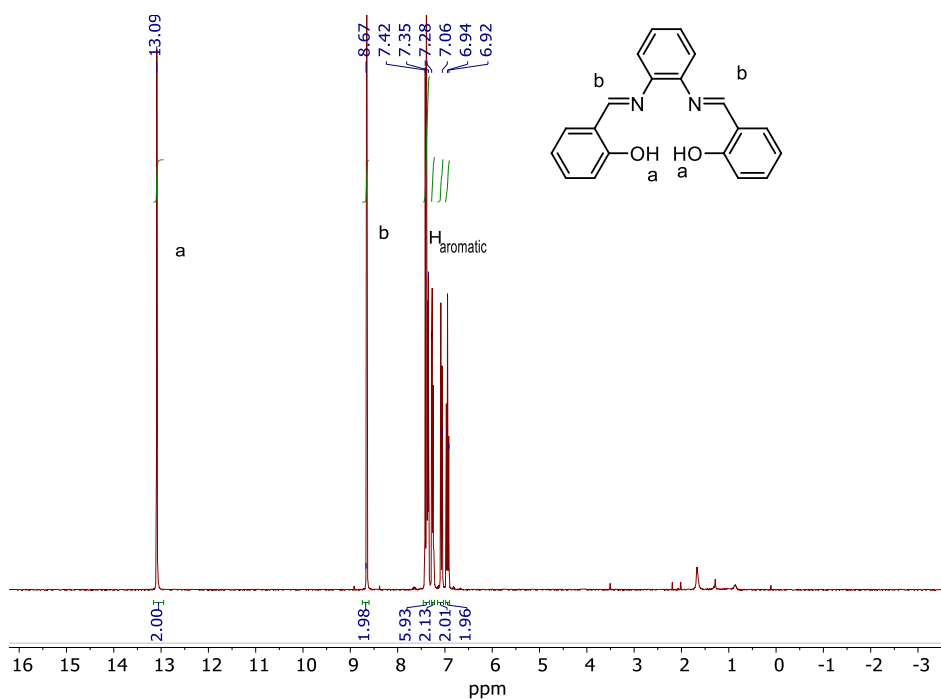


Figure 5.9 Scheme of the synthesis of Salphen

Figure 5.10 ^1H NMR of the salphen monomer (300 MHz, CDCl_3)

Once the Salphen was synthesized, it was metallized with cobalt, following the procedure reported,^[41] using Cobalt (II) acetate tetrahydrate and toluene and ethanol as solvents, obtaining *N,N'*-Bis(salicylidene)-1,2-phenylenediamine cobalt complex (Salphen-Co) structure was confirmed by ^1H NMR (Figure 5.11), observing that the signal due to free hydroxyl groups at ~ 13

ppm disappears due to the incorporation of the metal. In addition, displacement is observed in the rest of the signals as a result of the presence of the metal.

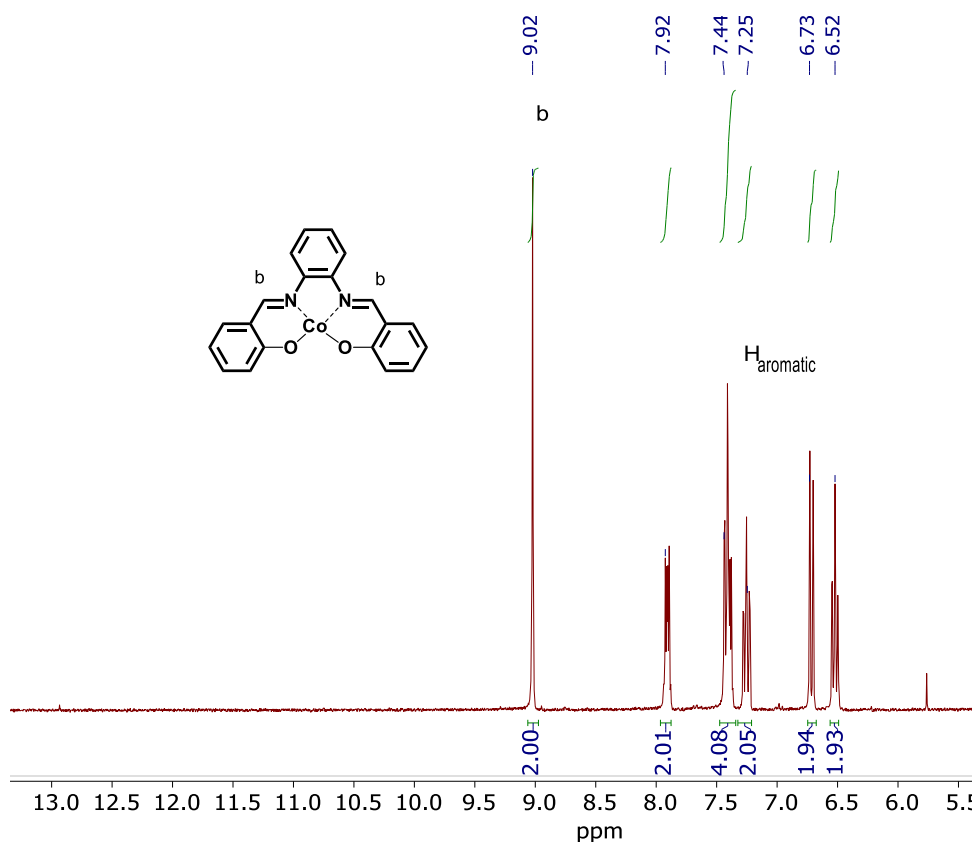


Figure 5.11 ^1H NMR of salphen-Co (300 MHz, CDCl_3)

5.3.2.2 Synthesis and Characterization of heterogenized Co-hypercrosslinked polymeric catalysts.

Finally, the Salphen-Co monomer was polymerized by mechanochemical synthesis in 55 min using AlCl_3 as catalyst and dimethoxymethane (DMM) as crosslinker. This mechanochemical synthesis has many advantages over conventional synthetic methods, which usually require the use of solvents, high temperatures and long reaction times. These characteristics have contributed to its growing relevance in the context of Green Chemistry.

The FTIR spectrum of HCP-Salphen-Co (Figure 5.12) shows a peak at 1609 cm^{-1} , accompanied by a neighboring peak at 1580 cm^{-1} , both of which are attributed to the strong interaction between the imine groups and the metal cations. The bands at 1538 cm^{-1} and 1435 cm^{-1} correspond to C=C stretching vibrations, while the peaks at 1210 and 1161 cm^{-1} are associated with the vibrations of the C-N and C-O bonds, respectively.

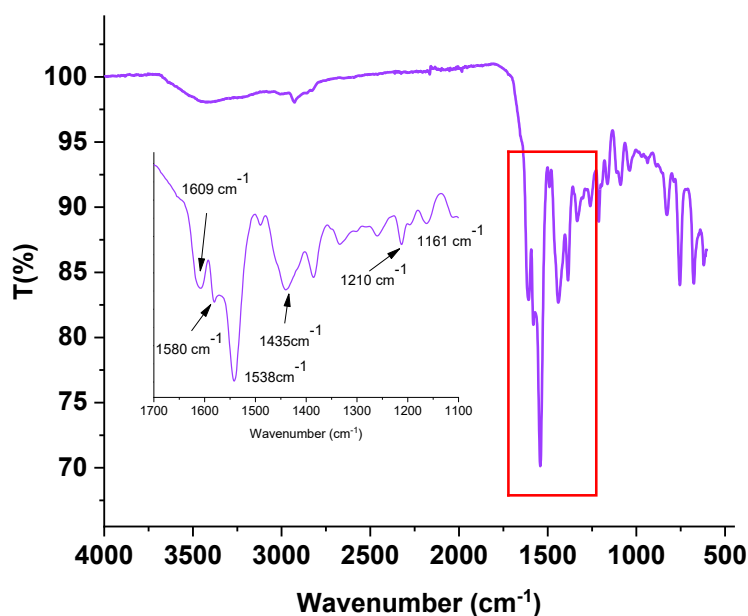
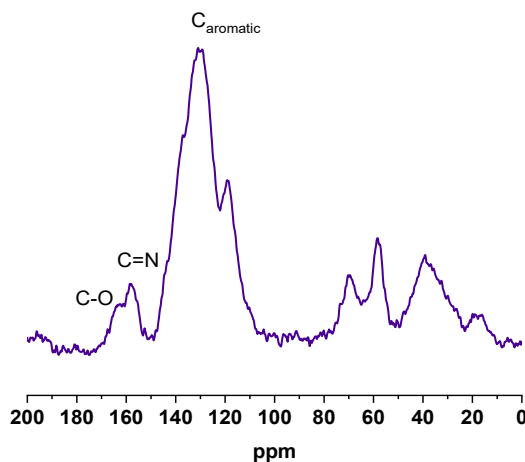


Figure 5.12 FTIR spectrum of HCP-Salphen-Co.

The ^{13}C NMR spectrum (Figure 5.13) showed an intense and broad signal between 110 and 140 ppm attributed to the aromatic carbons of the benzene rings. The signal corresponding to the oxygen carbon at ~ 160 ppm is also observable, and the imine groups around 150 ppm.

Figure 5.13 ^{13}C NMR spectra of HCP-Salphen-Co

Thermogravimetric analysis (Figure 5.14) indicated good thermal stability with an initial decomposition temperature of 400 °C. The presence of metal generates a percentage of residue due to the formation of metallic oxides during the thermogravimetric analysis. Thus, the amount of metal (Co) obtained from the TGA residue was 15.7%. which is very close to the one calculated (14.2 %).

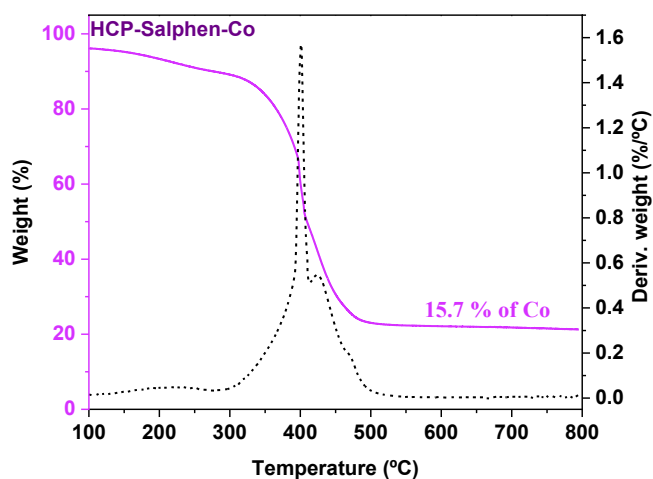


Figure 5.14. TGA of HCP-Salphen-Co.

The XPS survey spectrum shows the incorporation of cobalt to the network (Figure 5.15). This spectrum also confirmed the presence of C, N, and O elements in the structures. The C 1s XPS traces showed a dominant peak at 285.8 eV, attributed to C-C bonds (Figure A.25). The binding energies of O 1s for all the complexes of salphen 534.0 eV^[42] The presence of an intense peak at 402 eV in the N 1s XPS traces corresponds to the nitrogen coordinated with the metal.^[43, 44] The first peak at 783.85 eV is assigned to Co 2p_{3/2} and is attributed to the Co-N bond whereas the peak, at 799.51 eV is ascribed to Co 2p_{1/2}.^[45, 46]

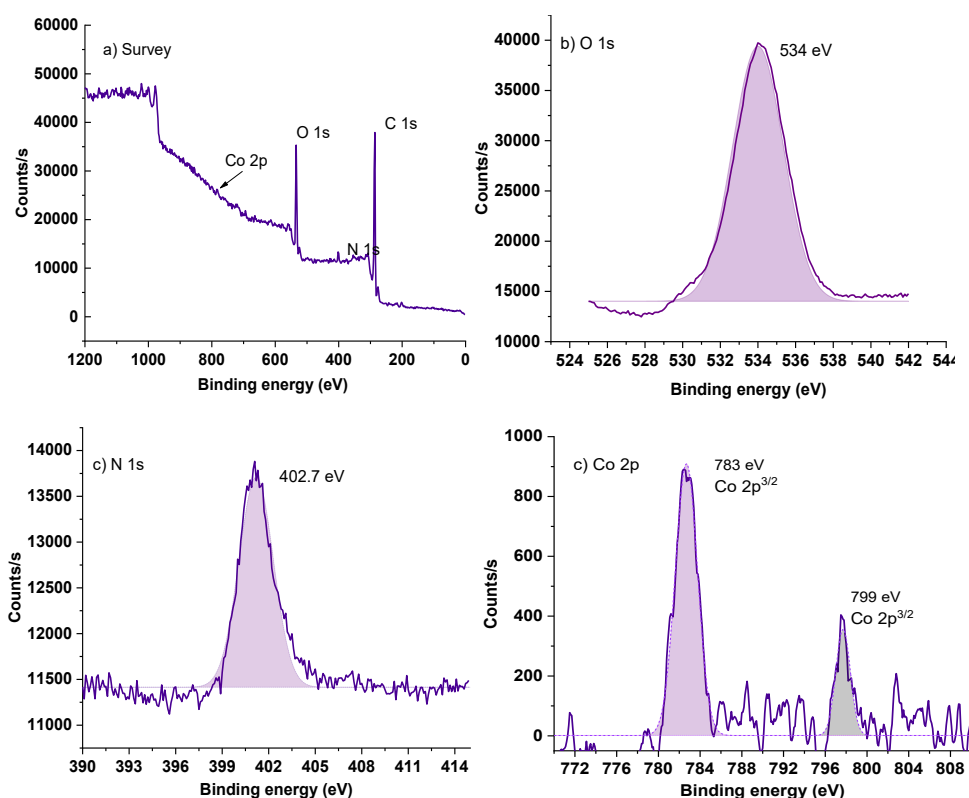


Figure 5.15 XPS a) Survey b) O 1s, c) N 1s and d) Co 2p traces of HCP-Salphen-Co.

The porous properties were evaluated by N₂ adsorption-desorption isotherms (Figure 5.16, left). HCP-Salphen-Co exhibited some N₂ uptake at low

pressure, which is attributed to the presence of micropores. The N_2 adsorption increased when the pressure was increased as is ascribed to porous materials showing a specific surface area of $99.1 \text{ m}^2/\text{g}$. In fact, the relatively low BET surface area might result from the incorporation of Co species. CO_2 uptake was measured using CO_2 adsorption isotherm (Figure 5.16, right), which indicated a value of CO_2 uptake of 1.32 mmol/g and a Langmuir surface area of $724.6 \text{ m}^2/\text{g}$. This is considered high compared to other previously reported HCPs, as the incorporation of cobalt into these crosslinked polymers enhances their CO_2 adsorption capacity. This improvement is attributed to the strong affinity between the active cobalt sites and the carbon dioxide molecules. [47, 48]

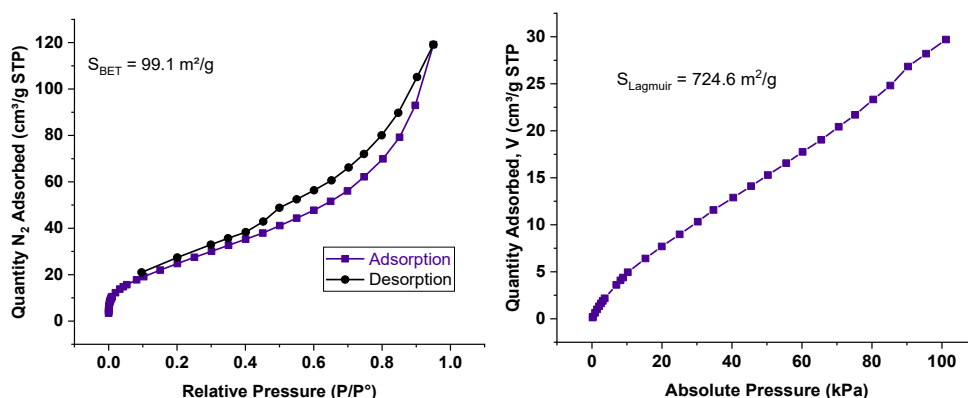


Figure 5.16 left N_2 adsorption/desorption, right CO_2 uptake of HCP-Salphen-Co.

The powder X-ray diffraction of HCP-salphen-Co (Figure 5.17) showed an amorphous nature for this catalyst, which is attributed to the absence of regularly stacked structures along the polymer network.

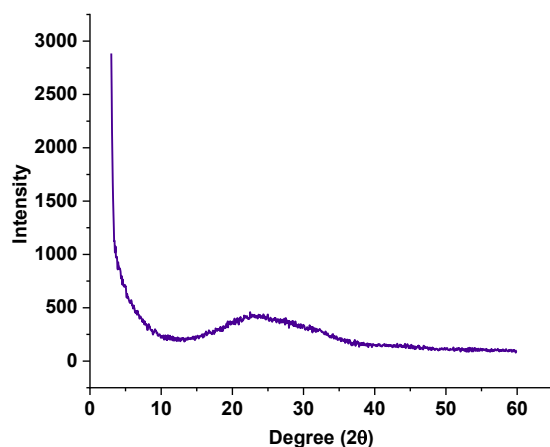


Figure 5.17 Powder X-ray diffraction of HCP-salphen-Co.

SEM images (Figure 5.18) demonstrated that the polymers consist of aggregates of particles with irregular shapes on a micrometer scale. Similarly, TEM images (Figure 5.19) revealed a significant degree of disorder, with certain areas displaying some microporosity in a comparably disordered fashion.

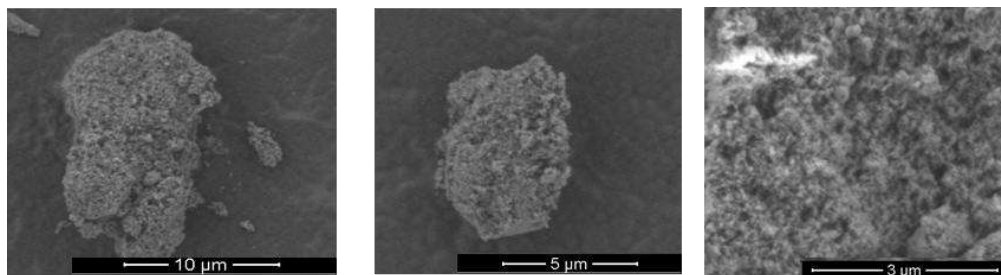


Figure 5.18. SEM images.

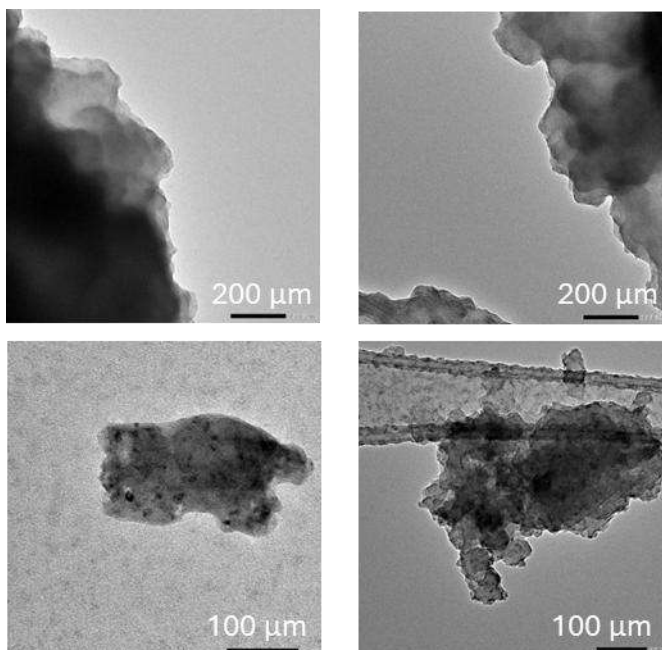


Figure 5.19 TEM images.

Once the catalyst was prepared and characterized, it was used to obtain the target molecule FDME following a procedure which involves a carboxylation reaction on the MF, in which the synthesized catalyst will be used followed by esterification, without the need to isolate the reaction intermediate. (Figure 5.20).

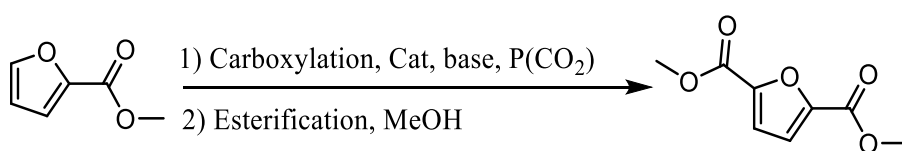


Figure 5.20 synthesis of FDME from MF.

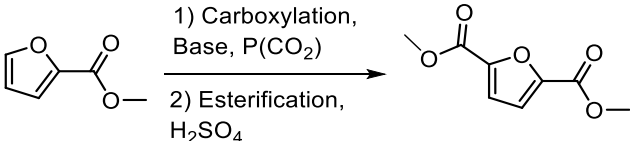
The esterification is a known reaction that was carried out in the same way in all cases, H_2SO_4 was added at room temperature and the mixture was heated at $80\text{ }^\circ\text{C}$ for 24 h.

To establish the reaction conditions of the first step, cobalt acetate was initially used as a catalyst (entries 1–5, Table 5.3). The ratio between 2-methyl furoate (MF) and cesium carbonate was 1:1, the temperature was fixed at 200 °C and the CO₂ pressure at 45 bar because they were conditions reported to promote C–H carboxylations.^[49]

The reactions were done at different reaction times, obtaining CO₂ with low yields (entries 1 and 2). However, when the time was fixed to 5 hours and the reaction was carried out at lower pressure, 20 and 10 bars, achieving FDME with a yield of 16 and 22% (entries 3 and 4). The increase in the amount of catalyst was negative since very low yields were obtained again (entries 5 and 6). Despite the low yields of the reaction, it should be mentioned that no other by-products were detected, so the selectivity towards the desired product was 100%. No traces of MF were observed either, which has made us think that during this step undetectable degradation compounds are being formed, as it was previously observed by Banerjee et al. in the carboxylation of 2-furanoic acid.^[49] Thus, keeping the reaction conditions of entry 4, HCP Salphen-Co was used as a catalyst obtaining FDME with a lower yield, of 12% (entry 7). To increase this yield, the reaction time, CO₂ pressure, temperature and addition of other base were investigated (entries 7–14). Extending the reaction time to 5 hours increased the conversion to 18% (entry 8). However, reducing the pressure to 8 bar resulted in lower yields (entry 9) confirming that the optimal pressure is 10 bar. Increasing the temperature also did not improve the results (entry 10), establishing the optimal temperature as 200 °C. Subsequently, the reaction time was extended to 6 and 7 hours. (entry 11 and 12). The best yield achieved was 30%, using a ratio 1:1 between 2-methyl furoate (MF) and cesium carbonate, 200 °C, 10 bars of CO₂ pressure and 6 hours of reaction (entry 11). Then alternative base mixtures were tested with no improvement in the results either (entry 13 and 14). Scaling up the

reaction by five times the amounts of reactants and catalyst led to a 28% yield (entry 15). The experiments in the absence of catalysts (entry 16) or under ambient pressure (entry 17) did not lead to the formation of any product.

Table 5.3 Optimization of the synthesis of FDME from MF ^{a)}

						
Entry	Cat. (%Co)	Base (mmol)	T (°C)	P (bar)	t (h)	Conv. (%)
1	Co(OAc) ₂ (1)	Cs ₂ CO ₃ (1)	200	45	12	<5
2	Co(OAc) ₂ (1)	Cs ₂ CO ₃ (1)	200	45	5	<5
3	Co(OAc) ₂ (1)	Cs ₂ CO ₃ (1)	200	20	5	16
4	Co(OAc) ₂ (1)	Cs ₂ CO ₃ (1)	200	10	5	22
5	Co(OAc) ₂ (1.5)	Cs ₂ CO ₃ (1)	200	10	4	<5
6	Co(OAc) ₂ (2)	Cs ₂ CO ₃ (1)	200	10	4	<5
7	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1)	200	10	4	12
8	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1)	200	10	5	18
9	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1)	200	8	5	8
10	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1)	220	10	5	10
11	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1)	200	10	6	30
12	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1)	200	10	7	20
13	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1.5)	200	10	6	<5
14	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (0.5) / K ₂ CO ₃ (0.5)	200	10	5	<5
15 ^{b)}	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (5)	200	10	10	28
16	-	Cs ₂ CO ₃ (1)	200	10	6	0
17	HCP-Salphen-Co (1)	Cs ₂ CO ₃ (1)	200	-	6	0

^{a)} 2-Methyl Furoate, MF, (1mmol), catalyst (0.18mmol). ^{b)} MF(5mmol), catalyst (0.9mmol)

To confirm the heterogeneity of the catalyst, the procedure was repeated six consecutive times (Figure 5.21). After each reaction, the HCP-Salphen-Co catalyst was recovered, washed with methanol, and dried under vacuum at 100 °C for 30 minutes before reuse. While performance decreased slightly in the initial cycles, it recovered in subsequent cycles, reaching a 32% FDME yield in the final run.

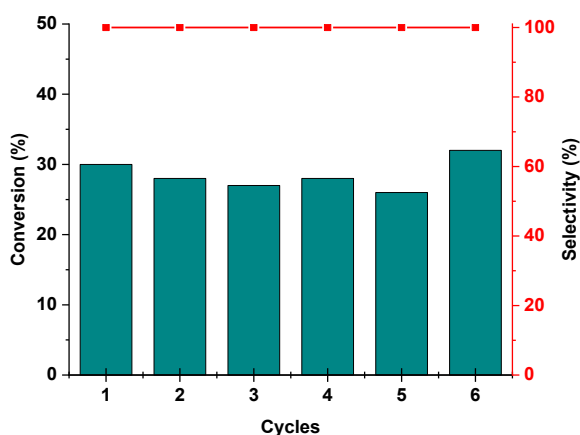


Figure 5.21 Recycling experiments of HCP-Salphen-Co in the synthesis of FDME from MF and CO₂.

FTIR and TGA analyses (Figure 5.22) confirmed the stability of the catalyst structure after six cycles. The FTIR spectra showed that the characteristic bands of the catalyst remained unchanged, while the TGA analysis revealed a similar thermal stability, but the amount of metal (Co) obtained from the TGA residue was 9%, decreasing from the 16,52% of the fresh one, indicating that there was no metal leaching during the reactions may be due to the reaction conditions.

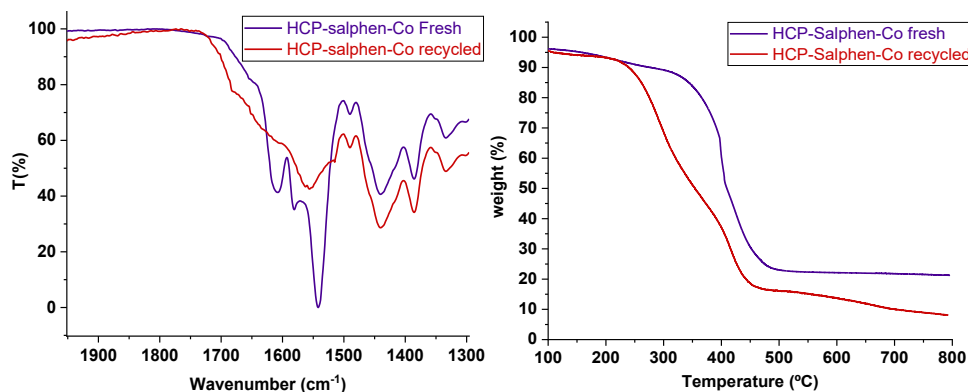


Figure 5.22 left FTIR and right TGA of recycled HCP-Salphen-Co.

5.3.2.1 Mechanism proposal

Based on previously reported mechanisms for metal-catalyzed carboxylation of sp^2 C–H bonds, a proposed mechanism for this reaction is outlined ^[50, 51] (Figure 5.23). The base, cesium carbonate, deprotonates the C–H bond at carbon 5 of 2-methyl furoate (**1**), enabling coordination with the catalyst. Subsequently, CO_2 inserts into the carbon–metal bond to form intermediate (**2**). After the reaction concludes, methanol is added to remove the catalyst. Following this step, a few drops of sulfuric acid are introduced, leading to the formation of cesium sulfate and furan-2,5-dicarboxylic acid (FDCA) (**3**). The cesium sulfate is removed by filtration, and FDCA is further heated with methanol to produce FDME (**4**).

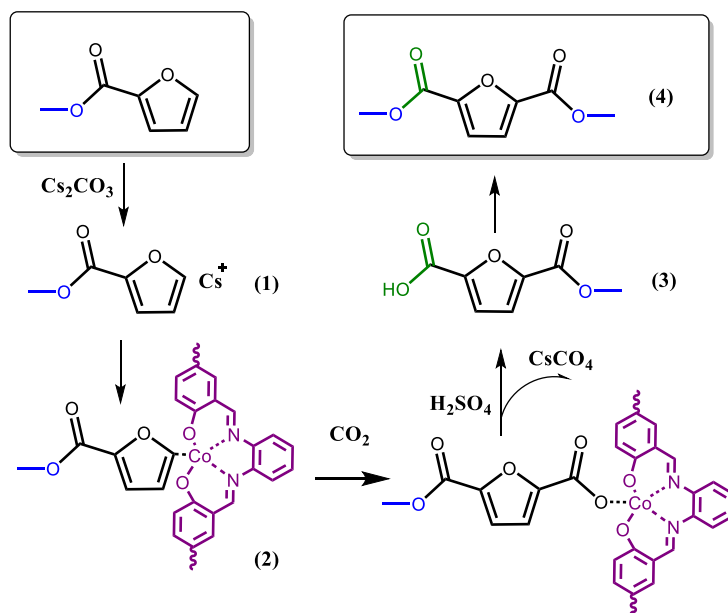


Figure 5.23 Proposed mechanism for the conversion of 2-methyl furoate into furfural dimethyl ester.

5.4 Conclusions

A new strategy has been described to prepare 2,5-furan dicarboxylic methyl ester (FDME) using CO₂ and Furfural as feedstocks following a three-steps process which involves an oxidative esterification, a carboxylation and a convectional acid esterification reaction.

The oxidative esterification of furfural to 2-methyl-furoate (MF) was done using 1-benzyl-3-methylimidazolium chloride (BzmimCl) or a hypercrosslinked ionic polymer prepared from it (HCP-BzmimCl) and the bases were Cs₂CO₃ or 1, 8-diazabicyclo [5.4.0] under- 7-ene (DBU). All catalytic systems worked in the presence of O₂ as the sole oxidizing agent, at 60°C with 24 h reaction times. The homogeneous catalytic systems produced MF with a yield of more than 92% and furfural conversions between 82% and 100%, improving the catalytic activity of other similar systems. The heterogeneous catalyst (HCP-BzmimCl) produced MF with a selectivity of 100% and almost complete furfural conversion. HCP-BzmimCl combined with strong bases becomes the first example of a heterogeneous ionic catalyst for this reaction, offering high yields of MF, although it showed better recyclability when Cs₂CO₃ was used as a base.

The carboxylation reaction was done using HCP-Salphen-Co catalyst prepared by mechanochemical polymerization, a more sustainable synthesis than the conventional one since it is faster (55 min vs. 24-72 h) and is solvent-free polymerization. The reaction was carried out at lower CO₂ pressures (10 bar) than other reported carboxylation (above 30 bars), at 200°C and in 6 hours. Despite the low yields of the carboxylation reaction (30%), it should be mentioned that no other by-products were detected, so the selectivity towards the desired product was 100%. The final acid esterification was quantitatively done under conventional conditions (H₂SO₄, MeOH and reflux for 24 h).

5.5 Experimental section

Oxygen (99.9% of purity) was supplied by air liquide; Furfural (99.0%), and Cesium carbonate (Cs_2CO_3 , 99.5%), were purchased from Acros Organics; 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 98.0%) was supplied by Sigma-Aldrich, Furfural (99.0%); anhydrous Aluminum chloride (AlCl_3 , 99.9%), 1-Butyl-3-methylimidazolium tetrafluoroborate (BmimBF_4) (98%) was purchased from Across Organics. Dimethoxymethane (98%) was supplied by Alfa Aesar; Cobalt (II) acetate tetrahydrate (98%) was supplied by Gute Chemie ABCR.

5.5.1 Synthesis of 2-methyl furoate from furfural

5.5.1.1 General procedure using Cs_2CO_3 as base

A mixture of furfural (1.0 mmol), an ionic-based catalyst (1.0 mmol), Cs_2CO_3 (0.5 mmol), and MeOH (2 mL) were placed into a glass reactor. The reactor was sealed, evacuated, filled with O_2 three times, and then pressurized with 5.0 bar of O_2 before being heated to 50°C . After 24 hours, the reactor was cooled to room temperature, depressurized, and opened. CH_2Cl_2 (10 mL) was added, and the mixture was washed twice with water (2×10 mL) and once with a saturated NaCl aqueous solution (1×10 mL). The organic phase was dried using anhydrous MgSO_4 , and the solvent was evaporated under reduced pressure to obtain MF as a yellow oil.

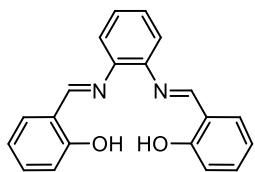
5.5.1.2 General procedure using DBU as base

Furfural (1.0mmol), ionic-based catalyst (0.4mmol), DBU (1.2mmol) and MeOH (2mL) were placed into a glass reactor. The reactor was sealed, evacuated, backfilled with O_2 three times and finally charged with 5.0 bar of O_2 and heated at 60°C . After 4h, the reactor was cooled to room temperature, depressurized and opened. CH_2Cl_2 (10mL) was added, and the resulting mixture was treated as in the previous case, obtaining MF as a yellow oil.

5.5.2 Recycling experiment

After each reaction is complete, the polymer HCP-BzmimCl was separated from the reaction media by filtration. In the case of using Cs_2CO_3 as a base, the catalyst was washed with CH_2Cl_2 and dried in an oven at 100°C for 12h. When DBU was used as a base, the catalyst was washed with diluted HCl, water, and methanol and dried in an oven at 100°C for 12h. After that, it was used in a fresh reaction.

5.5.3 Synthesis of N,N'-Bis(salicylidene)-1,2-phenylenediamine (Salphen).

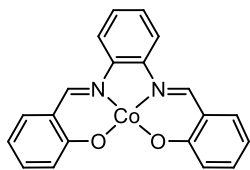


Salphen was prepared by reaction between salicylic aldehyde (4g, 32.8mmol) and *o*-phenylenediamine (1.7g, 16.4 mmol) were dissolved in 50 mL of methanol. The mixture was refluxed and heated at 70 °C for 3 h. After evaporating the solvent, crystallization was induced by adding petroleum ether. Afterward, the crystals obtained were filtered on a Buchner, yielding salphen as an orange solid. (5g, 16mmol, 95%)

^1H NMR (300 MHz, DMSO- d_6) δ 13.09 (d, 2H), 8.65 (s, 2H), 7.46 – 7.33 (m, 6H), 7.25 (m, 2H), 7.07 (m, 2H), 6.94 (m, 2H).

Elemental analysis, ($\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$) calculated: C, 75.93; H, 5.10; N, 8.86 Found: C, 77.25; H, 5.19; N, 7.84.

5.5.4 Synthesis of N,N'-Bis(salicylidene)-1,2-phenylenediamine cobalt complex (Salphen-Co).



Salphen (2.00 g, 6.32 mmol) dissolved in toluene (30 mL) was heated at 100 °C, 1h. After, a solution of 1 equiv of $\text{Co}(\text{OAc})_2(\text{H}_2\text{O})_4$ (1.57 g, 6.32 mmol) in ethanol (50 mL) was added. The mixture was heated at 100 °C for 15 min, and then the resulting solution was kept at 0 °C in an ice bath, affording a precipitate, which was collected and washed with ethanol to give Salphen-Co (2.22g, 5.94 mmol, 94%).

^1H NMR (300 MHz, DMSO- d_6) δ 9.02 (s, 2H), 7.91 (m, 2H), 7.47 – 7.34 (m, 4H), 7.25 (m, 2H), 6.72 (m, 2H), 6.52 (m, 2H). (Figure 5.11 ^1H NMR of salphen-Co (300 MHz, CDCl_3)

Elemental analysis, ($C_{20}H_{14}CoN_2O_2$) calculated: C, 64.35; H, 3.78; N, 7.5.

Found: C, 59.2; H, 4.47; N, 4.85.

5.5.5 Synthesis of HCP-Salphen-Co

The salphen-Co monomer (470 mg, 1.26 mmol) and aluminium (III) chloride (1 g, 6.1 mmol) was added to a zirconia vessel containing three zirconia balls. Then, dimethoxymethane (0.56 mL, 6.1 mmol) was added to this mixture and was ball-milled at 600 rpm for 55 min. Then, MeOH was added to the zirconia vessel and the product was filtered out. The solid was thoroughly washed with methanol, acetone, and water. Finally, the solid was purified by Soxhlet extraction with MeOH for 24 h and then, it was dried under vacuum at 100 °C for another 24 h. The hypercrosslinked polymer was obtained as a red powder (HCP-Salphen-Co) 435 mg (93% yield).

5.5.6 Synthesis of FDME from 2-methyl furoate and CO₂

2-methyl furoate MF (630 mg, 5 mmol) was introduced in a high-pressure autoclave engineers' reactor with HCP-Salphen-Co (750 mg, 1%Co) and Cs₂CO₃ (1.630 g, 5mmol) and 10 bar of CO₂. This mixture was heated at 200 °C for 6-8 h. After this time the reactor was opened and 50 mL MeOH was added, and HCP Salen-Co was removed by filtration. Then, H₂SO₄ was added at room temperature until cesium sulfate precipitated (pH = 7) (1.540 g), which was also separated by filtration. The mixture was heated at 80 °C for 24 h and then, by adding water, FDME was obtained as a beige solid with moderate yield (246 mg, 30%). The reactions were followed by TLC and proton nuclear magnetic resonance (¹H NMR).

Chapter 3

5.5.7 Recycling experiment

After each reaction is complete, the polymer HCP-Salphen-Co was separated from the reaction media by filtration. The catalyst was washed with CH_2Cl_2 , water and methanol dried in an oven at 100°C for 12h.

5.6 References

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Conclusions

This Doctoral Thesis has demonstrated that heterogeneous catalysts based on functionalized hyper-crosslinked polymers (HCPs) can be tailor-made to catalyze the desired transformations. Specifically, in this thesis, catalysts based on HCPs have been designed to carry out specific CO₂ conversions. All of them exhibited good catalytic performance in the corresponding reactions including their recoverability and reusability.

Chapter 1:

Hyper-crosslinked polymers based on imidazolium chloride (HCP-BzmimCl and HCP-*Bis*(BzmimCl), obtained directly from imidazolium chloride monomers, were found to be excellent heterogeneous catalysts for the synthesis of formamides from amines and CO₂, using phenylsilane (PhSiH₃) as reducing agent and DMF as key polar additive. This combination allows the activation of N-H and Si-H bonds, resulting in conversions in shorter reaction times than previously reported with other ionic liquid-based catalysts. The materials showed high recyclability, with HCP-BzmimCl retaining its activity for up to five cycles and HCP-*Bis*(BzmimCl) for up to ten cycles due to the stability of its imidazolium chloride groups.

Chapter 2:

The treatment with Ag₂O and CuI of the hyper-crosslinked polymers based on imidazolium chloride synthesized in Chapter 1, allowed to obtain four N-heterocyclic carbene complexes (two with silver and two with copper), which were used as heterogeneous catalysts for CO₂ fixation reactions in the synthesis of cyclic carbamates (2-oxazolidinones) and asymmetric carbonates. The study found that copper-based catalysts (especially HCP-*Bis*NHC-Cu) were more effective than silver-based ones for synthesizing cyclic carbamates from propargylic alcohol, CO₂, and primary amines. due to stronger π coordination

Conclusions

between Cu and propargyl alcohol as well as better CO₂ adsorption. Recycling studies confirmed their good stability and reusability, demonstrating their long-term applicability. In contrast, silver-based catalysts formed inactive nanoparticles, reducing their performance. In comparison, the synthesis of asymmetric carbonates from propargylic alcohol, CO₂, and primary alcohols was slower and less selective. A cyclic carbonate by-product formed early in the reaction, indicating a competing pathway that lowers selectivity.

Chapter 3:

A new strategy was proposed to synthesize FDME (2,5-furan dicarboxylic methyl ester) from CO₂ and furfural in three steps: oxidative esterification, carboxylation, and acid esterification.

The oxidative esterification of furfural to 2-methylfuroate (MF) was achieved with more than 92% yield using BzmimCl or its polymeric derivative HCP-BzmimCl preferably using Cs₂CO₃ as a base and O₂ as the sole oxidant. The heterogeneous system with HCP-BzmimCl achieved 100% selectivity and high furfural conversion, being the first example of a heterogeneous ion catalyst for this reaction. The carboxylation was carried out using the HCP-Salphen-Co catalyst, prepared by mechanochemical polymerization (faster and greener), at lower CO₂ pressures (10 bar). Although the yield of carboxylation was 30%, the selectivity was 100%, since no by-products were detected. Final esterification with sulfuric acid and methanol gave FDME with 100% yield.

Conclusiones

Esta Tesis Doctoral ha demostrado que los catalizadores heterogéneos basados en polímeros hiper-reticulados funcionalizados (HCPs) pueden diseñarse a medida y prepararse para catalizar las transformaciones deseadas. En particular, en esta tesis se han diseñado catalizadores basados en HCPs para llevar a cabo conversiones específicas de CO₂. Todos ellos mostraron un buen rendimiento catalítico en las reacciones correspondientes, incluyendo su recuperabilidad y reutilización.

Capítulo 1:

Los polímeros hiperreticulados basados en cloruro de imidazolio (HCP-BzmimCl y HCP-Bis(BzmimCl), obtenidos directamente a partir de monómeros de cloruro de imidazolio, resultaron ser excelentes catalizadores heterogéneos para la síntesis de formamidas a partir de aminas y CO₂, utilizando fenilsilano (PhSiH₃) como agente reductor y DMF como aditivo polar clave. Esta combinación permite la activación de los enlaces N-H y Si-H, dando lugar a conversiones en tiempos de reacción más cortos que los registrados anteriormente con otros catalizadores basados en líquidos iónicos. Los materiales mostraron una alta reciclabilidad, con el HCP-BzmimCl conservando su actividad hasta cinco ciclos y el HCP-Bis(BzmimCl) hasta diez ciclos debido a la estabilidad de sus grupos cloruro de imidazolio.

Capítulo 2:

El tratamiento con Ag₂O y CuI de los polímeros hiperreticulados basados en cloruro de imidazolio sintetizados en el Capítulo 1, permitió obtener cuatro complejos de carbeno N-heterocíclico (dos con plata y dos con cobre), que se utilizaron como catalizadores heterogéneos para reacciones de fijación de CO₂ en la síntesis de carbamatos cíclicos (2-oxazolidinonas) y carbonatos asimétricos. El estudio descubrió que los catalizadores basados en cobre (especialmente HCP-

Conclusiones

*Bis*NHC-Cu) eran más eficaces que los basados en plata para sintetizar carbamatos cíclicos a partir de alcohol propargílico, CO₂ y aminas primarias. debido a una coordinación π más fuerte entre el Cu y el alcohol propargílico, así como a una mejor adsorción de CO₂. Los estudios de reciclado confirmaron su buena estabilidad y reutilización, lo que demuestra su aplicabilidad a largo plazo. En cambio, los catalizadores basados en plata formaron nanopartículas inactivas, lo que redujo su rendimiento. En comparación, la síntesis de carbonatos asimétricos a partir de alcohol propargílico, CO₂ y alcoholes primarios fue más lenta y menos selectiva. Al principio de la reacción se formó un subproducto de carbonato cíclico, lo que indica una vía competidora que reduce la selectividad.

Capítulo 3:

Se propuso una nueva estrategia para sintetizar FDME Ácido 2,5-furano dicarboxílico (FDME) a partir de CO₂ y furfural en tres pasos: esterificación oxidativa, carboxilación y esterificación ácida.

La esterificación oxidativa de furfural (FA) a 2-metilfuroato (MF) se consiguió con más del 92% de rendimiento utilizando BzmimCl o su derivado polimérico HCP-BzmimCl preferentemente utilizando Cs₂CO₃ como base y O₂ como único oxidante. El sistema heterogéneo con HCP-BzmimCl alcanzó una selectividad del 100% y una elevada conversión de furfural, siendo el primer ejemplo de catalizador iónico heterogéneo para esta reacción. La carboxilación se llevó a cabo utilizando el catalizador HCP-Salphen-Co, preparado por polimerización mecanoquímica (más rápido y ecológico), a presiones de CO₂ más bajas (10 bar). Aunque el rendimiento de la carboxilación fue del 30%, la selectividad fue del 100%, ya que no se detectaron subproductos. La esterificación final con ácido sulfúrico y metanol dio FDME con un rendimiento del 100%.

Annexes

The materials synthesized in this work were characterized by the following instrumental techniques:

Microanalyses were made with a LECO CHNS-932 elemental analyzer (C, H, N). Residual aluminum contents were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on a Perkin Elmer OPTIMA 2100 DV.

FTIR spectra were recorded (cm^{-1}) on a PerkinElmer Spectrum Two spectrometer with a Fourier equipped with a diamond internal element.

Nuclear Magnetic Resonance spectra (^1H and ^{13}C NMR) were made in a VARIAN INOVA 300 MHz and a JEOL JNM-ECZ400R. The **solid-state ^{13}C NMR** spectra were taken in a Bruker AV-400-WB using a 4 mm triple channel probe with ZrO rotors and Kel-F plug at room temperature and 100.32 MHz. The speed of rotation is set at 10 KHz in all cases. ^{13}C NMR CP-MAS spectra were recorded using a spectral width of 35 kHz and the chemical shift refers to the CH signal of adamantane (29.5 ppm) as a secondary reference to TMS as the primary reference.

Thermogravimetric and differential thermal analyses were conducted on a with a TA Instruments Model TA-Q500 analyzer. The samples were heated from 40 to 800 °C under N_2 atmosphere with a heating rate 10 °C/min. Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 M surface and porosity analyzer. Prior to measurement, the samples were degassed for 12 h at 100 °C.

X-ray Photoelectron Spectroscopy (XPS) data were obtained with a SPECS GmbH system equipped with a hemispherical energy analyzer PHOIBOS 150 9MCD. A non-monochromatic Mg X-ray source was used with a power of 200 W and voltage of 12 kV. Samples were placed first in the pre-chamber at room

temperature and degassed for several hours before being transferred to the analysis chamber. Pass energies of 50 and 20 eV were used for acquiring both survey and high-resolution spectra.

Specific surface area measurements and porosity analysis were performed using **N₂ (adsorption isotherms)** on a Micromeritics, ASAP 2020 MICROPORE DRY Analyzer (P/P 0.01–1.0) using the BET theory, BJH and DFT methods. Before, the samples were degassed at 110 °C for 12.

High-resolution **isotherms of CO₂** were obtained at a series of temperatures in a Micromeritics ASAP 2010 volumetric instrument, using ~150 mg of powder sample. The sample was placed in a sample holder that was immersed into a liquid recirculating thermostatic bath (Julabo FP40-HL) able to control the adsorption temperature from 273 to 333 K. Before adsorption experiments, samples were outgassed at 423 K for 6 h under turbo-molecular high vacuum. The adsorption heat was estimated using the Clausius-Clapeyron equation from the CO₂ isotherms obtained at different temperatures.

X-ray powder diffractograms were recorded in a Bruker D8 diffractometer with a Sol-X energy dispersive detector, working at 40 kV and 30 mA and employing CuK α ($\lambda = 1.5418 \text{ \AA}$) filtered radiation. The diffractograms were registered with a step size of 0.02 and exposure time of 0.5 s per step and a 2θ range of 2.5-30. EPR spectra were recorded at 100k on a Bruker EMX-12 instrument operating in X band at 9.5GHz, modulation amplitude of 1G and modulation frequency of 100KHz.

Scanning electron microscopy micrographs were obtained with a Hitachi SU-8000 microscope operating at 0.5 kV. The samples were prepared directly by dispersing the powder onto a double-sided adhesive surface.

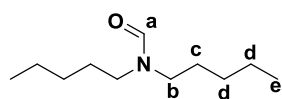
Transmission electron microscopy micrographs were recorded with a JEM2100F electron microscope (JEOL Ltd., Tokyo, Japan) operating at 200 keV.

Acquisition of **chromatograms (GC-MS)** was done using KONIK HRGC 4000B with KAP-120212 capillary column (30 nm, 0.25 mm, 0.25 μ m)

Chapter 1

Synthesis of the formamides obtained in the catalysis reactions

N,N-dipentylformamide: ^1H NMR (300 MHz, CDCl_3) δ 7.96 (s, 1H, H_a), 3.23 – 3.09



(m, 4H, H_b), 1.51 – 1.41 (m, 4H, H_c), 1.30 – 1.16 (m, 8H, H_d), 0.84 (td, 6H, H_e);

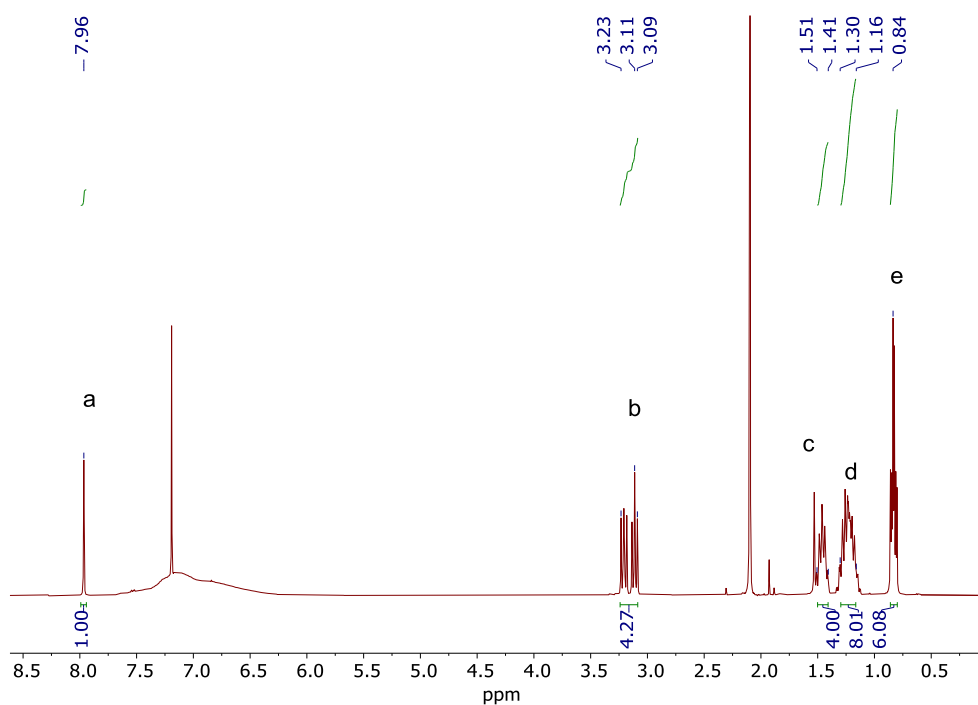


Figure A.1 ^1H NMR of N,N-dipentylformamide

N-methyl-N-phenylformamide ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.32 (m, 2H), 6.87 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.76 – 6.73 (m, 2H), 3.72 (s, 1H), 2.93 (s, 3H).

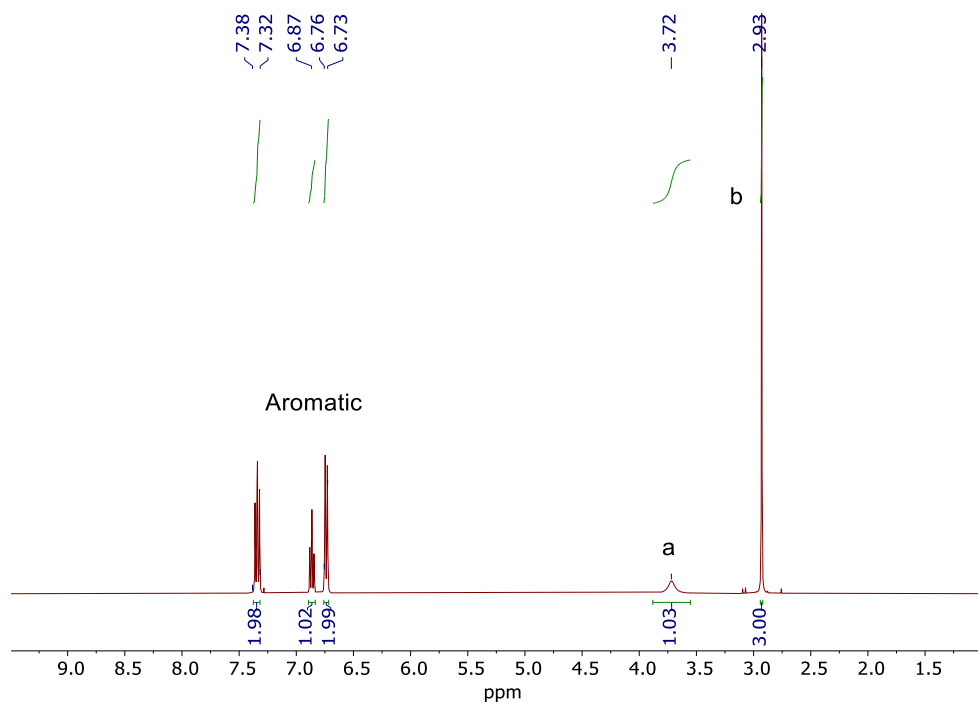
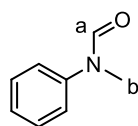


Figure A.2 ^1H NMR of N-methyl-N-phenylformamide

Piperidine-1-carbaldehyde: ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H, H_a), 3.42

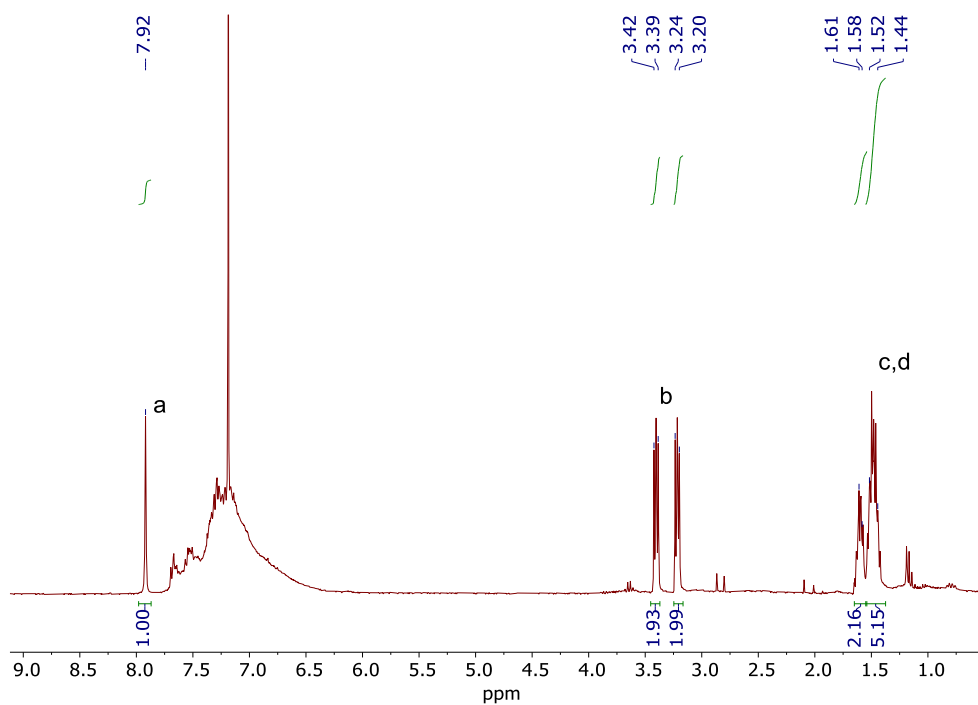
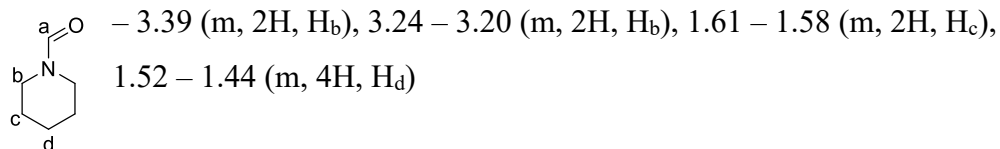


Figure A.3 ^1H NMR of Piperidine-1-carbaldehyde:

Morpholine-4-carbaldehyde: ^1H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1H, H_a),

3.59 – 3.27 (m, 8H, $\text{H}_{b,c}$),

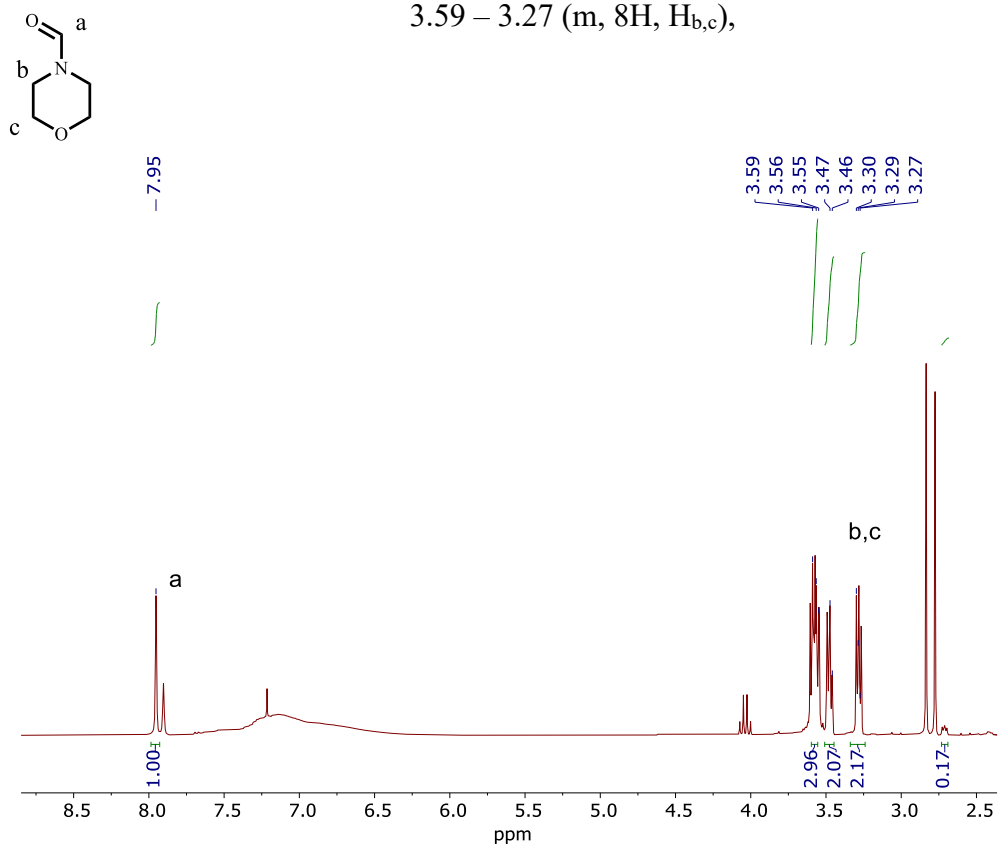


Figure A.4 ^1H NMR of Morpholine-4-carbaldehyde.

N,N-Bis(1-phenylethyl)formamide: ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H, H_a), 7.43 – 7.22 (m, 10H), 5.72 (d, 1H, H_b), 4.52 (d, 1H, H_b), 1.75 – 1.69 (m, 6H, H_c).

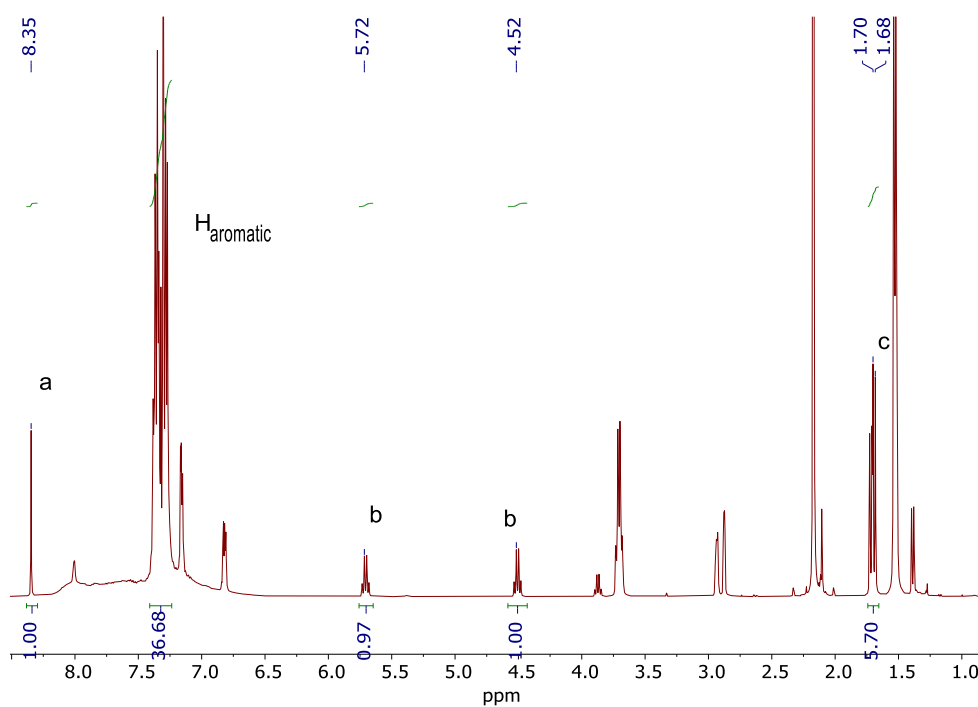
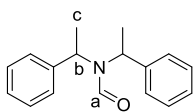


Figure A.5 ^1H NMR *N,N-Bis*(1-phenylethyl)formamide

Experiment to force Route 1

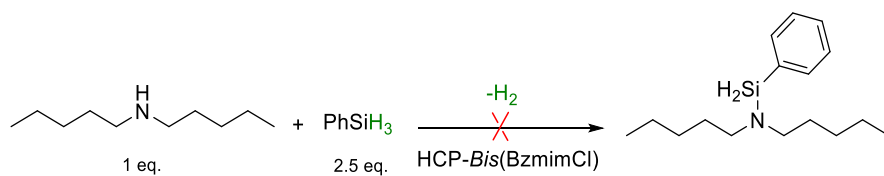


Figure A.6 Scheme to the reaction to force Route 1

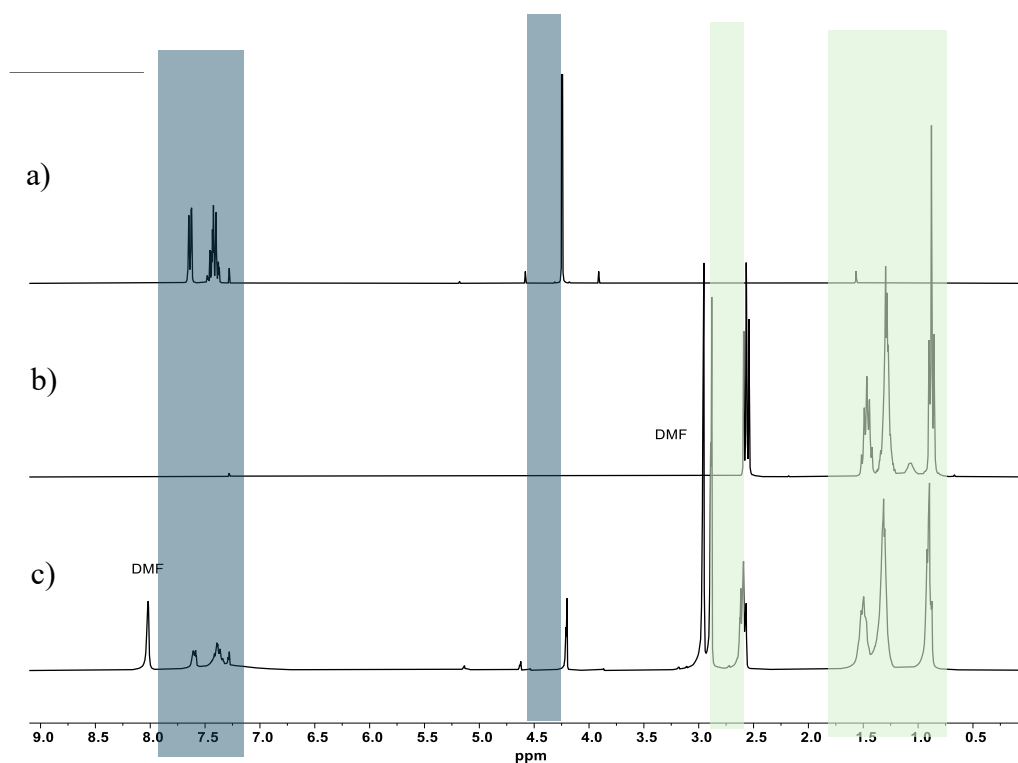


Figure A.7 ^1H NMR spectrum of a) phenyl silane, b) dipentylamina and c) reaction of between pentylamine and PhSiH_3 using HCP-Bis(BzmimCl) as catalyst .

Experiment to force Route 3

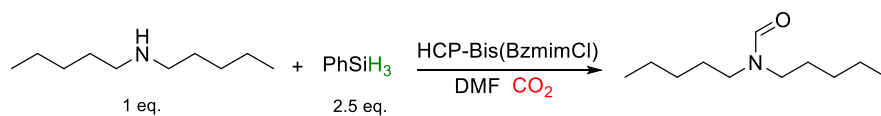
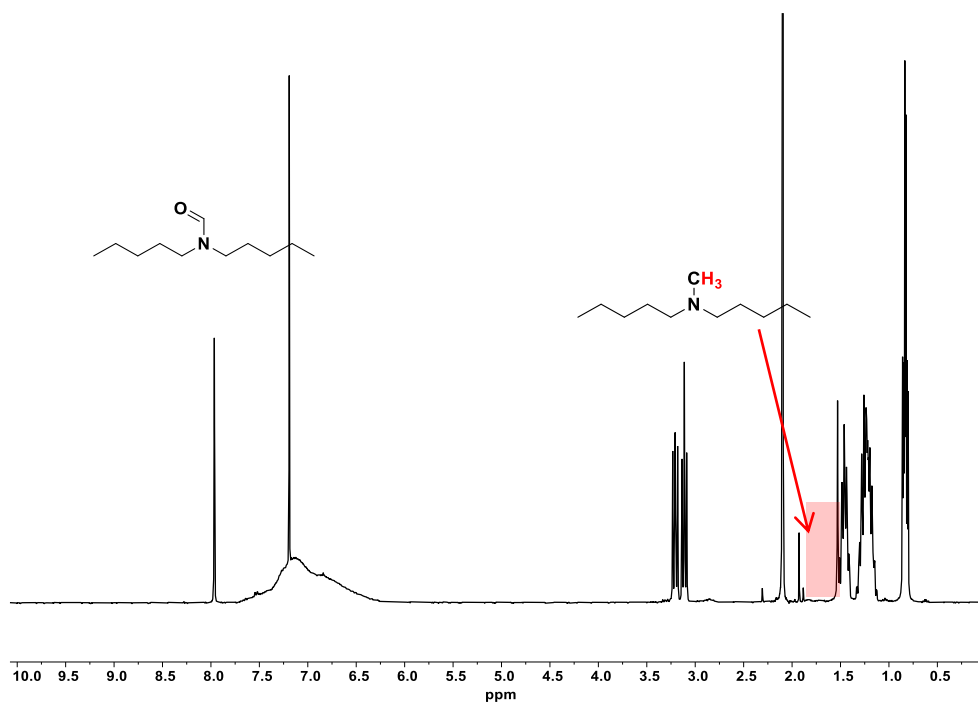


Figure A.8 Scheme to the reaction to force Route 3

Figure A.9 ^1H NMR spectrum of reaction between pentylamine, CO_2 , DMF and excess of PhSiH_3 using HCP-*Bis*(BzmimCl) as catalys

Chapter 2

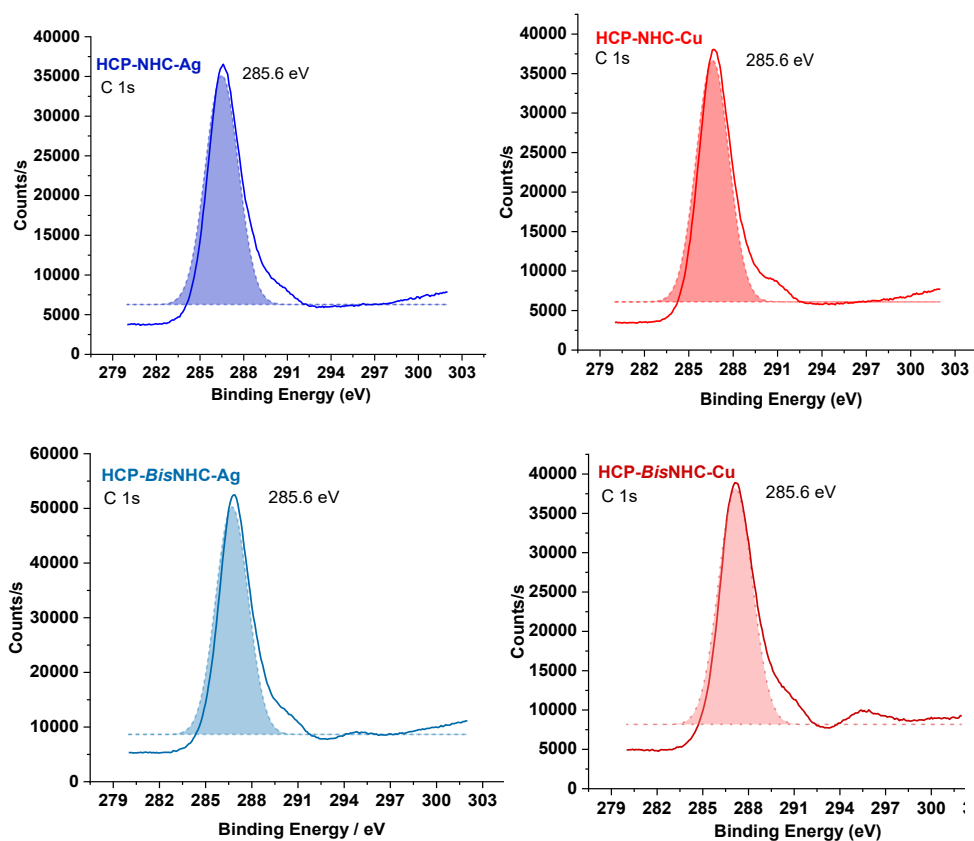


Figure A.10 C 1 s XPS spectra of the metal-HCP-NHCs catalysts

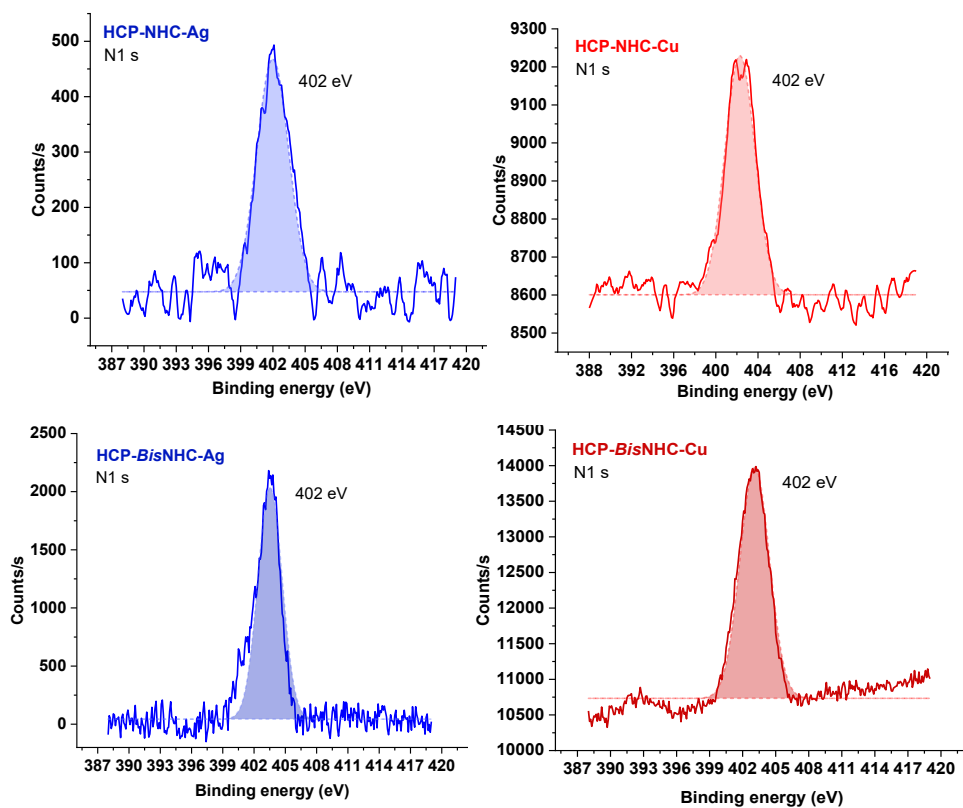


Figure A.11 N 1s XPS spectra of the metal-HCP-NHCs catalysts.

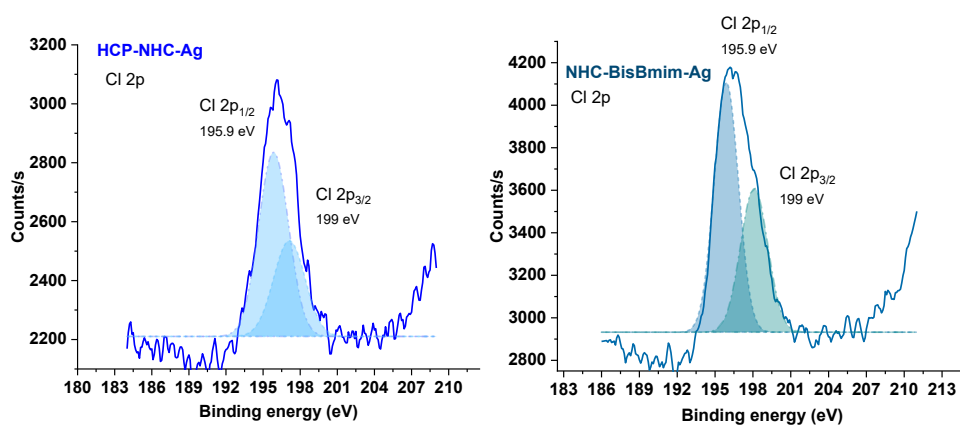


Figure A.12 Cl 2p XPS spectra of HCP-NHC-Ag and HCP-BisNHC-Ag.

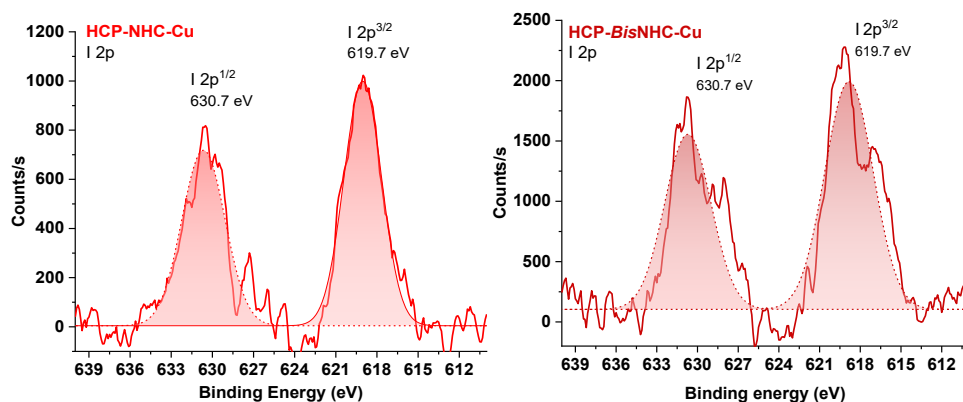


Figure A.13 I 2p XPS spectra of HCP-NHC-Cu and HCP-BisNHC-Cu.

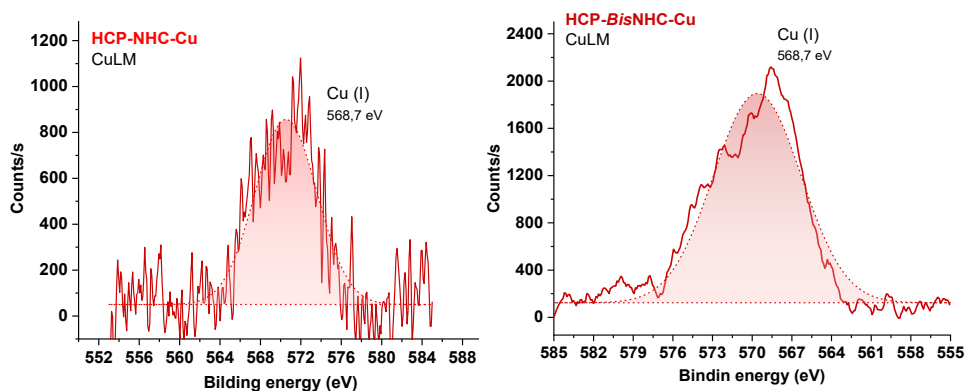


Figure A.14 CuLM XPS spectra of HCP-NHC-Cu and HCP-BisNHC-Cu.

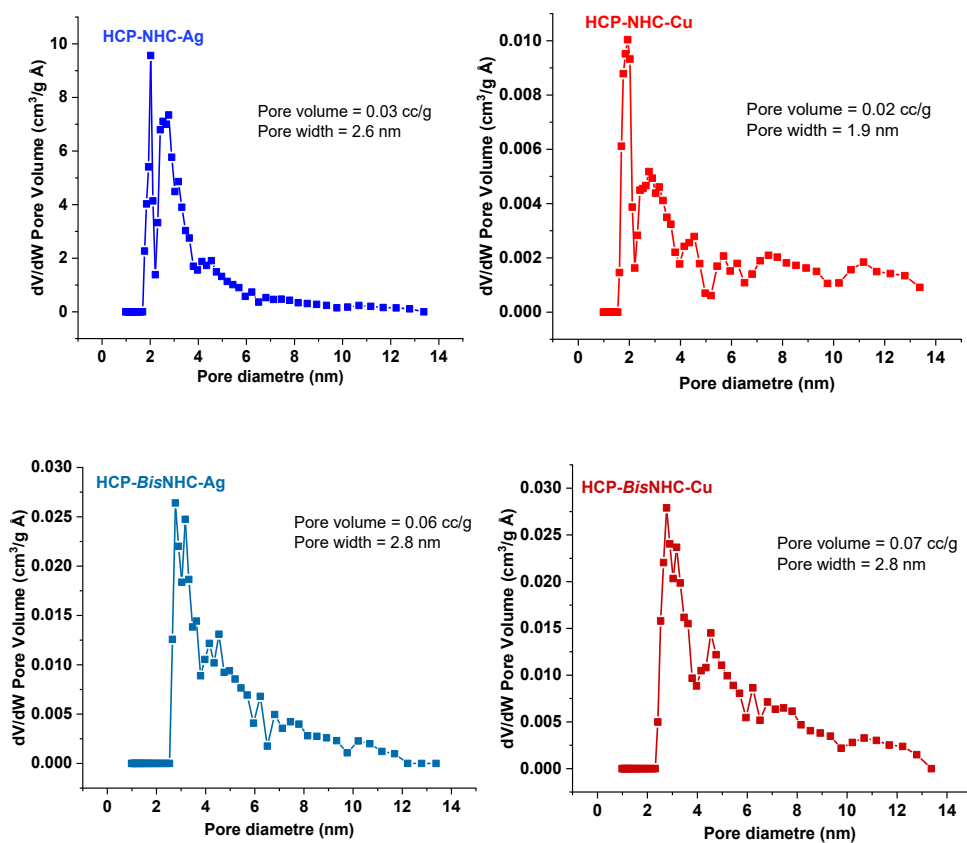
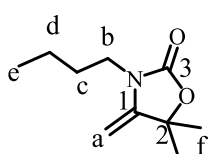


Figure A.15 Pore Size Distribution (DFT method).

3-butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one. Yield: 99% (Entry 4, Table



4.3) ^1H NMR (400 MHz, 25 °C, CDCl_3) δ 4.08 (d, 1H, Ha), 3.99 (d, 1H, Ha), 3.46 (t, 2H, Hb), 1.60 (dt, 2H, Hc), 1.57 (s, 6H, Hd), 1.36 (dq, 2H, He), 0.93 (t, 3H, Hf). ^{13}C NMR (300 MHz, 25 °C, CDCl_3) δ 155.66, 154.73(C3), 151.03 (C1), 83.46 (Ca), 81.92 (C2), 41.15 (Cb), 28.36 (Cc), 27.97 (Cf), 19.93 (Cd), 13.72 (Ce).

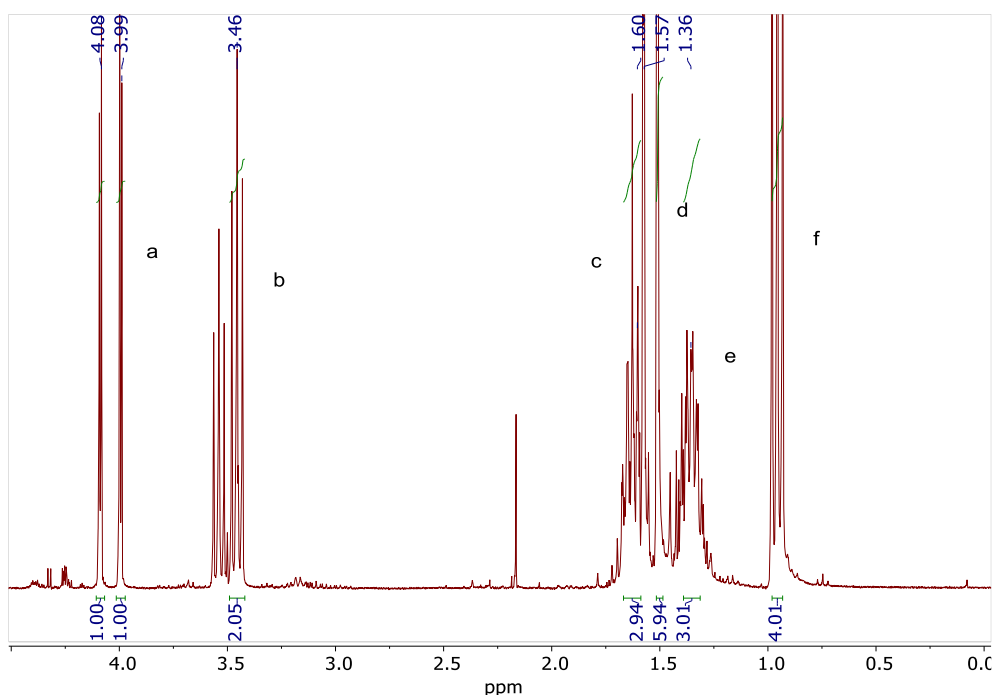


Figure A.16 ^1H NMR of 3-butyl-5,5-dimethyl-4-ethylenoxazolidin-2-one

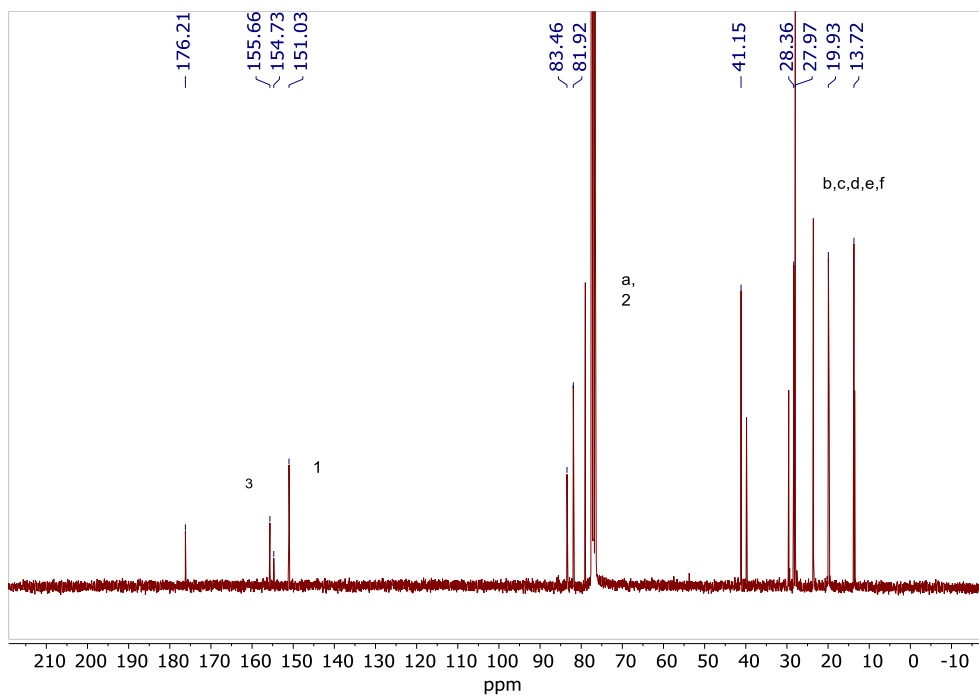
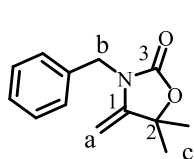


Figure A.17 ¹³C NMR of 3-butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one

3-benzyl-5,5-dimethyl-4-methyleneoxazolidin-2-one Yield: 99% (Entry 14 Table



4.3) ^1H NMR (400 MHz, 25 °C, CDCl_3) δ 7.39-7.39 (m, 5H, Ar-H), 4.67 (s, 2H, Hb), 4.03 (d, 1H, Ha), 3.98 (d, 1H, Hc), 1.56 (s, 6H, CH_3) ppm. ^{13}C NMR (300 MHz, 25 °C, CDCl_3) δ 155.89 (C3), 150.37 (C1), 134.85, 128.89, 127.08 (Ar-C), 85.48 (Ca), 82.29, 80.61 (C2), 45.21 (Cb), 27.95, 23.53. (Cc)

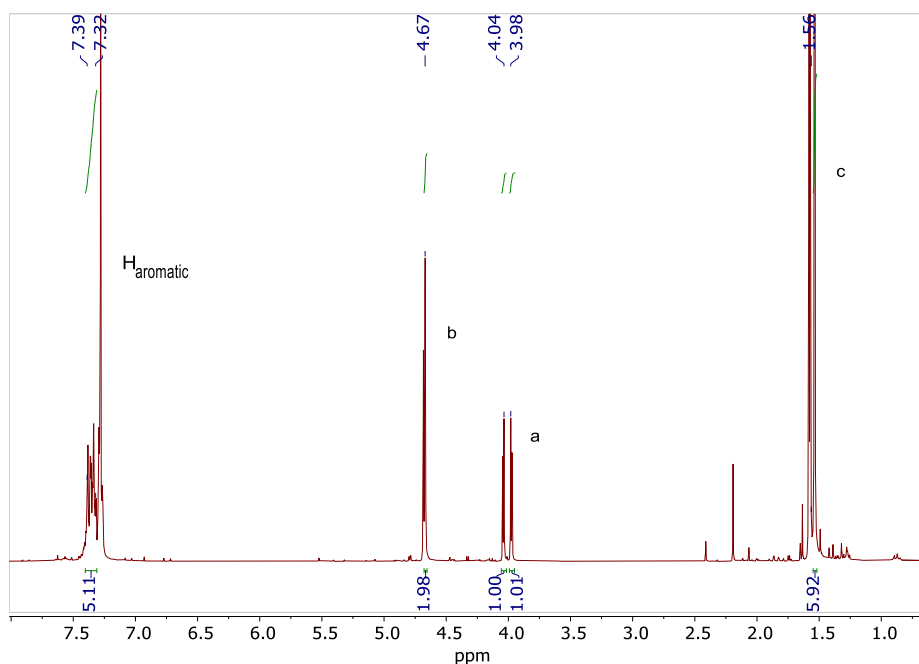


Figure A.18 ^1H NMR of 3-benzyl-5,5-dimethyl-4-methyleneoxazolidin-2-one.

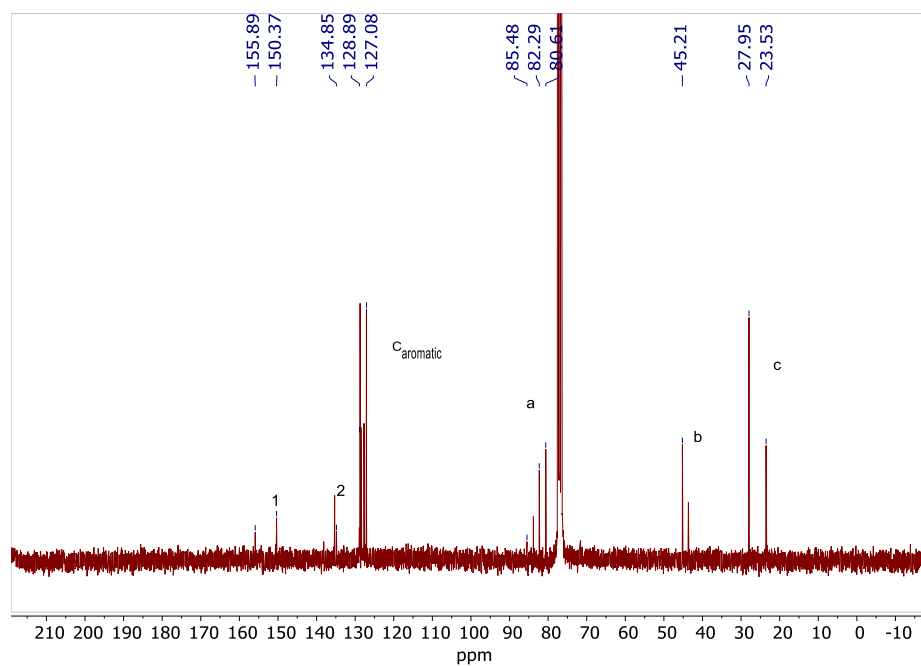
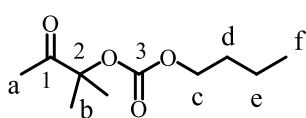


Figure A.19 ¹³C NMR of 3-benzyl-5,5-dimethyl-4-methyleneoxazolidin-2-one.

N-Butyl 2-methyl-3-oxobutan-2-yl carbonate Yield:90 % (Table 4.4). ^1H NMR



(400 MHz, 25 °C, CDCl_3): δ = 4.13 (t, 2H, Hc); 2.2 (s, 3H, Ha), 1.70 (m, 2H, Hd) 1.53 (s, 6H, Hb), 1.43-1.63 (m, 2H, He), 0.95 (t, 3H, Hf), ^{13}C NMR (300 MHz, 25

°C, CDCl_3): δ = 206.74 (C1) , 154.02 (C3), 85.38 (C2), 68.15 (Cc) ,30.62, ,(Cd) 24.20, (Cb), 18.87, (Ce), 13.74 (Cf)

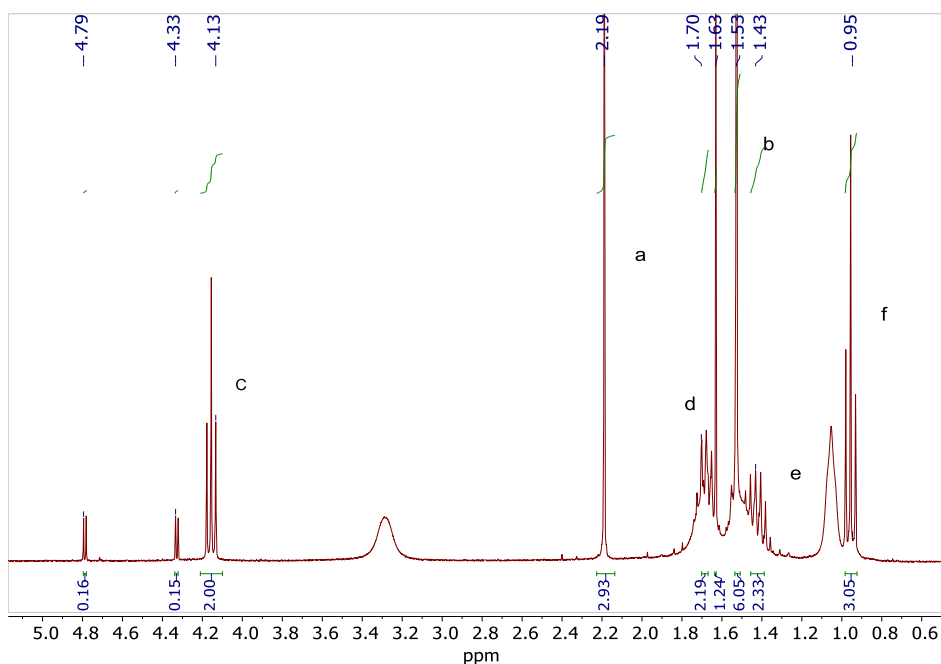


Figure A.20 ^1H NMR of n-Butyl 2-methyl-3-oxobutan-2-yl carbonate.

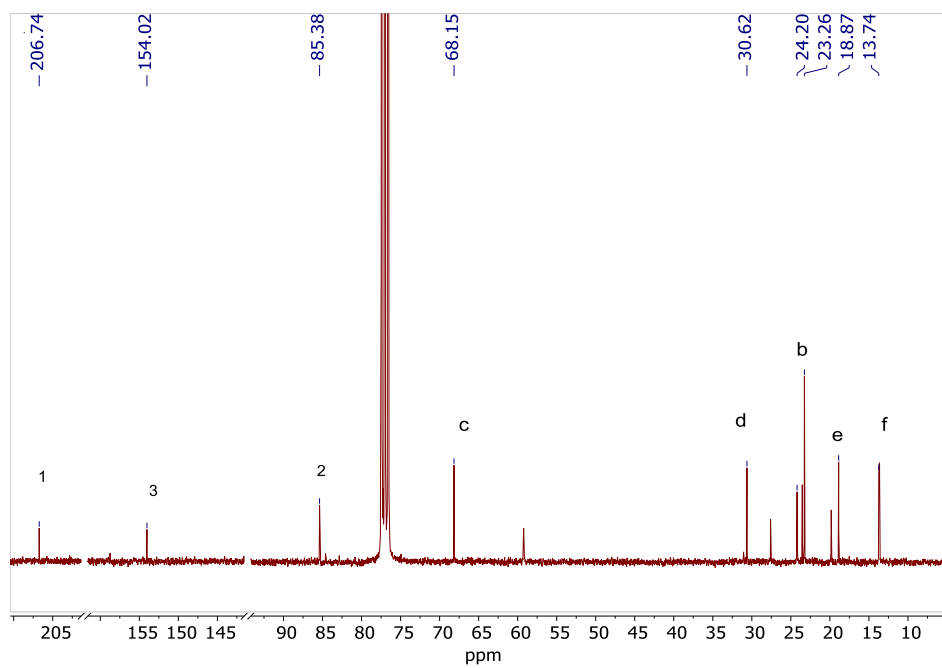
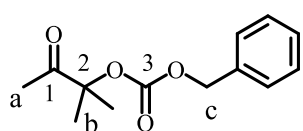


Figure A.21 ^{13}C NMR of n-Butyl 2-methyl-3-oxobutan-2-yl carbonate.

Benzyl (2-methyl-3-oxobutan-2-yl) carbonate, Yield: 95% (Table 4.4) ^1H NMR



(400 MHz, 25 °C, CDCl_3): δ = 7.39 (m, 5H, Ar-H), 5.17 (s, 2H, $-\text{OCH}_2-$), 2.14 (s, 3H, CH_3), 1.52 (s, 6H, CH_3). ^{13}C NMR (300 MHz, 25 °C, CDCl_3): δ = 206.61,

(C1) 153.84, (C3) 134.96, 128.68, 128.65, 128.38 (Ar-C) 85.80, (C2) 69.84, (Cc) 26.32, (Ca) 23.24 (Cb).

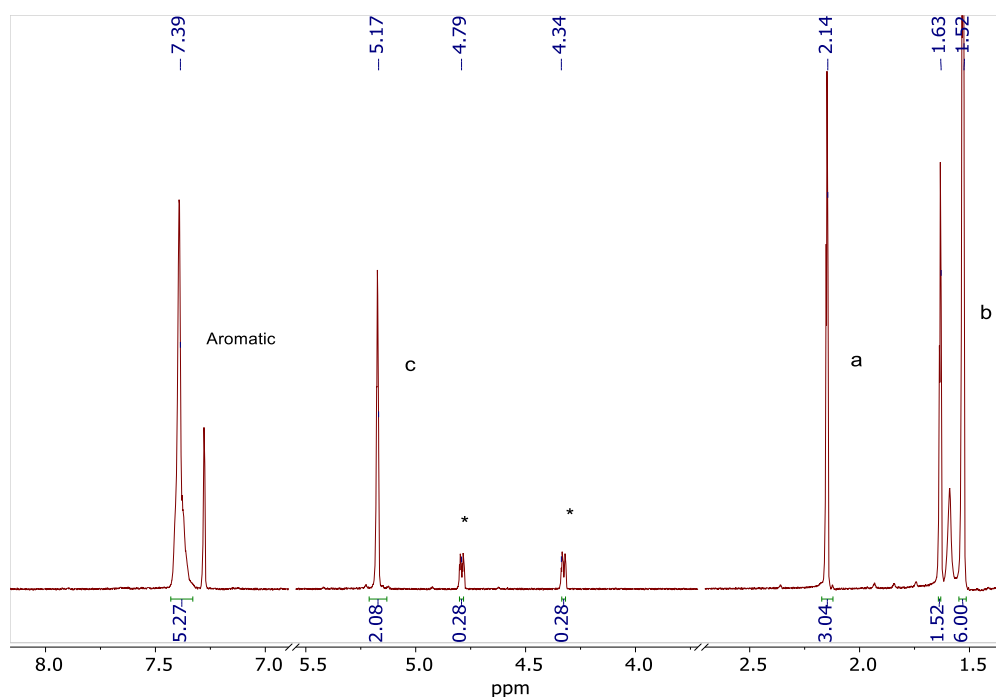


Figure A.22 ^1H NMR of benzyl (2-methyl-3-oxobutan-2-yl) carbonate.

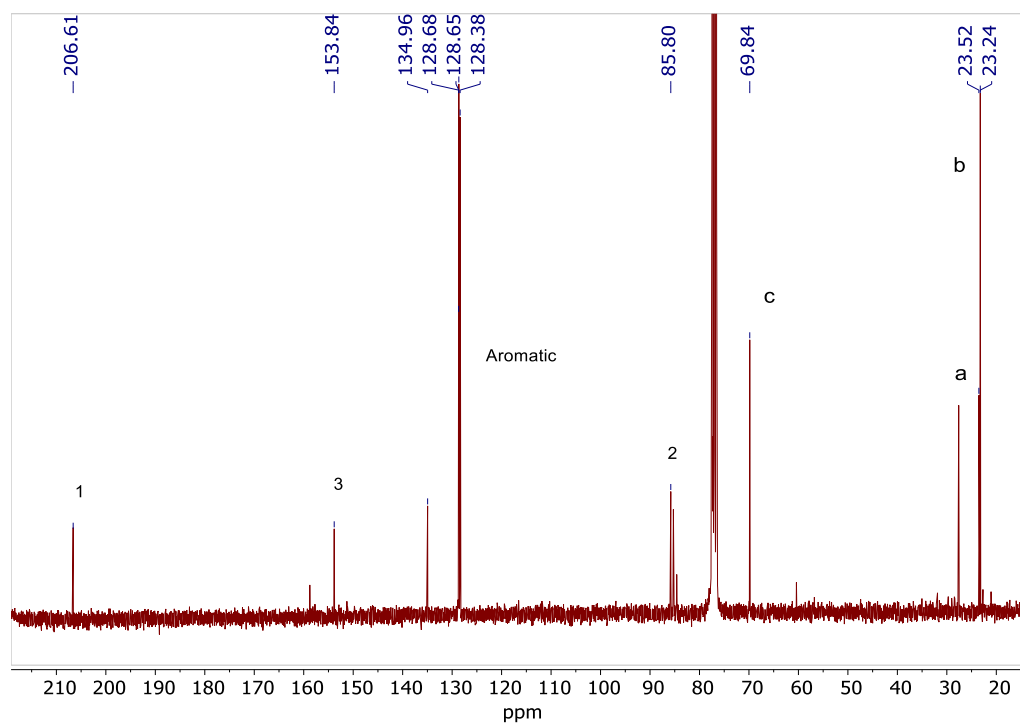
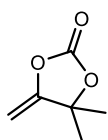


Figure A.23 ¹³C NMR of benzyl (2-methyl-3-oxobutan-2-yl) carbonate.

4,4-dimethyl-5-methylene-1,3-dioxolan-2-one ^1H NMR (400 MHz, 25 °C,



CDCl_3) δ = 4.78-4.76 (m, 1H), 4.33-4.30 (m, 1H), 1.62 (s, 6H).

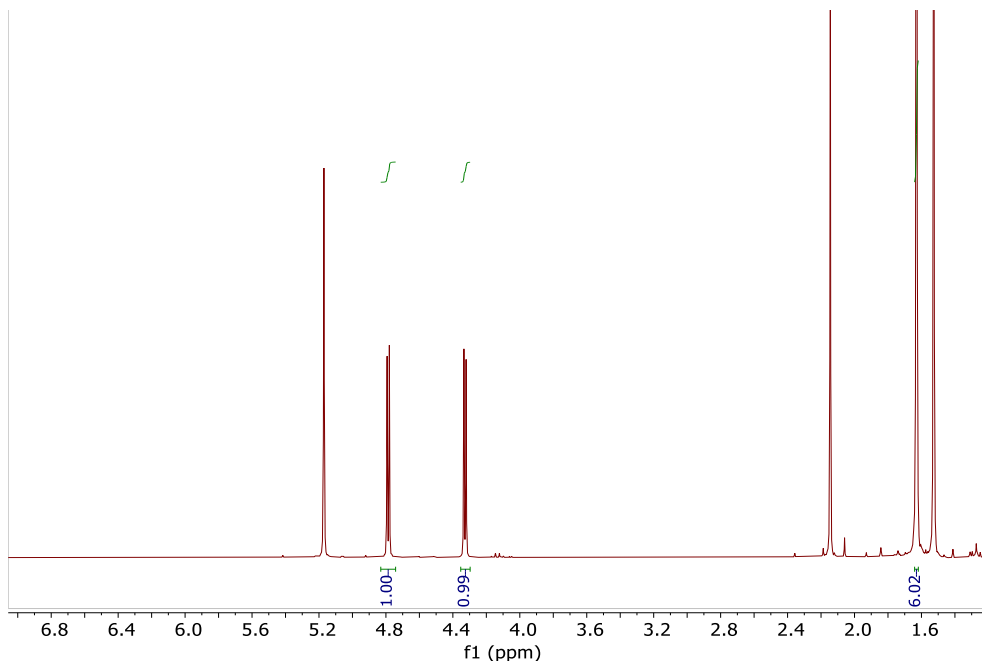


Figure A.24 ^1H NMR of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one.

The TOF (Turn over frequency) has been calculated from the following equation from the straight lines of maximum slope.

$$TOF (h^{-1}) = \frac{\Delta Conv(\%) * (mol\ substrate)}{\Delta time(h) * (mol\ cat)}$$

Chapter 3

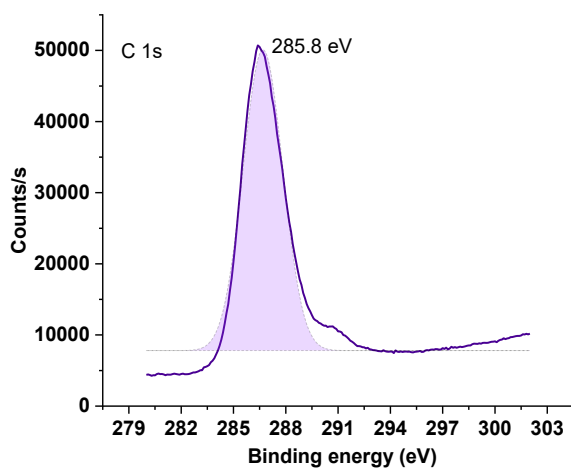


Figure A.25 C 1 s XPS spectrum of HCP-Salphen-Co.

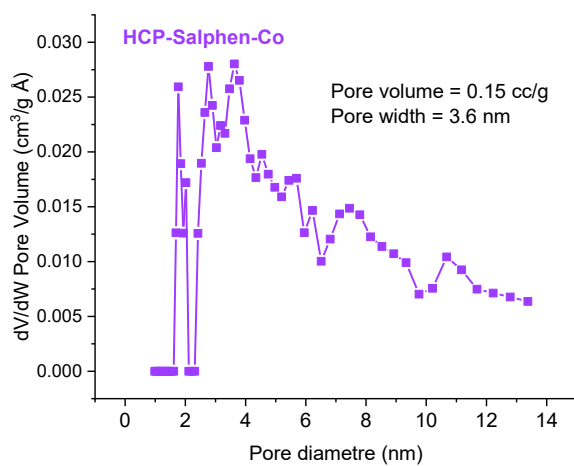


Figure A.26 Pore Size Distribution (DFT method).

Methyl furate: ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.54 (m, 1H, H_a), 7.19 (td, 1H, H_c), 6.51 (dt, 1H, H_b), 3.90 (d, 3H, H_d).

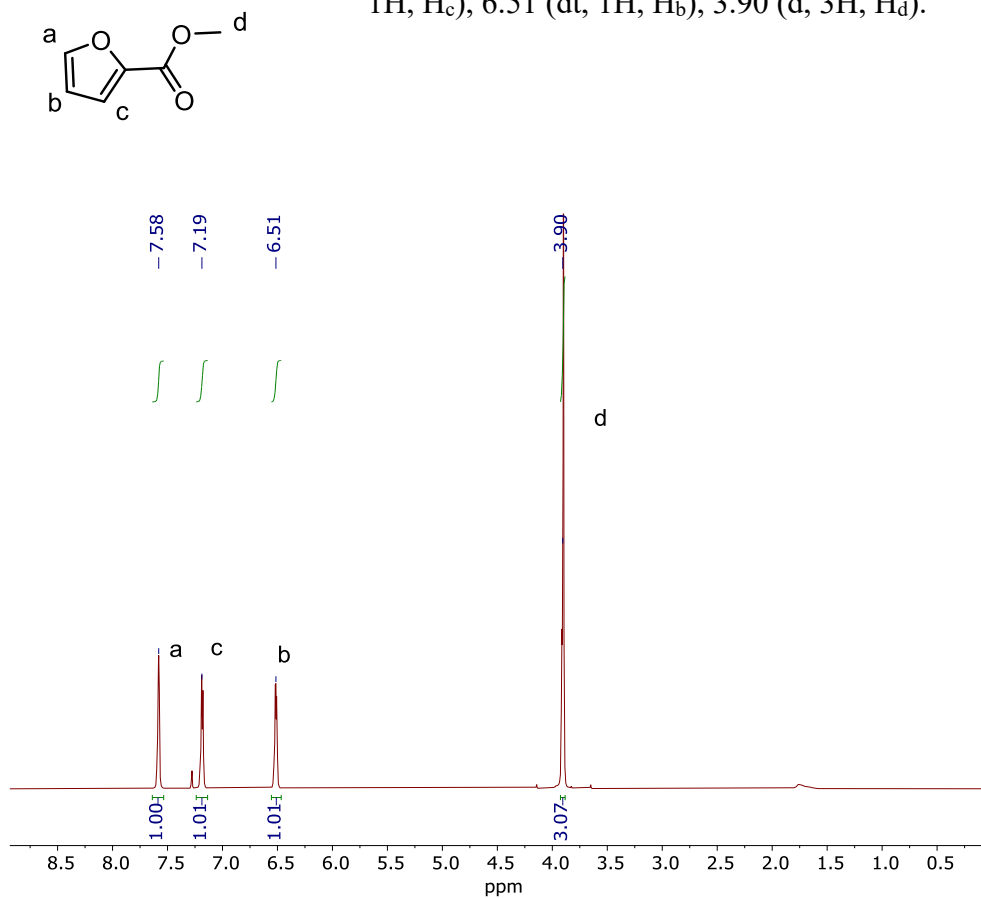


Figure A.27 ^1H NMR of 2-methyl furoate.

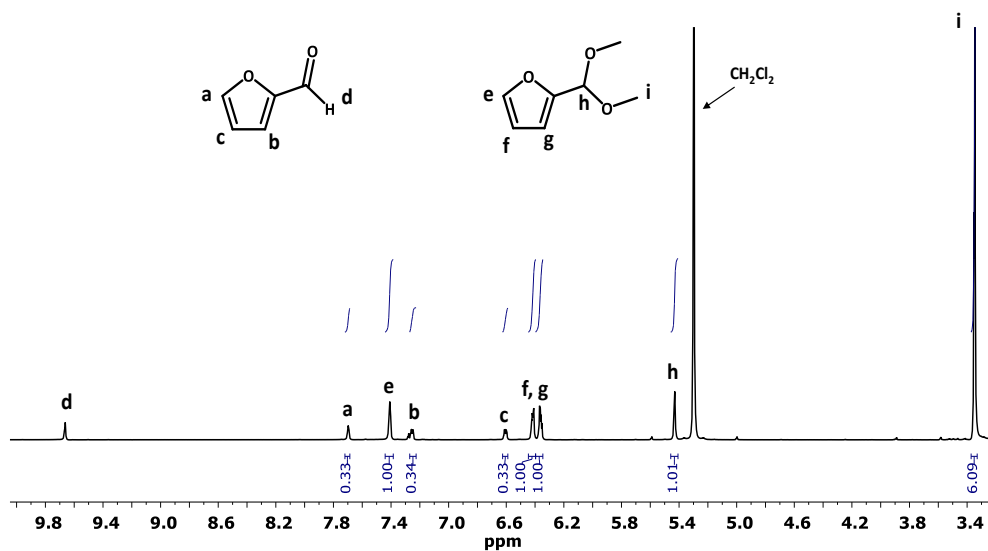


Figure A.28 ^1H NMR (CDCl_3) spectrum of entry 11, Table 5.1. FA(1mmol), HCP-BzmimCl(ammol), 60°C , 24h.

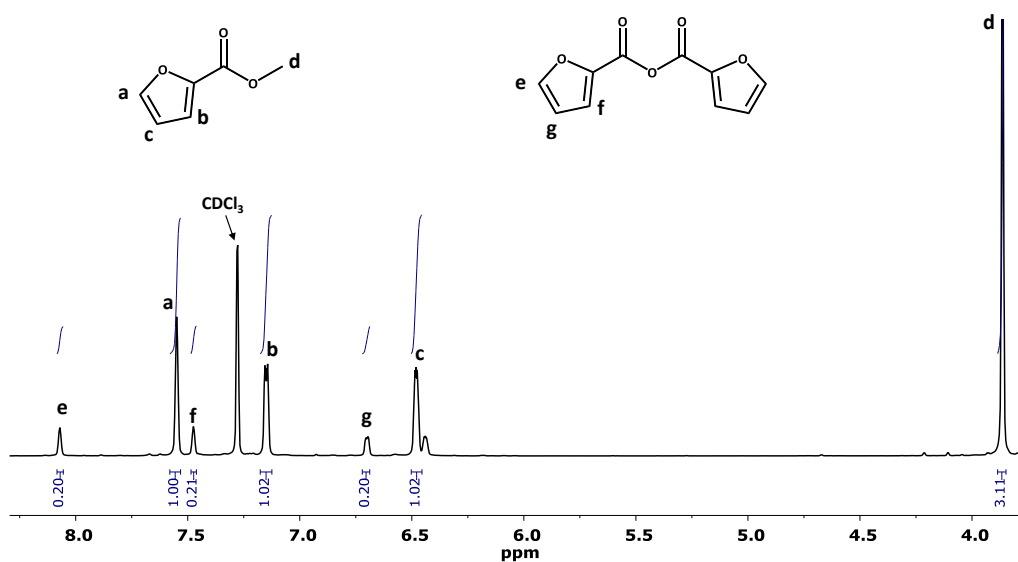


Figure A.29 ^1H NMR of entry 5 of Table 5.2, FA(1mmol), HCP-BzmimCl (0.5mmol), DBU (1,2 mmol), 4h.

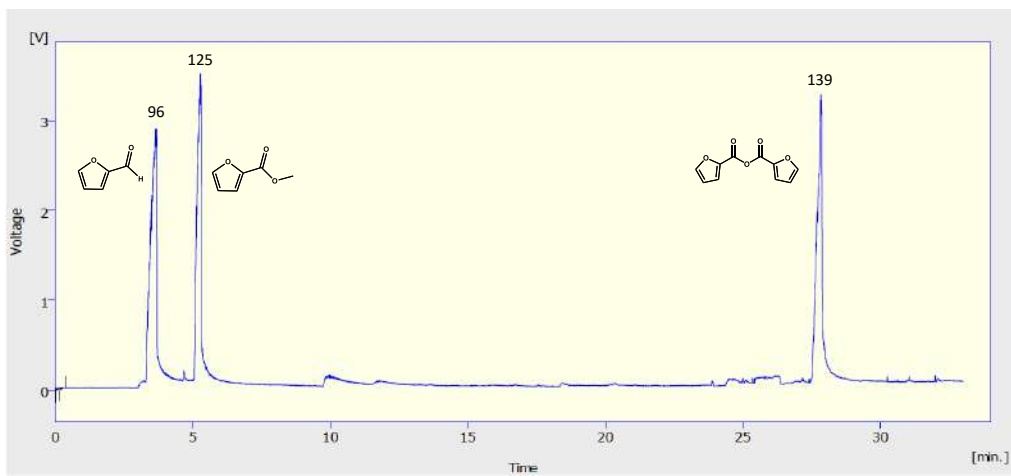
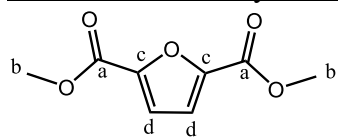


Figure A.30 GC Chromatogram of entry 5 of Table 5.2

2,5-Furan dicarboxylic methyl ester: ^1H NMR (400 MHz, CDCl_3) δ 7.24 (d, 2H,



H_a), 3.98 – 3.94 (m, 6H, H_b), ^{13}C NMR (300 MHz, 25 $^\circ\text{C}$, CDCl_3): δ 158 (H_a), 147 (H_c), 118 (H_d), 52 (H_b).

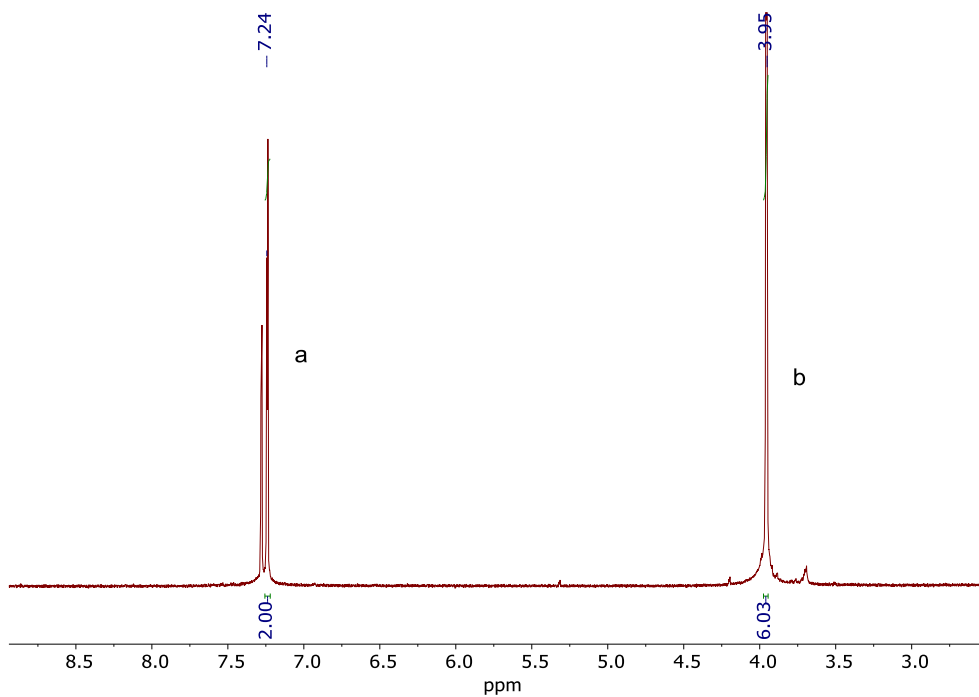


Figure A.31 ^1H NMR of 2,5-Furan dicarboxylic methyl ester.

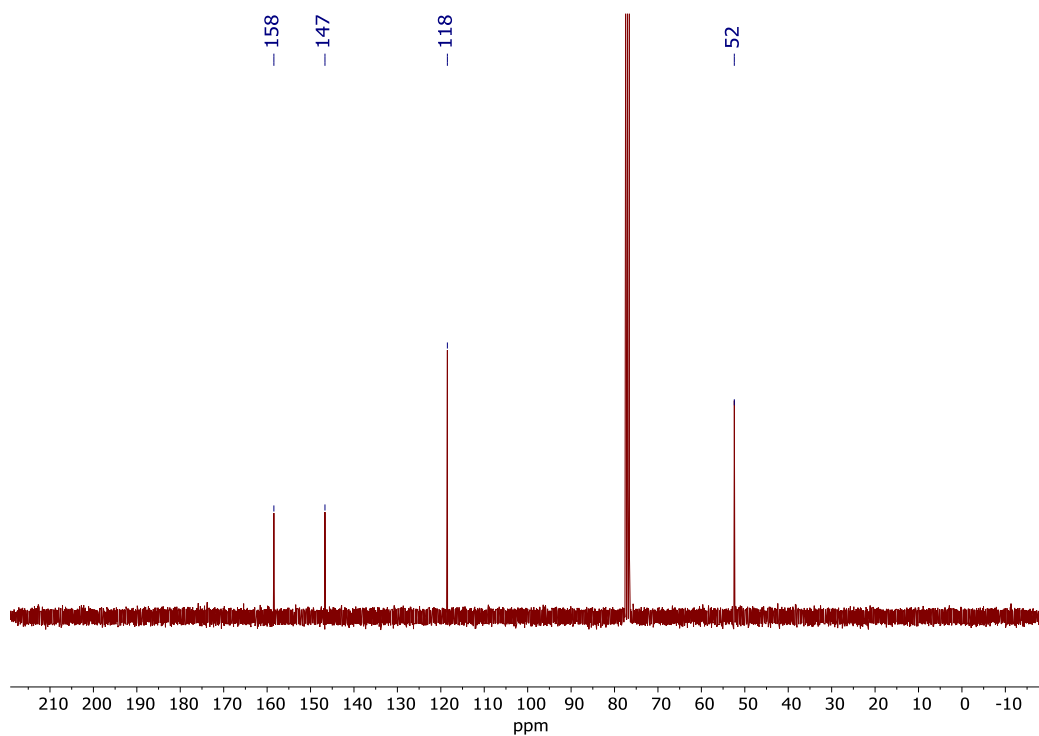


Figure A. 32 ^{13}C NMR of 2,5-Furan dicarboxylic methyl ester.

List of publications

The results of this thesis have been published in the following publication:

1. B. Fuerte-Díez, E. Rangel-Rangel, M. Iglesias, and E. M. Maya, Metal-free catalytic systems based on imidazolium chloride and strong bases for selective oxidative esterification of furfural to methyl furoate. *Applied Catalysis A: General*, 2023. 654, 119088
2. B. Fuerte-Díez, E. Rangel-Rangel, M. Iglesias, and E. M. Maya, Efficient DMF-assisted synthesis of formamides from amines using CO₂ catalyzed by heterogeneous metal-free imidazolium-hypercrosslinked polymers. *Journal of CO₂ Utilization*, 2024. 80, 102679.
3. E. Rangel-Rangel, B. Fuerte-Díez, M. Iglesias, and E. M. Maya. Insertion of CO₂ to 2-methyl furoate promoted by a cobalt hypercrosslinked polymer catalyst to obtain a monomer of CO₂-based biopolyesters. *RSC Sustainability*, 2024. 2(10), 2896-2902.
4. B. Fuerte-Díez, M. Iglesias, and E. M. Maya. Three-Component Coupling of CO₂ for the Synthesis of Carbamates and Carbonates using Metal-Supported Hypercrosslinked N-Heterocyclic Carbene Polymer (HCP-NHC) Catalysts. 2025 *Under preparation*.

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