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POSS-based 3D functional networks as catalysts for the conversion of carbon dioxide

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Preface

Today, the development of sustainable processes is in the spotlight due to the climate emergencies. Green Chemistry with its twelve principles developed by Paul Anastas, focuses on the development of alternative and more environmentally friendly processes. This branch of chemistry shows how concepts such as waste prevention, the use of renewable raw materials and catalysis are of great importance in making a process more sustainable. In this context, carbon dioxide (CO₂) represents one of the most abundant, non-toxic and renewable carbon feedstocks. The possibility of reusing CO₂ and transforming this molecule into value-added products such as cyclic carbonates, via addition into epoxides, makes this molecule interesting from a research point of view. Despite these interesting characteristics, the transformation of CO₂ has a very high energy thermodynamic requirement. To overcome this problem, a suitable catalyst is essential to decrease the activation energy of the process and make it work in milder condition. In this context this Ph.D. dissertation finds its outlines. Among all the possible catalysts proposed in literature, one class of catalysts that has been little explored is that of bifunctional materials. The excellent catalytic performance shown by these heterogeneous catalysts seems to narrow the gap in terms of catalytic activity between heterogeneous and homogeneous catalysis in relation to this reaction.

The first Chapter of the dissertation introduces the reader into the field of heterogeneous catalysis and in catalysis applied for the conversion of carbon dioxide in cyclic carbonates. After this introductory chapter, the dissertation is splitted into two main sections.

A first part concerning the Chapter III is related to the study of the stability during catalysis of different materials based on carbon nanoforms (CNFs). On the other hand, Chapters IV and V are related to the second part of the thesis that put its attention in the design of different bifunctional materials based on polyhedral oligomeric silsesquioxanes and their application as a catalyst for the conversion of carbon dioxide with epoxides.

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Special thanks go to my colleagues at both universities. Thanks to them I discovered how to rely on others, be loyal and work well in a team

I am grateful to *Prof. Eric Gaigneaux* and *Dr. Luca Fusaro*, my *comité d'accompagnement*, for the help and the advices they offered to me. I additionally wish to thank *Prof. Guillaume Berionni* for being part of the committee members.

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Finally, special thanks go to my family and my friends for their incredible support and love during these three years and during my entire life until now.

At real the end, I would like to thank myself for always being strong enough.

CHAPTER I:
General Introduction

1.1 Green Chemistry and Sustainable Development

Nowadays, the need of carrying out industrial processes in a sustainable way is indisputable. The continuous growth of interest in green chemical processes and technologies to reduce the production of wastes in industrial processes has given rise to a novel branch of chemistry: Green Chemistry.[1] The term green chemistry was coined by Paul Anastas of the US Environmental Protection Agency (EPA). In 1998 Anastas proposed 12 principles that should be considered as 12 guidelines to be followed in order to have a completely sustainable process (Figure 1).[2]

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Figure 1. The twelve principles of green chemistry.

A definition that can explain the main focus of Green Chemistry could be: “*green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.*”[3] It is clear from both the twelve principles and from this definition, that the main goal of a sustainable process is the waste prevention. Indeed, the better choice will be always to prevent and not to cure. Preventing a waste in fact involves performing fewer steps to obtain the final product during a chemical process. Reducing these steps avoids purification procedures of the reaction mixture in the work-up phases of the process under consideration. This results in an economic advantage for the industry as it also reduces waste sorting costs.

Moreover, it is worth looking to the sustainability of a process from another point of view. It is clearly important to prevent waste, but it is equally important to transform toxic or potentially dangerous substances into more useful and less harmful species. In this context, the perfect example could be the addition of CO₂ to epoxides to form cyclic carbonates. A reaction that is object of study in this Dissertation. This process will be deeply discussed in the end of this introduction Chapter. However, it is important to say now that the process allows the simultaneous conversion of a waste as carbon dioxide and toxic compounds such as epoxides to obtain useful and non-toxic products like cyclic carbonates.

The sustainable design of new materials, products and processes includes the key concepts of waste prevention: atom economy, E-factors as well as the use of renewable feedstocks. Atom economy and E-factor, in particular, are two of the most largely employed sustainability metrics used to quantify the sustainability of a chemical process.[4]

- Atom economy is a measure that considers how many atoms of reactants end up in the final product and how many ends up in by-products or waste. The main advantage of the atom economy is that this parameter can be calculated at a planning stage of the process since the stoichiometrically balanced reaction is sufficient. Just to make a simple example, addition reactions are a class of processes with an atom economy of 100%.
- E-factor is defined as the mass ratio of total wastes generated to the mass of the desired product. This parameter considers not only the eventual by-products formed but also the wastes from all auxiliary components, for example, solvent and the chemicals used in work-up step. In the evaluation of the E-factor, water (eventually formed in the reaction) is not considered as a waste since it is harmless, so its mass is usually omitted from the total mass of waste in the calculation. Moreover, when reactions are performed in aqueous medium, every species present is considered in the E factor, except the amount of water employed. The ideal E-Factor is zero and as logically expected, a high value of this parameter indicates a negative environmental impact of the considered process.[5]

It is worth to mention that atom economy is applied to individual steps, while the E factor, on the other hand, can easily be applied to a multistep process thus facilitating a holistic assessment of a complete process. The larger E factors in the fine chemical and pharmaceutical industries are also a consequence of the widespread use of classical stoichiometric reagents rather than catalysts. It is useful to stress how the importance of using sub-stoichiometric quantities and being able to recycle our resources is essential in order to have a highly sustainable process. In this regard, one of the most important pillars of Green Chemistry is the development of catalytic processes.[6] Catalysis offers many advantages from a Green Chemistry point of view, including lower energy requirements derived from the intrinsic characteristics of the catalyst. The correct design of a catalyst is essential in order to achieve excellent yields and selectivity towards the desired product. Even structural changes such as the choice of a binder or metal, or even a specific functional group, can lead to significant improvements in selectivity, energy consumption, and solvent utilization.

Catalysis can be classified in two different sub-disciplines: homogeneous catalysis and heterogeneous catalysis.[7, 8]

Homogeneous catalysis is a sequence of reactions involving a catalyst in the same phase as the reactants and solvents and generally uses organic molecules, organometallic complexes, acids/bases or salts as catalysts. Normally, in this type of catalysis, all the active sites of the catalyst are all available, thus making the process extremely productive. However, when talking about homogeneous catalysis, one must also consider all the post-reaction problems, such as the difficulty of purifying the mixture from the catalyst, the washing of the catalyst itself and its recycling.

Precisely for the latter reasons, it is certainly more appealing and convenient in the field of Green Chemistry to use heterogeneous catalysis. In heterogeneous catalysis, the catalyst (usually solid) is present in a different phase than the reaction medium (usually liquid or gas). The activity of the catalytic material is often lower in comparison with homogeneous catalysts due to the problems related to diffusion limitation. Despite these potential drawbacks, heterogeneous catalysts offer the

advantage that products are readily separated from the catalyst and also for that reason they are more easily recyclable.[9]

A heterogeneous catalyst is usually a material that is insoluble in the reaction mixture. Moreover, the use of a support ensures that many of its properties such as thermal or mechanical stability are retained in the final catalytic material. In addition, designing the correct catalyst and optimizing reaction parameters (temperature, pressure, reaction time...) also means optimizing factors such as stability, turnover number (defined by the ratio between moles obtained of the selected product and moles of active sites), Productivity (defined by the ratio between grams obtained of the selected product and grams of used catalyst), solubility and ease of separation from the product.

1.2 Solids Supports

It is evident from what has already been discussed that finding an ideal balance between homogeneous and heterogeneous catalysis is a challenging objective. On the one hand, homogeneous catalysts usually display high catalytic activity. However, as mentioned above, it sins in terms of reuse. On the other hand, heterogeneous catalysts are often less performants but present the advantage of a easier separation from the reaction mixture and reuse.

One of the cheapest methods to prepare heterogeneous catalytic materials is the polymerization process. Nevertheless, the resulting polymers could display poor catalytic performances due to diffusion limitations and sometimes they flaw in thermal or mechanical resistance. In this respect, different strategies have been developed for the design of heterogeneous catalyst via immobilization of molecular homogeneous catalysts onto a plethora of solid supports. Heterogenization of a catalyst can offer significant advantages in term of separation, reuse and robustness. One of the possible ways to obtain an heterogenized catalyst well resistant and active onto the target reaction can be to use a support. In this way, the final solid material will acquire the specific properties of the chosen support, while, hopefully, maintaining the catalytic activity of the molecule or polymer we have decided to support. The immobilization of the homogeneous catalyst can be done via the covalent or the non-covalent functionalization of the chosen supporting material. In

the case of covalent functionalization, the co-synthetic strategy is one of the easiest ways to obtain a supported material. In this method both the catalyst and the molecular precursors of the support are reacted together in order to obtain the final material by using a one-pot procedure.

Due to the importance of the solid supports in the field of heterogeneous catalysis, it is worth saying that a good support should have some properties such as:

- chemical, mechanical and thermal stability;
- large surface area;
- abundant surface functionalities;
- fast mass transport of the reagents and the products to and from the active sites.

Two classes of solid materials that satisfy the above-mentioned criteria are carbon nanoforms and the mesostructured silica.

1.2.1 Carbon Nanoforms

Carbon nanoform (CNF) refers to a family of allotropic carbon nanostructures with nanoscale dimension, whose functional properties strongly depends on the type and tridimensional arrangements. In Figure 2 are represented various members of this family such as fullerene, nanotubes, nano-onions, nano-diamonds, nanohorns, nanotori, graphene.[10]

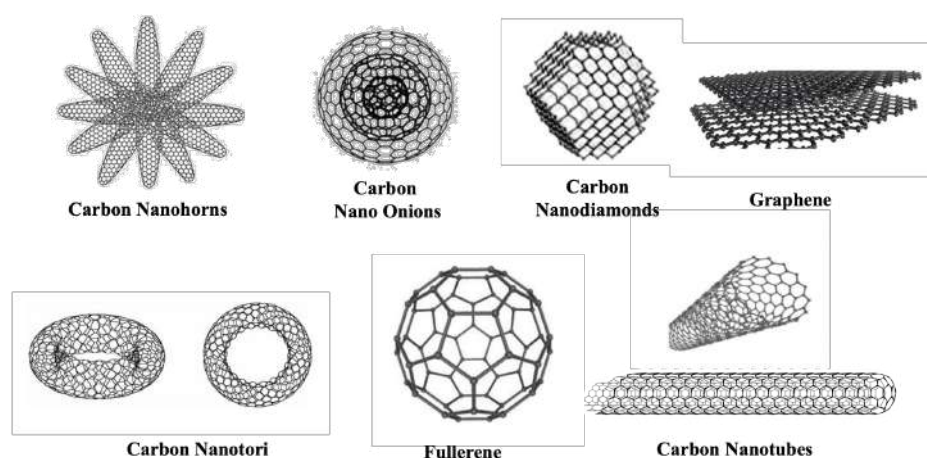


Figure 2. Different carbon nanoforms.

The applications of carbon nanoforms fade into various fields such as photonics, optoelectronics, nano-medicine and many more.[11-14] In this regard, nanocarbon-based materials showed to be suitable supports for heterogeneous catalysis, due to a series of features comprising high chemical inertness under many conditions, thermal stability and mechanical resistance.[15-17]

1.2.1.1 Carbon Nanotubes.

Carbon nanotubes (CNTs), discovered in 1991, immediately attracted the scientific community because of their special properties. Their structure can be considered as a graphene sheet rolled into a tube.[18]

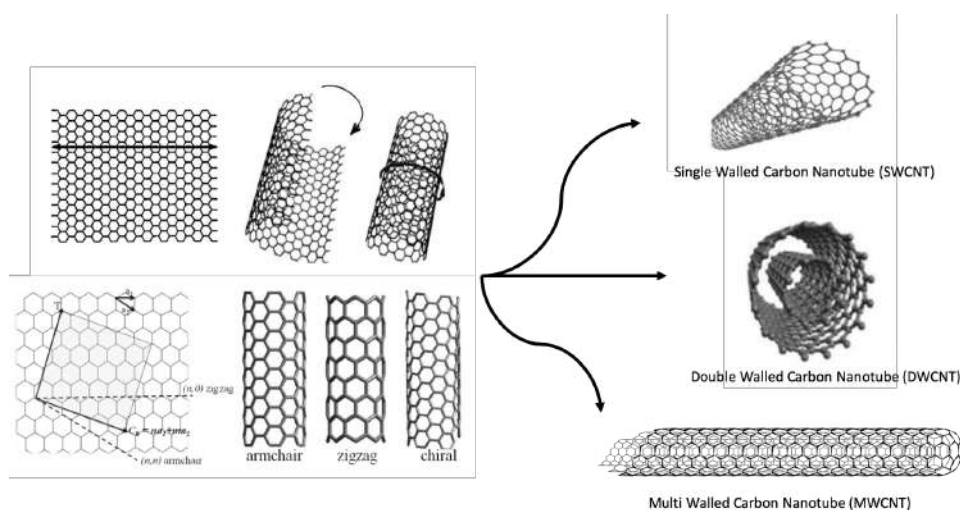


Figure 3. Functional way to represent CNT formation (left). Single walled carbon nanotube, double walled carbon nanotube and multi-walled carbon nanotube (right). A first division can be made on the basis of their morphology as shown in Figure 3. They exist in single-walled nanotubes (SWNTs), double-walled nanotubes (DWCNTs) and multi-walled nanotubes (MWNTs) of different lengths and diameters. SWCNTs external diameters are in the range between 0.4–4 nm, whereas in the case of MWCNTs the diameter is up to 100 nm with the inter-tubular space around 0.34 nm. Another kind of classification could be on the side of the way of rolling up the sheet of graphene. There are many ways to roll a graphene into a single-walled nanotube, with some of the resulting nanotubes possessing planes of symmetry both parallel and perpendicular to the nanotube axis. We can have three different CNTs configuration: zig-zag, armchair, chiral.[19]

A single sheet will generate single-walled nanotubes, while two or more sheets rolled up concentrically will lead to the formation of DWCNTs and MWCNTs respectively. The synthesis of CNTs can be carried out by using, in presence of a metal catalyst, different techniques such as arc-discharge, laser ablation, and chemical vapor deposition (CVD). Carbon nanotubes have high specific surface area and large aspect ratio. They show unique properties such as remarkably high mechanical strength, low density and large electrical and thermal conductivity which are relevant for various applications. Concerning MWCNTs it is worth saying that the outer wall of the multilayer structure protects the inner CNT from chemical interactions and improves their tensile strength over DWCNTs and SWCNTs.[20] Despite being endowed with extremely intriguing properties, pristine CNTs are not easily utilized as they present solubility and dispersion problems due van der Waals and π - π stacking interactions between the walls of the tubes. Through these forces, pristine CNTs generally tend to aggregate in bundles of various sizes. One method to increase their dispersion in a liquid medium could be the sonication, however, as soon as the exposure to ultrasound stops, the CNTs tend to aggregate again. The energy generated by ultrasounds overcomes the energy of the van der Waals and π - π stacking interactions between the walls of the nano-objects present in the solution which allows the pristine nanotubes to aggregate. As soon as the ultrasound is interrupted, the nanotubes start approaching each other thus forming again the bundles. It is therefore clear that the key to limit aggregation is the modification of the nanotube walls. This modification, properly called functionalization, allows the nanotubes to be coated with molecules of different natures. Through functionalization process and selecting the proper moieties, the interactions between the walls of the different nanotubes can be decreased. Moreover, this way to modify the walls of CNTs is also a good method to expand the field of applications.[21-23] As shown in Figure 4, CNTs can be chemically modified by the following strategies:

- functionalization of defects on the sidewall and on the rims;
- noncovalent interactions;
- sidewall covalent functionalization
- endohedral inclusion.

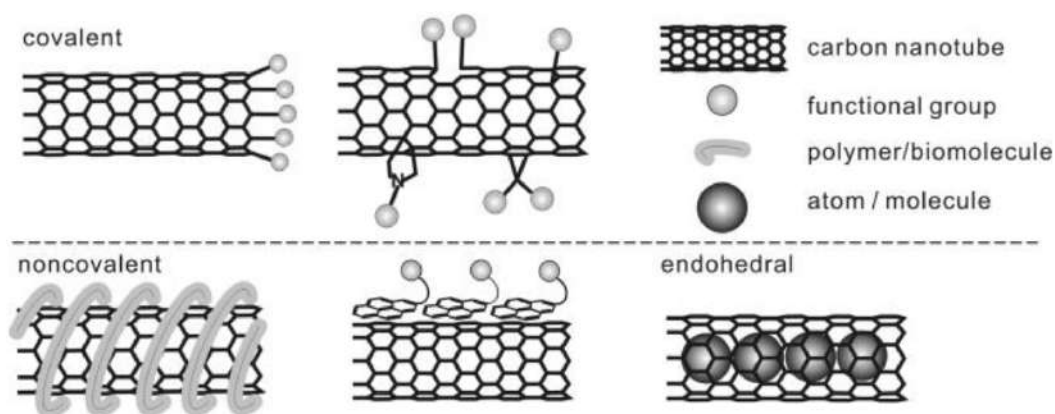


Figure 4. Different ways of CNTs functionalization

Among all the foregoing techniques, the covalent functionalization of CNTs offers the advantage of producing stable and strong interactions between the functional moieties and the CNTs matrix. In the case of supramolecular functionalization, weak interactions such as van der Waals and π - π stacking forces play a key role. In contrast, in the case of endohedral inclusion the issue is slightly more particular. Firstly, nanotubes are initially opened at their tips by annealing or oxidative treatment (i.e. $\text{H}_2\text{SO}_4/\text{HNO}_3$ or $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$). Subsequently, metal species smaller than the nanotube diameter or small organic molecules are included inside the tube by solvent evaporation or refluxing. This strategy can be used to produce nano-reactors or confined environments for stabilizing species at room temperature. [24] The functionalization of a CNTs, and in particular, covalent attachment of appropriate chemical entities is a good strategy to improve dispersibility in liquid media by disruption of the sp^2 system and lowering of the van der Waals forces responsible for the bundling. The oxidative pretreatment and the subsequent post-modification of CNTs is a good method to fulfil this purpose. However, it is clear from the Figure 5 that the oxidative pretreatment is not the only way to modify CNTs and other techniques to functionalize covalently pristine CNTs and CNHs were developed, including in situ radical polymerization and microwave-assisted functionalization, among others.[17, 25-26] Furthermore, when π -conjugated polymers have been used as dispersants, π - π interactions between the surface of CNTs and the polymer play a relevant role, with CNTs acting as a sort of templating agent for the wrapping of the polymeric coating around the CNTs surface. In

addition to non-covalent interactions, other studies show how different organic polymers roll up along the shape of the nanotube, as a result of an in situ radical polymerization.[22, 27, 28]

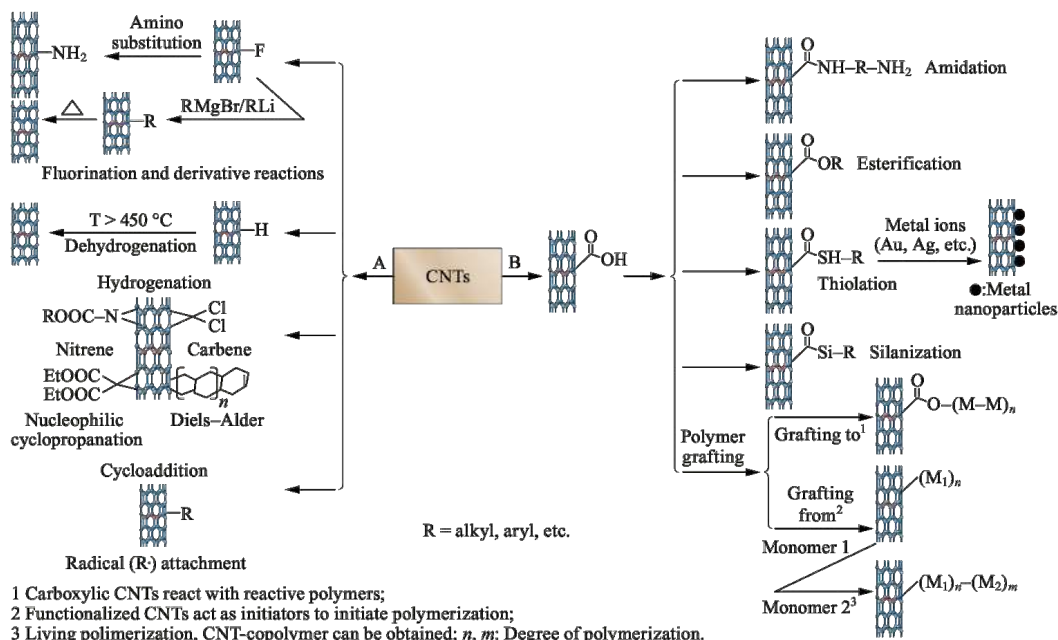


Figure 5.[19] Strategies for covalent functionalization of CNTs (A: direct sidewall functionalization; B: defect functionalization).

Due to this versatility in their functionalization, nanotubes cover an extremely wide range of applications such as components in electronics, solar cells, sensors, energy storage devices, filler in polymeric composites, drug carrier, or as support for catalyst.[29-33]

1.2.1.2 Carbon Nanohorns

Carbon Nanohorns (CNHs) are a particular allotropic form of carbon. They were first obtained in 1999 via CO_2 laser ablation of a graphite target, at room temperature under Ar, in high yield (75%) and purity (95%). Compared to all CNFs, CHNs attract the attention of research for their special structure and their high degree of purity due to the absence of metal during their synthesis.[34] The synthetic method consists in giving high energy to the system. This energy is able to vaporize and restructure a carbon target, followed by rapid quenching under inert

conditions. CNHs are conical carbon nanostructures made up of single rolled graphene sheets with cone caps resembling horns, with an average tubule diameter of 2-5 nm, tubule length of 40-50 nm, cone angle of 20° and aggregate diameter of 80 - 100 nm.

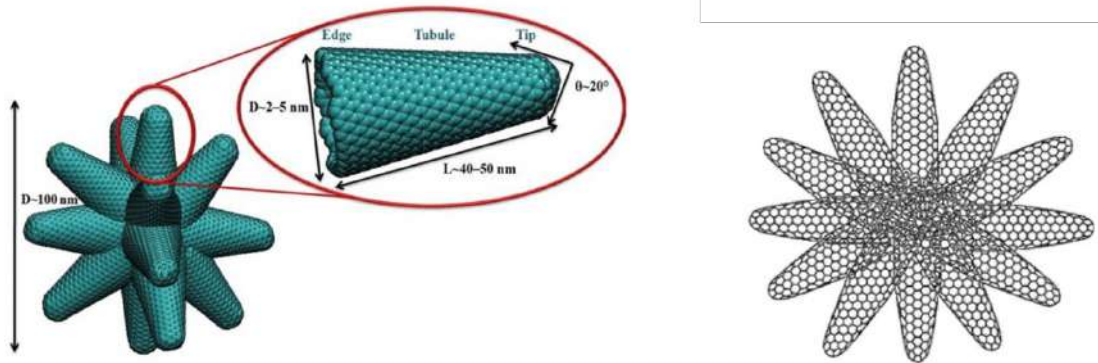


Figure 6. Pristine carbon nanohorns (dahlia like shape).

Pristine CNHs aggregate in a dahlia-like shape, as shown in Figure 6, while a large number of conical-shaped single-layered tips stick out in all directions of the spherical superstructure. Importantly, the surrounding tips are capped by highly stretched five-membered rings. It is reported that as-grown CNHs consist of 70% tubular, 15% defective (on tips), 12% graphitic and 2.5% amorphous carbon.[35] Furthermore, thanks to their special structure, CNHs have numerous properties: they possess good thermal stability, micro and meso-porosity, high surface area, and they also have good semiconductor properties. SWCNHs possess significant advantages compared with CNTs. First of all, the horn-like structure of SWCNHs makes them have more defects. The structure of CNHs imposes greater tension on the horn closure part. In this way, the shell part is more bent than CNTs, showing the presence of more 5 members rings and more defects. Thus, this feature imposes an higher reactivity of CNHs in functionalization compared to CNTs. Second, the preparation process without metallic catalysts averts interference from metal impurities. The synthesis of CNTs not only produces metal impurities, but also

carbon impurities. Accordingly, for CNTs, especially SWCNTs, an additional and complicated purification process is required to remove some of the impurities.[36] Following the research experience gained on the functionalization of carbon nanotubes, similar methodologies have been developed for the solubilization of CNHs. In general, dissolution of CNHs is achieved either by covalent chemical modification of the outer skeleton of CNHs or via non-covalent supramolecular means based on π - π stacking interactions between CNHs and aromatic organic units and/or synergistic electrostatic interactions.

Two are the main procedures followed for the covalent functionalization of CNHs, namely:

- sidewall attachment of organic addends. (*In situ* radical polymerization, 1,3-dipolar cycloaddition, microwave assisted functionalization etc...);
- modification of carboxylic group of oxidized-CNHs (ox-CNHs) through esterification or amidation coupling.

Carbon nanohorns, exactly like all members of the family to which they belong, as soon as they undergo functionalization processes can be used for a wide variety of applications. These mainly include their capability to adsorb gases or other molecules, to act as drug carriers, to construct effective biosensors and electrodes for electrochemical and photoelectrochemical purposes, or to act as catalyst supports and fuel cells.[37-41]

1.2.2 Silica

Silicon dioxide (SiO_2), generally named Silica, is the most common form of Silicon.[42] It is possible to find two different structures of silica:

- crystalline;
- amorphous.

The most commonly used matrices are porous (or mesoporous) silica-based materials (e.g. SBA-n, MCM-41 types), which are characterized by their low cost, high specific surface area, ordered porosity, well-defined pore geometry, and mechanical and thermal stability.[43] The synthesis of silica materials is most often performed using the sol-gel route (Figure 7). The first step in this synthetic route

involves the dispersion of an amphiphilic molecule (usually a surfactant) in a solvent (commonly water). Under appropriate reaction conditions, the surfactant molecules will rearrange to form micelles. At this point, the addition of a silica precursor (an alkoxide such as tetraethyl orthosilicate) under acidic or basic conditions allows, through a series of hydrolysis and condensation reactions, the formation of a series of Si–O–Si bonds along the micelle surfaces. Finally, the final step involves the removal of the surfactant trapped in the pores of the silica structure by calcination.

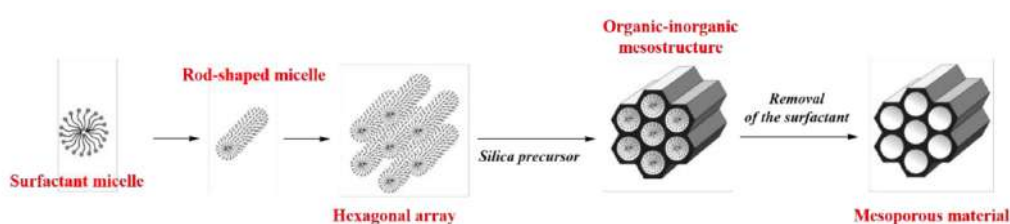


Figure 7. Synthesis of Silica mesoporous material.

The structural properties of the mesoporous material obtained at the end of the synthetic protocol, change depending on the reaction conditions used and on some specific parameters such as the solvent, the pH, nature of the template, its concentration, the temperature, the reaction time, the addition of a swelling agent or salt. By modifying these parameters, it is possible to tune different features (e.g., pore size, size of particles, the architecture of porosity), thus obtaining various materials and mesoporous structures. MCM-41 and SBA-15 deserve to be mentioned as two of the most representative members of mesoporous silicas with hexagonal phase.[44] For example, by changing the precursor used as templating agent and its ratio to silica, it is possible to obtain different pore geometries for the SBA type mesoporous silica: SBA-11 (cubic) to SBA-12 (3-d hexagonal) to SBA-15 (hexagonal) and SBA-16 (cubic cage-structured).[45]

The most important feature of silica-based materials is the presence of silanol groups (-Si-OH) on the surface, which can be exploited for a functionalization of the material through the condensation reaction with the appropriate organosilane.[46]

Thanks to the above-mentioned properties and the possibility of being functionalized, this class of materials is used as supports for immobilizing biomolecules, catalysts, agents for polymers reinforcement and templates for the synthesis of other materials.[47-50]

1.2.2.1 Polyhedral Oligomeric Silsesquioxanes (POSS)

Polyhedral Oligomeric Silsesquioxanes (POSS) represent a versatile class of organosilicon compounds with nanometrical dimensions. They are the smallest nanostructure with a well-defined inorganic framework made of Silicon (Si) and Oxygen (O) atoms. They respect the general formula $(\text{R-SiO}_{1.5})_n$, where n is commonly 6, 8, 10 and 12, the ratio O/Si is 1.5, and R is the vertex functional group. Among all the possible dimensions of the cage, Figure 8 shows the octameric structure with the formula $\text{R}_8\text{Si}_8\text{O}_{12}$ that it is also, the most investigated silica nanostructure. Octameric silsesquioxanes molecules have a cage-shaped three dimensional (3D) structure, and they consist of a rigid and inorganic silica core (length: 0.5-0.7 nm) surrounded by eight organic functional groups.[51, 52]

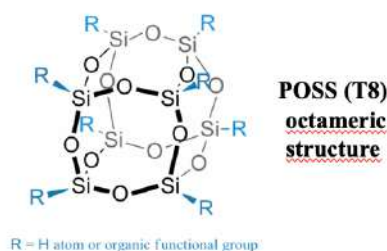


Figure 8. T8 POSS octameric nanocage.

The R groups at the corner can strongly influence the physical and chemical properties of the nanocage, while the silica core confers rigidity and thermal stability. Ideally, POSS are completely condensed structures but in reality, it is possible to find cages in which a vertex is not completely condensed. In this case the incomplete silsesquioxane cage has silanol groups (Si-OH), showing a more

complexed formula and becoming an ideal compound as ligand for metal coordinate complexes as shown in Figure 9.

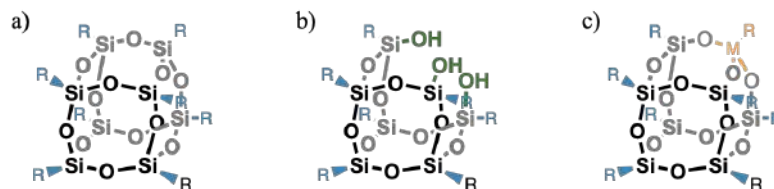


Figure 9. Different POSS structures: a) completely condensed cage, b) partially condensed and c) metallasilsesquioxane (M = metal).

From a synthetic point of view, this class of compounds can be prepared using different strategies as shown in Figure 11:

- the hydrolytic condensation of monosilanes;
- the corner capping of partially condensed silsesquioxanes;
- the chemical modification of the functional groups of an already T⁸ core to give a new POSS derivative.

Of the listed methods, the first one is the most widely used.[53] The synthetic hydrolysis and condensation pathway involves an initial hydrolysis step of a monosilane RSiX_3 , where R is an organic substituent, and X is a highly reactive substituent such as Cl or alkoxy, and the formation of the corresponding trisilanol RSi(OH)_3 . This intermediate will subsequently undergo through a series of chain condensations until the fully closed cage is obtained.

Despite being the most widely used method, it is influenced by many parameters to be controlled such as the nature of the organic group (R) and the nature of the exit group (X), the reaction time and temperature, the solvent used, the pH, the concentration of the monosilane, the amount of water.

Once the cage has been obtained, it can be post-functionalized.[54] This peculiar feature of being able to structurally change the organic group R attached to each silicon vertex makes POSS an extremely versatile and interesting class of compounds. From post-functionalization in fact it is possible to obtain inorganic oxygen-silicon scaffold with peculiar thermal and mechanical properties of the nano-silica compounds, in addition to enormous potential of the really big class of

organic molecules suitable for different fields, e.g. catalysis, polymer chemistry, photochemistry, chemistry of material, biomedicine.[55-64]

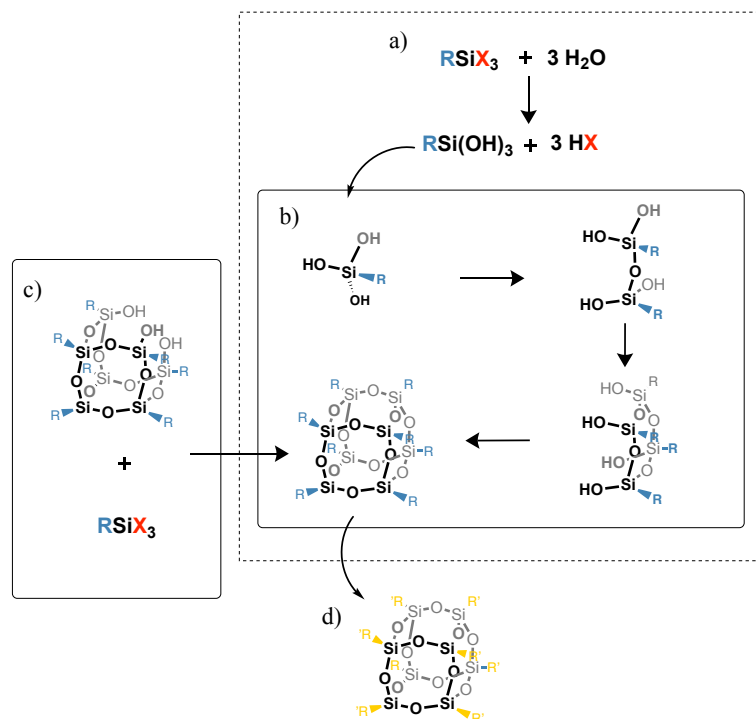


Figure 11. Schematic sequence of reaction for the mechanism of hydrolysis (a) and condensation (b), corner capping pathway (c) and post functionalization of the obtained silsesquioxane cage (d).

Once synthesized one possible technique that can easily describe and characterize them is the ^{29}Si Nuclear Magnetic Resonance. This is an easy notation to describe all the silica-based materials. It focuses on how many oxygen atoms are connected with a central silicon atom. Depending on this number, two different classes are possible. “Tⁿ” and “Qⁿ” are abbreviated from “triplet” and “quartet” from silicon NMR literature, indicating silicon atoms covalently connected to three or four oxygen atoms in POSS structures, respectively.[54, 65] Moreover an oxygen atom can be part of a hydroxy group or can be bonded to:

- Another silicon atom (the oxygen will be a bridge between two silicon atoms);
- An organic group R (alkoxide moiety).

From the above, in Figure 10 it is possible to find different Qⁿ and Tⁿ structures. In Qⁿ structure for example, a central silicon atom is bonded to four oxygens. On

the other hand, in T^n structure a central silicon bonded to three oxygen atoms and one R (organic moiety) group. For example, in Q^1 structure the silicon is bonded to 4 oxygen atoms but only one oxygen is bonded to another silicon atom. The other three oxygens can be hydroxy groups and/or alkoxy groups. In the case of Q^2 structure, one central silicon atom is bonded to four oxygens. Two of these oxygens are bonded with other two silicon atoms and the other two can be hydroxy groups and/or alkoxy groups. From the above, it is reasonable to expect that the Q^4 structure is the full condensed framework, where each oxygen makes a bridge bond between the central and others silicon atoms. By the same logic, therefore, the T^n class will also have geminal and isolated hydroxy (or alkoxy) groups in the T^1 and T^2 frameworks respectively, and the total absence of -OH (or -OR) groups in the total condensed T^3 frameworks.

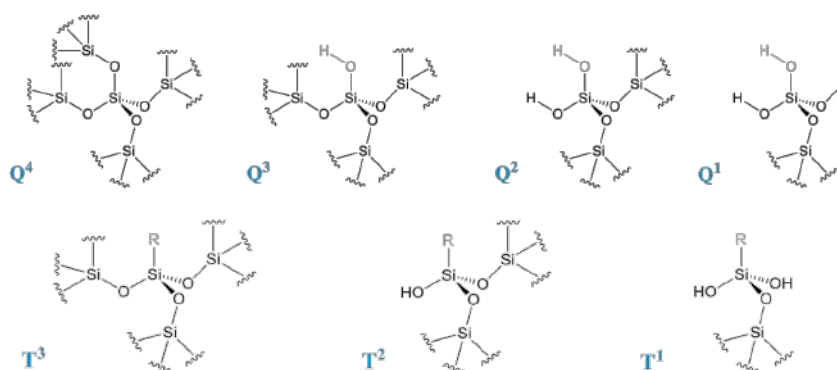


Figura 10. Q^n and T^n silicon unit nomenclature (represented only with -OH groups).

There are four main ways of using POSS molecules to form hybrid polymers and nanocomposites:

- Copolymerization of an organic monomer, such as vinyl, styrene, propylene, or methyl methacrylate, with POSS molecules bearing the same or similar functional group in one or all of their pendant arms. Depending on whether the POSS species has one or eight polymerizable functional groups, it can act here either as a pendant group or a cross-linker, respectively.

- Polymerization of classical monomers in the presence of POSS molecules bearing unreactive groups, commonly alkyl groups, or introduction of POSS molecules into the already prepared polymer matrix by physical mixing.
- Grafting of a POSS unit bearing a single reactive function onto a preprepared polymer or a support by the formation of covalent bonds. This method can produce either polymers with many pendant POSS cages grafted along the polymer backbone.
- Direct cross-linking of POSS units without using an additional polymer, either directly by reaction of appropriate POSS derivatives with each other or by covalent binding to small organic molecules to form a three-dimensional network.

In this context, and wanting to stress out a specific application, interesting materials for catalysis have recently been prepared that have shown remarkable performance in CO₂ conversion. Indeed, it has been observed that the possible functionalization of multiple cage vertices with catalytic active sites can create a sort of synergy and cooperation between the active sites that are precisely localized for the purposes of catalysis. In fact, it has been found that this proximity effect enables the catalyst supported on the silica nanocage to perform better than the unsupported one.[66]

1.3 CO₂ conversion

Carbon dioxide is a common product of biological processes, such as aerobic respiration or the alcoholic fermentation of sugars, and its emission can also be associated with the combustion of fuels derived from human activities for energy production, transport and industrial processes. The increase in carbon dioxide in the atmosphere corresponds to the beginning of the industrial revolution and the latest Intergovernmental Panel on Climate Change (IPCC) report warns of the impacts on climate change. From 1959, about 45% of the carbon dioxide released by burning fossil fuels is not absorbed by the land and oceans and remains in the atmosphere. The stable level of CO₂ of 260 ppm in the atmosphere at the beginning of the 19th

century, now increases constantly to reach 400 ppm becoming an environmental issue to be addressed.[67]

In this context carbon capture, utilization and storage is one of the most interesting routes. CO₂ has several applications (Figure 12) such as dry-cleaning, refrigerators, fire extinguishers, in the food or agrochemical industry.[68-70] Moreover, at 73.8 bar and 31 °C, it behaves as supercritical fluid. This state of matter is used in various chemical processes such as the extraction or as solvent and it is used for various chemical reactions like hydrogenation, synthesis of organometallic compounds, polymerization, and even for free radical reactions.[71]

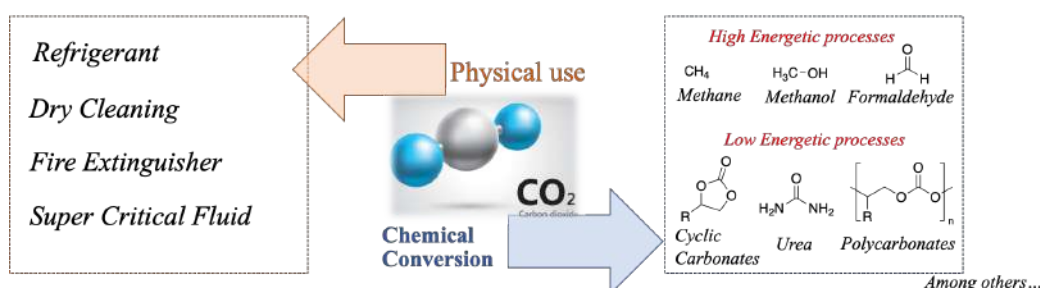


Figure 12. Some possible utilizations and some added value products of CO₂.

However, these uses of this molecule only concern the physical state in which it is or can be transformed. Much more interesting is the chemical transformation of CO₂ into high added value products. Carbon dioxide molecule can be considered as a nontoxic, highly available and renewable carbon feedstock. Despite these attractive features, the chemical transformation of CO₂ is challenging considering the high stability of this molecule (standard enthalpy of formation = -393.52 kJ/mol). The carbon atom in CO₂ is present in its most oxidized state resulting into a low molecular reactivity.

Processes in which carbon dioxide is involved can be categorized into two types:

- *high energy processes* (when during the process there is a reduction of the carbon atom oxidation state from 4 down to its minimum -4);
- *low energy processes* (when CO₂ is incorporated as the entire molecule into an organic or inorganic substrate).

For several years, scientists have been working on the production of fuels by catalytic hydrogenation of CO₂ to methane (CH₄), formaldehyde (HCOH) or formic acid (HCO₂H). It is also possible to produce urea from carbon dioxide. Ammonia or carboxylic acids can be produced by coupling with Grignard or organolithium reagents, themselves generated from an alkyl or aryl halide.[72]

Electro-reduction and photo-reduction of CO₂ are two different pathways to transform this molecule into different more useful products. The photo-reduction is bio-inspired by natural systems. It is sometimes called the artificial photo-synthesis.[73] The idea is to use the energy of the light to convert CO₂ into valuable chemicals. All mechanisms are based on the photoexcitation followed by a charge separation to generate the hole-electron pair. The available electron is then used to reduce the CO₂. On the other hand, instead of using the light to generate a photo-excited electron, there is a more straightforward mechanism to use: the electro-reduction. Here, it is about the direct use of electricity to perform a chemical reaction. This operation requires new catalysts and the ability to conduct current with metals.[74]

In low energy processes it is possible to overcome the problem of the high thermodynamic stability of the CO₂ molecule by using highly energetic starting materials such as hydrogen, epoxides, amines and among others that employed with a proper catalyst are able to decrease the activation energy of the selected reaction.[75]

This is the context for the work in this thesis, which aims to convert CO₂ into cyclic carbonates through its reaction with epoxides.

1.3.1 Carbon dioxide conversion into cyclic carbonates

Among the reactions mentioned above, the addition of carbon dioxide to epoxides is a relevant topic of research since it is a 100% atom economy reaction that can generate useful classes of compounds as cyclic carbonates and polycarbonates (Figure 13).[76]

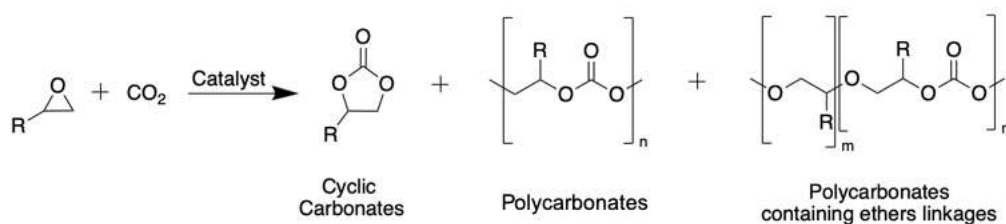


Figure 13. Possible products of the reaction between CO₂ and epoxides.

Both cyclic carbonates and polycarbonates are valuable compounds with many potential applications. In particular, cyclic carbonates are the thermodynamically favored products of the reaction, and they show properties such as low vapor pressure, high boiling point, low toxicity, and biodegradability. Such features lead these reaction products to have various applications such as aprotic high-boiling polar solvents, electrolytes for batteries, precursors for polymeric materials, fuel additives, plastic materials, and intermediates for the synthesis of fine chemicals.[77]

In industry, cyclic carbonates are traditionally prepared by synthetic methodologies involving the use of phosgene. This molecule is hazardous, toxic, corrosive, and difficult to handle. To overcome toxicity issues the reaction between CO₂ and epoxides is a valid sustainable alternative. The two C=O bonds are polar, implying that the carbon atom has a partial positive charge, and the oxygen atoms have a partial negative charge. Therefore, the carbon atom can act as an electrophile and the oxygen atoms as nucleophiles.[78] As mentioned in the previous paragraph, the use of epoxides alone is not enough to overpass the energy requirements of the process. In order to decrease the activation energy of the reaction, a catalyst is needed. It was demonstrated that the essential element in a proper catalyst for the target reaction is the nucleophilic species.[79] From a mechanistic point of view as shown in Figure 14a, the first step of the process is an epoxide-ring opening (1) by a nucleophilic attack from the anion of the salt. Then, the generated alcoholate attacks the electrophilic carbon of the CO₂ (2). The catalytic cycle ends with the 5-member ring closure and the regeneration of the initial anion (3). Hence the anion acts both as a nucleophile at the step (1) and as leaving group at the step (3).[80]

The activation energy of the reaction can be further decreased if species with Lewis acid properties (as Al, Cr, Mn, Co, Fe, Cu, Zn, Cd, Mg) or hydroxy-rich molecules able to form H-bonds are employed. The coordination bond between the oxygen of the epoxide and the Lewis acid species, or its H-bonding with H-bonding donors, promotes the progress of the reaction (Figure 14b).[81] As a result of the coordination bond, the opening of the epoxide can be favoured, as the electrophilic character of the carbon bonded to the coordinated oxygen increases. This coordination has been proved on various metal centres and complexes and the resulting enhanced electrophilicity was demonstrated by ^{13}C NMR and IR measurements.[82, 83]

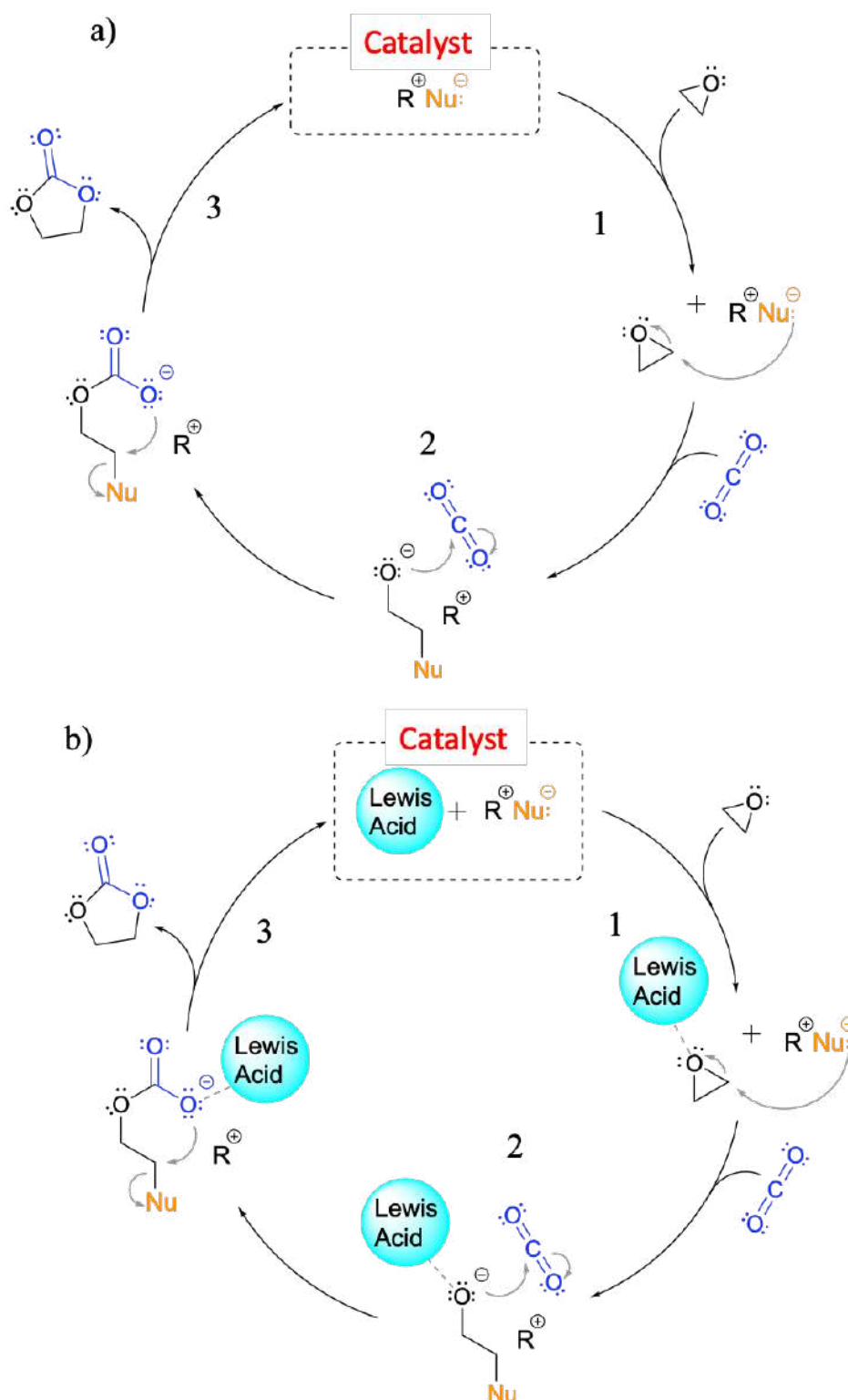


Figure 14. Proposed mechanism for the reaction between epoxides and CO₂. a) catalyzed by nucleophilic species only. b) catalyzed by nucleophilic species and co-catalyzed by Lewis acid species.

In addition to these mechanistic requirements, the addition reaction of CO₂ to epoxides is influenced by several parameters.

The selectivity of the reaction can be influenced not only by reaction conditions such as pressure and temperature, but also by the nature of the nucleophile and the metal species (catalyst), the presence and the nature of solvents and nature of substrate.[76, 84]

- Nucleophiles and metal species. It has been described in bifunctional catalytic systems that the nucleophilic anion plays a role in the reaction progress. In fact, catalytic results have shown that in catalysts containing a halide as a nucleophile, the order of catalytic activity is: $\text{Cl}^- \ll \text{Br}^- \leq \text{I}^-$. This is related to the halide's ability to act as a nucleophile, but also as a leaving group. A poor leaving group promotes polymer chain growth, while a good leaving group promotes the production of cyclic carbonate. Moreover, the strength of the bond between the metal and the oxygen and the nature of the substrate plays a crucial role on the selectivity of the process. A too strong metal-oxygen bond makes the intermediate inactive to another insertion or towards the ring closure. A proper choice of ligands that coordinate the metal as well as the nature of the metal itself are parameters to consider in the design of a good catalyst. Finally, it has been reported that the ratio of co-catalyst to catalyst plays a decisive role in determining selectivity towards cyclic or polymeric carbonates. A higher ratio of nucleophile to metal center may increase the selectivity towards cyclic carbonate. The presence of more nucleophile promotes the kinetics of the first reaction step related to the opening of the epoxy ring and the consequent increase in the formation of the metal-bonded carbonate intermediate, thus favoring the formation of the cyclic product.[85, 86]
- Substrate. The nature of groups on the epoxide or the dimensions of the heteroatomic ring can influence the selectivity of the reaction.[87, 88] This is essentially related to the preferential position of the nucleophilic attack (Figure 15). Substituted epoxides with electron-withdrawing (EWG) groups such as epichlorohydrin favor the formation of the cyclic carbonate, while alkyl chains with terminal epoxides or epoxides with the two secondary ring

carbons will tend to form the polycarbonate. In the first case (Figure 15 a), the preferential position is that of the carbon already bonded to the substituent promoted by the more electrophilic behavior due to the effect of the substituent. This favors the formation of an intermediate after insertion of the CO₂, that promotes ring closure. Whereas in the second case (Figure 15b), a monomeric intermediate favors the various combinations of polymeric chain possible formation.

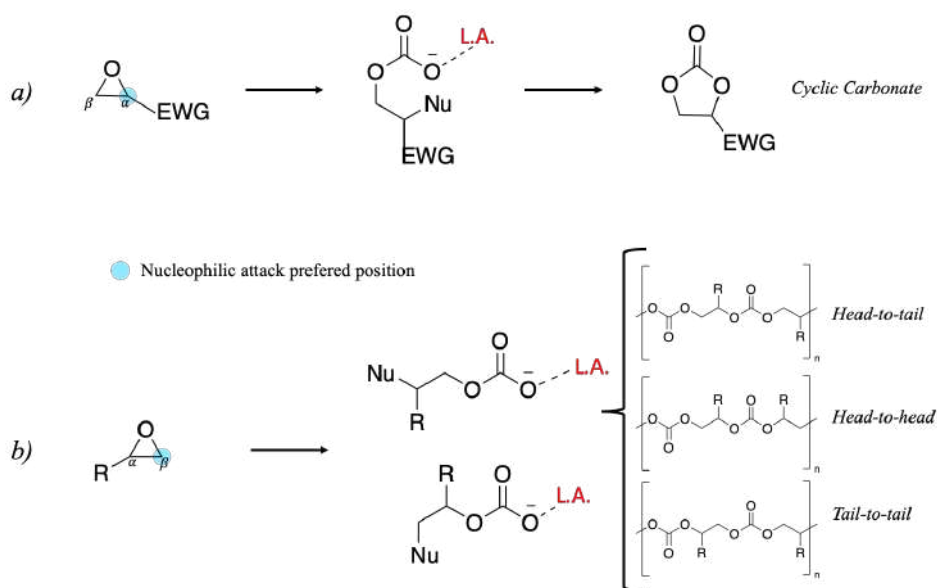


Figure 15. a) pathway of epoxides with electron-withdrawing groups as substituent. b) pathway of terminal epoxides.

On the other hand, oxetanes are characterized by lower ring strain, which implies that the ring opening step is more challenging. Furthermore, another main difference between epoxides and oxetanes is that for the former the five-membered cyclic carbonates are the thermodynamically favored products, while for the latter the polycarbonate is thermodynamically more stable than the six-membered cyclic carbonate.

1.3.2 Catalysts for carbon dioxide conversion into cyclic carbonates

The first catalysts used for this reaction were LiBr and NaBr.[89] Subsequently, various homogeneous catalysts were developed that offered excellent performance for the reaction of adding CO₂ to epoxides. In particular, the class of Ionic liquids (ILs) in Figure 16, such as ammonium, phosphonium, imidazolium, pyridinium or triazolium attracted the scientific community, as they can solubilize CO₂ very well. This feature enhances the rate of cycloaddition reactions between epoxides and CO₂. They could behave in various ways depending on the nature of either the cation or the anion. In the case of bulky and charge delocalized anions (e.g. BF₄⁻, PF₆⁻), the interaction between the epoxide and the anion is very weak and thus the nucleophilic attack on the epoxide is less feasible. On the other hand, also the structure of the cation has an influence on the catalytic performances. A bulky and delocalized cation will force itself away from the counter anion, and this less electrostatic interaction would make the anion more nucleophilic, while the less bulky and more nucleophilic cation, by binding the anion tightly, would decrease its availability for reaction with CO₂ or epoxides. For example, using a soft cation such as the aromatic imidazolium with the positive charge delocalized in the 5-membered ring leads the halide anion to be more available to proceed to the nucleophilic attack compared to the homologue KBr or KCl. Besides, some of the features like non-flammability, non-volatile, low vapour pressure and high melting points of ILs, make them suitable catalysts for CO₂ cycloaddition reactions. Among them, tert-butyl ammonium bromide emerged as the most industrially used for the production of cyclic carbonates until the 2000s. However, the harsh reaction conditions (80 bar and 220 °C) prompted researchers from both academia and industry to look for new solutions.[90-95]

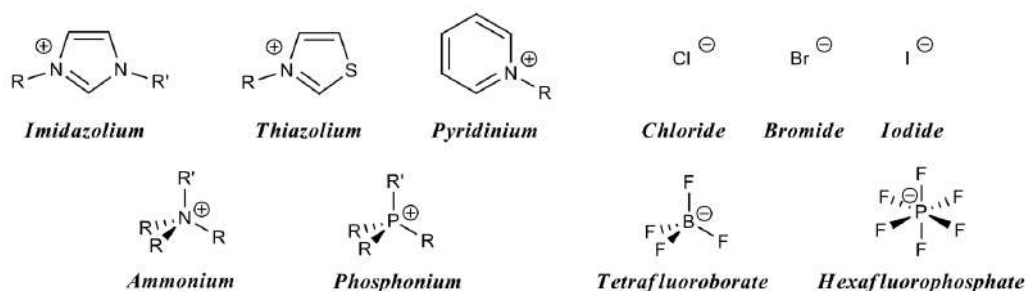


Figure 16. General representation of different ionic liquids.

In particular metal complexes such as salen complexes or metalloporphyrins have attracted the attention of researchers due to their good catalytic performance when used simultaneously with a nucleophilic species.[96-99] Porphyrins represent an interesting type of highly conjugated heterocyclic macromolecules with 18-electron π systems. Owing to the presence of four basic nitrogen atoms in the rigid and stable porphyrin ring, the structural feature endows them with excellent metal coordination abilities. Indeed, this type of square-planar coordination site leads to the easy incorporation of the vast majority of metal ions (e.g. Fe, Ni, Co, Zn, Cu, Sn, Al, and Mg) into the porphyrin center, thereby forming stable M-N4 coordination. It has also been proposed that this p-conjugated structure displays high affinity toward various small molecules including CO_2 molecules. Even though these structures allow for good cooperation between Lewis acids and Lewis bases, they always operate at the level of homogeneous catalysis. Therefore, their recovery and reuse are quite costly and tedious. For these reasons, various catalytic systems have been developed over the years that are capable of operating through heterogeneous catalysis. In this context, during last decades poly-ionic-liquids (PILs) have emerged as suitable catalysts for coupling CO_2 with epoxides. In addition, the polymerized ILs have several positive characteristics as catalysts, such as enhanced stability, improved processability, and increased flexibility and durability compared to the non-polymerized one. Han et al. first synthesized an active and insoluble PIL for the fixation of CO_2 into cyclic carbonates, which was supported with 3-butyl-1-vinylimidazolium chloride on a highly cross-linked polymer matrix.[100] Park et al. synthesized highly cross-linked porous poly(N-vinylimidazole-co-divinylbenzene) (PVIm) by suspension polymerization. The

surfaces of the PVIm were then modified with various alkyl halides to obtain various IL-grafted porous polymer beads (PVIm-RX), which were then used as effective heterogeneous catalysts for fixation of CO₂ with epoxides.[101] Moreover, recently in our group Calabrese et al. synthesized different solids based on CNHs as supporting material. Different imidazolium salts bearing bromide (Br⁻) or iodide (I⁻) as counter anion were successfully grafted onto CHNs via one-pot radical polymerization reaction. The solids showed outstanding performance onto the conversion of CO₂ into cyclic carbonates. In this context, different heterogeneous catalysts and co-catalysts have been prepared such as metal organic frameworks (MOFs)[102], covalent organic frameworks (COFs)[103], porous organic polymers (POPs).[104, 105] In particular metal-POPs or MOFs together with a nucleophilic catalyst (generally tetrabutylammonium bromide salt -TBAB-) are often known as binary catalytic systems in the cycloaddition reaction of CO₂ and epoxides. The cooperative effect between Lewis acidic metal sites and halogen anions can promote the CO₂ transformation. Yang and co-workers demonstrated a simple and convenient method for the preparation of porphyrin-based POPs by the direct condensation of pyrrole and aldehydic compounds in propanoic acid (Figure 17a). The synthesized P-POF-Zn showed good activity in presence of TBAB through the conversion of carbon dioxide with propylene oxide. The total conversion of the latter was observed after 5 h of reaction time at 100°C, 15 bar of CO₂ and with a catalyst loading of 0.1% mol.[106] Moreover, Jiang et al. synthesized an Al-MOF that was composed of alternating Al(III)-OH chain SBUs and 4,40-dibenzoicacid-2,20-sulfone linkers (Figure 17b). Al-MOF showed good catalytic activity in the cycloaddition of CO₂ and propylene oxide with the use of TBAB as a co-catalyst at room temperature under 1 bar CO₂ pressure, giving a high yield of propylene carbonate (81%).[107]

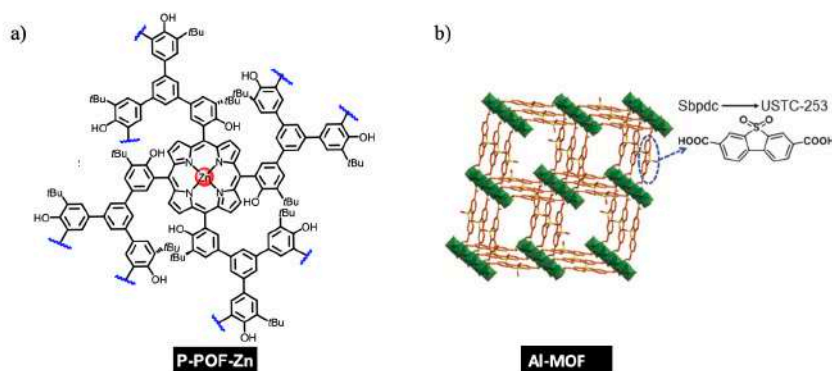


Figure 17. A) P-POF-Zn; b) Al-MOF

Although metal centers within the metal-POPs or MOFs are usually heterogeneous, the employed nucleophiles tend to be homogeneous in the catalytic systems. Thus, nullifying the benefits of using heterogeneous catalysis and making the process less sustainable. Among the different ways of heterogenizing a catalyst, different imidazolium salts and different metal complexes were immobilized on different supports such as carbon nanotubes, silica, alumina and others.[41, 58, 108-112]

In any case, it is fairly well known that materials in which the nucleophilic species is supported, manage to have moderate to average catalytic activity, whereas immobilized metal species alone do not show interesting catalytic activity except when homogeneous co-catalysis is added to the system by a nucleophilic species such as TBAB.

Therefore, a possible solution to this issue could be offered by the preparation of a heterogeneous bifunctional catalyst containing both the metal center and the nucleophilic species.[113-117] Sanjeevi Jayakumar et al. reported the immobilization of a zincporphyrin complexes on mesoporous SBA-15 by a simple one-pot method that involves 5,10,15,20-tetrakis(4-pyridyl)porphyrin zinc(II) (Zn-TPy), SBA-15 and 3-(trimethoxysilyl)propyl bromide (Figure 18).[116] The bifunctional obtained solid showed enhanced catalytic activity compared to the homogeneous counter-part in the conversion of CO₂. Moreover, porphyrin rings offer the possibility of being functionalized and playing a key role in the synthesis of porous and hypercrosslinked copolymers. Thanks to this feature, Yaju Chen et al. reported the synthesis of a bifunctional metalloporphyrin-based ionic

porous organic polymer by using Ni(0)-catalyzed coupling of brominated metalloporphyrin and brominated ILs. The Al/Br⁻ obtained catalyst was able to convert the 97% of propylene oxide in 3h at 40 °C and with a pressure of CO₂ of 10 bar.[118]

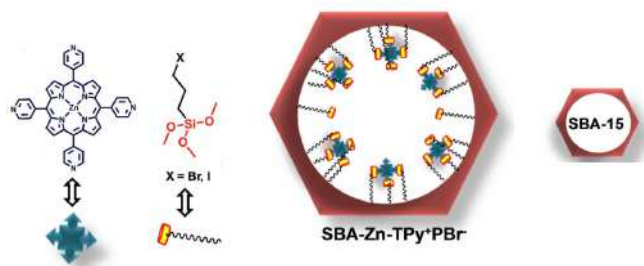


Figure 18. SBA-Zn-TPy⁺Br⁻

In this context, very recently in our laboratories, a polymeric material was synthesized using an Al-porphyrin ring functionalized with vinyl groups and a bis-vinyl imidazolium salt with bromide as counter-anion.[119] Taking advantage of radical polymerization, this copolymer was immobilized through a one pot synthesis on MWCNTs. The material exhibited surprising catalytic properties comparable to or even superior to the individual components. Whether the latter operated in monofunctional or bifunctional homogeneous catalysis. The enhanced catalytic performances of the prepared catalyst could be ascribed to the proximity between the porphyrin core and the bis-vinylimidazolium salt in the 3D polymeric network. This proximity allows a cooperation between the two co-catalytic species which act synergistically during the catalytic cycle as shown in Figure 19.

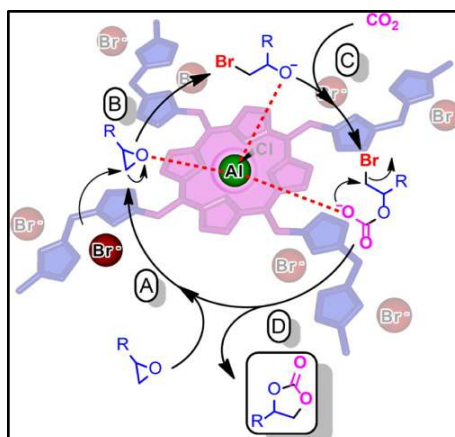


Figure 19.[119] Proposed proximity effect between halide anions (Br⁻) and metal (Al) centers in Imidazolium/Porphyrin catalytic system.

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CHAPTER II:
Objective and Strategies

2.1 Objective and Strategies

The main objective of this doctoral dissertation is the synthesis of hybrid organic-inorganic catalysts for the conversion of CO₂ in added value product such as cyclic carbonates.

As already explained in the previous chapter, this reaction is mainly possible by using high energy molecules such as epoxides in combination with a suitable catalyst. Moreover, the high energy requirement can be further reduced by the coordination of the oxygen of the epoxides with a co-catalytic Lewis acid species. The main focus will be on the design and the preparation of different bifunctional catalytic systems bearing simultaneously both the Lewis acid species and the nucleophilic species. The two elements, if close to each other in the structure of the final solid, can display excellent catalytic activity due to the proximity effect obtained thanks to the structure of the material. This proximity effect may allow to have a synergistic cooperation between the metal center and the nucleophile, thus showing a catalytic activity that could be higher than the corresponding homogeneous species.

During this thesis, all the catalysts were extensively characterized in order to well understand their structure and then, to explain their catalytic behavior.

The work of this project can be divided into two main parts:

- The heterogenization of a new bis-vinyl imidazolium salt in different carbon nanoforms and the study of their stability during catalytic tests and the recycling test of solids.
- The synthesis, characterization and study of the catalytic activity of new bifunctional materials based on polyhedral oligomeric silsesquioxanes (POSS).

2.1.1 First part: Carbon Nanoforms based catalysts

The materials prepared in this first part of the project are carbon nanoforms based materials.

A bis-vinyl imidazolium salt, bearing bromide as counter anion, will be polymerized in absence and in presence of different carbon nanoforms species. The

one-pot radical polymerization process should allow to obtain different heterogeneous materials.

All the materials will be tested in the reaction with CO₂ and styrene oxide. The comparison of the catalytic activity of all the materials will be done by using TON values.

Moreover, a study on the stability of the solids during recycling tests will be done. For these purpose materials will be characterized both in their fresh synthesized state and also, after their reuse in recycling test.

2.1.2 Second part: POSS based catalysts

The second part of this Thesis is focused on POSS based materials.

The main focus on this section will be the use of heterogeneous bifunctional materials.

In particular Chapter IV aims to investigate if the bifunctional heterogeneous material can display better catalytic performance than the separate species.

A porphyrin system complexed with aluminum is selected as Lewis acid source, meanwhile a bis-vinyl imidazolium salts bearing bromine as counter anion as nucleophilic source. The hybrid materials will be synthesized with a polymerization reaction in presence of a POSS cage as building block inorganic core.

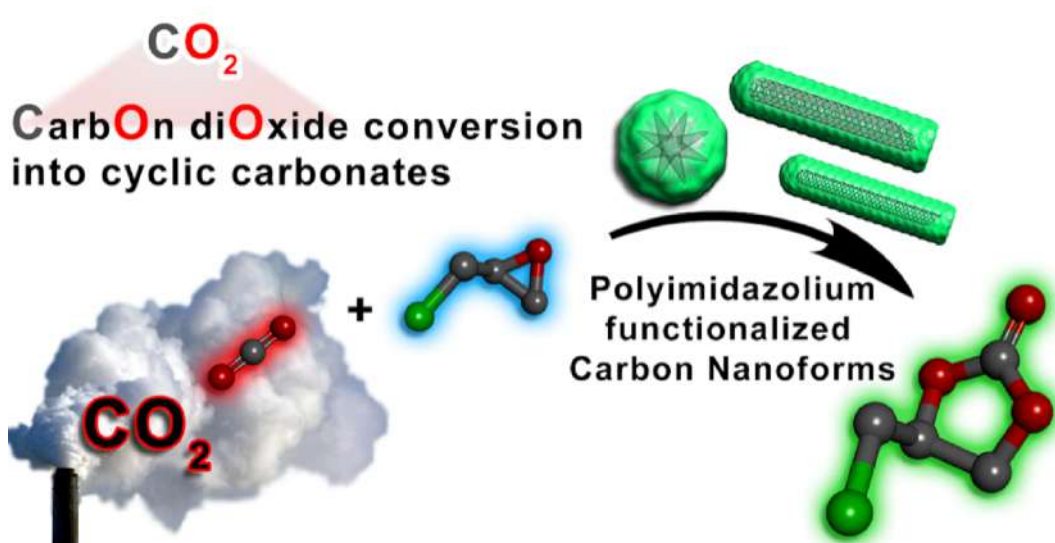
Different catalytic system operating both in homogeneous and heterogeneous conditions will be tested in the reaction between CO₂ and epoxides in order to compare the activity of single species (Lewis acid and nucleophile) with the activity of a heterogeneous bifunctional catalyst bearing in its structure both species simultaneously.

Finally, in Chapter V following the same class of POSS based materials, different POSS-Porphyrin-Imidazolium bifunctional materials will be prepared with the same radical polymerization reaction.

The main goal of this Chapter is to evaluate the co-catalytic effect of two different metals (Al and Zn) and also, the influence of different nucleophilic species (Cl⁻, Br⁻ and I⁻) on the catalytic performances of solids.

CHAPTER III:

Stability of Carbon Nanoforms–Polyimidazolium Network Hybrids in the Conversion of CO₂ into Cyclic Carbonates: Increase in Catalytic Activity after Reuse.



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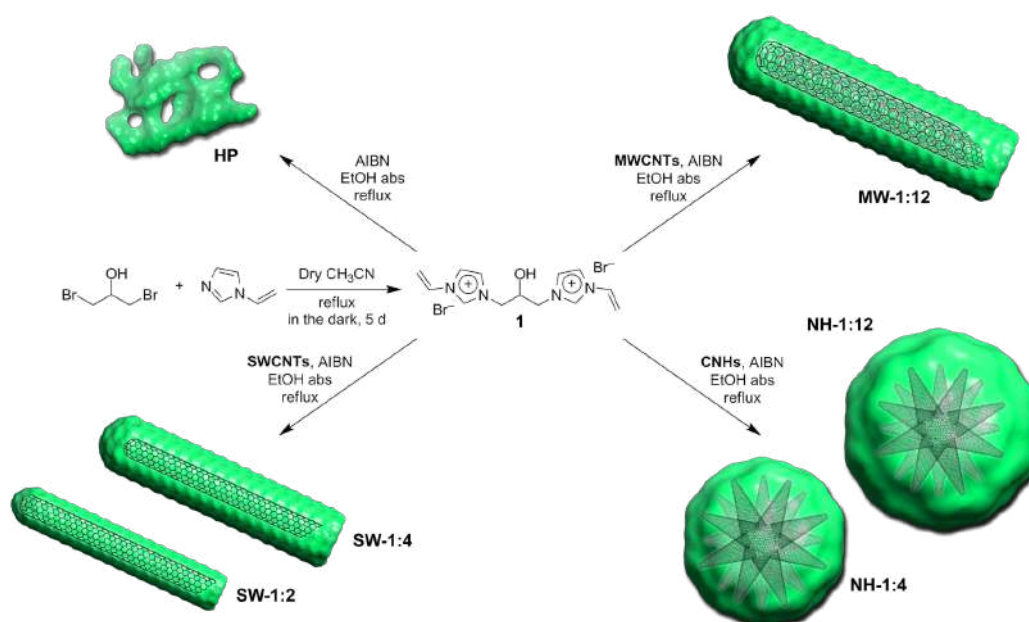
Nanomaterials **2021**, *11*, 2243.

3.1 Abstract

Three different carbon nanoforms (**CNFs**), single-walled and multi-walled carbon nanotubes (**SWCNTs**, **MWCNTs**) and carbon nanohorns (**CNHs**), have been used as supports for the direct polymerization of variable amounts of a bis-vinylimidazolium salt. Transmission electron microscopy confirmed that all **CNFs** act as templates on the growth of the polymeric network, which perfectly covers the nanocarbons forming a cylindrical (**SWCNTs**, **MWCNTs**) or spherical (**CNHs**) coating. The stability of these hybrid materials was investigated in the conversion of CO₂ into cyclic carbonate under high temperature and CO₂ pressure. Compared with the homopolymerized monomer, nanotube-based materials display an improved catalytic activity. Beside the low catalytic loading (0.05–0.09 mol%) and the absence of Lewis acid co-catalyst, all the materials showed high TON values (up to 1154 for epichlorohydrin with **SW-1:2**). Interestingly, despite the loss of part of the polymeric coating for crumbling or peeling, the activity increases upon recycling of the materials, and this behaviour was ascribed to their change in morphology, which led to materials with higher surface areas and with more accessible catalytic sites. Transmission electron microscopy analysis, along with different experiments, have been carried out in order to elucidate these findings.

3.2 Results and Discussion

In order to investigate the role of the support material, onto which the catalytic polymeric network is distributed, we have used three CNFs (*i.e.* SWCNTs, MWCNTs and CNHs) and changed the ratio CNF/poly ionic liquid. In addition, the reference homopolymer (**HP**), *i.e.* the monomer polymerized without the presence of a support, was also synthesized. As poly ionic liquid, we started from the monomer bis-vinylimidazolium salt (**1**), containing a 2-hydroxypropane-1,3-diyl as connecting linker (**Scheme 1**).



Scheme 1. Preparation of all the catalytic materials **HP**, **MW-1:12**, **NH-1:4**, **SW-1:4**, and **SW-1:2**.

Recently, the successful use of hydroxylated imidazolium ionic liquids, as catalysts for the synthesis of cyclic carbonates, has been described both in homogeneous and heterogeneous conditions [1,2]. Beneficial effect on the catalysis stems by the close proximity of three different hydrogen-bond donors, the hydroxyl group and two imidazolium cations, that activate the oxirane ring and stabilize the ring-opened intermediate.

The monomer bis-vinylimidazolium salt (**1**) was readily prepared from 1,3-dibromopropan-2-ol and 1-vinylimidazole. The synthesis of each material (Scheme 1) was performed by in situ polymerization of the same bis-vinylimidazolium salt

(1) in the presence of the proper carbon nanoform. The formation of an imidazolium cross-linked network was achieved using azobisisobutyronitrile (AIBN) as a radical initiator. In Table 1 are reported the catalytic systems prepared.

Table 1. Hybrid materials prepared with their imidazolium loading and specific surface area (SSA).

CATALYST	SUPPORT	1 [mg] (mmol)	SUPPORT / 1 WEIGHT RATIO	IMI ⁺ LOADING [mmol g ⁻¹] ¹	SSA [m ² g ⁻¹] ²
HP	none	[825] (2.03)	–	4.3	<10
MW-1:12	MWCNTs	[600] (1.47)	1:12	3.9	15
NH-1:12	CNHs	[600] (1.47)	1:12	3.8	24
NH-1:4	CNHs	[200] (0.49)	1:4	3.3	<10
SW-1:4	SWCNTs	[400] (0.98)	1:4	3.1	65
SW-1:2	SWCNTs	[400] (0.98)	1:2	2.6	196

¹ Imidazolium loading determined by thermogravimetric analysis. ² See Figures 1.

Catalyst **HP** was prepared without support, catalysts **MW-1:12** and **NH-1:12** were prepared using the same support/bis-imidazolium salt weight ratio (1:12) and using two different supports (MWCNTs and CNHs). Then, the ratio was changed to 1:4 and comparison was made using CNHs and SWCNTs (catalysts **NH-1:4** and **SW-1:4**). Finally, keeping the same support (SWCNTs) the support/bis-imidazolium salt weight ratio was changed to 1:2 (**SW-1:2**). The degree of functionalization of the supported carbon nanoform was estimated by thermogravimetric analysis (TGA, *vide infra*) (Table 1). Loadings were almost similar when the support/bis-imidazolium salt weight ratios were the same; the amount of supported imidazolium salt was, proportionally, slightly higher when a higher ratio was employed. It is worth saying that the radical polymerization is a totally random process. Indeed, it is possible that not all of the polymer will be supported on the chosen carbon nanoform. Indeed, when the monomer to support ratio is high enough, small soluble unsupported polymer or oligomers could be formed and eliminated during the work-up steps. This would explain why materials with identical synthetic monomer to support ratio have similar and not identical catalytic contents in imidazolium species. Moreover, in the case of **NH-1:12** and **NH-1:4** the loading in imidazolium of the two materials is similar despite the important difference in support/monomer

ratio employed to prepare the two solids. This behaviour can be due to the particular morphology of carbon nanohorns. The classical spherical Dahlia shape and the presence of more defects in the walls of the horns compared to the one of carbon nanotubes allows nanohorns to be more reactive and thus raises the chance that the monomer will polymerize on the carbon nanoform. Figure 1 shows the Nitrogen physisorption analysis of the solids. Specific surface areas (SSA) were estimated using the Brunauer-Emmett-Teller (BET) method [3,4]. Estimated SSA values were rather low, in the range $<10 - 24 \text{ m}^2 \text{ g}^{-1}$ except in the case of SWCNT-based materials, where higher values were obtained. Also, it is interesting to note how **SW-1:2** is the only solid that shows a meso-porosity. This can be explained by low monomer-support ratio selected during the synthetic procedure. Probably, the thin layer of polymer formed on the walls in the nanotube favour the presence of meso-pores. However, this mesoporosity is lost as the amount of monomer used during synthesis increases. In fact, after completing the formation of the first polymer layer around the chosen support, the polymer will begin to self-polymerize by thickening and forming dense and compacted layers thereby losing the specific surface area and porosity typical of the selected carbon nanoform. The self-polymerization process is confirmed also on the material **MW-1:12**. From an estimation of the average diameter on the fresh prepared material via TEM analysis (Figure 3; Figure 8) we were able to say that **MW-1:12** shows functionalized-tubes with a diameter of $83 \pm 21 \text{ nm}$ ($n = 110$ counts). This value is quite higher compared to the one of pristine nanotubes, that normally have a diameters values in the rage of 10-30 nm.

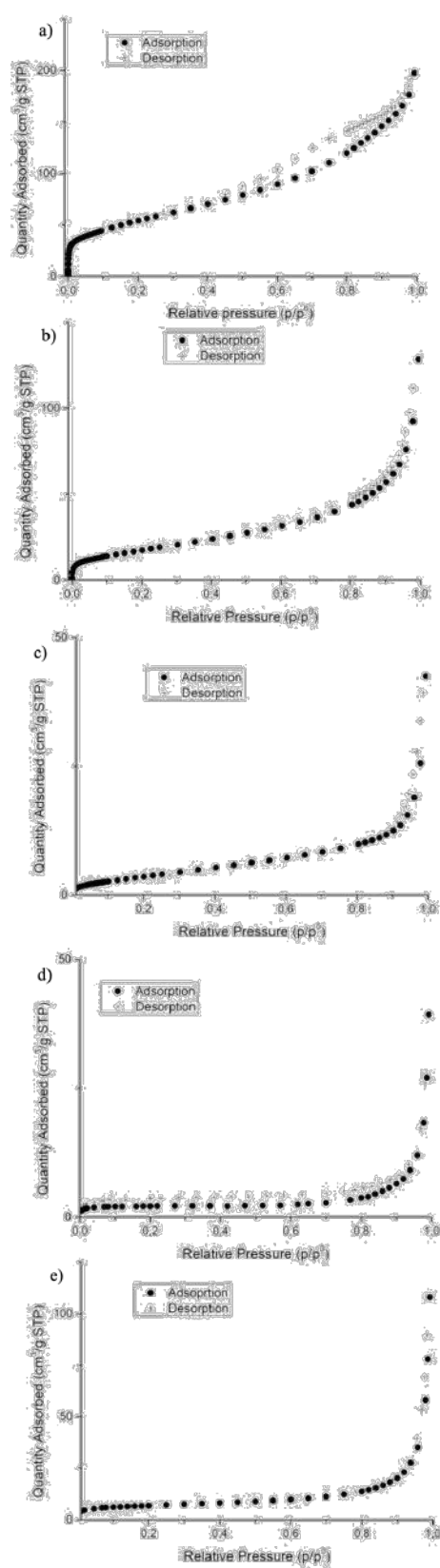


Figure 1. Isotherm of adsorption and desorption of material SW-1:2 (a); SW-1:4 (b); MW-1:12 (c); CNH-1:2 (d) and CHN-1:4 (e).

In Figure 2 the solid-state cross-polarization (CP) ^{13}C -NMR of material **HP** obtained employing a total suppression of spinning side bands (TOSS) pulse sequence is reported. The spectrum displays the presence of the signals of the imidazolium ring centred at 132 and 121 ppm, as well as those of the aliphatic moiety in the 30-70 ppm range.

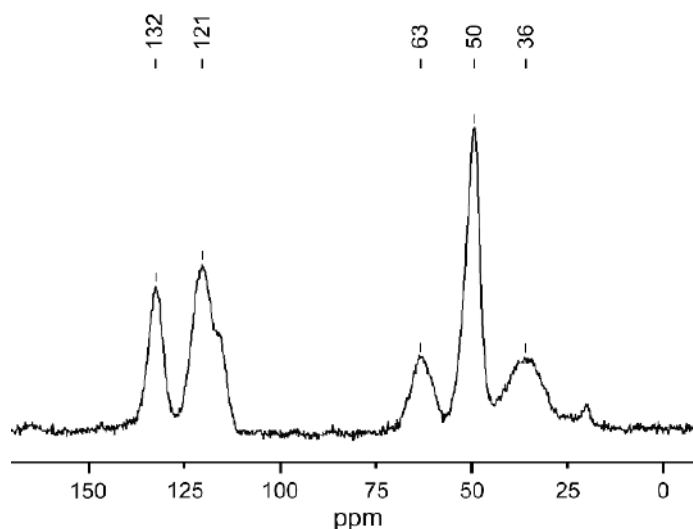


Figure 2. CP-TOSS ^{13}C -NMR solid state of material **HP**.

Transmission electron microscopy (TEM) was used to provide morphological information on all the prepared materials (Figure 3). The micrographs of **HP** show the presence of large and compact aggregates typical of the highly cross-linked homopolymer due to the random nature of the polymerization process (Figure 3a). This compact and amorphous shape is completely lost when the monomer is polymerized in the presence of a carbon nanoform, since they play a templating role during the polymerization. Despite the nature of the CNF and the ratio of support/bis-imidazolium salt **1**, the resulting grafted polymer perfectly covers the used CNF taking its shape, as clearly visible in Figure 2c,e,f,h,i. In this manner the catalytic polymer is spread over a larger area with respect to material **HP** forming a thicker layer as the CNF:**1** ratio increases [5].

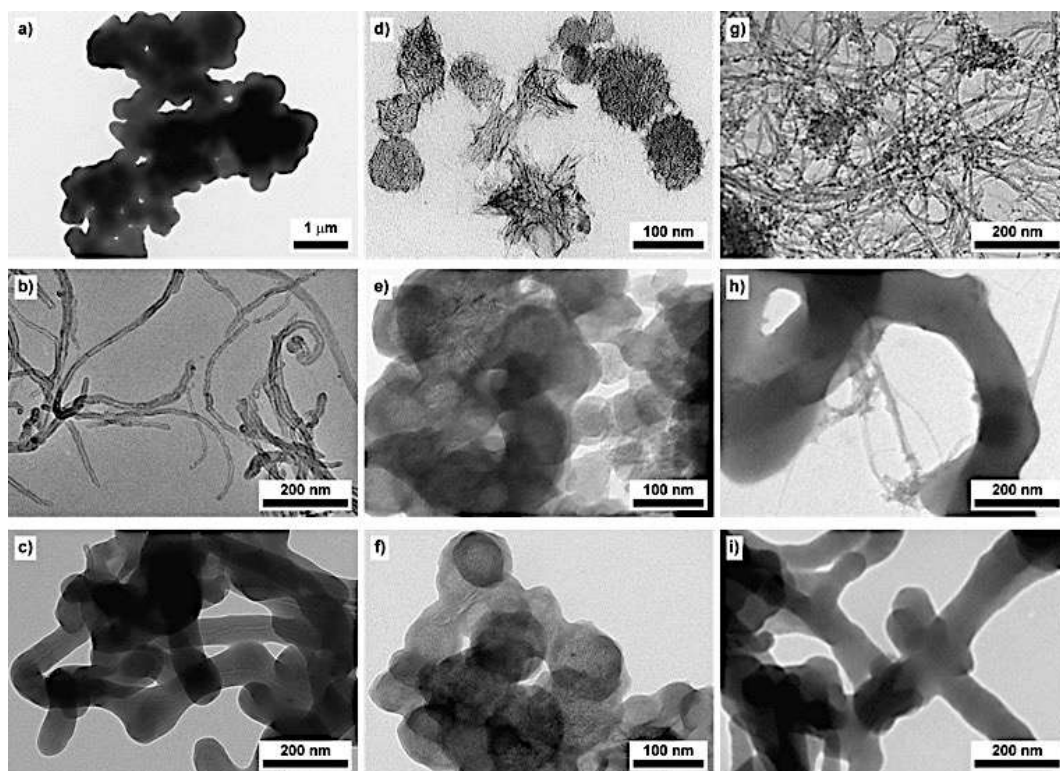


Figure 3. TEM images of: (a) homopolymer **HP**, (b) pristine MWCNTs, (c) **MW-1:12**, (d) pristine CNHs, (e) **NH-1:4**, (f) **NH-1:12**, (g) pristine SWCNTs, (h) **SW-1:2**, (i) **SW-1:4**.

After the preliminary characterization, the solid samples were tested as catalysts for the reaction of epichlorohydrin with CO_2 to give the corresponding cyclic carbonate under solvent-free conditions and without adding Lewis acids as co-catalytic species (Table 2). Due to the different imidazolium loading, the activity of the solids was compared in terms of TON (calculated as moles of epoxide converted/moles of imidazolium bromide). The conversion was estimated by ^1H -NMR analysis of the crudes.

Table 2. Catalytic activity of the hybrid materials in the reaction between epichlorohydrin and CO₂.¹

ENTRY	Catalyst	Loading [mol%]	Conversion [%] ²	TON
1	HP	0.09	49	575
2	MW-1:12	0.08	50	645
3	NH-1:12	0.08	38	504
4	NH-1:4	0.07	36	548
5	SW-1:4	0.06	56	922
6	SW-1:2	0.05	60	1154

¹ Reaction conditions: catalyst 60 mg, epichlorohydrin (306 mmol) CO₂ (40 bar), 150 °C, temperature ramp (1 °C min⁻¹), 3h. ²Determined by ¹H NMR; selectivity toward cyclic carbonate > 95%; yield ≥ 95 % (determined in selected cases by column chromatography of portions of crude reaction mixtures).

It is worth to note that despite the rather low catalytic loading and the absence of any Lewis acid co-catalyst, all the materials showed high TON values and good TOF and productivity (P) values of 385 h⁻¹ and 417, respectively, for entry 6 (P, defined as grams of cyclic carbonates per gram of catalyst). There is not a clear contribution of the CNHs support on the catalytic activity of **NH-1:12** and **NH-1:4** when compared to **HP**, resulting the latter a little more active than the CNH-based materials. On the other hand, CNTs-based catalysts **MW-1:12**, **SW-1:4** and **SW-1:2** showed enhanced activity in the title reaction with **SW-1:2** displaying a TON value double than that of **HP**, thus confirming that the immobilization of the cross-linked poly-bisvinylimidazolium bromide onto carbon nanotubes lead to more active catalysts. The lower activity of **NH-1:12** and **NH-1:4** compared with CNTs-based materials may be due to fact that the resulting hybrids seem to form big aggregates that limit the accessibility to the catalytic sites along with a lower SSA. On the contrary, both covered MWCNT and SWCNTs bundles are quite individualized having a higher number of active sites exposed for the catalysis. Next, the most active catalyst **SW-1:2** has been employed in recycling tests with a more challenging epoxide as styrene oxide. At the end of each catalytic cycle, the

catalyst was easily recovered from the reaction mixture by centrifugation, washed, and reused for the next cycle. The material showed an increase in the catalytic activity during the recycling from the first to the fourth cycle and a subsequent stabilization of the TON value in the fifth cycle while maintaining the selectivity towards cyclic carbonates (Figure 4). This behaviour was observed in a previous work, with a similar material based on polymerized bis-vinylimidazolium salt having a *p*-xylyl linker on CNHs [6].

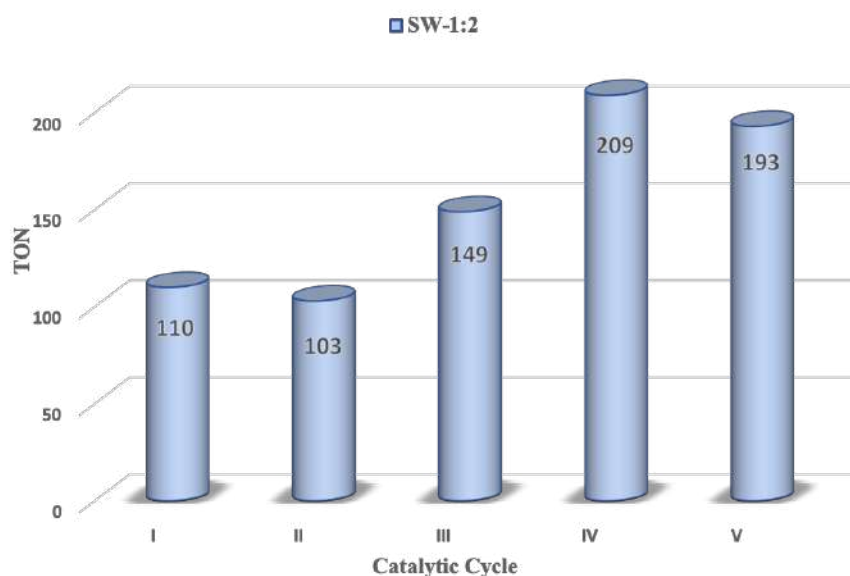


Figure 4. Recycling tests of catalyst **SW-1:2**. Reaction conditions: styrene oxide (209.7 mmol), CO₂ (40 bar), catalyst (300 mg; 0.8 mmol), 150 °C, 3h.

In Figure 5, TGA of fresh and recycled solid **SW-1:2** were compared in order to try to understand the reason of such increased activity upon recycling. Recycling tests were repeated twice in order to confirm the reproducibility of the catalytic behaviour.

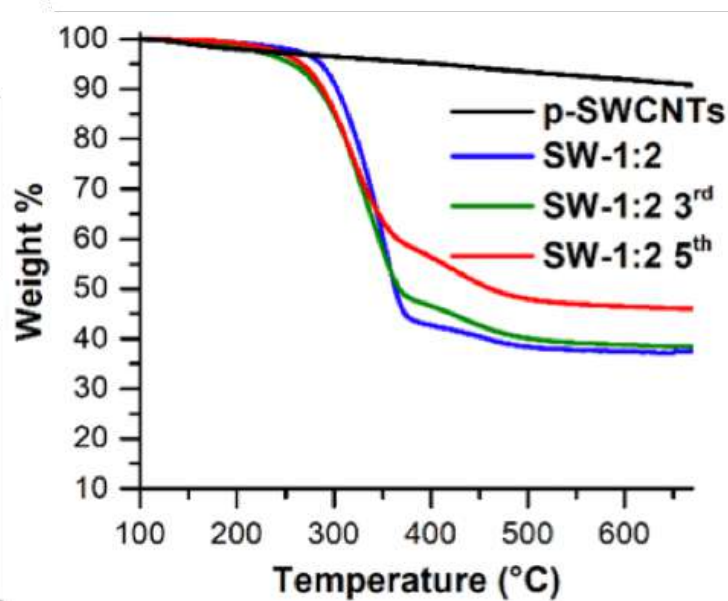


Figure 5. TGA analysis of fresh and reused SW-1:2.

At first, TGA of the fresh catalyst **SW-1:2** was compared with the TGA of same solid after the third cycle; then, two subsequent cycles were performed and the TGA of **SW-1:2** was repeated after the fifth cycle. As the TGA of freshly prepared catalyst shows, the polymeric networks grown on the CNF surface display good thermal stability. Indeed, the degradation of the material started at ca. 250 °C, which could be promising for the possible repeated use under heating regimes. The TGA profile of the hybrid material after three cycles appears very similar to the fresh catalyst with only a minor loss of organic material. On the other hand, TGA of **SW-1:2** after five cycles shows a slightly diminished thermal stability along with a minor weight loss of about 8% reflecting that some polymer has been lost during the recycling tests. Based on these interesting results, we decided to explore the catalytic activity upon recycling of materials **MW-1:12** and **SW-1:4** with styrene oxide for five cycles (Figure 6). As for catalyst **SW-1:2**, the hybrids **MW-1:12** and **SW-1:4** displayed increasing in the catalytic activity from the first to the fourth run with a stabilization in the fifth cycle.

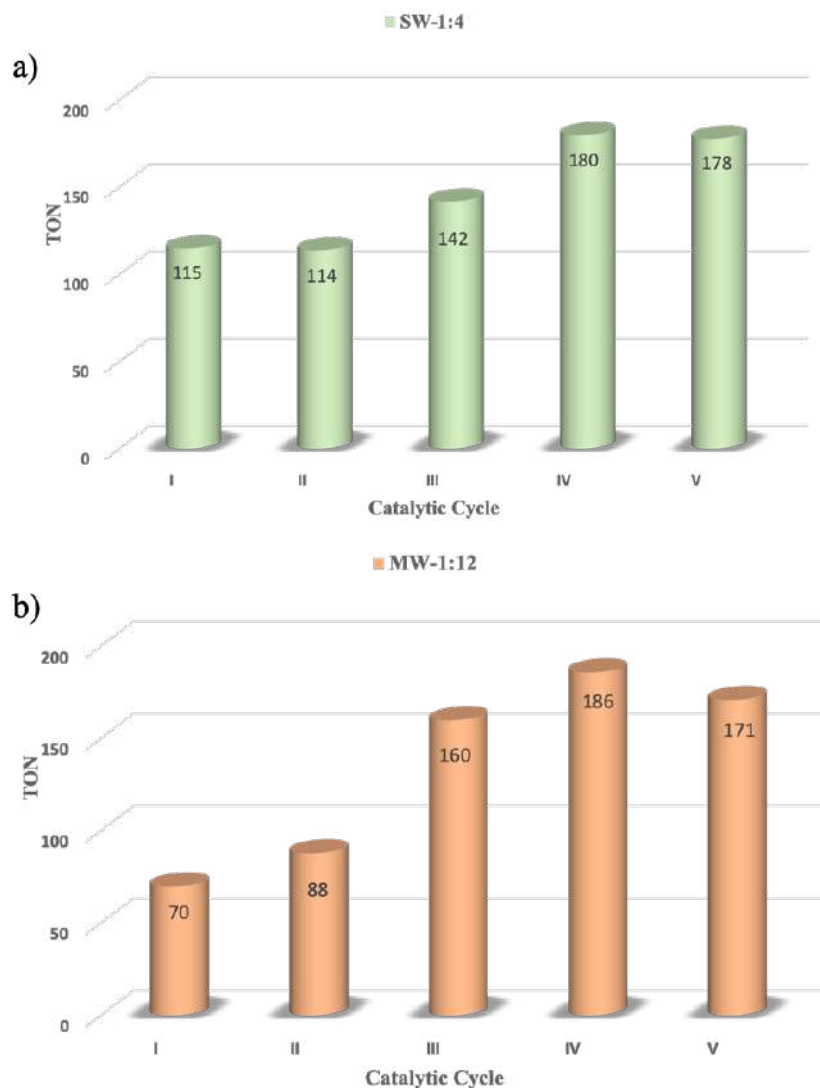


Figure 6. (a) Recycling tests of catalysts **SW-1:4** and (b) **MW-1:12**.

Reaction conditions: styrene oxide (209.7 mmol), CO₂ (40 bar), catalyst (300 mg; 0.9 mmol of **SW-1:4**, or 208 mg; 0.8 mmol of **MW-1:12**), 150 °C, 3h.

Figure 7 shows that also for these two materials, TGA of freshly prepared catalysts show a good thermal stability of the polymeric networks grown on the CNF surface.

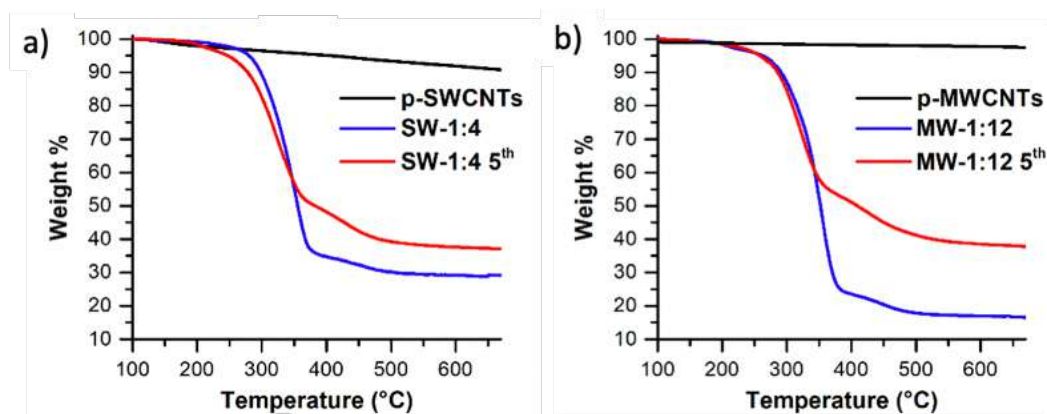


Figure 7. (a) TGA analysis of fresh and reused SW-1:4; (b) fresh and reused MW-1:12.

TGA profile of the hybrid material SW-1:4 after five cycles shows a slightly diminished thermal stability along with a minor weight loss of about 8-9% reflecting that some polymer has been lost during the recycling tests (Figure 7a). Conversely, TGA of recycled MW-1:12 shows that stability is not affected but it suffers of a sensible loss of poly ionic liquid phase during the five runs of ca. 20% (25% of the initial imidazolium loading; Figure 7b).

The results of these additional thermogravimetric analyses therefore led to a further TEM study of the morphology of the materials following the recycling tests. (Figure 8)

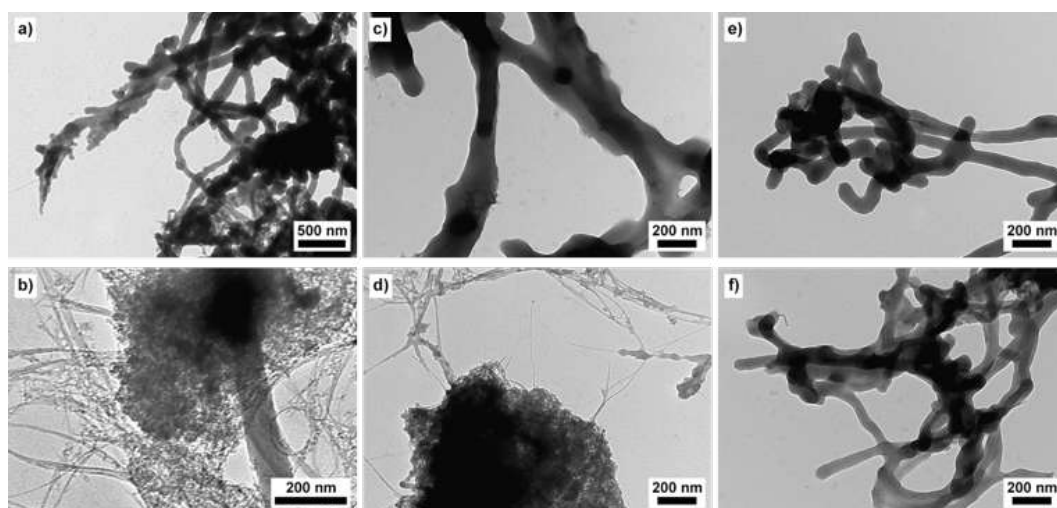


Figure 8. TEM images of fresh catalytic materials SW-1:2, SW-1:4 and MW-1:12 a), c), e) and after the fifth cycle b), d), and f).

In the TEM images of Figure 8 a comparison is made between the morphology of the fresh materials and that of the materials after the fifth cycle. Polymers supported on SWCNTs (**SW-1:4** and **SW-1:2**) showed a similar tendency to underexposure upon mechanical stress during catalytic tests. In this case, morphology of fresh and re-used material is deeply changed. Indeed, regardless of the support/monomer ratio, TEM pictures of re-used materials **SW-1:4** and **SW-1:2** (Figure 8b and 8d) show that the polymeric layer is no longer covering the SWCNTs surface but it is detached leaving the nanotube naked, forming big irregular aggregates constituted of small nanoparticles of crumbled poly-imidazolium bromide phase trapped on the SWCNTs network. On the one hand this finding justifies the small loss of organic material pointed out in the TGA analyses. On the other hand, it may explain the increasing activity since the resulting heterogeneous materials possess a higher amount of exposed and accessible catalytic sites after crumbling. In this regard, estimation of specific surface area of recycled **SW-1:4** after five cycles indicates an increasing value from 65 to 114 m²g⁻¹, whereas only a slight decrease was observed for **SW-1:2** (from 196 to 166 m²g⁻¹). Conversely, the images of the catalyst based on the MWCNTs (**MW-1:12**, Figure 8e, f) show how this material is quite mechanically resistant since its morphology is maintained during the reaction cycles thanks to a thicker polymeric coating resulting both from a higher monomer/MWCNTs ratio and a reduced number of nanoobjects to be covered in comparison with SWCNTs. An estimation of the average diameter on the fresh and used hybrid revealed that whereas the former value is 83±21 nm (n = 110 counts), the reused **MW-1:12** displays a lower value of 59±25 nm (n = 77 counts). Due to its more compact shape, some of the outer and fragile layers of the polymeric coerture is peeled off during the mechanical stirring just thinning the organic layer without affecting its morphology. The above finding is in very good agreement with the loss of organic material highlighted in TGA (Figure 7b). In addition, SSA value of **MW-1:12** increased from 15 to 53 m²g⁻¹ after five cycles.

On the grounds of these findings, additional experiments have been carried out with the aim to discern whether our materials act as pure heterogeneous catalysts or if a simultaneous action of heterogeneous and homogeneous catalysis, due to leaching phenomena, is taking place. It is worth saying that whenever the catalyst was

recycled, the ratio of the moles of epoxide to the amount of material was always respected. The amount of epoxide was decreased each time an amount of material was lost. In these cases, TON values were calculated on the basis of the amount of material weighed.

Figure 9 shows ^1H -NMR spectra of first, third and fifth cycles of reaction carried out with catalyst **SW-1:4** were analysed in order to investigate if released imidazolium species, which could act as homogeneous-like catalytic species, are present in the reaction mixture. Such spectra show very little signals that could be related to imidazolium species.

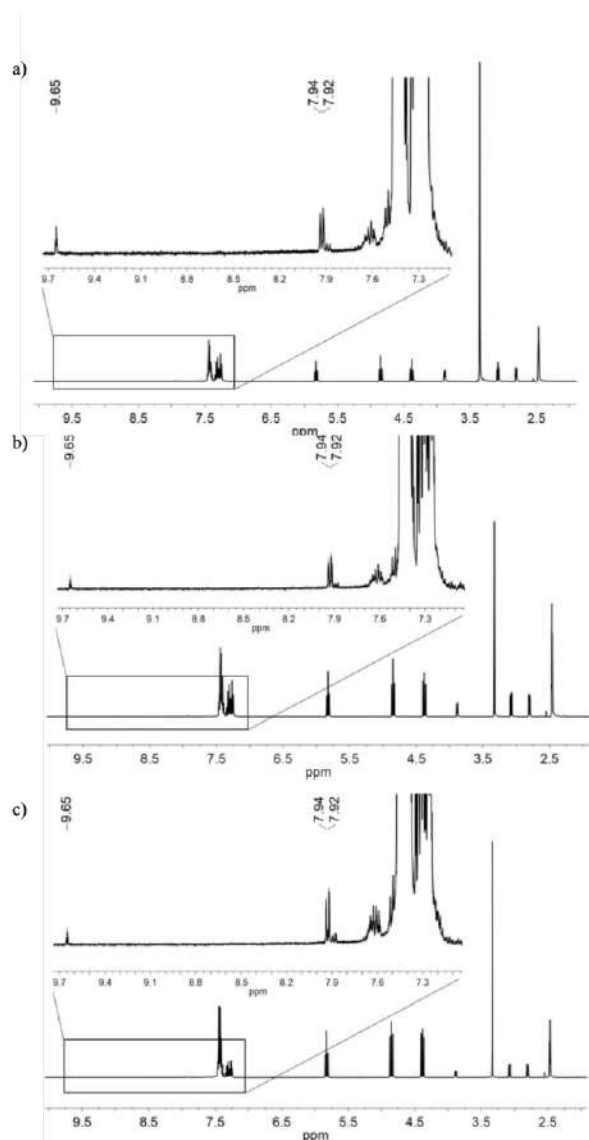


Figure 9. NMR spectra of I (a); III cycle (b) and V cycle (c) of the reaction between CO_2 and styrene oxide catalyzed by **SW-1 :4**.

Then, trying to explain the origin of the increased activity in recycling, further tests were carried out (Table 3).

Table 3. Additional experiments for establishing leaching contributes.

TEST TYPE	BEFORE REACTION (CONV. %) ¹	AFTER REACTION (CONV. %) ¹	ΔCONV. [%]
TEST 1 ¹	0	50	50
TEST 2 ²	50	78	28
TEST 3 ³	78	89	11
TEST 4 ⁴	0	34	34
TEST 5 ⁵	34	56	22
BLANK 1 ⁶	0	3	3
BLANK 2 ⁷	50	54	4
TEST 6 ⁸	0	17	17

¹ Same reaction between styrene oxide and CO₂ with catalyst SW-1:4 second cycle (see Table S2).

² Test performed with the reaction mixture of test 1 after removing the solid catalyst by centrifugation and filter the liquid mixture with a 0.2 μm filter. ³ Test performed with the reaction mixture of test 2 after filtering the liquid mixture with a 0.2 μm filter. ⁴ Reaction between styrene oxide and CO₂ with catalyst MW-1:12 second cycle. ⁵ Test performed with the reaction mixture of test 4 after removing the solid catalyst by centrifugation and filter the liquid mixture with a 0.2 μm filter. ⁶ Blank test: Test performed only with styrene epoxide (209.7 mmol), no catalyst, 150 °C, 3h.

⁷ Test performed with a mixture 50/50 [styrene carbonate/styrene oxide] and no catalyst. ⁸ Reaction condition: styrene oxide (209.7 mmol), CO₂ (40 bar), bis-vinylimidazolium dibromide 1 as catalyst (21.3 mg), 150 °C, 3h. I Selectivity >99%.

Test 1 corresponds to the second cycle carried out using styrene oxide in the presence of catalyst **SW-1:4** at 0.44 mol% loading. After 3 h at 150 °C a 50% conversion was obtained. Then, the solid catalyst was removed by centrifugation. Recovered catalyst **SW-1:4** was used for completing the recycling investigation whereas the supernatant was filtered using a 0.2 μm filter. Hence, the filtered mixture was allowed to react in the presence of CO₂ at 40 bar, 150 °C for 3h (*i.e.*, the usual reaction conditions) without any catalyst (Test 2). An additional 28% conversion increase was observed being the total conversion equal to 78%, representing a 56% conversion of the styrene oxide of the mixture. Although no visible particles were present, the mixture was filtered again through a 0.2 μm

membrane and a subsequent cycle was carried out, still without adding any catalyst. The final conversion was 89% with a further 11% increase in the conversion, a 50% of the remaining styrene oxide (Test 3). These results indicate that in the reaction mixture small oligomeric species smaller than 0.2 μm was present and possess catalytic activity. These polymeric species can be large enough to have broad and not highly intense signals from an NMR point of view hence not visible when recording ^1H -NMR spectra. Similar experiments were run with the filtered reaction crude of a second cycle in which catalyst **MW-1:12** was employed. Once again, an additional 22% conversion increase was noticed (Tests 4 and 5).

To dispel the last doubts, two blank experiments were also carried out, in order to exclude any possible transformation in the absence of catalysts under the adopted reaction conditions. The reaction carried out without catalyst showed a conversion of about 3 %. (Blank 1). A similar conversion was obtained when the reaction without catalyst was carried out using a 50/50 epoxide/carbonate mixture, just to exclude any possible concomitant autocatalytic process (Blank 2). These experiments indicate that leaching of catalytic species from the material is taking place, though the nature of the leached species is not clear. However, for the sake of clarity, the above species once leached are lost and absent in the subsequent cycles.

In order to evaluate the contribution of soluble leached species (*i.e.*, the bis-imidazolium unit), a homogeneous test was carried out using the starting bis-vinylimidazolium dibromide compound **1** as catalyst. This experiment was carried out by employing an amount of monomer **1** comparable to the material loss estimated by TGA (Test 6). Surprisingly, although the test shows a conversion of 17%, this result is much lower than those obtained with the leached species, excluding a strong contribution of homogeneous catalysis during the tests with the hybrid materials.

Hence, it can be assumed that for the CNTs-based catalysts, the mechanical disintegration of the active material into really fine particles able to pass through the 0.2 μm filter along with the increased specific surface area is responsible for the enhanced catalytic activity during the recycling. The crumbled (or peeled in the case of **MW-1:12**) cross-linked polymer has an improved accessibility for the

reactants to the catalytic sites with respect to the compact fresh polymer, but at the same time it is catalytically more active than the parent monomer, displaying a kind of synergetic action due to the concentration effect of active sites [7].

3.3 Conclusions

Three different CNFs, namely SWCNTs, MWCNTs, and CNHs were used as support for the polymerization of a bis-vinylimidazolium salt. All the materials prepared were characterized by means of several analytical and spectroscopic techniques and tested in the reaction between CO₂ and epoxides to form cyclic carbonates with the aim to investigate their stability under the reaction conditions adopted under repeated use. The comparison between the catalytic activity of the homopolymerized bis-vinylimidazolium salt and the CNFs-based materials showed that, in the present case, carbon nanohorns had no beneficial effect towards the synthesis of cyclic carbonates, whereas MWCNT-, and SWCNT-based materials showed an improved catalytic activity. Interestingly, both homopolymerized bis-vinylimidazolium salt and the CNFs supported materials were more active than the homogeneous bis-vinylimidazolium salt monomer, and this behaviour was probably due to the high local concentration of imidazolium moieties in such materials. The use of a supports increases the concentration of active sites localized in close proximity. This could explain the enhanced catalytic performances of the supported materials compared to the unsupported bis-vinylimidazolium salt. Recycling studies revealed that, for all the nanotube-based materials, the catalytic activity increases during reuse. Additional characterizations on the recycled catalysts with TEM, TGA and specific surface analyses showed that the SWCNT-based materials **SW-1:2** and **SW-1:4** suffer of a severe morphology change with the disintegration of the polymeric network, whereas **MW-1:12**, probably due to its higher polymeric loading, maintains its initial shape even if with a thinner polymeric coverture. Further experiments proved that there was a partial leaching into solution of the polymeric coating of the different CNF-supported materials. The leached species, though not clear in nature, showed a good catalytic activity, much higher than the monomer bis-imidazolium salt. However, despite the loss of part of the polymeric coating (proved by TGA), both MWCNT-, and SWCNT-based materials displayed an increase in catalytic activity during the recycling ascribed to their change in morphology that led to materials with higher surface areas and more accessible catalytic sites and to the contemporary presence of leached species. Further studies on the nature of such leached species may lead to

the development of new powerful catalytic systems for the synthesis of cyclic carbonates. The next step in our investigation is to better understand the nature of this leached species and also to keep ongoing with poly-imidazolium salts. In particular the object will focus on changing support in order to have a better stability to the mechanical stress of the material during catalytic tests. As mentioned in the introduction Chapter of this Thesis, POSS nanocages seem to be ideal candidates to solve this issue due to their rigidity and their thermal stability. Moreover, the possibility to have organic functionalities at the vertices of the cage structure allows selecting functionalized POSS such as the octavinylsilsesquioxane that is reactive to the radical polymerization process.

3.4 Experimental Section

Materials and Methods

Chemicals and solvents were purchased from commercial suppliers to be used without further purification. 1-Vinylimidazole (>98%), epichlorohydrin (>99%) and styrene oxide (>98%) were purchased from TCI Chemicals (Zwijndrecht, Belgium), 1,3- dibromopropan-2-ol (95%) was purchased from Sigma-Aldrich (Milan, Italy), azobisisobutyronitrile (AIBN) (98%) was purchased from Fluka (Milan, Italy) and recrystallized before use. CNHs were purchased from Carbonium (Selvazzano Dentro, Italy), SWCNT were purchased from Nanocyl (Sambreville, Belgium), MWCNT (10-30 nm) were purchased from Iolitec (Heilbronn, Germany). Absolute ethanol (>99.8%) and acetonitrile (99.9%) were purchased from VWR International (Milan, Italy). Nitrogen adsorption–desorption analyses were carried out at liquid nitrogen temperature with a volumetric adsorption analyser (Micromeritics 3Flex). Prior to the analysis, the samples were pre-treated at 90 °C for 1 h and then at 150 °C for 8 h under vacuum ($< 10^{-5}$ Torr). The Brunauer–Emmet–Teller (BET) method was applied in the 0.05–0.30 relative pressure range to calculate the specific surface area. Thermogravimetric analysis was performed on a Mettler–Toledo instrument in a sapphire crucible. The sample is allowed to stabilize at 100 °C for 30 min under a N₂ flow (60 mL/min). The oven heats up to 900 °C with a rate of 10 °C/min under N₂ flow (60 mL/min). Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai 10 microscope operating at 80 kV. Samples were prepared by dispersion of a small quantity of material in absolute ethanol and deposited onto a copper grid. All the solid-state MAS NMR experiments (¹³C) were performed at room temperature on a Bruker Avance 500 Spectrometer operating at 11.7 T, using a Bruker probe of 4 mm. CP-MAS-TOSS ¹³C-NMR spectra were recorded using a contact time of 2 ms and a spinning rate of 5 KHz. The chemical shift scale was calibrated with respect to a sample of adamantane. Liquid state ¹H NMR spectra were collected on a JEOL ECA spectrometer, operating at 9.4 T (400 MHz).

Synthesis of monomer Bis-Vinyl Imidazolium Salt 1

In a 50 mL flask, equipped with a magnetic stirring bar, 5 mmol of 1,3-dibromopropan-2-ol, 16 mmol of 1-vinylimidazole and 15 mL of acetonitrile were introduced. The system was sonicated for 10 min while simultaneously bubbling argon. The reaction mixture was refluxed at 80 °C for 5 days in a dark environment. When the reaction was complete, a highly viscous brown liquid formed. The solvent was removed under vacuum and the residue was solubilized in a small amount of methanol and precipitated with diethyl ether. The whole procedure of solubilization and precipitation was repeated several times. Once purified, the compound appeared as a white solid. Finally, the compound was dried under vacuum (4×10^{-4} mbar) at a temperature of 60 °C overnight. Yield 96%. ^1H -NMR (400 MHz, DMSO- D_6) δ 9.54 (s, 2H), 8.25 (s, 2H), 7.92 (s, 2H), 7.35 (dd, $J = 15.8, 8.8$ Hz, 2H), 6.02 (d, $J = 6.2$ Hz, 1H), 5.98 (dd, $J = 15.8, 2.4$ Hz, 2H), 5.41 (dd, $J = 8.8, 2.4$ Hz, 2H), 4.48 (dd, $J = 13.7, 2.8$ Hz, 2H), 4.30 (m, 1H), 4.18 (dd, $J = 13.6, 8.1$ Hz, 2H). ^{13}C -NMR (101 MHz, DMSO- D_6) δ 136.56, 129.35, 124.47, 119.46, 109.38, 67.84, 52.67.

Synthesis Homopolymer HP

In a 50 mL flask, equipped with a magnetic stirring bar, 0.812 g (2 mmol) of previously synthesized monomer 1, 0.033 g (0.2 mmol) of freshly recrystallized AIBN, and 15 mL of absolute ethanol were introduced. The system was placed under reflux overnight. At the end of the reaction, a white precipitate was formed. The homopolymer was purified by washing with hot methanol to remove traces of unreacted monomer. A final wash with diethyl ether was carried out and then the material was vacuum (4×10^{-4} mbar) dried at 60 °C overnight.

Synthesis of CNHs-1:12 and CNHs-1:4

Pristine CNHs (50 mg) were transferred to a 50 mL flask, equipped with a magnetic stirring bar. Absolute ethanol (15 mL or 10 mL) was added to the flask and the system was allowed to sonicate for 20 min. Bis-vinylimidazolium salt 1 (1.47 mmol or 0.49 mmol) was added to the CNHs. Argon was bubbled into the mixture for 10 min. Freshly recrystallized AIBN (5 mol% per vinyl group) was added to the

reaction mixture, which was then refluxed and stirred at 78 °C overnight. The hybrid solid material was recovered by filtration through a 0.1 µm membrane filter. The functionalized CNHs were washed with hot methanol, recovered from the filter, sonicated in methanol for 10 min, and filtered. This procedure was repeated several times. The last wash was performed with diethyl ether. The catalyst was dried under vacuum (4×10^{-4} mbar) at 60 °C overnight.

Synthesis SW-1:4 and SW-1:2

Pristine SWCNTs (100 or 200 mg) were transferred to a 50 mL flask equipped with a magnetic stirring bar. Absolute ethanol (10 mL) was added to the flask and the system was allowed to sonicate for 30 min and stirred at room temperature overnight. Bis- vinylimidazolium salt 1 (406 mg; 1 mmol) was added to the SWCNTs. The dispersion was sonicated for 20 min. Argon was bubbled into the mixture for 10 min. Freshly recrystallized AIBN (0.1 mmol, 5 mol% per vinyl group) was added to the reaction mixture, which was then refluxed and stirred at 78 °C overnight. The solid hybrid material was recovered by centrifugation. The functionalized SWCNTs were washed several times with hot methanol. Before each centrifugation, materials were sonicated for 15 min in the washing solvent. The last wash was performed with diethyl ether. The catalyst was dried under vacuum (4×10^{-4} mbar) at 60 °C overnight.

Catalytic Tests

Catalytic tests were performed in a Cambridge Design Bullfrogbatch reactor with temperature control, pressure monitoring and mechanical stirring, designed to operate at high temperature and pressure. In a typical experiment, the catalyst was highly dispersed in the epoxide and the reactor was closed, the mechanical stirring speed was set to 500 rpm. The system was purged with N₂ for 10 min and then pressurized with CO₂. The temperature was increased with a ramp of 1 °C/min and maintained 150 °C for 3 h. The reaction mixture was recovered and centrifuged to separate the solid catalyst from the reaction mixture. The supernatant solution was analysed by ¹HNMR spectroscopy.

Recycling Tests

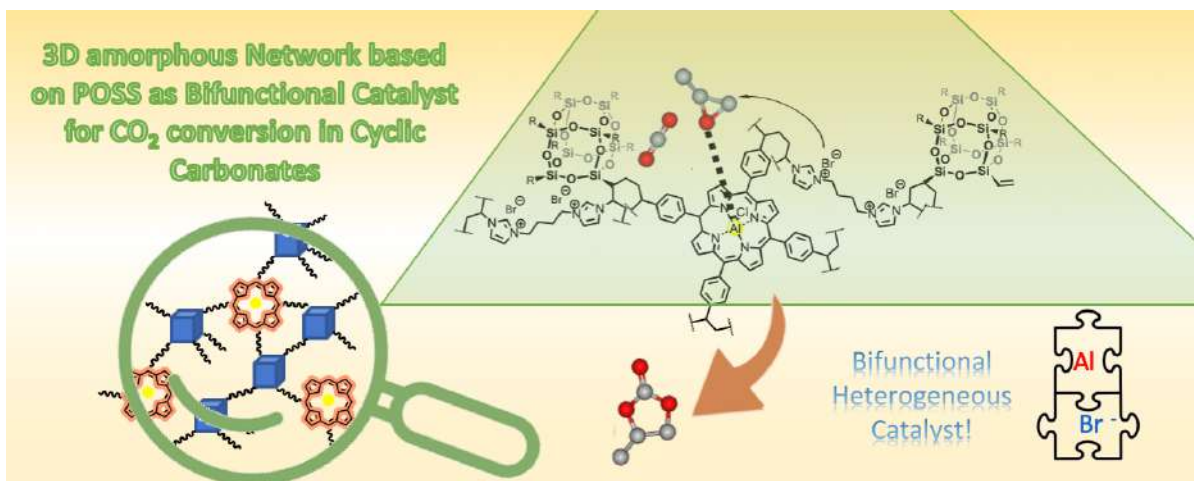
The recyclability of the catalyst was tested for the reaction between styrene oxide and CO₂. The catalyst was recovered by centrifugation and washed several times with toluene and ethanol. Before each centrifugation, it was sonicated for 15 min in the washing solvent. The last wash was performed with diethyl ether. The catalyst was dried under vacuum (4×10^{-4} mbar) at 60 °C. Once dried, it was used for the next cycle. Conversions were estimated by analysis ¹H NMR.

3.5 References

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CHAPTER IV

POSS-Al-porphyrin-imidazolium cross-linked network as catalytic bifunctional platform for the conversion of CO₂ with epoxides.



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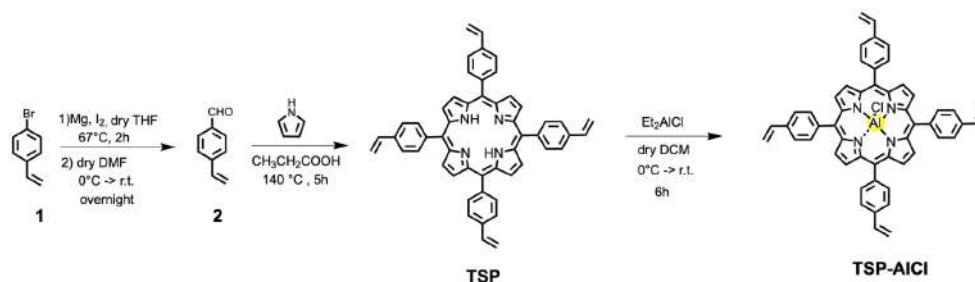
4.1 Abstract

Two heterogeneous catalysts were prepared with the aim of following the promising path of CO₂ fixation onto epoxides. The synthetic procedure involves a radical copolymerization of an octavinylsilsesquioxane as inorganic core building block and tetrastyrilporphyrin aluminum chloride monomer (**TSP-AlCl**) in presence (**POSS-TSP-AlCl-imiBr**) or in absence (**POSS-TSP-AlCl**) of a bis-vinylimidazolium bromide salt (**bis-imiBr**), in order to investigate if the bifunctional heterogeneous material can display better catalytic performance than the separate species. All the solids were fully characterized and tested in the synthesis of cyclic carbonates starting from CO₂ and several epoxides. The synergic cooperation of the two co-catalytic species (Lewis acid/imiBr) was observed. **POSS-TSP-AlCl-imiBr** showed to be a recyclable material with an excellent activity and TON and TOF values up to 16000 and 5000, respectively. These excellent results, even under mild reaction and solvent-free conditions, were attributed to a twofold effect: the proximity between the two active sites due to the direct covalent bond between the porphyrin and the imidazolium component and the increasing local concentration of active sites effect that is obtained by functionalizing the silica cage at all its vertices.

4.2 Results and Discussion

Continuing the desire to test the amazing catalytic performance of imidazolium salts towards the conversion of CO₂ into cyclic carbonates, two new POSS-based polymeric materials were prepared. As already described in the introduction to this manuscript, POSS are excellent building blocks for the synthesis of polymeric materials. Moreover, in order to be able to perform the reaction under milder conditions, a bifunctional material was prepared by introducing a porphyrin ring, suitably functionalized, complexed with aluminium to the polymer system. The synthesis of the material was conducted by exploiting the possible polymerization of the vinyl groups present in the three components.

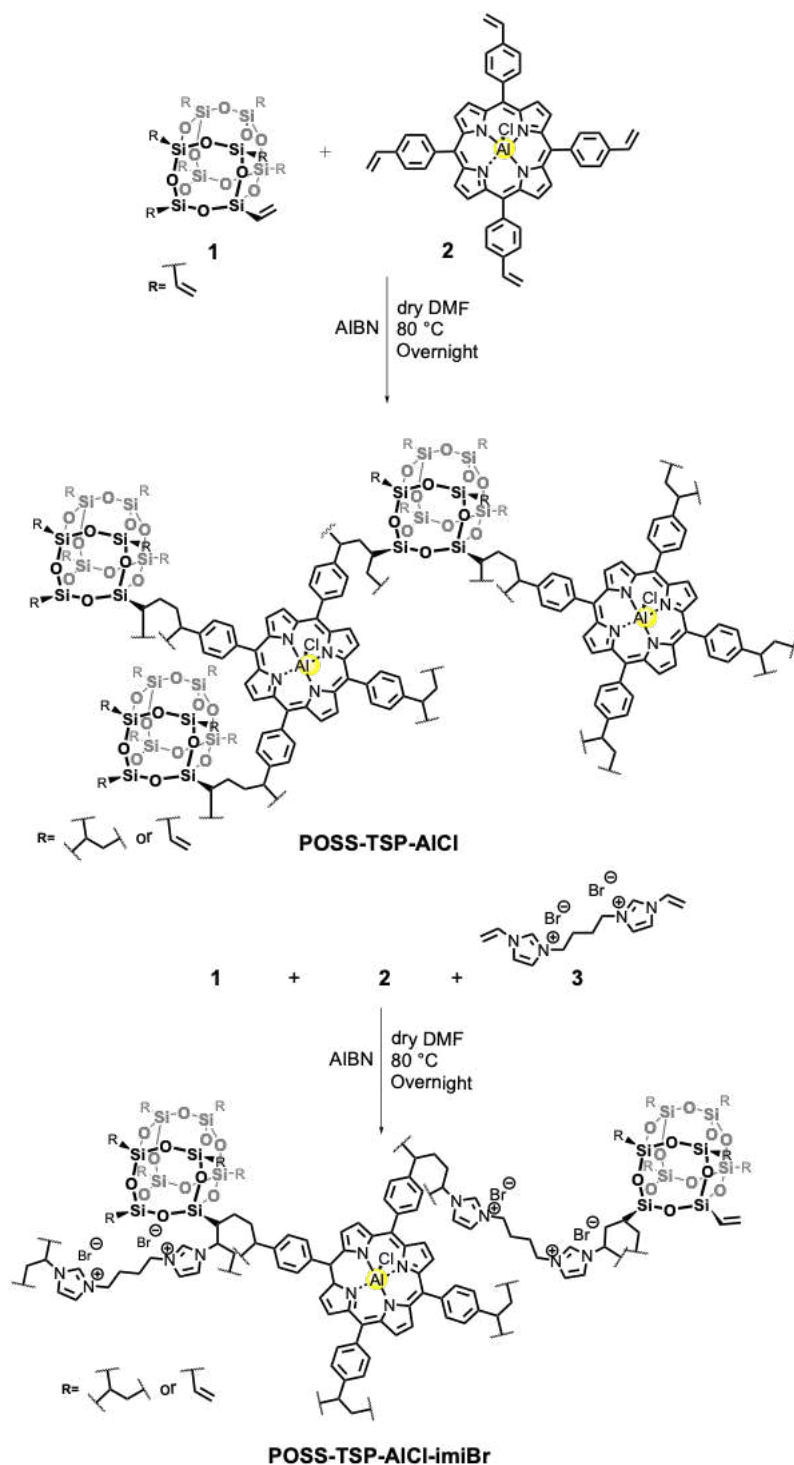
Tetrastyrilporphyrin (**TSP**) was obtained as shown in Scheme 1. Formylation of Grignard reagent arising from 4-bromostyrene **1** with dimethylformamide (DMF) gave 4-vinylbenzaldehyde **2**. Subsequently, **2** was reacted with pyrrole in propionic acid to obtain tetrastyrilporphyrin (**TSP**) through a cyclization process made up of a series aldolic reactions. The following reaction of **TSP** with Et₂AlCl led to the formation of tetra-styrilporphyrin aluminium chloride (**TSP-AlCl**) complex.



Scheme 1. Synthesis of tetrastyrilporphyrin aluminium chloride complex (**TSP-AlCl**).

TSP-AlCl complex was subsequently copolymerised with octavinyl-POSS by using α - α' -azoisobutyronitrile (AIBN) as radical initiator. The reactivity of vinyl groups in this radical reaction allowed obtaining the material **POSS-TSP-AlCl** and the material **POSS-TSP-AlCl-imiBr** when the polymerization process was carried out in presence of the bis-vinylimidazolium salt (**bis-imiBr**). The synthesis of material **POSS-TSP-AlCl** containing only the Lewis acid species was performed

to explore whether the simultaneous presence of both the nucleophilic species and the co-catalytic Lewis acid in the catalytic platform **POSS-TSP-AlCl-imBr** may lead to a synergic cooperation. The synthetic pathway chosen can have a double aspect. On the one side, the presence of POSS cages may allow to have an increased local concentration of catalyst or co-catalyst active sites in the system due to the functionalization of vinyl moieties in all the eight vertices. This vinyl groups can react with the vinyl groups of both porphyrin and imidazolium salt molecules. On the other side, the synthesis was performed with an excess of nucleophilic species compared to the Lewis acid species in order to enhance the selectivity through cyclic carbonates, according to literature (see Chapter I, paragraph 1.3.1). This excess of imidazolium species may allow for a better chance of forming covalent bonds with porphyrin rings via radical polymerization process and thus, enhance the possibility to maximize the synergistic cooperation between aluminium and bromide species. (Scheme 2)



Scheme 2. Synthesis of **POSS-TSP-AICl** and of **POSS-TSP-AICl-imiBr**.

The two materials **POSS-TSP-AICl** and **POSS-TSP-AICl-imiBr** were characterized via different techniques including ^{13}C and ^{29}Si cross-polarization magic angle spinning (^{13}C and ^{29}Si CP-MAS) NMR spectroscopy. ^{29}Si solid state

NMR spectra (Figure 1) of **POSS-TSP-AlCl-imBr** and **POSS-TSP-AlCl** revealed the presence of two main contributions centred at -65 and -79 ppm which can be both assigned to the T8 POSS cage with condensed structure. The two signals can be attributed to the ^{29}Si atoms linked to alkyl groups of reacted vinyl moieties (alkyl-Si) and unreacted vinyl groups (vinyl-Si), respectively. This interpretation agrees with the NMR data of POSS structures previously reported in the literature [1]. Moreover, it is reasonable to think that not all the vinylic moieties of the POSS reacted due to the steric hindrance obtained when POSS nanocages are functionalized with organic molecules such as porphyrin rings.

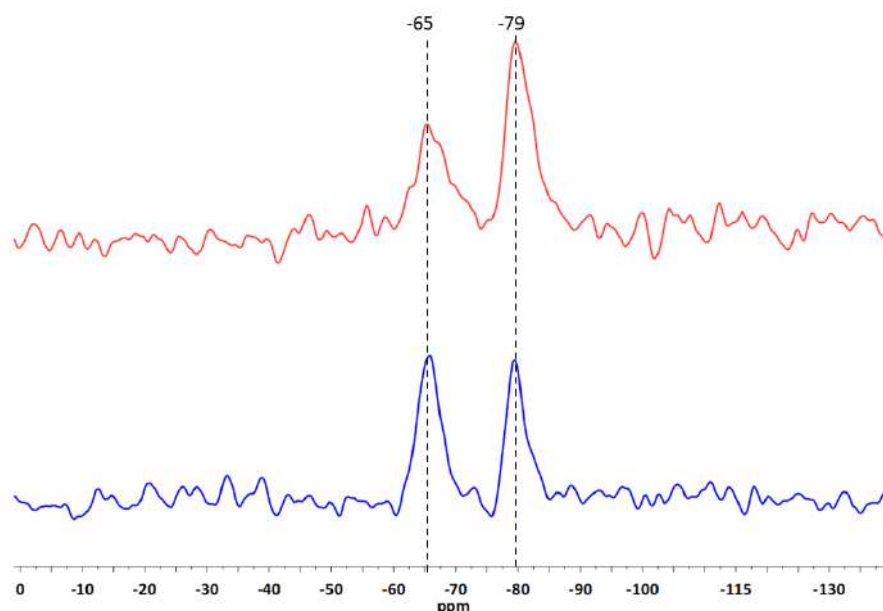


Figure 1. Solid state CP-MAS ^{29}Si NMR of **POSS-TSP-AlCl-imBr** (Blue Line) and **POSS-TSP-AlCl** (Red Line).

^{13}C Solid state NMR spectra of both materials (Figure 2) display the signals attributed to the carbon atoms of the porphyrin together with those of the imidazolium moieties and not reacted vinyl groups in the 115-150 ppm region. The contributions present in the 20-60 ppm region are assigned to the aliphatic carbon atoms generated upon the polymerization process and those of the butyl linker between the two imidazolium moieties.

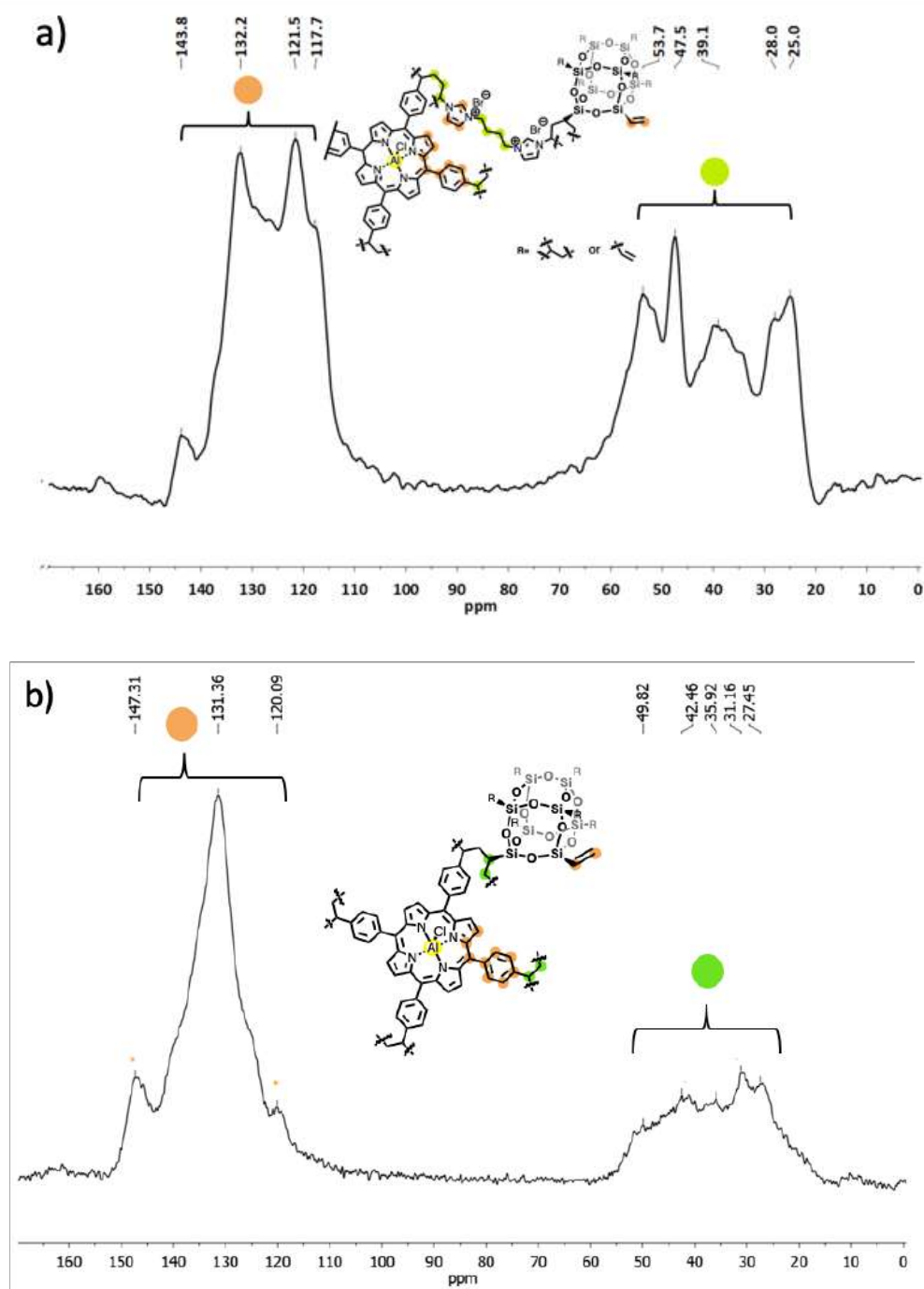


Figure 2. Solid state CP-MAS TOSS ^{13}C NMR of **POSS-TSP-AlCl-imiBr** (a) and **POSS-TSP-AlCl** (b).

Figure 3 shows the thermogravimetric analysis (TGA) carried out on the two solids under N_2 flow.

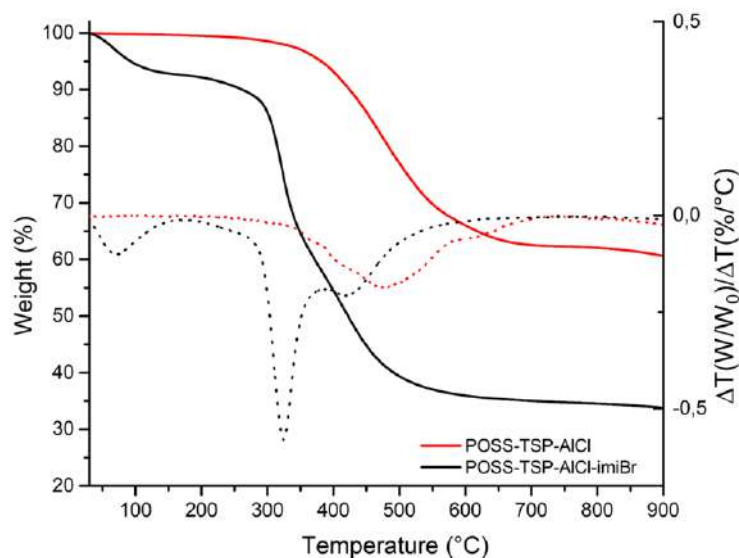


Figure 3. TGA (solid lines) and DTG (dotted lines) analysis in N₂ of **POSS-TSP-AlCl** and **POSS-TSP-AlCl-imBr**.

The solids display two different degradation profiles, showing appealing features for the reaction under study in this work. First, the presence of the imidazolium salt moieties in **POSS-TSP-AlCl-imBr** makes it more hygroscopic than **POSS-TSP-AlCl**, justifying the weight loss between room temperature and 100 °C. Interestingly, the two materials present a good thermal stability up to 300 °C. After this temperature they start to decompose with a first weight loss at *c.a.* 320 °C and another one centered at *c.a.* 418 °C for **POSS-TSP-AlCl-imBr**, and a degradation peak centered at 478 °C for **POSS-TSP-AlCl**, thus confirming the good thermal stability of both hybrids. Moreover, the appearance of the third degradation peak centered at 320°C in **POSS-TSP-AlCl-imBr** confirms the presence of the imidazolium species in the structure of the material. Another interesting details possible to catch from TGA analysis is related to the shift of 60°C concerning the degradation peaks of the porphyrin system in the two solids. On the one hand, the higher thermal stability of **POSS-TSP-AlCl** confirms the thermal benefits obtained by using POSS nanocage as support. On the other hand, the lower thermal stability of **POSS-TSP-AlCl-imBr** confirms the high number of covalent bonds between imidazolium species and porphyrin molecules. A lower stability is reasonable considering the fact that introducing a bis-vinylimidazolium species in the

polymerization process means introduce more organic cross-linker elements and thus, extend the organic structure in the morphology of the final solid. Finally, the study of thermal behaviour of these two cross-linked nanohybrid materials is of central importance because of their possible recycling under the heating regimes. X-ray photoelectron spectroscopy (XPS) was employed to understand the composition of the outer surface of the solids **POSS-TSP-AlCl** and **POSS-TSP-AlCl-imiBr**.

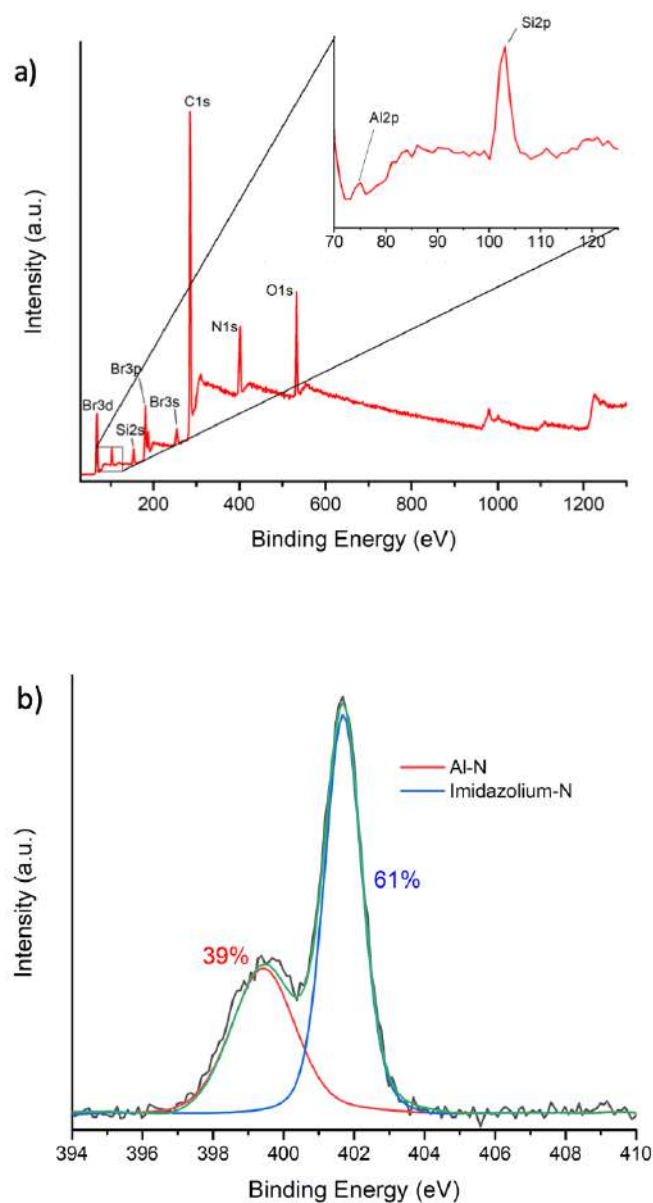


Figure 4. XPS Survey (a) and N1s High resolution (b) of **POSS-TSP-AlCl-imiBr**

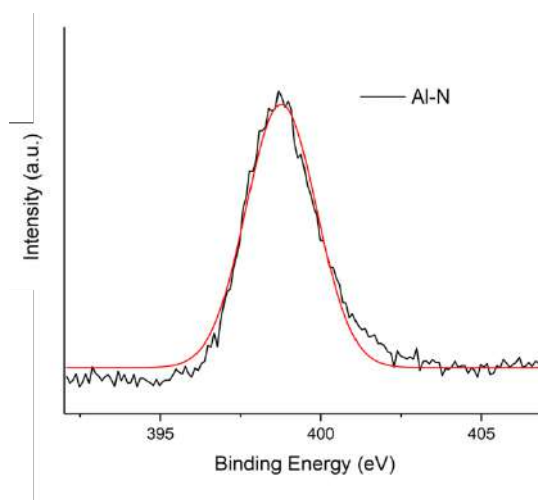


Figure 5. N1s High resolution of **POSS-TSP-AlCl**.

Figure 4a shows the XPS survey spectrum of **POSS-TSP-AlCl-imiBr** which displays the presence of Al and Br derived from the TSP-AlCl and bis-imiBr monomers, respectively. Figure 4b shows the high-resolution XPS spectra of the N1s region of **POSS-TSP-AlCl-imiBr** which can be deconvoluted into two contributions at 399.4 and 401.7 eV with atomic percentages of 39 % and 61 %. These two signals can be attributed to the nitrogen atoms of the porphyrin ring coordinated with aluminum (Al-N) and the nitrogen atoms of the imidazolium rings, respectively [2]. Moreover, in Figure 5, the high-resolution XPS spectra of the N1s region of **POSS-TSP-AlCl** shows only one peak centred at 399.4 eV related to the nitrogen atoms of the porphyrin ring coordinated with aluminum (Al-N) which is the only type present in the material. Once again, the higher contribution of imidazolium species allows to obtain 1:1.5 as ratio aluminium-bromide value, considering the ratio between the areas of the two peaks.

The amount of aluminum present in **POSS-TSP-AlCl** and **POSS-TSP-AlCl-imiBr** was estimated by inductively-coupled plasma atomic emission spectroscopy (ICP-OES) analysis resulting 0.40 and 0.32 mmol/g, respectively.

Finally, the morphology of the two catalysts **POSS-TSP-AlCl** and **POSS-TSP-AlCl-imiBr** was studied by using transmission electron microscopy (TEM). Figure 6 shows TEM images in which is evident that the two materials display irregular and amorphous porous structures with an accessible polymeric network.

Nevertheless, nitrogen physisorption shows values of specific surface area (SSA) below 1 m²/g. These low specific surface areas are probably due to presence of a broad and non-regular distribution of pores mainly in the macroporous region.

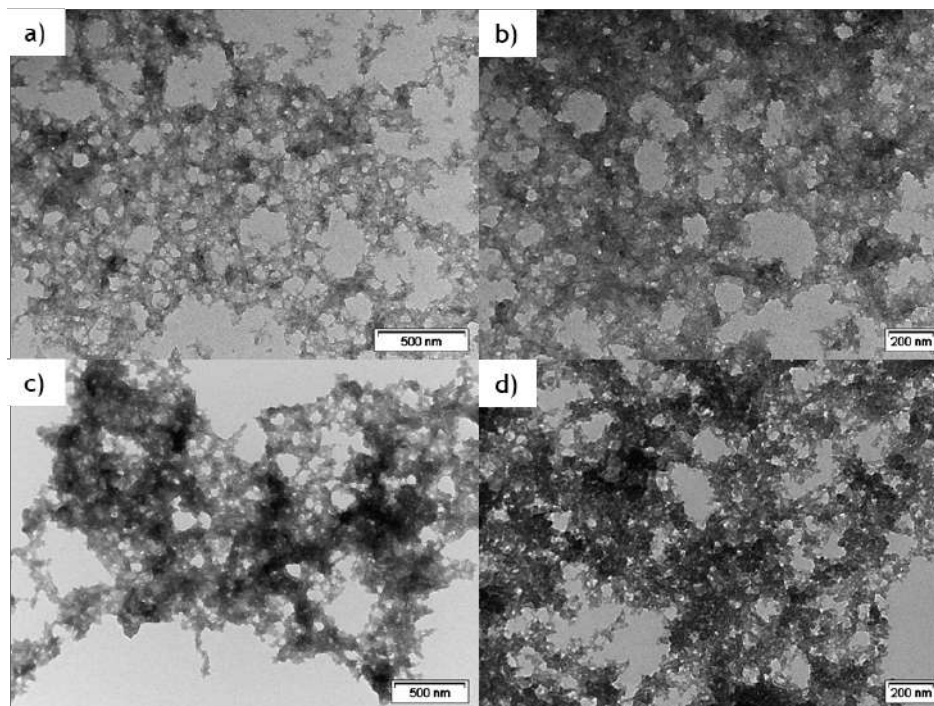
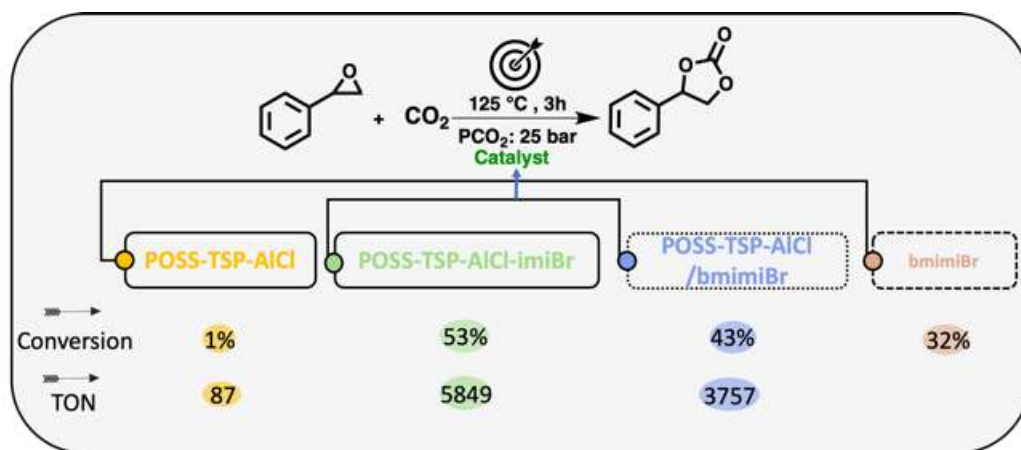


Figure 6. TEM images of **POSS-TSP-AlCl-imiBr** (a,b) and **POSS-TSP-AlCl** (c,d).

Once characterized, both materials were investigated in the conversion of carbon dioxide to cyclic carbonates by employing styrene oxide as benchmark reactant under solvent-free conditions as shown in Scheme 3. Due to the different content of active species in the two materials, a more specific comparison of the catalytic activity of **POSS-TSP-AlCl** and **POSS-TSP-AlCl-imiBr** solids was performed considering the turnover number values based on the aluminum content (TON_{Al}; defined as moles of epoxide converted/moles of Al active sites).

Initially, **POSS-TSP-AlCl** and **POSS-TSP-AlCl-imiBr** were tested in the reaction using the same mass amount obtaining a very different conversion of 1% and 53%, respectively (Scheme 2). The huge difference between the two reactions is ascribed to the absence of a nucleophilic source in **POSS-TSP-AlCl**, resulting thus essential in the target process. Two additional tests were performed: the first employing **POSS-TSP-AlCl** (0.024 mmol Al), as source of Lewis acid species, combined with

butylmethylimidazolium bromide salt (bmimBr, molar ratio 1:6), as the nucleophile source, and the second with bmimBr alone. It is worth to note that the former test displayed a higher conversion (43%) than the bmimBr alone (32%) but a TON sensibly lower (3757) than that obtained with the bifunctional heterogeneous system. Based on this last two results, it is evident how the presence of the co-catalytic species enhance the catalytic performance. It is worth saying also, that the higher TON and conversion values obtained with **POSS-TSP-AlCl-imibR** compared to the system bmimBr/**POSS-TSP-AlCl** allows evidencing the benefits of bearing in the same structure both the Lewis acid and nucleophilic species. Moreover, the test done using the system bmimBr/**POSS-TSP-AlCl** was carried out with a ratio aluminium-bromide 1:6, largely higher than the ratio estimated from XPS for **POSS-TSP-Al-Cl-imibR** (1:1.5). This last result could be ascribed to the proximity between the porphyrin core and the bis-vinylimidazolium in the 3D polymeric network of **POSS-TSP-AlCl-imibR**. This proximity allows a cooperation between the two co-catalytic species which act synergistically during the catalytic cycle. A similar synergistic activation was previously reported in the literature [2].



Scheme 3. Comparison of the catalytic activity of **POSS-TSP-AlCl** (60 mg; 0.024 mmol Al) and **POSS-TSP-AlCl-imibR** (60 mg 0.019 mmol Al), **POSS-TSP-AlCl/bmimBr** (0.024 mmol Al, 1:6 molar ratio) and **bmimBr** (30 mg) in the reaction of styrene oxide with CO₂. Reaction conditions: styrene oxide (209.7 mmol), catalyst (0.024 or 0.019mmol Al), 25 bar CO₂, 125 °C, 3 h, 500 rpm.

Afterwards, the promising bifunctional material was employed with styrene oxide to study the recyclability of the catalyst. Five consecutive runs were performed and after each cycle the material was easily recovered from the reaction mixture by centrifugation, washed with toluene, ethanol and diethyl ether and dried under vacuum at 60°C overnight. The results shown in Figure 7 indicate that **POSS-TSP-AlCl-imiBr** is a quite robust material under the selected reaction conditions and can be used for multiple cycles without any decrease of catalytic activity.

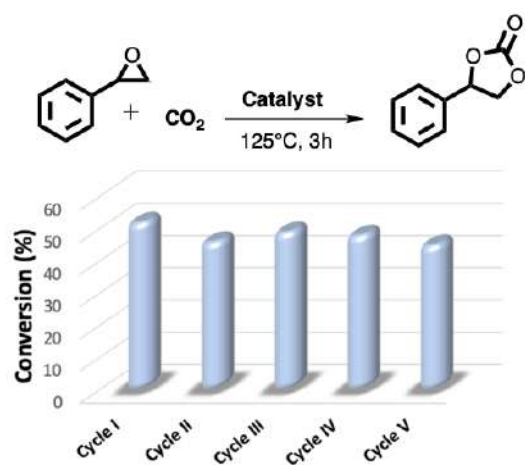


Figure 7. Recycling tests of **POSS-TSP-AlCl-imiBr**. Reaction conditions: styrene oxide (209.7 mmol), 60 mg of catalyst (0.019 mmol Al, 0.009 mol%), 25 bar of CO₂, 3h, 500 rpm.

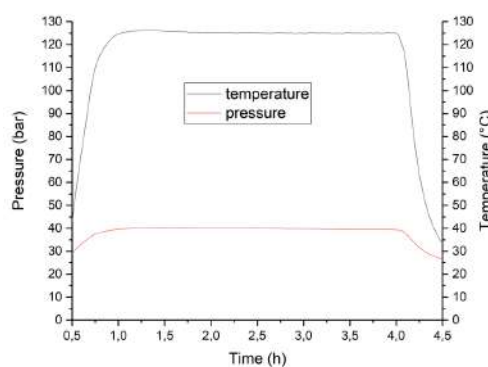


Figure 8. Pressure/Temperature vs. Time plot for the test with the mixture of the reaction between styrene oxide and CO₂, catalyzed by **POSS-TSP-AlCl-imiBr**.

Moreover, in order to confirm the absence of leached active species in the solution after the catalytic test, a further experiment was carried out. After the separation of **POSS-TSP-AlCl-imiBr** from the reaction mixture, the liquid phase was filtered using a 0.2 µm filter and was allowed to react under the same reaction conditions. Figure 8 shows an almost constant CO₂ pressure was detected during the reaction time, and the ¹H-NMR analysis at the end of the reaction showed only a small increase in conversion of 1.4%, confirming the absence of leached species.

The catalytic activity of **POSS-TSP-AlCl-imiBr** was also assessed using different epoxides (Table 1). Unless otherwise specified, a complete selectivity (>95%) toward cyclic carbonate has been achieved.

Table 1. Reaction conditions of different screening tests of **POSS-TSP-AlCl-imiBr** with different epoxides.

ENTRY	TESTS	SUBSTRATE	T. (°C)	CONV. ^a (%)	TON _{Al} ^b	TOF _{Al} ^b	P. ^c
1	I cycle	Styrene oxide (S.O.) (209.7 mmol)	125	53	5849	1950	304
2	I cycle	Glycidol (Gly.) (379 mmol)	50	44	8777	2926	328
3 ^d	I cycle	Glycidol (379 mmol)	50	41	8178	2726	306
4	I cycle	Glycidol (379 mmol)	30	16	3192	1064	119
5	I cycle	Epichlorohydrin (Epi.) (306 mmol)	100	91	14656	4885	634
6 ^e	I cycle	Epichlorohydrin (306 mmol)	100	>95	16105	5368	696
7	I cycle	Epichlorohydrin (306 mmol)	80	73	11756	3919	508
8	I cycle	Epichlorohydrin (306 mmol)	50	11	1772	591	77
9 ^f	II cycle	Cyclohexene oxide (Cy.Ox.) (237 mmol)	150	88 ^g	6518	272	296
10 ^h	III cycle	Oxetane (Ox.) (372 mmol)	150	>95 ^h	18600	775	600
11	IV cycle	Epichlorohydrin (306 mmol)	100	73	11596	3865	501

Reaction conditions: 24 mL of epoxides, 60 mg of catalyst (0.019 mmol Al), 25 Bar of CO₂, 3h, 500 rpm.

^a Determined by ¹H NMR; selectivity toward cyclic carbonate > 95%; yield ≥ 95 %.

^b TON and TOF values calculated on the basis of the Al content estimated by ICP analysis. (TON = mmol epoxide converted/ mmol Al); (TOF= TON/ time (h))

^c Productivity (P)= grams of product/grams catalyst considering 100 % selectivity

^d Constant pressure of 10 bar of CO₂

^e Refill at 40 bar of CO₂ after 1h of reaction time.

^f 100 mg of catalyst (0.032 mmol Al); reaction time of 24h

^g Selectivity toward cyclic carbonates 83 % (cis/trans ratio 72:28).

^h Reaction time of 24h; selectivity 99% toward polycarbonate.

Styrene oxide was converted into the corresponding cyclic carbonate with 53% of conversion when the material was employed at 125 °C for 3 h (Table 1, entry 1 and

Scheme 3). Conversions of 44 % or 41% were obtained for glycidol at 50 °C in 3 h when an initial pressure of 25 bar or a constant pressure of 10 bar was applied, respectively (entries 2 and 3). Moreover, decreasing the temperature from 50 °C to 30 °C allows converting 16% of glycidol in only 3 h (entry 4).

Epichlorohydrin was tested at different temperatures: 100, 80 and 50 °C applying a reaction time of 3 h. A conversion value of 91% was obtained at 100 °C in 3h (entry 5). Interestingly, a full conversion (>95%) of epichlorohydrin was obtained in the same conditions when the system was refilled with CO₂ after 1h (entry 6). Refilling the reagent in the gas phase after 1 h re-establishes good reaction kinetics as shown in Figure 9, where the comparison between the pressure profile during the reaction time of entries 5 and 6 shows how the kinetic of the process decreases during the consumption of CO₂. Decreasing the temperature to 80 °C and 50 °C results in conversion values of 73% and 11%, respectively (entries 7 and 8).

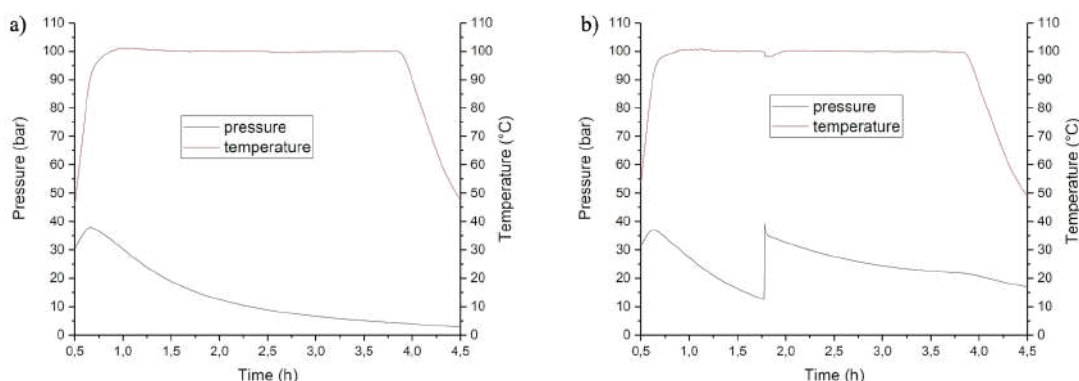


Figure 9. a) Pressure variation during the reaction time of the reaction between epichlorohydrin and CO₂ at 100 °C for 3h and without any pressure refill (entry 5, table 1); b) pressure variation during the reaction time of the reaction between epichlorohydrin and CO₂ at 100 °C for 3h and with a pressure refill after 1h (entry 6, table. 1).

A final step forward on the catalytic activity of **POSS-TSP-AlCl-imiBr** was made by recycling the material and subjecting it to different reaction conditions during catalysis between CO₂ and several more challenging-to-convert epoxides. As shown in Table 1 good conversions were obtained for cyclohexene oxide and oxetane at the first and the second reuse of the material. In the former case, a conversion of 88% was reached in 24h at 150 °C employing 100 mg (0.032 mmol

of Al) of catalyst (entry 9). Despite the good conversion, *cis*-cyclohexane carbonate was not the only product obtained. During the reaction also *trans*-cyclohexane carbonate and the poly-cyclohexane carbonate were formed with a selectivity toward cyclic carbonates of 83 % and *cis/trans* ratio of 72:28, according to the analysis of a study done on cyclohexane oxide conversion [3]. Finally, >95% of oxetane was converted in 24h at 150 °C with a full selectivity toward the corresponding polycarbonate (entry 10). This result agrees with the selectivity reported in the literature in the conversion of CO₂ by addition to oxetane when the coordinating metal is aluminum [4]. To better evaluate the robustness of the material after recycling, epichlorohydrin was tested again in the same condition of entry 5. A slightly decreased conversion (73%) was observed when the reused material was employed with respect to the reaction carried out in the presence of the fresh catalyst (entry 5).

Even with this diminished conversion, the material remains still active and quite efficient even after several consecutive uses under different reaction conditions contributing thus to making this class of materials promising for the conversion of CO₂ in cyclic carbonate.

Finally, a comparison with other catalytic systems is usually carried out; however, the reaction under examination has different experimental parameters and a close comparison is difficult to do. Aluminum-based catalysts are largely investigated for the above reaction, but we believe that a comparison should be made with bifunctional supported catalytic systems. In Table 2 are reported few examples. A first comparison between **POSS-TSP-AlCl-imiBr** and an analogous solid obtained via copolymerization in the absence of POSS (**TSP-AlCl-imi**) evidences the enhanced catalytic performances of the former (compare entries 1 and 2) thus further highlighting the importance of the POSS nanocage. Indeed, the unsupported polymer **TSP-AlCl-imi** has a lower TON of 3868 compared to 5849 that is the TON of the test carried out with **POSS-TSP-AlCl-ImiBr**. Then, we examined **POSS-TSP-AlCl-imiBr** and **MWCNT-TSP-AlCl-imi**, a previous material prepared by our group that was used under the same reaction conditions. Both materials possess the Al-porphyrin-imidazolium cross-linked network but on different supports, POSS and MWCNT respectively.

Table 2. Selected data for the reaction between epoxides and CO₂ in the presence of different catalytic systems.

ENTRY	CATALYST	SUBSTRATE	CONV. (%)	TON _{Al}	P ^a	REACTION CONDITION	REF.
1	POSS-TSP-AlCl ₃ -imiBr	S. O.	53	5849	304	25 bar; 3h; 125 °C	This Work
2	TSP-AlCl ₃ -imi	S. O.	49	3868	281	25 bar; 3h; 125 °C	[2]
3	MWCNT-TSP-AlCl ₃ -imi	S. O.	55	7649	316	25 bar; 3h; 125 °C	[2]
4	Al-iPOP-1	S. O.	52		51	1 MPa; 9 h; 40 °C	[5]
5	COP-Al	S. O.	91.5		50	1 MPa; 18 h; 90 °C	[6]
6	IM-iPHP-2	S. O.	84		5.5	1 bar; 72 h; 80 °C	[7]
7	V-iPHP-1	S. O.	93		6.1	0.1 MPa; 72 h; 80 °C	[8]
8	POSS-TSP-AlCl ₃ -imiBr	Epi.	91	14656	634	25 bar; 3h; 100 °C	This Work
9	MWCNT-TSP-AlCl ₃ -imi	Epi.	>95	20265	661	25 bar; 3h; 100 °C	[2]
10	Al-iPOP-1	Epi.	99		81	10 bar; 6h; 40 °C	[5]
11	COP-Al	Epi.	98		45	10 bar; 18h; 90 °C	[6]
12	IM-iPHP-2	Epi.	96		5.2	0.1 MPa; 48 h; 80 °C	[7]
13	V-iPHP-1	Epi.	97		5.3	0.1 MPa; 48 h; 80 °C	[8]
14	POSS-TSP-AlCl ₃ -imiBr	Cy. Ox.	88 ^b	6518 ^d	296 ^e	25 bar; 24 h; 150 °C	This work
15	MWCNT-TSP-AlCl ₃ -imi	Cy. Ox.	71 ^c	3352 ^d	119 ^e	25 bar; 24 h; 150 °C	[2]
16	Al-iPOP-1	Cy. Ox.	83		71	10 bar; 36 h; 40 °C	[5]

^a Productivity(P)= grams of product/grams catalyst; ^b selectivity toward cyclic carbonate, 83%; ^c selectivity toward cyclic carbonate, 74%; ^e TON based on cyclic carbonate: 5410 and 2480 respectively. ^d Productivity based on cyclic carbonate: 245 and 88 respectively.

The MWCNT-based material performs slightly better with styrene oxide compared to the POSS-based catalyst (entries 1; 3). On the one hand, the MWCNT performs better with epichlorohydrin in terms of conversion and TON values, though they showed similar productivity values (entries 8-9); on the other hand, the POSS-based

catalyst showed a very interesting result with the less reactive cyclohexene oxide in terms of conversion and selectivity toward the cyclic carbonate, TON and productivity values (entries 14-15). The latter two values, calculated on selectivity towards cyclic carbonate highlight the greater performance of the POSS-based catalyst. Catalytic materials based on bifunctional Al-porphyrin/imidazolium bromide system (Al-iPOP-1) or Al-salen/imidazolium bromide system (COP-Al) gave high conversions at milder conditions but using a large amount of catalytic materials as demonstrated by the productivity values (entries 4,5,10,11,16). The synergy between the metal center (Lewis acid) and the co-catalyst (halide ion) in **POSS-TSP-AlCl₃-imiBr** allows achieving enhanced catalytic performances with respect to POSS-based catalysts that do not contain Lewis acid. In the case of IM-iPHP-2 and V-iPHP-1 the reaction was assisted by many H-bondings. In these cases, the materials did not present a silica nanocage with a fully condensed (T8) arrangement, but it was shown that part of the cage was hydrolysed. This opening of the cubic structure led to the formation of silanol groups that can contribute to catalysis through hydrogen bonding between the hydrogen of the hydroxyl groups attached to the silicon atom and the oxygen of the epoxide.

4.3 Conclusions

Octavinylsilsesquioxane and aluminum chloride tetrastyrilporphyrin (**TSP-AlCl**) have been subjected to AIBN mediated radical polymerization in the presence (**POSS-TSP-AlCl-imBr**) and in absence (**POSS-TSP-AlCl**) of and bis-vinylimidazolium dibromide (**bis-imBr**). The corresponding cross-linked solids have been thoroughly characterized by means of several spectroscopic and analytic techniques such as TGA, ICP-OES, XPS, TEM, solid state NMR. Hybrid materials were used as heterogeneous catalysts in the cycloaddition reaction of CO₂ with epoxides to obtain the corresponding cyclic carbonates under solvent-free conditions. It has been shown how the presence of both Lewis acid and nucleophilic species within the same heterogeneous material **POSS-TSP-AlCl-imBr** leads to a catalyst with high catalytic performance due to the synergistic effects exerted by the metal centers and halide ions. This performance could be ascribed to a twofold effect. A first contribution is attributed to the close proximity between the metal centers and the bromide ions, which are able to cooperate and exert a synergistic effect during the catalytic cycle. A second contribution comes from the use of the POSS-silica nanocage used as a building block during synthesis. The possibility of functionalizing the POSS cage at its vertices ensures an increase in the concentration of active sites in the material at certain localized positions. The hybrid catalyst showed high catalytic activity with a range of different epoxides, with TON and TOF values of up to 16,000 and 5,000, respectively. **POSS-TSP-AlCl-imBr** was easily recoverable and recyclable for at least five cycles with unchanged activity, and no leaching phenomena have been observed during the performed tests. Based on these results, different catalytic systems can be easily designed by changing both the nature of metalloporphyrin and/or halide ion as well as the linker of the bis-imidazolium salt.

4.4 Experimental Section

Materials and methods

Octavinylsilsesquioxane, styrene oxide, epichlorohydrin and cyclohexene oxide were purchased from TCI. Glycidol and 2,2'-azobis(2-methylpropionitrile) (AIBN) and diethylaluminum chloride were purchased from Sigma-Aldrich. These chemicals were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer. Solid state ^{13}C CP-MAS TOSS NMR spectra were recorded at room temperature, on a Jeol ECZ-R 600 MHz spectrometer operating at 14.1 T, using a contact time of 2 ms, a spinning rate of 8 KHz and an automas probe of 3.2 mm with acquisition delay of 5 s and 5000 scans. Solid ^{29}Si NMR spectra were recorded at room temperature on a JEOL ECZ-R spectrometer operating at 14.1 T using a 3.2 mm automas probe and spinning frequencies of 10 kHz with acquisition delay of 10 s and 10000 scans. X-ray photoelectron spectroscopy (XPS) analyses were carried out in a ThermoFisher ESCALAB 250Xi instrument. Thermogravimetric analysis was performed under nitrogen flow from 25 to 900 °C with a heating rate of 10 °C/min in a Mettler Toledo TGA STAR system. Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai 10 microscope operating at 80 kV. The samples were prepared by dispersion of a small quantity of the material in absolute ethanol and deposited into a copper grid. Inductively coupled plasma optical emission spectroscopy. (ICP-OES) was performed in an Optima 8000 ICP-OES spectrometer.

Synthesis of bis-vinylimidazolium salt (bis-im i Br)

bis-im i Br was synthesized according to a reported procedure [2]. In a 10 mL round bottom flask, a solution of 1,4-dibromobutane (950 μL , 7.88 mmol) and 1-vinylimidazole (1.5 mL, 16.24 mmol) in methanol (2 mL) was stirred in the dark and under Ar atmosphere at 65 °C for 13 h. The solution was transferred in a 100 mL round bottom flask and the volume was reduced under vacuum before adding Et $_2$ O (70 mL). After sonication and vigorous stirring, a white precipitate was obtained, and the supernatant was removed by simple decantation. The white solid was again solubilized in methanol and precipitated in diethyl ether for three times

before drying it under vacuum (4×10^{-4} mbar) at 40 °C. bis-imBr was obtained as a white solid (3.128 g; 98 %).

Synthesis of Tetrastyrilporphyrin

Tetrastyrilporphyrin (**TSP**) was synthesized according to a reported procedure [2]. In a 250 mL two-neck round-bottom flask propionic acid (65 mL) was heated to 140 °C before adding pyrrole (500 μ L, 7.1 mmol) and 4-vinylbenzaldehyde (0.926 g, 7.1 mmol). The system was allowed to react for 5 hours before its cooling down, filtering and washing with methanol and ethyl acetate. After drying, the tetrastyrilporphyrin was obtained as a purple powder (415 mg; 27 %). ¹H NMR (300 MHz, CDCl₃, δ): 8.90 (s, 8 H), 8.19 (d, J = 7.9 Hz, 8 H), 7.81 (d, J = 8.0 Hz, 8 H), 7.07 (dd, J = 17.6, 10.9 Hz, 4 H), 6.08 (d, J = 17.6 Hz, 4 H), 5.51 (d, J = 10.9 Hz, 4 H), -2.73 (s, 2 H) ppm.

Synthesis of tetrastyrilporphyrin aluminum chloride (TSP-AlCl)

Tetrastyrilporphyrin aluminum chloride (**TSP-AlCl**) was synthesized according to a reported procedure [2]. In a 50 mL two-neck round-bottom flask, under Ar atmosphere, tetrastyrilporphyrin (200 mg, 0.28 mmol), was dissolved in 4 mL of dry dichloromethane. The mixture was cooled to 0 °C then a solution of diethylaluminum chloride (0.1 M solution in hexane, 170 μ L, 0.3 mmol) was added dropwise. Then the reaction mixture was stirred for 6 h at room temperature. After the reaction time the solvent was removed by rotary evaporation before adding methanol and transfer all the mixture in a centrifuge tube. Four centrifugations with methanol were carried out and the combined supernatants were evaporated under vacuum. Once again, the solid obtained was taken up with dichloromethane and all the insoluble residues were removed by filtration. The filtrate was concentrated under vacuum and **TSP-AlCl** was obtained as purple powder (115 mg; 53 %). ¹H NMR (300 MHz, CDCl₃, δ): 8.41 (s, 8 H), 7.49 (s, 16 H), 6.98 (dd, J = 17.6, 11.0 Hz, 4 H), 5.99 (d, J = 17.7 Hz, 4 H), 5.49 (d, J = 10.9 Hz, 4 H) ppm.

Preparation of POSS-TSP-AlCl

In a 25 mL two-neck round-bottom flask, octavinylsilsesquioxane (100 mg, 0.158 mmol) and **TSP-AlCl** (200 mg, 0.25 mmol) were solubilized in dry DMF (6 mL) and sonicated for 10 min. Then, AIBN (49 mg, 0.294 mmol) was added under argon and the reaction mixture stirred for 30 min at room temperature before increasing the temperature up to 80 °C. After 24 h the dark mixture obtained was cooled at room temperature and transferred in a centrifugation tube by adding a small amount of DMF. The residue mixture was subjected to centrifugation several times with different solvents. Two times in DMF, three times using a methanol/Et₂O (v/v) 3/1 mixture and two times with Et₂O. The solid was recovered and dried under vacuum (4×10^{-4} mbar) at 60 °C. **POSS-TSP-AlCl** was obtained as a dark powder (300 mg).

Preparation of POSS-TSP-AlCl-imiBr

In a 25 mL two-neck round-bottom flask, octavinylsilsesquioxane (150 mg, 0.237 mmol), **TSP-AlCl** (200 mg, 0.25 mmol), and **bis-imiBr** (404 mg, 1 mmol) were solubilized in dry DMF (8 mL) and sonicated for 10 min. Then, AIBN (108 mg, 0.657 mmol) was added under argon and the reaction mixture stirred for 30 min at room temperature before increasing the temperature up to 80 °C. After 24 h the dark mixture obtained was transferred in a centrifuge tube by adding a small amount of DMF. The residue mixture was subjected to centrifugation several times with different solvents. Two times in DMF, three times using a methanol/Et₂O (v/v) 3/1 mixture and two times with Et₂O. The solid was recovered and dried under vacuum (4×10^{-4} mbar) at 60 °C. **POSS-TSP-AlCl-imiBr** was obtained as a dark powder (660 mg).

Catalytic experiments

Catalytic experiments were carried out using a Cambridge Design Bullfrog batch reactor equipped with temperature control and mechanical stirring. In each test, the catalyst (see Table 1 for the corresponding amounts) and the proper epoxide (24 mL) were added to a Teflon vial and then the reactor was closed. After passing a flow of N₂ for 10 minutes and loading 25 bar of CO₂, the system was left to react at the target temperature reached by a ramp of 5 °C/min. In selected cases, a refill

of CO₂ was carried out during the experiment. In these cases, the initial pressure of CO₂ was never overpassed. After the proper reaction time (3 h or 24 h), the reactor was cooled down to room temperature, depressurized and, then, the catalyst was recovered from the reaction mixture by centrifugation (15 min at 4500 or 9000 rpm). The supernatant was analyzed by ¹H NMR in d₆-DMSO. Each catalyst was dried overnight under vacuum at 60°C prior to the catalytic test.

Recycles

Recycling tests were carried out employing styrene oxide. At the end of the catalytic experiment, after separation the catalyst from the reaction mixture, a small amount of solvent (toluene, then ethanol and finally diethyl ether) was added to the solid and the mixture was sonicated for 15 minutes. Then, the material was recovered by centrifugation. The recovered solid was dried overnight in a vacuum (4×10^{-4} mbar) oven at 60 °C. In order to maintain the same catalytic loading, the dried catalyst was weighed and reused in the same reaction, modifying, if necessary, the amount of epoxide.

Leaching test

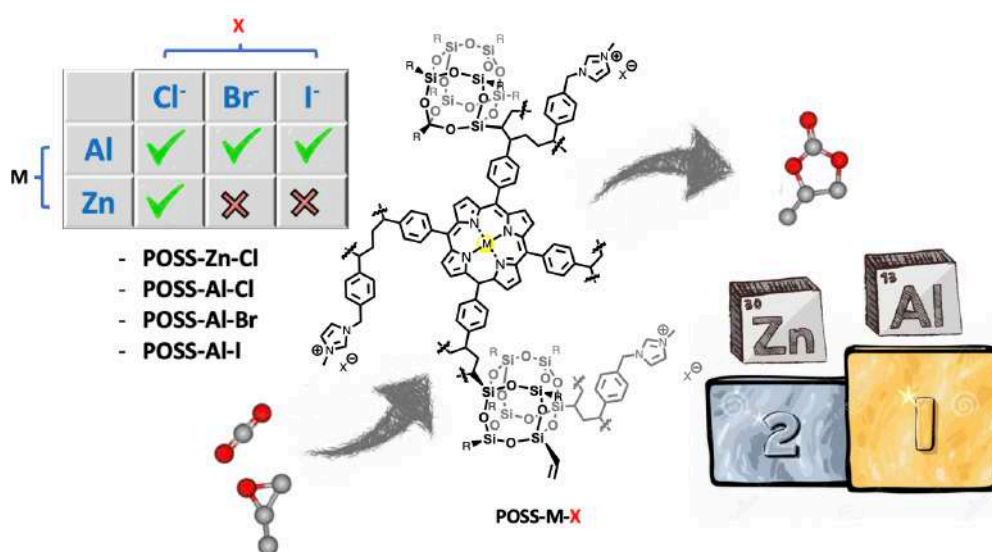
Styrene oxide was used for leaching test. At the end of the catalytic cycle, the catalyst was recovered from the reaction mixture via centrifugation during 15 min at 4500 rpm and the supernatant was analyzed by ¹H NMR in d₆-DMSO. Then, the liquid mixture was filtered through a 0.2 µm filter and allowed to react again in the same reaction condition. During the reaction time, no decrease of the CO₂ pressure was observed and no further conversion was detected by ¹H NMR analysis.

4.5 References

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CHAPTER V:

Comparison of polymeric networks based on POSS-Porphyrin-imidazolium systems as catalytic bifunctional platforms for the conversion of CO₂ with epoxides.



This chapter is based on a manuscript in preparation.

5.1 Abstract

Four heterogeneous catalysts were prepared with the aim of following the promising path of CO₂ fixation onto epoxides. The synthetic procedure involves a radical copolymerization of an octavinylsilsesquioxane as inorganic core building block and tetrastyrilporphyrin aluminum chloride monomer (**TSP-AlCl**) or tetrastyrilporphyrin Zinc monomer (**TSP-Zn**) in presence of an imidazolium salt bearing a specific counter anion (chloride, bromide or iodide). The synthetic procedure allows obtaining **POSS-Zn-Cl**, **POSS-Al-Cl**, **POSS-Al-Br** and **POSS-Al-I** in order to investigate first, the co-catalytic effect of two different metals (Al and Zn) and also, the influence of different nucleophilic species (Cl⁻, Br⁻ and I⁻) on the catalytic performances. All the solids were fully characterized and tested in the synthesis of cyclic carbonates starting from CO₂ and styrene oxide. **POSS-Zn-Cl** had the worst catalytic activity of the four prepared solids thus indicating that aluminium displays better performance as Lewis acid center. Moreover, **POSS-Al-Cl** was the less active in comparison to **POSS-Al-Br** and **POSS-Al-I**, but the latter two materials were not easily separable from the reaction mixture via simply filtration or centrifugation. On the other hand, **POSS-Al-Cl** was easily recoverable and used in four consecutive runs in the reaction with epichlorohydrin and carbon dioxide.

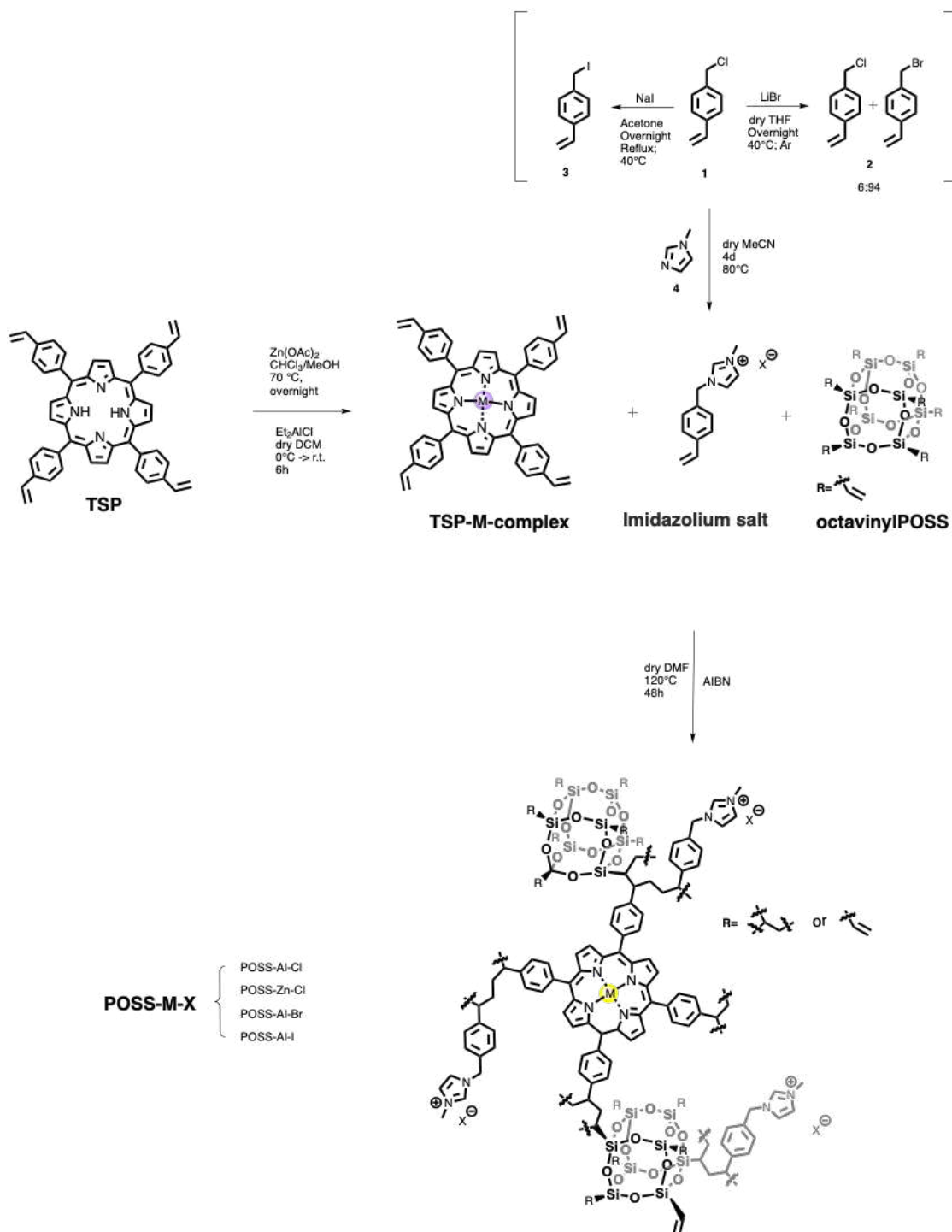
5.2 Results and Discussion

The interesting results obtained with the POSS-based bifunctional materials, i.e. those with a Lewis acid and a nucleophilic centre in the same structure, prompted our curiosity to investigate this promising class of catalysts. Furthermore, in this Chapter the investigation is extended to a comparison between two different metals Aluminium and Zinc (Al and Zn). As in the previous chapter, the synthesis of the materials was performed by exploiting the possible polymerization of the vinyl groups present in the monomers.

Firstly, as shown in Scheme 1, the tetrastyrilporphyrin (**TSP**) was reacted once with Et_2AlCl and once with $\text{Zn}(\text{OAc})_2$ in order to obtain tetrastyrilporphyrin aluminum chloride (**TSP-AlCl**) complex and tetra-styrilporphyrin zinc (**TSP-Zn**) complex, respectively.

Moreover, from 4-vinylbenzyl chloride (**1**) we were able to obtain, via substitution reaction, 4-vinylbenzyl bromide (**2**) and 4-vinylbenzyl iodide (**3**). In the case of 4-vinylbenzyl bromide the substitution was not complete (94:6 Br^-/Cl^- ratio). The precursor was used with this ratio without any further purification.

Afterwards, the three obtained precursors were reacted with 1-methyl imidazole (**4**) in dry acetonitrile for four days at 80 °C in order to obtain the three respective 1-methyl-3-(4-vinylbenzyl)imidazolium salts.



Scheme 1. Synthesis route of **POSS-M-X** materials.

TSP-AlCl and **TSP-Zn** complexes were subsequently copolymerized with octavinyl-POSS and 1-methyl-3-(4-vinylbenzyl)imidazolium chloride by using AIBN as radical initiator. The radical process allowed obtaining the material **POSS-Al-Cl** and **POSS-Zn-Cl**, respectively. Afterwards the same radical reaction was

used to obtain the other two materials **POSS-Al-Br** and **POSS-Al-I** in presence of the previous obtained imidazolium salts.

This line of materials aims to use octavinyl-POSS as inorganic building block core and also, together with porphyrin ring as cross-linker elements of the system.

The imidazolium salt containing only one vinyl unit in its structure, instead of the bis-vinyl imidazolium salt, was used with the aim to avoid increasing the number of cross-linker elements in the system.

The use of an imidazolium salt with a single vinyl moiety may give a less reticulate material and could optimize the proximity effect between the metal centres and the nucleophile moieties.

All the solids were characterized via different techniques including ^{13}C and ^{29}Si cross-polarization magic angle spinning (^{13}C and ^{29}Si CP-MAS) NMR spectroscopy. Considering the identical structure of the four solids, and that the only changes concerning the metal complexed by the porphyrin ring or the counter anion of the imidazolium salt do not lead to changes in the carbon or silicon NMR spectra of the compounds, only the spectra of **POSS-Al-Cl** are given as examples.

^{29}Si solid state NMR spectrum (Figure 1) of **POSS-Al-Cl** revealed the presence of two main contributions centered at -65 and -79 ppm. The two signals can be attributed to the ^{29}Si atoms linked to alkyl groups of reacted vinyl moieties (alkyl-Si) and unreacted vinyl groups (vinyl-Si), respectively. This interpretation agrees with the NMR data of POSS structures previously reported in the literature [1] and with the hypothesis done above (see Chapter IV, paragraph 2).

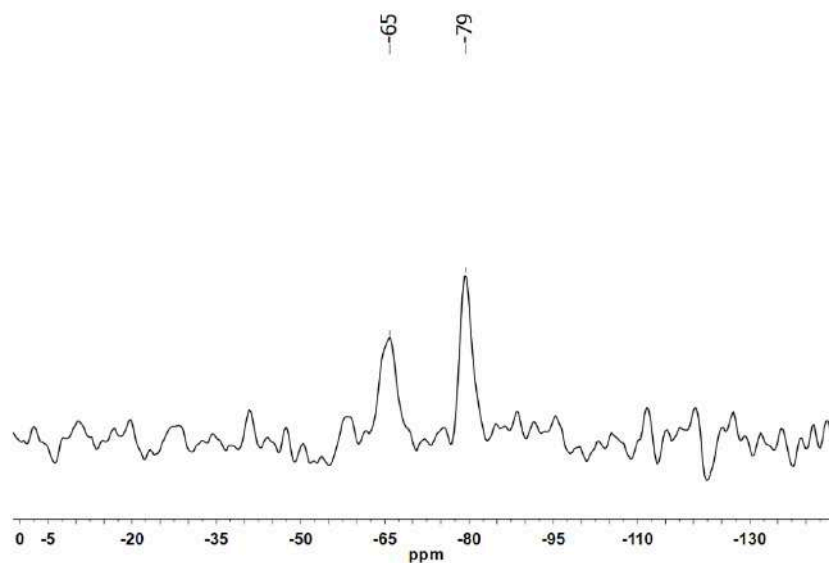


Figure 1. Solid state CP-MAS ^{29}Si NMR of **POSS-Al-Cl**.

^{13}C Solid state NMR spectrum of **POSS-Al-Cl** (Figure 2) displays the signals present in the 20-60 ppm region assigned to the aliphatic carbon atoms generated upon the polymerization process and to the methyl moiety linked to the nitrogen atom of the imidazolium ring. Signals in the region between 115-150 ppm are attributed to the carbon atoms of the porphyrin together with those of the imidazolium moieties and not reacted vinyl moieties.

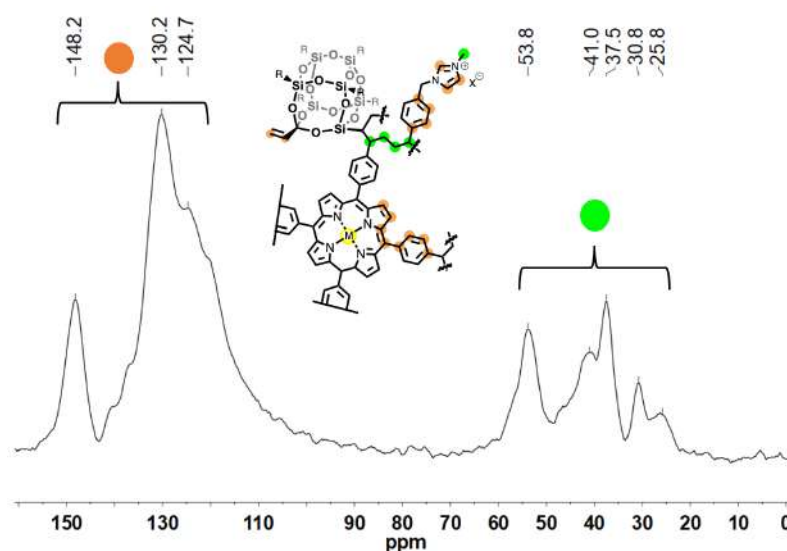


Figure 2. Solid state CP-MAS TOSS ^{13}C NMR of **POSS-Al-Cl**.

Figure 3 shows the thermogravimetric analysis (TGA) carried out on the four solids under air flow. TGA was carried out in air to be sure that all the organic part of the solids was degraded at high values of temperature and only silicon dioxide and aluminium oxide remain as residuals.

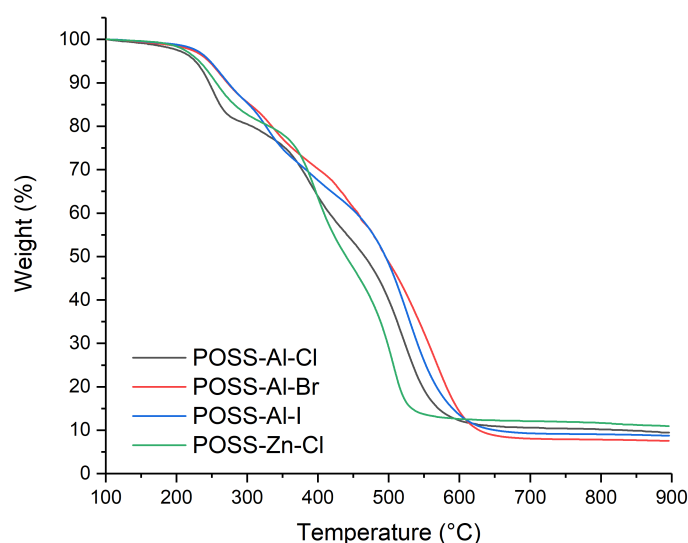


Figure 3. TGA analysis in Air of the reported solids.

All the solids display a similar degradation profile. The four materials start to degrade at values of temperature up to 250 °C. The study of thermal behavior of these cross-linked nanohybrid materials is of central importance because of their possible recycling under the heating regimes.

X-ray photoelectron spectroscopy (XPS) was employed to understand the composition of the outer surface of the four materials. The XPS survey spectra of the synthesized POSS based materials in figure 4 display the presence of the metal (Al or Zn) and relative counter anions derived from the TSP-M complex and imidazolium salt monomers, respectively. The presence of some Cl2p in the survey of **POSS-Al-Br** (Figure 4b) is due to the substitution ratio of 96:4 obtained during the synthesis of 4-vinylbenzyl bromide obtained from 4-vinylbenzyl chloride.

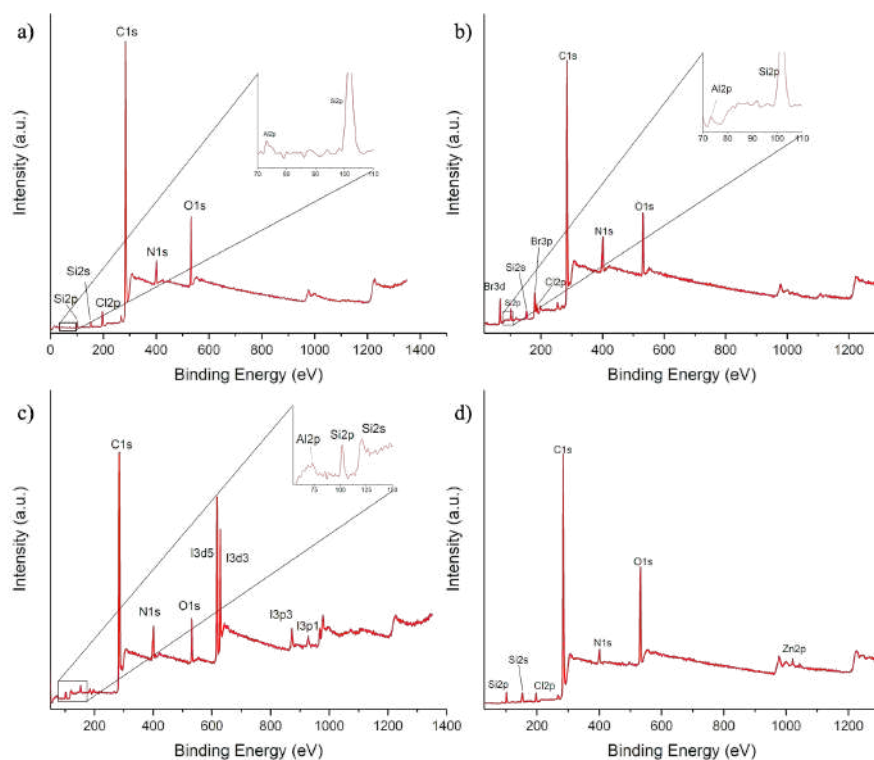


Figure 4. N1s High resolution of **POSS-Al-Cl** (a), **POSS-Al-Br** (b), **POSS-Al-I** (c) and **POSS-Zn-Cl** (d).

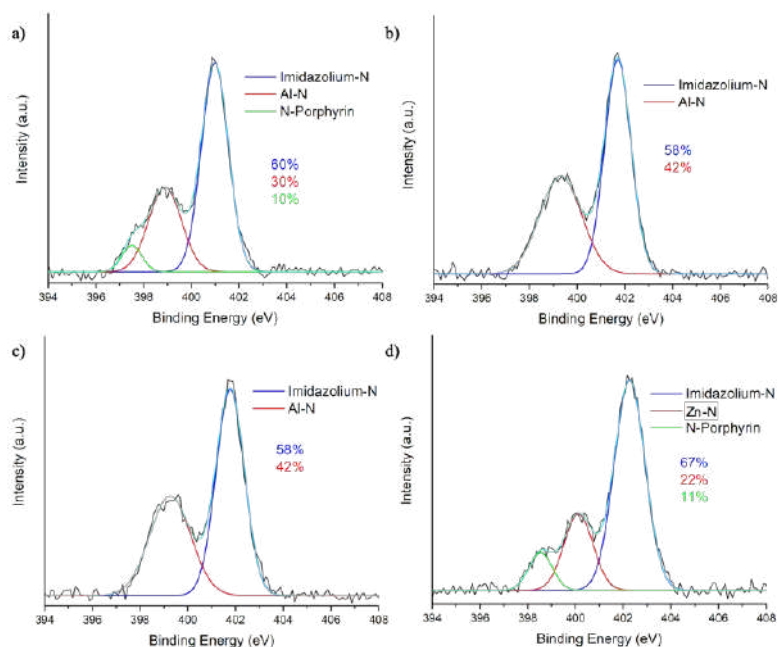


Figure 5. N1s High resolution of **POSS-Al-Cl** (a), **POSS-Al-Br** (b), **POSS-Al-I** (c) and **POSS-Zn-Cl** (d).

Figure 5 shows the high-resolution XPS spectra of the N1s region of **POSS-M-X**. From the deconvolution of the signals, it can be seen that all spectra show a contribution around 402 eV relative to the nitrogen atoms of the porphyrin ring coordinated with the metal (Al–N or Zn–N) and a contribution around 399 eV due to the nitrogen atoms of the imidazolium rings [2]. The contribution at about 398 eV in Figure 5a and 5d is due to a fraction of demetallized porphyrin [3-5].

Despite the small portion of decomplexed porphyrin, it is useful to note that in all aluminium solids the ratio between the porphyrin component and the imidazole component is approximately 1:1.5, meanwhile **POSS-Zn-Cl** has a slightly higher ratio of 1:2.

The amount of metal present in all the solids was estimated by inductively-coupled plasma atomic emission spectroscopy (ICP-OES) analysis and it is reported in Table 1.

Table 1. Loading of metal in the solids.

MATERIAL	METAL LOADING (mmol * g⁻¹)
POSS-Al-Cl	0.40
POSS-Al-Br	0.34
POSS-Al-I	0.38
POSS-Zn-Cl	0.60

Finally, the morphology of the catalysts was studied by using transmission electron microscopy (TEM). Figure 6 shows TEM images in which is evident that the four materials display irregular and amorphous structures. It can be seen from TEM images the solids are very compact polymers. The only one showing a subtle difference in its structure is **POSS-Al-Cl**, which shows a slightly more regular morphology.

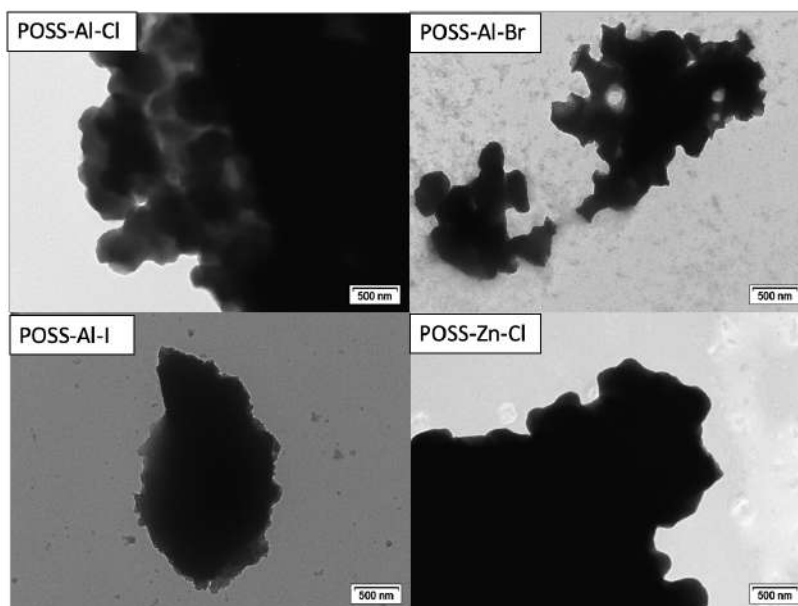
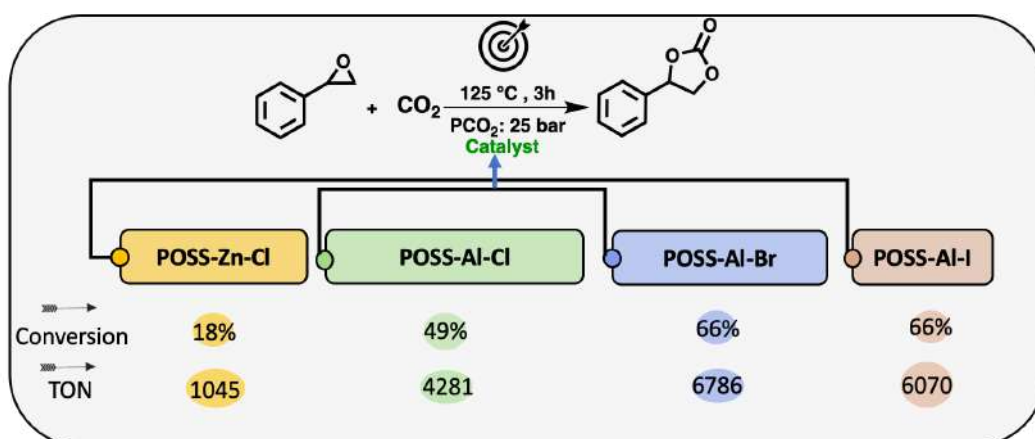


Figure 6. TEM images of the catalysts.

Once characterized, the four materials were investigated in the conversion of carbon dioxide to cyclic carbonates by employing styrene oxide as benchmark reactant under solvent-free conditions as shown in Scheme 2. Due to the different content of active species of the solids, a more specific comparison of the catalytic activity was performed considering the turnover number values based on the metal content (TON; defined as moles of epoxide converted/moles of M active sites).



Scheme 2. Comparison of the catalytic activity of **POSS-Zn-Cl** (60 mg; 0.036 mmol Zn) and **POSS-Al-Cl** (60 mg; 0.024 mmol Al), **POSS-Al-Br** (60 mg; 0.02 mmol Al) and **POSS-Al-I** (60 mg; 0.023 mmol Al) in the reaction of styrene oxide with CO₂. Reaction conditions: styrene oxide (209.7 mmol), catalyst (60 mg), 25 bar CO₂, 125 °C, 3 h, 500 rpm.

Initially, **POSS-Zn-Cl** and **POSS-Al-Cl** were tested in the reaction using the same mass amount obtaining a very different conversion of 18% and 49%, respectively (Scheme 2). The large difference in catalytic activity is even more evident if the TON is considered. **POSS-Zn-Cl** shows a TON of 1045, largely lower than 4281 which is the TON value when the test was carried out with **POSS-Al-Cl**. Considering from this result that there is a huge difference in the co-catalytic activity of the two selected metals, we decided to keep ongoing with Aluminum as Lewis acidic species. In order to evaluate the difference in activity of different halide as nucleophilic source a comparison between **POSS-Al-Cl**, **POSS-Al-Br** and **POSS-Al-I** was performed as well. The three tests were carried out with the same amount of material. The three materials show conversion values of 49% for **POSS-Al-Cl** and 66% for both **POSS-Al-Br** and **POSS-Al-I**. TON values confirm the same trend shown in conversion. Indeed, **POSS-Al-Cl** is the less active with a TON of 4862 while **POSS-Al-Br** and **POSS-Al-I** have almost the same activity showing TON values of 6740 and 6070, respectively. The slightly lower TON value of **POSS-Al-I** compared to **POSS-Al-Br** could be ascribed to the more compact morphology of the structure as previous shown with TEM images (see, Figure 6). Hence, it could be possible that some active sites in **POSS-Al-I** are not really accessible.

Afterwards, the promising bifunctional materials were employed with epichlorohydrin to study the recyclability of the catalysts. As expected, the materials containing the bromide ion or the iodide ion were more active than the material containing the chloride (see Chapter I, paragraph 1.3.1).

However, several problems with the handling of the reaction mixture were observed during the work-up steps of the catalytic test.

The materials were inseparable from the reaction mixture by centrifugation and also by filtration using a Millipore filter (0.2 μm PTFE membrane). The filter of the latter became clogged, not allowing the liquid phase to pass through. Different mixtures of solvents were added to the reaction mixture to favor the separation of the catalyst from the reaction mixture via centrifugation or filtration process. Even after several essays the solids were difficult to recover. This tendency could be

ascribed to the presence of the mono-vinylimidazolium salts. Perhaps, the reduced cross-linking causes the formation of a less rigid polymers together with small insoluble oligomers with an exceptional tendency to remain dispersed in the high viscosity mixture obtained at the end of the catalytic tests. The only material that was less tedious to recover from reaction mixture was **POSS-Al-Cl**. The material was used, for four consecutive runs with almost no loss in catalytic activity (Figure 7). After each cycle the solid was recovered from the reaction mixture by Millipore filtration, washed with toluene, ethanol and diethyl ether and dried under vacuum (4×10^{-4} mbar) at 60°C overnight. Further studies will be carried out in order to better understand the behavior of this catalytic solid.

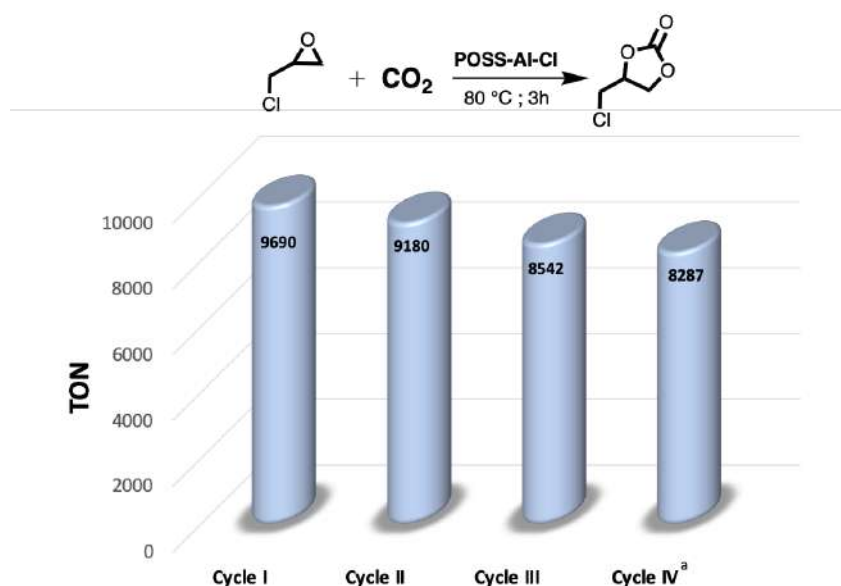


Figure 7. Recycling tests of **POSS-Al-Cl**. Reaction conditions: epichlorohydrin (306 mmol), 60 mg of catalyst (0.024 mmol Al, 0.008 mol%), 25 bar of CO_2 , 3h, 500 rpm. a) epichlorohydrin (280.5 mmol), 55 mg of catalyst (0.022 mmol Al, 0.008 mol%), 25 bar of CO_2 , 3h, 500 rpm.

5.3 Conclusions

Three different imidazolium salts, bearing chloride (Cl^-), bromide (Br^-) or iodide (I^-) as counter anion, were synthesized and successfully polymerized with aluminum chloride tetrastyrilporphyrin (**TSP-AlCl**) in presence of octavinylsilsesquioxane. The AIBN mediated radical polymerization in presence of this silica nanocage acting as building block precursor, allows to obtain **POSS-Al-Cl**, **POSS-Al-Br**, **POSS-Al-I** materials. Moreover, **POSS-Zn-Cl** was successfully prepared by the same synthetic route using zinc tetrastyrilporphyrin (**TSP-Zn**) instead of the aluminium one.

The obtained cross-linked networks have been thoroughly characterized by way of several spectroscopic and analytical techniques such as TGA, ICP-OES, XPS, TEM, solid state NMR. Hybrid materials were used as heterogeneous catalysts in the cycloaddition reaction of CO_2 with epoxides to obtain the corresponding cyclic carbonates under solvent-free conditions. An initial comparison between **POSS-Al-Cl** and **POSS-Zn-Cl** shows how aluminium (Al) is a better co-catalyst than zinc (Zn) in this class of materials. It has been shown also, how the presence of different Lewis species has an influence on the catalytic performance of the materials. Among the halide series of materials, bearing aluminium as co-catalytic species, as expected the **POSS-Al-Cl** resulted the less efficient catalysts in the reaction between styrene oxide and CO_2 . Meanwhile, **POSS-Al-Br** and **POSS-Al-I** showed the same conversion value. The slightly lower TON of the latter is maybe ascribed to the more condensed and inaccessible structure. Moreover, even if the chloride-based material was the less active, it was the only one to be recoverable. **POSS-Al-Br** and **POSS-Al-I** indeed, were really impossible to separate from the reaction mixture with common methods such as filtration or centrifugation. **POSS-Al-Cl** was recovered from the reaction mixture by filtration via Millipore membrane. The materials resulted recyclable for four times in a row with only a slight decrease in catalytic activity.

As future work could be interesting evaluate the performance of **POSS-Al-Cl** with different substrates and different reaction conditions in order to better understand the activity of this solid in the catalysis of CO_2 addition to epoxides.

5.4 Experimental Section

Materials and methods

Octavinylsilsesquioxane, styrene oxide, epichlorohydrin and were purchased from TCI. $\text{Zn}(\text{OAc})_2$, 4-vinyl benzyl chloride, Glycidol and 2,2'-azobis(2-methylpropionitrile) (AIBN) and diethylaluminum chloride were purchased from Sigma-Aldrich. These chemicals were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer. Solid state ^{13}C CP-MAS TOSS NMR spectra were recorded at room temperature, on a Jeol ECZ-R 600 MHz spectrometer operating at 14.1 T, using a contact time of 2 ms, a spinning rate of 8 KHz and an automas probe of 3.2 mm with acquisition delay of 5 s and 5000 scans. Solid ^{29}Si NMR spectra were recorded at room temperature on a JEOL ECZ-R spectrometer operating at 14.1 T using a 3.2 mm automas probe and spinning frequencies of 10 kHz with acquisition delay of 10 s and 10000 scans. X-ray photoelectron spectroscopy (XPS) analyses were carried out in a ThermoFisher ESCALAB 250Xi instrument. Thermogravimetric analysis was performed under air flow from 25 to 900 °C with a heating rate of 10 °C/min in a Mettler Toledo TGA STAR system. Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai 10 microscope operating at 80 kV. The samples were prepared by dispersion of a small quantity of the material in absolute ethanol and deposited into a copper grid. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed in an Optima 8000 ICP-OES spectrometer.

Synthesis of 4-vinyl benzyl bromide

The synthesis of 4-vinyl benzyl bromide was synthesized by adapting a reported procedure [6].

LiBr (5.65 g, 65 mmol) was solubilized in 10 mL of anhydrous THF. After a complete dissolution, 4-vinylbenzyl chloride (1.85 mL, 13 mmol) was added under Ar atmosphere and the reaction mixture was stirred at 40 °C for 24 h. After reaction time, the solvent was removed under reduced pressure. The residue then, was solubilized in water and extracted three times with diethyl ether. The organic layer was then washed with a Brine solution and dried with Na_2SO_4 . The solvent was

removed under reduced pressure to provide yellowish liquid (2.5 g, 96:4 ratio Br:Cl).

¹H-NMR (CDCl₃, 400 MHz): δ ppm 7.37 (m, 4H), 6.70 (dd, J = 17.69 Hz, 11.08 Hz, 1H), 5.77 (d, J = 17.57 Hz, 1H), 5.28 (d, J = 10.98 Hz, 1H), 4.47 (s, 2H).

Synthesis of 4-vinyl benzyl iodide

The synthesis of 4-vinyl benzyl iodide was synthesized by adapting a reported procedure [7].

NaI (2.8 g, 18.8 mmol) was solubilized in 15 mL of acetone. After a complete dissolution, 4-vinylbenzyl chloride (1.85 mL, 13 mmol) was added under Ar atmosphere and the reaction mixture was refluxed for 24 h. After reaction time, the solvent was removed under reduced pressure. The residue was solubilized in water and extracted three times with dichloromethane. The organic layer was washed with brine solution and dried (Na₂SO₄). The solvent was removed under reduced pressure to provide yellowish liquid (3.6 g, 99%).

¹H-NMR (CDCl₃, 400 MHz): δ ppm 7.38 (s, 4H), 6.74 (dd, J = 17.6, 10.7 Hz, 1H), 5.82 (dd, J = 17.6, 0.7 Hz, 1H), 5.32 (dd, 10.7, 0.7 Hz, 1H), 4.50 (s, 2H).

General synthesis of 1-Methyl-3-(4-vinylbenzyl)imidazolium Salts.

1-methylimidazole (1.1 g, 13 mmol) was dissolved in dry acetonitrile (11 mL). After the complete dissolution, 4-vinylbenzyl chloride (2.0 g, 13 mmol) or 4-vinylbenzyl bromide (2.3 g, 13 mmol) or 4-vinylbenzyl iodide (3.1 g, 13 mmol) was added dropwise. The resulting mixture was stirred at 80 °C for 96 h. Next, the solvent was evaporated under reduced pressure. Afterwards the resulted solid was solubilized in hot methanol and precipitated in diethyl ether several times and dried. (99 %)

¹H NMR (1-methyl-3-(4-vinylbenzyl)imidazolium chloride) (CD₃OD, 300 MHz): δ 9.04 (1H), 7.51 (1H), 7.40 (1H), 7.35 (2H), 7.26 (2H), 6.54 (1H), 5.62 (1H), 5.46 (2H), 5.16 (1H), 3.93 (3H, Me).

Synthesis of Tetrastyrilporphyrin (TSP)

Tetrastyrilporphyrin (TSP) was synthesized according to a reported procedure [2]. In a 250 mL two-neck round-bottom flask propionic acid (65 mL) was heated to

140 °C before adding pyrrole (500 μ L, 7.1 mmol) and 4-vinylbenzaldehyde (0.926 g, 7.1 mmol). The system was allowed to react for 5 hours before its cooling down, filtering and washing with methanol and ethyl acetate. After drying, the tetrastyrilporphyrin was obtained as a purple powder (415 mg; 27 %). ^1H NMR (300 MHz, CDCl_3 , δ): 8.90 (s, 8 H), 8.19 (d, J = 7.9 Hz, 8 H), 7.81 (d, J = 8.0 Hz, 8 H), 7.07 (dd, J = 17.6, 10.9 Hz, 4 H), 6.08 (d, J = 17.6 Hz, 4 H), 5.51 (d, J = 10.9 Hz, 4 H), -2.73 (s, 2 H).

Synthesis of tetrastyrilporphyrin aluminum chloride (TSP-AlCl)

Tetrastyrilporphyrin aluminum chloride (TSP-AlCl) was synthesized according to a reported procedure [2]. In a 50 mL two-neck round-bottom flask, under Ar atmosphere, tetrastyrilporphyrin (200 mg, 0.28 mmol), was dissolved in 4 mL of dry dichloromethane. The mixture was cooled to 0 °C then a solution of diethylaluminum chloride (0.1 M solution in hexane, 170 μ L, 0.3 mmol) was added dropwise. Then the reaction mixture was stirred for 6h at room temperature. After the reaction time the solvent was removed by rotary evaporation before adding methanol and transfer all the mixture in a centrifuge tube. Four centrifugations with methanol were carried out and the combined supernatants were evaporated under vacuum. Once again, the solid obtained was taken up with dichloromethane and all the insoluble residues were removed by filtration. The filtrate was concentrated under vacuum and TSP-AlCl was obtained as purple powder (115 mg; 53 %). ^1H NMR (300 MHz, CDCl_3 , δ): 8.41 (s, 8 H), 7.49 (s, 16 H), 6.98 (dd, J = 17.6, 11.0 Hz, 4 H), 5.99 (d, J = 17.7 Hz, 4 H), 5.49 (d, J = 10.9 Hz, 4 H).

Synthesis of tetrastyrilporphyrin zinc complex (TSP-Zn)

Tetrastyrilporphyrin (200 mg, 0.28 mmol) was dissolved in CHCl_3 (20mL) after that a solution of anhydrous $\text{Zn}(\text{OAc})_2$ (400 mg 2 mmol) in MeOH (6 mL) was added and the reaction mixture was stirred overnight at 70 °C. After the reaction time the solvent was removed via rotary evaporation. Once again, the solid obtained was taken up with dichloromethane and all the insoluble residues were removed by filtration. The filtrate was concentrated under vacuum and TSP-Zn was obtained as purple powder (218 mg; 99%).

¹H NMR (300 MHz, CDCl₃, δ): 8.41 (s, 8 H), 7.49 (s, 16 H), 6.98 (dd, J = 17.6, 11.0 Hz, 4 H), 5.99 (d, J = 17.7 Hz, 4 H), 5.49 (d, J = 10.9 Hz, 4 H).

Preparation of POSS-Al-Cl

In a 25 mL two-neck round-bottom flask, octavinylsilsesquioxane (150 mg, 0.237 mmol) and **TSP-AlCl** (200 mg, 0.25 mmol) and 1-methyl-3-(4-vinylbenzyl)imidazolium chloride (480 mg, 2 mmol) were solubilized in dry DMF (10 mL) and sonicated for 10 min. Then, AIBN (106 mg, 0.636 mmol) was added under argon and the reaction mixture stirred at 120 °C for 24h. After the reaction time the dark mixture obtained was cooled at room temperature and transferred in a centrifuge tube by adding a small amount of DMF. The residue mixture was subjected to centrifugation several times with different solvents. Two times in DMF, three times using a methanol/Et₂O (v/v) 3/1 mixture and two times with Et₂O. The solid was recovered and dried under vacuum (4*10⁻⁴ mbar) at 60 °C. **POSS-Al-Cl** was obtained as a dark powder (560 mg).

Preparation of POSS-Al-Br

In a 25 mL two-neck round-bottom flask, octavinylsilsesquioxane (150 mg, 0.237 mmol) and **TSP-AlCl** (200 mg, 0.25 mmol) and 1-methyl-3-(4-vinylbenzyl)imidazolium bromide (550 mg, 2 mmol) were solubilized in dry DMF (10 mL) and sonicated for 10 min. Then, AIBN (110 mg, 0.660 mmol) was added under argon and the reaction mixture stirred at 120 °C for 24h. After the reaction time the dark mixture obtained was cooled at room temperature and transferred in a centrifuge tube by adding a small amount of DMF. The residue mixture was subjected to centrifugation several times with different solvents. Two times in DMF, three times using a methanol/Et₂O (v/v) 3/1 mixture and two times with Et₂O. The solid was recovered and dried under vacuum (4*10⁻⁴ mbar) at 60 °C. **POSS-Al-Br** was obtained as a dark powder (480 mg).

Preparation of POSS-Al-I

In a 25 mL two-neck round-bottom flask, octavinylsilsesquioxane (150 mg, 0.237 mmol) and **TSP-AlCl** (200 mg, 0.25 mmol) and 1-methyl-3-(4-

vinylbenzyl)imidazolium iodide (670 mg, 2 mmol) were solubilized in dry DMF (10 mL) and sonicated for 10 min. Then, AIBN (115 mg, 0.690 mmol) was added under argon and the reaction mixture stirred at 120 °C for 24h. After the reaction time the dark mixture obtained was cooled at room temperature and transferred in a centrifuge tube by adding a small amount of DMF. The residue mixture was subjected to centrifugation several times with different solvents. Two times in DMF, three times using a methanol/Et₂O (v/v) 3/1 mixture and two times with Et₂O. The solid was recovered and dried under vacuum (4×10^{-4} mbar) at 60 °C. **POSS-Al-I** was obtained as a dark powder (502 mg).

Preparation of POSS-Zn-Cl

In a 25 mL two-neck round-bottom flask, octavinylsilsesquioxane (150 mg, 0.237 mmol) and **TSP-Zn** (200 mg, 0.25 mmol) and 1-methyl-3-(4-vinylbenzyl)imidazolium chloride (500 mg, 2 mmol) were solubilized in dry DMF (10 mL) and sonicated for 10 min. Then, AIBN (110 mg, 0.660 mmol) was added under argon and the reaction mixture stirred at 120 °C for 24h. After the reaction time the dark mixture obtained was cooled at room temperature and transferred in a centrifuge tube by adding a small amount of DMF. The residue mixture was subjected to centrifugation several times with different solvents. Two times in DMF, three times using a methanol/Et₂O (v/v) 3/1 mixture and two times with Et₂O. The solid was recovered and dried under vacuum (4×10^{-4} mbar) at 60 °C. **POSS-Zn-Cl** was obtained as a green powder (685 mg).

Catalytic experiments

Catalytic experiments were carried out using a Cambridge Design Bullfrog batch reactor equipped with temperature control and mechanical stirring. In each test, the catalyst and the proper epoxide were added to a Teflon vial and then the reactor was closed. After passing a flow of N₂ for 10 minutes and loading 25 bar of CO₂, the system was left to react at the target temperature reached by a ramp of 5 °C/min. After the proper reaction time, the reactor was cooled down to room temperature, depressurized and, then, the catalyst was recovered from the reaction mixture by Millipore filtration using a 0.2 µm PTFE membrane. The supernatant was analyzed

by ^1H NMR in $\text{d}_6\text{-DMSO}$. Each catalyst was dried overnight under vacuum (4×10^{-4} mbar) at 60°C prior to the catalytic test.

Recycles

Recycling tests were carried out employing epichlorohydrin. At the end of the catalytic experiment, after separation of the catalyst from the reaction mixture by Millipore filtration using a $0,2\ \mu\text{m}$ PTFE membrane, a small amount of solvent (toluene, then ethanol and finally diethyl ether) was added to the solid and the mixture filtrated again. The recovered solid was dried overnight in a vacuum (4×10^{-4} mbar) oven at $60\ ^\circ\text{C}$. In order to maintain the same catalytic loading, the dried catalyst was weighed and reused in the same reaction, modifying, if necessary, the amount of epoxide.

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CHAPTER VI:
General Conclusions

6.1 General conclusions

This Ph.D. thesis surveyed the development of novel hybrid materials as heterogeneous catalyst for CO₂ conversion in cyclic carbonates via its addition to epoxides under solvent free conditions. All the materials of this work were well characterized by means of techniques such as thermogravimetric analysis, multinuclear solid-state NMR, transmission electron microscopy, N₂ physisorption, X-ray photoelectron spectroscopy, inductively coupled plasma optical emission spectroscopy. The catalytic performances of all the hybrids were extensively evaluated in terms of selectivity, recyclability, productivity, and turnover number/turnover frequency values.

In the first part of the work an imidazolium salt bearing bromide as counter anion was grafted with a polymerization reaction in different carbon nanoforms (SWCNTs, MWCNTs, SWCNHs). The synthetic route allows us to obtain six different materials. All supported materials were tested in the reaction between CO₂ and styrene oxide and compared in catalytic activity each other using the unsupported homopolymer of the imidazolium salt as reference. Among all, SWCNTs and MWCNTs based materials were the most active of the series. Moreover, they showed also an increase of the catalytic activity during the recycling tests. This behaviour was ascribed to their change in morphology that led to materials with higher surface areas and more accessible catalytic sites and, possibly, to the contemporary presence of leached species.

Furthermore, a series of bifunctional materials based on POSS were synthesized. An Aluminium porphyrin complex was used as Lewis acid source and was polymerized in presence and in absence of a bis-vinyl imidazolium salt bearing bromide as nucleophilic species, with an octavinyl silsesquioxanes as inorganic building block core.

The heterogeneous bifunctional hybrid (**POSS-TSP-AlCl-imBr**) showed an excellent catalytic activity and resulted more active in CO₂ than the analogue single catalytic species acting simultaneously (**POSS-TSP-AlCl** and **bmimBr**).

Moreover, **POSS-TSP-AlCl-imBr** was tested in different reaction conditions. The material was recyclable for five consecutive time without losing catalytic activity

and also, it showed a recyclability in different reaction conditions and using different epoxides showing a slight decrease in catalytic activity.

Then, a final investigation was carried out by comparing different solids bearing different Lewis acid species and different nucleophilic species.

Four different POSS-porphyrin-imidazolium materials were synthesized with the same radical polymerization reaction.

An initial comparison was done with two materials (**POSS-Al-Cl** and **POSS-Zn-Cl**) bearing chlorine as nucleophile and different Lewis acid species, Aluminium and Zinc, respectively.

The better performance in catalytic activity of the former led us to keep ongoing in the investigation with Aluminium as co-catalyst.

For that reason, other two materials bearing Aluminium as Lewis acid but Bromide or Iodide as nucleophilic species were prepared (**POSS-Al-Br** and **POSS-Al-I**).

Among all Aluminium materials **POSS-Al-Cl** was the less active as expected, but nevertheless it was also the only one to be recoverable and recyclable. Indeed, **POSS-Al-Br** and **POSS-Al-I** were not really recoverable from the reaction mixture via simple filtration or centrifugation, losing in this way the advantages to use heterogeneous catalyst.

In this Ph.D. dissertation, all materials were active in the CO₂ conversion showing good performance and good selectivity toward the desired product. In particular POSS based materials showed outstanding performance compared to literature in terms of TON and Productivity. This performance could be ascribed to a twofold effect. A first contribution is attributed to the close proximity between the metal centers and the bromide ions, which are able to cooperate and exert a synergistic effect during the catalytic cycle. This proximity effect was enhanced when a mono vinyl imidazolium salt was selected as nucleophilic source instead of using a bis vinyl compound. In the conversion of styrene oxide with CO₂ the higher TON value showed by **POSS-Al-Br** compared to **POSS-TSP-AlCl₃-imiBr** supports the hypothesis that decreasing the crosslinker elements during the polymerization process can improve the proximity effect between the metal center and the nucleophilic source. A second contribution comes from the use of the POSS-silica nanocage used as a building block during synthesis. The possibility of

functionalizing the POSS cage at its vertices ensures an increase in the concentration of active sites in the material at certain localized positions.

It is worth saying that the reaction under examination has different experimental parameters and a close comparison is difficult to do. However, it is important also to stress out that our reactor operates with large amounts of epoxide (200 mmol) and the use of just an equivalent of CO₂ at atmospheric pressure would require the filling of a volume of almost 5 litres at room temperature. On the other hand, it must also be said that even with large amount of epoxide we are able to have almost total conversion using really a small amount of material (about 0.006-0.01 mol%). The industrial production of cyclic carbonates, such as propylene carbonate, is usually carried out within reactors operating at high pressures (8-60 bar) while still maintaining small excess of CO₂ (up to 1.5 equivalent with respect to propylene oxide) and temperatures between 110 and 180 °C, even when homogeneous catalysts are used. [1] One of the goals of process intensification is the reduction in the size and/or volume of all the process plant components. The use of high pressures makes it possible to reduce the reactor volume considerably, since working with atmospheric CO₂ pressure would require a considerably larger volume than with pressurised gas. Therefore, our experiments under the adopted reaction conditions assume considerable importance as they are very close to the conditions normally used on industrial scale and therefore only minor adjustments would be necessary to transpose the preparations reported here to a large scale.

6.2 Proximity effect and future perspectives

As already mentioned a lot of time during this dissertation, a twofold synergistic proximity effect between the metal centers and the nucleophilic species was found out during the study of the catalytic activity of these bifunctional materials based on POSS-porphyrin-imidazolium systems.

Preliminary evidences on a previous work based on functionalized SBA-15 with imidazolium modified polyhedral oligomeric silsesquioxanes show how the presence of POSS cages enhances the catalytic performances. The key point of this activity was ascribed to the increased concentration of imidazolium moieties around

the silica-nanocages. TON of about 4000 was reached at 150°C for 3h without adding any Lewis acid source in the system. [3]

In this context, **POSS-TSP-AlCl-ImiBr** combines the above-mentioned effect of silica nanocages with the proximity effect and the synergistic cooperation between the metal centers and the nucleophilic species due to the covalent bond obtained among the imidazolium moiety and the porphyrin molecules (Figure 1). [4]

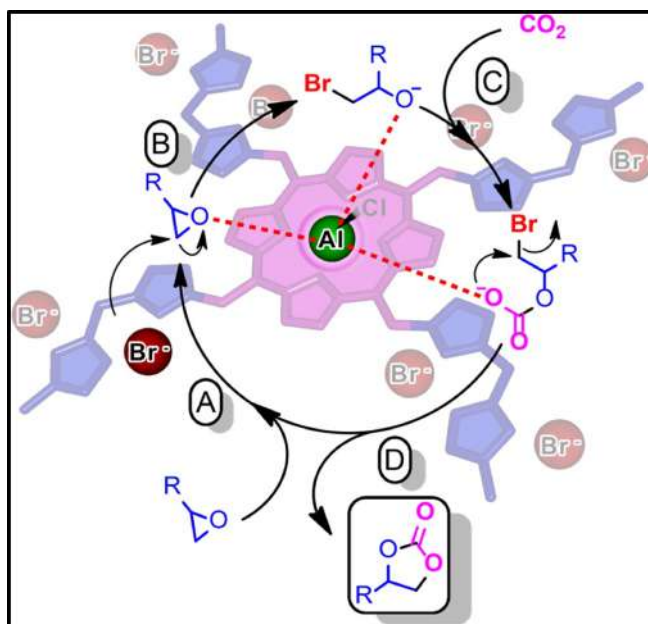


Figure 19.[4] Proposed proximity effect between halide anions (Br^-) and metal (Al) centers in Imidazolium/Porphyrin catalytic system.

The presence of an aromatic cation with a delocalized charge near the porphyrin metal center may allow the mobile counter anion of the imidazolium ring to be close enough to attack almost immediately the epoxides once that the oxygen of the latter is coordinated by the metal center.

This hypothesis should be addressed by different experimental studies supported with computational calculations.

At the moment **POSS-TSP-AlCl** demonstrated that the presence of the nanocages enhances the catalytic activity of the material. Indeed, the solid showed better catalytic performances in TON values compared to the unsupported **TSP-AlCl-imi** that could benefit only of the proximity effect between porphyrin and imidazolium.

Moreover, keeping ongoing with POSS based material, the latter mentioned effect was slightly improved when less inter-crossing systems elements participate to the synthetic process.

In the case of **POSS-Al-Br**, probably, the presence of a mono-vinylimidazolium moiety decreased the presence of inter-crossing system elements. As consequence of this hypothesis could be possible that more bonds porphyrin-imidazolium or imidazolium-POSS should be formed during the synthetic process.

This can allow to have more proximity among metal centers and nucleophile or have a local increase in imidazolium concentration in the structure of the solids, respectively.

Moreover, the polymerization process is a random process and it is difficult predict the final structure of the solid with a good precision.

Despite this, it is important make a final comparison between **POSS-Al-Br**, **POSS-TSP-AlCl-imiBr** and **TSP-AlCl-imi**. The three materials were able to convert styrene oxide at 125°C in 3h with TON values of 6786, 5849, 3869, respectively. This higher TON values of **POSS-Al-Br** compared to the others can suggest that this could be the correct way to explore more this particular behavior of POSS bifunctional systems.

One possibility to try to enhance both of the mentioned effect could be designing a metallo-porphyrin bearing four imidazolium moieties and let it react with a proper functionalized nucleophilic-POSS.

6.3 References

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ANNEXES

NMR experimental details.

^1H NMR spectra were recorded on a JEOL 400 MHz spectrometer with a pulse of 45° and a relaxation delay of 6.6 s.

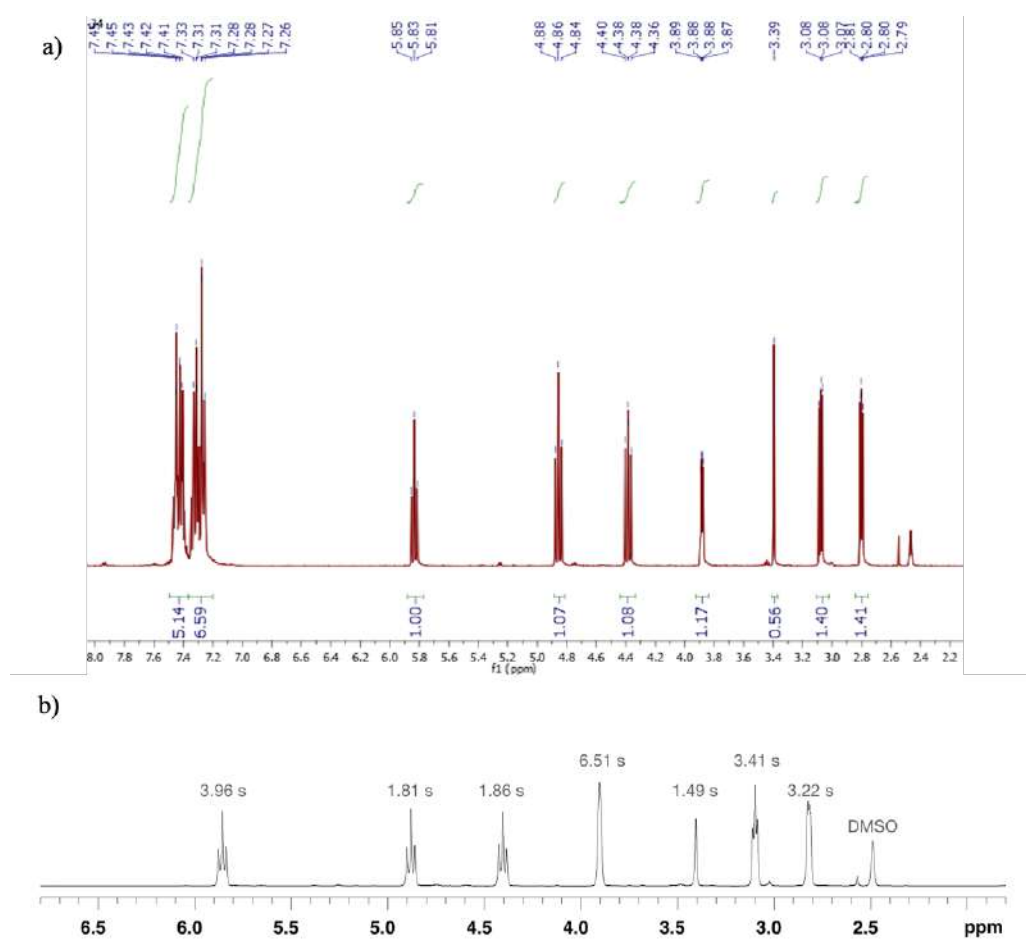


Figure 1. (a) Full spectra of the reaction mixture between styrene oxide and CO_2 ; (b) pattern of signals of the same spectra with the related relaxation time for each signal.

In order to estimate the error on the values of conversion obtained by proton NMR analysis, a more accurate study on the relaxation times was done on the reaction mixture concerning the conversion of styrene oxide in styrene carbonate. In Figure 1a is reported the full spectra of the reaction mixture, while in Figure 1b is reported the pattern of signals with the related relaxation time for each signal. From the

Figure 1b is clear that relaxation delays are different. A more accurate analysis showed that the correct parameters to do a correct quantitative analysis is to acquire the spectra on the JEOL 400 MHz spectrometer imposing a pulse of 90° and a relaxation delay of 39 s.

Despite this, the acquisition of the spectra was done 10 times with both conditions. This analysis showed that the error committed in the calculation of the conversion when the spectra is recorded with 45° as pulse and 6.6 s as relaxation delay is about 3-5% respect to the value obtained acquiring the spectra with a pulse of 90° and a relaxation delay of 39 s.

It is worth saying that 39 s is a really long relaxation delay and thus, keeping this time means longer analysis. In consideration of all this, we should say that a difference of 3-4% in conversion values is not a significant difference when we are studying the catalytic activity of two or more materials. It is almost impossible finds measurements without experimental errors and normally 5% confidence interval is accepted. Considering this, it reasonable make this small error but working with much lower analysis times. Generally, proton NMR is a fairly routine technique in the characterization of molecules. It is therefore essential to have fairly fast analysis times while lying a good degree of accuracy as sin this case.

In any case this example was done on styrene oxide, the analysis of relaxation time can be done for each substrate in order to find the optimum parameters and be able to be always inside of 5% error confidence interval.

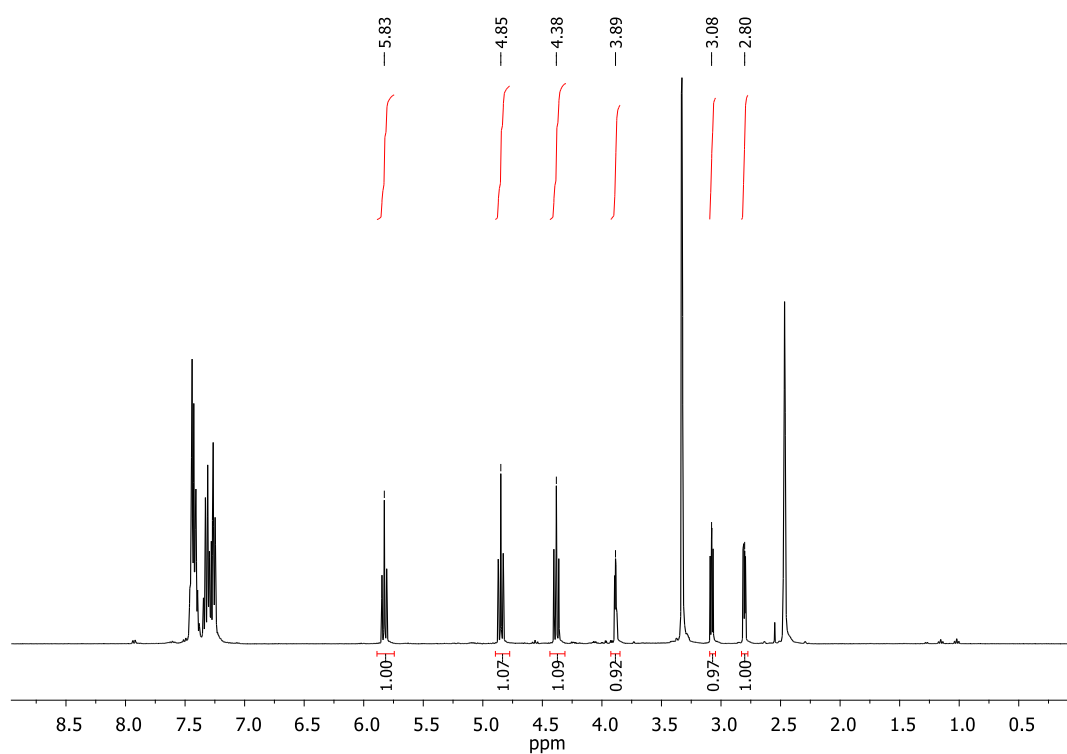


Figure 2. ^1H NMR (400 MHz, DMSO) of the reaction mixture I cycle (Chapter IV; Figure 7)

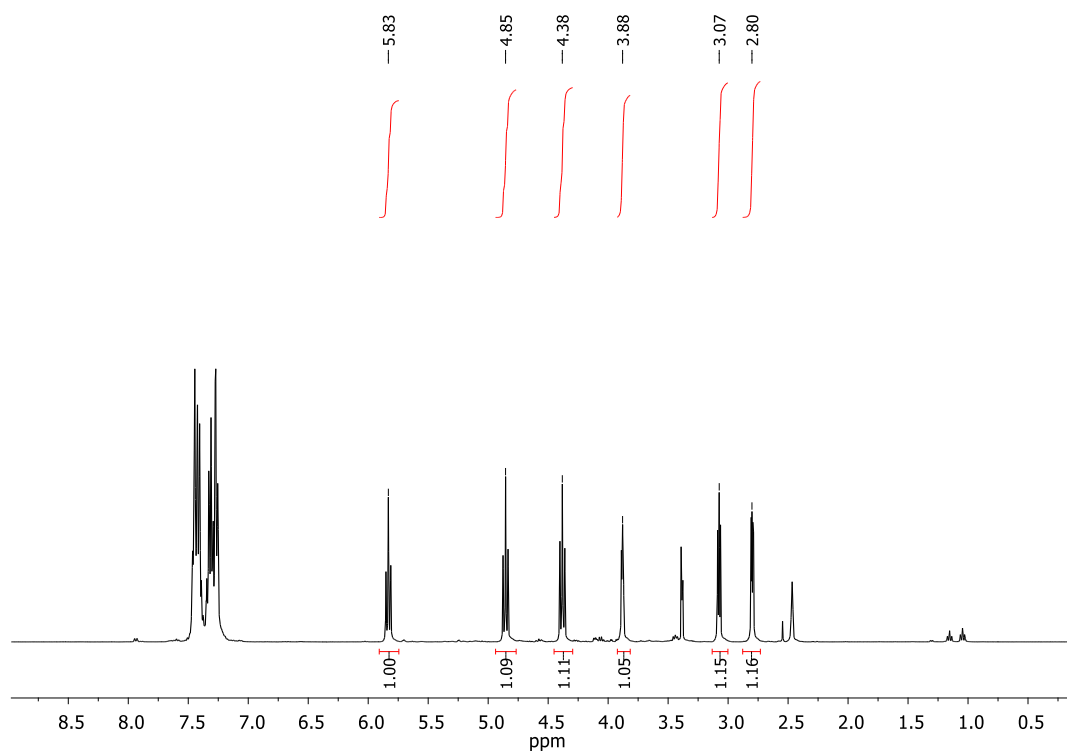


Figure 3. ^1H NMR (400 MHz, DMSO) of the reaction mixture III cycle (Chapter IV; Figure 7)

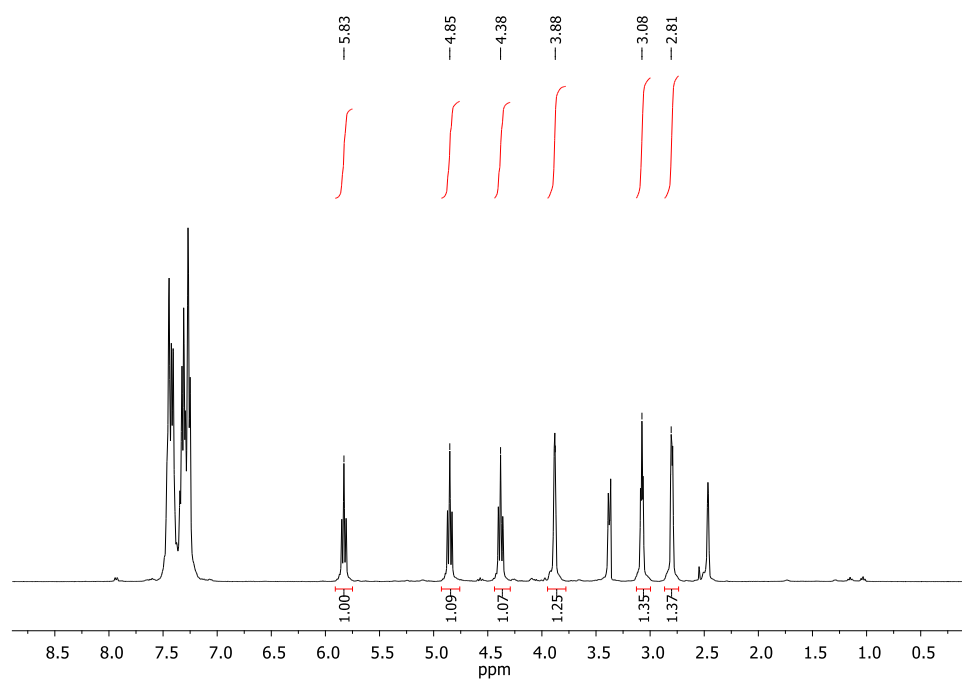


Figure 4. ^1H NMR (400 MHz, DMSO) of the reaction mixture V cycle (Chapter IV; Figure 7)

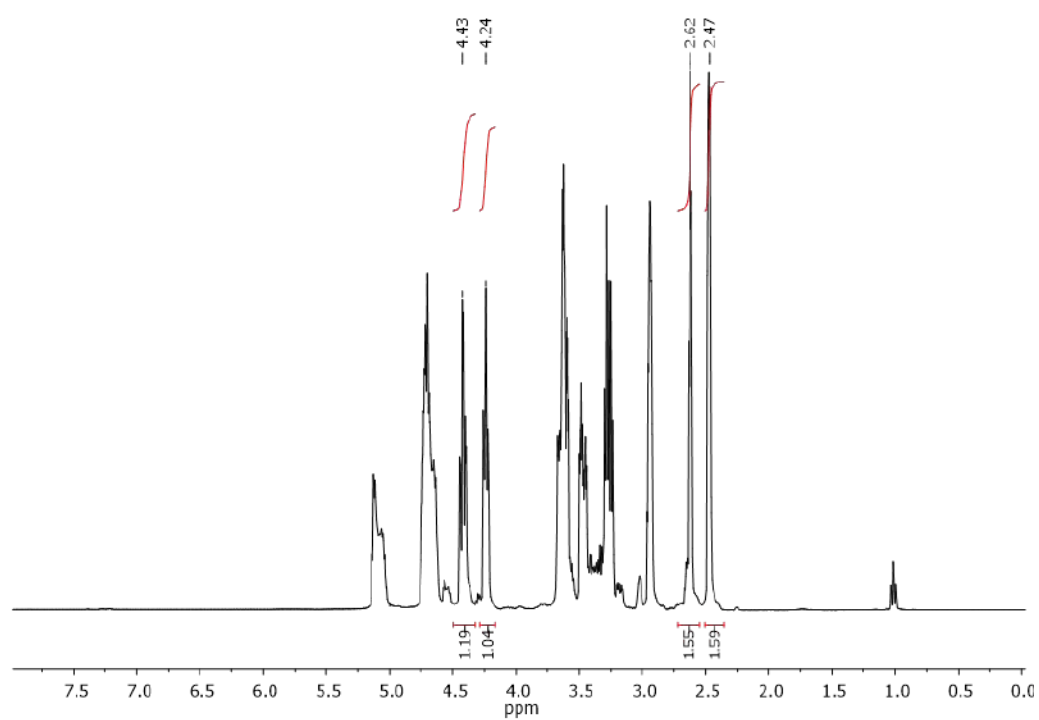


Figure 5. ^1H NMR (400 MHz, DMSO) of the reaction mixture Entry 2, Table 1, Chapter IV

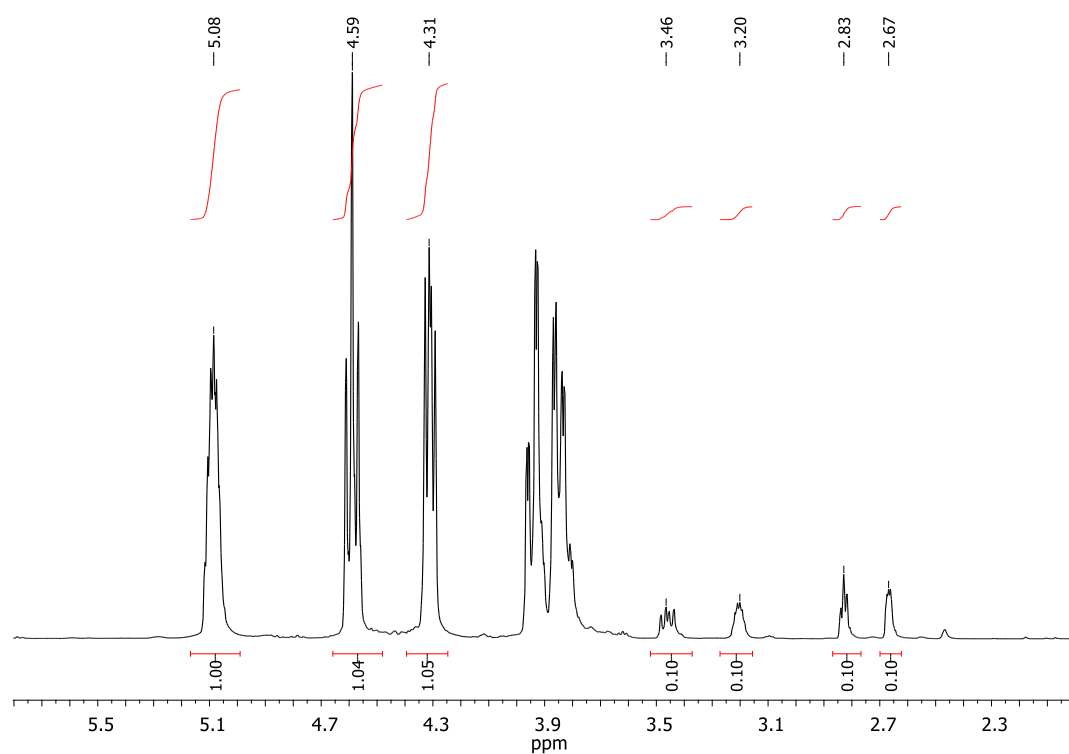
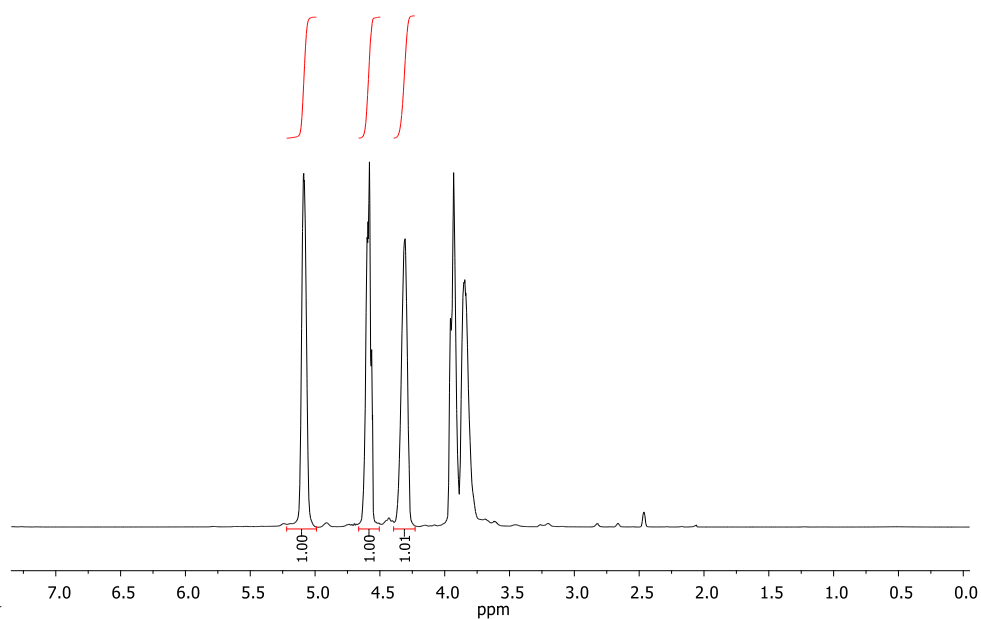


Figure 6. ^1H NMR (400 MHz, DMSO) of the reaction mixture Entry 5, Table 1, Chapter



IV

Figure 7. ^1H NMR (400 MHz, DMSO) of the reaction mixture Entry 6, Table 1, Chapter IV

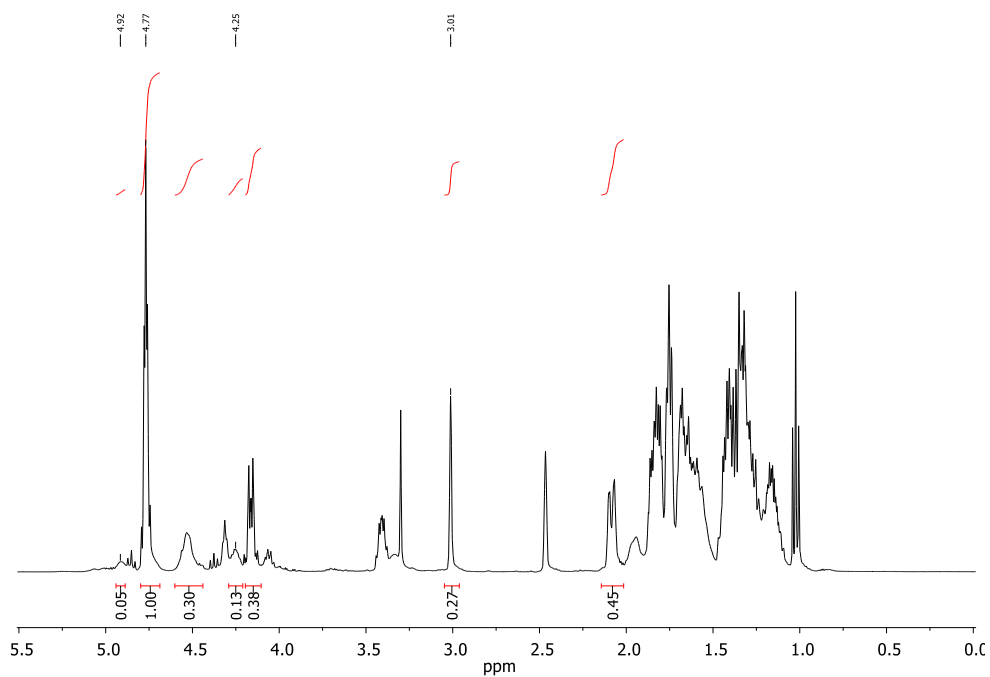


Figure 8. ^1H NMR (400 MHz, DMSO) of the reaction mixture Entry 9, Table 1, Chapter IV