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Phosphonium Salt/Al-Porphyrin Copolymer as Bifunctional Heterogeneous Catalyst for CO_2 Conversion to Cyclic Carbonates

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The effective chemical valorization of CO_2 by means of its conversion into valuable products is now more than ever a topic of considerable interest. It is on that basis that herein we have chosen the conversion of CO_2 and epoxides to cyclic carbonates as a convenient route to achieve this goal. A new bifunctional (Lewis acid/nucleophile) heterogeneous material, TSP-AlCl-PhospBr, was designed in order to guarantee a close proximity between the two active sites that can cooperate to the activation and opening of the epoxide ring. The prepared copolymer has been extensively characterized using various spectroscopic and analytical techniques. As a heterogeneous catalyst, it enables efficient chemical conversion of CO_2 and epoxides, even at low temperatures, down to 30 °C, without the use of solvents. In particular, the catalyst demonstrates high turnover numbers (TON) and frequency values (TOF). Recyclability studies on TSP-AlCl-PhospBr have shown its stability and reusability for consecutive cycles without the need of reactivation procedures.

Introduction

The high concentration of carbon dioxide (CO_2) in the atmosphere is responsible for the greenhouse effect and the consequent changes to the global climate. This increased emission is mainly due to fossil fuel combustion for energy production, transportation, and industrial processes. Against this background, the scientific community is committed to seeking alternative energy sources and developing systems for the chemical utilization of CO_2.[1] A viable strategy that enables the reduction of CO_2 emissions is the carbon capture and storage (CCS).[2] The CCS has emerged as a tangible process that aims to reduce negative impacts on humans and environment. On the other hand, carbon dioxide is an interesting raw material for the production of valuable chemicals.[3] Indeed, it is possible to consider this molecule as a source of renewable feedstock rather than as a "waste" product. Furthermore, it should be emphasized that this renewable source of carbon is abundant, economical, non-toxic and non-flammable. However, because of its low reactivity, processes that could use carbon dioxide as a sustainable resource requires the use of highly energetic starting materials such as hydrogen, epoxides, and amines employed in conjunction with a catalyst that can adequately decrease the activation energy of the selected reaction. A significant transformation is the incorporation of CO_2 into epoxides to generate cyclic carbonates.[2b,4] It is because of their interesting features, such as low vapor pressure, high boiling point, low toxicity, and biodegradability, cyclic carbonates find applications in both industry and academia. Their uses include those as polar solvents with a high boiling point, electrolytes for batteries, precursors for polymeric materials, and additives for fuels.[4a,5] Furthermore, organic carbonates are considered a green alternative to replace various toxic chemical reagents.[6] From the point of view of green chemistry and sustainability, the relevance of the synthesis of five-membered cyclic carbonates, from carbon dioxide and epoxides, lies in the transformation of a renewable source into a valuable chemical product, as well as in the possibility of carrying out the process under solvent-free conditions. In addition, the process exhibits 100% atom economy and the use of an easily recoverable heterogeneous catalyst can improve the greenness of the reaction.[7] Moreover, heterogeneous catalysts are often at the forefront of the chemical industry, as the possibility of recycling the material in a very simple way allows for a more economical process, increasing the turnover number of the process.[8] In this context, there is growing interest in the design of catalytic systems that include Lewis acid sites for electrophilic activation of the epoxy substrate and nucleophilic species for promoting epoxide ring opening. In the last years, several heterogeneous

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catalytic systems, such as polymeric matrix, covalent organic frameworks (COFs), porous organic polymers (POPs), porous ionic polymers (PIPs), have been developed with the goal of having the two active sites in the same structure.[9] Although homogeneous catalysts achieve high efficiency in the cycloaddition reaction of CO_2, the decision to rely on a heterogeneous bifunctional catalyst is probably more attractive than using a homogeneous catalytic system consisting of two separate components. This point could be advantageous in terms of environmental impact and cost-effectiveness. Indeed, when employing homogeneous catalysts, the recovery and recycling of the catalyst, along with the laborious purification process of cyclic carbonates, result in a significant consumption of time and energy.[10]

Porous organic polymers (POPs) are considered a suitable and safer alternative for sustainable process design due to their low cost, non-toxic nature, and simplified processing procedures. POPs are typically amorphous materials with disordered porosity. Despite their lack of ordered pores of defined size, POPs benefit from high thermal and chemical stability, thanks to which they can be reused in multiple cycles.[11] In particular, organic porous poly ionic liquids (PILs) are of special interest because of the variability of their monomeric building blocks, as well as their flexible ionic skeletons.[12] PILs featuring cationic skeletons with abundant nucleophilic counter anions play a crucial role in this reaction. Moreover, the incorporation of metal complexes, such as Al or Mg-porphyrin, into the structure of POP materials, resulted in reusable heterogeneous bifunctional catalysts with remarkable activity in the cycloaddition of CO_2 into epoxides under mild reaction conditions and low catalytic loading.[13]

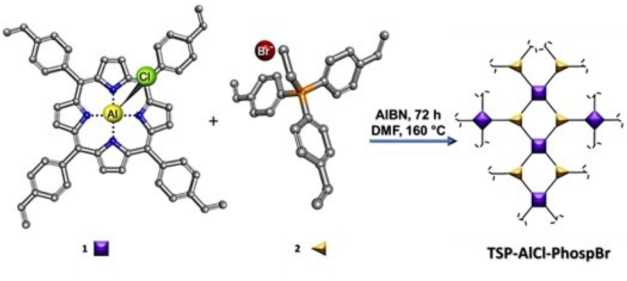
Even though the industrial production of cyclic carbonates is well known,[14] extensive research is needed to make the process more economical, productive, environmentally friendly and safe.[15] The smaller processing volumes handled in intensified systems offer the potential to reduce material costs and improve safety. Consequently, the use of pressurized CO_2 allows for a significant reduction of the reactor volume since the same amount of CO_2 at atmospheric pressure would require considerably more volume than pressurized gas. Furthermore, the use of these conditions may result in an easier scale-up of the process since high pressures of CO_2 are also used at the industrial level.[14]

Herein, following our previous studies on the design of novel bifunctional catalysts for CO_2 conversion, the radical copolymerization of a tetrastyrylporphyrin aluminium chloride monomer (TSP-AlCl) with a tris-vinylphosphonium salt bearing bromide anions as a counterion was performed to obtain porous ionic polymers as multifunctional catalyst for the conversion of epoxides (ca. 300 mmol scale) and pressurized carbon dioxide into cyclic carbonates.

Results and Discussion

An aluminium porphyrin based ionic porous cross-linked polymer was designed and prepared to be applied as heterogeneous bifunctional catalytic system in the conversion of CO_2 and epoxides into cyclic carbonates. The copolymer **TSP-AlCl-PhospBr** was obtained following a simple one-pot radical polymerization by mixing the thermal radical initiator 2,2′-azobis(2-methylpropionitrile) (AIBN) and the two building blocks: aluminium porphyrin (TSP-AlCl) **1** and vinyl-functionalized quaternary phosphonium salt monomer **2** (Scheme 1).

This simple approach allows an easy and effective synthesis of a material containing two active sites, the nucleophile species (catalyst) and the Lewis acid species (co-catalyst). This synthetic strategy is highly performing, as demonstrated by the excellent yield (96%). In order to study the thermal behaviour of the cross-linked material, thermogravimetric analysis (TGA) was performed under nitrogen flow (Figure 1). TGA profile of **TSP-AlCl-PhospBr** indicates good thermal stability of the solid up to 300 °C; above this temperature the degradation of the organic moieties with a first weight loss centred at 347 °C starts along with a second decomposition peak at 466 °C. In this regard, it should be highlighted that the good thermal stability of the solid represents a promising feature for its repeated use under heating conditions. Moreover, through the TGA thermogram under oxygen, the thermal stability of the copolymer was also corroborated under oxidizing conditions, as shown by the TGA profile under air, which exhibits a marked weight loss only after 300 °C (Figure S1).



Scheme 1. Schematic representation of the synthesis of **TSP-AlCl-PhospBr**.

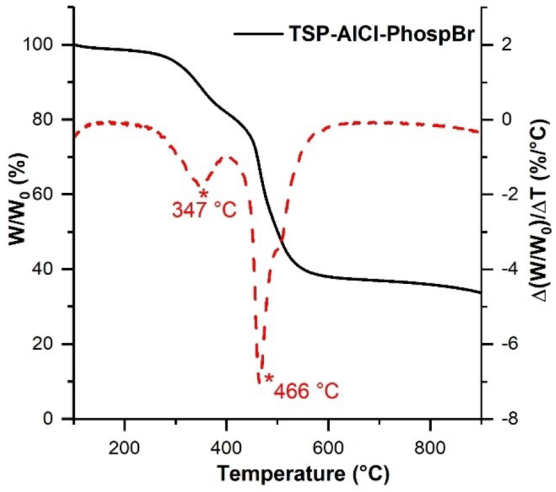


Figure 1. TGA profile (solid line) and derivative thermogravimetry (dotted line) of **TSP-AlCl-PhospBr**.

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The morphology of the bifunctional material was investigated by transmission electron microscopy (TEM). TEM analysis revealed that the copolymer forms a series of compact and large aggregates (Figure S2). Through the use of TEM-EDX, the presence of both catalytic active sites, aluminium and bromide, and especially an uniform distribution of these elements in the copolymer was confirmed (Figure S3). The textural property of the material was explored by means of N_2 adsorption/desorption measurements. The specific surface area (SSA), estimated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution analysed by applying the Barrett-Joyner-Halenda (BJH) method, were calculated to be 212 m^2/g and 0.17 cm^3/g, respectively. Based on the IUPAC classification, the N_2 physisorption isotherm of the hybrid copolymeric material exhibits typical type II isotherms with H4 hysteresis loop (Figure 2). The first proof of the copolymerization process was provided by Fourier-transform infrared (FT-IR) spectroscopy (Figure 3). FT-IR spectrum of **TSP-AlCl-PhospBr** was compared with those of its precursors.

In particular, some characteristics IR bands of both aluminium porphyrin (blue line) and phosphonium salt (red line) can be clearly identified in the spectrum of the copolymeric material (black line) as highlighted in Figure 3. The typical vibration of the metal-porphyrin ring around 1012 cm^{-1} as well as the intense absorptions at 1430 and 1109 cm^{-1} associated with the stretching and bending vibration modes of the P–C bond in the phosphonium moieties are revealed.[16] The copolymer spectrum also shows the band at 1595 cm^{-1} attributed to the stretching vibration mode of C=C–C bond of the phenyl units along with the symmetrical C–H stretching present in the aromatic core located in the region below 3000 cm^{-1}. Furthermore, the high hygroscopicity of the copolymer results in a large and strong absorption band at 3200–3800 cm^{-1} and a medium absorption band at 1628 cm^{-1}, arising from O–H stretching and H–O–H bending of water, respectively.

To further characterize **TSP-AlCl-PhospBr**, solid state ^{13}C NMR was employed by means of the Cross-Polarization Magic Angle Spinning Total Suppression of spinning side bands technique (CP-MAS-TOSS ^{13}C NMR). ^{13}C NMR spectrum, in Figure 4a, shows the signals attributed to the carbon atoms of the porphyrin ring along with the phenyl moieties of the phosphonium salt in the $\delta = 115–160$ ppm range, whereas the aliphatic ones are located in the range between $\delta = 6–50$ ppm. The highly shielded signal at $\delta = 6$ ppm corresponds to the -CH_3

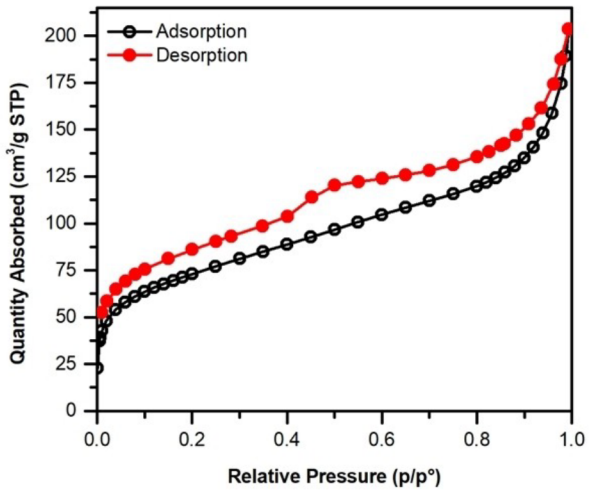

Figure 2. Nitrogen adsorption-desorption isotherms of **TSP-AlCl-PhospBr**.

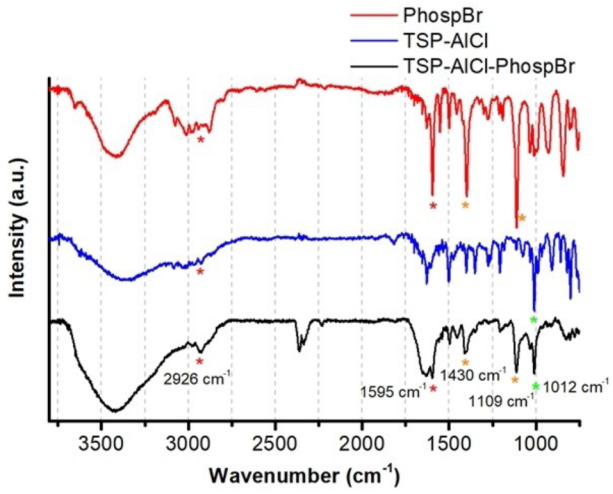

Figure 3. FT-IR spectra of Phosphonium salt (red line), TSP-AlCl (blue line) and **TSP-AlCl-PhospBr** (KBr pellet; black line).

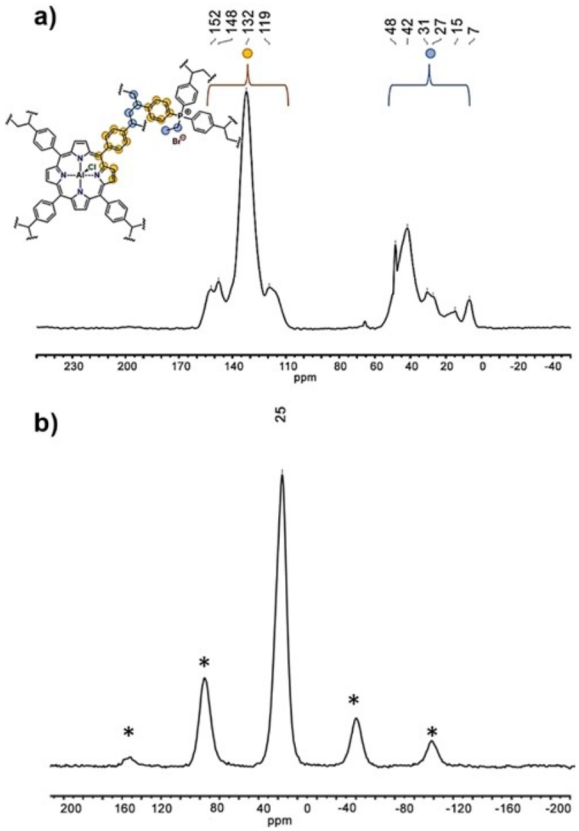

Figure 4. a) ^{13}C CP-MAS-TOSS NMR of **TSP-AlCl-PhospBr** and **b)** ^{31}P CP-MAS-NMR of **TSP-AlCl-PhospBr**. Asterisks indicate spinning side bands

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of the ethyl chain in the phosphonium salt structure. The ^{31}P NMR MAS analysis of the hybrid material was performed to verify the stability of phosphorus during the polymerization process. The spectrum in Figure 4b displays a single peak at 25 ppm, which is in accordance with theliterature; indeed, the typical signals of $(R)_4$ P^+ resonates in the range of 22 to 26 ppm. This analysis allowed to corroborate the preservation of phosphonium salt moieties in the copolymer skeleton.[17] By X-ray photoelectron spectroscopy (XPS), the chemical composition of the outer surface of the material was analysed (Figure 5). The survey spectrum shows the presence of the peaks relative to the Lewis acid (Al) and those of the nucleophile (Br^-).

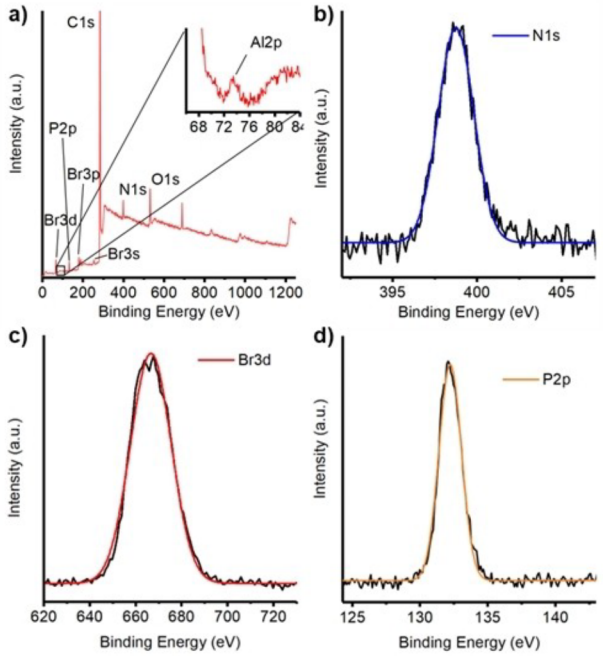

Figure 5. a) XPS survey spectrum of **TSP-AlCl-PhospBr**, b) N1s region, c) Br3d region and d) P2p region.

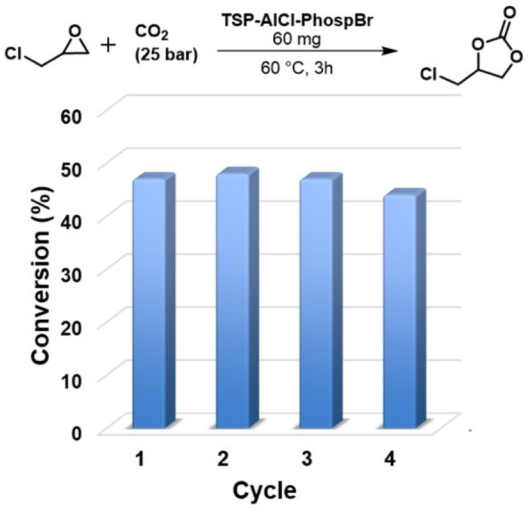

Figure 6. Recycling tests of **TSP-AlCl-PhospBr**. Reaction conditions: epichlorohydrin (307 mmol), 60 mg of catalyst (0.021 mmol Al) 25 bar of CO_2, 3 h, 60 °C, 500 rpm.

Consequently, the possibility of including both catalytic active sites in the structure of a bifunctional catalyst is confirmed. Furthermore, through the analysis of the high resolution XPS spectrum of the N1s region it was possible to verify the total complexation of the porphyrin ring with the metal. Indeed, the spectrum displays only a signal at 399.1 eV corresponding to the nitrogen atoms of the porphyrin ring coordinated with aluminium (Al–N).

Finally, the amount of aluminium in **TSP-AlCl-PhospBr** was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis (0.36 mmol/g). The copolymerized phosphonium-based salt was tested as heterogeneous catalyst for the conversion of CO_2 into cyclic carbonates under solvent-free reaction conditions. The formation of epichlorohydrin carbonate was chosen as benchmark reaction to verify the catalytic behaviour and the reusability of the catalyst. The recycling tests were carried out at non-quantitative conversion of epichlorohydrin. As illustrated in Figure 6, the catalytic material was employed for four consecutive runs at 60 °C without any considerable decrease of the performance. After each catalytic cycle, the copolymer was recovered by filtration and washed several times with toluene, ethanol and ethyl ether and dried under vacuum at 60 °C overnight.

These results demonstrated the robustness of the catalyst in being used in several cycles.

Based on these preliminary results, our focus has been on the catalytic activity of the material under different reaction conditions and using other substrates such as glycidol, styrene oxide and cyclohexene oxide (Table 1, Entries 1–10). The catalytic performances of the solid were evaluated in terms of turnover number (TON_{Al}, defined as moles of epoxide converted/moles of Al active sites), turnover frequency (TOF_{Al}; TON_{Al}/reaction time in hours) and productivity (P, calculated as grams of cyclic carbonates obtained *per* grams of catalyst). As shown in Table 1, some of the catalytic experiments were performed using reused **TSP-AlCl-PhospBr**, reflecting the versatility and good robustness of the material under different reaction conditions during catalysis between CO_2 and different epoxides (entries 2, 5, 7). Deeper investigations on epichlorohydrin conversion have been conducted (entries 1–6). It is worth mentioning that the catalyst can be employed at room temperature, achieving a conversion of 16% into the corresponding epichlorohydrin carbonate in only 3 hours with a TON_{Al} value of 2300 (entry 1). Nevertheless, the extension of the reaction time to 24 hours resulted in an increased conversion with a higher TON_{Al} value (entry 2). The same conversion value is obtained by reducing the reaction time to 3 hours and operating at a slightly higher temperature (entry 3). Higher conversion values and TON_{Al} are obtained when the reaction temperature is raised up to 80 °C (entries 4–6). These additional tests were carried out under the same conditions except for the amount of CO_2 used. When the system is filled with an initial pressure of 25 bar or a constant pressure of 10 bar is maintained, similar conversion values of 88% and 90% are obtained (entries 4 and 5). The analysis of the pressure/temperature *vs.* time graph (Figure S4a) of entry 4 revealed that a very low final pressure was reached indicating the plausible total consumption of CO_2. Conversely, a

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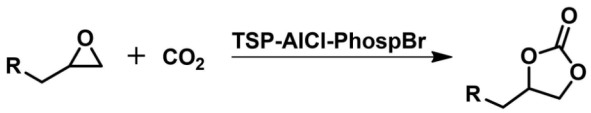
Table 1. Cyclic carbonate synthesis catalyzed by **TSP-AlCl-PhospBr**.

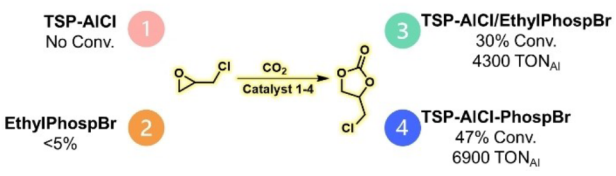


Entry	Test	Substrate	t (h)	T (°C)	Conv. (%)[a]	TON_{Al}[b]	TOF_{Al} (h^{-1})[b]	Productivity[c]
1[d]	fresh	 230 or 307 mmol	3	30	16	2300	800	111
2[e,f]	recycled		24	30	49	7000	300	340
3[d]	fresh		3	60	47	6900	2300	327
4[d]	fresh		3	80	88	12900	4300	612
5[e,f,g]	recycled		3	80	90	12900	4300	625
6[d,h]	fresh		3	80	>99	14500	4900	688
7[e,i]	recycled	 362 or 271 mmol	6	30	21	3600	600	149
8[h,j]	fresh		3	50	65	1100	3700	462
9	fresh	 210 mmol	3	100	34	3400	1100	285
10[k,l]	fresh	 237 mmol	24	150	31	1200	50	171

Reaction conditions: CO_2 (25 bar), catalyst 60 mg (0.021 mmol Al), 500 rpm. [a] Determined by ^{1}H NMR; [b] TON and TOF values calculated on the basis of the Al content obtained from ICP analysis; [c] Productivity: grams of product/grams of catalyst [d] 307 mmol of epichlorohydrin were used; [e] Catalyst 45 mg (0.016 mmol Al); [f] 230 mmol of epichlorohydrin were used; [g] CO_2 constant pressure 10 bar; [h] CO_2 constant pressure 25 bar; [i] 271 mmol of glycidol were used; [j] 362 mmol of glycidol were used; [k] Catalyst 170 mg (0.059 mmol Al); [l] Selectivity toward cyclic carbonates 80% (*cis/trans* ratio 70:30).

complete conversion and a corresponding TON_{Al} value of 14500 were reached when the system was charged and maintained at the CO_2 operating pressure of 25 bar (entry 6 and Figure S4b). The reactivity of glycidol was studied at two different temperatures, 30 and 50 °C (entries 7–8). Once again, the catalyst is shown to be active at room temperature, achieving a good conversion value of 21% in 6 hours, with a TON_{Al} value of 3550. In addition, decreasing the reaction time from 6 to 3 hours and operating at 50 °C clearly leads to an improvement in terms of conversion and TON_{Al}, 65% and 1100, respectively. With the more challenging styrene oxide, 34% conversion was achieved when the reaction was conducted at 100 °C for 3 h (entry 9). Cyclohexene oxide exhibited a conversion of 31% when the reaction was run at 150 °C for 24 hours (entry 10). *Cis*-cyclohexene carbonate was not the only product. In addition to *cis*-cyclohexene carbonate, the presence of poly(cyclohexene carbonate) and *trans*-cyclohexene carbonate can also be observed.

The formation of the *trans* isomer was attributed to a backbiting reaction, which can take place at the terminal end of the developing polymer chain Indeed, through ^{1}H NMR a *cis*/*trans*-cyclohexene carbonate ratio of 70:30 and a selectivity toward the corresponding cyclic carbonate of 80% can be observed.[2a,18] As previously reported, the use of the co-catalyst enables a cooperative effect during the CO_2 conversion with the epoxide to generate cyclic carbonates. To further corroborate this phenomenon, three additional tests were conducted as described in Scheme 2. These experiments involved the use of different catalytic systems under homogeneous conditions: the tetrastyrylporphyrin-aluminium chloride complex (**TSP-AlCl**) as Lewis acid, **TSP-AlCl** combined with ethyltriphenylphosphonium bromide as source of Br^- ions (**EthylPhospBr**), and the



Scheme 2. Comparison of the activity between the heterogenous bifunctional catalyst **TSP-AlCl-PhospBr** and the homogeneous systems **TSP-AlCl**, **EthylPhospBr** and **TSP-AlCl/EthylPhospBr** in the reaction between CO_2 and epichlorohydrin. Reaction conditions: epichlorohydrin (307 mmol), catalyst (0.021 mmol Al) 25 bar CO_2, 60 °C, 3 h, 500 rpm.

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employment of **EthylPhospBr** alone. Consistently, the amount of aluminium introduced for the reactions in the homogeneous setup corresponded to that of the **TSP-AlCl-PhospBr** (0.021 mmol).

Interestingly, the heterogeneous material, **TSP-AlCl-PhospBr**, showed higher activity than the homogeneous **TSP-AlCl/EthylPhospBr** combination, with conversion values of 47% and 30%, respectively. The reaction catalyzed by the Lewis base species alone (**EthylPhospBr**) showed lower activity, with a conversion $<5\%$, while the Lewis acid species alone does not lead to any conversion. These results demonstrate the importance of the presence of co-catalytic species in the system, but also the remarkable performance of the bifunctional heterogeneous material. The possible explanation for this result could be attributed to the spatial arrangement of the two distinct catalytic sites (aluminium and bromide ions) in the **TSP-AlCl-PhospBr** material. Actually, in the material the two active sites are directly linked, unlike the homogeneous **TSP-AlCl/EthylPhospBr** combination, which represents a relatively more disordered system. In particular, the structure of the polymeric network allows a close proximity between aluminium porphyrin core (Lewis acid) and phosphonium salt (bromide anion), resulting in a synergistic effect between the two active sites (Figure 7).

Conclusions

A copolymerized phosphonium cross-linked network was prepared by using aluminium chloride tetrastyrylporphyrin and vinyl-functionalized quaternary phosphonium salt monomer as molecular building blocks. A simple one-pot method of AIBN-mediated radical polymerization was followed for the synthesis of **TSP-AlCl-PhospBr** containing aluminium as Lewis acid species and bromide as nucleophilic species. Several spectroscopic and analytical methods were used to fully describe the cross-linked material including TGA, ICP-OES, FT-IR, XPS, TEM, solid-state NMR and porosimetry. The novel material was employed as heterogeneous bifunctional catalyst in the cycloaddition reaction of CO_2 with epoxides to obtain the corresponding cyclic carbonates under solvent-free conditions. Performance evaluation of the hybrid material was carried out taking into account some critical requirements, such as recyclability of the catalyst, turnover number (TON_{Al}) turnover frequency (TOF_{Al}) and productivity values. The catalyst was easily recyclable for four consecutive cycles in the reaction between CO_2 and epichlorohydrin. Moreover, its robustness was also confirmed after consecutive uses under different reaction conditions, making it a useful material for transforming CO_2 into cyclic carbonate. Remarkably, the catalyst could be successfully employed at room temperature, achieving excellent TON_{Al} value of 2300 in only three hours. The cross-linked material proven high catalytic activity and versatility with different epoxides, reaching high TON_{Al} and TOF_{Al} values. This outstanding catalytic performance can be attributed to the close proximity between the metal centres and the bromide ions due to the direct covalent bonding, which allows for the cooperative effect during the catalytic cycle enabling the obtainment of the desired cyclic carbonate in a short time as highlighted through the comparison experiment under homogeneous conditions. Recently Dai *et al.*[9i] demonstrate synergy in similar bifunctional systems based on a series of porous organic catalysts in which the two active sites are phosphonium chloride and magnesium porphyrin. In this report, the catalytic tests were carried out at 1 atm in a temperature range between 40 and 80 °C, using 10 mmol of epoxide with a loading of 0.05 mol% for long reaction times. Conversely, we applied higher pressures (25 bar) in a temperature range between 30 and 150 °C, to a significantly larger amount of epoxide (230 to 362 mmol). In addition, catalytic loadings were substantially lower, ranging from 0.02 mol% to 0.006 mol%, with shorter reaction times, allowing obtaining high TON and TOF values. These conditions acquire substantial relevance since they are similar to those often used on an industrial scale. As a result, only modest changes would be required to scale the cyclic carbonate synthesis described here on a large scale.[14]

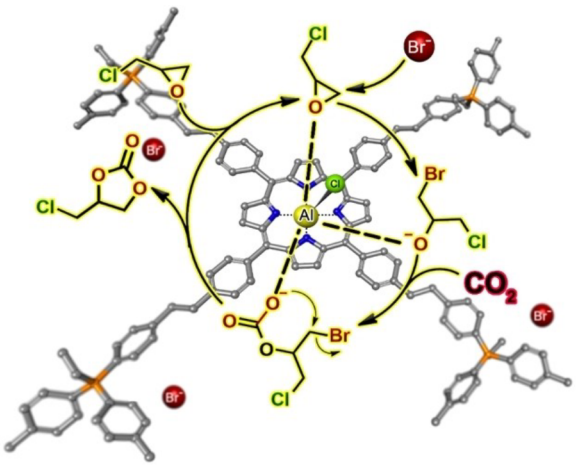

Figure 7. Schematic representation of the synergy between Al-porphyrin and phosphonium salt in the synthesis of cyclic carbonates.

Experimental Section

Ethyl bromide (98%), diethylaluminum chloride (25 wt. % in toluene), 1,2-dibromoethane (98%), magnesium turnings (98%), phosphorus(III) chloride (99%), 2,2′-Azobis(2-methylpropionitrile) (AIBN) (98%), magnesium sulfate (>99.5%) were purchased from Sigma Aldrich and used as received. Ethyltriphenylphosphonium bromide (>98%), pyrrole (>99%), 4-bromostryrene (>95%), styrene oxide (98%), epichlorohydrin (99%), cyclohexene oxide (98%) and glycidol (96%) were bought from TCI chemicals and used without any purification. Solvents (HPLC grade) were purchased from commercial suppliers without any further purification. Solid state ^{13}C spectrum was 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. ^{31}P-NMR spectrum was recorded at room temperature on a VARIAN Avance 400 at 9.1 T using a 4 mm probe and spinning frequencies of 10 kHz. ^{1}H-NMR spectra were collected on a JEOL 400 spectrometer or on a Bruker Avance 400 spectrometer. Thermogravimetric analysis (TGA) was performed in a Mettler Toledo TGA STAR system

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with a heating rate of 10 °C/min, under nitrogen flow from 25 to 900 °C or under oxygen flow from 100 to 1000 °C. N_2 adsorption-desorption measurement was carried out at 77 K by using a volumetric adsorption analyser (Micromeritics ASAP 2420). Before starting the analysis, the sample was pre-treated at 150 °C for 8 h under reduced pressure (0.1 mbar). The BET technique was used to calculate the specific surface area in the range p/p0 = 0.05–0.30, while the BJH method was used to estimate pore size distributions from the adsorption isotherm.[19] TEM micrographs were taken on a Philips TECNAI 10 at 80–100 kV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed in an Optima 8000 spectrometer. Analyses of X-ray photoelectron spectroscopy (XPS) were conducted in a ThermoFisher ESCALAB 250Xi instrument equipped with a monochromatic Al Kα X-ray source (1486.6 eV) and a hemispherical deflector analyser (SDA) working at constant pass energy (CAE), allowing for constant energy resolution across the whole spectrum. The experiments were carried out using a 200 μm diameter X-ray spot. The charge neutralization of the sample was achieved with a flood gun using low energy electrons and argon ions. The pressure in the analysis chamber was in the range of 10–8 Torr during data collection. Survey spectra were recorded with a 200 eV pass energy, whereas high-resolution individual spectra were collected with a 50 eV pass energy. Analyses of the peaks were carried out with the Thermo Avantage software, based on the non-linear squares fitting program using a weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood.

Synthesis of and ethyl-tris(4-vinylphenyl)phosphonium bromide

Ethyl-tris(4-vinylphenyl)phosphonium bromide was synthesized according to a reported procedure, with a few minor adjustments.[9h] In a 10 mL Schlaker tube, under argon atmosphere, tristyrylphosphine[20] (1.5 mmol; 530 mg) and ethyl bromide (20.2 mmol; 1.5 mL) were charged and the reaction mixture was stirred at 42 °C for 26 h. After cooling to room temperature, a white mixture was formed and was transferred to a round-bottom flask with chloroform and concentrated under vacuum. Phosphonium salt was obtained as white crunchy solid (650 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (ddd, J = 11.2, 10.2, 5.6 Hz, 1H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.96 (d, J = 17.6 Hz, 1H), 5.52 (d, J = 10.9 Hz, 1H), 3.85 (m, J = 14.8, 7.4 Hz, 1H), 1.38 (m, J = 20.1, 7.4 Hz, 1H) ppm. FT-IR (film): 3420, 2926, 2885, 1595, 1430, 1109, 1026, 995, 921, 839 cm^{-1}.

Synthesis of TSP-AlCl-PhospBr

In a two-neck round-bottom flask, tetrastyrylporphyrin aluminium chloride[9g] (0.13 mmol; 100 mg) and ethyl tris(4-vinylphenyl)phosphonium bromide (0.51 mmol; 230 mg) were transferred and dissolved in dry dimethylformamide (DMF) (5.1 mL). The reaction mixture was sonicated for 20 min, under argon atmosphere. After the addition of AIBN (10 mol%), the system was degassed by bubbling argon for 20 min and the temperature was gradually increased up to 160 °C. The reaction mixture was allowed to react at this temperature for 72 h. The solid was recovered by centrifugation and washed several times with DMF, methanol and diethyl ether. Before each centrifugation, the catalyst was sonicated for 10 min in the washing solvent. After drying under vacuum at 60 °C, **TSP-AlCl-PhospBr** was obtained as a brown solid (320 mg, 96%). FT-IR (KBr pellet): 3420, 2926, 1643, 1595, 1430, 1109, 1012, 823, 771 cm^{-1}.

Catalytic Tests

Catalytic experiments were carried out in a Cambridge Design Bullfrog batch reactor, with temperature control, pressure monitoring and mechanical stirring. In each run, a fine dispersion of the catalyst and the right amount of the selected epoxide was added to a Teflon vial. Then, the reactor was closed, and the mechanical stirring speed was set to 500 rpm. The system was purged with N_2 for 10 min, before the addition of 25 or 10 bar of CO_2. Subsequently, the temperature was gradually raised with a ramp of 5 °C/min and maintained at the required temperature during the proper reaction time. At the end of the reaction time, the reactor was cooled to room temperature and slowly depressurized. The separation of the catalyst from the reaction mixture was performed by filtration (Millipore filtration using a 0.45 μm PTFE membrane) or by centrifugation (4500 rpm for 10 minutes). The supernatant was analysed by ^{1}H NMR spectroscopy in $(CD_3)_2SO$.

Recycling Tests

The recyclability of the materials was verified in the reaction between epichlorohydrin and CO_2. After each catalytic test, the hybrid was recovered by filtration (Millipore filtration with 0.45 μm PTFE membrane) and washed several times with toluene, ethanol and diethyl ether. The catalyst was then dried overnight in a vacuum oven at 60 °C before being used in the next cycle. To maintain the ratio between moles of catalyst and moles of epoxide, the amount of epoxide was adjusted according to the recovered catalyst. The conversion of epichlorohydrin into cyclic carbonate was estimated by ^{1}H NMR analysis.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Carbon dioxide conversion 1 · bifunctional catalyst 2 · phosphonium salt · Al-porphyrin · cyclic carbonates

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