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A Rational Investigation of the Lewis Acid-Promoted Coupling of Carbon Dioxide with Cyclohexene Oxide: Towards CO₂-Sourced Polycyclohexene Carbonate under Solvent- and Cocatalyst-Free Conditions

Joseph Grondin, Christian Aupetit and Thierry Tassaing *

Institut des Sciences Moléculaires, UMR CNRS 5255, Université de Bordeaux, 351 cours de la Libération, 33405 Talence, France

* Correspondence: thierry.tassaing@u-bordeaux.fr; Tel.: +33-5400-028-92

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Abstract: We report a rational investigation of the selective synthesis of poly(cyclohexene carbonate) from CO₂ and cyclohexene oxide by using commercially available Lewis acids with nontoxic metal centers. After a preliminary screening, we focused on the use of zinc salts, and the effect of the pressure, the temperature, the catalyst loading, and the presence of cocatalyst or a solvent on the reaction yields, selectivity, and molar masses was evaluated for selected catalytic platforms. Thus, we found that ZnTosylate in catalytic amounts under solvent- and cocatalyst-free conditions enables the selective synthesis of poly(cyclohexene carbonate) with a molecular weight of about 62.1 kg/mol with about 70% yields at 343 K and 4 MPa. To the best of our knowledge, this is a rare example of high molar mass polycyclohexene carbonates that are moreover obtained under solvent- and cocatalyst-free conditions. The high selectivity of ZnTos towards the formation of poly(cyclohexene carbonate) was interpreted, thanks to in situ FTIR spectroscopy and DFT calculations, as resulting from its ability to coactivate CO₂.

Keywords: CO₂ valorization; Polycarbonate; Lewis acid catalyst

1. Introduction

The valorization of carbon dioxide (CO₂) as a renewable C1 feedstock to produce fine chemicals or polymers is of growing interest in academic laboratories and industries in the context of sustainable chemistry [1–11]. In this context, the coupling of CO₂ with epoxides that leads to the formation of cyclic carbonates or polycarbonates is a highly attractive 100% atom-economic reaction. Both products are valuable chemicals that should be selectively produced in order to minimize the separation and purification steps. The selectivity of this reaction is dependent on the nature of the substrate and the formation of either cyclic carbonates [12–15], polycarbonates [1,2,16–18], or polyethers is strongly related to the choice of an appropriate catalyst (Scheme 1).
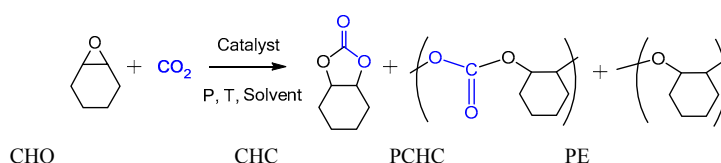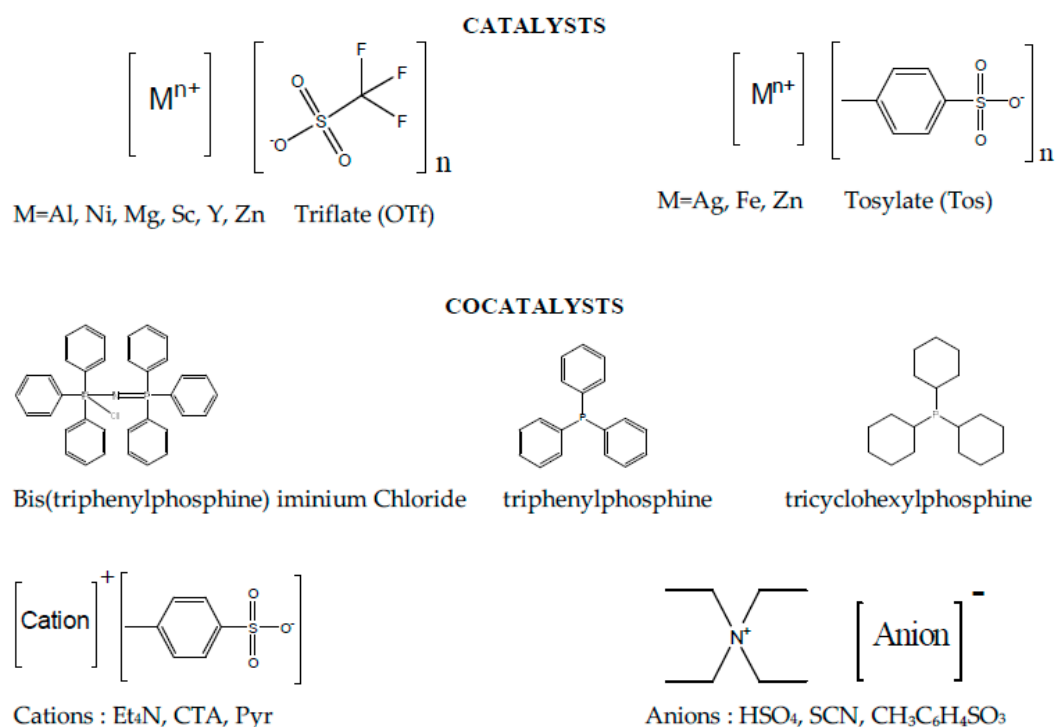

Scheme 1. The CO₂/cyclohexene oxide (CHO) coupling leading to various possible products: cyclic cyclohexene carbonate (CHC), poly(cyclohexene carbonate) (PCHC), and poly(cyclohexene ether) (PE).

The selectivity is also influenced by the reaction conditions (temperature, CO_2 pressure) as the activation barrier for the formation of polycarbonates is generally lower and cyclic carbonates are the thermodynamically favored products [4].

The common point between the most efficient catalysts is that they act as a Lewis acid/nucleophile couple, where the Lewis acid activates the epoxide for the ring opening of the epoxide by the nucleophile that allows the insertion of CO_2. Then, this intermediate can undergo a ring closure to produce the cyclic carbonate or undergo a nucleophilic attack towards another epoxide leading to the polycarbonate [7]. Thus, a nucleophilic species with a poor leaving ability will favor the growth of the polymer chain, whereas a nucleophile with a good leaving ability will promote the ring closure and formation of the cyclic carbonate product. By the same token, the molar ratio between the nucleophile and the Lewis acid site is expected to play a significant role on the selectivity [19]. Thus, for the selective and efficient synthesis of polycarbonates (PCs) from the copolymerization of CO_2 and epoxides, many Lewis acid catalysts such as organometallic complexes usually used in combination with a nucleophile have been developed. In particular, the important characteristics of metal-based catalysts (zinc [20–37], aluminum [38,39], chromium [40–43], cobalt [44–47], magnesium [48,49], iron [19,50–54], titanium [55,56], copper [57], ytterbium [58], ...) with a variety of ligands have been thoroughly discussed in recent reviews [59–61]. However, many highly active complexes including the types mentioned above are air- and moisture-sensitive, which is a serious limitation to their possible industrial application [62]. In addition, most of these systems require halogen-containing compounds as cocatalyst, such as ammonium and phosphonium salts. More recently, polycarbonates were successfully synthesized for the first time through the anionic copolymerization of epoxides with CO_2 under metal-free conditions using an organic Lewis acid (Triethyl borane) in combination with an organic initiator (onium halides or onium alkoxides) [63]. Although very attractive, this protocol still requires a combination of catalysts and the use of a solvent to reach relatively low molar masses (around 30 kg/mol). In the context of green chemistry, some recent investigations were devoted to the copolymerization and terpolymerisation of CO_2 with biobased epoxides precursors [64–66].

A recent review by Pescarmona et al. [17] offers an updated overview of the catalytic synthesis of polycarbonates, their physicochemical properties, and the growing applications of this class of green polymers. Therefore, this research field is still very active as further improvements are still needed in order to develop robust, active, and selective catalysts while respecting environmental and economic standards and improving the material properties of PCs that generally display low molar masses, hence severely limiting their usefulness. In this context, we have performed a rational investigation of the copolymerization of cyclohexene oxide (CHO) with CO_2 in the presence of commercially available Lewis acids under solvent-free conditions (Scheme 2). After a preliminary screening with metal center such as Zn, Mg, Al, Ni, Sc, Y, we focused on the use of commercially available Lewis acids with Zn as a nontoxic metal center. The influence of the pressure, the temperature, the catalyst loading, and the presence of a cocatalyst or a solvent on the reaction yields, selectivity, and molar masses has been evaluated for selected catalytic platforms. Interestingly, we have shown that the presence of ZnTosylate in catalytic amounts under solvent- and cocatalyst-free conditions enables the selective synthesis of poly(cyclohexene carbonate) (PCHC).

CATALYSTS

M=Al, Ni, Mg, Sc, Y, Zn   Triflate (OTf)   M=Ag, Fe, Zn   Tosylate (Tos)

COCATALYSTS

Bis(triphenylphosphine) iminium Chloride   triphenylphosphine   tricyclohexylphosphine

Cations : Et$_4$N, CTA, Pyr   Anions : HSO$_4$, SCN, CH$_3$C$_6$H$_4$SO$_3$

Scheme 2. Structures of the catalysts and cocatalysts investigated in this study.

2. Materials and Methods

2.1. Materials

Metal triflates complexes, Sc(OTf)$_3$ (Sigma-Aldrich, St. Louis, MO, USA, 99%), Y(OTf)$_3$ (Sigma-Aldrich, 98%), Ni(OTf)$_2$ (Sigma-Aldrich, 96%), Mg(OTf)$_2$ (Sigma-Aldrich, 97%), Al(OTf)$_3$ (Sigma-Aldrich, 99%), and Zn(OTf)$_2$ (Sigma-Aldrich, 98%), were used as received and stored under Argon. Organic cocatalysts, Bis(triphenylphosphine)iminium chloride (PPNCl, Sigma-Aldrich, 97%), Triphenylphosphine (P(Ph)$_3$, AlfaAesar, Haverhil, MA, USA, 99%), Tricyclohexylphosphine (P(Cy)$_3$, AlfaAesar, 96%), Tetraethylammonium hydrogensulfate (Et$_4$NHSO$_4$, Fluka, Charlotte, NC, USA, 99%), Tetraethylammonium thiocyanate (Et$_4$NSCN, Fluka, 99%), Tetraethylammonium p-toluenesulfonate (Et$_4$NTos, Fluka, 99%), Cetyltrimethylammonium p-toluenesulfonate (CTATos, Sigma-Aldrich, 99%), and Pyridinium p-toluenesulfonate (PyrTos, AlfaAesar, 98%), were used as received and stored under Argon. Metal tosylates complexes, Zincp-toluenesulfonate hydrate (ZnTos xH$_2$O, AlfaAesar), Silver p-toluenesulfonate (AgTos, AlfaAesar, 98%), and Iron p-toluenesulfonate hexahydrate (FeTos 6H$_2$O, Sigma-Aldrich), were stored under Argon. AgTos was used as received and anhydrous ZnTos and FeTos were obtained after drying for 1 h under vacuum at 160 °C using the protocol described in reference [67]. Carbon dioxide with a purity of 99.95% was purchased from Air Liquide and used as received.

2.2. Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)

Fourier transform infrared spectra were recorded using a Nicolet iS50 spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with a transmission or with a diamond attenuated transmission reflectance (ATR) device. Spectra were obtained in ATR mode as a result of 200 spectra in the range of 4000–400 cm^{-1} with a nominal resolution of 4 cm^{-1}.

2.3. High-Pressure Transmission Infrared Spectroscopy

In order to measure the spectrum of CO_2 in interaction with selected catalysts investigated in this study, we dispersed the solid catalyst in a KBr pellet (10 wt % of the catalyst, typically 0.012 g in 0.11 g of KBr). Then, the pellet was "stuck up" between the two ZnSe windows of a high-pressure transmission homemade cell (see ref [68] for details). A spectrum of the catalysts-loaded KBr pellet under atmospheric pressure was taken using the FTIR spectrometer described above (32 scans, 4 cm^{-1} resolution, in transmission mode) after which CO_2 was introduced into the cell at a pressure of 4 MPa.

2.4. Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR samples were prepared by dissolving about 5 mg of product in 600 µL of deuterated chloroform ($CDCl_3$, D = 99.96%, Euriso-top, Saint-Aubin, France). The NMR experiment was recorded on Brüker Avance 600 (Billerica, MA, USA) equipped with 5 mm BBI probe. ^{1}H NMR spectra was obtained at 600.16 MHz and chemical shifts from proton NMR spectra are reported in ppm relative to the CDCl3 peak at 7.26 ppm. ^{1}H NMR experiment was recorded using pulse sequences available from the Bruker sequence library. All NMR spectra were phased and baseline-corrected.

2.5. Steric Extrusion Chromatography (SEC)

SEC analyses were performed in Tetrahydrofuran (THF) (25 °C) on an Agilent PL GPC50 (Santa Clara, CA, USA)with four TSK columns: HXL-L (guard column), G4000HXL (particles of 5 mm, pore size of 200 A, and exclusion limit of 400,000 g/mol), G3000HXL (particles of 5 mm, pore size of 75 A, and exclusion limit of 60,000 g/mol), G2000HXL (particles of 5 mm, pore size of 20 A, and exclusion limit of 10,000 g/mol) at an elution rate of 1 mL/min. The elution times of the filtered samples were monitored using UV and RI detectors and SEC was calibrated using polystyrene standards.

2.6. Differential Scanning Calorimetry (DSC)

DSC thermograms were measured using a DSC Q100 apparatus from TA instruments (New Castle, UK). For each sample, two cycles from –50 to 200 °C at 10 °C·min^{-1} were performed and then the glass transition and melting temperatures were calculated from the second heating run. Thermogravimetric (TGA) analyses were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C·min^{-1} under nitrogen atmosphere from room temperature to 600 °C.

2.7. Coupling of Cyclohexene Oxide with CO_2: Catalysts Screening

In a representative experiment, a stainless-steel autoclave with a nominal volume of 2 mL, equipped with a magnetic rod, a manometer, and a gas inlet/outlet, was charged with 0.5 mL (0.0049 mol) of cyclohexene oxide and 1 mol % of catalyst. The autoclave was equilibrated at 70 °C for 30 min. Then, the reaction was allowed to run during 20 h at constant CO_2 pressure of 4 MPa. The crude reaction mixture was analyzed by the ATR-IR set-up described above in paragraph 2.2. The conversion and the selectivity towards the formation of the end-products reported in the tables below have been determined by ATR-IR. Indeed, as reported previously, ATR-IR spectroscopy is better adapted than ^{1}H NMR to determine the selectivity in particular between the cyclic carbonate and the polycarbonate [17]. Nevertheless, we checked for a few samples that the conversions and yields determined by ATR-IR were in accordance with the NMR results. Figure 1 illustrates the ATR-IR spectra of CHO, CHC, PCHC, PE.

The conversion of cyclohexene oxide was highlighted by the decrease of the CHO peak at 534 cm^{-1}. Meanwhile, formation of PCHC and PE were attested by the appearance of peaks at 1740 and 1080 cm^{-1}, respectively. The presence of CHC in the IR spectrum of the crude sample was revealed by a peak at 1803 cm^{-1} [69]. Then, the conversion of cyclohexene oxide and the selectivity towards the formation of the cyclic carbonate, the polycarbonate, and the polyether were determined by comparing the relative intensities of the characteristic peaks of each species defined above (see ESI 1 in

Supplementary Materials). The purification of the polycarbonate was carried out by precipitation from a dichloromethane solution of the crude mixture with acidic methanol, followed by repeated washing steps with methanol and drying under vacuum to obtain the purified polymer as a white powder. The ^{1}H NMR spectra of the purified sample is characteristic of the polycarbonate (PCHC) with almost exclusively carbonate linkages and traces of ether linkages (see ESI 2, Figure S1 in Supplementary Materials). In other words, the polyether segments obtained during the CHO/CO_2 copolymerization were produced as contaminant and were not along the polycarbonate chain. All the samples for SEC and DSC analyses were purified along the same protocol and were controlled by ^{1}H NMR.
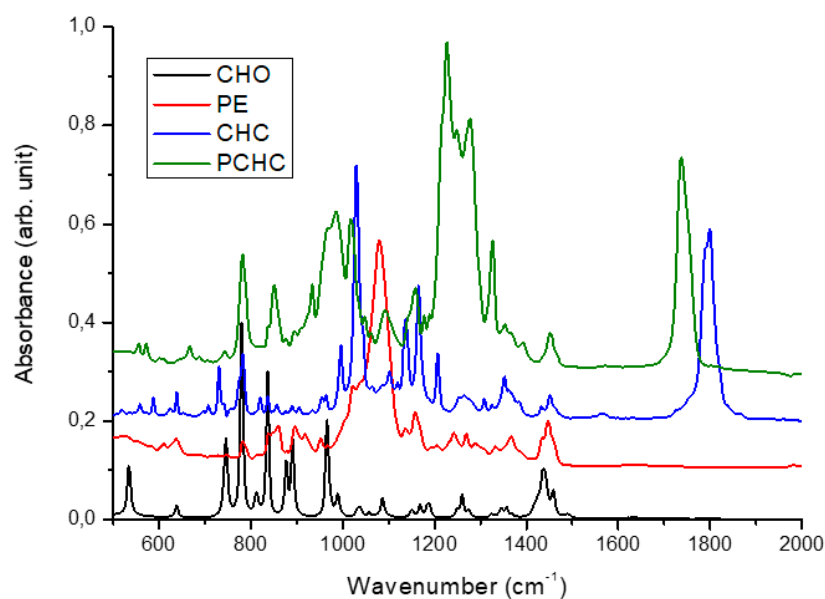
Figure 1. ATR-IR spectra of cyclohexene oxide (CHO), cyclic cyclohexene carbonate (CHC), poly(cyclohexene carbonate) (PCHC), and poly(cyclohexene ether) (PE).

3. Results and Discussion

3.1. Catalytic Studies Performed with Metal Triflates Complexes

Series of metal triflates complexes catalysts were screened in combination with nucleophilic cocatalysts for the solvent-free coupling of CO_2 with cyclohexene oxide which can lead to the formation of cyclic carbonate, polycarbonate, and polyether products (Scheme 1). This epoxide was chosen as its structure containing a six-membered ring is known to favor the production of polycarbonate over cyclic carbonate. The coupling reactions were performed for 20 h using 1 mol % of catalyst at different temperatures and pressures ranging between 60 and 90 °C and 2 and 7 MPa, respectively.

3.1.1. Influence of the Nature of the Metal

The influence of the metal cations of the Lewis acid catalysts with Triflate anion on their activity and selectivity was first evaluated (Table 1, entries 1–6). Interestingly, the cyclohexene oxide conversion was found to be higher than 85% whatever the nature of the metal cation with a general trend of high selectivity towards the formation of PE due to epoxide homopolymerization. In particular, for the Al, Ni, and Mg complexes (Table 1, entries 1–3), the selectivity towards the formation of PE was higher than 99%. However, we observed that for the Sc, Y, and Zn complexes (Table 1, entries 4–6), a small amount of polycarbonate could be obtained with a slightly better selectivity towards PCHC found for the Zn salt. Finally, we did not observe any formation of cyclic carbonates in any case. Thus, it appears clearly that these strong Lewis acid species that activate the epoxide towards ring opening allow mainly the consecutive insertion of two epoxides leading to the formation of polyethers. In order to favor the alternating copolymerization of CO_2 and cyclohexene oxide and thus improve the

selectivity of the Sc, Y, and Zn complexes towards the formation of PCHC, we investigated various cocatalysts of different types with different relative catalyst/cocatalyst ratios.

Table 1. Catalytic studies performed with metal triflates complexes [a].

Entry	Catalyst	Conv [b] (%)	S_{CHC} [c] (%)	S_{PCHC} [d] (%)	S_{PE} [e] (%)
1	$Al(OTf)_3$	99	0	0	>99
2	$Ni(OTf)_2$	99	0	0	>99
3	$Mg(OTf)_2$	89	0	0	>99
4	$Sc(OTf)_3$	85	0	4	96
5	$Y(OTf)_3$	99	0	7	93
6	$Zn(OTf)_2$	94	0	9	91

[a] Conditions: 5 mmoles cyclohexene oxide, 1 mol % catalyst, 60 °C, 20 h, 4 MPa CO_2; [b] Conv: CHO conversion; [c] SCHC: selectivity to cyclic carbonate; [d] SPCHC: selectivity to polycarbonate; [e] SPE: selectivity to polyether.

3.1.2. Influence of the Nature of the Cocatalyst

Preliminary investigations of the influence of a cocatalyst on the selectivity of the Sc and Y complexes towards the formation of PCHC were performed. The results are reported in the ESI 3, Table S1 (Supplementary Materials) and put in evidence only a slight improvement of their selectivity towards the formation of PCHC. The influence of different types of cocatalysts on the selectivity of the Zn complex towards the formation of PCHC was then evaluated (Table 2). PPNCl, P(Ph)$_3$, and P(Cy)$_3$, which have been reported previously as possible efficient cocatalysts for the PCHC synthesis, were tested (Table 2, entries 1–11).

Table 2. Catalytic studies performed with $Zn(OTf)_2$ catalyst using various cocatalysts [a].

Entry	Cat./cocat.	Cat./cocat Ratio	Conv [b] (%)	S_{CHC} [c] (%)	S_{PCHC} [d] (%)	S_{PE} [e] (%)
1	$Zn(OTf)_2$/PPNCl	1:1	69	0	10	90
2	$Zn(OTf)_2$/P(Ph)$_3$	1:1	79	0	12	88
3	"	1:2	76	0	15	85
4	"	1:3	74	0	14	86
5	$Zn(OTf)_2$/P(Cy)$_3$	1:2	76	1	20	79
6	"	1:3	63	6	36	58
7	"	1:3 [f]	82	6	54	40
8	"	1:3 [g]	90	10	58	32
9	"	1:3 [f,h]	76	1	39	60
10	"	1:3 [f,i]	75	3	46	51
11	"	1:3 [f,j]	77	2	23	75
12	$Zn(OTf)_2$/Et$_4$NHSO$_4$	1:3 [f]	87	1	11	88
13	$Zn(OTf)_2$/Et$_4$NSCN	1:3 [f]	50	48	52	0
14	$Zn(OTf)_2$/Et$_4$NTos	1:3 [f]	74	6	83	11
15	$Zn(OTf)_2$/CTATos	1:3 [f]	73	6	55	39
16	$Zn(OTf)_2$/PyrTos	1:3 [f]	48	8	14	78

[a] Conditions: 5 mmoles cyclohexene oxide, 1 mol % catalyst, 60 °C, 20 h, 4 MPa CO_2; [b] Conv: CHO conversion; [c] SCHC: selectivity to cyclic carbonate; [d] SPCHC: selectivity to polycarbonate; [e] SPE: selectivity to polyether [f] T = 70 °C; [g] T = 80 °C; [h] P = 3 MPa; [i] P = 5 MPa; [j] P = 7 MPa.

PPNCl at a catalyst/cocatalyst ratio of 1:1 allowed only a slight improvement of the selectivity towards PCHC at the expenses of a lower conversion (69% instead of 94%)(Table 2, entry 1). A similar conclusion is drawn from the results obtained with P(Ph)$_3$ (Table 2, entry 2). Higher catalyst/cocatalyst ratio between 1:2 and 1:3 slightly improved the selectivity towards the formation of PCHC from 12% to 15% and 14%, respectively (Table 2, entries 3–4), while a higher conversion between 74% and 79% was obtained in comparison with PPNCl. Finally, the use of P(Cy)$_3$ at 1:2 and 1:3 catalyst/cocatalyst ratio significantly improved the selectivity towards the formation of PCHC to 20% and 36%, respectively

(Table 2, entries 5–6). However, at the 1:3 catalyst/cocatalyst ratio, the conversion was decreased to 63% and a non-negligible contribution of 6% of cyclohexene carbonate was detected. Interestingly, increasing the temperature to 70 °C led to an increase of the conversion to 82% and improved the selectivity towards the formation of PCHC to 54% (Table 2, entry 7). A further increase of the temperature to 80 °C slightly improved the selectivity towards the formation of PCHC to 58% (Table 2, entry 8) at the expense of a significant increase of the production of cyclic carbonate to 10%. So, we do consider that the temperature of 70 °C is optimum for this catalytic platform. Finally, at 70 °C, when the pressure was changed between 3 and 7 MPa (Table 2, entries 9–11), it appears that the higher conversion and selectivity towards the formation of PCHC were obtained at P = 4 MPa. From these encouraging results, we investigated other types of cocatalysts in order to favor the CO_2-epoxide copolymerization. Firstly, we investigated different tetraethyl ammonium (Et_4N) salts with different counter-anion (HSO_4^-, SCN^-, $CH_3C_{36}H_4SO_3^-$ (Tos)) as potential efficient cocatalysts for this reaction under the optimized conditions obtained with $P(Cy)_3$ as cocatalyst. Et_4NHSO_4 displayed a good cocatalytic activity with a conversion of 87%, but at the expense of a low selectivity towards the formation of PCHC of about 11% (Table 2, entry 12). A low conversion of only 50% and selectivity towards the formation of PCHC of about 52% were observed with Et_4NSCN (Table 2, entry 13). Interestingly, Et_4NTos displayed a very good selectivity towards the formation of PCHC of about 83% with a good conversion (74%), the contribution of cyclohexene carbonate staying below 6% in both cases (Table 2, entry 14). As Et_4NTos was found to be the most effective cocatalyst, we then tested other tosylate-based salts with different cations, namely cetyltrimethylammonium tosylate (CTATos) and pyridinium tosylate (PyrTos). Although PyrTos was found to be an ineffective cocatalyst with a low conversion (48%) and low selectivity (14%) (Table 2, entry 16), CTATos displayed a good selectivity towards the formation of PCHC of about 55% with a good conversion (73%), the contribution of cyclohexene carbonate staying below 6% (Table 2, entry 15). The lower efficiency of PyrTos versus CTATos and Et_4NTos was probably due to a higher stabilization of the ion pair versus the "free" ions that might hamper the nucleophilicity of the tosylate anion. Then, in order to find the optimal catalytic performance of the two most efficient catalytic platforms reported above, namely ($Zn(OTf)_2/Et_4NTos$ and $Zn(OTf)_2/CTATos$), we investigated the effect of the catalyst/cocatalyst ratio on their catalytic activity and selectivity for the synthesis of PCHC (see Table 3).

Table 3. Catalytic studies performed with $Zn(OTf)_2/Et_4NTos$ and $Zn(OTf)_2/CTATos$ catalytic platforms using various catalyst:cocatalyst ratios [a].

Entry	Cat./cocat.	Cat.:cocat Ratio	Conv [b] (%)	S_{CHC} [c] (%)	S_{PCHC} [d] (%)	S_{PE} [e] (%)
1	$Zn(OTf)_2/Et_4NTos$	1:1	99	0	9	91
2	"	1:1.5	99	0	26	74
3	"	1:1.75	88	1	62	37
4	"	1:2	83	0	78	22
5	"	1:3	74	6	83	11
6	"	1:4	70	7	86	7
7	$Zn(OTf)_2/CTATos$	1:1	95	2	17	81
8	"	1:1.5	87	1	55	44
9	"	1:1.75	72	4	75	21
10	"	1:2	71	6	75	19
11	"	1:3	73	7	54	39
12	"	1:4	75	8	69	23

[a] Conditions: 5 mmoles cyclohexene oxide, 1 mol % catalyst, 70 °C, 20 h, 4 MPa CO_2; [b] Conv: CHO conversion; [c] S_{CHC}: selectivity to cyclic carbonate; [d] S_{PCHC}: selectivity to polycarbonate; [e] S_{PE}: selectivity to polyether.

The catalyst/cocatalyst ratio was varied from 1:1 to 1:4 for both systems. Whatever the nature of the cocatalyst, an increase of the cocatalyst content led to an increase of the cyclic cyclohexene carbonate production, probably due to an excess of nucleophile in the medium. Interestingly, an overall

increase of the selectivity towards the formation of PCHC was observed, although this tendency was only clearly observed in the case of $Zn(OTf)_2/Et_4NTos$. Thus, from these results, we consider that for both catalytic platforms, the best compromise between the conversion, the selectivity towards the formation of PCHC, and the quantity of cocatalyst is obtained for a catalyst/cocatalyst ratio of 1:2.

Finally, the synthesis of PCHC using $Zn(OTf)_2/Et_4NTos$ as the catalytic platform was performed in solvents of different polarity that have been used previously in the literature, namely, toluene, tetrahydrofuran, and dichloromethane (see ESI 4, Table S2 in Supplementary Materials). It was found that the conversion and selectivity towards the formation of PCHC remained relatively comparable to the one reported under neat conditions.

3.2. Catalytic Studies Performed with Metal Tosylates Complexes

The good results obtained above with the $Zn(OTf)_2/Et_4NTos$ catalytic platform prompted us to investigate the catalytic activity of a series of commercially available metal tosylates complexes for the synthesis of poly(cyclohexene carbonate) without the use of any cocatalysts. Unless mentioned otherwise, the coupling reactions were performed at 70 °C and 4 MPa for 20 h using 1 mol % of catalyst (Table 4). AgTos was found to be an ineffective catalyst with a low conversion (24%) and low selectivity (16%) towards the formation of PCHC (Table 4, entry 1). Although FeTos displayed a good catalytic activity with a conversion of 91%, a rather low selectivity towards the formation of PCHC of about 18% was obtained (Table 4, entry 2). Finally, it is noteworthy that ZnTos afforded a good conversion of 67% with a very high selectivity towards the formation of PCHC of about 97% (Table 4, entry 3). Thus, we emphasize that the performance of ZnTos in terms of selectivity towards the formation of PCHC was higher than that obtained with the $Zn(OTf)_2/Et_4NTos$ catalytic platform. Increasing the temperature to 80 °C slightly improved the conversion (72%) together with a high selectivity towards the formation of PCHC (95%) (Table 4, entry 4). A further increase to 90 °C did not improve the selectivity towards the formation of PCHC (94%) (Table 4, entry 5). At 80 °C, an increase of the catalyst concentration to 2 mol % allowed reaching an almost full conversion (98%) of cyclohexene oxide but at the expense of the selectivity towards the formation of PCHC (66%) (Table 4, entry 6). Interestingly, at 70 °C and decreasing the pressure to 2 MPa, a good conversion of 65% was observed together with a high selectivity towards the formation of PCHC (95%) (Table 4, entry 7). Finally, performing the reaction in toluene at different concentrations did not improve the conversion and had a detrimental effect on the selectivity towards the formation of PCHC in comparison to the one reported under neat conditions (Table 4, entries 8–10). The most promising poly(cyclohexene carbonate) samples in terms of yield and selectivity obtained in selected sets of experiments reported above were characterized by steric extrusion chromatography (SEC) (Table 5). The PCHC sample obtained with the $Zn(OTf)_2/P(Cy)_3$ catalytic platform displayed a molar mass of about 12 kg/mol (Table 5, entry 2/7). Interestingly, the PCHC sample prepared using $Zn(OTf)_2/Et_4NTos$ and $Zn(OTf)_2/CTATos$ led to a significant increase of the Mn from 12 to about 25 kg/mol with a dispersity of about 5 (Table 5, entries 3/4, 3/9). Thus, even if the selectivity toward PCHC of these three catalytic platforms is not optimal, they allow the synthesis of PCHC with molecular weights comparable to those obtained with other catalytic systems [7,17,19,51]. Then, the performance of ZnTos without the use of any cocatalysts was much better than that of the $Zn(OTf)_2/Et_4NTos$ catalytic platform as the obtained PCHC displayed a molar mass Mn of 62 kg/mol while the observed dispersity was maintained at about 4 (Table 5, entry 4/3). Increasing the temperature to 80 and 90 °C led to a decrease of the Mn to 42 and 39 kg/mol, respectively (Table 5, entries 4/4, 4/5), in accordance with the results previously reported by Werner et al. [21]. By the same token, at 70 °C and decreasing the pressure to 2 MPa led to a product with a lower molecular weight of 33 kg/mol and high dispersity of about 10 (Table 5, entry 4/7). Finally, even though the use of increasing concentration of toluene led to a product with higher molecular weight, the yield and the incorporation of CO_2 in the polymer chain decreased significantly (Table 5, entries 4/8, 4/9, 4/10). Thus, as a general comment regarding the observed broad dispersity reported in Table 5, this could be due to the presence of a small amount of water in the reaction medium that can deactivate

our catalyst during the reaction and/or act as a chain-transfer agent by reacting with the growing polymer chain to yield hydroxyl-terminated polycarbonates of various chain length, thus preventing the chain growth. Indeed, although our catalysts were handled and stored under argon, the CO_2/CHO coupling experiments were not performed under strict avoidance of water. In addition, as it is often observed for the copolymerization of cyclohexene oxide with CO_2, a bimodal M_n distribution was observed that has been also attributed to the presence of small amounts of water. The glass transition temperature (T_g) values determined by DSC and reported in Table 5 for four selected samples are in the range 120–125 °C. These values are comparable to the highest one reported in the literature for PCHC [17]. On the other hand, the fact that they were higher compared to previously reported T_g for poly(cyclohexene carbonate) obtained from the copolymerization of CO_2 and cyclohexene oxide mediated by zinc organyls [21] is ascribed to the higher molecular weight of our polymers. To conclude, under optimized conditions at 343 K and 4 MPa, we found that ZnTosylate in catalytic amounts (1% mol) under solvent- and cocatalyst-free conditions enables the selective synthesis of poly(cyclohexene carbonate) with a molecular weight of about 62.1 kg/mol (T_g = 124 °C) with about 70% yields.

Table 4. Catalytic studies performed with metal tosylates complexes [a].

Entry	Catalyst	Conv [b] (%)	S_{CHC} [c] (%)	S_{PCHC} [d] (%)	S_{PE} [e] (%)
1	AgTos	24	2	16	82
2	FeTos	91	0	18	82
3	ZnTos	67	0	97	3
4	ZnTos [f]	72	1	95	4
5	ZnTos [g]	62	2	94	4
6	ZnTos [h]	98	2	66	32
7	ZnTos [i]	65	1	95	4
8	ZnTos/Toluene (0.2 mL)	75	3	85	12
9	ZnTos/Toluene (0.4 mL)	63	3	82	15
10	ZnTos/Toluene (0.5 mL)	35	2	76	22

[a] Conditions: 5 mmoles cyclohexene oxide, 1 mol % catalyst, 70 °C, 20 h, 4 MPa CO_2; [b] Conv: CHO conversion; [c] S_{CHC}: selectivity to cyclic carbonate; [d] S_{PCHC}: selectivity to polycarbonate; [e] S_{PE}: selectivity to polyether; [f] 80 °C; [g] 90 °C; [h] 80 °C, 2 mol % catalyst; [i] 2 MPa.

Table 5. GPC data for the PCHC samples prepared using catalysts based on $Zn(OTf)_2$/cocatalysts [a].

| Table/Entry	Cat./cocat.	Solvent (ml)	Conv [b] (%)	S_{PCHC} [c] (%)	M_n (g.mol^{-1})	PDI [d]	T_g [e] (°C)
2/7	$Zn(OTf)_2$/P(Cy)$_3$	"	82	54	12,100	4.1	
3/4	$Zn(OTf)_2$/Et$_4$NTos	"	83	78	26,000	5.1	
3/9	$Zn(OTf)_2$/CTATos	"	72	75	24,800	5.3	
4/3	ZnTos	"	67	97	62,100	4.1	124.5
4/4	ZnTos [f]	"	72	95	42,400	6.9	123.7
4/5	ZnTos [g]	"	62	94	39,200	8.1	121.2
4/7	ZnTos [h]	"	65	95	33,500	9.9	
4/8	ZnTos	Toluene/(0.2)	75	85	41,400	10	
4/9	ZnTos	Toluene/(0.4)	63	82	69,300	6.3	
4/10	ZnTos	Toluene/(0.5)	35	76	109,300	4.5	124.8

[a] Conditions: 5 mmoles cyclohexene oxide, 1 mol % catalyst, 70 °C, 20 h, 4 MPa CO_2; [b] Conv: CHO conversion; [c] S_{PCHC}: selectivity to polycarbonate; [d] Polydispersity index defined as PDI = M_w/M_n; [e] Determined by DSC at 10 °C·min^{-1} from the second cycle; [f] 80 °C; [g] 90 °C; [h] 2 MPa.

Finally, in order to evaluate the performance of ZnTos with another monomer, we performed a few experiments using propylene oxide (PO) as a substrate. Under the optimized conditions found for CHO (5 mmoles PO, 1 mol % catalyst, 70 °C, 20 h, 4 MPa CO_2), a high conversion of PO of about 90% was obtained with a high selectivity of about 70% towards the formation of cyclic propylene carbonate

and a low selectivity of about 30% towards the formation of poly(propylene carbonate) PPC. To try to improve the selectivity towards the formation of PPC, the temperature was decreased to 40 °C. Although the selectivity towards the formation of PPC was increased to about 70% at the expense of the formation of cyclic propylene carbonate (30%), there was a strong decrease of the conversion of PO to about 30%.

3.3. Infrared Absorption Experiments

In order to put in evidence any specific interaction between CO_2 and the catalysts investigated in this study, we performed an infrared investigation of pressurized gaseous CO_2 in contact with some selected catalysts. In particular, we investigated the CO_2 bending mode in the spectral region of about 670 cm^{-1} that is known to be very sensitive to any specific solute–CO_2 interactions. Indeed, for isolated CO_2 molecules, the out-of-plane and in-plane bending modes are degenerated and display the same vibrational frequency. When CO_2 interacts with a solute, there is a removal of the degeneracy and the out-of-plane and in-plane bending modes display two distinct vibrational bands. For example, such splitting of the bending mode has already been reported to put in evidence CO_2–polymer [70], CO_2–ionic liquids [71], and CO_2–metal isopropoxide interactions [68]. Thus, we have reported in Figure 2 the infrared spectra of three selected catalysts dispersed in a KBr pellet, namely, ZnTos, Zn(OTf)$_2$, and Mg(OTf)$_2$ under a CO_2 pressure of 4 MPa. In order to reveal the spectrum of CO_2 interacting with each catalyst under a CO_2 pressure of 4 MPa, each spectrum was corrected from the contribution of the catalysts-loaded KBr pellet recorded under atmospheric pressure.
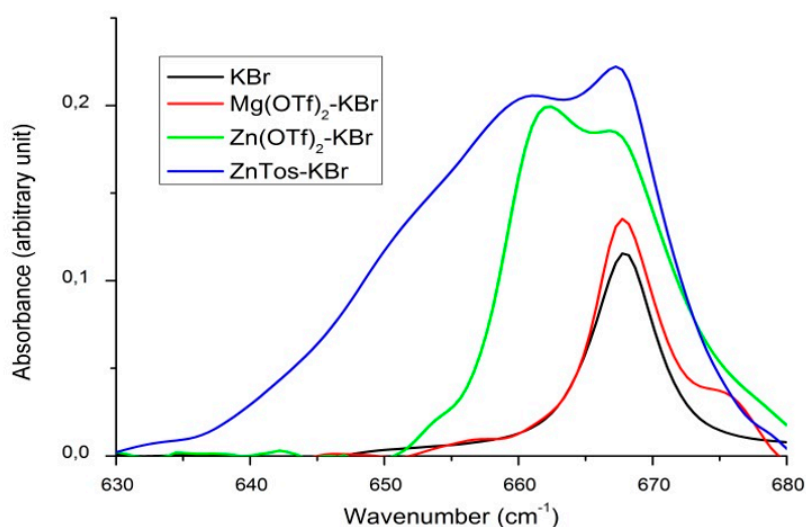

Figure 2. Infrared spectra of three selected catalysts dispersed in a KBr pellet, namely, ZnTos, Zn(OTf)$_2$, and Mg(OTf)$_2$ under a CO_2 pressure of 4 MPa corrected from the contribution of the catalysts-loaded KBr pellet recorded under atmospheric pressure. The spectrum of a KBr pellet under CO_2 pressure at 4 MPa is reported for comparison.

The spectrum of a KBr pellet under CO_2 pressure at 4 MPa reported for comparison displays a single narrow band at 668 cm^{-1} that is associated to the degenerated bending mode of CO_2, thus revealing that there is no specific interaction between KBr and CO_2. The same conclusion can be done in the case of Mg(OTf)$_2$-loaded KBr pellet. A different behavior is observed in the case of Zn(OTf)$_2$ and ZnTos. Indeed, an additional component is observed at about 662 and 660 cm^{-1} for Zn(OTf)$_2$ and ZnTos, respectively. Thus, from these observations, we can conclude that there is a specific interaction between CO_2 and both Zn(OTf)$_2$ and ZnTos. The higher shift, width, and intensity of the broad component observed for ZnTos can be interpreted as a signature of the stronger activation of CO_2 by ZnTos.

3.4. DFT Calculations

In order to support this experimental evidence, we performed DFT (Density Functional Theory) calculations on the 1:1 complex of CO_2 with ZnTos and $Zn(OTf)_2$. For the minimum energy structures of both complexes that are displayed in Figure 3, we observed that the CO_2 molecule acts simultaneously as electron donor towards the Zn atom and as an electron acceptor towards an O atom of the SO_3^- group. Although the stabilization energy of both complexes were nearly equal at –3.26 (ZnTos) and –3.36 kcal/mol ($Zn(OTf)_2$), the structures of both complexes were different as we observed that the interaction of CO_2 with the SO_3^- group was favored with ZnTos as shown by a shorter $C(CO_2)–O(SO_3^-)$ distance of about 3 Å instead of 3.5 Å in the $Zn(OTf)_2$ complex. This specific interaction led to an intramolecular OCO angle of CO_2 that was lower (178°) than that calculated for CO_2 in the $Zn(OTf)_2$ complex (179°), thus putting in evidence a stronger activation of CO_2 by ZnTos. Finally, from the calculated frequencies of the out-of-plane (ν_O) and in-plane (ν_i) bending modes of CO_2 in the ZnTos and $Zn(OTf)_2$ complexes, we found that the frequency gaps (ν_O-ν_i) were of about 12 and 4 cm^{-1} for the ZnTos and $Zn(OTf)_2$ complexes, respectively, which are consistent with the experimental infrared spectra reported above. Thus, these experimental and theoretical results are in line with the higher selectivity of ZnTos towards the formation of polycarbonate in comparison with $Zn(OTf)_2$ and $Mg(OTf)_2$, thus revealing that the ability of ZnTos to coactivate CO_2 is a key factor that governs its selectivity towards the formation of polycarbonates. In other words, although ZnTos is expected to activate the epoxide towards ring opening, the coactivation of CO_2 by ZnTos should favor the alternating copolymerization of CO_2 and cyclohexene oxide instead of the consecutive insertion of two epoxides that leads to the formation of polyethers.
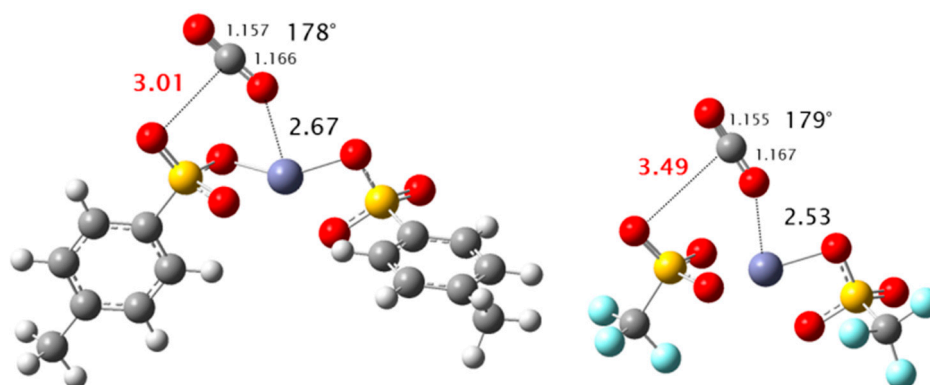
Figure 3. Optimized geometries (CAM-B3LYP/aug-cc-pVDZ) of the structures of the ZnTos-CO_2 (**left**) and $Zn(OTf)_2$-CO_2 (**right**) complexes. Bond lengths of interest are displayed in Ångström (dashed lines). The intramolecular C–O distances and OCO angle of CO_2 are also displayed.

4. Conclusions

The aim of this study was to investigate the copolymerization of cyclohexene oxide (CHO) with CO_2 in the presence of commercially available Lewis acids with metal centers such as Zn, Mg, Fe, Al, Ni, Sc, and Y. The influence of the pressure, the temperature, the catalyst loading, and the presence of a cocatalyst or a solvent on the reaction yields, selectivity, and molar masses has been evaluated for selected catalytic platforms. $Zn(OTf)_2$ in the presence of a tosylate-based cocatalyst has allowed the synthesis of PCHC in good to high yields. Then, the commercially available Zinc tosylate salt investigated under various thermodynamic conditions appears to be the most attractive simple Lewis catalyst that enables the selective synthesis of poly(cyclohexene carbonate) under solvent- and cocatalyst-free conditions. Thanks to in situ FTIR spectroscopy and DFT calculations, we have put in evidence a specific interaction between ZnTos and CO_2. Thus, we propose that, although ZnTos is expected to activate the epoxide towards ring opening, such catalytic performance is related to the

coactivation of CO_2 by ZnTos. This rational investigation is expected to help researchers to identify suitable catalysts that offer the best compromise in terms of activity, toxicity, and cost.

Supplementary Materials: The following are available online at http://www.mdpi.com/2311-5629/5/3/39/s1, ESI 1: Method for determination of conversion and selectivity, ESI 2-Figure S1: ^{1}H NMR spectra of polymer sample, ESI 3-Table S1: Sc and Y complexes investigation, ESI 4-Table S2: Solvent effect.

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