Adding Value to Power Station Captured CO_2: Tolerant Zn and Mg Homogeneous Catalysts for Polycarbonate Polyol Production

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Ⓢ *Supporting Information*

ABSTRACT: Using captured waste carbon dioxide (CCU) as a chemical reagent is an attractive means to add value to carbon capture and storage (CCS) and is a high-priority target for manufacturing. One promising route is to copolymerize carbon dioxide and epoxides, to prepare aliphatic polycarbonates. In this study, three homogeneous dinuclear Zn and Mg catalysts, previously reported by our group (see Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K *Angew. Chem., Int. Ed.* **2009**, *48*, 931−933 and Kember, M. R.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, *134*, 15676−15679) have been investigated using captured and contaminated carbon dioxide, with cyclohexene oxide, to produce polymers. Carbon dioxide captured from the carbon capture demonstrator plant at Ferrybridge Power Station, U.K., is applied for the efficient production of poly(cyclohexylene carbonate). Remarkably, the dinuclear Zn and Mg catalysts display nearly equivalent turnover numbers (TON) and turnover frequencies (TOF) using captured CO_2 versus those using purified CO_2. The tolerance of the catalysts to reactions contaminated with known quantities of exogenous water, nitrogen, SO_2, amine, and octadecanethiol are reported. The catalyst activities, productivities, and selectivities are presented, together with the polymers' number-average molecular weights (M_n), dispersities ($Đ$), and end-group analyses. The catalysts show high tolerance to protic impurities, including the addition of amine, thiol, and water. In particular, under certain conditions, efficient polymerization can be conducted in the presence of up to 400 equiv of water without compromising catalytic activity/productivity or selectivity. Furthermore, the catalysts can selectively produce polycarbonate polyols with molecular weights in the range of 600−9000 g/mol and disperities <1.10.

KEYWORDS: *carbon dioxide, copolymerization, polymerization, catalysis, homogeneous catalyst, zinc catalyst, magnesium catalyst, carbon capture and utilization, polycarbonate, controlled polymerization, carbon dioxide capture*
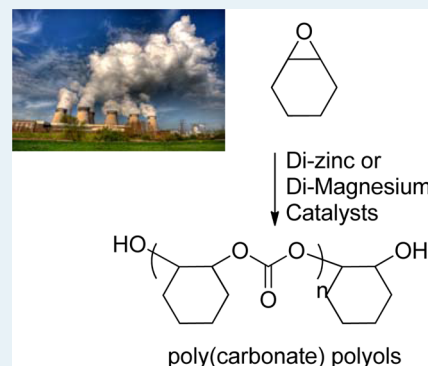
INTRODUCTION

Using waste CO_2 as a renewable raw material for the production of chemicals and materials is a particularly desirable means to add value to carbon capture and storage (CCS) and by analogy is frequently termed carbon dioxide capture and utilization (CCU).[1] Although CCU could be highly attractive from both an economic and environmental perspective, there are only a few practical examples of its implementation. One successful commercial process is the pilot-scale production of methanol, demonstrated by Carbon Recycling International, which applies waste CO_2 and H_2, produced by water electrolysis using renewable power.[2] Another example is the application of purified CO_2, captured from power generation, termed the "Dream" process and realized by Bayer for the production of poly(ether carbonates).[3]

In the context of CCU, the metal-catalyzed copolymerization of CO_2 with epoxides is interesting because of the high uptake of CO_2 into the product.[4] In an industry where raw material costs routinely account for >90% of production market prices, the substitution of costly petrochemical feedstocks with a low-cost feedstock such as CO_2 is an exciting prospect. Indeed, materials which are 30−50 mol % derived from CO_2 can be easily produced.[4] The product aliphatic polycarbonates are proposed as petrochemical substitutes in applications such as films, packaging, and rigid plastics.[5] Of particular interest are applications of low molecular-weight polycarbonate polyols as viable alternatives to the petrochemical polyols commonly applied in the manufacture of polyurethanes.[6] The commercialization of polycarbonate polyols, derived from CO_2, is an area of intense activity and pilot scale production is already underway.[7] Central to the viability of the copolymerization process is the selection of the catalyst; both homogeneous and heterogeneous catalysts are known. While heterogeneous catalysts are being commercialized, they can suffer from low rates, require high pressures of purified carbon dioxide, and result in rather low uptakes of CO_2, yielding poly(ether carbonates). Thus, if high CO_2 uptake and concomitant formation of polycarbonates is desired, then homogeneous catalysts may be preferable.

Currently, a rather limited range of homogeneous catalysts suitable for this catalysis have been described, most of which have been included in recent reviews.[4] Of these, significant

Table 1. Typical Composition of Various Post-Capture Carbon Dioxide Streams, According to Recommendations in both the EU and USA[a]

compound	US pipeline quality specifications[19c]	Weyburn enhanced oil recovery project[17d]	Dynamis pipeline quality specifications[19b]
CO_2	>95%	>96%	>95.5%
Ar			<4%
C_xH_y	<5%	<0.7%	<4% (saline aquifers), <2% (enhanced oil recovery)
CO		<1000 ppm	<2000 ppm
H_2O	0.4805 g/Nm^3	<20 ppm	<500 ppm
H_2S	10−200 ppm	<9000 ppmv	<200 ppm
N_2	<4%	<300 ppm	<4% (saline aquifers)
NO_x			<100 ppm
O_2	<10 ppm	<50 ppm	<4% (saline aquifers), 100−1000 ppm (enhanced oil recovery)
SO_x			<100 ppm

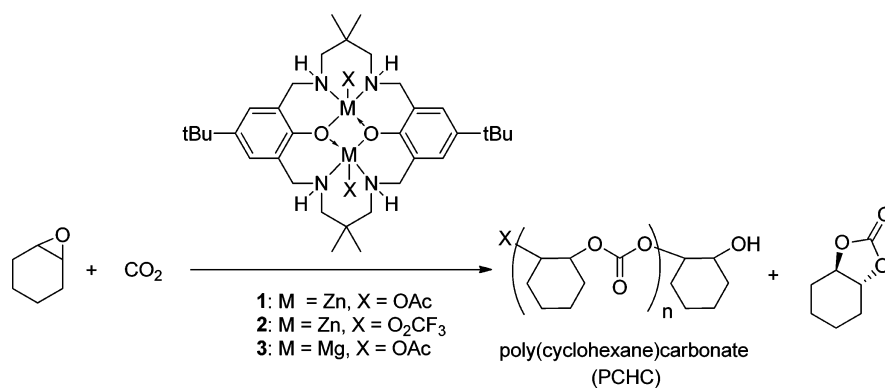[a]The table and contents are reproduced from Table 1 in ref 19a (with permission).

Figure 1. Molecular structures of the catalysts used for the production of poly(cyclohexene carbonate), and *trans*-cyclohexene carbonate byproduct, from cyclohexene oxide (CHO) and CO_2 under neat conditions at 100−120 °C, 1 bar of CO_2, and 3−6 h reaction time.

attention has focused on Co-salen complexes and their derivatives. The most effective of these have salen ligands incorporating ionic co-catalysts, commonly alkyl ammonium salts.[4] There have been several interesting reports of strategies to recycle and reuse these catalysts from polymerization reactors.[8] Although these catalysts exhibit high activities and selectivities, they also generally require higher CO_2 pressures and typically apply the highest purity epoxides, which are subsequently reacted under rigorously anaerobic and anhydrous conditions.[8,9] We have previously reported a series of homogeneous binuclear catalysts, comprising coordination complexes of macrocyclic ligands with dinuclear Zn(II),[10] Co(II/III),[11] Fe(III),[12] and Mg(II)[10g,h,13] metal centers. In particular, the colorless, air-stable, low-cost, dinuclear Zn or Mg catalysts showed highly competitive activities and selectivities even in the presence of an excess of water (up to 30 mol equiv vs catalyst).[13b] Additionally, these catalysts performed equivalently to some Co-salen complexes even at very low pressures of CO_2 (*ca.* 1−5 bar). A full kinetic study (Zn$_2$ catalysts) revealed a zero-order dependence on CO_2 pressure, over the range 1−40 bar.[10c] These promising characteristics prompted the current investigation into the tolerance of such dinuclear catalysts to a range of impurities found in captured CO_2. To the best of our knowledge, such studies are critical to successful CCU implementation yet have not been routinely investigated/published. A notable exception is a recent relevant study by Darensbourg and co-workers, where metal-organic frameworks were used to store pure CO_2 and then release it for subsequent copolymerization studies.[14] In other fields of carbon dioxide application, for example the production of cyclic carbonates, contaminated CO_2, simulating the composition of some waste

streams from power generation, has been used for the production of cyclic carbonates.[15] Xie and co-workers reported heterogeneous cobalt salen catalysts incorporated into conjugated microporous frameworks for use in simultaneous carbon storage and cyclic carbonate formation.[16] It should, however, be noted that the parallels between the catalysts for cyclic carbonate and polymerization are limited: cyclic carbonates are the thermodynamic products and as such are generally favored over polymers using most catalysts. Furthermore, polymerization catalysts are usually designed as "leave in" and thus recycling strategies are different.

Herein, the previously reported homogeneous dinuclear Zn/Mg catalysts are applied to the production of poly(cyclohexene carbonate) (PCHC), using *contaminated* waste CO_2.[10a,e,13b] The polymerizations are conducted under 1 bar pressure of CO_2, as model conditions for a desirable CCU process. Furthermore, the polymerizations have been conducted using concentrations of common poisons and contaminants higher than those commonly encountered in captured CO_2 to demonstrate the extent of the robustness of these systems.

◼ RESULTS AND DISCUSSION

CCU relies on recycling waste CO_2 streams as chemical feedstocks; in this context, CO_2 streams produced by power generation are some of the most contaminated.[1b] Therefore, in order to investigate the tolerance of the catalysis, such contaminated gases were targeted.

It is clear that carbon dioxide captured from any industrial source (power plant or other) will contain impurities and the most common of these include water, nitrogen, oxygen, and, if

Table 2. Comparison of Polymerization Results Using Catalysts 1−3 with Research Grade CO_2 (Entries A and B) and Captured CO_2 (Entries C−H)[a]

entry	catalyst	temp/°C	[cat.]/mol %	TON[b]	TOF/h^{-1}	selectivity[c]	M_n g/mol (Đ)[d]
A[10a]	1	100	0.1	527	25	94	7360 (1.21)
B[13b]	3	100	0.1	458	152	>99	11800 (1.03), 5900 (1.06)
C	1	100	0.1	121	20	99	1400 (1.18)
D	2	100	0.1	74	12	98	1720 (1.19)
E	3	100	0.1	436	73	99	6210 (1.04), 2760 (1.10)
F	3	120	0.1	384	64	99	4090 (1.30)
G	3	100	0.01	800	133	>99	1200 (1.19)
H	3	120	0.01	920	153	99	1120 (1.31)

[a]Reaction conditions: 5 mL of CHO, 3−6 h reaction time, 1.06 (captured CO_2)−1.62 (research grade, 99.999%, entries A and B) bar of CO_2. [b]TON = (mol of epoxide consumed)/(mol of catalyst). [c]Selectivity for polycarbonate vs cyclic carbonate, determined by ^{1}H NMR spectroscopy and comparison of the relative integrals of the lowest field resonances of poly(cyclohexene carbonate) at 4.65 ppm and cyclohexene carbonate at 4.05 ppm. No ether linkages were detected. [d]Determined by SEC.

Table 3. Performance of 3 in the Presence of Different Gas-Phase Additives[a]

entry	additive[b]	concn/vol %	TON[c]	TOF/h^{-1}	selectivity/%[d]	M_n g/mol (Đ)[e]
A	none		477	159	99	6300 (1.04), 2800 (1.09)
B	none[f]		305	101	99	5900 (1.03), 2700 (1.09)
C	H_2O	0.68	437	146	99	8300 (1.03), 4300 (1.09)
D	N_2	5	439	146	99	7300 (1.04), 3100 (1.12)
E	N_2	50	96	32	97	~600 (~1.2)[g]
F	N_2	75	88	29	95	~600 (~1.2)[g]
G	CH_4	5	447	149	99	7500 (1.05), 3200 (1.11)
H	O_2	5	458	153	99	9000 (1.04), 4000 (1.09)
I	H_2S	5	515	172	99	3000 (1.39)
J	SO_2	0.05	383	127	99	4600 (1.03), 2100 (1.09)

[a]Reaction conditions: 0.1 mol % of 3, 5 mL of CHO, 3 h reaction time, 1.06 bar of CO_2. [b]Pre-mixed into gas feed. [c]TON = (mol of epoxide consumed)/(mol of catalyst). [d]Selectivity for polycarbonate vs cyclic carbonate, determined by ^{1}H NMR spectroscopy, and comparison of the relative integrals of the lowest field resonances of poly(cyclohexene carbonate) at 4.65 ppm and cyclohexene carbonate at 4.05 ppm. No ether linkages were detected. [e]Determined by SEC using polystyrene calibrants. [f]Food grade CO_2 supplied from a balloon (ca. 1.06 bar measured overpressure). [g]Only approximate values are given, since part of this mass range is outside the calibrated weight range of SEC experiments.

coal is the power source, also sulfur oxides (SO_x) and nitrogen oxides (NO_x) as well as other traces of other organic/inorganic components. The type and nature of these impurities depend on a number of factors, including the type of capture process and the fuel source. A number of studies have investigated the composition of carbon dioxide streams from power plants;[17] these findings have been recently summarized by Race and co-workers.[18] Large-scale carbon dioxide capture schemes (CCS) will involve the transportation of carbon dioxide from the capture plan to the storage (or further reaction) site either via a pipeline network or by shipping networks.[19] Thus, it is informative to consider the recommended pipeline specifications for captured carbon dioxide, as presented in Table 1 for systems from both the USA[19c] and EU,[19b] as these provide an unambiguous qualification of the pipeline tolerances.[19a]

For this study, we were able to use authentic samples of post-combustion captured CO_2 supplied from a pilot plant in operation at Ferrybridge Power Station, Knottingley, West Yorkshire, U.K., which operates an amine-based carbon capture and separation process. While the precise composition of this gas is commercially sensitive, it falls within the range of typical compositions for post-combustion CCS and pipeline quality carbon dioxide (see Table 1). For more information regarding the process and typical gas specifications, the reader is referred to refs 17a and 19a. In addition to using this captured gas, the catalysts were also tested using CO_2 mixed with known contaminants as model gas compositions (vide infra). Three catalysts were tested, all of which have been reported

previously: two are based on Zn (1^{10a} and 2^{10e}), and one is based on Mg (3)[13b] (Figure 1). The catalytic tests were conducted under conditions identical with those for previously reported polymerizations, except that contaminated CO_2 was used. It should be noted that such conditions are non-optimized in terms of a commercial process and are used simply to be able to compare accurately the results obtained in this study against previous reports of these catalysts in the scientific literature. Gratifyingly, all three catalysts were found to retain the excellent activity and selectivity (Table 2) using post-combustion captured CO_2 from Ferrybridge Power Station. These results were observed in spite of contaminants present in the CO_2 feed and the very low overpressure of the supply (measured at 0.06 bar overpressure; see the Experimental Section for details). These results show that the activity/selectivity data compare favorably with those previously reported when using ultrapurified carbon dioxide (0.62 bar overpressure of research grade CO_2 99.9999% (BOC)) and purified epoxide.

In line with previous findings,[13b] the Mg-based catalyst 3 is significantly more active than either of the two Zn-based systems (1 and 2). Therefore, all subsequent testing was conducted solely using 3. The tolerance of the catalysis using 3 with captured CO_2 was explored under various different conditions, including different temperatures (Table 2, entries F and H) and catalyst loadings (Table 2, entries G and H). In all cases, the selectivity remains high for both polymer and carbonate linkages, while there is a slight increase in the

Table 4. Performance of 3 in the Presence of Different Solution-Phase Additives[a]

entry	additive[b]	amt of additive/molar equiv[c]	TON[d]	TOF/h^{-1}	selectivity/%[e]	M_n g/mol ($Đ$)[f]
A	none[g]		511	176	99	2900 (1.45)
B	HNEt$_2$	20	487	162	99	1200 (1.14)
C	MEA	20	306	102	99	1300 (1.18)
D	HS(C$_8$H$_{17}$)	20	521	173	99	1600 (1.13)
E	H$_2$O	39	294	98	99	~600 (1.2)
F	H$_2$O	68	200	67	99	oligomers
G	H$_2$O	109	120	40	99	oligomers

[a]Reaction conditions: 0.1 mol % of **3**, 5 mL of CHO, 3 h reaction time, 1.06 bar of CO$_2$. [b]Weighed directly into reaction vessel. [c]Based on **3**. [d]TON = (mol of epoxide consumed)/(mol of catalyst). [e]Selectivity for polycarbonate vs cyclic carbonate, determined by ^{1}H NMR spectroscopy, and comparison of the relative integrals of the lowest field resonances of poly(cyclohexene carbonate) at 4.65 ppm and cyclohexene carbonate at 4.05 ppm. No ether linkages were detected. [f]Determined by SEC using narrow molecular weight polystyrene standard as the calibrants. [g]Unpurified CHO from Acros Organics, 98% (GC).

formation of the cyclic carbonate side product (*trans*-cyclohexene carbonate) at low loadings and high temperature (Table 2, entry H). These findings are in line with the literature experiments, which used research grade carbon dioxide at 99.999% purity.[13b]

Although activity is an important parameter for any catalyst, it is also important to consider the nature of the polymer produced. To this end, the polymers were analyzed by size exclusion chromatography (Table 2). The molecular weights were all in the range 600−9000 g/mol, which is within the range targeted for polyols for polyurethane manufacture. As would be expected, higher catalyst loadings afforded a higher degree of monomer conversion, at fixed reaction times, and consequently higher molecular weight polymers. The dispersities were low in all cases and are consistent with well-controlled polymerizations as reported previously.[10a,e,13b]

To further demonstrate the practical utility of **3** in any CCU scenario, its tolerance to other CO$_2$ sources and to high levels of various model contaminants was investigated (Tables 3 and 4). Importantly, it was found that commercial "food-grade" CO$_2$ also resulted in activities and molecular weight distributions very similar to those in the aforementioned runs using captured CO$_2$ (Table 3, entry B).[20] The lower rates in this case are likely due to the significantly lower overpressure supplied by a balloon rather than a regulated supply from a cylinder. To simulate a truly "wet" feed, known volumes of H$_2$O and CO$_2$ were pre-mixed in a 2 L reactor held at 150 °C (ca. 0.6 bar overpressure), theoretically simulating 0.63 wt % H$_2$O contamination (Table 3, entry C). Once again, the catalysis proceeds at a very similar rate, producing polymers with very similar molecular weights, in comparison to using purified CO$_2$ supplied at the same overpressure (Table 3, entry A). Although it is difficult to ascertain and generalize the nature of the contaminants found in reclaimed CO$_2$, both reduced and oxidized compounds of nitrogen (N$_2$, amines, NO$_2$ and NO) and sulfur (H$_2$S, SO$_2$ and SO$_3$), O$_2$ and H$_2$O are common (Table 1). Of the other common gas-phase contaminants in addition to H$_2$O, relatively inert contaminants such as N$_2$, CH$_4$, and even O$_2$ have essentially no effect on rate or selectivity even at high loadings (Table 3, entries D, G, and H). However, extensive dilution of the CO$_2$ feed with N$_2$ does have an unfavorable effect at this pressure (Table 3, entries E and F). Upon dilution of the CO$_2$ feed by 50%, a non-linear decrease in rate is observed that is not affected significantly upon further dilution (to 25% CO$_2$). Moreover, with 75% N$_2$ present, the selectivity worsens significantly, and the SEC analysis reveals only low M_n species are formed (*ca.* 600 g/mol), which is due

to the much lower monomer conversions.[21] Curiously, a modest but consistent rate enhancement was observed when H$_2$S was present in the feed (Table 3, entry I). Although the origin of this enhancement in rate is not clear, analysis of the SEC data reveals a significant reduction in molecular weight, suggesting that H$_2$S may be acting as a CTA under these conditions (supported by solution-phase experiments using HSC$_{18}$H$_{37}$; see Figure S1 in the Supporting Information). While no detectable loss in selectivity was apparent by ^{1}H NMR spectroscopy, the MALDI-TOF MS using a thiol chain transfer agent does show the presence of polymer series in which one or two ether linkages are present (Figure S1). In addition to reduced sulfur contaminants, post-combustion feeds are often contaminated by oxidized sulfurous impurities, namely SO$_2$ and SO$_3$, albeit at very low concentrations (Table 1).[22] When the polymerization was carried out using a pre-mixed CO$_2$ feed containing 500 ppm of SO$_2$, there was a modest but reproducible reduction in TOF (Table 3, entry J). It is not clear if this reduction is due to a dilution and/or competitive inhibition effect, due to the greater solubility of SO$_2$ relative to CO$_2$, or to chemical reactivity.[23] For example, the insertion of SO$_2$ into Zn−alkyl bonds has been used to generate active catalysts for CHO/CO$_2$ copolymerization from alkylzinc complexes.[24] It could be envisaged that SO$_2$ might compete with CO$_2$ in the reversible insertion into the proposed propagating alkoxide bonds (Mg−OR). In any case, the concentration of SO$_2$ used corresponds to ca. 70 times the expected contamination level (Table 1) and thus it is not envisaged that "normal" levels of this contaminant would have a significant effect on the rate.

Having assessed the robustness of **3** to the presence of some common gas-phase contaminants pre-mixed into the gas feed, it was also prudent to investigate its tolerance to some other potential homogeneous contaminants present (Table 4). Using unpurified CHO resulted in a modest rate enhancement in comparison to distilled samples (Table 4, entry A; Figure S2, Supporting Information). Various types of amine-based solvents are commonly proposed for CO$_2$ capture technologies.[25] For this study, diethylamine and monoethanolamine (H$_2$N(CH$_2$)$_2$OH, MEA) were selected as practical model contaminants. When polymerizations were conducted using diethylamine, even at unrealistically high relative loadings (20 molar equiv based on **3** to investigate a "worst case" scenario; Table 4, entry B), the activity of **3** is marginally increased relative to the control (entry A, Table 3). As with H$_2$S, the unimodal molecular weight distribution and substantial decrease in M_n are indicative of chain transfer and both the
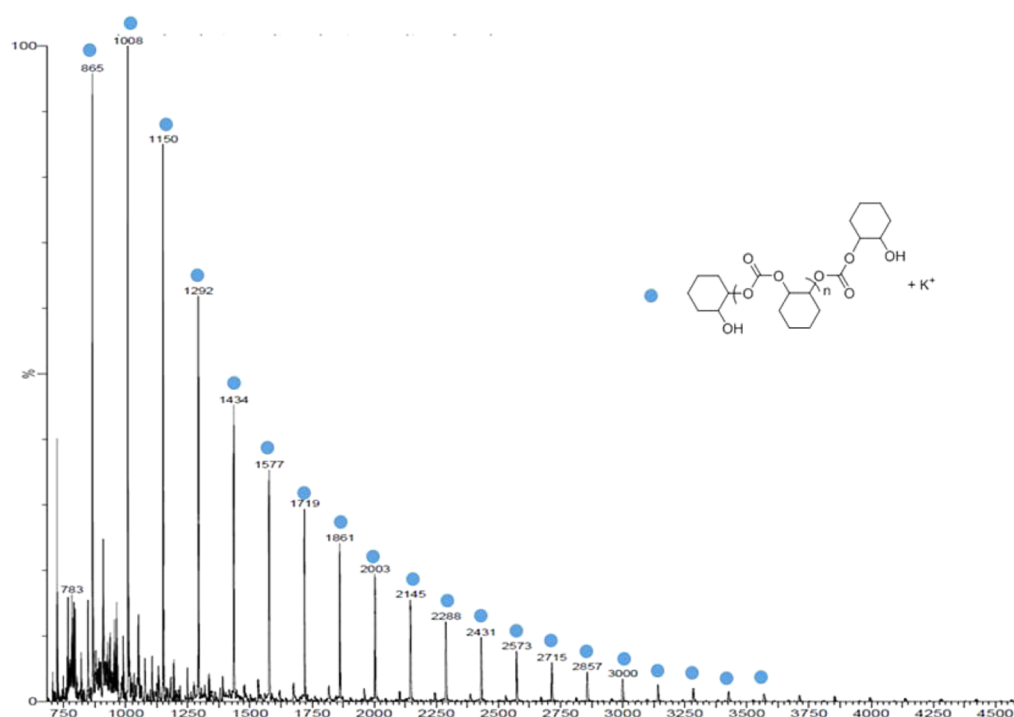
Figure 2. Representative MALDI-TOF spectrum of the isolated polymer from entry E, Table 4. The major series corresponds to dihydroxyl end-capped poly(cyclohexene carbonate) polyol.

Table 5. Polymerizations using 3 Conducted in a Mechanically Stirred Reactor[a]

entry	amt of **3**/mol %	$p(CO_2)$/bar	t/h	T/°C	amt of H_2O/equiv[b]	TON[c]	TOF	selectivity[d]/%	carbonate linkages[d]/%	M_n g/mol[e]	Đ
A	0.02	10	6	90	48	2300	400	99	99	5000	1.09
B	0.01	10	2	125	48	6700	3350	99	99	54900	1.22
C	0.01	40	2	125	48	5900	2950	99	99	43000	1.20
D	0.003	10	5	125	192	26900	5400	99	99	7200	1.06
E	0.003	10	4	125	400	9200	2300	99	99	2300	1.08

[a]Reaction conditions: see the Experimental Section. [b]Based on **3**. [c]TON = (mol of epoxide consumed)/(mol of catalyst). [d]Selectivity for polycarbonate vs cyclic carbonate, determined by ^{1}H NMR spectroscopy, and comparison of the relative integrals of the lowest field resonances of poly(cyclohexene carbonate) at 4.65 ppm and cyclohexene carbonate at 4.05 ppm. No ether linkages were detected (see carbonate linkages column). [e]Determined by SEC using narrow molecular weight polystyrene standards as the calibrants.

^{1}H NMR and MALDI-TOF MS spectra of the polymer produced in the presence of diethylamine clearly reveal −NEt$_2$ terminated polymers (Figures S3 and S4, Supporting Information). High loadings of MEA are tolerated less well by **3** (Table 3, entry C), giving a substantial drop in rate (ca. 30%) along with a reduction in M_n that is anticipated, given the presence of both primary hydroxyl and primary amino functionalities in MEA (see MALDI-TOF mass spectrum in Figure S5, Supporting Information). It is again worth drawing attention to the fact that high levels of MEA used in this experiment were chosen to represent an upper-end extreme scenario and are not anticipated to reach these levels in any real CCS process. To corroborate the previously determined rate enhancement in the presence of H$_2$S, HSC$_{18}$H$_{37}$ was selected as an easily handled solution-phase analogue for comparison. A consistent increase in TOF and reduction of M_n were again observed (Table 4, entry D). The presence of −SC$_{18}$H$_{37}$ end groups is easily identified in the MALDI-TOF MS spectra of the polymer and confirms the notion that it is acting as a CTA (Figure S6, Supporting Information). The propensity for thiols to function as chain transfer agents can be rationalized by the higher acidity of H$_2$S (pK_a = 7) in comparison to H$_2$O (pK_a =

15).[26] Taken together, it appears that the inclusion of small amounts of non-aqueous CTAs (such as amines, thiols, and the impurities present in unpurified CHO) actually give marginal increases in TOF.

The preceding experiments employing waste CO$_2$ (Table 2) and CO$_2$ contaminated with water (Table 3, entry C) as well as the previously published studies using carbon dioxide mixed with added H$_2$O have all demonstrated tolerance of **3** to H$_2$O and other contaminants in captured gas streams. It is, however, of interest to further examine the specific effect of added water, as this would be expected to be a common contaminant of both epoxides and carbon dioxide. It is clear that adding a large excess of water (>40 molar equiv vs **3**) exerts a negative effect on the relative activity of **3** (Figure 2) and reduces the M_n of the material produced (Table 4, entries E−G). The origin of the loss in activity is not clear but may result from competitive binding of water.[27] On the other hand, it does yield exclusively the dihydroxyl-terminated polymer (polyol) (Figure 2). This improvement in end-group selectivity is due to the ability of water to act as a chain transfer agent or to generate cyclohexenediol and to produce telechelic polymers. A major

application for these polymers is as polycarbonate polyols; thus, the production of dihydroxyl-terminated polymers is important.

Thus, these studies clearly reveal the promise for this class of homogeneous polymerization catalysts using captured or impure carbon dioxide gas streams. Although it is extremely difficult to unambiguously explain why these catalysts show such superior stabilities, factors such as catalyst structure and resting state are likely to be implicated. The high catalyst tolerance, particularly to protic impurities, relates to the catalyst structures where the chelate rings of the macrocycles and O,N donors stabilize the metals to ligand dissociation. Another factor is the stability of the initiating groups; the co-ligands are carboxylates, which show high stability to common impurities such as water/alcohols, as would be expected on the basis of pK_a values.

In order to fully investigate the influence of water tolerance, a series of experiments were conducted using a mechanically stirred stainless-steel autoclave (CO_2 pressures 10−40 bar, Table 5). Once again, it is important to note that these conditions are not optimized for catalyst performance but rather were conducted under typical and highly consistent laboratory conditions. These experiments revealed that, with efficient mechanical stirring but without any further process optimizaton, **3** can already exhibit outstanding performance that far exceeds the best results reported to date using these catalysts.[13b] In addition to high productivities and activities, catalyst **3** retains excellent selectivity at loadings considerably lower than those that had previously proved effective (vs experiments in standard laboratory glassware) (vide supra). Increasing the pressure from 10 to 40 bar (compare entries B and C) results in only a marginal reduction in rate, consistent with previous rate studies and presumably due to a relative dilution of monomer.[10c] Additionally, it is clear that **3** can also show much higher tolerance to water than is found for reactions in glassware; indeed, up to 400 equiv of water can be added in these reactor runs, at very low catalyst loadings, while maintaining excellent activity and selectivity. Furthermore, the molecular weights of the PCHC can be increased under these conditions, even in the presence of 48 equiv of water (entries B and C).

CONCLUSIONS

This work clearly demonstrates the utility of the previously reported Zn_2 complexes (**1** and **2**) and, in particular, Mg_2 complex **3**, as viable catalysts for the production of poly-(cyclohexene carbonate) polyols using CO_2 obtained from post-combustion CCS. Furthermore, these studies also highlight the tolerance of **3** to various impurities commonly found in captured carbon dioxide. It is notable that the catalyst continues to perform well even under high loadings of model contaminants, including compounds bearing S−H (H_2S, octadecanethiol), N−H (diethylamine, MEA), and O−H (H_2O, MEA, SO_2) functional groups. Under the best conditions tested, catalyst activity exceeds 5000 h^{-1} in the presence of excess added water (∼192 molar equiv vs catalyst). It is worth noting that the best conditions tested (mechanically stirred batch reactor, 10 bar, and 100 °C) are closely related to those used in the current industrial production of polyols. As expected, the molecular weights decrease with increasing water, or protic impurity, content, due to the chain transfer effect. However, this facilitates the selective production of low-molecular-weight polyols which could be suitable for further application in polyurethane manufacture. These findings

demonstrate the potential for this polymerization catalysis to integrate with carbon capture and to apply contaminated carbon dioxide as a raw material for polymer synthesis.

EXPERIMENTAL SECTION

All reactions were conducted in a nitrogen-filled glovebox or using standard Schlenk techniques. All glassware was dried at 160 °C for 20 h and cooled under vacuum prior to use. Catalysts **1**,[10a] **2**,[10e] and **3**[13b] were prepared by previously reported procedures and stored under nitrogen. Cyclohexene oxide was purchased from Alfa Aesar (98%) and fractionally distilled from CaH_2. Diethylamine (anhydrous) and octadecanethiol were purchased form Sigma-Aldrich and used as received. High-purity CO_2 (5.0 grade) was obtained by passing industrial grade CO_2 (BOC gases) through a high-performance purifier (Valco Instruments). Reclaimed CO_2 was received from Ferrybridge Power Station on August 20th, 2013. Ferrybridge operates a CCS demonstrator plan using amine-based post-combustion capture technologies. The CCS plant extracts up to 100 tons of CO_2/day from a coal-fired power station flue gas stream. More details regarding the typical operating parameters of amine-based carbon capture and separation technologies, including process schemes, can be found in ref 1. These processes typically comprise absorption of the gases by the liquid amine based solvent system, followed by desorption of the gases and solvent regeneration. The desorption processes typically involves a thermal treatment to accelerate the desorption of the carbon dioxide. The gas used from Ferrybridge was taken directly after desorption, and its pressure was approximately 1 bar. Data concerning typical carbon dioxide purity for postcombustion CCS can be found in Table 1 and in refs 1b, 17a, and 19a.

The samples were stored in Tedlar bags (with a volume of 10 L) each and at Econic Technologies were connected to the reaction apparatus via tubing, the entire system then being purged thoroughly with the sample gas. As a compression system was not available, a weight (∼2 kg) was applied to compress the bag and ensure a positive pressure of gas at all times in the apparatus. "Food" grade CO_2 was obtained from ISI and dispensed into a balloon reservoir. CO_2 containing 500 ppm of SO_2 was prepared by BOC using high-purity CO_2 and was used as received. A CO_2 feed containing 0.63% water was prepared by heating 0.32 mL of water and 50 bar of high-purity CO_2 in a 2 L reactor held at 150 °C.

^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker AV-400 instrument, unless otherwise stated. All mass spectrometry measurements were performed using a Fisons Analytical (VG) Autospec spectrometer. MALDI-TOF MS experiments were carried out using a dithranol matrix in THF at a loading of 1:5 with KOAc as the cationizing agent. SEC data were collected using an Agilent 1260 infinity instrument, with THF as the eluent, at a flow rate of 1 mL min^{-1}. Two Agilent Mixed E columns were used in series. Narrow M_w polystyrene standards were used to calibrate the instrument.

Polymerizations Conducted at Low Pressures. The appropriate quantity of catalyst (0.049 mmol) was weighed into a Schlenk tube, fitted with a magnetic stirrer, inside the glovebox. The tube was connected to a Schlenk line. Cyclohexene oxide (49 mmol, 5 mL) was added, via syringe, under a positive pressure of nitrogen. The tube was briefly degassed and then immediately refilled with CO_2, from the appropriate source, immersed in a pre-heated, stirred oil bath (defined as t_{start}), and maintained at the required temperature, with magnetic stirring at 750 rpm, for the duration of the reaction. At the end of the polymerization the reaction mixture was sampled via syringe while still hot and vigorously stirred (defined as t_{finish}) and an aliquot was analyzed by SEC and ^1H NMR spectroscopy. Any additives used in these experiments that were not present in the gas feed were weighed and added directly to the Schlenk tube inside the glovebox.

High Pressure Polymerizations. These reactions were conducted in a 1.8 dm^3 stainless steel reactor equipped with a mechanical anchor impeller with Teflon blades. Gaseous (CO_2) and liquid (CHO, water) reactants were fed via valve ports in the reactor lid. Defined amounts of the catalyst and CHO were loaded into a pressure-tight steel cylinder in the glovebox, and the cylinder was then attached to

the sealed, purged (CO_2) reactor (at room temperature), heated to the required temperature, and pressurized to the required pressure (defined as t_{start}). The pressure drop was monitored throughout, and CO_2 was repeatedly added to the reactor during polymerization to maintain a constant pressure. The polymerization was stopped by releasing the CO_2 pressure (over ca. 5 min, defined as t_{finish}). CHO was removed in vacuo (pulsed vacuum), and the crude product was dried with N_2 flushing. The crude product was weighed and analyzed by SEC and ^{1}H NMR spectroscopy. Calculation of the total polymer yield for the reaction at the sampling time was based on the overall isolated yield and ^{1}H NMR composition analysis of the withdrawn sample. Calculation of the final yield did not take into account the NMR sample, as this was deemed to be of negligible quantity and was constant across the series of experiments.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501798s.

MALDI spectra of the polycarbonates (PDF)

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Notes

The authors declare the following competing financial interest(s): C.K.W. is a director and founder of Econic Technologies. Econic Technologies seeks to commercialize polymers from carbon dioxide.

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(20) The composition of this CO_2 was not analyzed but is specified at >99.5% by the manufacturers. The principal contaminants are expected to be water and oxygen.

(21) Such low molecular weights are at the lower limit of the calibration of our SEC instrument, and thus only estimates are given on the basis of chromatograms within the calibrated region.

(22) Although the specific SO_3 tolerance could not be tested in isolation, the post-combustion reclaimed gas (vide supra) was not found to contain SO_3. Despite the precedent for using SO_3 as a contaminant in related studies (see ref 15), we found that addition of even milligram quantities of either SO_3 or H_2SO_4 to mixtures of **3** and CHO resulted in a vigorous exotherm, a blackening of the solution, and the formation of black smoke that presumably results from the rapid acid-catalyzed polymerization/decomposition of CHO and/or **3**. We do not recommend ever mixing these components.

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