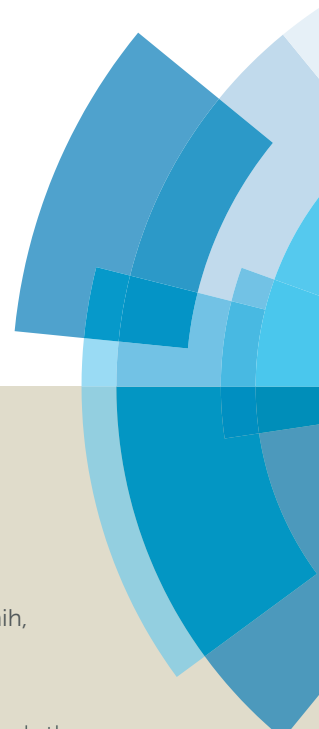


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Highly integrated CO₂ capture and conversion: Direct synthesis of cyclic carbonates from industrial flue gas

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Robust and selective catalytic systems based on early transition metal halides (Y, Sc, Zr) and organic nucleophiles were found able to quantitatively capture CO₂ from diluted streams via formation of hemicarbonates species and to convert it to cyclic organic carbonates under ambient conditions. This observation was exploited in the direct and selective chemical fixation of flue gas CO₂ collected from an industrial exhaust, affording high degrees of CO₂ capture and conversion.

The rising CO₂ levels in the atmosphere and the unavoidably related environmental concerns have been in the spotlight of international debates,¹ legislation² and research³ in the last decades. With the role of CO₂ in global warming,³ oceans acidification⁴ and global scale migration⁵ being ascertained, the attention has now shifted to the mitigation of the adverse effects⁶ and the development of efficient strategies for emissions reduction. It is becoming clearer that a major contribution to the reduction of the net amount of anthropogenic CO₂ released in the atmosphere will have to come from a decreased dependence from fossil fuels in favour of renewable energies and from higher energy efficiency.⁷ In parallel, chemistry-based strategies must be developed for the treatment of CO₂ in flue gases.⁸ Carbon capture by chemical sorbents⁹ has the advantage of handling large volumes of flue gas with a CO₂-recovery rate that is generally higher than 90 % and a purity up to 99 %.¹⁰ Geological storage of captured CO₂ (CCS) is a possibility for the disposal of large volumes of CO₂,¹¹ however, it encounters non-negligible limitations in terms of energy and capital costs, CO₂ transportation and durability of the sequestration.¹² On the other hand, the utilization of the CO₂ recovered after stripping for the

preparation of bulk commodity chemicals (carbon capture and utilization, CCU) could represent an optimal strategy to recycle CO₂ as a C-1 building block, thus reducing the dependence of the chemical industry on fossil fuels. The feasibility of this process has been demonstrated for the synthesis of organic chemicals.¹³ Nevertheless, in spite of the broad portfolio of chemicals accessible from CO₂¹⁴ and of the incessant development of new chemical processes,¹⁵ the amount of CO₂ utilized by the chemical industry is very small when compared to the volume of the anthropogenic emissions.¹⁶ This is in part determined by market size as only urea can count on a global demand above 100 Mt/year.^{11a,14b} Additionally, the reactions with CO₂ require in general a source of highly pure and compressed CO₂, its transportation to the reaction site and, often, high reaction temperatures. Even in the case of strongly exothermic processes, high energy co-reactants such as H₂ are required. Taken together with the purification process, these factors may easily offset the economical and environmental advantage of upscaling CO₂ recycling as an effect of indirect costs.¹⁷ In this context, highly integrated chemical processes able to capture and convert CO₂ to chemicals directly from flue gas "as it streams" from the point source could be able to maximize the benefits of CO₂ recycling without incurring in most of the indirect penalties.¹⁸ So far, very few processes have the potential to be applied for the direct conversion of CO₂ from flue gas. Amongst them, the non-catalytic mineralization of CO₂ to solid inorganic carbonates¹⁹ and CO₂ tri-reforming.²⁰ Both processes meet specific limitations and have not yet been implemented on a large scale.¹⁸

In an attempt to develop new, commercially attractive and environmentally benign processes for the direct conversion of CO₂ from flue gas, we considered that cyclic organic carbonates can be produced from CO₂²¹ under mild or even ambient conditions.²² Interestingly, they can be used as solvents for synthetic and catalytic applications²³ and are increasingly regarded as useful synthetic intermediates.^{15h,24} However, in spite of the burgeoning number of studies recently dedicated to this reaction,²⁵ no attempts have been made to use industrial flue gas as an impure CO₂ source for the synthesis of organic carbonates. To the best of our knowledge, efforts have been limited to the use of the CO₂ generated from the laboratory scale combustions of CH₄,²⁶ NO_x and

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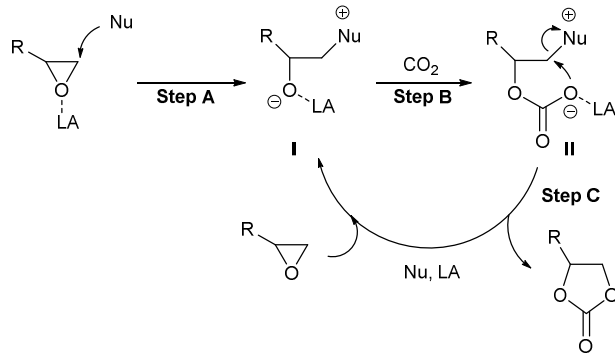
Electronic Supplementary Information (ESI) available: [General information and experimental methods, details on gas sampling and composition, *in situ* IR and kinetic studies and copies of NMR spectra]. See DOI: 10.1039/x0xx00000x

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SO_x doped CO₂,^{22h} or batches of catalyst exposed to flue gas from a power plant.²⁷ In this report we demonstrate the capability of simple metal halides-based catalysts to convert the CO₂ from diluted flows to cyclic carbonates under semibatch conditions.²⁸ With the catalytic and kinetic data at hand, the opportunity and the limitations of employing a flow of industrial flue gas as an impure CO₂ source for the synthesis of cyclic organic carbonates are assessed by employing the most active catalytic system. Thus, the first direct application of industrial flue gas for the synthesis of cyclic carbonates and, in general, the first application of flue gas in catalysis under ambient conditions is reported.

Under a mechanistic standpoint, previous kinetic and DFT investigation of the cycloaddition of CO₂ to epoxides have shown that the high Lewis acidity of early transition metal halides such as NbCl₅ facilitates the opening of the epoxide ring by the nucleophilic co-catalyst (scheme 1). As an effect, **step A** of Scheme 1 is nearly barrierless and highly exergonic; intermediate **I** can be considered as the resting state (most stable intermediate) of the catalytic cycle.²⁹ CO₂ insertion in **I** to afford hemicarbonatate **II** (**step B**, scheme 1) was found to proceed readily under ambient conditions and at low CO₂ concentration.^{29a} Therefore, we postulated that intermediate **I** would be readily formed from epoxide solutions of tetralkylammonium salts and early transition metal halides. Upon contact with CO₂, **I** can serve as a selective CO₂-capture unit by formation of **II** (Scheme 1, **step b**). This would be comparable to the formation of carbamate in amine scrubbing or of inorganic carbonates in mineral carbonation processes.³⁰ Cyclization of **II** to afford the organic carbonate (**Step C**) finally regenerates intermediate **I** for a new catalytic cycle.



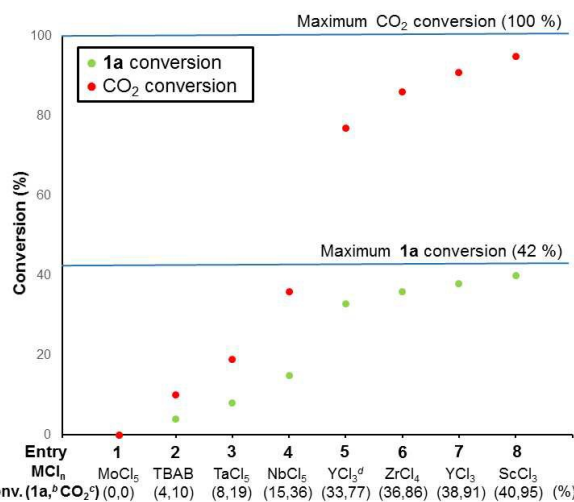
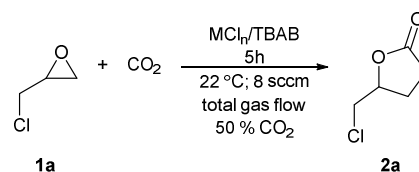
Scheme 1. Mechanistic overview of CO₂-capture and conversion by Lewis acidic halides and nucleophilic cocatalysts. Intermediate **I** can selectively activate CO₂ by formation of hemicarbonatate **II**.

Results and Discussion

The high potential of simple early transition metal halides combined with organic nucleophiles has been already demonstrated for the fixation of CO₂ into cyclic carbonates in previous studies under ambient conditions and at low CO₂ concentration.³¹ Surveying comparative homogeneous catalysts able to promote the title reaction under mild conditions,²² shows that early transition metal halides are both readily available and inexpensive as no long preparation is required to decorate them with elaborate organic ligands. The ability of early transition metal halides to promote the

cycloaddition of CO₂ to epoxides under reaction conditions roughly similar to those of a flue gas slipstream was initially assessed. Diluted flows of pure CO₂ were employed in a semi-batch process using the epoxides as a reaction medium and a reagent (See experimental section for details). We selected for this investigation the early transition metal halides having performed efficiently in previous studies.^{31a,d} They were used in combination with TBAB (tetrabutylammonium bromide) as a nucleophilic cocatalyst. The cycloaddition of CO₂ to non-volatile epichlorohydrin (**1a**) was chosen as a benchmark reaction (Chart 1, also refer to Table S3 in the ESI for additional experiments and blank reactions). A gas stream containing 50 % CO₂ (v/v, Ar was initially used as carrier gas) was bubbled through the epoxide (acting as a solvent and a reagent) solution. Under these conditions, CO₂ is the limiting reagent with a maximum **1a** conversion achievable of ca. 42 % for 100 % conversion of the CO₂ in the gas flow (horizontal asymptotes in Chart 1). The reactions were systematically monitored via *in situ* IR spectroscopy. This allowed the measurement of the kinetic profile of carbonate formation and of the apparent initial reaction rates (*k*_{rel}, Table S3).

Chart 1. Graphical representation of epoxide **1a** and CO₂ conversion for the cycloaddition of CO₂ to **1a** catalysed by metal halides and TBAB under flow conditions.^a



^a Epichlorohydrin 10 mL (11.8 g, 127.5 mmol), catalyst 1.275 mmol (1 mol%), TBAB 2.55 mmol (2 mol%), 5 h, 22 °C with a flow of 8 sccm (50 % v/v CO₂) using Ar as carrier gas. ^b Conversion of **1a** determined by ¹H-NMR by integration of the corresponding NMR signals of **2a** (4.56 ppm) and of **1a** (2.82 ppm, see Section 4 of the ESI). ^c Conversion of CO₂ calculated as the ratio between the moles of **2a** formed and the moles of CO₂ flowed through the reaction (1 sccm = 7.43·10⁻⁷ mol·s⁻¹; 53.51 mmol of CO₂ flowed through 5 h). ^d Using O₂ as the carrier gas.

Most of the halides tested were able to catalyse the conversion of CO₂ under these challenging reaction conditions. **2a** was generally

obtained selectively with the ^1H NMR spectra of the reaction mixture displaying additional signals attributable to the presence of the metal alcoholate (Intermediate I, Scheme 1, see Section 7 of the ESI). MoCl_5 is an exception as it led to polymerization of the substrate (Chart 1 entry 1). A blank experiment using only TBAB afforded just 4 % conversion of **1a** (Chart 1, Entry 2) using a flow containing 50 % CO_2 and no product formation when the concentration of CO_2 in the flow was reduced to 12.5 % (Table S3, Entry 2). ScCl_3 performed as the most active catalyst (Chart 1, entry 8) leading to the impressive conversion of 95 % of the amount of CO_2 passed through the reaction mixture. YCl_3 and ZrCl_4 (Chart 1, Entries 6, 7) were slightly less active than ScCl_3 , but demonstrated high degree of CO_2 conversion (91% and 86%, respectively). The runs using NbCl_5 and TaCl_5 showed lesser performances (36% and 19% CO_2 conversion respectively). A previous screening of early transition metal halides (that did not include Y- and Sc- halides) had revealed NbCl_5 as the most efficient catalyst for the conversion of propylene oxide (PO) to propylene carbonate (PC).^{31a} In this case, it was found to be less efficient than its Y, Sc and Zr counterparts. This can be explained in terms of the radically different reaction conditions with regards to CO_2 concentration and pressure, substrate, temperature and co-catalyst that were adopted in this study. ZnBr_2 has also been reported as an active catalyst for the title reaction under ambient conditions.³² It was slightly less performing than the most active early transition metal halides under identical reaction conditions (74 % CO_2 conversion Table S3, Entry 3). From a mechanistic point of view, all reactions displayed an identical profile of carbonate formation as observed by *in situ* IR (See the ESI file, Section 6). The spread between the initial reaction rates for each catalyst was found to be consistent with the degree of conversion observed at the end of the reaction (See Table S3). The formation of **2a** was generally preceded by an induction time of ca. 20 min in which a species with an IR absorption band centred at 1660 cm^{-1} formed, corresponding to the metal hemicarboxylate intermediate (Scheme 1, intermediate II and ESI file, Section 6).^{29a}

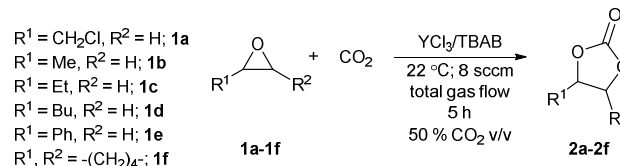
Based on these results, Y- and Zr-halides appear as the most promising candidates for feasibility studies on the direct conversion of CO_2 from flue gas. Scandium is a relatively rare and expensive metal and its application as a catalyst in a large scale seems unrealistic. YCl_3 was selected for further investigation and application with real flue gas. Yet it should be noted that, albeit less active, ZrCl_4 would be a more adequate alternative regarding costs. In order to explore the sensitivity of the Y-based catalytic system towards oxygen (an actual flue gas component), the YCl_3/TBAB pair was tested in the synthesis of **2a** using O_2 as a carrier gas (Chart 1, Entry 5). This led to a slightly lower catalytic efficiency. Nevertheless, in the perspective of the utilization of flue gas, O_2 was chosen in place of argon as a more realistic carrier gas for the remainder of this study.

In the light of the results obtained using epoxide **1a** as a substrate, we extended the application of the method to other mono- and di-substituted epoxides (Table 1). The use of propylene oxide (PO, **1b**) as a substrate is of particular interest as the corresponding carbonate product (propylene carbonate, PC, **2b**) finds various applications and could store CO_2 as a liquid and commercially attractive form.^{15j,24} A nearly quantitative conversion of CO_2 (with 37 % isolated yield of PC) was achieved using PO as a substrate and

a flow containing 50 % CO_2 (Table 1, Entry 2). Notably, no by-products were observed in the ^1H NMR spectrum of the reaction mixture. Within the **1a-1f** series of epoxides, substrate and CO_2 conversion were observed to decline by increasing the number of carbon atoms at the side chain (Table 1, entries 1, 2, 4-7). In this regard, styrene oxide (**1e**, Table 1, entry 6) proved to be a challenging substrate leading only to low styrene carbonate yields and low CO_2 conversion rates at room temperature. No formation of carbonate **2f** was observed in the case of di-substituted epoxide **1f** under the reaction conditions employed. In a mechanistic study on the cycloaddition reaction of CO_2 to various epoxides catalysed by Zn(salphen) complexes, Kleij, Bo et al. have shown that the low reactivity of epoxide **1f** is determined by steric effects, whereas, that of styrene oxide is dominated by electronic effects.³³ Steric effects might play a role in the reduced substrate reactivity within the **1b-1d** series.

As a potential drawback, a significant evaporation of volatile PO in the gas flow was observed by this method. This issue could be tackled by reducing the reaction temperature to $0\text{ }^\circ\text{C}$ at the cost of a lower reaction rate (Table 1, Entry 3; see also Section 4 of the ESI for further details and discussion). A good degree of CO_2 conversion (nearly 60 %) was observed at $0\text{ }^\circ\text{C}$ in 5 h.

Table 1. Screening of various epoxides for the cycloaddition reaction with CO_2 from diluted flows.^a



Entry	1	Yield (%) ^b (Conv. (%) ^c)	CO_2 conv. ^d (%)	TOF (h^{-1}) ^e
1 ^f	1a	(33)	77	6.6
2	1b	37	98 ^g	7.4 ^g
3 ^h	1b	21	56 ^g	4.2 ^g
4	1c	38 (39)	82 ^g	7.6 ^g
5	1d	(31)	58	6.2
6	1e	(8)	15	1.6
7	1f	0		

^a Unless otherwise noted, all reactions were carried out using epoxides **1a-1f** (100 equiv.), 1 mol % YCl_3 and 2 mol % TBAB at $22\text{ }^\circ\text{C}$ for 5 h with a total gas (50 % CO_2 v/v in O_2 flow of 8 sccm). ^b Isolated yield after column chromatography. ^c ^1H NMR conversion as per footnote b of Chart 1. ^d Determined as per footnote c of Chart 1 based on the amount of carbonate formed. ^e TOF (turnover frequency), calculated as TON/h (TON: turnover number; moles of **2a**/moles of YCl_3). ^f Taken from Chart 1, Entry 5. ^g Based on the actual isolated yields. ^h At $0\text{ }^\circ\text{C}$.

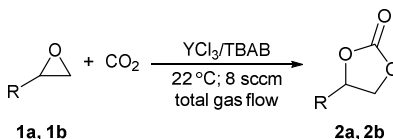
Prior to the application of flue gas as the CO_2 source for the cycloaddition reaction, we considered the possible interaction of the catalyst with main flue gas components such as O_2 and H_2O . Studies on the cycloaddition of CO_2 to epoxides catalysed under mild conditions by Al- and Zn-complexes have shown that these catalysts are compatible with the presence of O_2 in the reaction environment.^{24b,34,35} Also in our case, only a slight decrease in the performance of the catalyst has been observed by replacing Ar with O_2 as a gas carrier (Chart 1, Entries 5, 7). These observations suggest that the title reaction is generally O_2 -tolerant, at least when carried

out under mild conditions. Water can potentially have a detrimental effect on this reaction by leading to the formation of (poly)glycols and/or by affecting the stability of metal-based catalyst. Nevertheless, organometallic catalysts such as an aluminium amino-trisphenolate complex³⁵ and a tetranuclear Zn cluster³⁶ have been reported as robust and selective catalysts for the cycloaddition of CO₂ to epoxides in the presence of water. The addition of water has even been found to have a promoting effect on the title reaction catalysed by potassium iodide and ionic liquids by activation of the substrate via H-bond formation.³⁶ The influence of water on the cycloaddition of CO₂ to **1a** catalysed by YCl₃ and TBAB was investigated by adding variable amounts of water (0.5 - 25 mol %) to the reaction mixture under otherwise identical conditions. The results obtained show that the presence of water leads to a significant reduction of the reaction rate and epoxide conversion, although some catalytic activity is retained even in the presence of 25 mol % water (See in the ESI, Sections 3 and 5b for further considerations and concerning the moisture in the flue gas). This could be due to the hydration of YCl₃ altering its Lewis acidic properties.³⁷ In fact, large part of the moisture content of the flue gas was readily removed during sampling by condensation as an effect of the cooling of the flue gas below its dew point (See in the

ESI section) and it did not appear to affect our study at room temperature (*vide infra*). This suggests that the implementation of existing technologies designed to recover water from flue gas could be a beneficial and synergetic approach with the use of this catalyst.³⁸

The catalytic behaviour and the reaction kinetics of YCl₃/TBAB were investigated in the presence of increasingly diluted CO₂ flows and of industrial flue gas (containing 10.2 % v/v; for additional information about sampling and composition of flue gas see Section 3 of the ESI). The variation of other relevant reaction parameters (temperature, catalyst loading and reaction time) has also been considered (Table 2). In all cases, the desired carbonate was afforded. Focusing initially on the effect of CO₂ concentration in the gas flow ([CO₂]_g), it is evident that the initial apparent reaction rates decline with decreasing [CO₂]_g (Table 2, Entries 1, 3, 4, 11, 13 and 16-f, see also Figure 1 for a plot of **1a** and CO₂ conversion versus [CO₂]_g). Within the experimental error range, only a small difference in the apparent initial rates could be observed when using a stream of pure CO₂ or just 75 % CO₂ v/v (Table 1, Entries 1-3 and Figure 1). This may be due to the epoxide solution being already saturated with CO₂ under a flow containing just 75 % CO₂.

Table 2. Study of the cycloaddition of CO₂ to epoxides **1a** and **1b** under increasingly diluted CO₂ flows and of the effect of catalyst loading, temperature, reaction time and flue gas.^a



Entry	epoxide	[CO ₂] (v/v %)	Time(h)	Conv. (%) ^b	CO ₂ Conv. (%) ^c	TOF (h ⁻¹) ^d	k _{rel} (10 ³) ^e
1	1a	100	5	47	56	9.5	6.5
2	1a	100	3	35	70	11.7	6.9
3	1a	75	5	40	63	8.0	6.6
4	1a	50	5	33	77	6.6	4.4
5 ^f	1a	50	5	20	48	4.0	2.8
6	1a	50	3	20	79	6.7	4.4
7	1a	50	24	75	37	3.1	3.5
8 ^g	1a	50	24	86	43	1.8	3.5
9 ^h	1a	50	5	32	76	6.4	3.1
10	1b	50	5	37 ⁱ	98	7.4	3.1
11	1a	25	5	17	81	3.4	1.9
12	1b	25	5	10 ^j	55	2.0	1.3
13	1a	12.5	5	9	86	1.8	1.1
14	1b	12.5	5	3.2 ⁱ ,(4.3) ^j	34,(46) ^k	0.6,(0.8) ^k	0.8
15-f ^m	1a	10.2	5	0			
16-f	1a	10.2	5	8	92	1.6	0.9
17-f	1a	10.2	12	20,(16) ⁱ	97,(79) ⁿ	1.7,(1.4) ⁿ	0.9
18-f ^p	1a	10.2	5	27,(18) ^j ,(21) ^p		5.4 ⁿ	
19-f	1b	10.2	5	3.5 ⁱ ,(5.6) ^j	46,(73) ^k	0.7,(1.1) ^k	1.3

^a Unless otherwise noted, all reactions were carried out using **1a** (as per footnote a of Chart 1) or **1b** (as per footnote a of Table 1) at 22 °C by bubbling a mixture of carrier gas (O₂) and of CO₂ or flue gas through the reaction mixture with a total flow of 8 sccm. ^b ¹H NMR conversion as per footnote b of Chart 1, unless otherwise noted. ^c Calculated as per footnote c of Chart 1. ^d TOF (turnover frequency), calculated as TON/h (TON: turnover number; moles of **2a**/moles of YCl₃). ^e Apparent initial reaction rate as obtained from the profile of formation of **2a** (See the ESI, Section 6). ^f Using just 1.275 mmol (1 mol %) of TBAB. ^g Using 2.55 mmol YCl₃ (2 mol %) and 5.10 mmol TBAB (4 mol %). ^h At 40 °C. ⁱ Isolated yield after column chromatography. ^j Determined by NMR using an internal standard (See the ESI, Section 4). ^k Based on the NMR conversion as per footnote j. ^l The label "f" indicates the use of flue gas. ^m In the absence of the catalyst. ⁿ Based on the isolated yield. ^o Using flue gas in a batch process in a steel autoclave (4 bar, 110 °C, 5h). ^p NMR conversion to polyepichlorohydrin.

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Therefore, under a kinetic standpoint, nearly pure CO₂, as that recovered from flue gas by scrubbing, could be potentially converted *in situ* by this method to cyclic organic carbonates nearly as efficiently as pure CO₂, but without the need of purification, compression and transportation. Considering only the reactions with [CO₂]_g ≤ 75 %, the logarithmic plot of the initial reaction rates versus [CO₂]_g displays a linear correlation with a slope of 1 (See the ESI, Figure S9) indicating a first order dependency of the reaction rate on [CO₂]_g. Nevertheless, the portion of CO₂ converted to **2a** was found to increase linearly with the dilution of CO₂ (See Figure 1). The degree of CO₂ conversion achieved at [CO₂]_g = 12.5 % (86 %, Table 1, entry 13) is remarkable because [CO₂]_g in the slipstream is close to that observed in flue gas from large CO₂ emitters (such as power generation and steel production).³⁹ When the flow of pure gases was replaced by flue gas (Table 2, Entries 15-f to 19-f) we were delighted to observe the formation of **2a** and the conversion of over 90 % of the CO₂ contained in the slipstream (Table 2, Entries 16-f, 17-f). No background reaction was observed using flue gas in the absence of the catalyst (Table 2, Entry 15-f). Importantly, the values of **1a** conversion, apparent reaction rate and CO₂ conversion obtained for the flue gas matched the trends defined by the experiments using pure gases (Figure 1, See also Figure S10 and the discussion in the ESI file). Moreover, the kinetic profiles of **2a** (Fig. S7) and **2b** (Fig. S8) formation from flue gas are comparable to those obtained for the case of pure gases (Fig. S5) and do not hint at catalyst deactivation or poisoning from the use of flue gas. This demonstrates that at room temperature, the impurities contained in the flue gas sample have little or no influence on the catalytic performance of YCl₃/TBAB. Additionally, no new by-products were observed in the ¹H NMR of the reaction products confirming the selectivity of the catalyst (See the spectra in the ESI, Section 7).

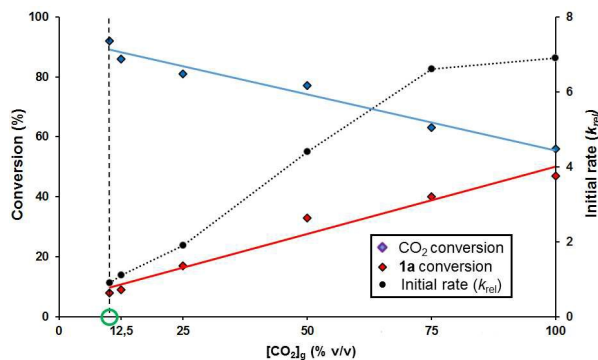


Figure 1. Plot of CO₂ conversion, **1a** conversion and apparent initial reaction rate as a function of [CO₂]_g. The green circle indicates the use of flue gas.

Longer reaction times, under otherwise identical conditions, led to higher yields of **2a** (Table 2, entries 1, 2, 6, 7). However, this corresponded to a lower fraction of CO₂ being captured and converted due to the progressive slowing-down of the reaction kinetics upon formation of **2a**. The use of a higher catalyst loading afforded nearly quantitative conversion of **1a** in 24 h (Table 2, entry 8) with 43 % overall CO₂ conversion. Finally, increasing the reaction temperature to 40 °C did not improve the yield of **2a** (Table 2, entry 9) as the effect of temperature was possibly offset by lower CO₂ solubility.

Given that the temperature of the flue gas at the sampling point is around 170 °C, we speculated that under harsher reaction conditions flue gas components such as moisture, NO_x and SO_x could have a stronger impact on the outcome of the reaction. Indeed, when the cycloaddition of CO₂ to **1a** was carried out from flue gas in a batch experiment (110 °C, 4 bar, Table 2 Entry 18-f), the ¹H NMR spectrum of the reaction mixture displayed, along with the carbonate product **2a**, a broad signal in the 3.5–4.0 ppm region (See the ESI, Section 7). This can be considered as an indication of the formation of large amounts of polyepichlorohydrin and polymeric material in general.⁴⁰ This result implies that the temperature at which flue gas is introduced in the reactor needs to be controlled if this process is to be carried out directly at the source of emission. Therefore, it appears that allowing the flue gas to cool below its dew point before reaction is crucial to lower the moisture content by condensation and to avoid the formation of by-products. In the case of PO a different trend was observed. The portion of CO₂ converted declined with the [CO₂]_g in the gas flow (Table 2, Entries 10, 12, 14) showing that the conversion of **1b** is highly sensitive to the amount of CO₂ available in solution. Nevertheless, when flue gas was employed a moderate degree of CO₂ conversion was observed with the formation of **2b** (Table 2, Entry 19-f). Within the limits of experimental error, this result is in line with what observed using pure gases. To note, the ¹H NMR spectra of the reactions carried out using **1b** and flue gas at 22 °C shows no polymeric material or other by-products; it is nearly identical to those obtained using streams of pure gases thus confirming the excellent selectivity of the catalyst developed in this study (See the ESI, Section 7).

Conclusions

The extraordinary catalytic activity of simple early transition metal halides in the well-known cycloaddition reactions of CO₂ to epoxides to afford cyclic carbonate was exploited in a semi-batch process to capture and convert CO₂ from

diluted slipstreams. For this purpose, early transition metal halides (in the presence of TBAB as a nucleophilic co-catalyst) have been applied as selective catalysts under a stream of either pure gases or industrial flue gas. YCl_3 -, ScCl_3 - and ZrCl_4 - based catalysts performed very well with both high activity and selectivity. In the case of sterically undemanding epoxides such as epichlorohydrin or industrially attractive propylene oxide, high degrees of conversion of the CO_2 in the gas flow to organic cyclic carbonates were observed. When flue gas was used as a diluted and impure CO_2 source at room temperature, YCl_3/TBAB was able to capture and convert a significant portion of the CO_2 in the flow. From a kinetic standpoint and at room temperature, flue gas was found to behave similar to a mixture of pure gases. For the case of epichlorohydrin, a CO_2 recovery rate from flue gas of over 90 % was observed; a performance comparable to that of chemical sorbents in industrial CO_2 scrubbing. It is noteworthy that the process described here presents the advantage to transform gaseous CO_2 to value added liquid chemicals. Yet epoxides are oil derivatives with a non-negligible C-footprint,⁴¹ therefore, the feasibility and the sustainability of this process needs to be evaluated carefully through LCA analysis of costs, energy and mass flows at the point source. Nevertheless, the process presented in this manuscript represents a remarkable advance in the treatment of flue gas and towards its direct catalytic conversion to chemicals at the emission source. Given the high activity displayed under flows of nearly pure CO_2 , this method could also be applied to the conversion of sequestered CO_2 as an alternative to geological storage. Future work will be focused on the preparation of highly active, halogen free,^{31b} supported^{29b} early transition metal catalysts for the cycloaddition of CO_2 from flue gas to industrially relevant epoxides such as propylene and ethylene oxide.

Experimental

Detailed experimental procedures are reported in the ESI file.

Acknowledgments

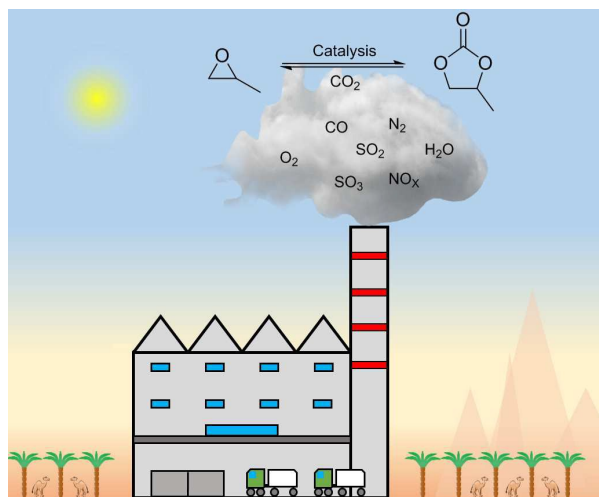
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The ability of early transition metal halides to capture and convert CO₂ from diluted gas flows has been exploited in the cycloaddition of CO₂ to epoxides using industrial flue gas as an impure source of CO₂.

