Faraday Discussions

RSCPublishing Faraday Discussions

FDCDU15 - Carbon Dioxide Utilisation: New catalysts for carboxylation of propylene glycol to propylene carbonate via high-throughput screening

Journal:	Faraday Discussions
Manuscript ID:	FD-ART-05-2015-000061.R1
Article Type:	Paper
Date Submitted by the Author:	26-May-2015
Complete List of Authors:	Heyn, Richard; SINTEF Materials and Chemistry, Process Chemistry North, Michael; University of York, Department of Chemistry comerford, james; york univsersity, ; University of York, Department of Chemistry Osma, Jose; University of York, Chemistry Tangstad, Elisabeth; SINTEF Materials and Chemistry,

SCHOLARONE[™] Manuscripts

Journal Name

ARTICLE



Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

New catalysts for carboxylation of propylene glycol to propylene carbonate via high-throughput screening

José A. Castro-Osma,^a James W. Comerford,^a Richard H. Heyn,^{*,b} Michael North^a and Elisabeth

High throughput methodologies screened 81 different metal salts and metal salt combinations as catalysts for the carboxylation of propylene glycol to propylene carbonate, as compared to a 5 mol % Zn(OAc)₂/p-chlorobenzene sulfonic acid benchmark catalyst. The reactions were run with added acetonitrile (MeCN) as a chemical water trap. Two new catalysts were thereby discovered, zinc trifluoromethanesulfonate (Zn(OTf)₂) and zinc p-toluenesulfonate. The optimal reaction parameters for the former catalyst were screened. Zn(OTf)2 gave an overall propylene carbonate yield of greater than 50 % in 24 h, twice as large as the previous best literature yield with MeCN as a water trap, with 69 % selectivity and 75 conversion of propylene glycol at 145 °C and 50 bar CO2 pressure. %

Introduction

Research on carbon dioxide (CO₂) utilization (CDU) has been gaining momentum over the past decade. While the motivation for this surge in interest may well be a response to the increasing levels of CO_2 in the atmosphere and the need for mitigating CO₂ emissions, the shear volumes of CO₂ emitted¹ and relatively modest contribution CDU can make toward mitigation of these emissions, at least in terms of chemical production volumes, strongly suggest that a more proper motivation is the development of CO₂ as a sustainable C₁ source for the chemical industry. CO₂ is renewable, easily handled and stored and essentially non-toxic. The challenge in its use arises from its thermodynamic and kinetic inertness. Advances in catalysis and process engineering are therefore necessary in order to overcome these barriers. Some of these issues can be and have been addressed by the use of high energy chemical reactants, as exemplified by the production of aliphatic polycarbonates from CO₂ and epoxides, which is on the cusp of industrial implementation.²

Tangstad^D

One class of compounds that have generated considerable interest as products for CDU is the organic carbonates, both open, linear carbonates such as dimethylcarbonate (DMC) and closed, cyclic carbonates such as propylene carbonate (PC). These molecules can be synthesized from CO_2 with two equivalents of an alcohol (methanol, for DMC) or one equivalent of a diol (1,2-propanediol, for PC). The latter can

also be prepared from CO₂ and propylene oxide by appropriate choice of catalyst, and the cyclic carbonates can be undesired by-products in the production of aliphatic polycarbonates.³

The reaction between CO_2 and alcohols or diols is thermodynamically unfavorable,⁴ with water as the other reaction product (See Scheme 1). Without any added water trap, the yield of PC from 1,2-propanediol (propylene glycol, PG) is 0.5 % at 130 °C with $CeO_2 \cdot ZrO_2$ as a heterogeneous catalyst.⁵ The addition of physical or chemical water traps will pull the equilibrium toward products, and this has most recently been successful with a $CeO_2/2$ -cyanopyridine system (20 mol % CeO_2 and 10-fold excess 2-cyanopyridine based on PG), which is able to provide nearly quantitative yield of PC from PG and CO_2 within 1 h at 130 °C and 50 bar CO_2 , with 2acetamidopyridine as the by-product from the chemical trapping of the co-produced water.⁶

The effect of water traps on the synthesis of organic carbonates from CO_2 and alcohols or diols has recently been reviewed.⁷ The majority of the other investigations into this reaction have used acetonitrile (MeCN) as the chemical water trap. One drawback with MeCN is the formation of a number of by-products from the water-trapping reaction, including acetamide, acetic acid, and acetylated glycols (See Scheme 1). The most efficient catalytic system (as based on time-yield) reported thus far is 2.5 mol % Zn(OAc)₂ with a 1.8 fold excess of MeCN at 160 °C and 30 bar CO₂, which provided a 12 % yield of PC with a 64 % selectivity after 2 h.8 A second report also indicates $Zn(OAc)_2$ as the best $M(OAc)_2$ catalyst (M = Co, Ni, Cu, Mn, Mg, Ca), but the reported time-yield is poorer (24 % yield and 62 % selectivity within 12 h at 170 °C and 100 bar CO_2).⁹ In addition to Zn(OAc)₂, inorganic carbonates (K₂CO₃ and $Cs_2CO_3/(NH_4)_2CO_3)$,¹⁰ organic bases (TBD = 1,5,6triazabicyclo[4.4.0]dec-5-ene)¹¹ and modified ZnO (KI/ZnO)¹² have been identified as the best catalysts in individual studies.

^{a.} University of York, Department of Chemistry, Green Chemistry Center of Excellence, York YO10 5DD, North Yorkshire, England.

^{b.} SINTEF Materials and Chemistry, P. O. Box 124 Blindern, 0314 Oslo, Norway. Email: rhh@sintef.no.

Electronic Supplementary Information (ESI) available: ¹H NMR spectrum of a typical PG to PC product mixture; List of all HT screened catalyst formulations. See DOI: 10.1039/x0xx00000x



Direct comparison between these catalysts is difficult since there is always variation in the reported reaction pressures, temperatures, times and catalyst loadings.

Considering the relatively limited number of compounds that have been tested for this reaction, we undertook a high throughput (HT) screening of 81 different metal salts and salt combinations. This contribution describes the selection of the benchmark catalyst for the HT studies, trends gleaned from the HT studies, and a parameter screening for an improved catalyst system found during the HT screening.

Results and Discussion

Catalyst pre-screening and choice of benchmark

This study started with a small catalyst pre-screening for determination of a suitable benchmark catalyst for the carboxylation of PG into PC at 145 °C and 60 bar CO₂. Reactions were carried out in the presence of either methanol or MeCN as solvent for 16 hours using 2.5 mol% of catalyst (Table 1). These conditions were chosen as an average between the conditions provided in the two previous papers reporting the catalytic activity of Zn(OAc)2.8,9 As shown in Table 1, zinc salts displayed higher catalytic activity than other metal salts, and Zn(OAc)₂ was, perhaps unsurprisingly, the most active catalyst. Additionally, reactions carried out in MeCN showed higher conversions than those carried out in methanol supporting previous results that MeCN not only acts as solvent but as dehydrating agent and shifts the reaction to the formation of products. As a catalyst, Zn(OAc)₂ showed some problems with reproducibility; a series of 6 runs gave a 39 ± 7 % conversion of PG and a 18 ± 5 % yield of PC with a 41 ±4% selectivity.

One of the main routes for the synthesis of cyclic carbonates is the transesterification reaction between DMC and diols.¹⁴ Similarly, the synthesis of diphenyl carbonate (DPC) can be carried out by a transesterification reaction between DMC and phenol,¹⁵ and it was found that using sulfonic acids as Page 2 of 6

 Table 1. Synthesis of PC from PG and CO2 with different catalysts.^a

Entry	Catalyst	Solvent	Yield PC ^b (%)
1	[SalenAl] ₂ O ^c	MeCN	0
2 ^d	[SalenAl] ₂ O + TBAB	MeCN	0
3	Tetrabutylammonium bromide	MeCN	0
4	K ₂ CO ₃	MeCN	0
5	Bu ₂ Sn(OAc) ₂	MeCN	<1
6	Mn(OAc) ₂	MeCN	7
7	Mn(OAc) ₂	MeOH	0
8	Fe(OAc) ₂	MeCN	<1
9	Fe(OAc) ₂	MeOH	0
10	Co(OAc) ₂	MeCN	8
11	Ni(OAc) ₂	MeCN	0
12	Cu(OAc) ₂	MeCN	5
13	Cu(OAc) ₂	MeOH	0
14	ZnBr ₂	MeCN	<1
15	Znl ₂	MeCN	<1
16	Znl ₂	MeOH	0
17	Zn(acac) ⁻ H ₂ O	MeCN	15
18	Zn(OAc) ₂	MeOH	<1
19 ^e	Zn(OAc) ₂	MeOH	0
20 ^e	Zn(OAc) ₂	MeCN	1
21	Zn(OAc) ₂	MeCN	27

^{*a*}Reactions carried out at 145 ^oC and 60 bar CO₂ pressure for 16 hours using 2.5 mol% of catalyst and 10 ml MeCN or MeOH. ^{*b*}Yield of PC determined by ¹H NMR spectroscopy of the crude reaction mixture (see Supplementary Material). ^{*c*} see ref. 13. ^{*d*}2.5 mol% tetra-butylammonium bromide (TBAB) used. ^{*e*}13X molecular sieves added (200mg).

co-catalysts improved both the conversion of DMC and the isolated yield of DPC.¹⁶ Therefore, the addition of a sulfonic acid as a co-catalyst for the synthesis of PC from PG was investigated. As shown in Table 2, the addition of 5 mol % p-chlorobenzene sulfonic acid (p-CBSA) gave higher PC yields and larger PG conversions. The yields of PC in Table 2 were the highest overall yields that have been reported in the literature for systems that employ MeCN as a water trap. The 5 mol % $Zn(OAc)_2/p$ -CBSA system was therefore chosen as the benchmark catalyst for the high throughput screening

High throughput screening

The high throughput (HT) screening experiments included a total of 81 different metal salts, combinations of metal salts and combinations of metal salts and strong acids. These screening experiments also included some metal salts tested in the pre-screening activity, as an additional check of the

Table 2. Synthesis of PC from PG and CO_2 with $Zn(OAc)_2$ and sulfonic acids as catalysts.^a

Entry	Sulfonic acid	Yield	Conversion	Selectivity	Isolated PC
		PC (%)	PG (%)	(%)	yield (%) ^P
1 ^c	p-CH ₃ C ₆ H ₄ SO ₃ H	22	48	44	-
2 ^d	p-CH ₃ C ₆ H ₄ SO ₃ H	28	69	41	18
3	C ₆ H₅SO ₃ H	29	72	40	17
4	p-ClC ₆ H₄SO ₃ H	33	73	45	25
5 ^e	p-ClC ₆ H₄SO ₃ H	35	84	42	34
6 ^f	p-CH₃C ₆ H₄SO₃H	26	63	41	27

^a Reactions carried out with 5 mol % Zn(OAc)₂ and 5 mol % sulfonic acid, at 145 [°]C and 60 bar CO₂ for 16 h. Product distributions based on ¹H NMR spectra of the crude reaction mixtures. ^b Yield of PC isolated by flash chromotography. See Experimental Section. ^c Used 2.5 mol % Zn(OAc)₂ and 2.5 mol % p-CH₃C₆H₄SO₃. Average values for 3 runs. ^d Average of three runs. ^e Dry MeCN. ^f 64 h reaction time.

Journal Name

reproducibility of the HT system. The screened catalyst systems can be loosely grouped into four categories: simple Zn salts, other late transition metal salts, combinations of Zn salts with other reagents, and Lewis acidic triflate salts. The first three categories included combinations with strong acids. In addition to the p-CBSA and p-toluene sulfonic acid (p-TSA) used in the pre-screening, the HT studies also used 4nitrobenzene sulfonic acid and dibenzenesulfonimide, as acids with different pK_a values (from 6.60 for 4-nitrobenzene sulfonic acid to 11.34 for dibenzenesulfonimide) in MeCN.¹⁷ The Lewis acids and other reagents were chosen since they have been shown to be effective transesterification catalysts. Specifically, lanthanide triflates have been shown to catalyze the transesterification of DMC with ethanol.¹⁸ The other reagents, KI, KOH, K₂CO₃ and NEt₄Br, have been shown to be catalysts or co-catalysts in the synthesis of DMC from CO₂, MeOH and epoxides.¹⁹ The results from the catalysts tested in the pre-screening compared well with the results from the same catalysts tested in the HT experiments. Table 3 compares PC yield of five catalysts studied both in the pre-screening and the HT experiments. The qualitative comparison as based on the yield of the benchmark catalyst is good, providing support of the validity of the results from the HT screening experiments. The larger differences for Co(OAc)₂ and $Zn(acac)_2 \cdot H_2O$ may be attributed to the different catalyst loadings in the different experiments.

All 81 screened catalyst formulations are provided in the Supplementary Material. For HT screening experiments, an important decision point is the definition of a "hit". For this study, any screened catalyst formulation that gave a better PC yield than that of the benchmark was deemed a "hit" and worth potential follow-up in a bench top reactor. It must be emphasized that the HT experiments are designed simply to identify potential lead catalyst candidates. The absolute PC yield for any one screened catalyst formulation was considered as merely suggestive. The list of catalyst formulations considered as lead candidates is shown in Table 4. These 16 catalyst formulations represent 20 % of all screened catalysts. Given that the hits for zinc trifluoromethanesulfonate $(Zn(OTf)_2)$ and zinc p-toluenesulfonate hydrate $(Zn(Tos)_2 \cdot H_2O)$ with acids are likely simply due to the Zn salts, these successful catalyst combinations can essentially be reduced to four lead candidates: Zn(OTf)₂, $Zn(Tos)_2 \cdot H_2O$, hexafluoroacetonylacetate dihydrate, and Zn(OAc)₂ with Lewis

Table 3. Comparison of selected catalysts in the pre-screening and HT experiments. $^{\rm a}$

Catalyst	PC yield relative to benchmark			
	Pre-screeing	HT		
Co(OAc) ₂	24 %	48 %		
Cu(OAc) ₂	15 %	10 %		
Zn(acac) ₂ ·H ₂ O	45 %	81 %		
Zn(OAc) ₂	82 %	97 %		
Zn(OAc) ₂ + p-TSA ^b	85 %	89 %		

^a Pre-screening data with 2.5 mol% catalyst, HT data with 5 mol % catalyst. Entry 4 in Table 2 used as benchmark catalyst yield. HT results based on HeadSpace GC analyses. ^b 5 mol % catalyst in the pre-screening experiment.

Table 4. Lead catalyst candidates from the HT screening.^a

Catalyst	Relative %	Catalyst	Relative %
	PC yield ^b		PC yield
Zn(OTf) ₂ + 4-NO2-		7n(OAc) + 5m(OTf)	1 1 1
benzenesulfonic acid	1.01	$2\Pi(OAC)_2 + 3\Pi(O\Pi)_3$	1.11
ZnI2 + p-TSAd	1.02	Zn(OTf) ₂ + p-TSA	1.11
$\frac{7}{2}$	1.02	Zn(OTf) ₂ +	
211(F6-acac)	1.03	dibenzenesulfonimide	1.12
Zn(F ₆ -acac) + p-CBSA	1.07	Zn(OAc) ₂ + LiOTf	1.18
Zn(OTf) ₂ + p-CBSA	1.08	Zn(OAc) 2 + Mg(OTf)2	1.25
Zn(OTf) ₂	1.08	Zn(OAc) 2 + Yb(OTf)3	1.30
Zn(Tos) ₂ ·H ₂ O + p-TSA	1.09	Zn(Tos) ₂ ·H ₂ O	1.31
Zn(OAc) ₂ + p-TSA ^d	1.09	Zn(OAc) 2 + Ca(OTf)2	1.35

^a HT reaction conditions: 145 °C, 50 bar CO₂, 16-18 h reaction time. ^b Data based on comparison to benchmark data, as determined from GC HeadSpace data. ^c F_{6^-} acac = hexafluoroacetylacetonate. ^d10 mol %.

acidic triflate salts. On the basis of performance and the preference for a single-component catalyst, $Zn(OTf)_2$ and $Zn(Tos) \cdot H_2O$ were chosen for bench top validation experiments.

The data for the carboxylation of PG to PC using 5 mol % $Zn(OTf)_2$ and $Zn(Tos)_2$ ·H₂O are shown in Table 5. In particular, $Zn(OTf)_2$ showed a significantly improved catalytic performance over previously studied catalysts. Over 50 % yield with nearly a 70 % selectivity was observed for the $Zn(OTf)_2$ catalyst. The observed PC yield for $Zn(OTf)_2$ is double the best reported overall yield in the literature for those systems that used MeCN as the chemical water trap.

Parameter screening for Zn(OTf)₂

Given the superior catalytic performance of $Zn(OTf)_2$ in the HT screening and validations studies, this catalyst was chosen for a parameter optimization. The effect of the reaction parameters of pressure and temperature and the amount of $Zn(OTf)_2$ on the conversion to PC and the overall selectivity of the reaction were screened in a bench top pressure reactor, and the results are presented in Figures 1, 2 and 3, respectively.[‡] There is very little effect of a change in pressure from 30 to 70 bar CO₂ on the product distribution. The yield of PC is essentially constant above 40 bar, and there is a slight increase in the side products with increasing pressure, as indicated by the increase in the overall conversion of PG and the decrease in selectivity.

The effect of temperature is more profound. At 85 °C, the yield of PC is only 4 %. The yield increases monotonically with an increase in temperature up to 135 °C; at this temperature the yield of PC, the overall selectivity and the conversion of PG are at their maximum values. Higher reaction temperatures show a decrease in PC yield and selectivity, while the conversion of PG remains constant, indicating that reaction temperatures

Table 5. Lead candidate validation results.

Catalyst	Time	p(CO ₂)	PC yield	PG conversion	Selectivity
	(h)	bar	(%)	(%)	(%)
Zn(OTf) ₂	24	53	52	75	69
Zn(Tos) ₂ H ₂ O	25	47	48	77	62

 $^{\rm a}$ Conditions: 20.7 g (2.72 mmol) PG, 31.45 g (766 mmol) MeCN, 145 °C, time from start of heating, product ratios from integration of $^1{\rm H}$ NMR spectra.

ARTICLE

Figure 1. Effect of different pressures on the yield of PC with 5 mol % Zn(OTf)₂ as



higher than 135 °C only increase side product formation. Similarly, an increase in the mol % catalyst from 1 to 5 mol % provides a monotonic increase in the PC yield, from 17 to 42 %. There is a concomitant increase in PG conversion, while the selectivity remains essentially constant. Increasing the catalyst amount from 5 to 10 mol % does not appreciably increase the PC yield. The overall conversion of PG does slightly increase, but this is mainly due to a greater increase in the formation of side products, as shown by the decrease in selectivity. **Discussion**

On the basis of the over 80 different catalyst formulations that have been screened, either in a bench top reactor or in a HT system, in this work, certain trends can be identified. One, transition metal salts apart from Zn salts are not very good catalysts for this reaction. None of the Ni or Cu salts showed any significant catalytic activity, even in the presence of strong acids. Salts of Mn, Fe and Co showed better activities; while the screened salts did not fare as well as the Zn salts, examples with different coordination spheres may prove to be viable candidates. Two, Lewis acidic triflate salts, based on Group 1, 2 and Lanthanide metals, are also very poor catalysts, although some of these salts showed promise in combination with Zn(OAc)₂ and are under further study. Three, the pK_a of the added acid had in general no effect on catalytic activity. Four, a strong acid than they did alone. For example, both ZnBr₂ and







 ${\sf ZnI}_2$ when combined with either p-CBSA or p-TSA, showed much better catalytic activities in the HT screening experiments than the simple salts did in the pre-screening experiments.

One hypothesis for the improved catalytic activity of $Zn(OTf)_2$ and $Zn(Tos)_2 \cdot H_2O$ over the benchmark system is that they do not need other reagents to produce open metal coordination sites. The activity of the benchmark catalyst (and other Zn salts) in combination with sulfonic acids may well be attributed to the formation of HOAc and some Zn^{2+} species with a labile coordination sphere. That other Zn salts with ostensibly poorly coordinating anions such as $Zn(BF_4)_2$ fail to show appreciable catalytic activities even in the presence of strong acids suggests that $Zn(OTf)_2$ and $Zn(Tos)_2 \cdot H_2O$ may impart other, asyet unknown, benefits towards catalysis of this reaction.

Experimental

General considerations

All reagents were commercially available (Alfa Aeser, Sigma-Aldrich, Fluka, TCI or Acros) and were used as received. Metal salts for the high throughput studies were in general anhydrous. See Supplementary material for further information. The bimetallic aluminium salen complex was prepared as previously reported.¹³ Carbon dioxide was purchased from BOC or Yara and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Jeol Oxford 400 spectrometer or on a Bruker UltraShield 400 spectrometer at resonance frequencies of 400 and 100 MHz, respectively.

Initial screening

Reactions were magnetically stirred in a 300 mL stainless steel pressure reactor heated in an oil bath. Product compositions were then analysed by ¹H NMR spectroscopy without any purification to determine the conversion and selectivity, as based on the integration of the Me signals of PC, side products and PG; see Supplementary Material.

Journal Name

PG (7.35 mL, 100 mmol), $Zn(OAc)_2$ (0.917 g, 5 mmol), p-CBSA (1.07 g, 5 mmol) and MeCN (10 mL, 191 mmol) were placed in a 300 mL stainless steel pressure reactor heated in an oil bath. The reaction mixture was magnetically stirred and heated to 145 °C. Then, the reactor was pressurized to 60 bar of carbon dioxide and the reaction mixture was stirred for 16 h. The conversion of PG to PC was then determined by analysis of a sample by ¹H NMR spectroscopy. The remaining sample was evaporated *i vacuo* to give mixture of PC, PG, propylene glycol acetate and propylene glycol diacetate. The mixture was purified by flash chromatography using dichloromethane as eluent to give the pure PC.

High throughput screening

High throughput experiments were conducted in an in-house constructed HT reactor featuring four rows of six reactor wells, with each row of reactors have a common gas feed. Each well was 9 cm high and had an inner diameter of 1.5 cm, with an effective reactor volume of approximately 11 ml. All wells were closed during the reaction to avoid well-to-well contamination. On a benchtop, the catalyst formulation (metal salts, acids, ligands) were added to each well of the reactor. The amount of catalyst was kept to ca. 5 mol % of the amount PG. A 1 ml aliquot of PG (13.6 mmol) and a 2 ml aliquot of MeCN (38.3 mmol) was then added by autopipette. Three steel balls (5 mm diameter) were added to each well to ensure proper mixing. The set of 24 reactor wells was then attached to the gas inlet portion of the reactor under a flow CO₂, placed in an oven and warmed up to 145 °C under 2-3 bar CO₂ pressure. After reaching the reaction temperature, the CO_2 pressure in each row of 6 reactors was sequentially increased to 50 bar. Mixing was accomplished with the help of a variable speed vortex (shaker). Reactions were run overnight, usually between 16-18 h from the time of pressurizing the reactors to 50 bar CO₂ until cooling was initiated. Approximately two hours were required to cool the reactor sufficiently before the CO₂ pressure could be released. Once the reactors reached a sufficiently low temperature, the pressure was carefully released overnight to a holding container. The initial HT experiment contained the benchmark catalyst system in each of the 24 reactor wells. No significant internal variation was observed, apart from a small, reproducible decrease in benchmark catalyst yields in the row of 6 reactors closest to the oven door. Comparison of PC yields for the screened catalysts were therefore made on a row-by-row basis, and in order to ensure reproducibility of each high-throughput experiment, the benchmark catalyst was placed in one randomly chosen well in each row of 6 reactors. The placement of the 20 other catalyst formulations in each high throughput experiment was also randomized.

Product analysis was conducted on a Teledyne Tekmar HT3 HeadSpace analyzer coupled to a Agilent 6890 gas chromatograph, using a DB-WAX column (30 m x 0.320 mm x 0.5 μ m) and flame ionization detector. Samples were subjected to a 140 °C, 15-minute temperature profile.

Analyses were conducted on two 10 μl samples withdrawn from the high-throughput reactor wells.

Validation experiments

Results from selected catalysts from the high throughput experiments were validated in a 300 ml Parr reactor with mechanical stirrer and heating jacket. On a bench top, a glass liner for the reactor was charged with the chosen catalyst formulation (ca. 5 mol % based on PG), PG (ca. 20.7 g, 0.272 mol) and MeCN (ca. 31.5 g, 0.767 mol). The reactor top was mounted under a flow of $\ensuremath{\text{CO}}_2.$ After the reactor had been assembled, it was flushed with CO₂ three times, and the temperature was raised to 145 °C under a slight pressure of CO₂ (2-3 bar). Finally, the pressure was raised to ca. 50 bar and the CO₂ feed was closed. The reaction was stopped by simply removing the heating jacket and allowing the reactor to cool to room temperature, followed by a slow release of CO₂. The reactor was cleaned with hot isopropanol and dried between runs. Product distributions were determined by the established ¹H NMR method.

Parameter screening for Zn(OTf)₂.

The reactor was dried at 100 °C under vacuum for a minimum of one hour and cooled to <40 °C before use. The reactor was then charged with anhydrous $Zn(OTf)_2$ and 10 ml (191 mmol) of dry MeCN stored under Ar. 60 mmol PG and a magnetic stirring bar was subsequently added. The reactor was then sealed, pressurized to 20 bar with CO_2 and heated to the desired temperature. Once this temperature had been reached, the CO_2 pressure was increased to the desired value. After 16 hours, the reactor was cooled in a bath of liquid nitrogen or dry ice/acetone until the internal temperature dropped below 30 °C, at which time the reactor was depressurized. Yields and selectivities were determined from integration of the ¹H NMR spectra of the products.

Conclusions

Due to its thermodynamic stability and kinetic sluggishness, CO₂ needs catalysts in order to be transformed into useful chemical products. In this study, we have endeavoured to apply high throughput techniques so as to more rapidly screen a host of different metal salts as catalysts for the carboxylation of propylene glycol to propylene carbonate. Our initial prescreening results found an improved catalyst system - 5 mol % Zn(OAc)₂/p-chlorobenzene sulfonic acid – that showed an improvement in PC yield over data reported in the literature. With this benchmark catalyst system in hand, 81 different metal salts and metal salt combinations were screened. This resulted in the discovery of two new catalysts for this reaction, $Zn(OTf)_2$ and $Zn(Tos)_2 \cdot H_2O$, the activities of which were validated in a bench top reactor. The Zn(OTf)₂ system underwent a further bench-top screening, in order to establish the optimal reaction parameters. The Zn(OTf)₂ catalyst has shown an overall PC yield at least twice as large as the best catalyst system hitherto reported in the literature that uses

Journal Name

ARTICLE

MeCN as a water trap. The activity of the new catalyst is still inferior to that obtained with CeO_2 and 2-cyanopyridine.⁶

We are continuing our studies into these new Zn catalyst systems, and variations on the basic $Zn(OTf)_2$ catalyst and investigations into the mechanism of the reaction will be reported in due course.

Acknowledgements

The authors would like to thank the European Union Seventh Framework program (FP7/2007-2013) project "CyclicCO2R", under grant agreement number 309497, for financial support. R. H. H. and E. T. would like to thank Kari Anne Andreassen, Anne Andersen, Aud M. Bougza, Dr. Silje F. Håkonsen and Ruth Elisabeth Stensrød for experimental assistance.

Notes and references

* Note that the amount of MeCN and the reaction time in the parameter screening experiments are less than those for the validation experiments. These differences, in addition to differences in protocol and reactor set-up, are the likely reasons for the slightly poorer overall results in the parameter screening experiments, as compared to those in the validation experiments.

- 1 G. M. Bond, J. Stringer, D. K. Brandvold, F. A. Simsek, M.-G. Medina and G. Egeland, *Energy Fuel*, 2001, **15**, 309-316.
- J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner and C. Gürtler, *Green Chem.* 2014, 16, 1865-1870. A. M. Chapman, C. Keyworth, M. R. Kember, A. J. J. Lennox and C. K. Williams, *ACS Catal.* 2015, 5, 1581-1588.
- 3 For a recent review, see C. Martin, G. Fiorani and A. Kleij, ACS Catal. 2015, 5, 1353-1370.
- 4 The standard Gibbs energy of reaction in the ideal gas state $\Delta^R g^{IG}$ is calculated to be \approx +37 kJ/mol for synthesis of open carbonates such as DMC from CO₂ and 2 equiv of an alcohol. K. Müller, L. Mokrushina and W. Arlt, *Chem. Ing. Tech.*, 2014, **86**, 497-503.
- 5 K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li and K. Kunimori, *Green Chem.* 2004, **6**, 206-214.
- 6 M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa and K. Tomishige, *ACS Catal.* 2014, **4**, 1893-1896.
- 7 M. Honda, M. Tamura, Y. Nakagawa and K. Tomishige, *Catal. Sci. Technol.* 2014, **4**, 2830-2845.
- 8 X. Zhao, N. Sun, S. Wang, F. Li and Y. Wang, *Ind. Eng. Chem. Res.* 2008, **47**, 1365-1369. After 6 h reaction, the yield of PC had increased to 19 %, while the selectivity had decreased to 51 %.
- 9 S. Huang, S. Liu, J. Li, N. Zhao, W. Wei and Y. Sun, J. Fuel Chem. Technol. 2007, **35**, 701-705.
- 10 S. Huang, S. Liu, J. Li, N. Zhao, W. Wei and Y. Sun, *Catal. Lett.* 2006, **112**, 187-191.
- 11 S. Huang, J. Ma, J. Li, N. Zhao, W. Wei and Y. Sun, *Catal. Commun.* 2008, **9**, 276-280.
- 12 S. Huang, S. Liu, J. Li, N. Zhao, W. Wei and Y. Sun, *Catal. Lett.* 2007, **118**, 290-294.
- 13 J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323–3326. M. North and R. Pasquale, *Angew. Chem.*, *Int. Ed.*, 2009, **48**, 2946–2948. J. A. Castro-Osma, M. North and X. Wu, *Chem. Eur. J.*, 2014, **20**, 15005-15008.
- 14 J. R. Ochoa-Gomez, O. Gomez-Jimenez-Aberasturi, B. Maestro-Madurga, A. Pesquera-Rodriguez, C. Ramirez-Lopez, L. Lorenzo-Ibarreta, J. Torrecilla-Soria and M.C. Villaran-

Velasco, *Appl. Catal. A*, 2009, **366**, 315-324. A. Kumar, K. Iwatani, S. Nishimura, A. Takagaki and K Ebitani, *Catal. Today*, 2012, **185**, 241-246.

- 15 M. Fuming, J. Mol. Catal. A: Chem, 2002, 184, 465-468.
- 16 H. Lee, S. J. Kim, B. S. Ahn, W. K. Lee and H. S. Kim, Catal. Today, 2003, 87, 139-144.
- A. Kütt, I. Leito, I. Kaljurand, L. Sooväli, V. M. Vlasov, L. M. Yagupolskii and I. A. Koppel, *J. Org. Chem.* 2006, **71**, 2829-2838. F. Eckert, I. Leito, I. Kaljurand, A. Kütt, A. Klamt and M. Diedenhofen, *J. Comput. Chem.* 2009, **30**, 799-810. The pK_a's for p-CBSA and p-TSA in MeCN are 7.16 and 8.01
- 18 F. M Mei, E. X. Chen and G. X. Li, *Kinet. Catal.* 2009, **50**, 666-670.
- 19 N. A. M Razali, K. T. Lee, S. Bhatia and A. R. Mohamed, *Renew. Sustain. Energy Rev.* 2012, **16**, 4951-4964.