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A Gas-Phase Flow Reactor for Ethylene Carbonate Synthesis from Waste Carbon Dioxide

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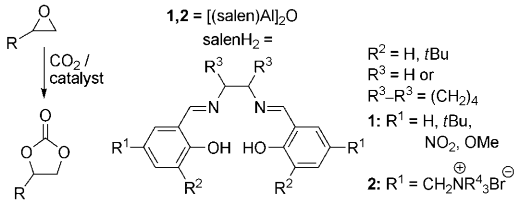
The conversion of carbon dioxide into useful chemicals is attracting increasing interest, both to provide an alternative, sustainable feedstock for the chemicals industry and to help to mitigate global warming.[1] For the latter application, it is essential that processes are developed, which operate at atmospheric pressure and at temperatures at which they can utilise waste heat from other processes to avoid more carbon dioxide being generated than is utilised.[2] One already commercialised reaction of carbon dioxide is its 100% atom economical reaction with epoxides to form cyclic carbonates (Scheme 1, R = H, Me are commercially important). However, current catalysts for this process require the use of high reaction temperatures and high pressures of pure carbon dioxide and reactions are carried out in batch reactors.[1,3]



Scheme 1. Synthesis of cyclic carbonates from epoxides and CO_2.

We have reported the development of bimetallic aluminium(salen) complexes **1**, which when used in conjunction with tetrabutylammonium bromide are capable of catalysing the insertion of carbon dioxide into terminal epoxides at one atmosphere pressure and at ambient temperature.[4] These extremely mild reaction conditions allowed us to carry out the first mechanistic study of this important reaction,[5] which showed that catalyst **1** retained activity even when the carbon dioxide concentration was reduced to less than 5% (the output of a fossil fuel power station is typically 6–13% carbon dioxide) and revealed that a previously unanticipated role for the tetrabutylammonium bromide was to generate tertiary amines in situ. On this basis, a one-component catalyst system **2** was developed and was also shown to be active at atmosphere pressure and at ambient temperature.[6] In this communication we show how the structure of catalysts **2** allows them to be immobilised on inorganic support materials and used to catalyse cyclic carbonate synthesis in a gas-phase flow reactor operating at atmospheric pressure. Previous reports[7] of continuous flow systems for cyclic carbonate synthesis have all relied on solution-phase reactions carried out at high pressures in supercritical carbon dioxide. Thus, our work represents the first demonstration of a system which could be directly attached to the exhaust stream of a fossil fuel power station (or other fixed site carbon dioxide producer) to convert the waste carbon dioxide into a valuable chemical commodity.

A variety of silica based solid supports were investigated[8] and these were coupled to previously reported,[6] bimetallic aluminium(salen) complexes **3a**,**b** to give immobilised complexes **4a**–**d**, which were quaternised by treatment with excess benzyl bromide to give silica supported catalysts **5a**–**d**, as shown in Scheme 2.[9] The loading of catalyst on each support (0.20–1.03 mmol g^{-1}) was determined by ICP-MS analysis of the aluminium content of digested samples.

The catalytic activity of supported complexes **5a**–**d** was first tested in a batch reactor at room temperature for 20 h with styrene oxide as substrate, a carbon dioxide atmosphere (1 atmosphere) and propylene carbonate as solvent, using 2.5 mol% of supported complex. Each complex was found to be catalytically active, giving conversions of styrene oxide to styrene carbonate of 69% (**5a**), 57% (**5b**), 52% (**5c**) and 78% (**5d**).[9] The recyclability of catalyst **5a** was also investigated. Thus, reactions were carried out with neat

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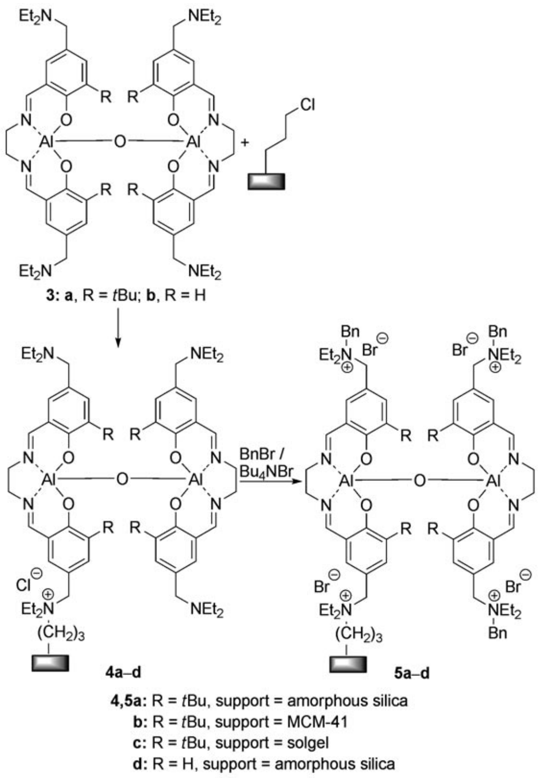

Scheme 2. Synthesis of supported catalysts **5a**–**d**.

propylene oxide as substrate under the above conditions. After a 20 hour reaction time, propylene carbonate and unreacted propylene oxide were distilled from the flask (at 170 °C) and the residue (catalyst **5a**) reused. Figure 1 shows

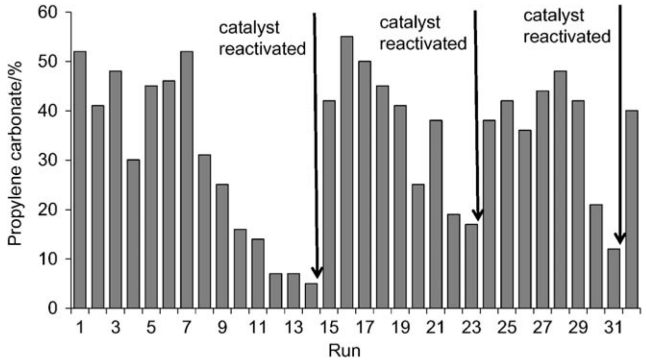

Figure 1. Reuse of supported catalyst **5a**.

the outcome of a series of 32 sequential reactions with the same batch of supported catalyst.[9] The catalyst was found to lose activity over the first 11 reactions. However, this was entirely attributed to the dequaternisation of the quaternary ammonium salts, as we have previously described.[5] Thus, full activity could be restored to the supported catalyst simply by retreating it with benzyl bromide. Similarly, the catalyst was again reactivated after reactions 23 and 31 and in each case this restored full catalytic activity. Hence, the core bimetallic aluminium(salen) unit does not decompose during reaction cycles, even with repeated heating at 170 °C. This indicated that the catalysts would be suitable for prolonged usage in a continuous flow reactor, even if elevated temperatures were required to achieve good conversions, but that occasional reactivation of the catalyst might be required.

The design of a gas-phase flow reactor suitable for use with catalysts **5a**–**d** and ethylene oxide is shown in Figure 2. This was constructed entirely from stainless steel. Commercial cylinders of ethylene oxide (b.p. 11 °C) supply liquid rather than gas. To avoid temperature and pressure control problems associated with vaporising the liquid ethylene oxide, liquid ethylene oxide was placed in a beaker inside a stainless steel pressure vessel fitted with gas inlet and outlet tubes on its upper surface. The pressure vessel was placed in a cryostatically controlled bath, and the combination of bath temperature and gas flow rates were used to ensure that the ethylene oxide evaporated at a constant, known rate. Thus, carbon dioxide and nitrogen were supplied from cylinders via mass-flow controllers into the cylinder containing ethylene oxide. The resulting gas stream was fed into a packed bed reactor (1 cm diameter, 3–15 cm length) containing catalyst **5a**–**d** and placed in a thermostatically controlled water bath (reaction temperatures up to 60 °C) or a thermostatically controlled Kugelrohr oven (reaction temperatures > 60 °C). The outlet from the reactor column was fed first to a receiving vessel to collect ethylene carbonate and then to a GC system fitted with gas sampling valves to allow online monitoring of the system.

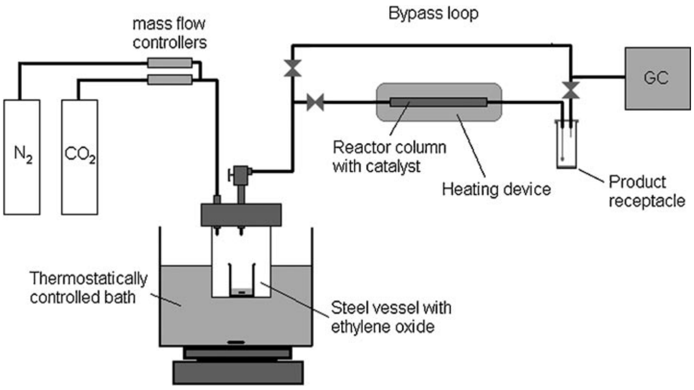

Figure 2. Diagram of the gas-phase continuous flow reactor.

Initial reactions were carried out by using a gas stream composed of 21 % carbon dioxide (total flow rate 4.7 mL min^{-1}) and a reactor length of 15 cm filled with catalyst **5a** (Table 1). Under these conditions at 20 °C, only a low rate of synthesis of ethylene carbonate was observed and only 6 % of the carbon dioxide was removed from the gas stream (entry 1). However, on warming the reactor the rate of reaction increased significantly until at 60 °C virtually all of the carbon dioxide had been converted into ethylene carbonate (entries 2 and 3). To further increase the TOF,

Table 1. Synthesis of ethylene carbonate in the flow reactor.[a]

Entry	Catalyst **5a–d** [g]	Reactor T [°C]	Reaction t [h]	CO_2 reacted [%][b]	TOF [h^{-1}]
1	**5a** (2.17)[c]	20	120	6	0.15
2	**5a** (2.17)[c]	50	19	82	2.2
3	**5a** (2.17)[c]	60	7	97	2.6
4	**5a** (0.43)[d]	150	6	57	7.6
5	**5b** (1.57)[c]	60	7	95	8.3
6	**5b** (0.32)[d]	60	6	23	8.9
7	**5b** (0.32)[d]	100	6	54	21
8	**5b** (0.32)[d]	150	6	66	26
9	**5c** (1.94)[c]	60	7	97	5.2
10	**5d** (2.17)[c]	60	7	98	1.1

[a] In each case the evaporation rate of ethylene oxide was 0.15 mLh^{-1}, and the flow rates of CO_2 and N_2 were 1.0 mLmin^{-1} and 2.5 mLmin^{-1} so the initial composition of the gas stream was 21% CO_2, 25% ethylene oxide and 54% N_2. [b] Based on mass of purified ethylene carbonate produced. [c] reactor length 15 cm. [d] reactor length 3 cm.

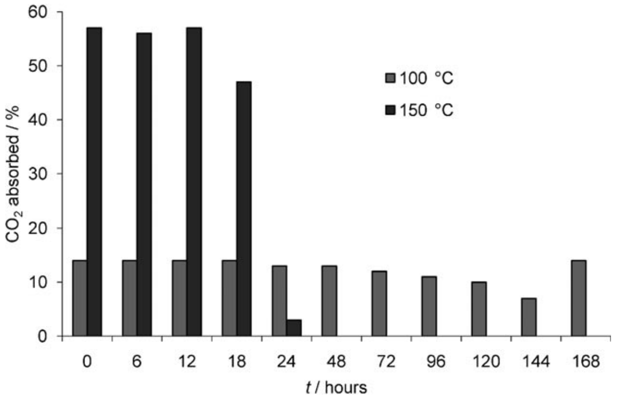

Figure 3. Lifetimes of catalyst **5a** in the continuous flow reactor. The catalyst was reactivated before the start of the final 100 °C reaction.

the column length was reduced to 3 cm and the reaction temperature raised to 150 °C. Under these conditions, 57% of the carbon dioxide was converted into cyclic carbonate corresponding to a TOF of 7.6 h^{-1} (entry 4). The reactions corresponding to entries (1–3) were completed by using the same batch of catalyst without any reactivation between experiments. This catalyst was then used in repeated experiments at 60 °C until catalyst deactivation was observed. The catalyst was then reactivated by treatment with benzyl bromide and used for the experiment at 150 °C (entry 4).

A similar trend in results was observed for catalyst **5b**, though the intrinsic reactivity of this catalyst appears to be about four times higher than that of catalyst **5a** (entries 5-8). Thus at 60 °C in a 15 cm reactor, essentially all of the carbon dioxide reacted, giving a TOF of 8.3 h^{-1} (entry 5). Reducing the reactor length to 3 cm resulted in only 23% of the carbon dioxide reacting, but the TOF remained essentially unchanged as expected (entry 6). Raising the reaction temperature further to 100 and 150 °C resulted in up to 66% of the carbon dioxide reacting even in the short path-length reactor, and corresponded to a TOF of up to 26 h^{-1} (entries 7 and 8). Sol–gel supported catalyst **5c** appeared to have intermediate activity to catalysts **5a** and **5b** (compare entries 3, 5 and 9), whereas catalyst **5d** displayed lower intrinsic activity (entry 10). All of the reactions in Table 1 produced ethylene carbonate as the only isolated product. In particular, no evidence for formation of poly(ethylene carbonate) or ethylene glycol was detected in any of the experiments.

Catalyst lifetime was investigated under continuous flow conditions using catalyst **5a** in the 3 cm reactor and results are shown in Figure 3. At 150 °C, the catalyst was found to give consistent results for just the first 18 h of operation. After this time, the % CO_2 absorbed decreased to zero over the next 18 h and the purity of the ethylene carbonate produced also decreased dramatically from 100 to just 5% as determined by both ^{1}H NMR spectroscopy and GCMS. After 36 h, the catalyst could not be reactivated by treatment with benzyl bromide, was found to have turned white (all of catalysts **5** are yellow when initially prepared) and ICPMS indicated that no aluminium was present. This indicated that prolonged heating of the catalyst to 150 °C resulted in cleavage of the salen units from the silica support.

At 100 °C however, far more promising results were obtained. The catalyst was used continuously over a period of seven days and the amount of ethylene carbonate formed was monitored every 24 h. Even after seven days, the catalyst still retained 50% of its original activity as shown in Figure 3. Furthermore, after this time the catalyst could be reactivated by treatment with benzyl bromide and restored to its original activity, indicating that the loss of catalyst activity was due to loss of quaternary ammonium groups and not to cleavage of aluminium(salen) units from the silica support. This was confirmed by ICPMS analysis of catalyst samples before and after the seven days of reaction, which showed that there has been no loss of aluminium from the supported catalyst. Finally, a series of experiments were carried out to mimic various modes of power station operation. Thus, a batch of catalyst was first subjected to a series of six reactions in which cyclic carbonate synthesis was carried out for six hours a day and the reactor allowed to cool and stand unused for 18 h between each reaction, to mimic its use with a "peak demand" power station. Subsequently, the same batch of catalyst was operated 24 h a day for eight days to mimic operation in a "base load" power station. During this sequence, the catalyst activity dropped to one eighth of its original value, but complete activity could be restored by reactivating the catalyst, and ICPMS again showed no decrease in the amount of aluminium attached to the silica support.[9]

The formation of ethylene carbonate from ethylene oxide and carbon dioxide is a highly exothermic process ($\Delta H_r = -140$ kJmol^{-1}).[10] Therefore, a scaled up version of this flow reactor could easily reach temperatures > 150 °C even if no waste heat was available locally. Scaling up a flow reactor operating under the conditions of Table 1: entry 8, suggests that a column packed with 50 tonnes of catalyst would be sufficient to totally remove 92,000 tonnes of carbon dioxide per annum from the exhaust gases of a fossil-fuel power station or other fixed site carbon dioxide producer. This would produce 184,000 tonnes per annum of ethylene carbonate which is sufficient to meet the current demand for cyclic carbonates and products derived from them,[1e,11] though there is a projected demand of over 30 Mtonnes per annum[1c,12] if the cost of production of cyclic carbonates can be reduced from the current level. For commercial applications, it is also notable that the experiments reported in Table 1 were carried out at an initial concentration of carbon dioxide of 20 %, which compares favourably with the 6–13 % carbon dioxide present in the exhaust gases from a fossil-fuel power station, whilst chemical plants produce waste carbon dioxide of much higher purity. In addition, catalysts **1**, **2** and **5** are unaffected by water and reactions using these catalysts can be carried out using wet cardice pellets as the carbon dioxide source.

In summary, we have developed silica immobilised catalysts **5a–d** for the synthesis of cyclic carbonates from epoxides and waste carbon dioxide. When incorporated into a gas-phase flow reactor, the catalysts could convert up to 98 % of the carbon dioxide flowing through the reactor into ethylene carbonate. Since ethylene oxide is manufactured globally on a >13 Mtonnes per annum scale,[13] the technology has the capability to be scaled up to remove a significant percentage of the carbon dioxide generated by a fossil fuel power station or other major fixed-site carbon dioxide producer.

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Keywords: aluminum · carbon dioxide fixation · heterogeneous catalysis · oxygen heterocycles · Schiff base

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