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Sustainable metal–based catalysts for the synthesis of cyclic carbonates containing five–membered rings

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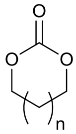
The use of sustainable metal–based catalysts for the synthesis of five–membered ring containing cyclic carbonates from epoxides and carbon dioxide is critically reviewed. Coverage is restricted to catalysis by the abundant metals: sodium, potassium, aluminium, calcium, titanium and iron and the relative merits and limitations of each catalyst system are compared.

1. Introduction

Cyclic carbonates have general structure **1** and the most important cyclic carbonates[1] contain a five–membered ring (**2**). Compounds **2** have many applications including as polar aprotic solvents[1,2] capable of replacing traditional solvents such as DMF, DMSO, NMP and acetonitrile which are likely to be banned under the European REACH regulations and which generate NO_x or SO_x when incinerated. Cyclic and acyclic carbonate mixtures are also used as the electrolytes in lithium–ion batteries[3] which power a profusion of portable electronic devices and are increasingly used in electric vehicles. Cyclic carbonates are also intermediates in the synthesis of other small molecules[4] and polymers.[5] They are also found in natural products[6] and potential pharmaceuticals.[7]



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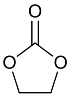

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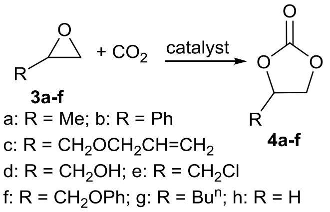
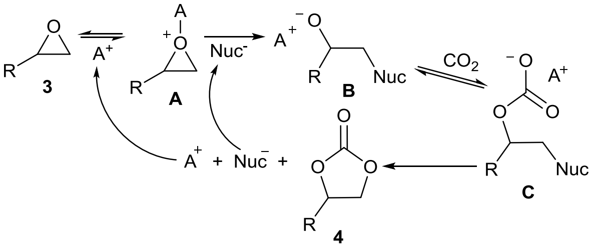
Five–membered ring containing cyclic carbonates can be prepared from either the corresponding 1,2–diols[8] or epoxides[9] and a one–carbon source. For synthesis from diols, phosgene and its oligomers can be used as the one–carbon source,[10] but greener alternatives such as urea, dimethyl carbonate or carbon dioxide are now available.[8] However, at present the most important and commercial[11] route to cyclic carbonates is the 100% atom–economical reaction between an epoxide **3** and carbon dioxide shown in Scheme 1. This reaction is one of the few currently known, commercially important reactions which uses carbon dioxide as a chemical feedstock. The use of (waste) carbon dioxide and (waste) biomass as chemical feedstocks has the potential to provide a sustainable basis for a future chemicals industry. However, for any reaction involving carbon dioxide, the thermodynamics of the process are of critical importance since if a large energy input is required, then this will generate more carbon dioxide than is consumed by the reaction unless the reaction can be linked to renewable or nuclear power. This reaction does not occur spontaneously even though it is highly exothermic as the uncatalysed reaction is calculated to have a rather high activation energy (ca 50–60 kcal mol^{-1} depending on the epoxide and calculation method).[12] A vast range of metal–based and metal–free catalyst systems have been developed for the synthesis of five–membered ring containing cyclic carbonates and DFT calculations indicate that the catalyst generally lowers the activation energy to 25-35 kcal mol^{-1}.[12]



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

There is a general mechanism (Scheme 2) for the synthesis of cyclic carbonates from epoxides whichever catalyst is used, though there are also variations on this general mechanism. Thus, the catalyst will optionally provide a Lewis– or Brønsted–acid to activate the epoxide. The catalyst then always provides a good nucleophile to ring–open the (activated) epoxide (**A**), forming an alkoxide (**B**) which reacts with carbon dioxide to form a carbonate (**C**). The nucleophile provided by the catalyst must also be a good leaving group as in the final step of the mechanism this is displaced intramolecularly by the carbonate to form the five–membered ring and regenerate the catalyst. Halides (especially bromide and iodide) make both good nucleophiles and good leaving groups and many catalyst systems developed for the conversion of epoxides **3** into cyclic carbonates **4** contain a halide as part of their structure. Indeed, commercial processes use tetraalkylammonium or phosphonium halides as catalysts.[11] These have the advantage of relative low cost and simplicity, but lack any acid component to activate the epoxide and as a result require the use of elevated temperatures and pressures. Therefore, many two–component catalyst systems have been developed in which a

Lewis– or Brønsted–acid is combined with a group–five halide salt to allow cyclic carbonate synthesis to occur under milder conditions. However, the halide does not have to be part of a group–five salt, and many simple metal halides are also known to form effective one–component catalysts. Catalyst systems are also known in which the nucleophile / leaving group is not a halide, for example 4–dimethylaminopyridine can perform this role in some catalyst systems.[9]



Scheme 2. General mechanism for cyclic carbonate synthesis.

The use of metal–free systems (and particularly the use of ionic liquids as catalysts) for the synthesis of cyclic carbonates **2** has been extensively reviewed recently[13] and so will not be covered in this critical review. Rather, the emphasis here will be on metal–based systems which, due to the presence of a good Lewis–acid within the catalyst, tend to have higher intrinsic catalytic activity. Current commercial catalysts for cyclic carbonate synthesis are based on non-metallic, quaternary ammonium or phosphonium salts.[9] There is however, extensive research into the use of metal based systems as these would allow the synthesis of cyclic carbonates to be carried out at lower temperatures and / or at higher substrate to catalyst ratios than current commercial processes, thus reducing the carbon footprint of cyclic carbonate synthesis. Throughout this review, when discussing two–component catalyst systems, the metal–based component will be described as the catalyst and the non–metallic component as a co–catalyst. However, some papers in the literature use the opposite convention. In general, the co–catalyst does not interact directly with the catalyst (e.g. modifying its coordination sphere), but rather both catalyst components interact with the epoxide, behaving as a bifunctional catalyst system.

It has recently been recognised that global supplies of many of the most useful metal ores are being exhausted and this, combined with supplies of some metals being restricted to a small number of geographical areas and low recycling rates for many metals has led to a compilation of ‘endangered elements’.[14] Whilst no such analysis can ever be 100% accurate and will change with time as new mineral seams are discovered and uses for elements change (increased or decreased demand), it nevertheless provides a useful guide to chemists seeking to carry out sustainable synthesis. Figure 1 shows a pictorial representation[15] of endangered elements within the periodic table. Only six metals are classified as abundant: the alkali metals sodium and potassium; the alkali Earth metal calcium; the group three metal aluminium and the first–row transition metals titanium and iron. Aluminium, iron, calcium, sodium and potassium are respectively the first to fifth most abundant metals in the Earth’s crust with titanium being the ninth most abundant. Iron, sodium and aluminium are also the three most produced metals and all six of these metals are widely distributed. Thus, they are the optimal metals to consider for the development of catalysts for the large scale production of cyclic carbonates. Salts and / or complexes or all of these metals are known to form catalysts for cyclic carbonate synthesis, and this review will concentrate exclusively on the use of sustainable catalysts based on these six metals.

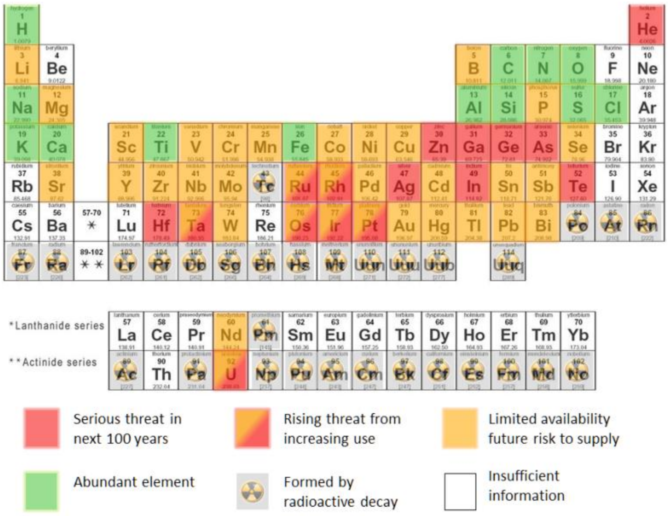


Figure 1. Pictorial representation of elemental sustainability.

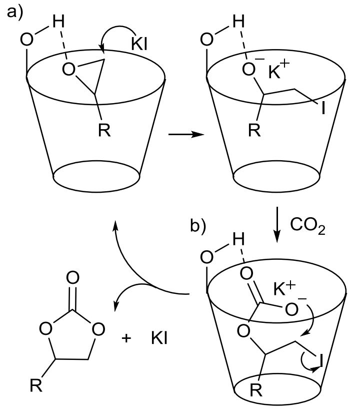
2. Alkali metals (sodium and potassium)

There is a significant quantity of literature associated with the use of alkali metal salts as catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide. However, this review will not discuss the use of lithium[16] due to its sustainability issues and will instead focus on sodium and potassium salts. By far, the dominant amongst these is the use of potassium iodide and as such, this will be discussed first.

2.1 Potassium Iodide

2.1.1 Potassium iodide with hydroxyl functionalised co–catalysts. The literature shows that potassium iodide has limited activity when used alone in cyclic carbonate synthesis. Due to this, the large majority of papers published in this field focus on development and application of co–catalysts to enhance conversions. Han et al[17] demonstrated how hydroxyl containing *β*–cyclodextrin has a dramatic effect when used as a co–catalyst with potassium iodide, building upon previously reported crown–ether work.[18] Conversion of propylene oxide **3a** into propylene carbonate **4a** increased from 27% using 2.5 mol% potassium iodide to 98% using 2.5 mol% potassium iodide and 8 wt% *β*–cyclodextrin after 4 hours at 120 °C with 60 bar pressure of carbon dioxide. Increased temperature, pressure and reaction times were not beneficial. Potassium chloride and bromide salts only gave conversions of 0% and 3%, increasing to 4% and 48% when the salts were used in combination with the *β*–cyclodextrin co–catalyst. It should be noted that poor performance from the chloride and bromide salts in comparison with the iodide salt is seen frequently in the literature. This is attributed to the increased ability of iodide to act as a leaving group.[17] A 94% conversion of styrene oxide **3b** to styrene carbonate **4b** was achieved using potassium iodide with *β*–cyclodextrin as co–catalyst, albeit after an extended reaction time of 12 hours, the need for which was attributed to the steric effect of the phenyl group. It is suggested that the enhanced activity observed when using *β*–cyclodextrin is due to hydrogen bond donating hydroxyls on the cyclic oligosaccharide being able to both activate the epoxide (Scheme 3a) and stabilise the alkylcarbonate anion (Scheme 3b).

Similarly, Han[19] found that cellulose enhanced potassium iodide's catalytic activity. Studies were limited to the synthesis of **4a** from **3a** and a conversion of 99% was achieved in 2 hours at 110 °C and 20 bar pressure of carbon dioxide using 2 mol% of potassium iodide and 66wt% of cellulose. Although an increased quantity of cellulose is used relative to *β*–cyclodextrin, it is an abundant, renewable material[20] that offers high yields in a shorter reaction time and under comparatively mild conditions. Subsequently, a number of small primary and secondary diol containing species were investigated as co–catalysts, the best being cyclohexane–1,2–diol, propylene glycol and ethylene glycol, which gave conversions of 96%, 96% and 92% respectively for the conversion of **3a** into **4a**. Conversions were reduced when using mono alcohols such as methanol (56%) and ethanol (48%). Comparable work has been reported by Hou et al[21] on the use of pentaerythritol. A 17wt% quantity of premixed (1:2.5) potassium iodide / pentaerythritol catalyst gave a conversion of 95% for both **3a** to **4a** and **3b** to **4b** after 2 and 4 hours respectively. The conditions employed were similar to the previously reported syntheses and used 25 bar pressure of carbon dioxide and a 130 °C reaction temperature.



Scheme 3. Han's suggested reaction mechanism.

Lignin was investigated as a co–catalyst with the aim of identifying the influence of surface hydroxyl concentrations on conversions. Interestingly, Liu et al [22] demonstrated that although an excess of potassium iodide relative to hydroxyl species was necessary to achieve high yields, varying the ratio of potassium iodide to co–catalyst did not have a substantial effect. The optimum molar ratio of potassium iodide to lignin–OH was found to be 3:1, giving an isolated yield of **4a** of 92% after 12 hours at 140 °C and 10 bar pressure of carbon dioxide. The yield only reduced to 87% when a 1:1 ratio was used. Consistent with previous work, the corresponding potassium chloride and bromide salts were poor in comparison, achieving yields of only 13% and 36% respectively. Synthesis of styrene carbonate **4b** using the potassium iodide / lignin–OH system gave an isolated yield of 87% after 12 hours using the optimum conditions. It should be noted that the sustainable nature and low cost of cellulose and lignin co–catalysts, offers both economic and environmental benefits, making these syntheses particularly attractive in spite of the relatively large quantity of catalyst required for high conversions.

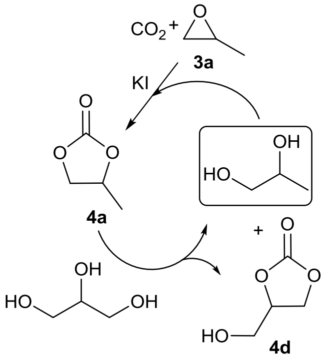
Yuan et al [23] showed that inorganic hydroxyl containing species can also act as effective co–catalysts. Magnesium hydroxyl chloride gave a **4a** yield of 98% after 4 hours using 30 wt% of magnesium hydroxyl chloride / potassium iodide as catalyst (1:2 ratio) and 60 bar pressure of carbon dioxide at 130 °C. The yield reduced to 87% after five reuses of the catalyst. The conversion of **3b** to **4b** was found to be 76% using the same conditions. Variation in catalyst to co–catalyst ratios and temperature did not improve the catalyst activity. Magnesium hydroxyl iodide was investigated using the conditions described above and gave a good conversion of 96% of **3a** to **4a** using 30 wt% of catalyst, though this was not investigated further. Although reasonably good conversions were obtained using this system, the future risk to supply and limited availability of magnesium[24] makes this synthesis potentially unsustainable.

Park et al [25] employed microwave chemistry as a green technology for the synthesis of cyclic carbonates using potassium iodide with formic acid as a co–catalyst to achieve high conversions in very short reaction times. A conversion of 60% of **3a** to **4a** was achieved in only 15 minutes using 200 Watts power in a microwave reactor, 1.6 mol% of potassium iodide, 14.5 mol% of formic acid and 9.6 bar pressure of carbon dioxide. Conversion of **3b** to **4b** was 82% using the same conditions. The high activity of the microwave system is thought to relate to the effective polarisation of the catalyst when irradiated with microwaves. Increasing the microwave power above 200 Watts slightly reduced conversions, possibly due to a reduction of carbon dioxide solubility in the reaction mixture. As a comparison, conventional heating was used, giving 87% conversion in 3 hours using 1.6 mol% of potassium iodide, 14.5 mol% of formic acid and 9.6 bar pressure of carbon dioxide at 120 °C. Using co–catalysts with long chain lengths, such as acetic and propionic acid reduced conversions, which is thought to be due to increased steric effects and hydrogen bonding between acids. The Park microwave synthesis offers significant energy savings along with the use of a low hazard, simple and green co–catalyst available in large quantities. Interestingly, water was found to be an effective co–catalyst for potassium iodide catalysed cyclic carbonate synthesis, giving 83% conversion of allyl glycidol **3c** to allyl glycidyl carbonate **4c** as opposed to a 94% conversion when using formic acid under the same microwave reaction conditions described above; a thermal reaction comparison was not performed in this case. This supports similar observations seen by Sun et al[26] where 0.5 mol% of potassium iodide, 33.5 mol% of water and 20 bar pressure of carbon dioxide at 125 °C using conventional heating, gave a 78% conversion of **3a** to **4a** in 1 hour; a 60% conversion was achieved with potassium bromide.

Han et al[27] reported that metal organic frameworks (MOFs) gave high conversions to cyclic carbonates when used as a co–catalyst. MOF–5 was investigated (comprised of $Zn_4O(BDC)_3$, where BDC is benzene–1,4–dicarboxylate). A conversion of 98% of **3a** to **4a** was obtained after 2 hours using 2.5 mol% potassium iodide, 0.1 grams of MOF–5 and 60 bar pressure of carbon dioxide at 90 °C. No conversion was observed when using either the potassium iodide or MOF–5 alone. A 95% conversion of **3b** to **4b** was obtained in 7 hours using the same conditions. Use of zinc oxide as a co–catalyst with potassium iodide gave a poor 5% conversion of **3a** to **4a**. Use of potassium bromide and potassium chloride with a MOF–5 co–catalyst gave significantly lower conversion of **3a** to **4a**, 1.2% and 0.2% respectively. Despite promising conversions, the

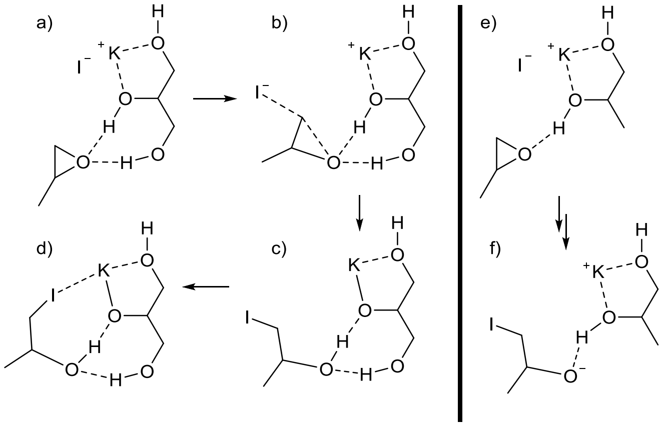
MOF–5 co–catalyst suffers from the same drawbacks as the magnesium hydroxyl halide systems where the supply of zinc may be under serious threat within the next 100 years.[24]

2.1.2 Potassium iodide and propylene oxide **3a** coupling agent. Han et al[28] discussed an interesting scenario, (albeit with quite a limited application), whereby a propylene glycol by–product and glycerol starting material both co–catalysed the cycloaddition of carbon dioxide to propylene oxide **3a** using potassium iodide as the catalyst. This was followed by trans–esterification of glycerol and propylene carbonate **4a** in an attempt to avoid the thermodynamic limitations of the direct synthesis of glycerol carbonate **4d** from glycerol (Scheme 4).



Scheme 4. Use of propylene glycol by–product as diol co–catalyst

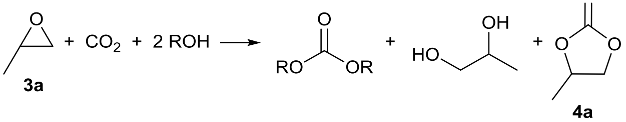
Glycerol was converted into glycerol carbonate **4d** (77% GC conversion), with 98% of **3a** being converted into 39% propylene glycol and 59% **4a** after 1.5 hours. Reaction conditions were 115 ^{o}C, 20 bar carbon dioxide pressure using 0.75 mol% of potassium iodide relative to **3a**. Similar to previous reports, potassium chloride and bromide salts were found to give reduced conversions from propylene oxide **3a** of 13% and 62% respectively. However, sodium iodide gave an excellent yield of 58% **4a** and 70% **4d** under the same conditions. Subsequently, Han et al[29] used density functional theory (DFT) modelling to explore how 1,2–diols affected potassium iodide activity. Fundamentally, the reaction system is reliant upon the synergistic effect of the K^+ and I^- ions, whereby the iodide anion is able to ring–open the epoxide, whilst the potassium cation stabilises the resulting anionic species and enhances the iodide's ability to leave the alkylcarbonate. In essence, the model suggests that when glycerol is introduced into the system, the hydroxyl groups coordinate with both the potassium cation and **3a**, (Scheme 5a). This may be followed by simultaneous protonation of the epoxide followed by ring–opening by the iodide (Scheme 5b), leading to formation of a potassium alkoxide intermediate (Scheme 5c). Stabilisation of the intermediates by the hydroxyl groups, along with electrostatic attraction from the potassium ion (Scheme 5d) increasing the leaving group ability of the iodide, is thought to lower reaction energy barriers from 36–41kcal mol^{-1} when using potassium iodide catalyst alone, to 29 kcal mol^{-1} when using a hydroxyl containing co–catalyst. Similarly, propylene glycol is able to hydrogen bond to potassium iodide and the epoxide, though without the additional hydroxyl group, it is less able to stabilise the transition state compared with glycerol, resulting in higher energy barriers, (Scheme 5e–f).



Scheme 5. Suggested intermolecular interactions between KI, **3a** and glycerol.

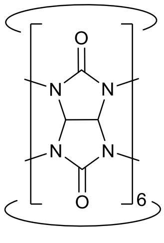
2.1.3 Potassium iodide with macromolecular and polymer based co–catalyst. Early work by Kuran et al[30] showed that 18–crown–6 exhibits good conversions as a co–catalyst with potassium iodide under relatively mild conditions. A 90% conversion of **3a** to **4a** was achieved using 0.67 mol% potassium iodide and 0.2 mol% 18–crown–6 at 120 ^{o}C and 40 bar carbon dioxide pressure after 4 hours with conversion of **3b** to **4b** being 68% under the same conditions. Other co–catalysts were investigated using the synthesis of 4–(chloromethyl)–1,3–dioxolan–2–one **4e** from 3–chloropropylene oxide **3e** as a test reaction. It was found that 15–crown–5, 18–crown–6, dibenzo–18–crown–6 along with benzyltriethylammonium chloride, 1,4–diazabicyclo[2.2.2]octane and tetramethylethylenediamine had high activities, giving conversions of over 90% within 24 hours; use of amine based co–catalysts will be discussed further in section 2.1.4.

Zhu et al[31] reported the use of polyethylene glycol (PEG) as an effective co–catalyst, giving a 100% conversion of **3a** to **4a** using 1 mol% of PEG (M_n 400) and 0.33 mol% of potassium iodide at 20 bar carbon dioxide pressure and 150 ^{o}C after 5 hours, with a 91% conversion achieved after 2.5 hours. A reduction in temperature to 100 ^{o}C caused the conversion to drop to 75% after 5 hours. It was found that upon increasing the molecular weight of the PEG the conversion to propylene carbonate **4a** decreased to 93% using 600 M_n PEG and 86% using 1000 M_n PEG (similar findings were reported by Kuran[30]). To add further value to this synthesis, aliphatic alcohols and NaOMe were introduced into the reaction in an attempt to transesterify propylene carbonate to form dialkyl carbonates in situ (Scheme 6). The simple synthesis of PEG from ethylene glycol suggests that this method will have economic benefits over the use of macromolecular ether based co–catalysts, although its substrate scope requires a more detailed study to support such a conclusion.



Scheme 6. Synthesis of **4a** with in situ transesterification to dialkyl carbonates.

More recently, use of macrocyclic cucurbit[6]uril[32] **5** as a co–catalyst has been shown to give a conversion of 98% of **3a** to **4a** using 1.5 mol% of potassium iodide and 0.5 mol% of **5** at 120 ^{o}C and 40 bar carbon dioxide pressure after 2 hours; in comparison, potassium chloride / **5** gave 7% and potassium bromide / **5** gave a 31% conversion under the same conditions. A conversion of 95% of **3b** to **4b** was achieved in 5 hours under the same conditions. The conversion of **3a** to **4a** increased with increasing temperature and reaction time, reaching a plateau at 120 °C and 2 hours. Carbon dioxide pressures above and below 40 bar were found to have a negative impact upon the conversion which is thought to be due to the low carbon dioxide concentration at low pressures and the low **3a** concentration at high pressures. Reusability of the potassium iodide / **5** catalyst was found to be excellent as the reduction in activity was negligible, even after five reuses. It is thought that the protruding carbonyls of **5** are able to coordinate with potassium cations, encouraging nucleophilic attack from the iodide to ring–open the epoxide. Therefore, acetylacetone **6** and polyvinylpyrrolidone **7** were investigated as co–catalysts in an attempt to support this mechanistic theory. Both gave a conversion of 98% of **3a** to **4a** under the same reaction conditions used with co–catalyst **5**.



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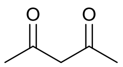

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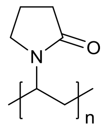

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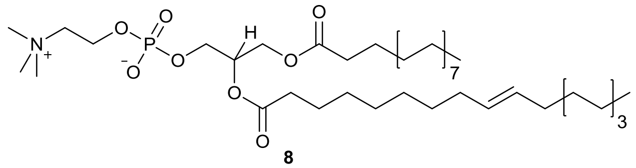
2.1.4 Potassium iodide with amine/ammonium salt co–catalyst.

Kuran's[30] early work showed that simple amines and amine salts are able to catalyse the cycloaddition of carbon dioxide to epichlorohydrin **3e**. Conversion to carbonate **4e** using 1,4–diazabicyclo[2.2.2]octane was found to be 95% after 24 hours, using 0.66 mol% of potassium iodide and 0.5 mol% of 1,4–diazabicyclo[2.2.2]octane at 40 bar carbon dioxide pressure at 120 °C. Conversions of 92% and 91% were achieved using 0.94 mol% of tetramethylethylenediamine and 0.49 mol% of benzyltriethylammonium chloride respectively under the same conditions. Similar observations were made by Ramidi et al, who found that 0.1 mol% of 4–dimethylaminopyridine along with 0.1 mol% of potassium iodide gave 73% conversion of **3a** to **4a** after 3 hours at 20 bar pressure of carbon dioxide and a reaction temperature of 130 °C.[33] When using potassium chloride and bromide salts, the conversions reduced to 62% and 69% respectively. It is thought that DMAP is able to activate carbon dioxide via a carbamate intermediate, allowing it to be attacked by the alkoxide intermediate. The highest conversion (91%) was actually observed when using lithium bromide rather than potassium iodide, whilst the lowest conversions were found when using triethylamine (32%), pyridine (25%), NMP (14%), *N,N*–diethylaniline (0.4%), tripropylamine (0.4%) and benzylidenemalononitrile (0.4%) with lithium chloride. The use of these amines with potassium salts was not reported.

Han et al[34] found lecithin **8** to be an effective co–catalyst, giving a conversion of 98% of **3a** to **4a** after 4 hours using 1.25 mol% of potassium iodide and 1.25 mol% of **8** at 20 bar carbon dioxide pressure and a reaction temperature of 100 °C. Conversion of **3b** to **4b** was found to be 94% after 6 hours using the same conditions. Carbon dioxide pressures below 20 bar and above 60 bar were found to have a negative impact upon conversions, whilst increased reaction time and temperature had a positive effect, supporting observations discussed previously. The optimal ratio of potassium iodide to **8** was reported to be 1:1; a reduced ratio of **8** gave lower conversions, but higher ratios of **8** were not investigated. The ability of **8** to form quaternary ammonium iodide **9**, thus increasing the nucleophilicity of the iodide, is thought to be the reason for the co–catalysts effectiveness. Simpler zwitterionic betaine **10** was also investigated as a co–catalyst and gave comparatively poor conversion (12%) of **3a** to **4a**. It was suggested that this may be due to poor solubility of **10** in the reaction mixture, whereas the large diglyceride chains found in **8** avoid such issues. There was no discussion of the relative importance of the phosphate group versus the carboxylate group in co–catalysts **8** and **10**.



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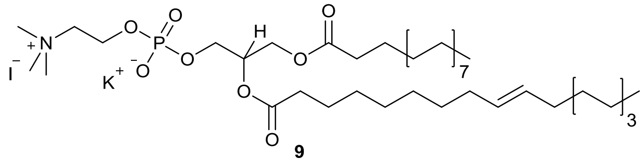

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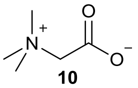

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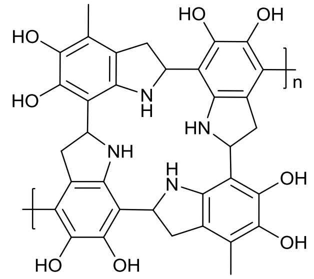
Yang et al[35] recently reported that polydopamine **11** has good activity as a co–catalyst in the conversion of **3a** into **4a**, giving 53% conversion using only 0.6 mol% of potassium iodide and 0.6 mol% of **11** at 120 °C and 20 bar pressure of carbon dioxide after 1 hour. Varying the ratio of **11** to potassium iodide gave lower conversions. High temperatures had a significant effect, increasing conversions after 1 hour to 91% at 130 °C and 96% at 140 °C. Despite this exceptional activity for propylene carbonate synthesis, conversion of **3b** to **4b** was relatively poor in comparison to cucurbit[6]uril **5**, being only 35% after 5 hours at 120 °C. (It should be noted however, that this system used half the carbon dioxide pressure used with co–catalyst **5**, so it is not directly comparable). Disubstituted epoxides such as 1,1–dimethyl–oxirane also gave poor conversions (30% after 10 hours). Mechanistically, Yang suggests that polydopamine has a dual function, activation of the epoxide through its hydroxyl groups and adsorption of carbon dioxide onto the amine to form a carbamate, (Scheme 7). The activity of the catalyst remained constant, even after being reused six times.

Similarly, Xiao et al[36] showed that triethanolamine had high activity as a co–catalyst. A 91% conversion of **3a** to **4a** was achieved in 1 hour using 1 mol% of potassium iodide, 1 mol% of triethanolamine and 20 bar pressure of carbon dioxide at 110 °C; conversion of **3b** to **4b** was found to be 96% in 6 hours. When using 2.8 mol% (8 wt%) of catalyst / co–catalyst in a 1:1 ratio the conversion to **4a** increased to 99%. These conversions are high considering the relatively mild reaction conditions and short reaction time. An increase in temperature, reaction time and catalyst quantity gave higher conversions, whereas molar ratios of triethanolamine to potassium iodide above 1:1 and pressures above 20 bar had a negative impact. Reduction in activity after reuse was negligible. Use of analogous co–catalysts such as ethanolamine (54%), diethanolamine (70%), triethylamine (25%) and ethanol (5%) gave reduced conversions of **3a** to **4a**, as did the use of potassium chloride with triethanolamine (2%) or potassium bromide without co–catalyst (5%). Similarly to the polydopamine system, the catalytic activity of triethanolamine is thought to be due to its ability to activate carbon dioxide by formation of a carbamate salt, whilst the hydroxyl groups promote ring–opening of the epoxide. Analogous work was reported by Werner[37], where an isolated yield of 98% of **3a** to **4a** was achieved in 2 hours using 2 mol% of potassium iodide, 2 mol% of triethanolamine and 10 bar pressure of carbon dioxide at 90 °C. A yield of 69% of **4b** from **4a** was obtained using the same conditions. Similar to Xiao's findings, the use of ethanolamine and diethanolamine gave reduced conversions.



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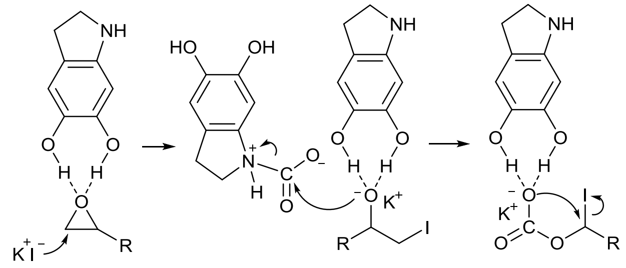
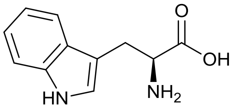


Scheme 7. Yang's suggested method of activation for epoxide and CO_2

More recently, Yang et al[38] demonstrated the effectiveness of amino acids as multi–functional co–catalysts. A 99% conversion of **3a** to **4a** was achieved in 1 hour using 1 mol% (*S*)–tryptophan (**12**) co–catalyst, 1 mol% potassium iodide and 20 bar pressure of carbon dioxide at 120 °C. After five reuses conversion only decreased to 96%. However, the conversion of **3b** to **4b** was only 22% after 2 hours. The catalytic activity of (*S*)–tryptophan is again thought to be due to the ability of its amine to form a carbamate salt with carbon dioxide and of its acid to accelerate epoxide ring–opening. This theory is supported by the observation of a reduced conversion (74%) of **3a** to **4a** when using 3–indolepropionic acid as co–catalyst and an even lower conversion when using indole (58%) and 1–methylindole (24%) as co–catalysts.

In a subsequent study, Park et al[39] showed the importance of the amine functionality with amino acid co–catalysts. Out of a wide range of (*S*)–amino acids screened it was found that (*S*)–histidine **13** gave the highest conversions (99%) for **3a** to **4a** after 3 hours using 0.2 mol% of potassium iodide, 0.2 mol% of **13** and 10 bar pressure of carbon dioxide at 120 °C. Conversion of **3b** to **4b** was 97% under the same conditions. A 1:1 ratio of potassium iodide to histidine was found to give the highest activity. Other amine functionalised (basic) amino acids such as (*S*)–arginine **14** and (*S*)–lysine **15** gave conversions of **3a** to **4a** of 75% and 82% respectively. Neutral amino acids with hydroxyl functionalised side–chains such as (*S*)–serine **15** and (*S*)–threonine **16** gave lower conversions of 51% and 57% for **4a** synthesis from **3a**.



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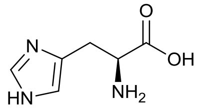

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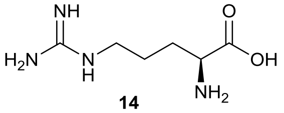

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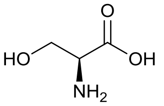

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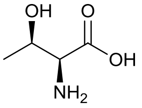

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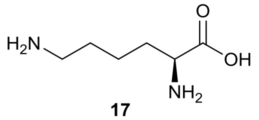

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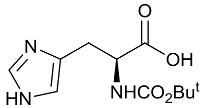

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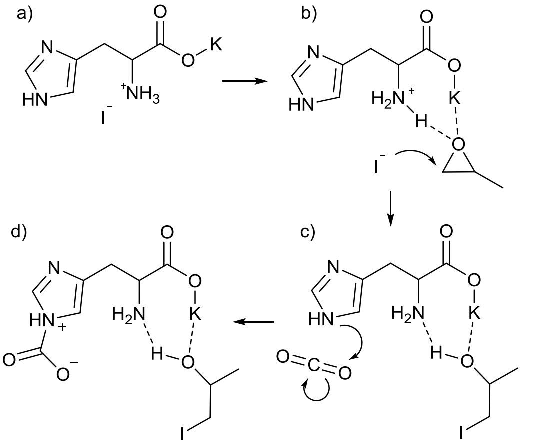
Tert–butyloxycarbonyl protected histidine **17** gave a reduced conversion of 63% for **3a** to **4a**, demonstrating the importance of the amine in the synthesis, analogous to Yang's findings.

Mechanistically, the system is again thought to be similar to polydopamine, where hydrogen bonding to the carboxylate salt and the amine conjugate acid promote ring–opening of the epoxide, (scheme 8b). Carbon dioxide is activated by formation of the carbamate salt on imidazole, (Scheme 8c,d), ready for the attack by the alkoxide intermediate.



Scheme 8. Park's suggested method of activation of epoxide and CO_2 using histidine **13** co-catalyst

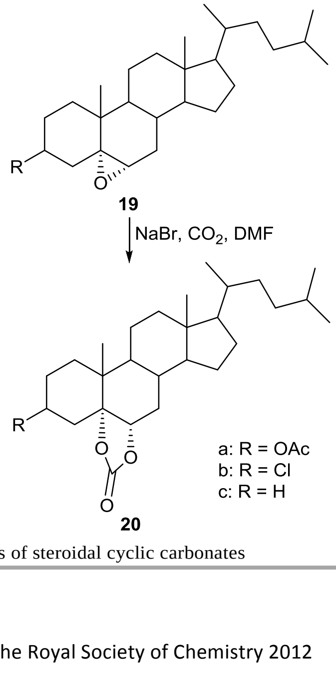
2.1.5 Supported potassium iodide. Sun et al[40] reported high conversions to cyclic carbonates by supporting potassium iodide onto a zinc oxide framework. A conversion of 94% for **3a** to **4a** was achieved after 2 hours using 8.6 wt% catalyst (with a potassium iodide loading of 3 mmol g^{-1}) and 50 bar pressure of carbon dioxide at 150 °C. Loading had a significant effect on conversions since 0.06 mmol g^{-1} of potassium iodide on zinc oxide gave 41% conversion using the same conditions. Thus, despite the 50 fold decrease in potassium iodide loading, the conversion only halved in the same reaction time. Other inorganic supports gave good conversions of **3a** to **4a** when using 3 mmol g^{-1} of potassium iodide, including, alumina (94%), zirconia (90%), NaX zeolite (82%) and silica (83%). When lower loadings of potassium iodide were used, conversions for these supports were much lower, in the range of 2–14%.

More recently, Zhou et al[41] showed that potassium iodide supported on MCM-41 was able to give high conversions after a reasonable reaction time. A conversion of **3a** to **4a** of 99% was achieved after 5 hours using 0.25 g (21.6 wt%) of potassium iodide supported on MCM-41 (35 wt% loading of potassium iodide on MCM-41) and 30 bar of carbon dioxide at 130 ^{o}C. A conversion of 95% of **3b** to **4b** was obtained using the same conditions. Increasing the amount of potassium iodide supported onto MCM-41 above 35 wt% had a negative effect on conversions to **4a**, since a 45 wt% loading gave 67% conversion, 55 wt% gave 95% and 65 wt% gave 93%. Recyclability of the catalyst was good although conversions reduced with several reuses achieving a 60% conversion to **4a** on the fourth reuse.

2.2 Sodium Bromide

Sodium halide catalysts have been significantly less studied than potassium halides, though there are a few good examples in the literature. Endo et al[42] showed that sodium bromide was an effective catalyst when used in *N*–methylpyrrolidinone (NMP) solvent. A conversion of 88% of **3f** to **4f** was achieved after 4 hours using 3 mol% sodium bromide, 11 ml of N–methylpyrrolidinone (108 mmol, 980 mol%) and 1 bar pressure of carbon dioxide at 100 ^{o}C; conversions of **3a,b** to **4a,b** were not reported. Increasing the catalyst concentration to 5 mol% increased the conversion of **3f** to **4f** to 98% after 4 hours. Contrary to the halide effect seen in potassium salt based systems, use of 5 mol% sodium iodide gave a lower conversion (88%) using the same conditions, though sodium chloride still gave a low conversion (41%). Though the reaction conditions are relatively mild, the N–methylpyrrolidinone solvent is a reproductive toxicant, making the methodology less attractive.

Ghosh et al[43] discussed the synergistic effect between metal halides and Lewis bases with sodium bromide and sodium chloride being two of the catalysts investigated. A 56% conversion of **3a** to **4a** was achieved after 3 hours using 0.1 mol% of sodium bromide, 0.1 mol% 4-dimethylaminopyridine co–catalyst and 20 bar pressure of carbon dioxide at 130 ^{o}C. The conversion increased to 78% when using sodium chloride in place of sodium bromide. However, lithium bromide gave the highest conversion, 91% after 3 hours.



Scheme 9. Synthesis of steroidal cyclic carbonates

Baqi et al[44] showed sodium bromide to be an effective catalyst for the reaction between carbon dioxide and steroidal epoxides **19a–c** (scheme 9). The exact quantity of sodium bromide used was not reported, a few crystals of sodium bromide were used with 2.52 mmol of epoxide in 30 ml of dimethylformamide (DMF) and carbon dioxide was bubbled through the reaction mixture for 30 minutes at 100 ^{o}C. Conversions to cyclic carbonates were: 70% for **19a–20a**, 68% for **19b–20b** and 69% for **19c–20c**. The focus of this work was synthetic, so the reaction mechanism was not investigated.

As mentioned in section 2.1.1, Sun et al[26] showed that water enhanced the catalytic activity of metal halides. It was found that 33.5% water co–catalyst with 0.5 mol% sodium bromide, and 20 bar pressure of carbon dioxide at 125 ^{o}C gave a 40% conversion of **3a** to **4a** after 1 hour. The highest conversion (100%) in this study was achieved by using PPh$_3$BuI as catalyst. Such observations are common in the literature where it is often the case that sodium bromide activity is reported alongside superior catalysts.

Jagtap et al[45] reported high activity when sodium bromide was used as part of a supported liquid phase catalytic system. The supported liquid phase catalyst (SLPC) was prepared by stirring PEG–600 acting as a dispersed phase, porous silica gel and the alkali metal salt (5 wt%) together, allowing good dispersion of the polyethylene glycol onto the silica surface. An 80% conversion of **3a** to **4a** was achieved after 6 hours using 34.5 wt% sodium bromide–SLPC (1 gram), 20 ml toluene solvent and 45 bar pressure of carbon dioxide at 150 ^{o}C. Sodium chloride–SLPC and sodium iodide–SLPC gave conversions of 65% and 70% respectively. Using 5 wt% of sodium bromide alone gave a 96% conversion of **3a** to **4a** after 2 hours. Sodium bromide–SLPC was able to achieve 85% conversion of **3b** to **4b** using 16.7 wt% sodium bromide–SLPC (1 gram), 20 ml toluene and 45 bar pressure of carbon dioxide at 150 ^{o}C. The effect of sodium bromide loading was investigated and the conversion was found to increase up to a loading of 7.5 wt%, above this there was no significant benefit. The key objective of this study was to develop a reusable catalyst and as such the sodium iodide–SLPC was recycled four times with no appreciable loss of activity or leaching of the alkali metal salt into the organic phase.

2.3 Sodium Iodide

Use of sodium iodide as a catalyst for cyclic carbonate synthesis is often limited to very specific reaction conditions, usually twinned with the use of a triphenylphosphine co–catalyst and a polar aprotic solvent which limits the sustainability of the process as phosphorus is an endangered element. Endo et al[46] showed this system to be effective in the reaction of carbon dioxide with polyglycidyl methacrylate. Incorporation of carbon dioxide into the polymer was quantified by ^{1}H NMR and found to be 89% after 24 hours using a polymer concentration of 1 mol L^{-1} in dimethylformamide, 1.5 mol% of sodium iodide, 1.5 mol% of triphenylphosphine and 1 bar pressure of carbon dioxide at 100 ^{o}C. Use of dimethylacetamide or *N*-methyl-2-pyrrolidone solvents gave a carbon dioxide incorporation of 84%. Interestingly, use of 2.5 mol% of sodium iodide alone gave 94% incorporation of carbon dioxide, suggesting that a co–catalyst was not necessary in this particular system.

Shi et al[47] demonstrated how high conversions could be obtained with the use of phenol as a second co–catalyst. A 100% yield of **4a** was obtained after 4 hours using 2 mol% of sodium iodide, 2 mol% of triphenylphosphine, 2 mol% of phenol and 40 bar pressure of carbon dioxide at 120 ^{o}C. An 85% conversion of **3b** to **4b** was obtained under the same conditions. A 1:1:1 ratio of catalyst to co–catalysts was necessary to obtain high yields. It is presumed that phenol acts as a Brønsted acid to promote ring–opening of the epoxide through hydrogen bonding.

2.4 Alkali metal summary

Of the alkali metals discussed, potassium iodide is superior to other potassium and sodium based catalysts in nearly all cases. As such, the systems discussed below refer to potassium iodide catalysed reactions, with conversions referring to **3a** to **4a** unless otherwise stated.

Conversions obtained when using potassium iodide with a co–catalyst tend to be 90+% within 1–4 hours. Use of potassium iodide with formic acid co–catalyst gave 60% conversion in only 15 minutes using a microwave reactor. The thermally heated equivalent only gave a conversion of 87% after 3 hours, showing that the high reaction rate is associated with use of microwave technology. Triethanolamine, (*S*)–tryptophan and polydopamine co–catalysts gave conversions of 91%, 99% and 96% in 1 hour. However, triethanolamine required an increased quantity of catalyst (1 mol%), (*S*)–tryptophan gave a poor conversion (22% after 2 hours) of **3b** to **4b** and polydopamine used a higher reaction temperature (140 ^{o}C). Water co–catalyst gave a good conversion (78% in 1 hour) when used with potassium iodide.

Typically, alkali metal salt catalysed cyclic carbonate syntheses used carbon dioxide pressures between 20 and 40 bar. The formic acid co–catalysed system used only 9.6 bar of carbon dioxide, with the (*S*)–histidine co–catalysed system using 10 bar pressure. The use of sodium bromide with *N*-methyl-2-pyrrolidone co–catalyst achieved a conversion of 88% of **3f** into **4f** using only 1 bar pressure of carbon dioxide, though its application to other substrates is unknown. *β*-cyclodextrin and MOF–5 co–catalysts used the highest carbon dioxide pressure (60 bar) and the supported potassium iodide catalysts (3mmol g^{-1} on zinc oxide, alumina and silica) used 50 bar pressure.

The most common reaction temperatures reported are 120–130 ^{o}C. Despite requiring high carbon dioxide pressures, the MOF–5 system used a reaction temperature of only 90 ^{o}C, achieving a conversion of 98% in 2 hours. The lecithin **8** co–catalysed system used a 100 ^{o}C reaction temperature and gave 98% conversion in 4 hours. Polyethylene glycol co–catalyst and supported potassium iodide catalysts (3 mmol g^{-1} on zinc oxide, alumina and silica) used the highest reaction temperatures (150 ^{o}C). The use of sodium bromide in a supported liquid phase catalyst system also used a 150 ^{o}C reaction temperature.

The quantity of alkali metal salt used typically ranged from 0.5–2.5 mol%, with a wide range of co–catalyst concentrations from 0.2 to 33.5 mol% and 8 to 66 wt%. The (*S*)–histidine co–catalysed system used only 0.2 mol% of both catalyst and co–catalyst and gave 99% conversion in 3 hours. The water co–catalysed system used 0.5 mol% of potassium iodide, giving a conversion of 78% in 1 hour, albeit using 33.5 mol% of water. Polydopamine used 0.6 mol% of both the co–catalyst and potassium iodide catalyst, giving a conversion of 96% after 1 hour. Use of sodium chloride with DMAP only required 0.1 mol% of both catalyst and co–catalyst to achieve 78% conversion in 3 hours.

Overall, the potassium iodide / water system offers the advantage of using a benign, low cost co–catalyst, however conversions are lower than the average and the system was not applied to more challenging substrates such as styrene oxide **3b**. Co–catalysts such as triethanolamine, *β*–cyclodextrin, cellulose, formic acid and lecithin offer the benefit of being inexpensive and simple or natural products and readily available, however they often require higher loadings of catalyst and harsher reaction conditions to achieve good conversions. The amino acid co–catalysts appear to be a good compromise. For example, the (*S*)–histidine system uses low concentrations of both catalyst and co–catalyst (0.2 mol%), an average reaction temperature of 120 ^{o}C, low carbon dioxide pressure (10 bar) and can achieve conversions of 99% and 97% for **3a,b** to **4a,b** respectively in 3 hours.

3. Group two metal (calcium)

Calcium salts have been known to be catalysts for the coupling of epoxides with carbon dioxide since the 1950s, however they have not been studied to the same degree as alkali metal or magnesium salts. The use of calcium chloride is described in a patent granted to Cline on behalf of the Mathieson Chemical Corporation in 1951.[48] This patent covers the use of several metal salts, describing calcium chloride as "particularly suitable". 1–2 wt% of the catalyst was used at around 200 °C for up to 2 hours using 1–2 molar equivalents of carbon dioxide. The patent also describes the use of these conditions in a continuous reactor.

The use of calcium chloride with an 'onium salt' co–catalyst such as tetrabutylammonium halides was reported by Kossev et al.[49] The authors show that combining calcium chloride with the onium salt results in significantly improved rates of reaction beyond the sum of the rates of each catalyst alone. Propylene oxide **3a** gave propylene carbonate **4a** with 96% conversion in 4 hours at 170 °C and 40 bar pressure of carbon dioxide using a 2:1 ratio of tetrabutylammonium chloride to calcium chloride as the catalyst system. Similarly, the use of calcium chloride with polymer–supported ammonium salts is mentioned by Siewniak et al although these are not the main focus of their work.[50] This system gave 54% conversion of **3a** to **3b** after 3 hours at 110 °C and 9 bar carbon dioxide pressure using a substrate: polymer supported salt: calcium chloride ratio of 714:7:2.

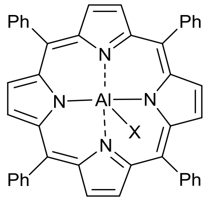
Other than the above examples using calcium chloride, the most notable area of interest concerning calcium–based catalysts is the use of processed blast furnace slags as catalysts for cyclic carbonate synthesis. Although primarily calcium based, these are not pure materials and aluminium, magnesium, manganese, titanium and iron are also present in significant amounts. Yamashita et al report a hydrocalumnite heterogeneous catalyst produced by the acid treatment of blast furnace slag to be a useful catalyst for several reactions including the addition of carbon dioxide to epoxides.[51, 52] Styrene oxide **3b** (4 mmol) was converted into cyclic carbonate **4b** in 90% yield after 48 hours using 0.5g catalyst in DMF at 1 bar carbon dioxide pressure and 100 °C. High yields were reported under the same conditions for several other terminal epoxides. It is believed that both Lewis acid and base sites exist within the catalyst in close proximity, explaining why a co–catalyst is not necessary.

The most interesting results found when using calcium containing catalysts are those obtained using processed blast furnace slags since this is an excellent example of green chemistry: using the waste of one process to facilitate a second process. The reaction conditions for the slag catalysed process are also very mild, especially the use of 1 bar carbon dioxide pressure. However, the use of DMF as a solvent is a significant drawback and the use of greener polar aprotic solvents should be explored. Additional mechanistic studies to determine if calcium or metal impurities present in the slag are the catalytically active species would also be of value.

4. Group Three Metal (aluminium)

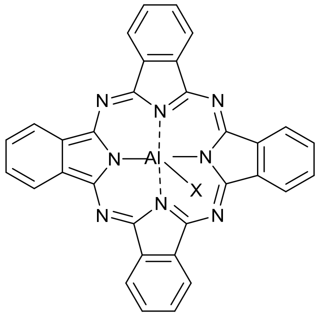
4.1 Monomeric aluminium–based complexes

4.1.1 Aluminium porphyrin and phthalocyanine complexes. In 1978, Inoue et al reported the synthesis of propylene carbonate **4a** catalysed by aluminium porphyrin complex **21a** in the presence of *N*–methylimidazole (NMI) as co-catalyst.[53] The reaction was carried out at room temperature and one bar pressure, employing 5 mol% of catalyst **21a** and 8 mol% of NMI. A 39% yield of **4a** was isolated after a reaction time of 45 hours. Spectroscopic methods were also used to study the reaction mechanism using aluminium phorphyrin **21b** as a postulated active species.[54]

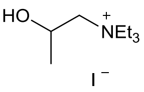


21a: X = OMe
21b: X = 1-chloro-3,3-dimethyl-2-butoxide

Later, Kasuga et al developed aluminium phthalocyanine complexes **22a,b** for the transformation of **3a** to **4a**, in conjunction with quaternary ammonium salt **23** or NMI.[55] Disappointingly, these systems do not exhibit high catalytic activity and the conversion to the desired product is typically only 2%. It was noteworthy, however, that the process was carried out at room temperature and one bar pressure of carbon dioxide. Subsequently, He et al showed that at 140 °C, aluminium phthalocyanine complex **22b** together with NMI afforded **4a** in 96% yield after a reaction time of 72 minutes.[56] Aluminium phthalocyanine complex **22b** was also anchored onto mesoporous MCM–41 silica.[57]



22a: X = OH
22b: X = Cl



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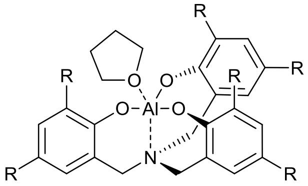
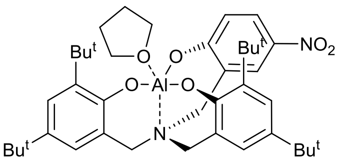
4.1.2 Aluminium triphenolate complexes. Aluminium(III)–aminotris(phenolate) complexes have been studied as Lewis acid catalysts.[58] In light of their previous work with Fe(III)–aminotris(phenloate) complexes,[59] Kleij et al have investigated the catalytic potential of hexachlorinated aluminium(III)–aminotris(phenolate) complex **24a** for the preparation of organic carbonates.[60] Initial experiments were carried out using 1,2–epoxyhexane **3g** as substrate and tetrabutylammonium iodide as co–catalyst. At a catalyst loading of 0.05 mol% and co–catalyst loading of 0.25 mol%, quantitative conversion to cyclic carbonate **4g** was achieved at 90 °C and 10 bar carbon dioxide pressure within 2 hours. To further improve the catalyst activity, a number of Al(III)–aminotris(phenolate) analogues **24b–d** as well as a nonsymmetrical aluminium complex **25** were synthesised and their activities tested under the same conditions. Amongst these catalysts, **24a** was found to be the most active. Finally, to demonstrate the wide applicability of Al(III)–aminotris(phenolate) **24a**, a range of terminal epoxides bearing various functional groups, as well as internal epoxides were transformed into the corresponding cyclic carbonates, employing low amounts of catalyst (0.05 mol%–0.10 mol%) and co–catalyst (0.25 mol%–0.50 mol%).



24a: R = Bu^t **24c**: R = H
24b: R = Me **24d**: R = Cl



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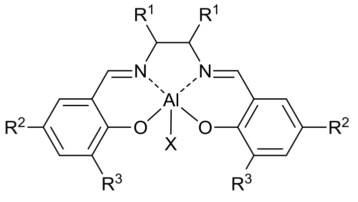
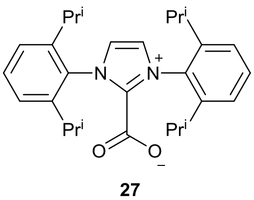
4.2 Aluminium(salen) complexes

4.2.1 Homogeneous aluminium(salen) complexes. Following the pioneering work of Darensbourg et al on the formation of polymeric and cyclic carbonates catalysed by chromium(salen) complexes,[61] He et al described their results for the synthesis of ethylene carbonate **3h** catalysed by Al(salen)Cl **26a** with tetrabutylammonium bromide as co–catalyst.[62] The homogeneous catalytic formation of ethylene carbonate **4h** from a mixture of supercritical carbon dioxide and **3h** proceeded rapidly at 110 °C and 150 bar pressure, with a substrate to catalyst to co–catalyst ratio of 5000:1:1. In the absence of the co–catalyst, complex **26a** still exhibits catalytic activity under the same conditions. The conversion of **3h** to **4h** is however, reduced significantly. Furthermore, high pressure is critical for the synthesis, as when the reaction was carried out at less than 40 bar pressure, the rate of conversion was only half of the rate observed at 150 bar pressure of carbon dioxide.



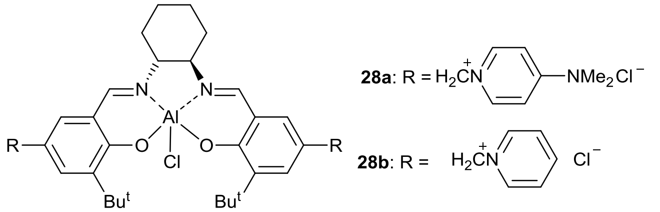
26a: X = Cl, R^1 = R^2 = R^3 = H
26b: X = Et, R^1 = R^2 = R^3 = H



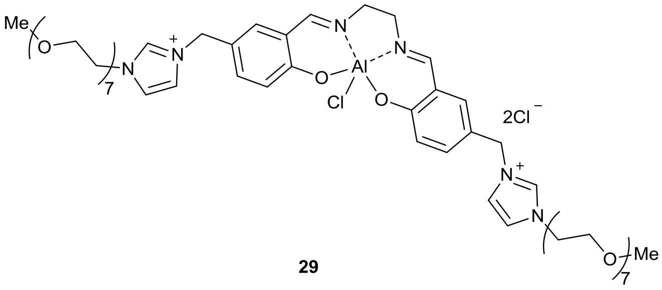
27

In 2002, Lu et al reported a cooperative bifunctional catalyst system of Al(salen)Et complex **26b** in conjunction with 18–crown–6/KI, for the addition of carbon dioxide to epoxides.[63] The reaction conditions are extremely mild compared to those previously reported (25 °C and 6 bar carbon dioxide pressure). Using a **3a** to catalyst to co–catalyst ratio of 400: 1:1, **4a** was isolated in 98% yield after a reaction time of 12 hours. Under the same conditions, use of 0.125 mol% complex **26a** and tetrabutylammonium iodide gave **4a** in 61% yield after a reaction time of 8 hours.[64] A binary catalyst system consisting of complex **26b** and *N*,*N*'–disubstituted imidazole(in)ium–2–carboxylate **27** has also been used in the reaction of carbon dioxide with terminal epoxides.[65] Whilst a quantitative yield of **4a** can be obtained using only 0.25 mol% of **26b** and 0.5 mol% of **27**, a much higher temperature and carbon dioxide pressure (120 °C and 20 bar) are necessary.

Darensbourg et al have designed and developed a series of one–component aluminium(salen) complexes bearing appended pyridinium salt substituents.[66] At 120 °C and 30 bar carbon dioxide pressure, complexes **28a**,**b** both proved to be highly efficient catalysts for the synthesis of **4a** from **3a** at a substrate to catalyst ratio of 2000:1. Changing the nature of the cation from 4–dimethylaminopyridinium (**28a**) to pyridinium (**28b**) led to a decrease in conversion from 74% to 51% after 5 hours, presumably because of a decrease in acidity of the quaternary ammonium salt. Catalysts **28a,b** also showed good recyclability without significant loss in catalyst activity.

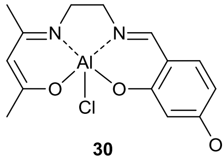


Similarly, a series of aluminium(salen) complexes (**29**) bearing imidazolium–based ionic liquid moieties and containing polyether chains has been introduced by Ji et al.[67] The optimized process for the synthesis of **4a** catalysed by **29** operates at 10 bar carbon dioxide pressure and 100 °C with 0.5 mol% of catalyst. Complete conversion of **3a** to **4a** was reached within 2 hours. The high catalyst efficiency could be attributed to the 'carbon dioxide expansion effect' of the polyethylene oxide chain.[68] Catalyst **29** could be recovered easily and used six times without significant loss of activity or selectivity.



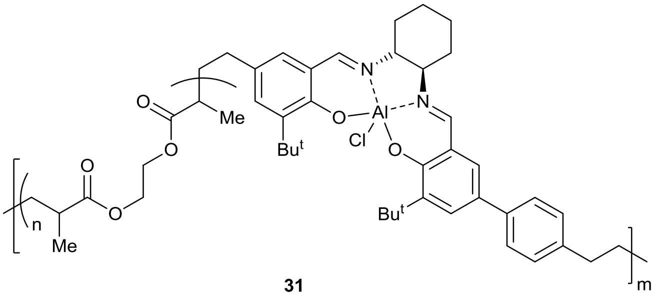
29

Recently, the development of non–symmetrical Al(salacen) complex **30** and its catalytic activity with tetrabutylammonium bromide as co–catalyst for the conversion of styrene oxide **3b** to styrene carbonate **4b** has been reported.[69] The use of dichloromethane as a solvent was found to be essential for the reaction. With 1 mol% of both complex **30** and tetrabutylammonium bromide, 90% conversion of **3b** to **4b** was observed at 100 °C and 1 bar carbon dioxide pressure after 48 hours. However, using 1 mol% of tetrabutylammonium bromide on its own, the conversion still reached 73%. This shows that aluminium catalyst **30** is not necessary for cyclic carbonate synthesis under these conditions, though it does increase the conversion.



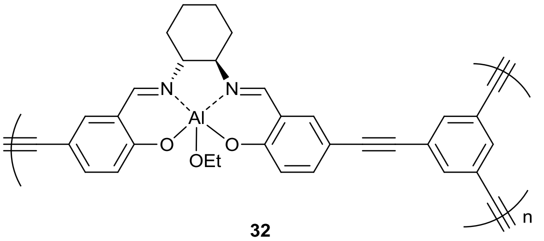
30

4.2.2 Aluminium(salen) based heterogeneous catalysts. In 2005, polymers of Al(salen)Cl complexes were synthesised and tested in the formation of styrene carbonate **4b** from styrene oxide **3b** and supercritical carbon dioxide at 80 °C and 100 bar.[70] Complex **31** supported on poly(ethylene glycol bis–methacrylate), used in conjunction with NMI afforded styrene carbonate **4b** in 78% yield after 15 hours. Unfortunately, the reusability of catalyst **31** was poor and a significant loss of activity was observed after its first use.



31

Xie et al reported the synthesis of aluminium–coordinated conjugated microporous polymers as heterogeneous catalysts for the coupling of carbon dioxide and **3a** to afford **4a**.[71] At ambient temperature and 1 bar pressure of carbon dioxide, the reaction of **3a**, 0.5 mol% (with respect to aluminium loading) of microporous aluminium–based polymer **32** and 7 mol% of tetrabutylammonium bromide as co–catalyst, proceeded within 48 hours to afford **4a** in 78% yield. When the temperature and pressure were increased to 100 °C and 30 bar respectively, a 91% yield of **4a** was obtained after 1 hour. Microporous polymer **32** exhibits high carbon dioxide absorption, indicating that it is a good carbon dioxide capture material. This could explain its enhanced performance compared with monomeric aluminium complexes.

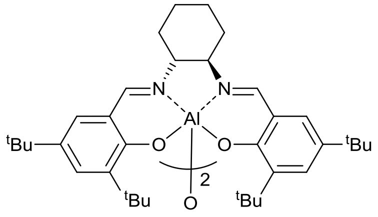


32

4.3 Bimetallic aluminium–based complexes

In 2007, North et al found bimetallic Al(salen) complex **33** and tetrabutylammonium bromide to be exceptionally effective in catalysing the coupling of various terminal epoxides and carbon dioxide, to provide the corresponding cyclic carbonates under extremely mild and solvent–free conditions.[72] When the reaction was carried out using 2.5 mol% of both catalyst **33** and tetrabutylammonium bromide at room temperature and 1 bar carbon dioxide pressure, styrene oxide **3b** was 62% converted into styrene carbonate **4b** after 3 hours and 98% converted after 24 hours. Using just 1 mol% of catalyst **33** together with tetrabutylammonium bromide, 86% conversion of **3b** to **4b** was observed after 24 hours. The addition of tetrabutylammonium bromide as a co–catalyst is essential to perform this coupling reaction smoothly and both complex **33** and the ammonium salt have a significant effect on the catalytic performance. At 0 °C, the catalyst system was still active, and using just 1 mol% of catalyst **33** and the co–catalyst, **3a** was 40% converted into **4a** after 3 hours.

A series of kinetic studies revealed that the reaction was first order with respect to the epoxide, carbon dioxide and **33**, but second order with respect to tetrabutylammonium bromide.[73] Furthermore, it was found that tetrabutylammonium bromide decomposes to tributylamine under the reaction conditions. On the basis of these findings, a reaction mechanism was proposed, which explains the high catalytic activity of bimetallic complex **33**, in comparison to its monometallic analogues.[74] Complex **33** could be reused over 60 times without loss of catalytic activity, though periodic addition of tetrabutylammonium bromide was necessary.

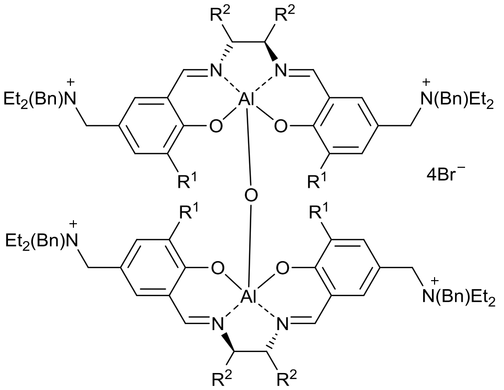


33

The effect of moderate temperatures (22–100 °C) and pressures (1–10 bar) on the synthesis of cyclic carbonates from epoxides and carbon dioxide catalysed by the combination of bimetallic aluminium complex **33** and tetrabutylammonium bromide has also been investigated by North et al.[75] As expected, at higher temperatures and pressures, the catalytic activity of complex **33** and tetrabutylammonium bromide increased 20 fold as measured by turnover numbers. Furthermore, the high catalytic activity seen at elevated temperature and pressure allowed the synthesis of disubstituted cyclic carbonates from disubstituted epoxides and carbon dioxide. These reactions were found to go with complete retention of the epoxide stereochemistry.

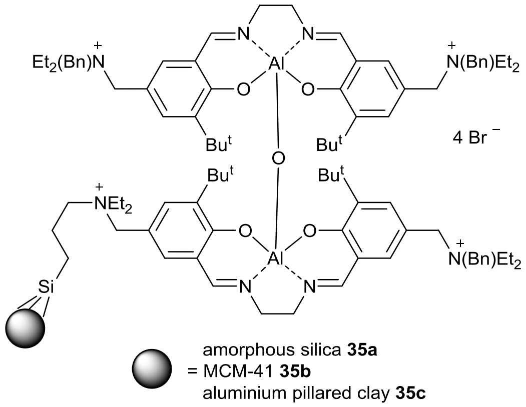
An integrated system that generates energy by the combustion of methane in a pure oxygen atmosphere, and produces glycerol carbonate **4d** from glycidol **3d** and the waste carbon dioxide generated during the combustion has been developed.[76] This demonstrated that catalyst **33** was compatible with the moisture and impurities present in the carbon dioxide gas stream.

North et al have also developed one–component bimetallic aluminium catalyst systems.[77] Rather than using tetrabutylammonium bromide as a co–catalyst, the quaternary ammonium bromides were covalently attached to the salen ligands to give catalysts **34a–d**. One–component catalysts **34a–d** were also found to be extremely active for the formation of cyclic carbonates from their corresponding epoxides under very mild conditions. At room temperature and pressure, one–component catalysts **34a–d** all converted **3b** into **4b**, with the most hydrophobic complex, **34a**, giving the best results (71% conversion after 3 hours and 97% conversion after 6 hours using 2.5 mol% of catalyst **34a**). Further investigation of the catalyst system showed that a wide range of functional groups were tolerated and, under the same reaction conditions, most terminal epoxides were converted into the corresponding cyclic carbonates in excellent yields.[78]



34a: $R_1 = Bu^t$, $R_2 = (CH_2)_4$
b: $R_1 = Bu^t$, $R_2 = H$
c: $R_1 = H$, $R_2 = (CH_2)_4$
d: $R_1 = H$, $R_2 = H$

To further demonstrate the utility of the one–component catalyst system, immobilised versions of catalysts **34** were prepared using several sources of solid support. Since heterogeneous catalysts no longer require the active site to be soluble, the relatively expensive 1,2–diaminocyclohexane unit was discarded in favour of the much less expensive 1,2–diaminoethane unit. The best solid–supported catalyst was found to be silica–supported catalyst **35a**. An 86% conversion of **3b** to **4b** was observed using **35a** (2.5 mol% of active sites) at 25 °C and 1 bar pressure of carbon dioxide under solvent–free conditions. Catalyst **35a** was also tested in batch reactions with **3a** as substrate. Due to the low boiling point of **3a**, the reaction was carried out at 0 °C and gave 73% conversion to **4a** after 24 hours. Catalyst **35a** could be recovered by distillation of **4a** and reused repeatedly. Even though the catalyst activity dropped off noticeably over a number of recycles, full catalyst activity could be restored by treatment of **35a** with benzyl bromide to reform the quaternary ammonium salt.



amorphous silica **35a**
= MCM-41 **35b**
aluminium pillared clay **35c**

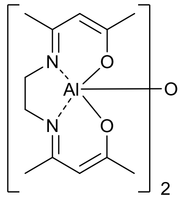
A gas–phase flow reactor was designed and catalyst **35a** was then used to prepare ethylene carbonate **4h** in flow–mode reactions.[79] The optimal reaction conditions were to use a gas stream composed of 21% carbon dioxide (total flow rate 4.7mL/min) and a reactor length of 3 cm filled with catalyst **35a**. Under these conditions at 150 °C, 57% of the carbon dioxide was converted into **4h** after 6 hours. However, when catalyst lifetime was investigated under these continuous flow conditions, it was found to retain its activity for the first 18 hours, after which time the percentage carbon dioxide absorbed decreased to zero over the next 18 hours and the purity of the **4h** produced was also decreased from 100 to just 5%. ICP–OES analysis of the catalyst indicated that no aluminium was present. This suggested that prolonged heating of the catalyst to 150 °C resulted in cleavage of the salen units from the silica support. Fortunately, catalyst deactivation studies carried out at 100 °C showed much better results and catalyst **35a** still retained 50% of its original activity after seven days. Furthermore, reactivation of the catalyst by treatment with benzyl bromide could restore it to its original activity.

To further improve the activity of silica–supported aluminium catalysts, the influence of various sources of silica and the linker on the activity and lifetime of the catalysts were investigated.[80] Seven types of silica with different physical properties were chosen and their corresponding silica–supported aluminium(salen) catalysts were made. Subsequent tests of the synthesis of cyclic carbonates from epoxides and carbon dioxide in both batch and gas–phase flow reactors showed that while the silica pore size had little effect on catalyst activity, the particle size was important with smaller particle sizes (<80 um), such as Fluorochem LC301, the standard amorphous flash silica that was used for the synthesis of heterogeneous catalyst **35a**, being advantageous to the catalytic activity. The stability of silica–supported catalysts was also affected by the nature of the silica support and catalyst **35a** has the highest intrinsic activity and the lowest rate of deactivation. The linker between the silica and the aluminium complex unit was also investigated by extending the three–carbon linker present in catalyst **35a** to an eleven–carbon linker. The resulting silica–supported catalyst was found to give a catalyst loading three times higher than that of the shorter linker. The catalyst activity, however, was only one third of catalyst **35a**.

It is highly desirable to develop catalyst systems that are compatible with waste carbon dioxide in order to reduce costs associated with purification of carbon dioxide. Using waste carbon dioxide present in either simulated or real power station flue–gas generated from combustion of gas or coal, and which contains a mixture of NO_x, SO_x, water, CO, O_2, N_2 and solid particles, complex **35a** was tested as catalyst for the synthesis of **4h** from **3h**.[81] Although exposure of catalyst **35a** to flue–gas from combustion of coal has some detrimental effect on catalyst activity in batch reactions, when catalyst **35a** exposed to flue–gas from combustion of coal was used in the gas–phase flow reactor, no decrease in catalyst activity relative to a control sample was observed. Initially, catalyst **35a** has 95% of the activity of the control sample (measured as the turn over frequency) and lost 21% of its activity over the first eight days of reaction. After the eighth day, the catalyst was reactivated by treatment with benzyl bromide and activity of the catalyst was restored to 97% of its original value.

In order to improve the potential application of aluminium–based catalysts on industrial scales, the cost of their production has been evaluated and optimisation of the synthesis of the catalysts has been carried out.[82] It was shown that the major chemical costs for the production of aluminium–based catalysts were the aluminium triethoxide and tetrabutylammonium bromide. The iodine–catalysed in situ formation of aluminium triethoxide from aluminium foil and ethanol was used for the formation of complex **33**. By using the revised procedure, the chemical cost of the production of **33** was reduced by 63% whilst the catalytic activity was retained at the same level as for **33** prepared from commercially sourced aluminium triethoxide.

An alternative class of bimetallic aluminium complex was also synthesised to reduce the cost of bimetallic aluminium(salen) complexes. Thus, the salicylaldehyde was replaced with pentan–2,4–dione to give aluminium(acen) complex **36**.[83] The cost of production of acen complex **36** is 22% lower than the cost of production of salen complex **33**. Complex **36** did however exhibit a slightly lower level of catalyst activity than complex **33**. Thus, using 2.5 mol% of complex **36** and 2.5 mol% of tetrabutylammonium bromide, **3b** is converted into **4b** (85%) after 24 hours. By replacing the commercial aluminium triethoxide with in situ formation of aluminium triethoxide, the cost of production of complex **36** could be further reduced to just 13% of its original cost and 10% of the cost for the production of complex **33**.

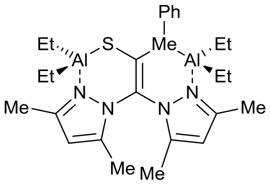


36

For the synthesis of one–component catalyst **34b,d** and silica–supported catalyst **35a**, benzyl bromide can provide the halide source. Therefore, tetrabutylammonium bromide could be completely omitted from the synthesis of these catalysts, resulting in a cost saving of 72%. Finally, the replacement of acetonitrile as a solvent in the production of aluminium–based catalysts was investigated. It was found that by replacing acetonitrile with propylene carbonate **4a**, an environmentally friendly, polar aprotic solvent, together with replacing the aluminium triethoxide and omitting tetrabutylammonium bromide, the combined effect resulted in the chemical cost for production of these catalysts being just 21–23% of their original values. The catalytic activity was investigated in the formation of **4b** from **3b**, and showed that there is no significant loss of catalytic activity associated with these changes in the preparation of the catalysts.

4.4 Complexes of aluminium and other ligands.

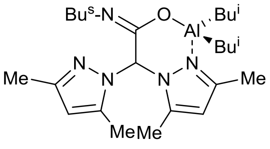
In 2012, North et al reported the utilisation of a series of aluminium complexes derived from bis–pyrazole ligands as catalysts for the formation of cyclic carbonates from terminal epoxides and carbon dioxide.[84] In the presence of 10 bar carbon dioxide pressure at room temperature, 5 mol% of complex **37** together with 5 mol% of tetrabutylammonium bromide catalysed the formation of styrene carbonate **4b** from styrene oxide **3b** with 96% conversion being obtained after 24 hours. A lower conversion (69%) was observed at 1 bar carbon dioxide pressure. A kinetic study revealed that the reaction is first order with respect to epoxide, complex **37** and tetrabutylammonium bromide and a catalytic cycle for cyclic carbonate synthesis catalysed by complex **37** was proposed.



37

Following on from the synthesis of helical aluminium complex **37**, North et al reported the development of several aluminium scorpionate–based catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide.[85] The catalytic activity of these catalysts have been investigated using **3b** as substrate, with 5 mol% of both catalyst and tetrabutylammonium bromide at 10 bar carbon dioxide pressure and room temperature for 24 hours. Mononuclear complex **38** with a single bis–pyrazole ligand catalysed the formation of **4b** and gave 79% conversion, while mononuclear complex **39** with two bis–pyrazole ligands gave only 51% conversion. The low conversion obtained when using complex **39** could be due to the aluminium ion being sterically hindered between the two large ligands, so that the Lewis acidic site is less accessible to coordinate to the epoxide. Binuclear complex **40** and trinuclear complex **41a–d** all have exceptionally good activity and transformed **3b** into **4b** with 92–100% conversion. Furthermore, at 1 bar carbon dioxide pressure, binuclear complex **40** afforded **4b** with 77% conversion, and trinuclear complex **41d** gave 100% conversion. This result suggested that trinuclear complex **41d** together with tetrabutylammonium bromide is the best catalyst system for the coupling of carbon dioxide and **3b** under the reaction conditions. When the loading of both complex **41d** and the co–catalyst was reduced to 2.5 mol%, only 40% conversion of **3b** into **4b** was observed at 1 bar carbon dioxide pressure.

Since complex **41d** contains seven aluminium methyl groups in three different environments, and to understand its mode of action, the influence of water on the catalytic activity of complex **41d** was investigated. It was found that the addition of up to 0.75 mol% of water had no detrimental effect on the catalytic activity when 5 mol% of complex **41d** and tetrabutylammonium bromide were used as catalysts. The addition of 2.5 mol% of water to the catalyst system, however, reduced the conversion of **3b** to **4b** dramatically to just 14%. This suggests that the active species of complex **41d** is a dimer or higher oligomer with oxygen bridges between aluminium units replacing some of the methyl groups. The addition of too much water, however, resulted in over hydrolysis to either a cross–linked catalytically inactive polymer or to aluminium oxides. A kinetic study was carried out and showed that the reaction was first order with respect to epoxide, complex **41d** and tetrabutylammonium bromide. A similar mechanism to that proposed for reactions catalysed by complex **37** was thus suggested for the synthesis of cyclic carbonates from epoxides and carbon dioxide catalysed by complexes **41**.



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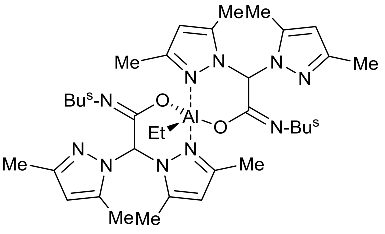

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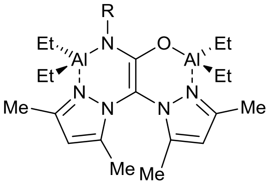
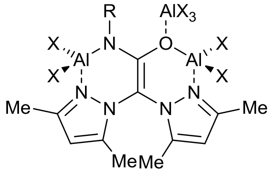
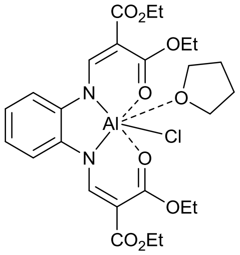


40 R = (*S*)-CH(Ph)Me



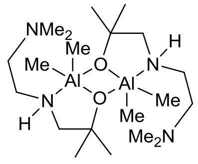
41a R = $\mathrm{Bu^s}$, X = Et
b R = (*S*)-CH(Ph)Me, X = Me
c R = (*S*)-CH(Ph)Me, X = Et
d R = Ph, X = Me

Recently, Zevaco et al reported the synthesis of aluminium complex **42** and its catalytic activity was first tested for producing poly(cyclohexenecarbonate).[86] Interestingly, when propylene oxide **3a** was used as a substrate, together with 0.2 mol% of catalyst **42** and 0.2 mol% of tetrabutylammonium bromide as a co–catalyst at 50 bar carbon dioxide pressure and 80 °C, propylene carbonate **4a** was formed in 94% yield after 20 hours. The addition of a co–catalyst was essential to obtain satisfying conversions. However, the study of complex **42** for the formation of cyclic carbonates was very brief and only propylene oxide **3a** was investigated.



42

In 2014, Kim et al reported the synthesis of dinuclear aluminium complexes bearing multidentate aliphatic aminoethanol–based ligands, and their utility was demonstrated by the addition of carbon dioxide to **3a** in the presence of tetrabutylammonium iodide as a co–catalyst.[87] The reaction was carried out at 10 bar carbon dioxide pressure and 70 °C for 24 hours, with a substrate to catalyst to co–catalyst ratio of 1000:1:1. Aluminium complex **43**, which has two methyl groups per aluminium centre, gave **4a** in 77% conversion, while aluminium complex **44**, with one methyl group per aluminium, gave a slightly lower conversion (66%). Other co–catalysts were tested and tetrabutylphosphonium bromide was found to be optimal. Thus, for reactions catalysed by complex **43**, an increase in conversion from 77% to 84% was observed.



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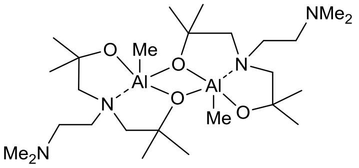

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4.5 Summary of aluminium complexes

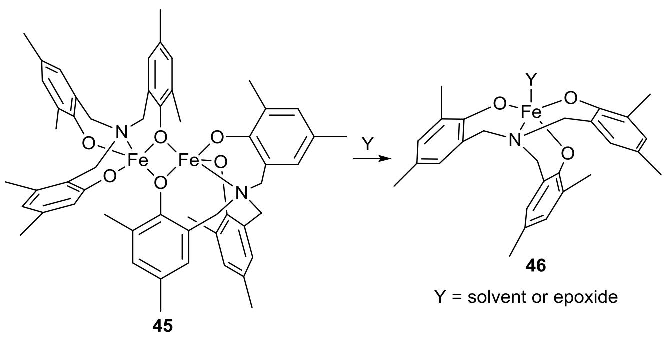
Aluminium based catalyst systems are generally active, for the synthesis of cyclic carbonates from epoxides and carbon dioxide but require high temperatures and pressures. Thus, the catalyst system of bimetallic aluminium complex **33** and tetrabutylammonium bromide is exceptionally active, using 2.5 mol% of both catalyst and co–catalyst at room temperature and pressure, a 98% conversion of styrene carbonate **4b** from styrene oxide **3b** was achieved after 24 hours. The related silica–supported aluminium catalysts **35** have been developed for both batch reactions and gas–phase flow reactions. Catalyst **35a** was tolerant of impurities present in flue gas, allowing the development of an integrated system for energy production with utilisation of waste carbon dioxide in cyclic carbonates synthesis.

Another powerful catalyst system for the formation of cyclic carbonates is aluminium(aminotris(phenolate)) complex **24a** together with tetrabutylammonium iodide. Using 0.05 mol% of catalyst and 0.25 mol% of the co–catalyst, quantitative conversion of epoxide **3g** to cyclic carbonate **4g** was achieved at 90 °C and 10 bar carbon dioxide pressure within 2 hours. Furthermore, this catalyst system is also active for the synthesis of cyclic carbonates from epoxides with a variety of functional groups, as well as for disubstituted epoxides, albeit at higher temperature and pressure.

5. Transition Metals (Iron and Titanium)

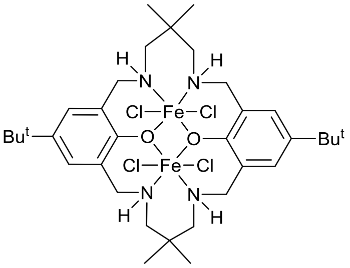
5.1 Iron Catalysts.

Several well–defined iron complexes have been used to catalyse the formation of cyclic carbonates by reaction of epoxides with carbon dioxide. One of the most important classes of iron catalysts are those developed by Whiteoak et al based on the iron(III) aminotriphenolate unit.[59,88,89,90] These are formed as oxo–bridged dimers **45** with the monometallic complex **46** being formed under the reaction conditions by coordination of the epoxide substrate or through addition of a coordinating solvent (Scheme 10). These systems displayed a wide scope in terms of substrate, including the ability to promote the synthesis of cyclic carbonates from internal epoxides such as cyclohexene oxide, provided the most suitable co–catalyst was chosen.[88,90] Also of note is that complex **46** was capable of converting oxetanes into six–membered cyclic carbonates. Control over the stereochemistry of the cyclic carbonate product was also possible by careful selection of co–catalyst and the catalyst to co–catalyst ratio.[59] Yields for formation of propylene and styrene carbonates **4a,b** were relatively modest (74% and 56% respectively) under standard conditions: 2 bar carbon dioxide pressure, 25 °C, 18 hour reaction time, using 0.5 mol% of catalyst and 5 mol% of co–catalyst in methyl ethyl ketone. Under the same conditions, yields for more lipophilic terminal epoxides were considerably higher (>90% for some examples).



Scheme 10. Conversion of bimetallic complex **45** to monometallic complex **46**

Williams et al have used a bimetallic iron(III) complex **47** to form cyclic carbonates from epoxides and carbon dioxide.[91] As this group is focused primarily on the production of polycarbonates, the cyclic carbonate chemistry or substrate range was not fully explored. However, Williams showed that in the presence of bis(triphenylphosphine)iminium chloride (PPNCl) as a co–catalyst, complex **47** was capable of inducing 90% conversion of cyclohexene oxide to cyclohexene carbonate under mild conditions: 1 bar carbon dioxide pressure, 80 °C, 24 hour reaction time using 1 mol% of catalyst and 2 mol% of PPNCl. However, PPNCl cannot be considered to be truly sustainable as phosphorus is an endangered element according to Figure 1.



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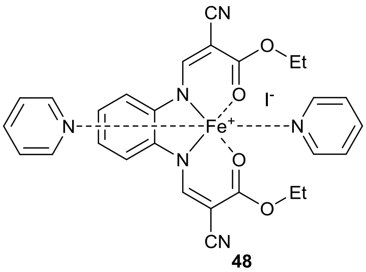
Recently, Döring reported monometallic catalysts which, the authors emphasize, are made in a high–yielding two–step synthesis from cheaply available starting materials.[92] The most active iron(III) catalyst (**48**) incorporated iodide as a counterion and two coordinated pyridines which were interpreted to be acting as a nucleophilic co–catalyst, thus making addition of further halide co–catalyst unnecessary. This catalyst gave 99% conversion of **3a** to **4a** after 20 hours using only 0.2 mol% of catalyst at 50 bar carbon dioxide pressure and 80 °C. The catalyst was shown to be effective on a range of monosubstituted terminal epoxides including **3b** which gave 96% conversion to **4b** under the same conditions.



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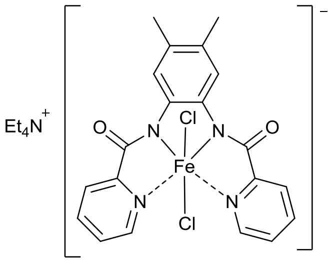

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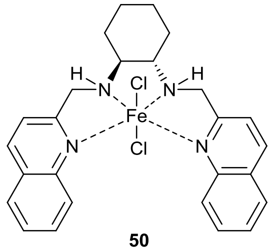

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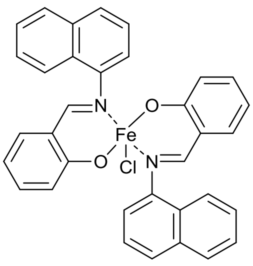
The same group also reported iron catalyst **49** based on a pyridine amide ligand that was effective both for the conversion of **3a** to **4a** and for the production of polycarbonate when presented with cyclohexene oxide as a substrate.[93] The formation of **4a** proceeded to 91% yield after 20 hours at 80 °C, and 35 bar pressure of carbon dioxide using 0.5 mol% catalyst. Again, no co–catalyst was needed as complex **49** contains chlorides. The versatility of this system was not demonstrated as the authors concentrated instead on the analogous cobalt catalysts. This work was, the authors acknowledge, inspired by Rieger's preparation of a one–component iron(II) tetraamine catalyst (**50**) which was itself capable of achieving complete conversion of **3a** to **4a** within 2 hours at 100 °C and 15 bar carbon dioxide pressure using 1.5 mol% of catalyst.[94]

Somewhat similar in terms of ligand structure is the recent work of Sunjuk et al concerning complexes **51**–**54**.[95] The authors focussed predominantly on the conversion of **3b** to **4b** and also discussed cobalt and chromium analogues of complex **51**. Of the iron complexes tested in this work, **51** was the most active catalyst, giving a turn over frequency (TOF) of 73 at 130 °C, 5 bar carbon dioxide pressure and a catalyst to tetrabutylammonium bromide to epoxide ratio of 1:1:2556.



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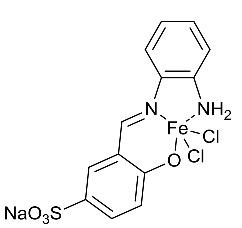

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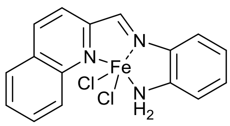

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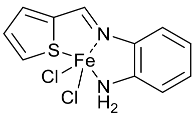

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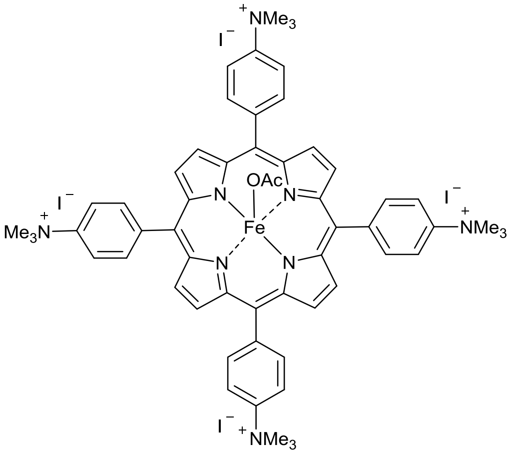
Iron(III) porphyrin complexes have been used as Lewis acid catalysts for cyclic carbonate synthesis by Bai et al.[96] Porphyrin complex **55** did not require a co–catalyst as the complex contained iodides which can perform this function. In this case the sustainable iron complex was outperformed by the (less sustainable) cobalt catalyst and so was not investigated in detail. The unoptimised iron complex was capable of converting **3a** to **4a** in 73% yield after 15 hours at 6.7 bar carbon dioxide pressure and 80 °C using 0.1 mol% of catalyst. The authors also emphasized the ease of recovery of the catalyst and demonstrated recycling complex **55** for five sequential reaction cycles with no significant reduction in activity.

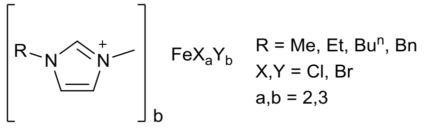


55

Lermontov et al discussed a halide–free route from epoxides to cyclic carbonates using hydroxyquinoline salts, including iron.[97] However, their use of triphenylphosphine oxide as a co-catalyst reduces the sustainability of the process and the conditions used were relatively harsh (15–100 bar carbon dioxide pressure and 140 °C) by comparison to more recent work.

In contrast to the systems discussed above which all use well-defined complexes which must be synthesised prior to use, Bok et al demonstrated the use of transition metal chlorides as catalysts with tetrabutylammonium acetate as co–catalyst.[98] Remarkably, given the simple and convenient catalyst system, these salts were effective under mild conditions for simple terminal epoxides and even for cyclohexene oxide. Propylene oxide **3a** was 90% converted to propylene carbonate **4a** after 4 hours at 90 °C and 15 bar pressure of carbon dioxide using 0.33 mol% of iron(III) chloride and tetrabutylammonium acetate. Under similar conditions but with 1 mol% catalyst loading, styrene oxide **3b** gave styrene carbonate **4b** with 90% conversion after 5 hours. This represents one of the more convenient systems, eliminating the need for multistep synthesis of the catalyst prior to use.

Bridging the gap between well–defined homogeneous catalysts and solid catalysts are those based upon ionic liquids. Kim et al used imidazolium metal halide salts **56** containing various alkyl substituents as catalysts for the coupling of CO_2 and epoxides.[99] However, the iron catalysts showed TOFs of around 420 h^{-1} for converting **3a** to **4a**, which was less than half the TOFs obtained for analogous but less sustainable zinc and manganese catalysts. These reactions were performed at 100 °C for 1 hour under 3.5 bar pressure of carbon dioxide using a 1:2000 ratio of catalyst to **3a**.



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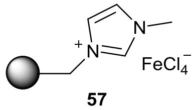


57

A similar catalyst, **57,** was used by Gao et al, where the imidazolium component was supported on crosslinked polystyrene, resulting in a heterogeneous, immobilised ionic liquid catalyst.[100] The catalyst was reasonably successful for use with a range of terminal epoxides, giving a conversion of 88% of **3a** to **4a** using 1 mol% of catalyst at 80 bar carbon dioxide pressure and 100 °C with a reaction time of 6 hours.

Qu et al also developed a heterogeneous catalyst for cyclic carbonate synthesis, in this case based upon magnetic "flower–like" iron oxide core/shell particles.[101] These were shown to be effective for the coupling of carbon dioxide with several terminal epoxides and with **3a** gave a 94% isolated yield of **4a** at a catalyst loading of 2 mg per mmol of epoxide, 1 mol% of potassium iodide co–catalyst, 125 °C and 20 bar carbon dioxide pressure. The magnetic nature of the catalyst particles facilitated recycling and reuse of the catalyst.

5.2 Iron catalysts summary

The use of simple iron(III) chloride and ammonium acetate by Bok and co–workers is arguably the most experimentally convenient method for carrying out this reaction using iron catalysts.[98] This method achieved a high conversion (90% for propylene oxide **3a** to the carbonate **4a**) without the need to carry out prior catalyst synthesis and, as is of prime importance for industrial applications, did not require very high pressure. This method was also effective on cyclohexene oxide, which implies a degree of substrate tolerance.

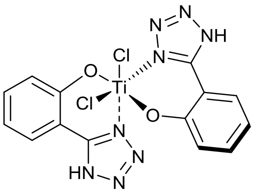
Whiteoak's catalysts[59,89,90] are also notable for their versatility, with **46** being very unusual in having the capability to also convert 4-membered oxetanes to 6-membered cyclic carbonates. This family of catalysts also demonstrated some degree of stereochemical control and could be used at 25 °C and 2 bar carbon dioxide pressure, the lowest temperature and pressure of any iron catalyst.

Where simple catalyst recovery and recyclability is a primary concern, the choice is between the porphyrin catalysts developed by Bai et al,[96] or a heterogeneous catalyst. The most convenient catalyst in terms of simple recovery must be the magnetic inorganic particles developed by Qu.[101] These particles, in addition to simplified recovery and recycling, gave very respectable yield (94% of **4a**) under mild pressure and temperature conditions (20 bar CO_2, 125 °C).

5.3 Titanium catalysts

Perhaps the most obvious titanium–based catalytic systems are those based on titanocene and other cyclopentadienyl titanium systems. Bai et al used bis–cyclopentadienyl titanium chloride and tetrabutylammonium bromide as their catalyst system.[102] They reported a 98% isolated yield of propylene carbonate **4b** from a 15 minute reaction in pyridine at 150 ^{o}C and 12 bar carbon dioxide pressure using 1 mol% of catalyst and co–catalyst. In the absence of pyridine, the same reaction took 24 hours to achieve a more modest 67% yield, whereas without tetrabutylammonium bromide the reaction proceeded to 98% yield in 75 minutes, indicating that tetrabutylammonium bromide was less active than the pyridine solvent as a Lewis base in this reaction. The system was shown to work for a range of terminal epoxides and cyclohexene oxide. The same group had previously published the use of potassium iodide as a co–catalyst for this reaction,[103] achieving a 98% yield of **4a** in 4 hours at the same pressure and temperature described above, but with THF as the solvent.

Go et al described an interesting system based on a tetrazole ligand.[104] Although mixed–ligand complexes with cyclopentadiene and THF are reported, the bis–tetrazole complex **58** was shown to be the most active catalyst, giving 86% conversion of **3a** to **4a** in 4.5 hours using 0.1 mol% of catalyst and tetrabutylammonium iodide co–catalyst at 75 ^{o}C and 22 bar carbon dioxide pressure. No other substrates were studied.



58

Brunner et al reported a method for the kinetic resolution of racemic epoxides using chiral binol ligands on titanium.[105] The authors formed the active chiral complex in situ by simply adding together a titanium acetate salt and one equivalent of the enantiopure binol ligand. Both epichlorohydrin **3e** and styrene oxide **3b** were studied, with the best result being for **3b**, which, at a conversion of 41% gave 24% ee for unreacted epoxide and 35% ee for cyclic carbonate **4b** ($s = k_{fast}/k_{slow} = 2.6$) in a reaction carried out at room temperature for 24 hours using 5 bar carbon dioxide pressure, 1 mol% catalyst and binol and 4 mol% of tetrabutylammonium iodide.

Titanium is also used in a different form for catalysis with titanosilicate molecular sieves. These are very attractive heterogeneous catalysts as they are commercially available, inexpensive and recyclable. Srivastava et al demonstrated the use of TS-1 titanium silicate molecular sieves in the coupling of epoxides with carbon dioxide and showed a 77% conversion of propylene oxide **3a** to propylene carbonate **4a** with high selectivity (88%) in the absence of solvent (100 mg molecular sieves, 0.0072 mmol DMAP as co-catalyst, 18 mmol epoxide, 6.9 bar, 6 hours at 120 °C).[106] Doskocil has also used titanosilicate molecular sieves for this reaction,[107] however the focus of this work was on the interaction of the carbon dioxide with the ion-exchanged ETS-10 sieves rather than preparatory chemistry and only modest yields were achieved (< 15%).

5.4 Titanium summary

The work of Bai et al using titanocene catalysts is very promising,[102,103] giving essentially quantitative conversion of propylene oxide **3a** to propylene carbonate **4b** in only 15 minutes with 1% catalyst loading without the use of excessive temperature or pressure. However, this method has the disadvantage that both pyridine and, for the fastest reaction, tetrabutylammonium bromide were required which may complicate purification and reduce the atom efficiency of the process.

The use of titanosilicate molecular sieves as catalysts has obvious appeal in terms of recyclability and cost. The use of dimethylaminopyridine as a co-catalyst is however problematic as this is highly toxic.[106] It is to be hoped that further research in this area can overcome these limitations.

Conclusions

The 100% atom–economical reaction between epoxides and carbon dioxide to produce cyclic carbonates has great potential to be a key reaction in a future green chemicals industry. The cyclic carbonate products already have numerous applications and these will surely expand further as the importance of green and sustainable chemistry increases in coming decades. The developments described in this review show that in addition to using 'waste' carbon dioxide as a feedstock, this reaction can be catalysed under mild reaction conditions using catalysts derived only from Earth abundant (strictly Earth crust abundant) metals. All six metals which fit this criterion have been used to catalyse cyclic carbonate synthesis, with particular success being achieved using potassium, aluminium and iron. The remaining challenges in this area include development of sustainable routes to epoxides, more examples of immobilised catalysts suitable for use in flow reactors and more examples of catalysts which tolerate the impurities present in 'waste' carbon dioxide.

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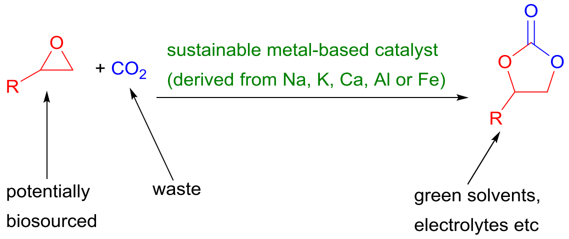
Graphical Abstract



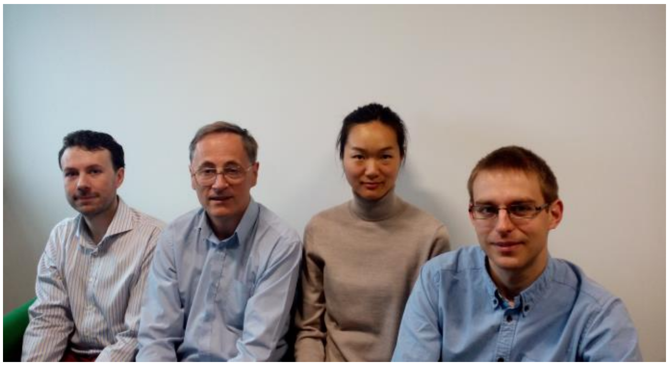
Biographies

James Comerford received his BSc, MRes and PhD from the University of York between 2005 and 2010 and part qualified as a patent attorney in 2012 from the University of Bournemouth. He is a post–doctoral teaching and research fellow at the Green Chemistry Centre of Excellence at York, working on the synthesis of glycerol carbonate from carbon dioxide and glycerol. His research interests cover the development of clean synthetic routes through the utilization of: renewable resources, green solvents and heterogeneous catalysts, as well as by the application of clean technologies including continuous flow, microwave and cold plasma reactors.

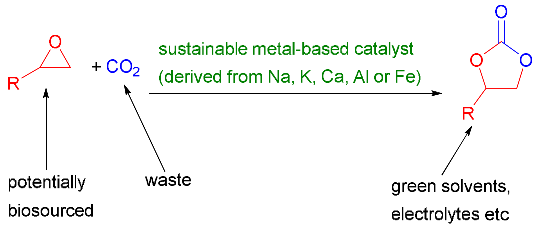
Ian D. V. Ingram graduated from the University of Oxford in 2009 and obtained his PhD in 2013 from the University of Manchester, UK. His PhD research, in Prof. Michael L. Turner's group, concerned the synthesis of state-of-the art semiconducting polymers and their application in unusual planar electronic devices. He briefly worked as a post-doctoral researcher at Manchester, on functional-polymer based electronic sensors, before joining Prof. Michael North's group within Green Chemistry at the University of York in May 2014. His current research is focussed on developing green routes from waste carbon dioxide and biomass to a variety of polymers.

Michael North graduated from Durham University in 1985 and obtained his D.Phil from the University of Oxford in 1988. He then had a two year postdoctoral position at the University of Nottingham before starting his academic career at the University of Wales in 1990. He moved to academic positions at the University of London and Newcastle University before moving to the University of York in 2013 as Professor of Green Chemistry. Professor North won the Descartes Prize in 2001 and the RSC Green chemistry award in 2014. His research interests focus on sustainable catalysis, especially carbon dioxide utilisation.

Xiao Wu gained her PhD at the University of York, supervised by Professor Peter O'Brien. Her doctoral thesis concerned the synthesis of fragrance molecules and the asymmetric synthesis of P-stereogenic compounds using organolithium chemistry. Xiao is currently working as a postdoctoral research associate in Professor Michael North's group on the design and development of both homogeneous and heterogeneous catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide.



From left to right: James Comerford, Michael North, Xiao Wu and Ian Ingram



The synthesis of cyclic carbonates from epoxides and carbon dioxide using sustainable metal–based catalysts is critically reviewed.