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**Comparison of the catalytic potential of  
ionic liquids and heterogeneous metallic  
catalysts to prepare cyclic carbonates  
from carbon dioxide and epoxides**

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## Abstract

The fixation of CO<sub>2</sub> to produce useful chemicals has been studied for a long time. Particularly the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides has been studied extensively. This report has looked at two different types of catalysts and their potential for catalysing the synthesis of cyclic carbonates. One is ionic liquids (IL) and the other is metal containing heterogeneous catalysts. For good selectivity and yield, the reaction should proceed at a pressure of 3 Mpa of CO<sub>2</sub> at 140 °C. The IL catalysts have an anion to promote the reaction and the rate of the reaction increases with nucleophilicity. The reaction speed is higher with IL catalysts than the metallic ones. IL catalysts lose more catalyst when it is regenerated and requires more energy per cycle to separate the product and regenerate the catalyst than metal heterogeneous catalysts. There are ways to mitigate loss and energy consumption to make them more similar. In total IL catalysts due to their higher reactivity seem more promising than metallic catalysts.

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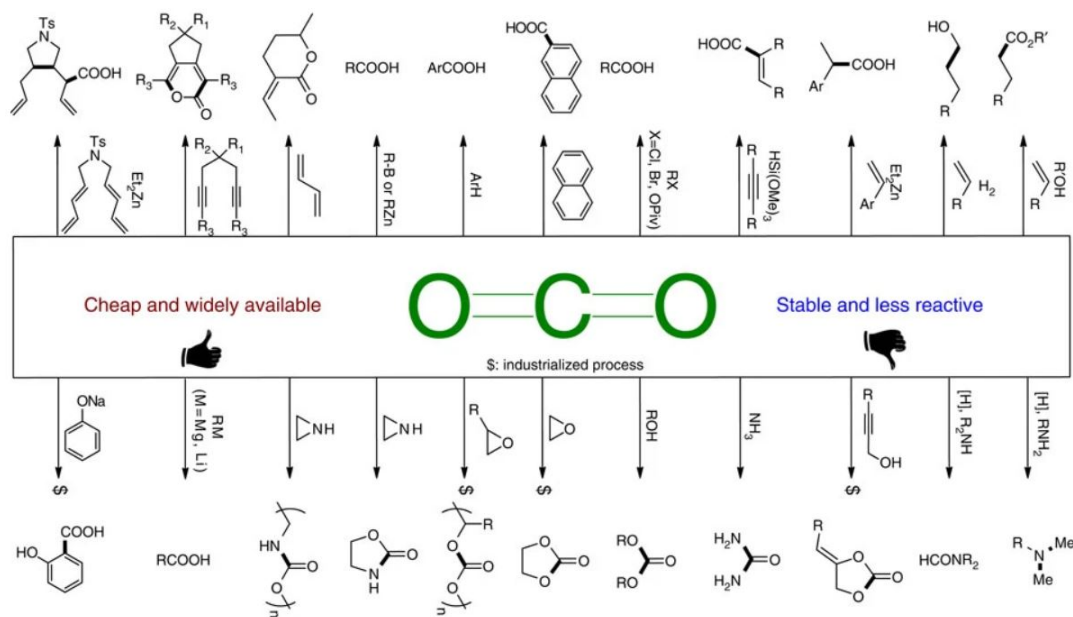
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## Abbreviations

C1	1 carbon
IL	Ionic liquid
LA	Lewis acid
M	Metal
MO	Metal oxide
Cat	Catalyst
MOF	Metal organic framework
DMAPH	4-(dimethylamino)pyridine
[HDBU]Cl	1,8-diazabicyclo[5, 4, 0]undec-7-enium chloride
[N5]Br3	Amino-pyrridinium-pyrrolidinium bromide
BTC	1,3,5-benzenetricarboxylate
Mn-BTC	$[(\text{CH}_3)_2\text{NH}_2][\text{Mn}_3(\text{BTC})(\text{HCOO})_4(\text{H}_2\text{O})]\text{H}_2\text{O}$
TOF	Turnover frequency
TON	Turnover number

# 1 Introduction

In organic synthesis the utilization of carbon dioxide as a 1 carbon (C1) building block is desirable due to its availability in the atmosphere and the fact that most carbon materials come from oil and natural gas which society wants to phase out[1]. Reactions with CO<sub>2</sub> however prove to be difficult due to the fact that CO<sub>2</sub> is a rather inert molecule, so often metallic catalyst which can be expensive or not ideal from an environmental perspective need to be utilized. From a green chemistry perspective it is interesting to look at different potential catalysts with good yields and chemo selectivity so that catalysts with large downsides to the environment or the industry can be phased out. The multitude of potential reactions that CO<sub>2</sub> might be a substrate in are shown in Scheme 1 and of these the reaction between epoxides and CO<sub>2</sub> show promise industrially.



Scheme 1: Shows an overview of the many reaction Schemes in which CO<sub>2</sub> can be a reactant, reprinted with permission from[1].

This report intends to put the focus on the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>. The reaction is often catalyzed by a catalyst that acts both as a Lewis acid and Lewis base[2][3]. Lewis acids are often protons or metals and Lewis bases are generally nitrogen, oxygen or halides[4][5][6]. The metal (M) is often a transition M which can be environmentally harmful like La or Zn[7][8], and often allow for good heterogeneous catalysts because they can be part of a metal oxide (MO) or a metal organic framework (MOF) that are insoluble in the solvent used for the reaction[9]. There are however catalysts that don't need a transition metal though these are not always heterogeneous, but rather homogeneous like ionic liquids (IL) which don't need metals, but they often need a halide or halide containing anion which also is not environmentally the best due to the production of the IL with a halide[10].

It would therefore be interesting to further review the usage and differences between MOF and MO catalysts versus IL catalysts. In this regard it would be interesting to compare the stability and reusability of the different catalysts given the fact that reaction proceeds under quite harsh conditions and decomposition of the catalyst[11]. For IL catalysts this report would like to focus on the catalyst 4-(dimethylamino)pyridine hydrobromide ([DMAPH]Br) and 1,8-diazabicyclo[5,4,0]undec-7-enium chloride ([HDBU]Cl). Two heterogeneous catalysts it would be interesting to evaluate are zirconium oxide doped with lanthanum and a zinc based MOF structure are evaluated[5][6]. Also looking at other similar MOFs to the zinc one with different M might provide further insight into MOF catalysts. With respect to chemo selectivity the main by product is a polymer structure that might form from repeating epoxides and CO<sub>2</sub>[12]. Alternatively the epoxide might further isomerize and hydrolyze[13]. It would also be interesting to look at how to reduce the formation of these byproducts. Another side warranting comparison is the separation of product and catalyst

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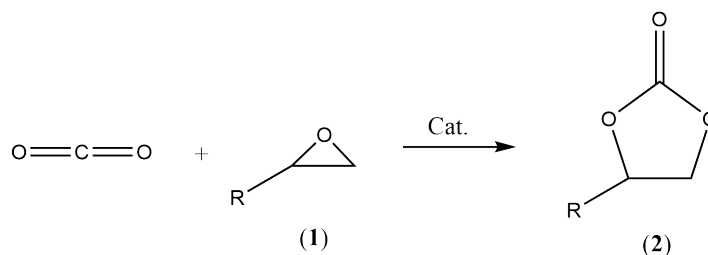
which does differ from heterogeneous and homogeneous catalysts.

## 2 Theory

### 2.1 Synthesis of cyclic carbonates

The general synthesis of cyclic carbonates using CO<sub>2</sub> as a reagent under mild conditions can be tricky due to the fact that CO<sub>2</sub> is an inert molecule that does not have a dipole moment and is in carbon's most oxidized state[1]. The catalysts utilized are often organometallic complexes with transition metals that work as Lewis acids with a supporting halide to promote the reaction or a nitrogen within the MOF to act as a Lewis base[6]. This can often be classified as metal organic framework (MOF). This type of catalyst is either floating freely in solution or connected to a larger heterogeneous network[14][15][2]. One study found that a structure of zirconium oxide doped with lanthanum gave a certain Lewis acid and base structure to promote the reaction[5]. This indicates that the catalyst types can vary a lot but need a good Lewis acid and base[5]. Alternatively ionic liquid or nitrogenous organic compounds in solution with halide counter ions have shown to also work as a catalyst[3][11]. Common for all catalytic systems are that they all utilize a Lewis acid and base interaction to catalyze the reaction.

The general reaction can be described as one CO<sub>2</sub> molecule reacting with an epoxide that can have an aromatic, alkylic or any other sort of side chain, catalysed by a catalyst (Cat), to produce a cyclic carbonate as show in Scheme 2[16][17].



Scheme 2: General reaction between carbon dioxide and epoxide with a catalyst to produce a cyclic carbonate.

For the homogeneous IL catalysts in solution there seems to be two clear mechanisms for how the reaction takes place. There is debate as to which is the primary mechanism but both mechanisms seem possible for these types of catalysts[16][17][4][18]. More details about IL catalysts and the two mechanisms is described in Section 2.2. When the catalyst is a transition metal in an organometallic complex or bound to a silica backbone via oxygen or amines an alternative mechanism where the amine or oxygen acts as a Lewis base and the metal coordinates with CO<sub>2</sub> and the oxygen in the epoxide is proposed[15]. Theory about heterogeneous catalysts is presented in Section 2.3.

### 2.2 Ionic liquid catalysts

The reaction utilizing an ionic liquid catalyst can be seen as the catalyst being homogeneous in solution. A proposed mechanism is shown in Scheme 3[18]. In this Scheme the halide allows a ring opening to occur so that the alkoxide can nucleophilically attack the CO<sub>2</sub> and then back-bite on the carbon bound to the halide to produce a ring[19][20]. Many Schemes from articles do not show the alkoxide of compound **5** attacking the CO<sub>2</sub> but that it just attaches to form compound **6** as show, however one article shows a metallic catalyst where the analogous alkoxide of compound **5** nucleophilically attacks the CO<sub>2</sub> to form a compound similar to **6**[19]. When looking at this proposed mechanism the Lewis acid (LA) would be a proton or tertiary nitrogen in IL[17]. With respect to this reaction the proton can protonate the oxygen in the epoxide promoting ring opening[20][11]. For most of the common catalysts this protonating hydrogen is bonded to a nitrogen that has

a positive charge due to having 4 bonds. An example of this catalyst is [DMAPH]Br (**10**) that is shown in Figure 2 or compound **3** in Figure 1. The epoxide oxygen can be directly bonded to a quaternary nitrogen as shown by compound **4** in Figure 1[3]. The nitrogen often sits within a pyridine like heterocyclic structure which experimentally seems to have higher reactivity than nitrogen structures with less spread charges[13]. This might be due to the delocalization of charges and then increased nucleophilicity of the accompanying halide[18][11].

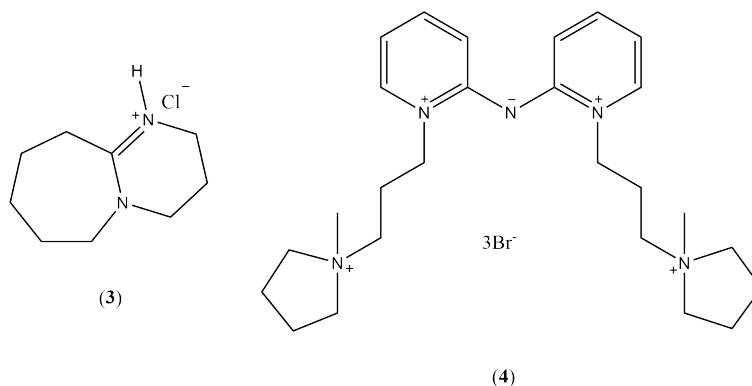
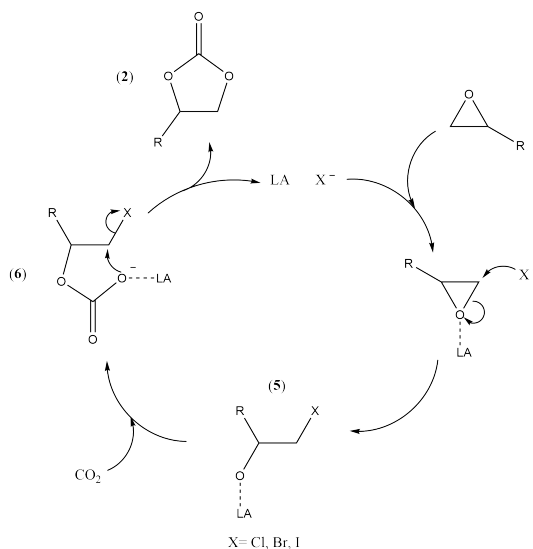


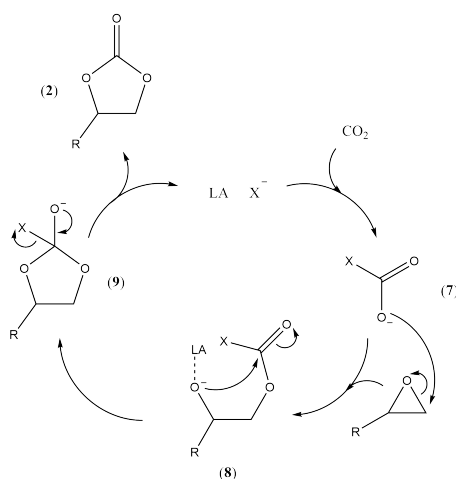
Figure 1: Structure of IL catalysts 1,8-diazabicyclo[5,4,0]undec-7-enium chloride (**3**) and aminopyrrolidinium-pyrrolidinium bromide (**4**).



Scheme 3: General reaction mechanism for homogeneous catalysts[3][11][18]. X is a halide and LA is a Lewis acid part of the catalyst.

There is a secondary proposed mechanism for the fixation of  $\text{CO}_2$  to epoxides as shown in Scheme 4[16][18]. It is thought that both these mechanisms happen at the same time, but that the one shown in Scheme 3 is the primary one. This mechanism differs from the one proposed in Scheme 3 by that the ring opening is instead performed by  $\text{CO}_2$  that has been nucleophilically attacked by a halide anion or halide containing anion to form compound **7**. Schemes from literature often do not show that the halide attacks as a nucleophile but it seems to be the clear mechanism. Then a nucleophilic attack on the backside of the carbonyl produces the cyclic structure. It seems to be a secondary mechanism for the reaction shown in Scheme 2 according to literature[16]. This is because most small nucleophiles directly attack the epoxide and go through the mechanism shown in Scheme 3[21]. Alternatively the existence of compound **7**, according to literature, is determined by a  $\text{CO}_2$  equilibrium and therefore more prevalent at higher pressures of  $\text{CO}_2$ [16].

The reaction to affix  $\text{CO}_2$  to epoxides often needs quite harsh conditions and depends on the catalyst used. Decent yields of cyclic carbonates is reported at temperatures of 80-140 °C and at around 3 Mpa of  $\text{CO}_2$  was used[16][18][11].



Scheme 4: Secondary proposed reaction mechanism for homogeneous catalysts[16][19]. X is a halide or halide containing anion and LA is the Lewis acid part of the catalyst.

One particular IL catalyst that has shown good promise is [DMAPH]Br(**10**) shown in Figure 2. It seems to follow the reaction mechanism proposed in Scheme 3 and mechanism is shown in Scheme 5. It seems to have good selectivity, being reported as 99% and does therefore not produce much of bi products such as polymerized epoxide[11]. It has show good recyclability retaining above 90% conversion over 5 trials[11]. Generally the reaction conditions for the reaction shown in Scheme 2 need harsh conditions, but it has been reported that (**10**) could attain a 92% yield at 99% selectivity when the substrate was styrene oxide and the product was styrene carbonate[22].

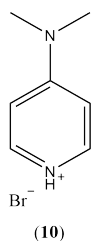
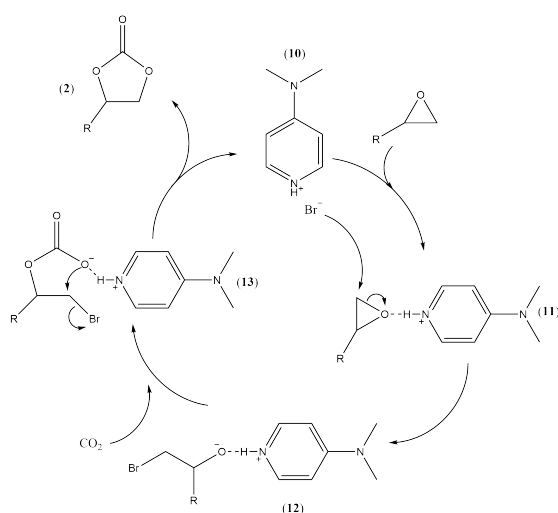


Figure 2: Shows the structure of [DMAPH]Br(**10**).



Scheme 5: Proposed mechanism for the preparation of cyclic carbonates using the catalyst [DMAPH]Br(**10**)[11].



## 2.3 Heterogeneous catalysts

MOFs that act as catalysts are often heterogeneous and can vary a lot in their structure to give more or less selectivity for different products due to pore sizes though since they are comprised carbon-carbon and other organic bonds they are less stable than inorganic structures[23]. When it comes to the reaction for affixing CO<sub>2</sub> to epoxides to produce cyclic carbonates a high temperature and sometimes high pressure is required which limits the types of MOFs that can be used. There are still many MOFs that meet the criteria to catalyze these reactions like Zn<sub>2</sub>(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>)(C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>)(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>3</sub> MOF which is a zinc based MOF catalyst that catalyses the formation of cyclic carbonates[6]. The structure of the zinc based MOF is shown in Figure 3. Since the MOFs that catalyze the reaction shown in Scheme 2 need a Lewis base they often have a nitrogen within the structure to act as this Lewis base. This appearance of nitrogen as a Lewis base is again reinforced by the structure of a manganese based MOF [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Mn<sub>3</sub>(BTC)(HCOO)<sub>4</sub>(H<sub>2</sub>O)]H<sub>2</sub>O (**Mn-BTC**), the structure of which is shown in Figure 3[24].

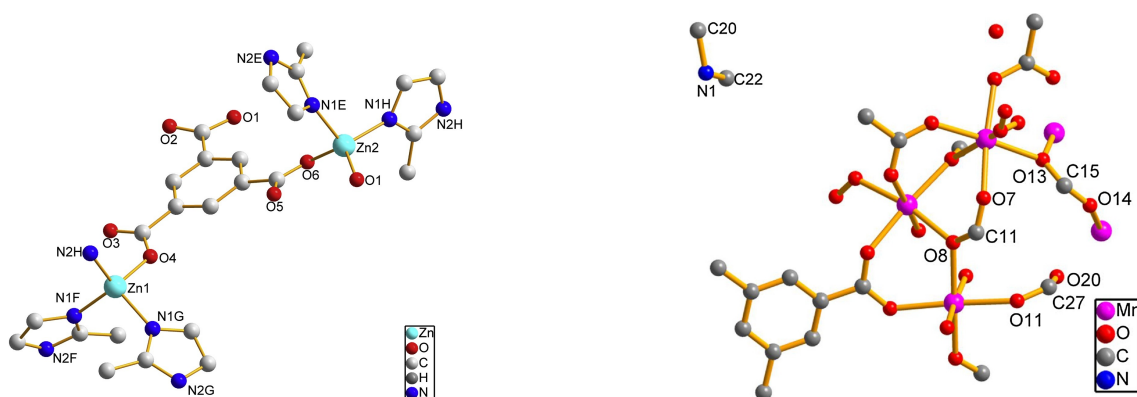
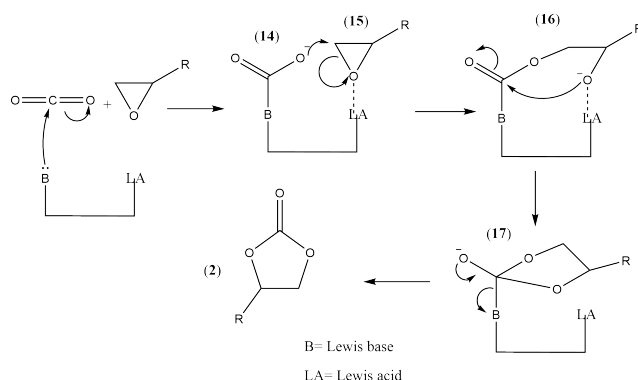


Figure 3: To the left is Zinc MOF monomer reprinted from[6]. To the right is Mn MOF (**Mn-BTC**) monomer reprinted from [24].

When looking at the reaction in Scheme 2 MOFs generally react a bit different from ionic liquids. The reaction instead uses a Lewis base component in the backbone of the framework to assist the metal holding the substrate in this case the epoxide[25][26]. The Lewis base is often a nitrogen as in the case of the Zn<sub>2</sub>(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>)(C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>)(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>3</sub> MOF[6]. This base can then bind to the electrophilic CO<sub>2</sub> to promote the reaction occurring. The mechanism utilizing a metal and nitrogen on the same structure is show in Scheme 6[15]. Here the ring opening is performed by compound **14** attacking the carbon in the epoxide ring of **15** to form compound **16**[2]. This mechanism for the reaction is only valid if halides are not present and the nitrogen is close to the metal in the framework. This is because if halides are present a reaction similar to the one shown in Scheme 3 may happen[2].



Scheme 6: Proposed reaction mechanism for heterogeneous catalysts. B is a Lewis base and LA is a Lewis acid part of the catalyst.

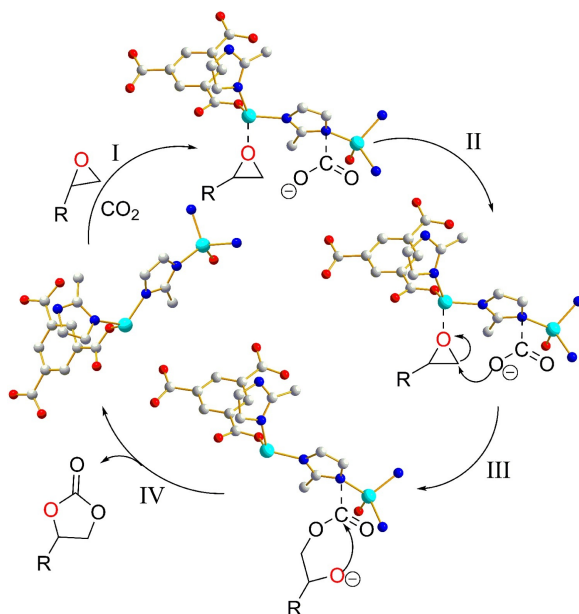
Another type of catalyst that is quite common is a metal oxide structure that has many similar

characteristics to the MOF catalysts[5]. As mentioned earlier a zirconium doped with lanthanum provides acidic sites from  $\text{ZrO}_2$  and basic sites from  $\text{La}_2\text{O}_3$  and it is assumed that this reacts via a mechanism similar if not the same as the one shown in Scheme 6[5]. It is primarily carbon in  $\text{CO}_2$  interacting with oxygen on lanthanum that stabilizes the  $\text{CO}_2$  and the epoxide is stabilized by its oxygen interacting with the zirconium. A similar interaction pattern can be found in other oxides, where two different metals aluminum and magnesium, producing electronegative differences needed for Lewis acid and base interactions[9].

The cyclic carbonates seem to be more thermodynamically stable than the other side products so at high temperatures the reaction from Scheme 2 yields mostly cyclic carbonates rather than polymers[12][6]. Similar to the reaction with IL catalysts, the conditions for the reactions using MOF catalysts are very harsh[2].

The  $\text{Zn}_2(\text{C}_9\text{H}_3\text{O}_6)(\text{C}_4\text{H}_5\text{N}_2)(\text{C}_4\text{H}_6\text{N}_2)_3$  MOF, which used  $100^\circ\text{C}$  and close to 30 atm  $\text{CO}_2$  gas, gave decent yields and recyclability above 90% conversion and above 98% selectivity for five trials with the regenerated catalyst[6]. This specific reaction mechanism is shown in Scheme 7.

The oxides also handled quite high temperatures of  $100\text{-}120^\circ\text{C}$  and 5 atm of  $\text{CO}_2$ . The recycling of the different heterogeneous catalysts mentioned here seem to be quite good, as they were able to be used three times with little loss to yields and catalytic potential[6][5][9]. The catalyst **Mn-BTC** which is similar to the  $\text{Zn}_2(\text{C}_9\text{H}_3\text{O}_6)(\text{C}_4\text{H}_5\text{N}_2)(\text{C}_4\text{H}_6\text{N}_2)_3$  MOF was simply washed with water and alcohol to remove organic material but lost about 10% yield from trail 2 to 3[24].

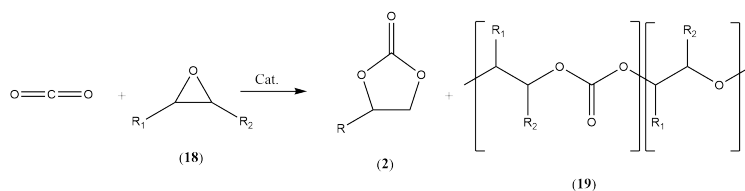


Scheme 7: Zinc MOF Scheme reprinted with permission[6].

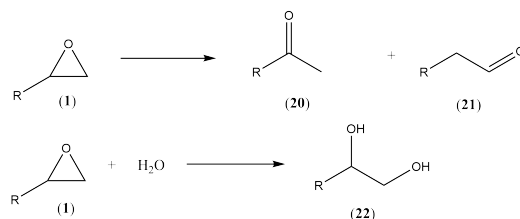
## 2.4 Side reactions

The fixation of  $\text{CO}_2$  to epoxide has some notable side reactions which are the formation of a polymer with ether and ester bonds as shown in Scheme 8[19], and epoxide isomerization giving **20** and **21** and hydrolysis giving **22** as shown in Scheme 9[13]. The selectivity of the cyclization of epoxides is affected by the type of IL and whether the catalyst is protonated like  $[\text{DMAPH}]\text{Br}$  or  $[\text{HDBU}]\text{Cl}$  and it favors the formation of cyclic carbonates rather than the polymer shown in Scheme 8[12]. For both heterogeneous and homogeneous catalysts the increase in temperature promotes the cyclization due to the cyclic carbonates being more thermodynamically stable and potential depolymerization to produce cyclic carbonates from polymer[14][6][5].

If there is no Lewis base co-catalyst present to act as a nucleophile the reactivity is quite low at a turnover frequency (TOF) of  $4\text{ h}^{-1}$ [12]. For IL the counter ion can be acetate to avoid the use



Scheme 8: Shows the reaction for production of polymer from epoxide and CO<sub>2</sub>[19][12].



Scheme 9: Shows isomerization and hydrolysis of epoxides[13].

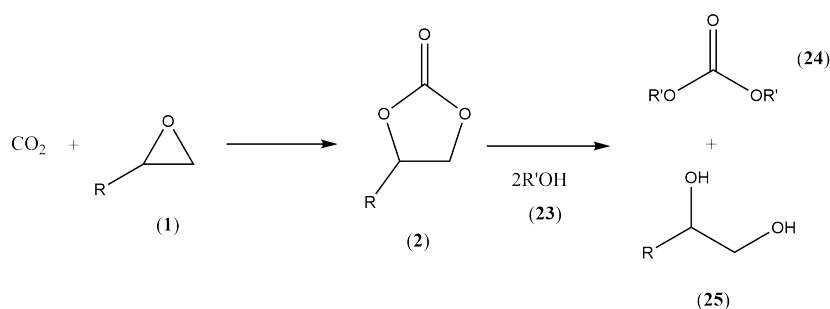
of halides and it has good yield and selectivity at 86% and 90% respectively[13]. Both selectivity and yield of the reaction shown in Scheme 2 increase with the catalyst amount, but more than 1% mol catalyst has a diminishing effect. It is shown that if the reaction is allowed to run for longer reaction time it will favor the formation of cyclic carbonates if the reaction is occurring between 120 and 150 °C which is attributed to it being more stable than the polymers that can form from CO<sub>2</sub> and epoxides[13]. The pressure of CO<sub>2</sub> will also affect the potential yield of the reaction[6][5][13]. There seems to be an optimal pressure for each catalyst, but it seems generally to be around 3 MPa. Too low pressure means low activity and other things than product is produced. Too high pressure makes too few available active seats so yield again falls. Alternatively the optimum has been attributed to the super critical pressure of CO<sub>2</sub>[14].

The type of epoxide also seems to affect the yield of the reaction shown in Scheme 2[12][13][11]. It seems that the more electron withdrawing the R group of an epoxide like compound **1** has the more reactive it is. A mono chlorinated methyl side group has better yield than a methyl one, 99% vs 97%. A phenyl side group has lower yield than a methyl group, 87% vs 97%. If both oxygen bonded carbons on the epoxide have a side group like in cyclohexene oxide, the yield will be very low at 19%.

### 3 Discussion

The study of catalysts for cyclic carbonate synthesis from epoxides and CO<sub>2</sub> has been ongoing for a couple of decades and therefore a lot of the articles cited in this text are review articles, but some are of course research papers since there are so many catalyst types[1]. This implies that the credibility is decent due to the fact that the data being referenced in the articles has been looked over by multiple scientists and deemed good enough to be include in a review article.

The synthesis of cyclic carbonates can be utilized as a step in a further synthesis of other carbonates and alcohols as shown in Scheme 10[14]. Epoxides can easily be converted to diols with water and a Lewis acid as a catalyst[27]. So cyclic carbonate synthesis as part of a synthetic pathway is much more interesting for the production of various carbonates by varying the alcohol that is compound for the reaction in Scheme 10. The choice of **23** does not affect the diol that is produced, but rather the R groups attached to the carbonate in compound **24**. This gives the synthetic pathway good selectivity for the acyclic carbonate being synthesised. The synthesis of other non cyclic carbonates might be interesting for varying chemical properties like solubility, boiling point, stability or perhaps a halide free carbonate[4]. This is because epoxide **1** used to synthesize the carbonate might have chlorinated side groups since this provides better reactivity for the synthesis of **2**[13].



Scheme 10: Shows synthesis of non cyclic carbonates form epoxides and  $\text{CO}_2$ [14].

Broadly two types of catalysts have been highlighted in this article, those with a metal or metallic ion and those without. The non metallic catalysts have all been of the type IL and the metallic have been a doped oxide and two types of MOFs with zinc and manganese as metals. These have all been shown to have yields close to 100% and selectivity's above 90%[6][24][5][12][13][11]. This seems to be mostly due to using high temperatures around 120-140 °C and the good thermodynamic selectivity of cyclic carbonates being produced form the reaction shown in Scheme 2. This high temperature gives almost no polymer side product since it is converted to cyclic carbonates at high temperatures[14]. It therefore seems that for good yields the focus should be on selecting a reactive epoxide with an electron withdrawing side group.

For further optimization it seems that the cyclization reaction is decently affected by the pressure of  $\text{CO}_2$ . This pressure optimum varies but tends to fall around 3 Mpa for most catalysts and activity slowly decreases at higher pressures and the reactivity is quite low if the pressure is low at under 0.5 Mpa[13]. At low pressure it seems that this can be mostly attributed to the  $\text{CO}_2$  not filling all the active sites and giving poor reactivity. At higher pressures there seems to be two differing explanations. One is that the high pressure makes the  $\text{CO}_2$  occupy the active sites and hinder the reaction[6]. The other explanation is that the  $\text{CO}_2$  enters a supercritical state and interacts poorly with the catalyst giving low reaction rates[14]. The supercritical explanation seems somewhat faulty because the optimum for most reactions has been around 3 MPa and  $\text{CO}_2$  does not enter a super critical state until 7.38 MPa[28]. At very high pressures the supercritical state of  $\text{CO}_2$  might explain a lowered reactivity but since it starts decreasing long before the super critical conditions this feels like a lacking explanation.

The reactivity is also affected by the accompanying nucleophile and the reactivity seems to increase with nucleophilicity as the backside attack to form **5** via Scheme 3 is a nucleophilic attack and is the rate determining step[20]. Mostly data supports the increasing size of anions to give more reactivity[11][20] and this is probably due to the environment being protic giving lower nucleophilicity to smaller anions. An older data set[16] concludes that smaller anions are more reactive, but seeing as in that report the environment is aprotic the general conclusion that reactivity increases with nucleophilicity stands. Since Scheme 4 also has a nucleophilic attack to produce **7** it should follow the same trend.

Many of the articles that have been studied for this report describes reactions at an analytical scale (mmols) rather than an industrial scale. It is therefore important to evaluate larger reaction batches. This is relevant because the ultimate goal is to stop relying on petroleum based carbon for organic synthesis[1]. This seems utopian today, but it highlights the importance of improving the reaction because for  $\text{CO}_2$  based organic compounds to compete with petroleum based ones it needs to be cheap, fast to produce and low in energy consumption. A higher TOF is therefore desirable because this is needed in order to be scaled up to an industrial level. The less time the reaction has to run, the cheaper the production is and less energy is needed to maintain the 140 °C needed for the reaction.

Interestingly, one point in which IL and metallic catalysts do diverge is the rate of the reaction or the TOF[29]. Generally the TOF of IL appears to be larger or equal to other heterogeneous metallic complex catalysts and oxide catalysts[14]. The TOF for IL is often 1000  $\text{h}^{-1}$  or above and have large electron donating side groups, and also often the side group expands the conjugated

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system connected to the nitrogen that acts as a Lewis acid. For the oxides and metallic complexes some have TOFs above  $1000 \text{ h}^{-1}$  if they utilize zinc or aluminum, but else the TOF is quite low. This shows a greater potential for catalysis when utilizing ILs, but they often use halides and are homogeneous. Heterogeneous catalysts are often better for industry since they are more recyclable and much easier to recover due to being in separate phases. An important point to raise is the comparability of TOF values as it is attained by the turnover number (TON) value which is relative to the amount of catalyst. The comparison of TOF data is tricky because it depends on amount of catalyst being used. This can easily be accounted for by looking at TOF data where similar amounts of catalyst mol percent wise is being used. This has been taken into account when looking at the data so the conclusion made above should still be valid.

Good reaction rates are of course desirable, but after the reaction is finished the components have to be separated. It is therefore productive to discuss how the separation of the product and catalyst varies for the two types of catalysts. In general it seems that the way to separate and clean heterogeneous catalysts is much easier as they are solid and do not mix with the product or reactant phases which are most often liquid at room temperature or a bit above. This lack of mixing between the phases allows for just draining the end product and centrifuging to regain the catalyst[6][30]. The catalyst can then be washed and some loss might have occurred, but empirically it seems to be low, at less than 10% over 5 cycles. This is in contrast to using homogeneous catalysts where the phases don't separate nicely so one of multiple energy consuming separation techniques have to be utilized. For this IL catalyst separation there seems to be 3 types which are distillation, and liquid-liquid extractions with either water or alcohols. The normal distillation is an energy intensive process due to the heating requirements and potential loss of energy through cooling[31]. The more promising techniques seem to be the liquid-liquid extractions which need much less energy, but since it is an extraction technique the selection of IL and what product is being made is very important to optimize the alcohol being selected for the extraction. The energy needed for water seems to be greater than when using alcohols so this makes the alcohol extraction more favorable. When using water only the IL and product can be changed so it also more limiting and the alcohol separation seems wholly more productive. Example wise utilizing water liquid-liquid extraction gave only about 10% loss of catalyst over 5 runs[11].

Another prominent aspect to evaluate is the environmental impact of the different catalysts. A macro scale analysis show that an industrial scale production of polypropylene carbonate and cyclic propylene carbonate has a net negative carbon imprint[30]. An important thing to note is that this does not account for the carbon imprint of the IL and propylene oxide production so whether the process is totally carbon negative is something to be sceptical of. As discussed the recycling of catalyst and refinement of product has a lot simpler procedure if the catalyst is heterogeneous. This is often done with metals through MOFs, oxides or metallic complexes. From a green chemistry perspective this is not favorable as many of the catalytically active metals like zinc or nickel are bad for the environment. Notably as can be seen in Scheme 7 certain MOFs have the potential to not need external nucleophiles. These nucleophiles are often halides which makes the choice of catalyst a trade off to some extent. This is assuming that the IL is using a halide, but in that case it would be weighing the environmental impact of producing halide containing ILs vs metals. The TOF data[14] indicates that IL systems are more reactive and to this extent a perhaps more optimal and more green catalyst is the one which an IL structure is attached to a non reactive backbone like a polymer. This would give it a heterogeneous character and ILs are generally cheap so from an industrialisation perspective it does hold merit.

Looking at the temperature varying data set for the Mn-BTC and the zinc MOF their yields both peak at about  $100 \text{ }^\circ\text{C}$  and it decreases rapidly if temperature increases[6][24]. The articles attribute this to the release of water which hydrolyses the epoxide as shown in Scheme 9. This might be a phenomenon unique to these MOFs as they are quite similar, but still it indicates that certain MOF structures have problems working at high temperature.  $100 \text{ }^\circ\text{C}$  might be a bit low for optimal yields and selectivity when looking at the desired conditions for the reaction. IL catalysts don't show any specific decomposition or loss of catalytic activity at relevant reaction temperatures.

Since metallic catalysts are still interesting due to their ease of being made heterogeneous, it is interesting to look at less toxic metals that might be used in catalysts. In this regard aluminum catalysts show great promise due to good reactivity if the right conditions and Lewis base is

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used[14]. This avoids many of the environmental issues associated with metals as catalysts seeing as though aluminum is not the most harmful metal. Also from a cost perspective aluminum is cheap and mass produced so cost wise it is decent. As a catalyst it is interesting because it shows potential for good reactivity if the right conditions and Lewis base is used[14].

If an IL based catalyst is used it is preferable to use halide free catalysts mostly from an environmental prospective, but the potential for use of different Lewis bases might give rise to cheaper alternatives since small nucleophiles can be a byproduct of many reactions. Like acetate which has shown good potential as a halide free replacement[13]. One interesting aspect to note is that larger halide containing anions that act as a Lewis base tend to react via the mechanism shown in Scheme 4. As discussed this mechanism might favor higher pressures of CO<sub>2</sub> due to equilibrium properties of compound 7. This might mean that if carboxylate groups are used as Lewis bases the pressure might have to be increased compared to halides for good yields. Though that is speculative so many non halide nucleophiles should be tested for pressure optimums and general yield to find suitable replacements to halides.

## 4 Conclusion

Both metallic and IL catalysts show good reactivity, but it seems that ILs might perform slightly better. They both have environmental issues, for ILs it is finding non halide nucleophiles to act as Lewis bases and for metallic catalysts the point of interest is finding metals that impact the environment less. Over all though it would seem that since ILs are more reactive it would be more interesting to find halide free nucleophiles since ILs are quite cheap and readily available. The reaction can regardless of the catalyst have above 90% yield and selectivity if temperature is 120-140 °C and the pressure around 3Mpa. Using a more nucleophilic anion increases reactivity. It seems that ILs hold up better at higher temperatures than MOFs due to their high stability. Oxides also seem quite stable at higher temperatures. For separation it seems that heterogeneous catalysts perform better for catalyst loss and energy consumption. Given this it might be interesting to develop heterogeneous IL catalysts that are also halide free.

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