

Greenhouse Gas Conversion by Homogeneous Salen Catalyst Systems under Very Mild Reaction Condition

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One of the main scientific challenges in the 21st century is the global warming due to the increasing level of carbon dioxide.¹ The consumption of fossil fuels is continue to increase with emitting substantial amount of green house gas.² The solution currently considered is capturing and storing of carbon dioxide which compressing carbon dioxide and then storing it into oil wells or under the ocean.³ The other solution include converting the carbon dioxide into useful chemicals with significant commercial demand,⁴ but low chemical reactivity of carbon dioxide restricts the chemical reactions.

One of the facile reactions of carbon dioxide includes inserting carbon dioxide into epoxides to generate cyclic carbonates or a polycarbonate.⁵⁻⁷ Several olefin cyclic carbonates were manufactured commercially and reduced atmospheric carbon dioxide up to 120 million tons per year if the process designed economically.³

Salen aluminum complexes were developed for the synthesis cyclic carbonates,⁶ which have an axial aluminum chloride and could effectively catalyze the reaction between carbon dioxide and epoxides to form cyclic carbonates. Porphyrin complexes were designed at the beginning but the preparation of salen complex is much easier and less expensive.⁷

This research include the preparation of several aluminum-Salen complexes and modification of the amount of moisture and ammonium salt for searching the optimum condition under ambient temperature and atmospheric pressure. Moisture and ammonium salt could function as a co-catalyst at the cyclic carbonate forming reaction.

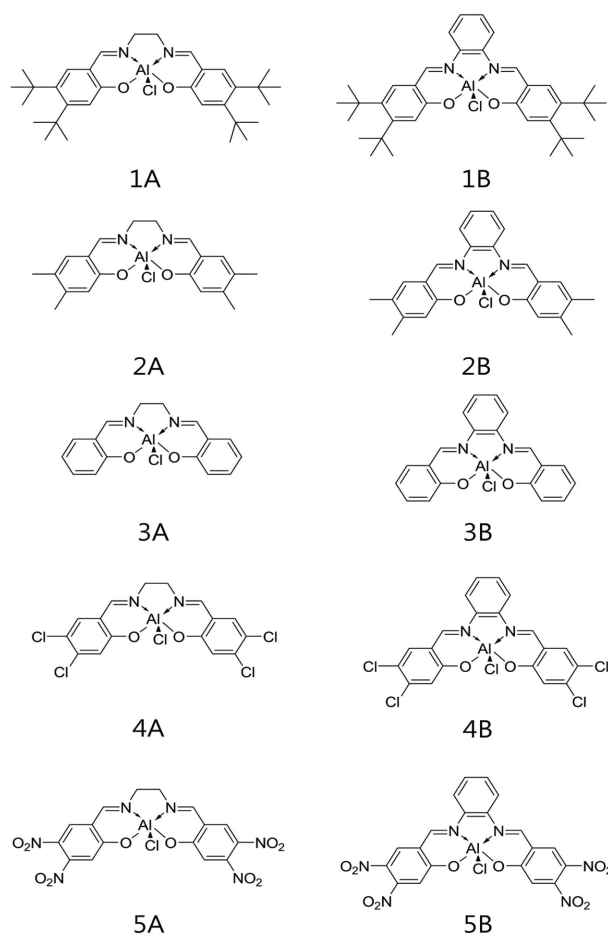
After the reaction complete, the product was examined with GC/MS analysis. The product cyclic carbonate was detected with the TOF more than 60 and the resulting catalyst was continuously recycled. The catalyst reactivity maintained more than 5 days.

It is apparent that adding moisture significantly increased

the conversion TOFs (Fig. 2). Also addition of ammonium salt increased the conversion efficiency significantly.

Without using the salen complex did not make any product. This means moisture and ammonium salts are co-catalyst which help the function of salen complex.

Salen complex to tetrabutylammonium bromide ratio



Scheme 1. Synthesized salen aluminum complexes attached with various functional groups.

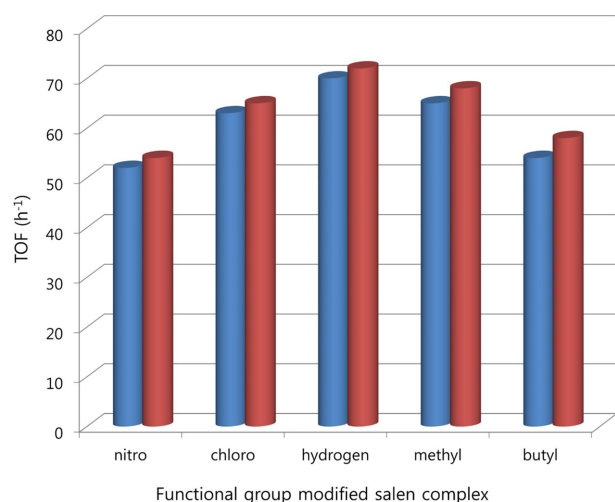
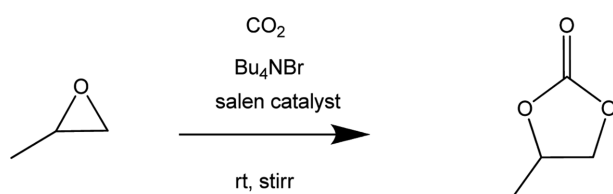


Figure 1. Results of cyclic carbonate synthesis using modified salen aluminium catalyst (the functional group number is the same as entry number as shown in Table 1).



Scheme 2. Experimental scheme for cyclic carbonate synthesis using carbon dioxide.

Table 1. Results of cyclic carbonate synthesis using modified salen aluminium catalyst

Compounds	TOF (h ⁻¹)	Catalyst and ammonium salt amount (mol%)	Water amount (mol%)
1A	52	5	2.5
1B	54	5	2.5
2A	63	5	2.5
2B	65	5	2.5
3A	70	5	2.5
3B	72	5	2.5
4A	65	5	2.5
4B	68	5	2.5
5A	54	5	2.5
5B	58	5	2.5

^aCarbon dioxide bubbling at the flow rate of 50 ml/min at 24 h and the product was determined by GC-MS analysis

was investigated (Fig. 2b). The amount catalyst 3B was fixed at 5 mol% and the amount of tetrabutylammonium bromide was varied 0–5 mol%. The results indicate that at least same mol% of both catalyst and ammonium salt is required to reach maximum catalytic performance. The highest TOF appeared when catalyst 1B and co-catalyst

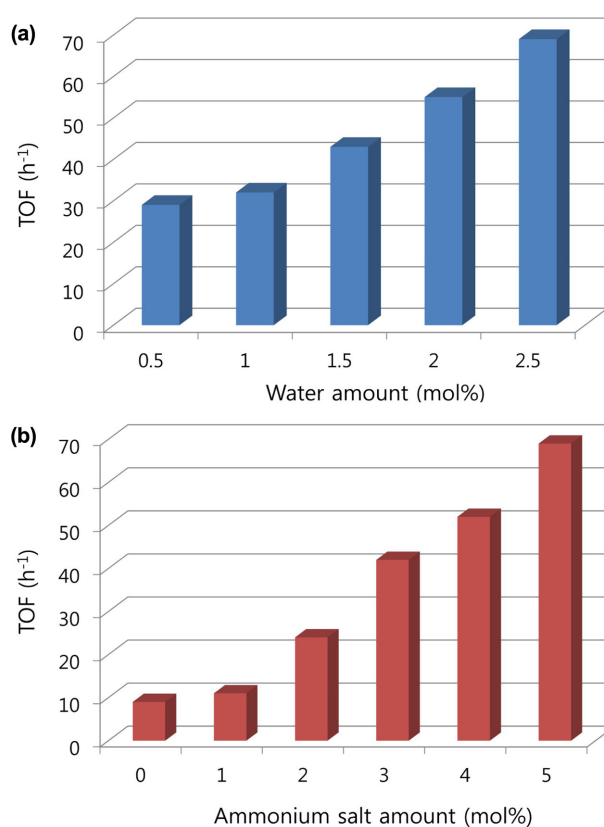


Figure 2. (a) Cyclic carbonate yields by modification of the water amount. (b) Cyclic carbonate yields by modification of the ammonium salt amount.

combination of salen complex : moisture : ammonium salt = 1:1:1.

Since salen complexes and *n*-Bu₄NY are easily dissolved in propylene oxide, the catalyzed reaction between CO₂ and epoxides does not require any solvent. No by-product such as polycarbonates or polyester was detected at the GC/MS analysis. However, in the absence of the quaternary ammonium salt, the polycarbonates (1730 cm⁻¹ in FTIR) and propylene carbonate were formed with a very low rate at room temperature. For catalyst 3b alone, neither propylene carbonate nor polymer formed. It is important to note that these quaternary ammonium salts by themselves showed no catalytic activity under the mild conditions. A rate conversion profile (TOFs) for the transformation of reactant to product indicated that the complex salen-ammonium salt system showed 700-fold rate enhancement and 200-fold rate enhancement by adding moisture. The results indicate a synergistic effect in the formation of propylene carbonate from CO₂ and propylene oxide by salen catalyst in conjunction with a quaternary ammonium salt and moisture. Mechanistic investigation on the acti-

Table 2. Results of cyclic carbonate synthesis using several salts and catalyst 3B

Anion salt	TOF (h ⁻¹)	Salen and salt amount (mol%)	Water amount (mol%)
<i>n</i> -BuNI	72	5	2.5
<i>n</i> -BuNBr	68	5	2.5
<i>n</i> -BuNCl	55	5	2.5
KI	20	5	2.5
KBr	18	5	2.5
KCl	11	5	2.5
BMIMBF ₄	15	5	2.5
BMIM PF ₆	18	5	2.5

^aCarbon dioxide bubbling at the flow rate of 50 ml/min at 24 h and the product was determined by GC-MS analysis

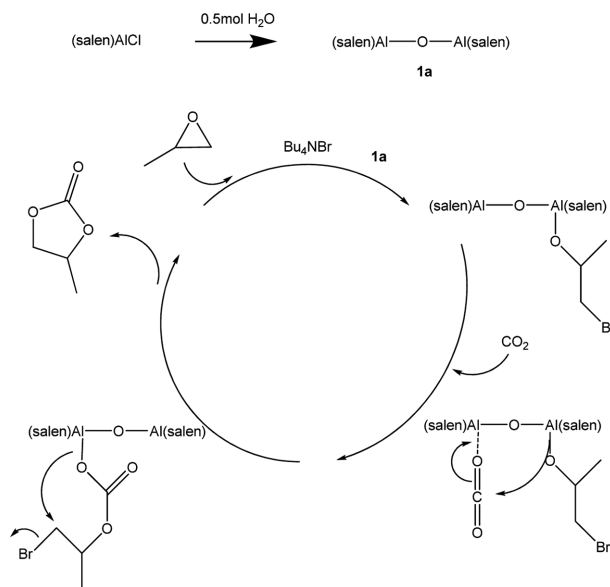
vation of CO₂ and epoxides in the presence of the catalysts are currently in progress by femto second Raman spectroscopy. This catalyst system can operate very efficiently even at low temperature of 298K and atmospheric pressure of CO₂ environment.

The anion of salt significantly affected the catalytic activities of the salen catalysts (Table 2). Especially quaternary ammonium halide showed a considerably high activity probably due to having moderate nucleophilicity and high leaving ability. Either potassium salts or ionic liquids did not exhibit any high reactivity under the same condition.

Although KI or KBr anion has higher nucleophilicity, salen-ionic liquid system showed very low activity probably due to low leaving ability of the anion. When the anions have not strong nucleophilicity, such as BMIM BF₄ or BMIM PF₆, have high leaving ability, salen-ionic liquid systems showed very low reactivity.

Several salen complexes with varying substituent groups on the aromatic rings were investigated as catalysts for the coupling of CO₂ and PO (Fig. 1). Complex 3B exhibited the highest catalytic activity in these catalysts and is 20% better active than either nitro or tert-butyl group attached one. The order of the activity is not consistent with the order of electrophilicity of these aluminum complexes. The results indicate that the neutral electronic ability and the sterically less clouded one affect the catalytic properties. The bridged phenyl ring could not help the reactivity. The structural flexibility might affect the performance of catalysts because the ethyl group would be more flexible than phenyl group.

Catalytic reaction mechanism is represented (Scheme 3). Exactly 0.5 mol amount of moisture enhanced the maximum catalytic reactivity. This means that the moisture reacts - with the salen aluminium chloride to form dimer.

**Scheme 3.** Possible catalytic reaction mechanism.

This oxo bridged dimer (1a) is participated into the reaction. Ring opening of the epoxide by aid of bromide ion results in aluminium bound alkoxide. Then the carbon dioxide is coordinated on to the other aluminium ion, followed by intramolecular electron transfer to make carbonate. Finally the cyclic carbonate is detached from aluminium complex and the detached bromide ion is recycled.

CONCLUSION

Homogeneous salen catalyst systems were investigated for the conversion of greenhouse gas into cyclic carbonate under room temperature and atmospheric pressure. Salen complexes were more active than salophen complexes. Neither electron withdrawing nor donating group showed lower conversion efficiency. Co-catalysts such as moisture or ammonium salt increased the conversion efficiency dramatically. These results have potential to decrease carbon dioxide emitted from fossil fuel combustions under mild condition.

EXPERIMENTAL

Propylene oxide was heated at reflux over a mixture of KOH and CaH₂ and fractionally distilled under a nitrogen atmosphere. CO₂ was purified by passing through a column packed with 4 molecular sieve before use.

Modified salen ligands were synthesized by a single-step Mannich condensation between the phenylene diamine,

ethylene diamine, formaldehyde and the substituted phenol.^{8,9} The synthesized salen compounds are shown in *Scheme 1* the structures of synthetic compounds are confirmed with the spectroscopic data.^{8,9}

The Schiff base aluminum complexes were prepared by the reaction of the corresponding free bases with Et₂AlCl according to the literature methods.^{8,9} These complexes are all sensitive to air or moisture and should be stored in a nitrogen atmosphere. The coupling reaction with epoxide was carried out in a 50 ml test tube with CO₂ bubbling at 50 ml/min (*Scheme 2*).

In a typical procedure, to a test tube (50 ml) were added salen catalyst (5 mol%) and *n*-Bu₄NY (5 mol%) under dry nitrogen. Propylene oxide (50 ml) and water (5 mol%) were introduced and CO₂ gas was bubbled for 24 h at 50 ml/min. The remaining mixture was degassed and fractionally distilled under reduced pressure to afford pure cyclic carbonates.

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REFERENCES

1. Arkawal, H. *Chem. Rev.* **2001**, *101*, 953.
2. Xiaoding, X.; Moulijin, J. A. *Energy Fuels* **1996**, *10*, 305.
3. Aresta, M.; Dibenedetto, A. *Catal. Today* **2004**, *98*, 455.
4. Omae, I. *Catal. Today* **2006**, *115*, 33–52.
5. Coates, G. W.; Moore, D. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6618–6639.
6. Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. *Acc. Chem. Res.* **2004**, *37*, 836–884.
7. Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155–174.
8. Peri, D.; Meker, S.; Manna, C. M.; Tshuva, E. Y. *Inorg. Chem.* **2011**, *50*, 1030–1038.
9. Peri, D.; Meker, S.; Shavit, M.; Tshuva, E. Y. *Chem. Eur. J.* **2009**, *15*, 2403–2415.