

Multi- metal cyanide와 이온성 액체 혼합 촉매를 이용한 allyl glycidyl ether와 CO₂로부터 cyclic carbonate의 합성

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Synthesis of Cyclic Carbonate from Allyl Glycidyl Ether and Carbon Dioxide Using Mixed Catalysts of Ionic Liquid and Multi-metal Cyanide

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Introduction

The reactions of carbon dioxide with oxiranes leading to five-membered cyclic carbonates are well-known among many examples. These cyclic carbonates can be used as aprotic polar solvents, electrolytes for batteries and sources for reactive polymer synthesis [1].

Double metal cyanide complexes(DMC) catalysts were discovered in the decade of the 1960s, and were found to have significant catalytic activity in a variety of reactions, particularly polymerizations. Recent improvements have made double/multi metal cyanide catalysts much more attractive for commercial manufacture of polyoxypropylene polyols[2-6].

Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted [7]. Room temperature ionic liquids have negligible vapor pressure, excellent thermal stability and special characteristics in comparison with conventional organic and inorganic solvents. Many reactions catalyzed with ionic liquids and showing high performance have been reported [8]. In particular, ionic liquids based on imidazolium cations and chloroaluminate anions, such as 1-butyl-3-methylimidazolium aluminium chloride ([BMIm]Cl/AlCl₃), have attracted growing interest in the last few years [10,11]. More recently, propylene carbonate has been synthesized from CO₂ and propylene oxide with 1-butyl-3-methylimidazolium (BMIm) salt ionic liquid [7].

In the present work, ionic liquids of different alkyl groups and different anions were used to understand the catalytic role of the ionic liquids. The mixed catalysts of multi-metal cyanide(MMC) and the ionic liquid were also studied for the cycloaddition of carbon dioxide to allyl glycidyl ether (AGE).

Experimental

Allyl glycidyl ether (purity; 99 %) was purchased from Aldrich. Ionic liquids based on 1-ethyl-3-methylimidazolium (EMIm), 1-butyl-3-methylimidazolium (BMIm) and 1-hexyl-3-methylimidazolium (HMIm), 1-octyl-3-methylimidazolium (OMIm) with different anions such as Cl⁻, BF₄⁻, PF₆⁻ were prepared according to the procedures reported previously. The purities of

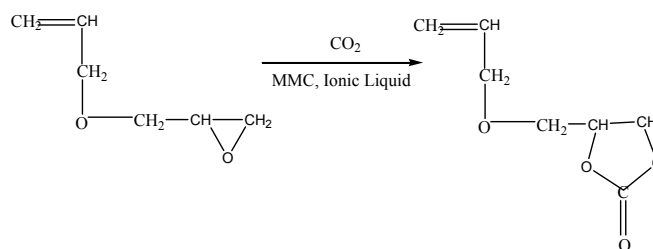
all the ionic liquids were over 96 % and the carbon dioxide (purity; 99.99 %) was used without further purification.

Quaternary ammonium salts were purchased from Aldrich and used without further purification. Typical multi-metal cyanide complex(MMC) catalyst with complexing agent (CA, tertiary butyl alcohol) has been prepared according to the literature procedures[9]. A solution of $ZnBr_2$ (220 mmol) dissolved in distilled water (115 mL) and $tBuOH$ (21 mL) is taken in the first beaker (solution 1). $K_3[Co(CN)_6]$ (0.01 mol) and $K_3[Fe(CN)_6]$ are dissolved in distilled water (42 mL) in the second beaker (solution 2). The third beaker contains a mixture of distilled water (1 mL), $tBuOH$ (20 mL) and polytetramethylene ether glycol (PTMEG, Mw = 1800, 3.5 g) (solution 3). Solution 2 is added to solution 1 dropwise for a period of over 60 min. at 50 °C with continuous mixing using a mechanical stirrer. Solution 3 is then added and the mixture is stirred for an additional 3 min. The mixture is centrifuged. The resulting catalyst cake is dried at 60 °C under vacuum (30 inHg) to a constant weight. The synthesis of cyclic carbonate from allyl glycidyl ether (AGE) and CO_2 using MMC and ionic liquid was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, MMC(20 mg) and ionic liquid (0.5 mmol) and allyl glycidyl ether (40 mmol) were charged into the reactor without solvent, and then purged several time with CO_2 . The reactor was then pressurized with CO_2 to a present pressure, at 120 psig (8.2atm) for batch operations, at room temperature. The reactor was heated to a desired temperature, and then the reaction was started by stirring at 300 rpm. The reactor pressure increased about 5 - 15 psia due to vapor pressure of the reactants depending on the reaction temperature.

The product was analyzed by a gas chromatograph (HP 6890N) equipped with a FID and a capillary column (HP-5,5% phenyl methyl siloxane). The identification of the five-membered cyclic carbonates was performed by FT-IR (ASI Model 1000, KBr).

Result and Discussion

The cyclic carbonate was synthesized from AGE and carbon dioxide using MMC and various ionic liquid catalysts under carbon dioxide pressure as shown in Scheme 1.



Scheme 1. Synthesis of cyclic carbonate from AGE and CO_2

The catalytic activity of ionic liquids usually depends on the corresponding catalyst cation and counter anion [10,11]. In order to understand the effects of cation structure on the conversion of AGE, the mixed of MMC and 1-alkyl-3-methylimidazolium salt or quaternary ammonium salt of different alkyl groups and anions were used at 50 °C and CO_2 pressure of 120 psig for 6 h. Table 1 summarizes the effects of ionic liquid structure on the conversion of AGE.

The order of the allyl glycidyl ether conversion increased as the size of the cation of the imidazolium salt ionic liquid increased from $EMIm^+$ < $BMIm^+$ < $HMIm^+$. Conversions for quaternary ammonium salt also increased in the order of TPA^+ < TBA^+ < THA^+ < TOA^+ . However, for TDA^+ and $OMIm^+$, the decomposition of the cyclic carbonate to AGE occurred and the conversion of AGE decreased.

The conversion of AGE increased in the order of $\text{PF}_6^- < \text{BF}_4^- < \text{Cl}^-$, which is consistent with the order of the nucleophilicity of the anions. More nucleophilic anion will be easier to attack the epoxide ring to form reaction intermediate. However, BMImBF_4 showed no activity for the reaction of AGE and CO_2 at $50\text{ }^\circ\text{C}$, 6 h. Bulky ionic liquid, having longer distance between cation and anion, may be considered to have higher anion activation ability. This explains why they are more effective in nucleophilic attack of the anion to the oxirane ring of AGE.

Table 1. Effects of structure of ionic liquid on the conversion of AGE.

Run	Catalyst	Temp ($^\circ\text{C}$)	Time (h)	Pressure (psig)	Conversion (%)
1	Zn-Co-Fe(III)MMC +EMImCl	50	6	120	10.8
2	Zn-Co-Fe(III)MMC +BMImCl	50	6	120	25.5
3	Zn-Co-Fe(III)MMC +HMImCl	50	6	120	38.7
4	Zn-Co-Fe(III)MMC +OMImCl	50	6	120	26.0
5	Zn-Co-Fe(III)MMC +BMImPF ₆	50	6	120	17.1
6	Zn-Co-Fe(III)MMC +EMImBF ₄	50	6	120	21.5
7	Zn-Co-Fe(III)MMC +TPAC	50	6	120	25.9
8	Zn-Co-Fe(III)MMC +TBAC	50	6	120	27.4
9	Zn-Co-Fe(III)MMC +THAC	50	6	120	32.4
10	Zn-Co-Fe(III)MMC +TOAC	50	6	120	44.1
11	Zn-Co-Fe(III)MMC +TDAC	50	6	120	38.6
12	Zn-Co-Fe(III)MMC +TBAB	50	6	120	40.5
13	Zn-Co-Fe(III)MMC +TBAI	50	6	120	42.0
14	Zn-Co-Fe(III)MMC +TBAH	50	6	120	34.7

The increase in the solubilities of CO_2 in the solution of AGE and ionic liquid with lengthening alkyl chain of the ionic liquid could also be a reason of the increase of AGE conversion. Kawanami et al.[12] reported the increase of reactivity when the alkyl chain length increased from C_2 to C_8 in 1-alkyl-3-methylimidazolium tetrafluoroborate $[\text{C}_x\text{MIm}]^+[\text{BF}_4]^-$ for the synthesis of propylene carbonate using a high pressure CO_2 - ionic liquid system.

Table 2. Effects of reaction temperatures on the conversion of AGE.

Run	Catalyst	Temp ($^\circ\text{C}$)	Time (h)	Pressure (psig)	Conversion (%)
2	Zn-Co-Fe(III)MMC +BMImCl	50	6	120	25.5
15	Zn-Co-Fe(III)MMC +BMImCl	70	6	120	34.5
16	Zn-Co-Fe(III)MMC +BMIMCl	100	6	120	64.1
17	Zn-Co-Fe(III)MMC +BMImCl	120	6	120	70.0
18	Zn-Co-Fe(III)MMC +BMImCl	140	6	120	68.5
8	Zn-Co-Fe(III)MMC +TBAC	50	6	120	27.4
19	Zn-Co-Fe(III)MMC +TBAC	70	6	120	31.6
20	Zn-Co-Fe(III)MMC +TBAC	100	6	120	63.3
21	Zn-Co-Fe(III)MMC +TBAC	120	6	120	75.5
22	Zn-Co-Fe(III)MMC +TBAC	140	6	120	70.6

Table 2 lists the conversion of AGE at different reaction temperature. The AGE conversion increased with increasing reaction temperature from 50 to $120\text{ }^\circ\text{C}$. But the conversion remained nearly constant over $120\text{ }^\circ\text{C}$, probably due to the partial decomposition of the cyclic carbonate to monomeric AGE at high temperatures.

Table 3 summarizes the conversion of cyclic carbonate at different reaction time. When the reaction time increased from 6 h to 36 h, the AGE conversion greatly increased.

Table 3. Effects of reaction time on the conversion of AGE.

Run	Catalyst	Temp (°C)	Time (h)	Pressure (psig)	Conversion (%)
2	Zn-Co-Fe(III)MMC +BMImCl	50	6	120	25.5
23	Zn-Co-Fe(III)MMC +BMImCl	50	12	120	67.6
24	Zn-Co-Fe(III)MMC +BMIMCl	50	24	120	87.4
25	Zn-Co-Fe(III)MMC +BMImCl	50	36	120	100
8	Zn-Co-Fe(III)MMC +TBAC	50	6	120	27.4
26	Zn-Co-Fe(III)MMC +TBAC	50	12	120	37.5
27	Zn-Co-Fe(III)MMC +TBAC	50	24	120	39.7
28	Zn-Co-Fe(III)MMC +TBAC	50	36	120	57.7

Conclusion

Carbon dioxide can be effectively added to the epoxide ring of allyl glycidyl ether (AGE) to produce the corresponding five-membered cyclic carbonate by using the mixed catalysts of MMC and ionic liquid without any solvent. The order of the AGE conversion increased as the size of the cation of ionic liquids increased from EMIm⁺ < BMIm⁺ < HmIm⁺. Imidazolium salts, having longer distances between cations and anions, seem to exhibit higher activity in activating anions. The catalytic activity also increased with increasing the nucleophilicity of the anion of BMIm⁺X⁻ ionic liquid: PF₆⁻ < BF₄⁻ < Cl⁻. The conversion of AGE is increased with increasing reaction temperature and reaction time.

Acknowledgements

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