

Synthesis of ethylene carbonate from supercritical carbon dioxide/ethylene oxide mixture in the presence of bifunctional catalyst

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Abstract

Ethylene carbonate was rapidly synthesized from supercritical carbon dioxide/ethylene oxide mixture by using as catalyst the system of tetradentate schiff-base aluminum complexes (designated as SalenAlX) coupling with a quaternary ammonium or phosphonium salt. The high rate of reaction was attributed to rapid diffusion and high miscibility of ethylene oxide in supercritical carbon dioxide under employed conditions. Various reaction periods present different formation rate of ethylene carbonate, mainly due to the existence of phase change during the reaction. The synergistic effect of the binary catalyst for ring-opening of ethylene oxide results from nucleophilicity of highly reactive anions of quaternary salts and the electrophilic interaction of SalenAlX with ethylene oxide. The activation of CO₂ was generally initiated by nucleophilic attack of the alcoholate(OCH₂CH₂BrN(Bu)₄) at the carbon atom of CO₂, and weak interaction between the central metal ion of SalenAlX and the lone pairs of one oxygen atom of CO₂. It resulted in the insertion of CO₂ to Al–O bond of Salen(X)Al–OCH₂CH₂BrN(*n*-Bu)₄ or SalenAl–OCH₂CH₂X to form linear carbonate which was transformed into ethylene carbonate by intramolecular substitution of halides. The experimental results demonstrate that supercritical carbon dioxide could be used as not only an environmentally benign solvent but also a carbon precursor in synthesis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical carbon dioxide; Ethylene carbonate; Salen-aluminum complexes; Synergistic effect; Phase change

1. Introduction

The use of supercritical fluids, particularly carbon dioxide, as a substitute solvent for chemical synthesis is a very attractive area in view of resource utilization and environmental problems [1–4]. Since CO₂, which has an easily accessible critical point with a T_c of 31 °C and a P_c of 7.3 MPa, is nontoxic, nonflammable and inexpensive, it can replace hazardous organic

solvent and thereby provides a valuable pollution prevention tool. As with other supercritical fluids, the solvent properties of supercritical carbon dioxide (designated as sc-CO₂) can be tuned by variation of pressure and temperature [5], therefore, selective separation directly from the reaction mixture seems possible. Furthermore, sc-CO₂ may be a particularly advantageous reaction medium when CO₂ serves as both a reactant and a solvent. The improved rates for catalytic hydrogenation of CO₂ to formic acid in supercritical conditions provided support for this approach [6,7]. Another class of reaction which utilizes CO₂ is the catalytic copolymerization of epoxides

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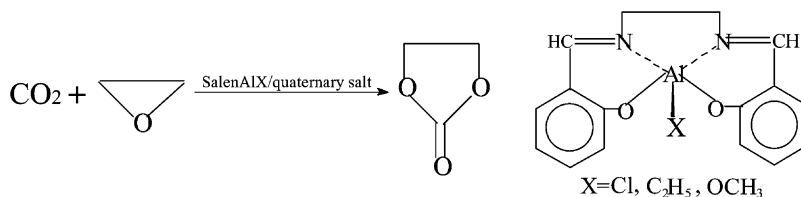
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with CO₂ to form polycarbonates. The precipitation copolymerization of CO₂ and propylene oxide in sc-CO₂ has been reported using zinc(II) glutarate as a heterogeneous catalyst [8]. Compared to that in non-critical conditions, polymerization performed in CO₂ above the critical pressure had an increased percentage of carbonate linkages relative to the ether linkages. Propylene carbonate was also produced as a byproduct, and its yield was increased with reaction temperature. Costello et al. [9] reported a CO₂-soluble catalyst for cyclohexene oxide/CO₂ copolymerization in the absence of any additional organic solvents under supercritical conditions. The zinc-based catalyst was soluble in CO₂ over a wide pressure range, but at 90 °C, irreversible phase separation occurred. The turnover numbers of up to 400 g of polymer/g Zn obtained for this catalyst are among the highest reported for the copolymerization of epoxides and CO₂. However, the first attempt for this strategy may be the reaction of hex-3-yne with CO₂ under supercritical conditions to produce tetraethyl-2-pyrone using [Ni(cod)₂]/Ph₂P(CH₂)₄PPh₂ as the catalyst [10].

For a long time, the search for environmentally benign processes has been the impetus for much of the research involving epoxide and CO₂ coupling. The synthesis of cyclic carbonates (which may be used as aprotic polar solvents and are also monomers for polymer synthesis) was performed, using catalyst such as alkali metal salts, quaternary salts [11], Ph₃SnI [12,13] or Ph₃SbX₂ [14] with a high temperature or high catalyst concentration. It has been reported that in the presence of 1-methylimidazole, aluminum porphyrin [15,16] or phthalocyanine [17,18] having an axial aluminum alkoxide or chloride could effectively catalyze the reaction between CO₂ and epoxides to form cyclic carbonates, involving the insertion of CO₂ into the aluminum alkoxide bond. Le Borgne and

co-workers [19] and Le Borgne et al. [20–22] have developed a new class of initiators for oligomerization of heterocycles, leading to oligomers with controlled structure. These initiators are aluminum complexes derived from tetradentate Schiff's bases (Salen), which are reminiscent of tetraphenylporphyrin or phthalocyanine. The Salen ligands feature two covalent and two coordinate covalent sites situated in a planar array, but their preparation is generally easier and more inexpensive than that of porphyrin derivatives. The high coordinative activity of the Salen ligands towards metallic ions has led to their extensive use in transition-metal chemistry, particularly in modeling enzymes and in catalysis [23,24]. However, only sporadic reports of main-group-Salen complexes have appeared [25,26]. Despite the similarity between the 3rd main-group elements and the trivalent transition metals, very little work has been done in this area until recent times. Aluminum-Salen complexes have been proved effective initiator for the living polymerization of epoxides [19,20,27]. The novel properties of these aluminum complexes motivate us to investigate their new application in catalysis and synthesis.

On the other hand, it is generally known that CO₂ exhibits high solubility in various epoxides. In fact, epoxides can also be dissolved in sc-CO₂ under certain conditions. The cycloaddition reaction of CO₂ to epoxides in sc-CO₂ should be different from that in non-critical condition. In this paper, the catalytic formation of ethylene carbonate from supercritical carbon dioxide/ethylene oxide mixture (ethylene oxide used as a model epoxide) was carried out by utilizing the binary catalyst of tetradentate schiff-base aluminum complexes (designated as SalenAlX) coupled with a quaternary ammonium or phosphonium salt (Scheme 1). The mechanism of ring-opening of ethylene oxide and activation of CO₂ will be discussed.



Scheme 1. The cycloaddition reaction of CO₂ with ethylene oxide and structure of SalenAlX.

2. Experimental

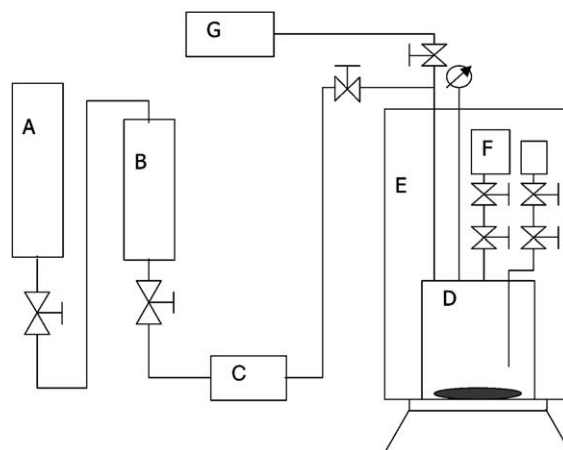
2.1. Materials

The Schiff-base ligand [Salen: *N,N'*-bis(salicylidene)ethylene diamine] was synthesized from salicylaldehyde and ethylenediamine in ethanol and recrystallized from chloroform/ethanol. Tetrabutylammonium bromide, chloride and iodide were synthesized by quaternization of tributylamine with the corresponding butyl halides and purified by recrystallization from ethanol. Triethylaluminum (Et_3Al) and diethylaluminum chloride (Et_2AlCl) were purified by fractional distillation under reduced pressure in a nitrogen atmosphere. Ethylene oxide was distilled after refluxing over a mixture of potassium hydroxide and calcium hydride. Methanol and ethanol were distilled after refluxing over the corresponding magnesium alkoxides under nitrogen atmosphere. CO_2 was purified by passing through a column packed with 4 Å molecular sieves before use.

2.2. Preparation of catalysts

A round-bottom flask equipped with a three-way stopcock containing the Salen ligand of 1.340 g (5 mmol) was purged with dry nitrogen, and anhydrous chloroform (40 ml) was added via syringe in a nitrogen atmosphere to dissolve the ligand. To this solution was slowly added of Et_2AlCl of 0.602 g (5 mmol) under constant stirring. The reaction was highly exothermic and resulted in a yellow solution and pale yellow solid. The mixture was allowed to stir for 4 h at ambient temperature, and then filtered under a nitrogen atmosphere. The solid was washed with anhydrous chloroform for three times and dried in vacuo, yielding 1.477 g (90%) of SalenAlCl . ^1H NMR (CDCl_3/TMS): δ 3.74 (m, 2H, CH_2), 4.22 (m, 2H, CH_2), 6.74–7.44 (m, 8H, PhH), 8.35 (s, 2H, PhCH). FT-IR (KBr, cm^{-1}): 3050 m, 1641 s, 1550 s, 1478 s, 1340 s, 909 m, 759 s. Anal. Calcd: C, 58.46; H, 4.29; N, 8.52. Found: C, 58.18; H, 4.42; N, 8.35.

The method used in the preparation of SalenAlEt was as the same as the described above and similar to the literature method [28]. ^1H NMR (CDCl_3/TMS): δ 0.36 (q, 2H, AlCH_2), 0.73 (t, 3H, CH_3), 3.65 (m, 2H, CH_2), 4.01 (m, 2H, CH_2), 6.65–7.38 (m, 8H, PhH), 8.24 (s, 2H, PhCH).



Scheme 2. Equipment used for the reaction in supercritical carbon dioxide. A: CO_2 tank; B: drying column; C: pump; D: autoclave or equilibrium cell (150 ml); E: oven; F: sampling vessel; G: injection system of ethylene oxide.

SalenAlOCH_3 was obtained from the reaction of SalenAlEt with methanol [22]: δ 2.89 (s, 3H, AlOCH_3), 3.71 (m, 2H, CH_2), 4.14 (m, 2H, CH_2), 6.72–7.41 (m, 8H, PhH), 8.19 (s, 2H, PhCH). These complexes are all sensitive to air or moisture and should be stored in a nitrogen atmosphere.

2.3. Procedure

The cycloaddition reaction of CO_2 with ethylene oxide was carried out in a 60-ml stainless autoclave with magnetic stirrer (Scheme 2). The autoclave with weighted catalyst was sealed and purged with CO_2 for three times. The autoclave was put into a constant bath and heated to the desired temperature. Then, ethylene oxide and liquid CO_2 were charged into the autoclave, respectively. After the expiration of the desired reaction time, the autoclave was half-submerged in a bath of ice/water mixture. When the autoclave was cooled to room temperature and the excess gases were vented. The remainder mixture was degassed and dissolved in methanol for the measurement of ethylene carbonate. Pure ethylene carbonate could be obtained via distillation under reduced pressure and recrystallization in Et_2O . The spectra data are listed as follows: IR: $\nu_{\text{C}=\text{O}}$ 1775, 1805 cm^{-1} ; $\nu_{\text{C}-\text{O}}$ 1163, 1072, 973 cm^{-1} ; ^1H NMR (CDCl_3/TMS): δ 4.51 (s, 4H); T_m : 36.5 °C.

Safety warning: The high-pressure equipment such as that required for these experiments should be equipped with a relief valve and/or (preferably) a rupture disk for minimizing the risk of personal injury.

2.4. Analysis of ethylene oxide

The ring-opening reaction of ethylene oxide with sulfuric acid can be quantitatively proceeded in the saturated solution of magnesium chloride at low temperature (less than 1 °C). Based on this principle, the samples from the uppermost and lowermost phase of the autoclave were slowly discharged into the saturated solution of MgCl₂, comprised 0.01000 mol H₂SO₄ at 0 °C. The solution was stirred about 20 min at 0 °C. The excess acid in the solution was titrated by using standard solution of NaOH with bromocresol green as indicator. The analyses of ethylene oxide are estimated to be accurate to within ±0.5%. However, errors in the reported phase compositions are due not only to errors in the analyses, but also to errors resulting from the sampling process. The maximum error in the phase compositions reported here, due to all causes, is estimated to be 2.0%.

2.5. Analysis of ethylene carbonate

The samples from the uppermost and lowermost phase of the autoclave, which comprised CO₂, ethylene oxide and ethylene carbonate, were transferred into sampling vessels and cooled to ambient temperature. After the slow removal of volatile materials, the remainder was dissolved in methanol. Ethylene carbonate was analyzed on a model 103 gas chromatography made by Shanghai analytic instrument factory, with butyl acetate as an internal standard. A constant relative response factor (ethylene carbonate/butyl acetate) of 2.23 was used in the analyses, based on calibration employing mixtures of known composition.

2.6. Measurement

Infrared spectra were measured using a Nicolet 50X FT-IR spectrophotometer. ¹H NMR spectra were recorded by a Varian INOVA-400 type spectrometer at 399.7 MHz. The chemical shifts were determined in ppm using TMS as an internal standard. Elemental

analyses were obtained on a Perkin-Elmer 2400 analyzer.

3. Results and discussion

3.1. Investigation of phase behavior

Reactions in supercritical fluids are strongly affected by phase changes during reaction [29]. For this reason, quantitative measurements of ethylene oxide and ethylene carbonate were also performed. Samples from the uppermost and lowermost phase of the autoclave under various conditions were transferred into the sampling vessels for the measurements of the densities and composition of phases present. The results are shown in Figs. 1 and 2 and Table 1. In these systems, only comprising ethylene oxide, the density of gas phase rapidly increases with the increase of the temperature, but its value is not higher than 0.04 g cm⁻³ at temperature less than 120 °C. The volume of liquid phase slightly increases with temperature.

However, in these systems composed of ethylene oxide and CO₂ at the same temperature, the situation is dramatically different (Fig. 1). The temperature and the composition of the binary systems have great effects on the densities and composition of phases present. At temperature below 31 °C (critical temperature of CO₂), the density of liquid phase in system only depends on the molar ratio of CO₂ to ethylene oxide in this phase and hardly changes with temperature, due to liquid CO₂ being completely miscible with liquid ethylene oxide. The gas phase contains very little ethylene oxide and its density is very low. At temperature between 31 °C and the critical temperature of CO₂/ethylene oxide mixture, CO₂ exists not only in the uppermost phase (gas phase) but also in the lowermost phase (liquid phase), due to its high solubility in ethylene oxide (Fig. 2). The density and the concentration of ethylene oxide in the uppermost phase increase with temperature, while the volume of the lowermost phase rapidly decreases near the critical temperature of the mixture. Above the critical temperature, the systems only exist a single phase, namely supercritical phase.

In the systems composed of CO₂/ethylene oxide/ethylene carbonate at 110 °C, the uppermost phase

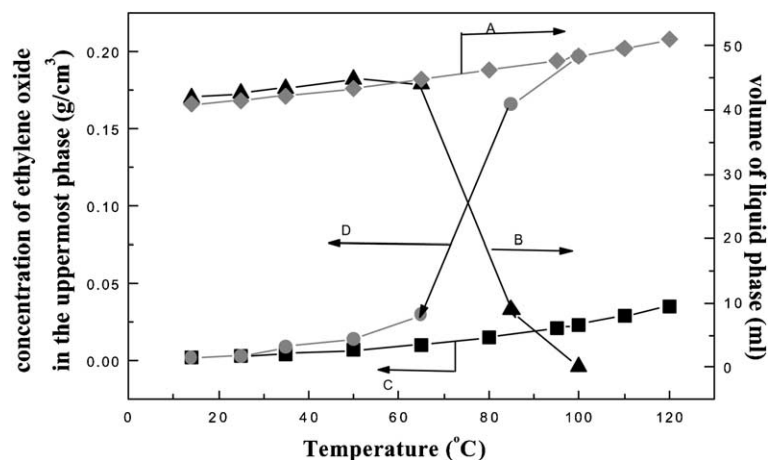


Fig. 1. Plots of the concentrations of ethylene oxide (curve C, D) in the uppermost phase and volume of liquid phase (curve A, B) in the equilibrium cell vs. temperature. Curve A and C are for the system consisted of only ethylene oxide; curve B and D are for the system consisted of CO₂ and ethylene oxide; average density of phases present in the equilibrium cell is 0.6 g cm⁻³.

mainly comprises CO₂, ethylene oxide and trace ethylene carbonate, while the lowermost phase consists of ethylene carbonate, CO₂ and ethylene oxide. The results are shown in Table 1. The concentration of ethylene carbonate in the uppermost phase increases with increasing the density of sc-CO₂/ethylene oxide mixture in the autoclave. The experimented result

indicates that phase change must occur during the cycloaddition reaction of sc-CO₂ and ethylene oxide, thus may affect the reaction rate significantly.

Although sc-CO₂ is a good solvent for most non-polar and some polar organic compounds with low molecular weight, it hardly dissolves not only quaternary salts such as tetrabutylammonium bromide

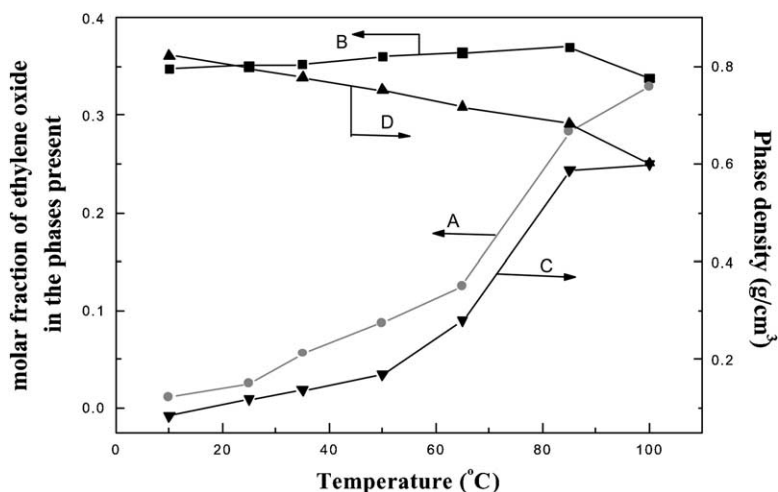


Fig. 2. Plots of compositions (curve A, B) and densities (curve C, D) of the phases present for sc-CO₂/ethylene oxide system vs. temperature. Curve A and C are for the uppermost phase; curve B and D are for the lowermost phase. Equilibrium condition: ethylene oxide/CO₂ = 1/2 (mol/mol); equilibrium time, 36 h. Average density of phases present in the equilibrium cell is 0.600 g cm⁻³.

Table 1

Phase equilibrium for carbon dioxide, ethylene oxide and ethylene carbonate system at 110 °C

EC ^a /EO/CO ₂ (molar ratio)	Average density ^b (g cm ⁻³)	Phase compositions						Phase densities (g cm ⁻³)	
		Vapor			Liquid			Vapor	Liquid
		X ₁	Y ₁	Z ₁	X ₂	Y ₂	Z ₂		
1/2/4	0.667	0.716	0.274	0.010	0.442	0.293	0.265	0.480	0.905
1/2.5/5	0.792	0.664	0.285	0.051	0.552	0.301	0.147	0.624	0.895

^a EC: ethylene carbonate; EO: ethylene oxide. X, Y and Z are the molar fractions of CO₂, EO and EC in the vapor or liquid phase of the equilibrium cell, respectively.

^b Average density of phases present in the equilibrium cell. Equilibrium time: 36 h.

(*n*-Bu₄NBr), but also these aluminum complexes derived from Schiff's bases. On the contrary, SalenAlCl and tetrabutylammonium bromide were found to dissolve in sc-CO₂/ethylene oxide mixture, perhaps resulting from their solubility in ethylene oxide. It is very difficult to investigate their accurate solubility in sc-CO₂/ethylene oxide, because either *n*-Bu₄NBr or SalenAlCl by oneself can catalyze the reaction of CO₂ with ethylene oxide to form ethylene carbonate under employed conditions.

3.2. Cycloaddition reaction of CO₂ with ethylene oxide

The homogeneous catalytic formation of ethylene carbonate from sc-CO₂/ethylene oxide mixture proceeds rapidly with the use of SalenAlCl/*n*-Bu₄NBr as catalyst (Table 2). The formation rate of ethylene carbonate is about two times that under 4.0 MPa CO₂ pressure at same temperature. Various reaction periods present different formation rate of ethylene carbonate,

Table 2

The formation rate of ethylene carbonate from sc-CO₂/ethylene oxide mixture under various conditions^a

Entry	CO ₂ /EO (mol/mol)	Catalyst	Temperature (°C)	TOF ^f (turnovers/h)
1	2	SalenAlCl/ <i>n</i> -Bu ₄ NBr	110	2220
2 ^b	–	SalenAlCl/ <i>n</i> -Bu ₄ NBr	110	1140
3	2	SalenAlCl	110	174
4	2	<i>n</i> -Bu ₄ NBr	110	78
5	2	<i>n</i> -Bu ₄ NCl	110	48
6	2	<i>n</i> -Bu ₄ NI	110	126
7	2	SalenAlCl/ <i>n</i> -Bu ₄ NCl	110	2190
8	2	SalenAlCl/ <i>n</i> -Bu ₄ NI	110	2360
9 ^c	2	SalenAlCl/ <i>n</i> -Bu ₄ NBr	110	1960
10 ^d	2	SalenAlCl/ <i>n</i> -Bu ₄ NBr	110	1730
11 ^e	2	SalenAlCl/ <i>n</i> -Bu ₄ NBr	110	1690
12	2	SalenAlCl/ <i>n</i> -BuPPh ₃ Br	110	1990
13	2	SalenAlOCH ₃ / <i>n</i> -Bu ₄ NBr	110	2060
14	2	SalenAlCl/ <i>n</i> -Bu ₄ NBr	100	1520
15	2	SalenAlCl/ <i>n</i> -Bu ₄ NBr	120	3070
16	3	SalenAlCl/ <i>n</i> -Bu ₄ NBr	110	1810
17	4	SalenAlCl/ <i>n</i> -Bu ₄ NBr	110	1210

^a Reaction condition: catalyst/EO = 1/5000 (mol/mol); time: 1 h; pressure: 15–16 MPa; density of reactants in the autoclave: 0.6 g cm⁻³.

^b Reaction was carried out under 4.0 MPa CO₂ pressure.

^c Reaction proceeded without stirring.

^d CH₂Cl₂ of 10 ml was also charged into the autoclave together with ethylene oxide and CO₂.

^e Ethylene carbonate of 10 g was put into the autoclave together with ethylene oxide and CO₂ before reaction.

^f TOF = mole of product(ethylene carbonate)/mol of catalyst per h.

Table 3

The formation rate of ethylene carbonate in various reaction periods^a

Reaction period	First hour	Second hour	Third hour
TOF (turnovers/h)	2220	1580	1090

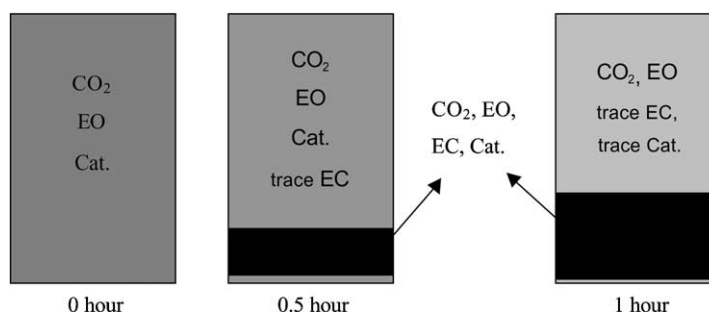
^a Reaction condition: SalenAlCl/*n*-Bu₄NBr/EO/CO₂ = 1/1/5000/10000 (molar ratio); density of reactants in the autoclave: 0.6 g cm⁻³.

as shown in Table 3. The rate is expressed in terms of the turnover frequency (TOF) (TOF = turnovers/h = mol of product/mol of catalyst/h). The fastest reaction with a TOF of 2220 h⁻¹ is in the first hour. The rate decreases to 1580 h⁻¹ in the second hour and 1090 h⁻¹ in the third hour. The main reason is the existence of phase change during the reaction. The typical reaction process (Scheme 3) is present as follows: at the start of the reaction, the reactants and catalyst are present only one phase (namely supercritical phase), but as the reaction proceeds, produced ethylene carbonate precipitates on the bottom of the autoclave and the phase separation arises.

Although SalenAlCl itself can effectively catalyze the reaction of CO₂ and ethylene oxide to synthesize ethylene carbonate at similar conditions, existence of tetra-alkyl ammonium halides such as *n*-Bu₄NBr could promote the conversion of the epoxide to cyclic carbonate at the same temperature, as shown in Table 2. To the best of our knowledge, the catalytic activity is one of the highest for the cycloaddition of CO₂ to epoxides amongst the reported catalysts. It is interesting that the cycloaddition reaction of CO₂

with ethylene oxide did not have obvious relevance to the nucleophilic abilities of anions of quaternary salts. On the other hand, with quaternary salt alone as catalyst, the reaction appeared to be dependent of the nucleophilicity of anions under the same condition. The Schiff-base aluminum complexes having an axial aluminum alkoxide, in company with *n*-Bu₄NBr, also present high catalytic activities towards this reaction. In the presence of ethylene oxide, CH₂Cl₂ is a good solvent for SalenAlCl, and *n*-Bu₄NBr, but its existence in reaction systems did not improve the formation rate of ethylene carbonate. Without stirring, the cycloaddition reaction of CO₂ with ethylene oxide still proceeds rapidly at the same condition. These results further confirm that the catalytic reaction was carried out in homogeneous condition.

The reaction temperature has a great effect on the catalytic activity of the binary catalyst. The formation rate of ethylene carbonate increases remarkably with the enhancement of reaction temperature. The molar ratio of CO₂ to ethylene oxide also affects the reaction rate. From Table 2, it can be observed that the formation rate of ethylene carbonate decreases with the increase of the molar ratio of CO₂ to ethylene oxide, when the ratio is higher than 2. Indeed, the solubility of ethylene carbonate in sc-CO₂/ethylene oxide mixture relies on not only the density, but also the composition of the supercritical fluid, because ethylene carbonate easily dissolves in ethylene oxide rather than pure sc-CO₂. The higher solubility for ethylene carbonate should be present in the supercritical fluid with the lower molar ratio of CO₂ to ethylene oxide. The lower the solubility of ethylene carbonate in the



Scheme 3. Schematic diagrams of phase behavior during the cycloaddition reaction of CO₂ with ethylene oxide in the presence of binary catalyst, showing the major components of each phase and the relative volume. EO = ethylene oxide; EC = ethylene carbonate; catalyst/EO/CO₂ = 1/5000/10000 (molar ratio); average density of phases present in the autoclave: 0.6 g cm⁻³.

supercritical fluid is, the faster the phase separation during the reaction occurs. Therefore, the lower rate for the system of the higher molar ratio of CO₂ to ethylene oxide probably mainly results from the faster phase separation during the reaction. On the other hand, further kinetic study confirms that ring-opening of ethylene oxide is key step for the formation of ethylene carbonate in the present case. Thus, change in the composition of the supercritical fluid probably also changes the reaction rate to a certain extent.

3.3. Cycloaddition mechanism

The formation of ethylene carbonate from CO₂ and ethylene oxide can proceed via various reaction pathways: direct insertion of CO₂ into the C–O bond of ethylene oxide, cyclic elimination of linear carbonate formed, polymerization/depolymerization process, and etc. These pathways may not operate exclusively each other, but one of them might be expected to predominate for a given catalytic system, or under certain experimental condition [30]. It is very difficult to investigate the reaction mechanism under supercritical condition by using in situ spectroscopic methods, due to limitation of high pressure required. However, some general comments can be made from the present data.

It has been reported that Schiff-base aluminum complexes were effective initiators for homopolymerization of epoxides [19,20], which were the same as the results of our experiment. In the meantime, we found that the polymerization reaction could be accelerated in the presence of a quaternary ammonium or phosphonium salts. The synergistic effect of the binary catalyst probably results from nucleophilicities of highly reactive anions of quaternary salts and the

electrophilic interaction of SalenAlCl with ethylene oxide. Inoue groups [31] have reported the living and alternating copolymerization of CO₂ and epoxides to produce linear polycarbonates of controlled molecular weight with a narrow distribution, catalyzed by the aluminum porphyrin-quaternary organic salt system at ambient temperature. However, in the catalytic system of SalenAlCl coupling with a quaternary salt, reaction between CO₂ and ethylene oxide mainly produces ethylene carbonate rather than polycarbonates, even low to 10 °C. The infrared spectra of the reaction mixture after the complete consumption of ethylene oxide show strong absorption characteristic of ethylene carbonate at 1805 and 1775 cm⁻¹. On the contrary, in the absence of quaternary salt, the polycarbonates (1733 cm⁻¹) and ethylene carbonate are formed with a low formation rate at room temperature (Table 4). Increasing reaction temperature, the yield of ethylene carbonate increases and that of polycarbonates reduces. The fact that higher temperature resulted in increased yield of cyclic carbonate demonstrates that cyclic carbonates are more thermodynamically stable than polycarbonates and are not intermediates during polycarbonates formation.

It is well known that opening-ring of epoxides is generally described in terms of two pathways: an acid-catalyzed cleavage and a base-catalyzed cleavage. In the present case, ethylene oxide is ring-opened according to base-catalyzed cleavage, as similar to the cases of propylene oxide with Al(L)TPP [15,16] or Al(L)Pc(*t*-Bu)₄ [17,18]. Monomeric SalenAlCl has a structure of 5-coordinate square-pyramidal Al³⁺ strongly bound to both the oxygen and nitrogen ligand atoms, as similar to that of SalenAlEt [28]. Indeed, because of the electrophilicity of Al³⁺ and the

Table 4
Conditions and results of the reaction of CO₂ with ethylene oxide at low temperature^a

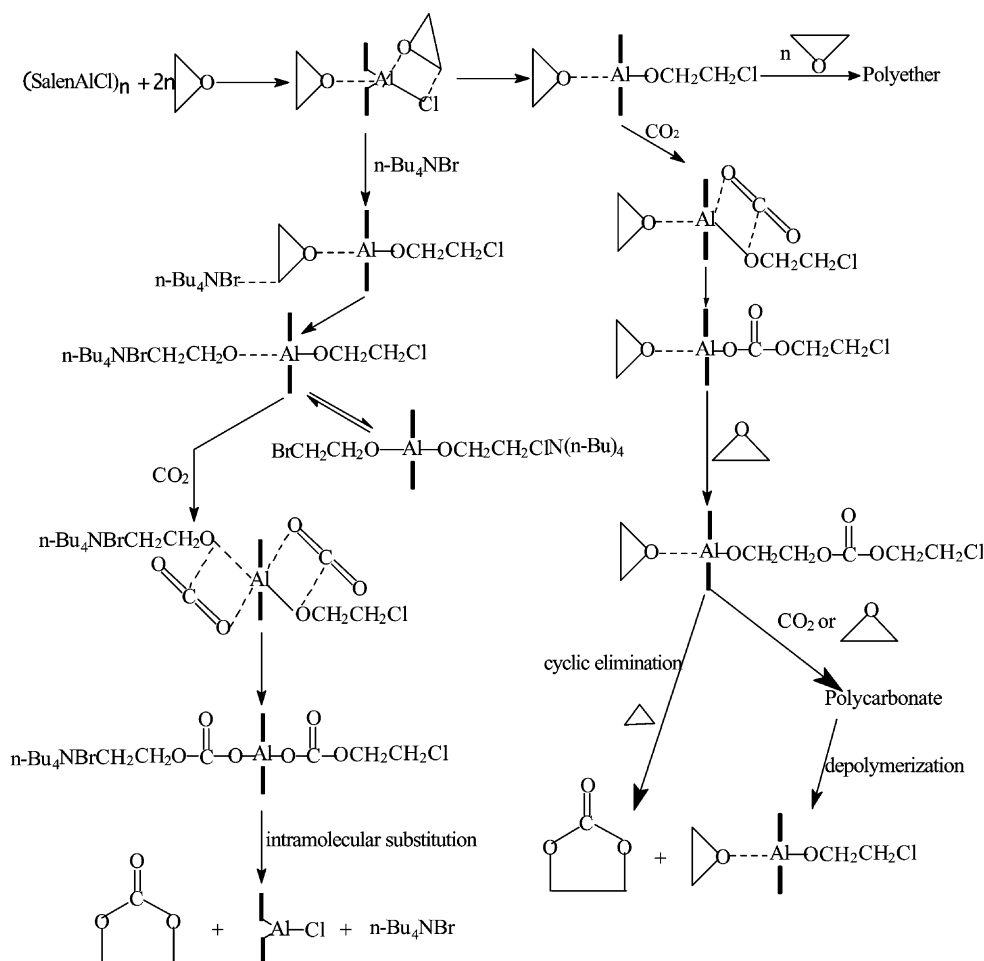
Catalyst	Temperature (°C)	Time (h)	Conversion ^b (%)	
			Ethylene carbonate	Polycarbonate
SalenAlCl	30	120	2	2
SalenAlCl	50	72	9	<1
<i>n</i> -Bu ₄ NBr	30	120	2	0
SalenAlCl/ <i>n</i> -Bu ₄ NBr	10	120	30	<1
SalenAlCl/ <i>n</i> -Bu ₄ NBr	30	72	96	0

^a SalenAlCl/*n*-Bu₄NBr/epoxide = 1/1/1000 (molar ratio); in CH₂Cl₂ of 10 ml under 2.5 MPa pressure of CO₂.

^b Based on ethylene oxide in the autoclave.

nucleophilicity of Cl^- , SalenAlCl usually exists in dimeric [32] or polymeric state by Cl^- bridge bond, and thus leads to its low solubility in most solvents. On the other hand, in the presence of base ligands such as *N*-methyl imidazole, SalenAlCl exhibits higher solubility in most solvents. Surprisingly, in the presence of ethylene oxide, SalenAlCl can be dissolved in CH_2Cl_2 or CHCl_3 with a higher solubility; but without ethylene oxide, the solubility is very low. It may be resulting from the coordination of ethylene oxide towards central Al^{3+} ion of SalenAlCl , and thus favoring monomeric aluminum complex. Smaller binding constants of epoxides or thiiranes to cadmium, zinc, or magnesium α , β , γ , δ -mesotetraphenylporphyrins

have been detected spectrophotometrically [33], and the first crystal structure of a metal epoxide complex been reported for a ruthenium porphyrin derivative of styrene oxide [34]. For mimicking the catalytic properties of the more reactive, poorly characterized catalysts derived from Zn(II) dicarboxylate. Darenbourg et al. [35] have investigated well-characterized metal-epoxide complexes based on Cd(II) dicarboxylate with Tris-3-phenylpyrazole hydroborate ligand. Furthermore, they had observed coupling of the epoxide ligand with the carboxylate group in these metal complexes to subsequently provide oligomers of the epoxide with terminal ester groups. In analogous reactions carried out in the presence of CO_2 ,



Scheme 4. The possible formation mechanism of ethylene carbonate from CO_2 and ethylene oxide in the presence of binary catalyst.

cyclic carbonates were also formed. Compared to these Cd(II), Zn(II), or Mg(II) complexes, analogous Al(III) complexes have higher electrophilicity and easily trend to form complexes with electron-donor ligands. Of course, due to the low electron-donor ability of ethylene oxide, the hexacoordinated complex formed from ethylene oxide and SalenAlCl is not stable, but the coordination effect is sufficient to lead to the destroy of bridging bond of polymeric SalenAlCl. Besides, interactions between ethylene oxide and SalenAlCl have another types: nucleophilic attack resulting from Cl⁻ ion of SalenAlCl towards ethylene oxide. The both interactions have synergistic effect each other. The formation of hexacoordinated complex could cause electronic transfer from oxygen atom of ethylene oxide to central metal ion of SalenAlCl, and thus reduced the Al–Cl bond. This might be beneficial for the insertion of ethylene oxide into the Al–Cl bond of SalenAlCl. On the other hand, the coordinated ethylene oxide is readily ring-opened in view of nucleophilic attack of even low nucleophilic reagents. It has been reported that polymerization of lactone catalyzed by Tris(*iso*-propoxy)aluminium(III) proceeded via a four-centered intermediate [36]. In the present case, the insertion of ethylene oxide into the Al–Cl bond of SalenAlCl, as well as CO₂ into Al–O bond of SalenAl–OCH₂CH₂(OCH₂CH₂)_nCl or Salen(Cl)Al–OCH₂CH₂BrN(*n*-Bu)₄ might proceed via the four-centered intermediate, as shown in Scheme 4, although the intermediates are not confirmed by means of spectroscopic methods, perhaps resulting from their less stability.

Based on the facts described above, some plausible mechanisms are proposed as shown in Scheme 4. In the ethylene oxide/SalenAlCl system, the sole product is polyether (SalenAl–OCH₂CH₂(OCH₂CH₂)_nCl), due to the insertion of ethylene oxide towards Al–Cl bond of SalenAlCl. In the presence of CO₂, the insertion of CO₂ to Al–O bond of SalenAl–OCH₂CH₂(OCH₂CH₂)_nCl results in the formation of linear polycarbonates. The enhancement of temperature increases the rate of reaction of CO₂ with ethylene oxide, but it is beneficial for the formation of cyclic carbonate rather than polycarbonates, due to more thermodynamical stability of five members cyclic.

By using SalenAlCl coupling with a quaternary salt as catalyst, the situation is very different in the absence of quaternary salt. The ethylene oxide coordinated

with SalenAlCl is readily ring-opened by nucleophilic attack of highly reactive anions of quaternary salt. The activation of CO₂ is generally initiated by nucleophilic attack of the alcoholate (OCH₂CH₂BrNBu₄) at the Lewis acid carbon atom of CO₂, and weak interaction between the central metal ion and the lone pairs of one oxygen of CO₂. The synergistic effect is sufficient to support the insertion of CO₂ to Al–O bond of Salen(Cl)Al–OCH₂CH₂BrN(*n*-Bu)₄ or SalenAl–OCH₂CH₂Cl, and thus leads to the linear carbonate which is transformed into ethylene carbonate by intramolecular substitution of halides.

4. Conclusion

Ethylene carbonate could be rapidly and high selectively synthesized from supercritical carbon dioxide/ethylene oxide mixture by using as catalyst the system of tetradentate schiff-base aluminum complexes coupling with a quaternary ammonium or phosphonium salt. The high rate of reaction is attributed to rapid diffusion and high miscibility of ethylene oxide in supercritical carbon dioxide under employed conditions. Various reaction periods present different formation rate of ethylene carbonate, mainly due to the existence of phase change during the reaction.

In the presence of SalenAlCl, ethylene oxide was ring-opened according to base-catalysed cleavage. The existence of a quaternary salt could promote the opening-ring reaction, due to the nucleophilicity of its anion. The activation of CO₂ was generally initiated by nucleophilic attack of the alcoholate(OCH₂CH₂BrNBu₄) at the Lewis acid carbon atom of CO₂, and weak interaction between the central metal ion Al³⁺ of SalenAlX and the lone pairs of one oxygen of CO₂. The synergistic effect resulted in the insertion of CO₂ to Al–O bond of Salen(Cl)Al–OCH₂CH₂BrN(*n*-Bu)₄ or SalenAl–OCH₂CH₂Cl to form linear carbonate. The linear carbonate formed ethylene carbonate by intramolecular substitution of halides. However, the formation rate of ethylene carbonate from sc-CO₂/ethylene oxide did not have obvious relevance to the nucleophilicity of anions of quaternary salts in the binary catalysis.

The process described in this report, and other processes based on sc-CO₂ as both a reactant and a

solvent, demonstrate that sc-CO₂ could be used as not only an environmentally benign solvent but also a carbon precursor in organic synthesis. Furthermore, compared to liquid phase reactions, the supercritical fluids reduce mass transport restrictions at the surface of catalyst, and thus make them more suitable for a flow reactor rather than batch reactor. On the other hand, the use of an immobilised homogeneous catalyst can overcome not only catalyst recovery problem, but also the influence of phase change during reaction. Based on this idea, continuous catalytic production of ethylene carbonate from sc-CO₂/ethylene oxide mixture using an immobilized homogeneous catalyst is under investigation in our laboratory.

References

- [1] C.A. Eckert, B.L. Kuntson, P.G. Debenedetti, *Nature* 283 (1996) 313.
- [2] J.M. Desimone, Z. Guan, C.S. Elbernd, *Science* 257 (1992) 945.
- [3] M.J. Burk, S.G. Feng, M.F. Gross, W. Tumas, *J. Am. Chem. Soc.* 117 (1995) 8277.
- [4] S. Hadida, M.S. Super, E.J. Beckman, D.P. Curran, *J. Am. Chem. Soc.* 119 (1997) 7406.
- [5] M.E. Paulaitis, G.C. Alexander, *Pure Appl. Chem.* 59 (1987) 61.
- [6] P.G. Jessop, T. Ikariya, R. Noyori, *Nature* 368 (1994) 231.
- [7] P.G. Jessop, T. Ikariya, R. Noyori, *Science* 269 (1995) 1065.
- [8] D.J. Darensbourg, N.W. Stafford, T. Katsurao, *J. Mol. Cat. A: Chem.* 104 (1995) 1.
- [9] C.A. Costello, E. Berluche, S.J. Han, D.A. Sysyn, M.S. Super, E.J. Beckman, *Polym. Mater. Sci. Eng.* 74 (1996) 430.
- [10] M.T. Reetz, W. Konen, S. Thomas, *Chimia* 47 (1993) 493.
- [11] D.J. Darensbourg, M.W. Holtcamp, *Coord. Chem. Rev.* 153 (1996) 155.
- [12] R. Nomura, A. Ninagawa, H. Matsuda, *J. Org. Chem.* 45 (1980) 3735.
- [13] R. Nomura, M. Kimura, S. Teshima, A. Ninagawa, H. Matsuda, *Bull. Chem. Soc. Jpn.* 55 (1982) 3200.
- [14] A. Baba, T. Nozaki, H. Mastuda, *Bull. Chem. Soc. Jpn.* 60 (1987) 1552.
- [15] N. Takeda, S. Inoue, *Bull. Chem. Soc. Jpn.* 51 (1978) 3564.
- [16] T. Aida, S. Inoue, *J. Am. Chem. Soc.* 105 (1983) 1304.
- [17] K. Kasuga, S. Nagao, T. Fukumoto, M. Handa, *Polyhedron* 15 (1996) 69.
- [18] K. Kasuga, T. Kato, N. Kabata, M. Handa, *Bull. Chem. Soc. Jpn.* 69 (1996) 2885.
- [19] V. Vincens, A. Le Borgne, N. Spassky, *Makromol. Chem. Rapid. Commun.* 10 (1989) 623.
- [20] A. Le Borgne, M. Moreau, V. Vincens, *Macromol. Chem. Phys.* 195 (1994) 375.
- [21] A. Le Borgne, V. Vincens, M. Jouglard, N. Spassky, *Makromol. Chem., Macromol. Symp.* 73 (1993) 37.
- [22] A. Le Borgne, M. Wisniewski, N. Spassky, *Polym. Prepr.* 36 (1995) 217.
- [23] W.A. Herrmann, M.U. Rauch, G.R. Artus, *Inorg. Chem.* 35 (1996) 1988.
- [24] E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, *J. Am. Chem. Soc.* 113 (1991) 7063.
- [25] A.L. Singer, D.A. Atwood, *Inorg. Chim. Acta* 277 (1998) 157.
- [26] S.C. Ball, I. Cragg-Hine, M.G. Davidson, R.P. Davies, M.I. Lopez-Solera, P.R. Raithby, D. Reed, R. Snaith, E.M. Vogl, *J. Chem. Soc., Chem. Commun.* (1995) 2147.
- [27] H. Sugimoto, C. Kawamura, M. Kuroki, T. Aida, S. Inoue, *Macromolecules* 27 (1994) 2013.
- [28] S.J. Dzugas, V.L. Goedken, *Inorg. Chem.* 25 (1986) 2858.
- [29] J.A. Darr, M. Poliakoff, *Chem. Rev.* 99 (1999) 495.
- [30] W.J. Kruper, D.V. Dellar, *J. Org. Chem.* 60 (1995) 725.
- [31] T. Aida, M. Ishikawa, S. Inoue, *Macromolecules* 19 (1986) 8.
- [32] D.A. Atwood, J.A. Jegier, D. Rutherford, *Inorg. Chem.* 35 (1996) 63.
- [33] P. Dumas, P. Guerin, *Can. J. Chem.* 56 (1978) 925.
- [34] J.T. Groves, Y. Han, D. Van Engen, *J. Chem. Soc., Chem. Commun.* (1990) 436.
- [35] D.J. Darensbourg, M.W. Holtcamp, B. Khandelwal, K.K. Klausmeyer, J.H. Reibenspies, *J. Am. Chem. Soc.* 117 (1995) 538.
- [36] P. Dubois, R. Jerome, P. Teyssie, *Macromol. Chem., Macromol. Symp.* 42 (1991) 103.