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Synthesis of cyclic carbonate from allyl glycidyl ether and CO_2 over silica-supported ionic liquid catalysts prepared by sol-gel method

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Abstract−A silica-supported ionic liquid (Im-IL) was proven to be an effective heterogeneous catalyst for solventless synthesis of cyclic carbonate from allyl glycidyl ether (AGE) and carbon dioxide. Im-IL catalysts were prepared by sol-gel method. The synthesis of cyclic carbonate from AGE and CO_2 was carried out in a batch autoclave reactor. Im-IL with shorter alkyl chain length showed the highest conversion of AGE, probably due to the steric hindrance for the formation of intermediate from the catalyst prepared by using longer alkyl chains and AGE. High temperature and high pressure were favorable for the conversion of AGE. Im-IL can be reused for the reaction up to two consecutive runs without any considerable loss of its catalytic activity.

Key words: Immobilization, Ionic Liquid, Sol-Gel Method, Allyl Glycidyl Ether, Carbon Dioxide

INTRODUCTION

The conversion of carbon dioxide to industrially useful compounds is a very attractive subject in view of environmental protection and resource utilization. The reactions of carbon dioxide with oxiranes leading to five-membered cyclic carbonates are well known among many examples. These carbonates can be widely used for various purposes, such as electrolytic elements of lithium secondary batteries, polar aprotic solvents, intermediates for organic and polymeric synthesis, and ingredients for pharmaceutical/fine chemicals in biomedical applications [1].

The use of ionic liquids as environmentally benign media for catalytic processes or chemical extraction has received much interest during the last few years because they possess some very important features, such as the negligible vapor pressure, unique solvation properties, good ion conductivity as well as good catalytic activity and selectivity [2-6]. Many reactions catalyzed with ionic liquids and showing high performance have been reported [7]. In the last decades of the 20th century, numerous catalytic systems [8-13] were developed for the coupling of carbon dioxide and epoxides, such as alkali metal salts [14], metal oxides [15,16], ionic liquid [17-24], porphyrin [25], and transition-metal complexes [26-29]. However, currently, all these catalysts suffer from low catalytic activity and/or selectivity, low stability; a co-solvent is needed, and high pressure and/or high temperature are required.

Development of a highly efficient and environmentally benign catalyst system for the chemical fixation of carbon dioxide with epoxides under mild conditions still remains a challenge. At the same time, the major problem associated with most homogeneous catalyst systems is the separation of catalysts from the reaction mixture and the recycling of the catalyst [30].

In the present work, we report the synthesis of five-membered cyclic carbonate from allyl glycidyl ether and carbon dioxide using immobilized imidazolium salt ionic liquid on as-synthesized silica. The effects of alkyl chain length, carbon dioxide pressure, and reaction temperature are discussed to better understand the reaction mechanism.

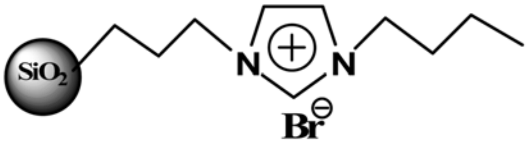
EXPERIMENTAL

1. Materials

Tetraethyl orthosilicate (TEOS, Aldrich), 3-chloropropyltriethoxysilane (ClPTES, Aldrich) and allyl glycidyl ether (AGE, Aldrich) were commercially available, and they were used without further purification. Carbon dioxide with a purity of 99.99% (Hanyu Chemicals) was also commercially available.

2. Preparation of Immobilized Ionic Liquid

Preparation of immobilized ionic liquid on silica was conducted by the previously reported method [31]. Imidazol was dissolved in toluene, and 3-chloropropyltriethoxysilane was added to the solution and the mixture was refluxed for 3 h under an argon atmosphere. The solvent was distilled under vacuum to yield 3-(N-imidazolyl) propyltriethoxysilane (I). Then (I) was reacted with 1-bromobutane in toluene under refluxing for 24 h and the solvent was distilled off under vacuum to produce 1-(triethoxysilylpropyl)-3-n-butylimidazolium bromide (II). 40 mmol of II together with 40 mL of TEOS, 10 mL of ethanol and 12 mL of water was added into a round bottom flask with a magnetic stirrer. After the formation of a clean and homogeneous liquid mixture, 5 ml of HCl (35 wt%) was added and the resultant mixture coagulated gradually. After ageing at 60 °C for 12 h, the mixture was then dried in vacuum at 80 °C



Scheme 1. Immobilized imidazolium salt ionic liquid on silica.

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for 5 h. The resulting solid contained 1-propyl-3-n-butylimidazolium bromide groups bonded to surface silicon atoms as show in Scheme 1.

3. Cycloaddition of CO_2 to AGE

The synthesis of cyclic carbonate from allyl glycidyl ether (AGE) and CO_2 using the supported ionic liquid (0.5 g) was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical batch operation, the immobilized ionic liquid (2 mmol) and AGE (42.5 mmol) were charged into the reactor without solvent, and then purged several times with CO_2. The reactor was then pressurized with CO_2 to a preset pressure, at 0.51-3.55 MPa, at room temperature. The reactor was heated to a desired temperature, and then the reaction was started by stirring the solution at 300 rpm. The reactor pressure increased about 0.03-0.11 MPa, depending on the reactor temperature.

4. Analysis

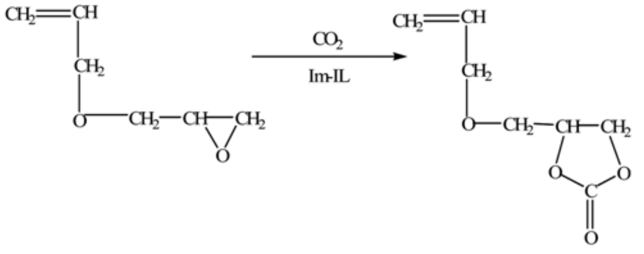
The amount of attached ionic liquid on SiO_2 surface was determined from elemental analysis (EA, Varioel 3) of nitrogen. The product was analyzed by a gas chromatograph (HP 6890N) equipped with an FID and a capillary column (HP-5, 5% phenyl methyl siloxane). The identification of the five membered cyclic carbonate was performed by FT-IR (ASI Model 1000, KBr), ^{1}H-NMR and ^{13}C-NMR (Varian Gemini 2000 spectrometer in $CDCl_3$), TMS as an internal standard.

RESULTS AND DISCUSSION

Surface area and pore volume of the immobilized ionic liquid (Im-IL) catalysts are measured by a nitrogen adsorption with a BET apparatus (Micromeritics, ASAP 2010), and the results are shown in Table 1. One can see that the Im-IL catalysts have very low surface area and very small pore volume. It seems that the inside pores are not well developed. The amount of immobilized imidazolium salt measured by the elemental analysis is also listed in Table 1. Im-IL-2 showed the highest amount of attached IL, 1.86 mmol/g. Im-IL-3 showed the lowest amount of attached IL, probably due to the increase of steric hindrance for long alkyl chain of octyl bromide. The attached amounts of IL on this amorphous silica were lower than that on a mesoporous MCM-41, of which the result will be published later. The surface area of the ordered MCM-41support was also much higher than this amorphous silica.

Table 1. BET surface area, pore volume and amount of immobilized imidazolium salt of silica-supported ionic liquid catalysts

Catalyst	Alkyl bromide	BET area (m^2/g)	Pore volume (cm^3/g)	Attached IL (mmol/g)
Im-IL-1	ethyl bromide	0.38	<0.01	1.38
Im-IL-2	butyl bromide	0.39	<0.01	1.86
Im-IL-3	octyl bromide	0.37	<0.01	1.26



Scheme 2. Synthesis of cyclic carbonate from AGE and CO_2.

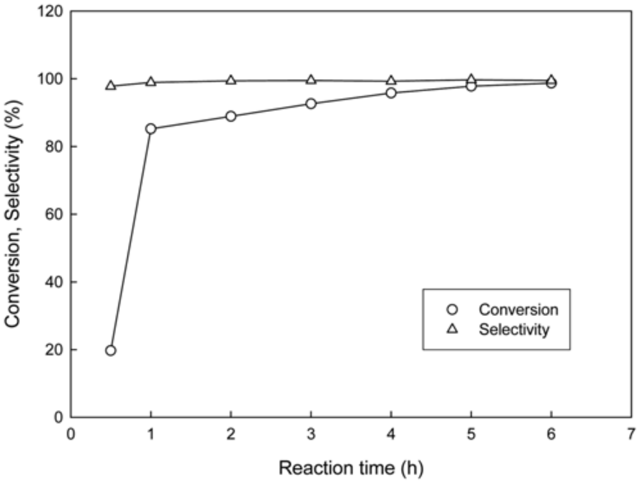


Fig. 1. Variation of AGE conversion and cyclic carbonate selectivity vs time on stream with Im-IL-2 catalyst at 110 °C and 1.76 MPa of CO_2 pressure.

The synthesis of cyclic carbonate from AGE and CO_2 was carried out by using various ionic liquids as shown in Scheme 2.

The formation of the five-membered cyclic carbonate was characterized by IR spectroscopy. By comparison of the relative intensities of the two carbonyl bands at 1,750 (linear carbonate) and 1,800 cm^{-1} (cyclic carbonate) in the IR spectrum, the amount of polycarbonate was estimated to be less than 2%.

The influence of reaction time on the cyclic carbonate synthesis using Im-IL-2 is given in Fig. 1. The reactions were performed in the presence of 0.5 g of Im-IL-2 at 110 °C under CO_2 pressure of 1.76 MPa. The AGE conversion at 30 min was low (19.6%) and it increased to 85.2% after 1 h. The rate-determining step for the reaction is known to be the attack of the anionic part of the catalyst such as formation of bulky imidazolium salt by oxirane [14]. Therefore, there appears to be an induction period for an irreversible reaction to proceed between the intermediate complex and CO_2 to form the cyclic carbonate. One can see that the reaction proceeds rapidly within first 3 h, while the selectivity of cyclic carbonate almost remains constant during the reaction course. It is important to note that within 6 h, an almost quantitative yield could be achieved with higher than 99% of the cyclic carbonate selectivity. In other words, a reaction time of 6 h is needed to complete the AGE conversion, which shows that the silica supported $[BMIm]^+[Br]^-$ is an effective heterogeneous catalyst for the synthesis of cyclic carbonate from AGE and CO_2. Therefore, all the following experiments were performed for 6 h.

The effects of the alkyl chain length of Im-IL catalysts were studied at 120 °C and CO_2 pressure of 0.86 MPa for 6 h. A relatively low CO_2 pressure was applied to compare the reactivity of the different catalysts. At high CO_2 pressure, as in Fig. 1, all the catalysts showed more than 97% of AGE conversion after 6 h of reaction.

Table 2 shows the conversion of AGE and selectivity to the cyclic carbonate for the immobilized ionic liquid catalysts of different alkyl-

Table 2. Synthesis of cyclic carbonate from AGE and CO_2 using the silica supported IL catalysts

Catalyst	AGE conversion (%)	Selectivity (%)
Im-IL-1	56.7	81.1
Im-IL-2	53.4	90.5
Im-IL-3	49.1	76.8

Reaction conditions: AGE=42.5 mmol, Catalyst=0.5 g, P (CO_2)=0.86 MPa, Temp.=120 °C, Time=6 h

Table 3. Effect of reaction temperature and CO_2 pressure on the synthesis of cyclic carbonate from AGE and CO_2 using Im-IL-2 catalyst

Temp. (°C)	P (MPa)	AGE conversion (%)	Selectivity (%)
80	0.86	47.2	89.4
100	0.86	51.3	86.8
120	0.86	53.4	90.5
140	0.86	64.4	69.0
160	0.86	62.3	64.2
110	0.51	37.7	79.6
110	0.86	52.9	89.3
110	1.76	98.7	94.1
110	3.55	97.3	96.8

Reaction conditions: AGE=42.5 mmol, Catalyst=0.5 g, Time=6 h

bromide used in the preparation step. The catalytic activity of ionic liquids usually depends on the corresponding catalyst cation and anion [32,33]. Bulky ionic liquid, having longer distance between cation and anion, may be considered to have higher anion activation ability. However, in the present study of immobilized ionic liquid catalysts, Im-IL-1 having the smallest alkyl chain shows the highest AGE conversion. The order of AGE conversion decreased in the order Im-IL-1>Im-IL-2>Im-IL-3, even though Im-IL-2 showed the highest amount of immobilized IL. This may due to the steric hindrance of bulky alkyl chain length for the formation of active intermediate complex between Im-IL catalyst and AGE, which is generally known as the rate-limiting step for the cycloaddition of CO_2 to epoxides [14,25].

Table 3 shows the effects of temperature and pressure of carbon dioxide on the conversion of AGE. AGE conversion increased with increasing reaction temperature from 80 °C up to 140 °C. At 160 °C AGE conversion decreased slightly due to the decomposition of the cyclic carbonate or to the side reaction to produce glycol. High temperature operation is one of advantage of imidazolium salt ionic liquid. Quaternary ammonium salt ionic liquid is reported to degrade at 140 °C in the presence of strong base [34].

In order to understand the effect of pressure on the reactivity of Im-IL-2 catalyst, the pressure of CO_2 was varied between 0.51 and 3.55 MPa. The AGE conversion increased as CO_2 pressure increased up to 1.76 MPa. However, it decreased at 3.55 MPa. There exists an optimum CO_2 pressure for the conversion of AGE. The decrease in the activity with increasing pressure of carbon dioxide at high pressure range was also reported previously [31,35]. It can be inferred that the introduced CO_2 dissolves in AGE or liquefies through the formation of a CO_2-AGE complex [36]. Too high CO_2 pressure may inhibit the interaction between AGE and the catalyst, and could cause a low concentration of AGE in the vicinity of the catalyst due to the so-called dilution effect.

Table 4. Reactivity of recycled Im-IL-2 catalyst

Recycle no.	AGE conversion (%)	Selectivity (%)
fresh	95.9	95.6
1	92.7	95.1
2	89.3	94.4
3	86.4	89.4

Reaction conditions: AGE=42.5 mmol, Catalyst=0.5 g, P (CO_2)=1.76 MPa, Temp.=80 °C, Time=6 h

A series of catalytic cycles were carried out to investigate the stability of the catalytic activity and recycling. In each cycle, the catalyst was separated by filtration and then used directly for the next run. Table 4 shows the activity of the reused Im-IL-2 catalyst. It shows that the catalyst can be reused at least twice with a slight loss of activity, while the selectivity of the product remains almost the same. At the third recycle, the catalyst showed about 10% loss of its initial reactivity. This loss might originate from the less stable structure of the amorphous silica support. Some of the imidazolium group can be detached from the surface of the silica support.

CONCLUSIONS

Silica-supported imidazolium salt ionic liquids prepared by sol-gel method were effective catalysts for the synthesis of cyclic carbonate from AGE and CO_2. High conversion of AGE together with good selectivity of the cyclic carbonate was achieved in less than 6 h. High temperature and high carbon dioxide pressure was favorable for the synthesis of the cyclic carbonate. The supported ionic liquid as heterogeneous catalyst was easily recovered and reused over two times with slight loss of its catalytic activity.

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