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Synthesis of cyclic carbonate through microwave irradiation using silica-supported ionic liquids: Effect of variation in the silica support

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ABSTRACT

Microwave-assisted cycloaddition of CO_2 to phenyl glycidyl ether (PGE) was carried out under solvent-free conditions using silica-supported ionic liquids as catalysts. Various immobilized ionic liquid catalysts were prepared with different silica supports such as commercial and amorphous silica, SBA-15, and MCM-41. The effect of these supports on the cycloaddition reactions of CO_2 to PGE was studied under optimized reaction conditions of microwave power and irradiation time. The catalytic activity was found to depend strongly on the morphology of the support. Comparative studies with conventional heating reactions showed that microwave-induced reactions were greatly superior, with very high PEG conversion and high selectivity of cyclic carbonate within 15 min of reaction time.

1. Introduction

Reducing the amount of atmospheric greenhouse gases has recently become an important concern of environmentalists and scientists owing to their great influence on climatic changes. The sequestration of CO_2, the principal greenhouse gas, would be considered a major breakthrough for researchers. The chemical use of CO_2 as a renewable feedstock through cycloaddition or copolymerization of CO_2 with epoxides has proven to be a worthwhile step toward this goal. Cyclic carbonates are a useful industrial chemical with various applications in synthetic organic chemistry [1–4]. Until recently, several catalysts, including homogeneous and heterogeneous catalysts, were used for cyclic carbonate synthesis; they include simple alkali metal salts, ionic liquids (ILs), phosphines, main group metal complexes, transition metal complexes, and porous metal oxides [5–12].

The unique properties of ILs, such as high thermal stability, a broad range of temperature over which they are liquids, and tunable acidity, make them appealing media for a broad range of catalytic applications [13–20], including the chemical fixation of CO_2 [21,22]. The major drawback of IL catalysis is the complexities of catalyst recovery from the reaction mixture and catalyst recycling. The chemical industry has always preferred to use a heterogeneous catalyst owing to the ease of separation and the ability to use a fixed-bed reactor. Given the economic concerns and the possible toxicity of available solvents, the immobilization of ILs on a solid support is highly advantageous. Immobilized ILs have been used for hydroformylation, hydrogenation, and the Friedel–Crafts alkylation and cycloaddition reactions. In our previous reports [23–27], we used various types of silica as a support for the reaction of CO_2 to epoxides under conventional reaction conditions.

Microwave-assisted organic synthesis has recently gained importance. A few successful reports of microwave-assisted CO_2 use have been published [28–30]. Owing to the high polarity of ILs, IL-mediated organic synthesis under microwave irradiation is useful for effective and rapid heating [31]. In this work, we studied the effects of variations in the morphology of silica supports and the reaction parameters on the cycloaddition reaction of CO_2 and phenyl glycidyl ether (PGE) under microwave irradiation (Scheme 1).

2. Experimental

2.1. Materials

All materials for the catalyst synthesis and reaction studies were purchased from Aldrich and used without further purification. CO_2 gas (99.999% pure) was purchased from Hanyu Chemicals and used as supplied for the reactions. All solvents were received from SK Chemicals, Korea, and used without any modification.

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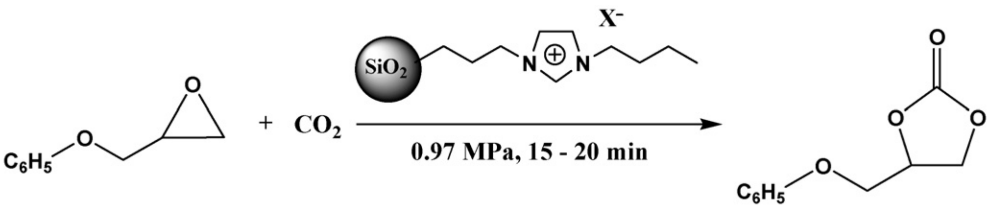

Scheme 1. Cycloaddition of PGE and CO_2 using silica supported ionic liquid.

2.2. Synthesis of silica-supported ionic liquids

2.2.1. Commercial silica support

Before immobilization, commercial silica was pretreated at 200 °C under vacuum for 4 h to remove physisorbed water. The pre-activated silica and the IL were dispersed in anhydrous toluene in a 500-mL round-bottom flask. The mixture was refluxed for 24 h under a nitrogen atmosphere. The resulting product was filtered and washed with dichloromethane to remove the unreacted IL. The catalyst was obtained after drying the sample at 60 °C under reduced pressure for 24 h.

2.2.2. Amorphous silica support

Imidazole (5.1 g, 79.5 mmol) was dissolved in 75 mL of dry toluene, to which 3-chloropropyltriethoxysilane (ClPTES, 18 mL, 75 mmol) was added, and the mixture was refluxed for 12 h under an argon atmosphere. An oil containing 3-(N-imidazolyl)propyl triethoxysilane was obtained, and to it was added 1-bromobutane, followed by refluxing for another 12 h under argon to yield 1-(triethoxysilylpropyl)-3-*n*-butylimidazolium bromide. This is denoted as IL-functionalized organosilane (IFOS). The molar ratio of the constituents of the synthetic mixture was optimized according to our previous report [24]; 0.818 TEOS:0.182 IFOS:5.61 HCl:153.9 H_2O, where the ratio of tetraethyl orthosilicate (TEOS) to IFOS was 4.5. In a typical synthesis, a 500-mL polypropylene (PP) bottle, fitted with a wheel-type magnetic bar and brought to 40 °C, was charged with 100 mL of water, followed by 25 mL of 35% HCl. After 15 min of stirring, a clear solution was obtained. Before 8.01 mL of TEOS was added, it was placed in the open PP bottle and stirred for 3 h at 40 °C for pre-hydrolysis and expulsion of ethanol from the reaction mixture. 4.64 mL of the IFOS–ethanol mixture was then added (initial organosilane mixed with 15 mL of ethanol to avoid errors in the measurement of the more viscous IFOS) into the aforementioned solution and stirred for 24 h at 40 °C; it was subsequently heated another 24 h at 60 °C in a hot-air oven in the PP bottle. The solid product was recovered and mixed with 50 mL of ethanol, filtered, and dried at 60 °C for 12 h.

2.2.3. SBA-15 support

The molar ratio of various constituents in the synthesis mixture was: $(1-X)$ TEOS: X ClPTES:0.016 P123:5.62 HCl:5.26 NaCl:181.3 H_2O, where $(1-X)/(X)$ is 4.5, and X is 0.1817. In a typical synthesis, 4 g of Pluronic P123 was added to 75 mL of water; after 90 min of stirring, a clear solution was obtained, and a solution containing 13.3 g of NaCl with 50 mL of water was added. Thereafter, 25.1 mL of 35% HCl was added, and the solution was stirred for another 2 h. Then 8.01 mL of TEOS was added to the surfactant–HCl mixture and mixed for 3 h for pre-hydrolysis at 40 °C. Subsequently, 1.99 mL of ClPTES was added to the above-mentioned solution, and the solution was stirred for 20 h at 40 °C. The solution was transferred to a PP bottle and heated for 24 h at 100 °C in a hot-air oven. The solid product was recovered by filtration without cooling and then washed with ethanol and water and dried at 60 °C for 24 h. The template was removed by Soxhlet extraction using ethanol at 60 °C for 24 h. The sample was washed with ethanol and water and dried at 60 °C overnight.

Immobilization was performed under a nitrogen atmosphere. The above synthesized sample was pre-activated at 200 °C under vacuum for 4 h to remove physisorbed water. 5 g of SBA-15 was treated with imidazole (5 mmol/g) using dry toluene (10 mL/g) under reflux conditions for 12 h. Alkyl halide (10 mmol/g) was then added, and the mixture was stirred for 12 h. The excess imidazole and alkyl halide were removed by filtration followed by repeated washing with 2 L dichloromethane (2 L/5 g of catalyst). The obtained solid was dried under vacuum at room temperature.

2.2.4. MCM-41 support

The molar ratios of the organically modified MCM-41 material synthesized using the constituents in the synthesis mixture are as follows: 1 TEOS:0.222 ClPTES:0.29 C_{16}TMABr:0.58 TMAOH:81.67 H_2O [23]. In a typical synthesis, TEOS (19.45 mL) was mixed with ClPTES (4.84 mL) to form Solution A. Solution A was added to Solution B (18.35 g of tetramethylammonium hydroxide (TMAOH) and 18 g of H_2O) and stirred for 5 min to form Solution C. Solution C was added to Solution D (9.1 g of cetyltrimethylammonium bromide (CTMABr) dissolved in a mixture of 30 g of H_2O and 45 mL of ethanol) and stirred vigorously at room temperature for 45 min. The resulting mixture was then heated in a water bath at 80 °C for 45 min to remove the added alcohol as well as that produced by alkoxide hydrolysis. Finally, 54 g of H_2O was added slowly to the solution, during which the clear liquid became a turbid gel. The gel was aged for 20 h (pH = 12.1) with continuous stirring. The pH of the resulting gel was adjusted to 11.3 with 4 N HCl. The resulting solution was stirred for 4 h and then heated in a Teflon-coated stainless steel autoclave at 140 °C for 48 h. The template was removed by Soxhlet extraction using ethanol at 60 °C for 24 h, and the sample was washed with ethanol and water and dried at 60 °C overnight. Mesoporous molecular sieves (chloropropyl-functionalized MCM-41, CP-MCM-41) were pre-activated at 175 °C under a vacuum for 4 h to remove physisorbed water. Five grams of CP-MCM-41 was immobilized by the procedure described in Section 2.2.3.

2.3. Sample characterization

The surface area, pore volume, and pore size distribution were measured by nitrogen adsorption at −195 °C using an ASAP2010 system purchased from Micromeritics. The solvent-extracted samples were degassed at 110 °C and 10^{-5} Torr overnight before the adsorption experiments. The mesoporous volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 by assuming that all mesopores were filled with condensed nitrogen in the normal liquid state. The pore size distribution was estimated using the Barrett, Joyner, and Halenda (BJH) algorithm software from Micromeritics built into the ASAP2010 system. Elemental analysis was performed using a Vario EL III in which 2.0 mg of each sample was subjected to 1100 °C with sulfanilic acid used as the standard.

Table 1
The physico-chemical properties of immobilized IL on different supports.

Catalyst	Silica source	S_{BET} (m^2/g)	D_p (nm)[a]	IL amount (mmol/g)[b]
CS-BImBr-1	Commercial	101	7.9	0.36
CS-BImBr-2	Commercial	209	1.9	1.30
CS-BImBr-3	Commercial	38	1.5	1.00
AS-BImBr	Amorphous	477	4.2	0.61
SBA-BImBr	SBA-15	856	4.7	2.53
MCM-BImBr	MCM-41	614	2.2	2.93

[a] Average pore diameter measured by N_2 adsorption using BJH method.
[b] Amount of immobilized ionic liquid estimated by the nitrogen content from elemental analysis.

3. Results and discussion

3.1. Characterization of silica-supported ionic liquid catalysts

The surface area and average pore diameter were estimated by the N_2 adsorption–desorption isotherm; the data are shown in Table 1. An IL attached to commercial silica (CS-BImBr-1) showed the biggest pore diameter, 7.9 nm. CS-BImBr-3 showed the smallest pore size. An IL attached to CP-MCM-41 (MCM-BImBr) had a smaller pore diameter than an IL attached to SBA-15 (SBA-BImBr) or amorphous silica (AS-BImBr). The nitrogen content of BMImBr in the different immobilized catalysts was analyzed by elemental analysis, and the amount of immobilized IL is also shown in Table 1. The amount of IL in MCM-BImBr and SBA-BImBr was higher than in the other immobilized IL catalysts, probably because of their high surface area. ^{29}Si NMR, ^{13}C NMR, and Fourier transform infrared (FT-IR) analysis of the ILs immobilized on silica materials confirmed the presence of IL attached to the silica surface [23].

3.2. Catalyst activity under microwave heating

The catalytic activity of these supported catalysts was tested for the cycloaddition of CO_2 and PGE under microwave irradiation, and the reaction conditions were optimized. To understand the influence of microwave heating on the catalytic properties of supported ILs for this particular reaction, cycloaddition was performed by varying the reaction conditions, such as microwave power level, catalyst concentration, and microwave irradiation time. Finally, various types of silica support were tested, and the activity of the immobilized ILs was measured in terms of PGE conversion.

The microwave power during the reaction significantly affected the reaction profile. As shown in Fig. 1, when the microwave power was increased from 100 to 500 W, the conversion decreased considerably. The yield also decreased with increasing microwave power; however, the selectivity of phenyl glycidyl carbonate (PGC) remained almost 100%, indicating that the catalyst promoted only the formation of cyclic carbonate, and no other side products were observed under these reaction conditions. This decrease in conversion and yield at higher microwave powers could be explained as follows. The reaction profile depends on the dissolution of CO_2 and its incorporation into the reaction mixture. Hence, for cyclic carbonate to form, both CO_2 and epoxide molecules should be activated. With increasing microwave power, the dissolution of CO_2 could decrease because of the sudden temperature increase; therefore, sufficient CO_2 molecules were not available for cycloaddition to epoxides. Since the catalyst is highly selective toward cyclic carbonate formation, high selectivity was observed even at higher microwave powers.

Since microwaves are a very efficient tool for activating the reaction mixture within a fraction of a second, the influence of the irradiation time was studied to measure the catalytic activity of supported catalysts. The reaction mixture was irradiated for 5–60 min; Fig. 2 shows the effect of irradiation time. PGE conversion increased with increasing irradiation time, reaching a maximum between 15 and 20 min, after which the activity did not significantly improve.

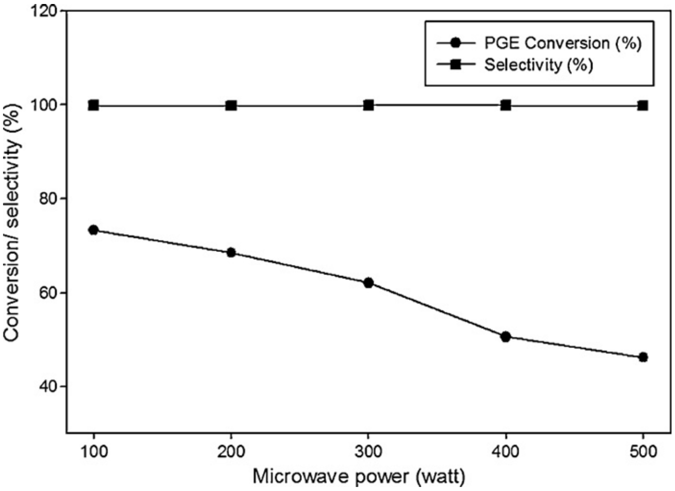

Fig. 1. Effect of microwave power on PEG conversion and PGC selectivity (PGE = 37.4 mmol; catalyst (SBA-BImBr) = 0.25 g; $P_{CO_2} = 0.97$ MPa; 20 min; 140–150 °C).

The temperature of the reaction mixture during various reaction conditions was measured at frequent intervals. Fig. 3 shows the temperature of the reaction mixture versus the irradiation time with 100 W of microwave power. The temperature increased very rapidly, reaching 128 °C after 10 min and 140 °C after 20 min. Then it increased slightly to 150 °C after 60 min.

The silica supports were varied by selecting commercial or amorphous silica, SBA-15, or MCM-41 as the source. The results are given in Table 2. CS-BImBr-1, AS-BImBr, and SBA-BImBr showed higher activity toward cyclic carbonate conversion. The results clearly show that supports with a higher pore diameter (D_p) yielded high conversion and selectivity irrespective of the surface area. This could be due to the geometry-based selectivity of cyclic carbonate from PGE, the significant production of which can occur only with large-pore supports having D_p higher than 4 (Runs 1, 4–8). Also, the lower conversion of PGE for the remaining supports having lower D_p could be expected from the activity of reactive species at the

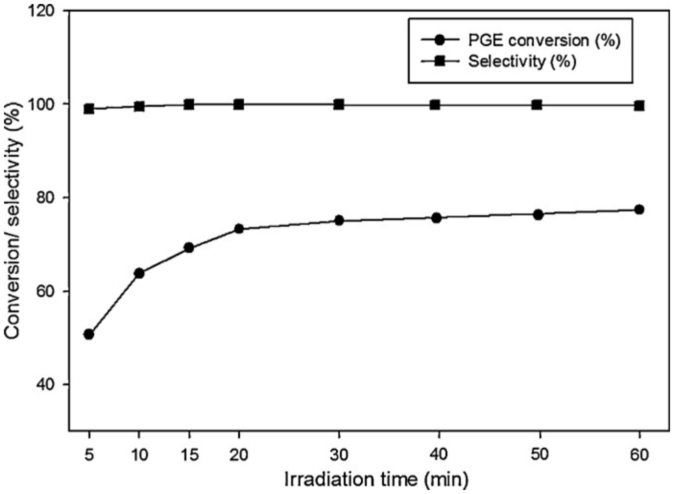

Fig. 2. Effect of irradiation time on PEG conversion and PGC selectivity (PGE = 37.4 mmol; catalyst (SBA-BImBr) = 0.25 g; $P_{CO_2} = 0.97$ MPa; 100 W; 140–150 °C).

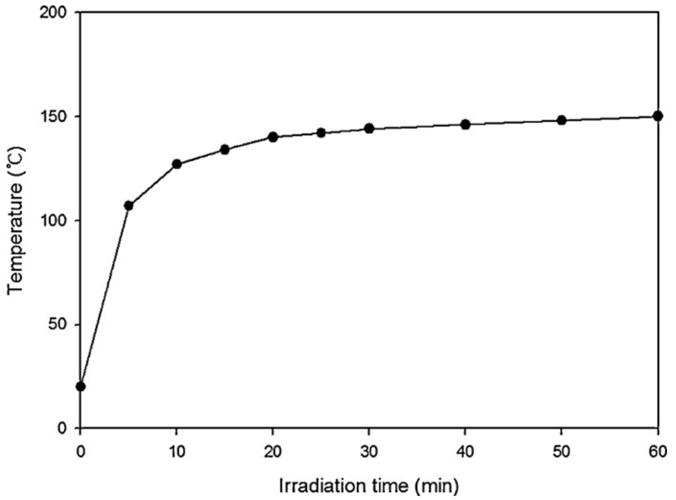

Fig. 3. Temperature profile for the reaction mixture (PGE = 37.4 mmol; catalyst (SBA-BImBr) = 0.25 g; $P_{CO_2} = 0.97$ MPa, 100 W).

surface. This is again clarified by the lower selectivity toward cyclic carbonate formation. The effect of the amount of catalyst on conversion and selectivity has also been established through Runs 4, 5, 6, and 7. The reaction data show a slight improvement in conversion when the amount of AS-BImBr or SBA-BImBr increases from 0.25 to 0.5 g.

The effect of the alkyl chain length of the supported IL is studied by varying the substituent on the SBA-15 support from ethyl to butyl with bromide as the anion. Generally, a free IL having a longer alkyl chain shows higher activity owing to an increase in anion activation ability. In the present scenario, the ethyl substituent showed higher activity (Run 8, 90.5%) than the butyl one (Run 7, 77.3%). From this observation, we can conclude that ILs that are active for the reaction are attached mainly inside the pores rather than on the surface; hence, a bulky substituent may cause stronger steric hindrance to the diffusion of the reactant molecule.

Interestingly, the temperature of reaction mixtures having conversions higher than 70% falls in the range of 140–150 °C (Runs 1, 4–8). Those systems showing low reactivity reached a reaction mixture temperature of only around 70 °C. This phenomenon suggests that microwave heating of the porous silica material by the reaction mixture can be affected by the pore structure; further detailed studies are needed.

Table 2
Effect of various silica supports on the cycloaddition reaction of PGE and CO_2.

Run	Catalyst	Catalyst amount (g)	Conversion (%)	Selectivity (%)
1	CS-BImBr-1	0.5	73.6	100
2	CS-BImBr-2[a]	0.25	11.6	97.4
3	CS-BImBr-3[a]	0.25	8.9	76.2
4	AS-BImBr	0.5	80.0	100
5	AS-BImBr[b]	0.25	71.5	100
6	SBA-BImBr[b]	0.25	73.3	100
7	SBA-BImBr	0.5	77.3	100
8	SBA-EImBr	0.5	90.5	100
9	MCM-BImBr[c]	0.25	9.5	77.1
10	MCM-BImBr[d]	0.25	61.7	64.5

Reaction condition: PGE = 37.4 mmol; $P_{CO_2} = 0.97$ MPa; 100 W; 140–150 °C; 15 min.

[a] 20 min; 70 °C.

[b] 20 min; 140–150 °C.

[c] 30 min, 70 °C.

[d] Reaction by conventional heating after 6 h at 140 °C.

Microwave heating was compared with conventional heating for the MCM-BImCl catalyst (Runs 9 and 10). Conventional heating showed much higher PGE conversion (61.7%) than the corresponding microwave heating (9.5%). This is not typical for homogeneous catalyst that the microwave heating showed much lower reactivity than the conventional heating. However, for the immobilized catalyst MCM-BImBr in microwave heating system, the small pore size might inhibit the effective penetration of microwave to active sites inside the MCM-41 support. The temperature of the reactor in Run 9 was much lower than Run 6 with SBA-BImBr having bigger pores.

4. Conclusion

Rapid, selective, and solventless synthesis of cyclic carbonate from PGE and CO_2 has been established through microwave heating using supported IL catalysts. Different catalysts were synthesized by varying the silica supports, using commercial and amorphous silica, SBA-15, and MCM-41. The effect of the structure of the silica support on the cycloaddition reaction was studied using a microwave reactor system under solvent-free conditions. IL catalysts immobilized on silica supports with relatively large pore diameters (greater than 4 nm) showed good catalytic activity. A comparison with conventional heating reactions showed that microwave-induced reactions were greatly superior to the former, with very high PGE conversion and high selectivity of PGC within 15 min of reaction time.

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