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Synthesis of cyclic carbonates from carbon dioxide and epoxides using alkali metal halide supported liquid phase catalyst

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Supported liquid phase catalysts (SLPC) were prepared from high surface area porous silica, polyethylene glycol (PEG), alkali metal halides and used for the synthesis of cyclic carbonates from carbon dioxide and epoxides. These catalysts was found to be highly active and selective for the synthesis of cyclic carbonates. The catalytic activity strongly depends on the nature of the supported alkali metal halide. The amount of alkali metal salt incorporated in the catalyst is one of the most important factor governing the catalytic performance. Effect of various reaction parameters such as pressure, temperature, catalyst loading, surface area of support was also studied in detail.

KEY WORDS: cyclic carbonates; supported liquid phase catalyst (SLPC); alkali metal halides; carbon dioxide fixation; oxiranes; silica.

1. Introduction

Carbon dioxide is one of the green house gas arising from human activities, which leads to environmental pollution. In recent years considerable attention is given for development of environmentally benign processes based on chemical fixation of carbon dioxide [1]. Several methodologies are developed for chemical fixation of carbon dioxide to valuable chemicals [2] and the synthesis of five membered cyclic carbonates via, the cycloaddition of CO_2 to epoxides is one of the promising reactions in this direction replacing existing poisonous phosgene based synthesis. The five membered cyclic carbonates have several application such as they act as a precursor for polycarbonates and other polymeric materials [3] they are also used as an intermediate for glycol, carbamates, pyrimidines, purines and so on [4]. In recent decades numerous homogenous and heterogeneous catalyst system such as alkali metal salts alone [5] or in combination with crown ether [6], quaternary ammonium salt or phosponium salt [7,8] ionic liquids [9], halostannanes [10] other organic bases [11–13], mixed oxides [14–17] smectite [18,19], zeolite [20,21] titanosilicates[22], metal complexes [23–29], and have been explored for this transformation. Most of these systems suffer from the problems associated with low catalyst reactivity, catalyst/product separation, expensive catalysts, sophisticated techniques and lower yield of the products. Hence there is a need for development of a highly active and recyclable catalyst system.

Various soluble alkali metal halides [30] are reported as a catalyst for the synthesis of cyclic carbonates. The catalyst product separation was the major disadvantage with this system due to homogenous nature of the catalyst and to over come this problem in this work we report silica supported liquid phase catalyst (SLPC) in which alkali metal halides are effectively anchored on the surface of high surface area silica. This catalyst is not overly sensitive to the air and moisture and could be subjected to utilization for several recycles without obvious loss of activity.

2. Experimental

2.1. Preparation of catalysts

Typical SLPC catalyst containing alkali metal halides were prepared by using polyethylene glycol (PEG 600) e.g. 1 g, as a dispersed phase and 5 g porous silica gel (Aldrich Davisil grade) with BET surface area of 800 m^2/g. PEG (1 g) and alkali metal salt (e.g. NaBr) 375 mg was added into 50 ml round bottom flask and mixed at 60–70 °C to get an homogenous mixture, then silica was added and the mixture was further magnetically stirred for 3–4 h at room temperature in order for the PEG phase to disperse well on the surface of silica gel.

2.2. Cycloaddition reactions

All the reactions were carried out in 250 ml stainless steel autoclave. Typical reaction procedure is as follows, 20 ml toluene, 50 mmol propylene oxide and 1 g SLPC catalyst prepared as mentioned above, were charged in

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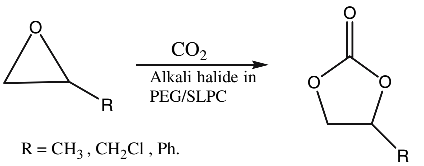
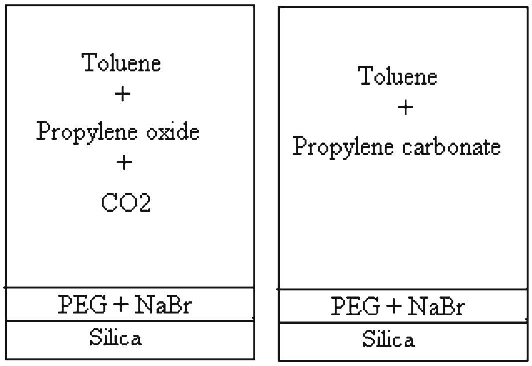
to the reactor. The reactor was heated up to 150 °C. Then CO_2 was injected up to 4.5 MPa. The reaction mixture was stirred for 6 h (800 rpm). After the completion of reaction the reactor was cooled and depressurized. The liquid reaction mixture was analyzed compared with authentic sample by gas chromatography. The GC analysis shows quantitative yield of propylene carbonate, no other side product were observed.

3. Results and discussion

The cycloaddition of carbon dioxide to epoxide was performed using SLPC catalyst described in experimental section. The typical reaction scheme is as follows,





Scheme 1. Schematic illustration of heterogeneous SLPC catalyst system for CO_2 fixation reaction.

In literature several different catalysts are reported for this reaction. They have disadvantage with respect to selectivity recyclability and activity (many of them requires prolonged reaction time) performance. Ionic liquids are found to be effective for this reaction however they are expensive and required sophisticated techniques for the preparation. In this view there is ample scope to investigate catalyst, which is simple and commercially available. Nobuhiro et al. reported various homogeneous alkali metal salts for this transformation. However, as these catalysts are homogenous in nature and hence poses problem associated with catalyst/product separation and recyclability of the catalyst which limits practical application. In this work we investigate to development of a catalyst system, which will heterogenies these homogenous soluble salts. Supported aqueous phase catalyst has gained considerable attention in recent years for heterogenisation of various transition metal complex catalysts and they can be used for the present reaction. Alkali metal halides are practically insoluble in aromatic solvents, particularly in presence of hydrophilic solvents. This property can be extended to develop such type of recyclable catalyst. The catalyst was prepared by solubilising alkali metal halide in PEG and anchoring this solution on high surface area porous hydrophilic silica. The catalyst was found to be effective and results are described as follows.

Table 1
Effect of activity of various salts on CO_2 fixation reaction

Catalyst	% Wt of salt	% Yield of PC[a]
None	–	19
SiO_2	–	15
[b]NaBr	5	96.39
[c]NaCl	5	71.54
NaBr/silica	5	80.36
NaCl/silica	5	65.39
NaI/silica	5	69.85
NaOAc/silica	5	21.00
KBr/silica	5	56.87
KCl/silica	5	34.93
TBAB/silica	5	73.67
TBAI/silica	5	67.69

Reaction Conditions: Propylene oxide: 50 mmol, catalyst: 1 g, toluene: 20 ml, CO_2 pressure 5.5 MPa, temp. 150 °C, time 6 h.
[a] Yield of PC determined by GC analysis.
[b, c] Reaction carried out for 2 h.

3.1. *The effect of the nature of alkali metal halide*

The effect of the nature of alkali metal halide is described in table 1. It was observed that nature of both cation and anion plays significant role in the reactivity. Bromides gives higher yield as compared with chlorides and iodides. Sodium salts was found to be highly effective than potassium salt. Phase transfer agents such as TBAB and TBAI are also effective for this reaction; however, leaching of catalyst was observed this case.

3.2. *Influence of NaBr loading*

Since the performance of sodium bromide was satisfactory it was studied for next optimization studies. The loading of the catalyst is represented in figure 1. It can seen that 7.5 wt%. NaBr gives the best performance.

3.3. *Influence of silica surface area*

Surface area of the catalyst plays an important role in the reaction. The effect of silica having different surface area was used for catalyst preparation. It was observed that yield of the reaction was highly depends on the surface area of the catalyst, with increase in the surface area the yield was found to be increases as shown in the figure 2. The increase in surface area of silica increases surface area of supported liquid film which leads to facilate gas- liquid- liquid mass transfer, thereby increases the reaction rate and conversion. The trend is

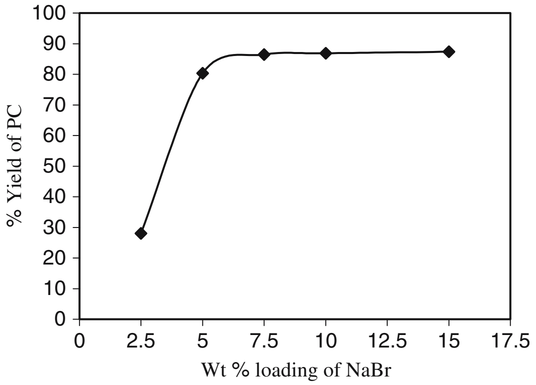


Figure 1. Influence of wt% loading of NaBr per gram of silica on the yield of reaction. Propylene oxide: 50 mmol; catalyst: 1 g; toluene: 20 ml; CO_2 pressure 5.5 Mpa, time 6 h.

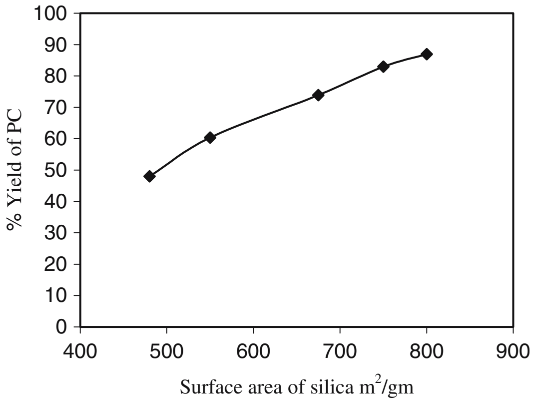


Figure 2. Influence of surface area of silica on yield of reaction. Propylene oxide: 50 mmol; catalyst: 1 g; l toluene: 20 ml; CO_2 pressure 5.5 MPa temp. 150 °C, time 6 h.

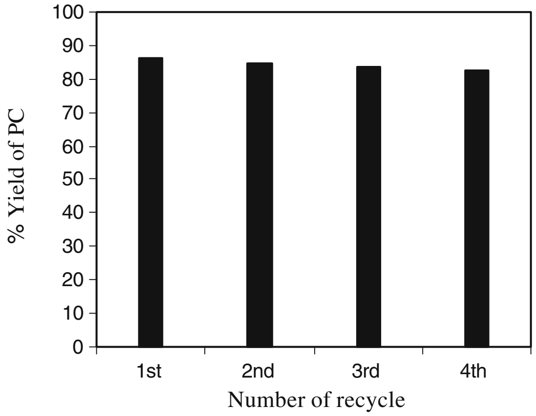


Figure 3. Recycling of SLPC catalyst. Propylene oxide: 50 mmol; catalyst: 1 gm; toluene: 20 ml, CO_2 pressure 5.5 MPa, temp. 150 °C, time 6 h.

also been reported for earlier studies using SLPC for other reactions [31].

3.4. Recycling of SLPC catalysts

The main objective of this work is to develop a recyclable catalyst. Hence recyclability experiment was performed and typical experimental results are shows in figure 3. It can be seen that catalyst retains its activity and selectivity performance as well as separated easily from the reaction mixture. Figure 3 shows that propylene carbonate was produced in quantitative yield with NaBr/silica catalyst system in which NaBr/silica was recovered and was subjected to utilization for several recycle without obvious loss of selectivity and activity performance. The leaching of NaBr was not observed in the organic phase.

3.5. The influence of the nature of supported liquid film

The influence of the nature of supported liquid film was also studied, various hydrophilic liquids such as polyethylene glycol (PEG), ethylene glycol (EG), and water, have been tested as a dispersion phase. Figure 4. shows the result using these dispersion liquids, showing higher yield for the reaction with PEG and EG as compared with water. It has been observed that water gives lower yield and EG film tend to leach from the surface of the silica. Also requirement of higher temperature such as 150 °C for the present reaction restricts application of water and EG as a supported liquid and hence PEG based catalyst was developed.

3.6. Effect of temperature

The reaction was appeared to be temperature dependent and the catalyst was not sensitive to air and moisture. To study the effect of the moisture on the catalyst activity, the reaction is carried out by adding 20% of water w.r.t. weight of PEG (fairly large amount as to check effect of moisture) and results shows 79.3% yield of PC was obtained using 5 wt% NaBr catalyst and this catalyst was found to be recyclable up to the fourth cycle without loss in activity. The higher

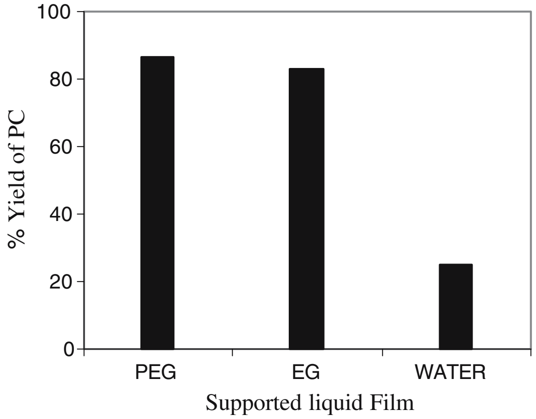


Figure 4. Influence of the supported liquid phase on yields of reaction. Propylene oxide 50 mmol, catalyst1 gm, toluene 20 ml, CO_2 pressure 5.5 MPa, temp.150 °C, time 6 h.

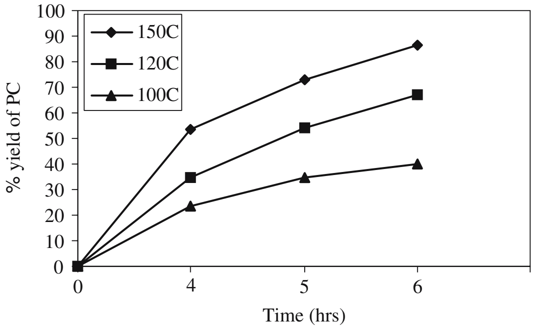


Figure 5. Effect of temperature on yield of reaction. Propylene oxide 50 mmol, catalyst 1 g, toluene 20 ml, CO_2 pressure 5.5 Mpa, time 6 h.

temperature was of great advantage to catalytic insertion of carbon dioxide into the C–O bond of epoxide thus resulting in the rapid conversion of epoxide to cyclic carbonate figure 5 .

3.7. *The effect of pressure*

The effect of pressure was also studied for the reaction and it was observed that the pressure also played an important role on the yield of cyclic carbonate. Experimental result shown in the figure 6 indicates the influence of CO_2 pressure in the catalytic conversion of epoxide to cyclic carbonate. These results are unexpected as Nobuhiro et al. observed that homogenous salts could give formation of epoxides at atmospheric pressure. However in this case high-pressure up to 4.5 MPa is required. Heterogenization of homogeneous catalysts often needs to enhance reaction conditions is well known fact and reported elsewhere for several other reaction systems [32]. In the present work homogeneous NaBr or alkali halide catalyst heterogenized for the conversion of CO_2 and epoxide to corresponding cyclic carbonates. Homogeneous catalyst system are gas-liquid in nature therefore catalyst have access to reactants, whereas the catalyst reported here is present in the another film of PEG hence, it is gas–liquid–liquid in nature. Therefore in order to increase reaction rates we need to enhance reaction conditions

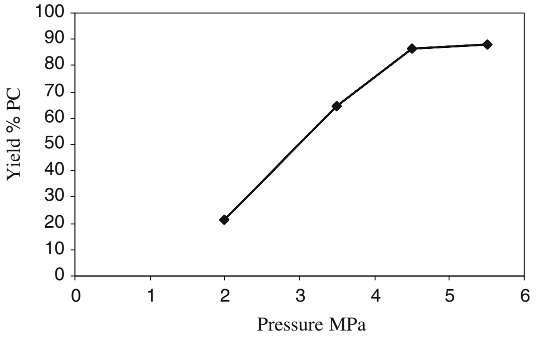
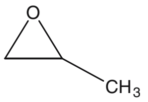
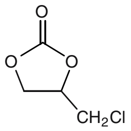
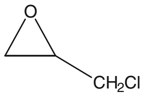
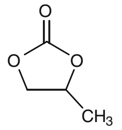
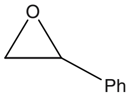
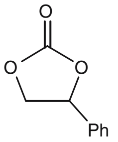


Figure 6. Influence of the pressure on yield of PC. Propylene oxide 50 mmol, catalyst 1 gm, toluene 20 ml, temp. 150 °C, time 6 h.

Table 2

Synthesis of various carbonates in presence of SLPC system at 150 °C for 6 h in CO_2

No	Reactant	Product	Pressure/MPa	% yield
1			4.5	89.67
2			4.5	86.43
3			4.5	84.78

Reaction conditions: Propylene oxide: 50 mmol; catalyst: 1 gm; l toluene: 20 ml; CO_2 pressure 4.5 MPa, temp. 150 °C.

3.8. *Substrate study*

A series of epoxide substrate was examined for the synthesis of the corresponding carbonates in presence of SLPC system at 150 °C and 4.5 MPa pressure of CO_2 carbonates with alkyl side chain group were successfully from each epoxide in nearly quantitative yield (Table 2). Propylene oxide was found to most reactive, while epichlorohydrin exhibit relatively low activity, among the epoxide surveyed lower yield was also obtained for styrene oxide this is due to low reactivity of β-carbon atom

4. Conclusion

Silica supported liquid phase catalyst system is found to be highly efficient heterogeneous catalyst and exhibited very high catalytic activity for the formation of various cyclic carbonates from corresponding epoxides and carbon dioxide. The catalyst was recycled several times and did not lose its activity.

Acknowledgments

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