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# Ionic liquid functionalized silica gel: novel catalyst and fixed solvent

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**Abstract**—Imidazolium cation-based ionic liquid functionalized silica gel was prepared, and Knoevenagel condensation as well as cycloaddition of propylene oxide and carbon dioxide without any additional organic solvents has been investigated. It was found that imidazolium cation-based ionic liquid functionalized silica gel was an effective recyclable catalyst.

Room temperature ionic liquids, entirely constituted of ions with negligible vapour pressure, excellent chemical and thermal stability, have attracted considerable attention as novel and environmentally friendly benign media. Many organic reactions have been reported to proceed in room temperature ionic liquids with excellent yields and chemo- and/or enantio-selectivities.[1–3] Although the application of ionic liquids in diverse areas has been well developed over the last two decades, problems such as cost and better recycling methods need to be addressed. In view of the increasing necessity for clean manufacturing processes and environmentally benign technologies, solvent-free and highly efficient catalytic technologies for chemical production are highly desirable. In fact, one of the continuing efforts of several groups is to develop new catalytic processes using supported ionic liquid catalysis.[4–6]

Knoevenagel condensation of aldehydes and/or ketones is a fundamental transformation in organic synthesis and one of the most powerful means of effecting carbon–carbon bond formation. The classical Knoevenagel condensation was catalyzed by ammonia and ammonium salts, primary and secondary amines and their salts in a liquid phase system with pronounced solvent dependency, and therefore environmentally undesirable organic solvents have been inevitably employed.[7] Knoevenagel condensation can be catalyzed by ionic liquids under organic solvent-free conditions.[8] The cycloaddition of carbon dioxide to propylene oxide with ionic liquids as catalyst without any additional organic solvents had also been investigated.[9–11] Though the ionic liquid used as catalyst was recyclable by distillation of the product from the resulting mixture, simpler catalyst separation processes still remains a challenge. Very recently, phosphonium salts immobilized onto silica for synthesizing propylene carbonate with excellent catalytic activities have been reported.[12]

Herein, we report the Knoevenagel condensation as well as cycloaddition of propylene oxide and carbon dioxide with imidazolium cation-based ionic liquid functionalized silica gel **2**[13,14] as recyclable catalyst and fixed solvent.

Knoevenagel condensation of ethylcyanoacetate and malononitrile with a variety of aromatic aldehydes with ionic liquid functionalized silica gel **2** as catalyst were investigated (Scheme 1). The results are summarized in Table 1.

Results listed in Table 1 show efficient Knoevenagel condensation of aromatic aldehydes with active methylene compounds in the presence of catalyst **2**. Aromatic aldehydes with electron-drawing or electron-donating

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*Keywords*: Ionic liquid functionalized silica gel; Knoevenagel condensation; Cycloaddition; Recyclable.

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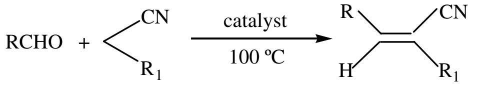


R = $C_6H_5$, 4-($CH_3O$)-$C_6H_4$, 4-(Cl)-$C_6H_4$, 2-(Cl)-$C_6H_4$, 4-($NO_2$)-$C_6H_4$, 4-(OH)-$C_6H_4$, 4-($CH_3$)-$C_6H_4$,

$R_1$ = $CO_2Et$, CN

**Scheme 1.**

**Table 1.** Knoevenagel condensation catalyzed with ionic liquid functionalized silica gel **2**[15]

| Entry | R | $R_1$ | Reaction time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | $C_6H_5$ | $CO_2Et$ | 5 | 95.2 |
| 2[a] | $C_6H_5$ | $CO_2Et$ | 5 | 93.3 |
| 3[b] | $C_6H_5$ | $CO_2Et$ | 5 | 91.8 |
| 4 | 4-$CH_3O$–$C_6H_4$ | $CO_2Et$ | 5 | 60.4 |
| 5 | 4-Cl–$C_6H_4$ | $CO_2Et$ | 5 | 93.7 |
| 6 | 2-Cl–$C_6H_4$ | $CO_2Et$ | 5 | 91.4 |
| 7 | 4-OH–$C_6H_4$ | $CO_2Et$ | 5 | 96.9 |
| 8 | 4-($NO_2$)–$C_6H_4$ | $CO_2Et$ | 5 | 95.1 |
| 9 | 4-$CH_3$–$C_6H_4$ | $CO_2Et$ | 5 | 87.8 |
| 10 | $C_6H_5$ | CN | 4 | 93.1 |
| 11 | 4-$CH_3O$–$C_6H_4$ | CN | 4 | 94.9 |
| 12[a] | 4-$CH_3O$–$C_6H_4$ | CN | 4 | 93.8 |
| 13 | 4-Cl–$C_6H_4$ | CN | 4 | 96.8 |
| 14 | 2-Cl–$C_6H_4$ | CN | 4 | 97.1 |
| 15 | 4-OH–$C_6H_4$ | CN | 4 | 96.4 |
| 16 | 4-($NO_2$)–$C_6H_4$ | CN | 4 | 97.6 |
| 17 | 4-$CH_3$–$C_6H_4$ | CN | 4 | 95.6 |

Reaction conditions: aldehyde 25 mmol, active methylene compound 25 mmol, 100 °C, catalyst 80 mg.

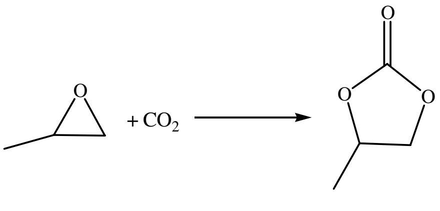
[a] The second run.

[b] The third run.

substituents could react very well with malononitrile and excellent yields were achieved. In addition, the catalyst was recyclable.

Our attention then turned to study the utility of this type of catalyst and/or fixed solvent in cycloaddition of propylene oxide and carbon dioxide (Scheme 2). As mentioned above, imidazolium-based ionic liquids have been introduced as effective catalysts for the fixation of carbon dioxide to cyclic carbonate, and the catalytic activity can be significantly enhanced by the co-catalyst zinc chloride.[16] The results of recycle experiments are summarized in Table 2.

After the catalyst **3**[13,14] had been used 4 times, the catalytic activity showed a small decrease, indicating that the ionic liquid functionalized silica gel catalyst **3** is recyclable for the cycloaddition.



**Scheme 2.**

**Table 2.** Cycloaddition of propylene oxide and carbon dioxide[17]

| Run | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Amount of $CO_2$ added (g) | 8.5 | 9.1 | 8.4 | 8.3 |
| Conversion (%) | 86.3 | 84.5 | 88.6 | 74.7 |

In summary, Knoevenagel condensation of a series of aromatic aldehydes with active methylene compounds proceeds smoothly in the presence of ionic liquid functionalized $SiO_2$ without any additional volatile organic solvents. The results have shown that this ionic liquid functionalized $SiO_2$ co-presented with zinc chloride was an effective catalyst for the cycloaddition of carbon dioxide with propylene to form propylene carbonate. And the catalyst can be recyclable. Our experiments show that imidazolium cation-based ionic liquid functionalized silica gel can be used as recyclable catalyst and/or fixed solvent in some organic reactions. Novel applications of this type of catalyst and/or fixed solvent are ongoing.

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13. Preparation of 1-methyl-3-(3-triethoxysilylpropylimidazolium chloride **1**: (3-Chloropropyl)triethoxysilane (48.2 g, 0.2 mol) and *N*-methylimidazole (16.4 g, 0.2 mol) were placed in a 100 mL stainless steel autoclave, which was evacuated and sealed, then heated to 120 °C for 24 h. The sticky residue was washed with ethyl acetate/diethyl ether and dried at 60 °C in vacuum to afford **1** (58.1 g, 90% yield), a white solid under room temperature.
14. Preparation of imidazolium cation-based ionic liquid functionalized silica gels **2** and **3**: Tetraethoxysilane (41.6 g, 0.2 mol) and **1** (32.2 g, 0.1 mol) were dissolved in 80 ml of ethanol, then 9.2 mL of 1% HCl aqueous was added. The resulting solution was stirred at 55 °C for 6 h

and at room temperature for 24 h, and then the mixture was evaporated to dryness under reduced pressure. The residue was heated to 200 °C for 8 h to form **2** quantitatively (Scheme 1). Catalyst **2** (7.82 g) and zinc chloride (1.414 g) were suspended in methylene dichloride (50 mL), after stirring overnight at room temperature. Evaporation of the suspension afforded zinc chloride co-presented catalyst **3**, which was used as catalyst for synthesis propylene carbonate from carbon dioxide and propylene oxide.

15. Typical Knoevenagel condensation experimental procedure: A mixture of 25 mmol of aldehyde and 25 mmol of ethyl cyanoacetate or malononitrile and 80 mg of **2** were charged into a 50 mL round-bottomed flask equipped with a magnetic stirrer. The reaction proceeded at 100 °C with constant stirring for 4–5 h. After cooling to room temperature, the resulted solid mass was ground and washed with a cool solution of 1% aqueous alcohol, filtered and dried in vacuum at 40 °C for 24 h to afford products with high purity (>99.5% purity as judged with GC–MS). The product was further purified by flash chromatography. All compounds were characterized by MS, $^{1}$H and $^{13}$C NMR.
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17. Cycloaddition of propylene oxide with $CO_2$: Cycloaddition reactions were performed in a 100 mL stainless steel autoclave equipped with a magnetic stirrer. Propylene oxide (7.0 mL, 0.10 mol) and 1.025 g of **3** were successively charged into the reactor, then $CO_2$ was introduced, and the amount of $CO_2$ added was measured by weight. The autoclave was heated up to 120 °C with stirring for 8 h. After cooling the remaining $CO_2$ was released, the resulting mixture was filtered, and the filtrate was analyzed by GC–MS, while the catalyst was charged with propylene and $CO_2$ into the autoclave for the next run.