

Chemical Fixation of Carbon Dioxide Catalysed by Multilayered Supported Ionic Liquids

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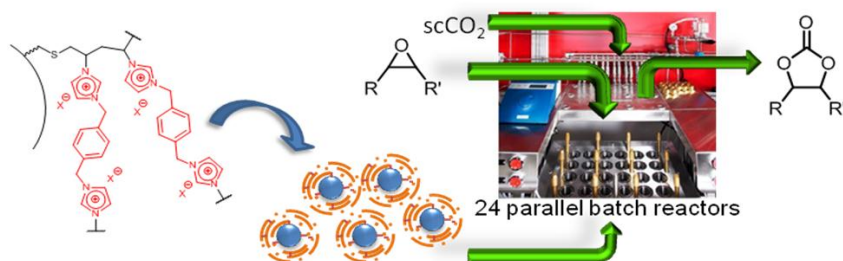
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Introduction

The chemical fixation of carbon dioxide is an attractive topic due to possibility of recycling the greenhouse gas CO₂ and, at the same time, converting it into valuable products such as cyclic carbonates [1]. Recently, simple supported ionic liquids with halides counter-ions have been successfully employed as catalysts for the chemical fixation of carbon dioxide [2]. Here, we report the synthesis of a new class of supported ionic liquid phase with excellent catalytic activity in the cycloaddition of carbon dioxide to epoxides yielding cyclic carbonates.



Experimental

Multilayered supported ionic liquids were synthesised by covalently grafting of bis-vinylimidazolium salts on a thiol-functionalised solid support (amorphous and ordered mesoporous SBA-15 silica; polystyrene) through the reaction of the S-H bonds with the terminal double bonds of the imidazolium salts (Fig. 1). The materials were characterised by solid-state ¹³C NMR, isothermal N₂ adsorption/desorption, elemental analysis, and were tested as catalysts in the synthesis of cyclic carbonates from epoxides. Supercritical CO₂ (scCO₂) was used with the double role of reagent and solvent. The tests were performed using a unique,

novel High-Throughput unit allowing the parallel testing of 24 catalysts in scCO₂. Conversion and selectivity were determined by GC.

Results and Discussion

A series of multilayered supported ionic liquids with different counterions (Cl, Br) were successfully synthesised, as demonstrated by combined characterisation with ¹³C NMR, N₂-sorption isotherms and elemental analysis. Since the ionic liquid was added in excess relatively to the amount of -SH groups on the support, a network of cross-linked imidazolium was obtained through self-addition reaction of the double bonds. This multilayered ionic liquid phase grants a very high loading of ionic liquids.

The materials were tested as catalysts in the synthesis of cyclic carbonates by the cycloaddition of CO₂ to epoxides. Three different epoxides were selected as substrates in order to investigate the versatility of our catalysts. In all cases, the best results were obtained with the bromide bis-imidazolium salts supported on SBA-15 (Fig. 1). This catalyst achieved very high conversion and selectivity in the reaction with propylene and styrene oxides (90% styrene carbonate yield after 3h reaction at 80 bar and 150°C). Thanks to its multilayered structure, the productivity of this catalyst ($\frac{g_{\text{product}}}{g_{\text{catalyst}}}$) is higher than that of other supported ionic liquids reported in the literature. The catalyst can be easily recovered and recycled in consecutive catalytic runs without loss of activity. Rapid screening and reliable comparison of the catalytic behaviour of the materials was made possible by the use of the High-Throughput unit.

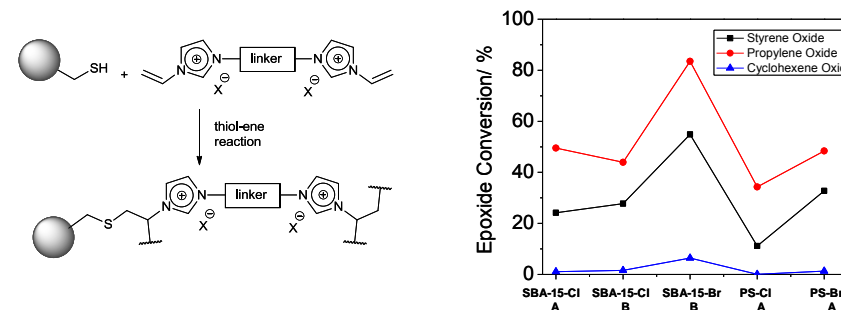


Figure 1. Synthesis of the multilayered supported ionic liquids (left) and their catalytic activity in the cycloaddition of carbon dioxide to different epoxides (right).

References.

1. D. H. Gibson, *Chem. Rev.*, **96**, 2063 (1996).
2. Y. Xie, Z. F. Zhang, T. Jiang, J. L. He, B. X. Han, T. B. Wu and K. L. Ding, *Angew. Chem. Int. Ed.*, **46**, 7255 (2007).