Bridging homogeneous and heterogeneous catalysis: grafted ionic liquids for the selective CO_2 conversion into limonene-based cyclic carbonates

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Highlights

- Ionic liquids were successfully grafted on solid supports.
- The grafting parameters were systematically investigated.
- The grafted catalyst were used for the first time in the carbonation of limonene diepoxide.

1. Introduction

Five-membered cyclic carbonates (5CCs) are highly attractive chemicals as precursors for bio-polymers such as polycarbonates and isocyanate-free polyurethanes (NIPU) [1]. 5CCs are typically synthesized via 100% atom economy by cycloaddition of CO_2 to epoxides [2]. Recent research has focused on the utilization of bio-based epoxides derived from vegetable oils, sugars and terpenes [1,3]. Among all, limonene diepoxide (LDO), obtained from limonene, a terpene abundantly found in citrus peel, is a promising precursor for the synthesis of 5CCs [4]. Carbonation of LDO can produce a monofunctional 5CC i.e., limonene carbonate (LC) and a bifunctional 5CC i.e., limonene dicarbonate (LDC) [5]. Valorization of limonene as a renewable feedstock is particularly appealing since large quantities of waste are generated by citrus processing i.e., up to 50% of the fruit mass during juice production [5]. Despite its potential, the use of LDO for 5CC production has been scarcely investigated, and mainly by using homogeneous catalysts. Shifting from homogeneous to heterogeneous catalysts and carrying out cycloaddition reactions under solvent-free conditions would be desirable from the viewpoint of green chemistry and process intensification. Heterogenization of homogeneous catalysts can be done by grafting. The present work explores a broader range of grafted catalyst designs and fine-tuning the synthesis conditions to improve the activity towards the carbonation of limonene diepoxide. Various grafted catalysts were synthesized and tested under solvent-free conditions. Several grafting parameters, including the nature of the ionic liquid, functionalization time, support acidification, and the introduction of a Lewis acid center, were investigated systematically. A series of characterization techniques were employed to correlate structural and morphological changes with catalytic performance [6].

2. Methods

SiO_2 gel, Al_2O_3, and SBA-15 were used as support materialss for producing grafted catalysts in a two-step procedure. The supports were pre-functionalized with (3-chloropropyl)trimethoxy-silane in toluene under nitrogen, then anchored with ionic liquids i.e., 4-pyrrolidinopiridine (4PP), 1-methylimidazol (1MI), triethylamine (TEA) and tributylamine (TBA). Structural and chemical characterizations via FT-IR, NMR, BET, CHNS, IC, TGA, SEM/EDX, TEM were employed to verify the chemical functionalization and determine the ionic liquid content and final morphology of the catalysts. The catalysts were tested for the CO_2 cycloaddition of limonene diepoxide under solvent-free conditions at 140 °C and 30 bar CO_2 in a pressurized reactor vessel. CO_2 was continuously added to the reactor system to maintain constant pressure. Recycling and leaching tests were performed to assess the catalyst stability.

3. Results and discussion

The successful functionalization of the ionic liquids on the solid supports was confirmed by different techniques such as solid-state NMR and SEM/EDX (Figure 1a). The catalytic activity was significantly affected by the ionic liquid structure (Figure 1b). The ionic liquids possessing aromatic/heteroaromatic nature, such as 4PPCl and 1MICl, showed superior performance, with 4PPCl exhibiting the highest activity. This observation can be attributed to the enhanced nucleophilicity and charge delocalization in these structures. The grafting time was directly correlated with catalytic efficiency. Increasing the grafting time from 12 to 48h improved the activity, probably due to a higher loading of the ionic liquid. The support nature played a crucial role. SiO_2 and Al_2O_3 performed similarly well, while SBA-15 showed a lower catalytic activity, due to adsorption of viscous reactants. Treatment of the support with nitric acid increased the mesoporosity and OH content, thereby increasing the grafting efficiency and catalytic activity. Recycling experiments showed that the catalysts retained most of the ionic liquid content, but partial deactivation occurred because of accumulation of residues, highlighting the need for improved cleaning procedures or the use of greener solvents [6]. Kinetic experiments were carried out with SiO_2-4PPCl-24h-A.T. at different reaction temperatures and the apparent activation energy was estimated to be 61 kJ/mol, in line with previously reported values for the CO_2 cycloaddition to epoxides.

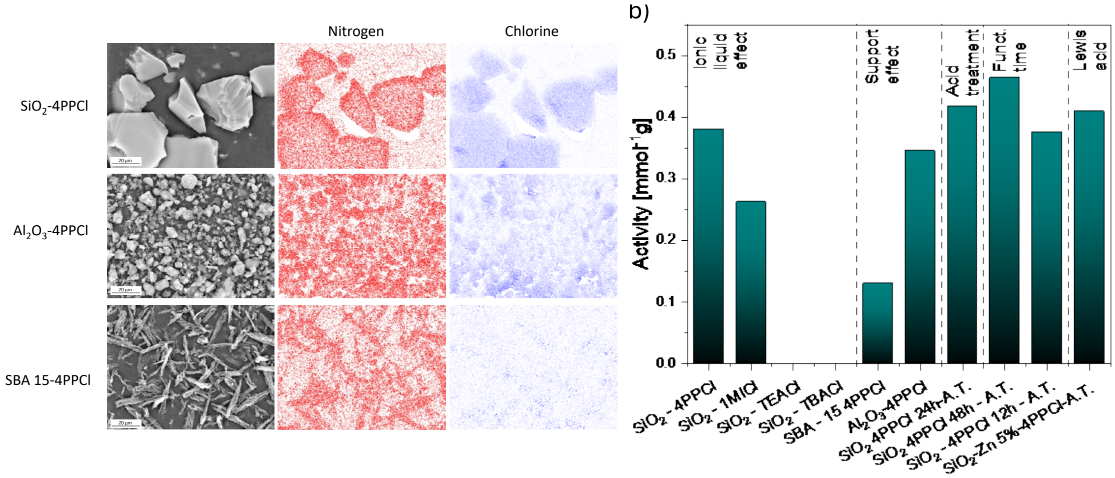

Figure 1. a) SEM/EDX of SiO_2-4PPCl, Al_2O_3-4PPCl and SBA 15-4PPCl. **b)** Comparison of the catalytic activity of the grafted catalysts separated by the investigated effects [6].

4. Conclusions

This work demonstrated how rational catalyst design, combining tailored ionic liquids with optimized supports and grafting time, can promote efficient valorization of carbon dioxide into bio-based cyclic carbonates. The catalytic activity resulted to be significantly affected by the ionic liquid structure and grafting time. The IL containing aromatic/heteroaromatic nature, i.e., 4-pyrrolidinopyridinium (4PPCl) showed superior performance which improved by increasing the grafting time from 12 to 48 hours. The pretreatment of the support prior to the functionalization with nitric acid also enhanced the grafting efficiency by increasing the mesoporosity and OH content.

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Keywords
Grafted catalysts, CO_2 utilization, limonene, cyclic carbonates