



Synthesis of cyclic carbonate from carbon dioxide and epoxides with polystyrene-supported quaternized ammonium salt catalysts

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ABSTRACT

Polystyrene-supported quaternized ammonium salt catalysts (PS-alkyl-AX) were synthesized and characterized by various physicochemical analytic methods such as EA, FT-IR, XPS, and SEM. The reactivity of the catalysts was investigated for the synthesis of allyl glycidyl carbonate from CO₂ and allyl glycidyl ether under mild reaction conditions. The PS-alkyl-AX catalysts showed good catalytic activity without using any solvent due to the synergistic effect of NH functional group and quaternary ammonium salt structure. Theoretical studies using density functional theory (DFT) was applied to investigate the reaction mechanism. The PS-hexyl-Mel catalyst was readily recoverable and reusable in subsequent reaction cycles without a significant loss in its activity.

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1. Introduction

Although CO₂ is thermodynamically stable, its desirable physical properties such as nontoxicity and nonflammability, along with its ready abundance, have attracted researchers to employ it as an environmentally friendly substitute for harmful chemicals such as phosgene and carbon monoxide, in the interest of environmental preservation and better resource utilization [1–5].

Thus, the chemical fixation of CO₂ owing to its low cost is a field of interesting research with multiple objectives such as reducing the atmospheric CO₂ concentration and synthesizing industrially important chemicals. In this context, the reaction of CO₂ with epoxides as an atom-efficient synthesis of cyclic carbonates is a dynamic field of interest.

Five-membered cyclic carbonates are industrially valuable chemicals widely employed as aprotic solvents, electrolytes in lithium-ion batteries, monomer units of polycarbonates, and so on [6,7]. Their challenging synthesis has led to the development of an appreciable number of catalyst systems, including room-temperature and task-specific ionic liquids (ILs), metal complexes

of salen and porphyrins, organometallic catalysts, quaternary ammonium salts, organic bases, and immobilized catalysts [7–22].

The immobilization of a catalyst and reagents on a variety of polymeric supports is attracting considerable attention as “green chemistry” in both industrial and laboratory chemical processes because of the ease of handling and recycling and the unique microenvironment formed by the reactants within the polymeric support [23–25]. Recently, polymer-supported ILs have been exploited as heterogeneous catalysts in the synthesis of cyclic carbonates and were found to offer the dual features of a homogeneous IL and a heterogeneous catalyst. Compared to pure ILs, such heterogeneous catalysts have additional advantages such as a reduction in the amount of ILs employed, recovery of the catalyst from the reaction mixture, and ease of separation [26–28].

Divinylbenzene (DVB) cross-linked polystyrene is one of the most useful polymers owing to its compatibility with a wide range of reaction conditions. Furthermore, because of its simple preparation, recyclability, environmental stability, low cost, and nonsolubility in commonly used organic solvents and water, DVB cross-linked polystyrene has attracted much attention as an efficient heterogeneous catalyst support [28–31].

In our previous work [32], we immobilized the imidazolium salt IL onto the Merrifield resin by alkoxylation with bromoalcohol followed by quaternization with methylimidazole.

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In this study, different polystyrene-supported quaternary ammonium salts were prepared by the reaction of PS and alkyl diamine followed by quaternization with an alkyl halide, with varying chain lengths of the alkyl diamine and different cation and anion of the alkyl halide. The performance of these catalysts in the synthesis of cyclic carbonate from allyl glycidyl ether (AGE) and CO₂ was investigated. These catalysts containing NH₂ group between the PS and quaternized ammonium group, can activate the epoxide ring, and therefore, showed better catalytic performance compared to the PS-supported quaternary ammonium salts without NH₂ group in the linker [33]. For a better understanding of the reaction mechanism, DFT studies were performed. The effects of the catalyst structure, CO₂ pressure, and reaction temperature were also discussed. A recyclability test of the catalyst was carried out to assess the stability of this catalyst system.

2. Experimental

2.1. Synthetic scheme

The synthesis of the quaternized ammonium salt anchored to PS was carried out via two steps as shown in Fig. S1 (Supporting Information). First, a mixture of PS (Merrifield peptide resin, Aldrich, 1% DVB, 4.5 mmol Cl/g) and acetonitrile was stirred for 12 h at 25 °C, then alkylene diamine was added with KOH, and this mixture was stirred for 48 h at 80 °C to yield alkylendiamine-anchored PS (PS-alkyl-diamine). The second step is the quaternization of the PS-alkyl-diamine to form PS-alkyl-AX by its reaction with an alkyl halide for 72 h at 50 °C. The precipitate was filtered and washed with ethanol and then dried in a vacuum oven for 12 h at 60 °C to prepare PS-alkyl-AX.

2.2. Characterization of the catalyst

Elemental analysis (EA) was carried out using Vario EL III. The samples (2 mg) were heated to 1100 °C, and sulfanilic acid was used as a standard. Fourier transform infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm⁻¹. XPS analyses were performed using an X-ray photoelectron spectrometer (VG, ESCALAB 250) with monochromatic Al K α radiation ($h\nu = 1486.6$ eV). The surface morphology was observed using an S-4200 field emission scanning electron microscope (FE-SEM, Hitachi-3500N).

2.3. Synthesis of AGC from AGE and CO₂

Allyl glycidyl carbonate (AGC) was synthesized by the coupling reaction of AGE and CO₂ in the presence of PS-alkyl-AX. All the reactions were carried out in a 60-mL stainless-steel batch reactor with a magnetic stirrer at 600 rpm. In a typical batch reaction, a predetermined amount of catalyst was charged into the reactor containing 52.3 mmol of AGE. The reaction was carried out under a constant pressure of CO₂ at different temperatures. After the completion of the reaction, the reactor was cooled to 0 °C, and the products were identified by gas chromatography (Agilent HP 6890 A) with a capillary column (HP-5, 30 m \times 0.25 μ m) using a flame ionized detector. The product yield was determined using an internal standard method with biphenyl (0.05 g) as the standard.

3. Results and discussion

3.1. Characterization of the catalysts

The organic compositions of PS, PS-alkyl-diamine, and PS-alkyl-AX were determined by elemental analysis (EA), and the results

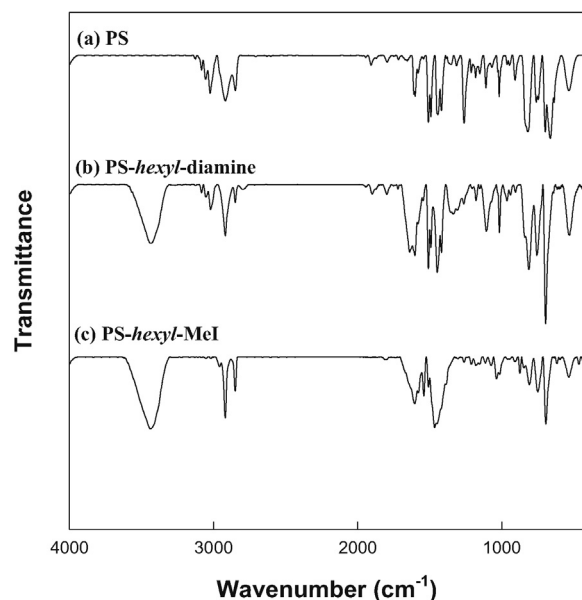


Fig. 1. FT-IR spectra of (a) PS, (b) PS-hexyl-diamine and (c) PS-hexyl-MeI.

are summarized in Table 1. The increase in the amount of nitrogen from PS to PS-alkyl-diamine indicated that the Cl of the DVB cross-linked chloromethylated polystyrene reacted with the NH₂ of the alkyl diamine to form N–C bonds and eliminate HCl during covalent anchoring to the polystyrene resin. The amount of PS-alkyl-QA immobilized on the polystyrene support varied from 2.0 to 2.7 mmol/g-cat.

The successful immobilization of the quaternary ammonium salt on the surface of the polystyrene support was confirmed using FT-IR spectroscopy (Fig. 1). In the FT-IR spectral analyses of PS-hexyl-diamine, PS-hexyl-MeI, and MPR, the characteristic peak corresponding to the stretching frequency of the CH₂Cl functional group (1265 cm⁻¹) disappeared in the spectra of PS-hexyl-diamine and PS-hexyl-MeI, suggesting the complete modification of MPR [26–28]. New peaks were observed for PS-hexyl-MeI in the regions 1560–1650 and 3400 cm⁻¹, which were absent from the MPR spectrum; these peaks are associated with the NH₂ bending and stretching frequencies [34].

Further corroboration of the successful quaternization under microwave irradiation was provided through XPS analyses. The N 1s spectra of PS-hexyl-diamine and PS-hexyl-MeI are presented in Fig. 2. While PS-hexyl-diamine (Fig. 2b) showed a sole characteristic amine nitrogen 1s peak at 399.4 eV, the quaternized species (PS-hexyl-MeI; Fig. 2a) exhibited one additional peak centered at 402.4 eV, which is consistent with the literature data for the 1s binding energy of quaternized nitrogen (–N⁺Me₃) species. This observation could be rationalized by the fact that the exposed amine groups of PS-hexyl-diamine indeed underwent a successful quaternization. The new peak (402.4 eV) observed in the characteristic region for the nitrogen atom provided conclusive evidence for the successful quaternization of PS-hexyl-diamine [35–37]. Moreover, the I 3d spectra of PS-hexyl-MeI were acquired to identify the bonding nature of the halogen associated with the metal species, as illustrated in Fig. S2. The I 3d peak was observed at 619.6 eV in the case of PS-hexyl-MeI, which indicated the anionic state of iodine [38,39]. The aforementioned results are a clear indication of the successful immobilization of the quaternized ammonium salt on the support, as shown in Fig. S1.

The SEM images of PS, PS-alkyl-diamine, and PS-alkyl-MeI are presented in Fig. 3. The images show that the diameter of the

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