Catalysis Communications 59 (2015) 201–205

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Supported imidazole as heterogeneous catalyst for the synthesis of cyclic carbonates from epoxides and CO_2

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ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form 21 October 2014
Accepted 28 October 2014
Available online 1 November 2014

Keywords:
Cyclic carbonates
CO_2 utilization
Anchored imidazole
Epoxides

ABSTRACT

Imidazole anchored onto a silica matrix, by means of a propyl linkage, is found to be an effective heterogeneous catalyst for the synthesis of cyclic carbonates from epoxides and CO_2 in near quantitative yield. The versatility of this catalyst is demonstrated by using different substrates (epichlorohydrin, propylene oxide, butylene oxide and styrene oxide) for this cycloaddition reaction. These CO_2 insertion reactions were typically carried out in the temperature range of 343 to 403 K at 0.6 MPa CO_2 pressure under solvent-free conditions. Several spectroscopic methods were used to characterize the catalyst and study the integrity of the fresh and spent catalysts.

1. Introduction

Utilization of renewable feedstock to value added chemicals is an attractive and important area of research [1–3]. Carbon dioxide (CO_2) is an abundant, safe, inexpensive and renewable C-1 feedstock for producing a number of industrially important chemicals [3–6]. However, owing to the thermodynamic stability of CO_2, its utilization in making organic compounds is a challenging topic [1,3,7]. Among various possible transformations, the atom-economic synthesis of cyclic carbonates from epoxides and CO_2 has been of great interest both industrially and academically (Scheme 1) [1,3,6,7]. Cyclic carbonates are used in the synthesis of many industrially important compounds like dimethyl carbonate and polycarbonates and they find applications as solvents and intermediates for the synthesis of fine chemicals [1,8–10]. Conventionally, these cyclic carbonates are synthesized using phosgene or CO, which are hazardous and environmentally unfriendly [3,4,7].

A number of catalysts have been reported for this method of synthesizing cyclic carbonate [11]. Although homogeneous catalysts are efficient in many cases, catalyst separation from the reaction mixture is difficult [12–14]. To overcome this, a number of solid catalysts have also been reported, for example, Yasuda et al. [15] have reported SmOCl-based catalyst to obtain higher selectivity without any additive under *sc*CO_2, but the yield was poor without an additive like DMF. Yamaguchi et al. [16] reported a mixed metal oxide catalyst, but with a higher catalyst loading for this cycloaddition reaction. Other reported heterogeneous catalysts include Nb_2O_5, Ti-SBA-15 and other metal oxide-based materials [17–19]. Unfortunately, these solid catalysts suffer one or more of the following disadvantages: need for solvent or co-catalyst, requirement of higher temperature and pressure, longer duration for the completion of reaction or high cost involved in the materials synthesis. Initially, we reported a Zn-W polyoxometalate-based catalyst for the synthesis of cyclic carbonate with a very high turnover number, but with homogeneous 4-(*N*,*N*-dialkylamine)pyridine (DMAP) as a co-catalyst [10]. During that study, we found that DMAP (lewis-base) alone can catalyze this cycloaddition reaction [10]. Shiels et al. [18] followed up this lead and anchored DMAP in SBA-15 and reported it as an effective heterogeneous catalyst for the synthesis of cyclic carbonate. Similarly, other N-containing organic bases have been anchored on metal oxide supports as were reported as heterogeneous catalysts for this reaction. Zhang et al. [19] anchored 1,5,7-triazabicyclo[4,4,0]dec-5-ene on fumed silica matrix and reported that as an efficient catalyst for the cyclic carbonate synthesis. However, the performance of the recovered catalysts decreased with a reduced selectivity for cyclic carbonate. Recently, Miralda et al. [20] reported a zeolitic imidazole framework-8 catalyst for the insertion of CO_2 to epichlorohydrin to form chloropropene carbonate. Although, this catalyst is active at relatively lower temperature, i.e., 353 K, the selectivity for the cyclic carbonate was reported to be less because of the formation of diol by-products. A number of groups have reported imidazolium-based ionic liquids supported on mesoporous silica [21], commercial silica surfaces [22], SBA-15 [23] and polymers [24,25] as effective

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http://dx.doi.org/10.1016/j.catcom.2014.10.026
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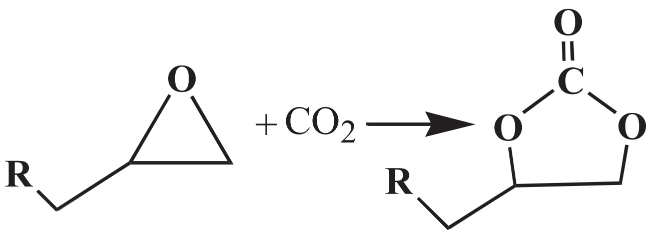

Scheme 1. Synthesis of cyclic carbonate from epoxide and CO_2.

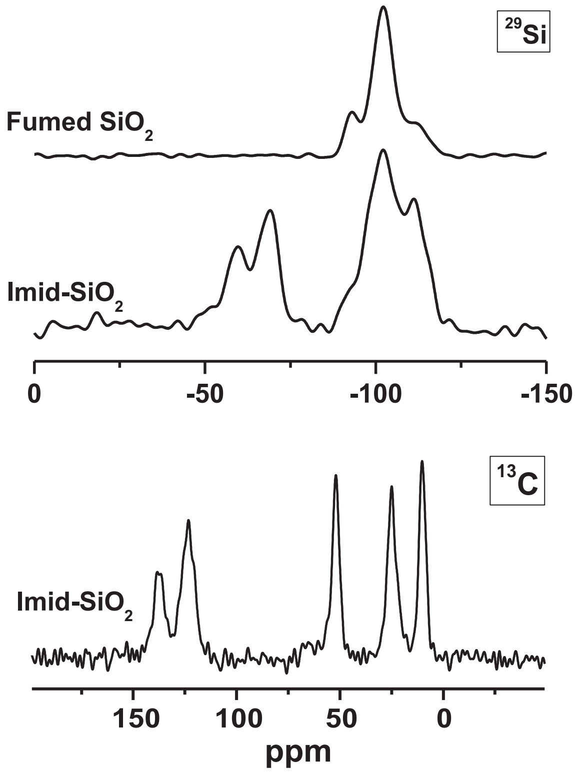

Fig. 1. ^{13}C and ^{29}Si CP-MAS NMR spectra of the silica-3-(2-imidazolin-1-yl) propyltriethoxysilane catalyst (Si-Imid) and ^{29}Si CP MAS NMR spectrum of neat silica support. All spectra were recorded at 298 K.

catalysts for this transformation. Most importantly, these catalysts are not active without the halide anions present in the ionic liquids. Many reviews have been published on supported ionic liquids catalysts for this cyclo-addition reaction [26,27]. However, it is highly desirable to design an active catalyst without any halide ions present. Following our earlier lead, our hypothesis was to anchor a simple organic base onto a metal oxide and use it as a heterogeneous catalyst for this reaction.

Based on that hypothesis, here we report the synthesis, characterization of imidazole anchored onto SiO_2 (Si-Imid) through a propyl linkage and its efficiency as heterogeneous catalyst for the synthesis of cyclic carbonates from epoxides and CO_2. The present catalyst has many advantages over the supported ionic liquid-based catalysts; easy to synthesize, cost effective and more importantly does not contain any halide ions [26,27]. This catalyst is effective to produce high yield of cyclic carbonate at relatively moderate temperature and CO_2 pressure, interestingly, under solvent-free conditions as well. In a mechanistic perspective, this catalytic system further substantiates our previous hypothesis that a Lewis base alone, without any halide ions, can catalyse the synthesis of cyclic carbonates using CO_2.

2. Experimental

A detailed materials and methods sections, explaining catalyst preparation, catalyst characterization and testing are provided as supplementary information.

3. Results and discussion

3.1. Solid-state NMR studies

The Si-Imid samples were characterized by multinuclear, solid-state (CP-MAS) NMR studies. ^{29}Si CP-MAS NMR spectra of Si-Imid along with that of the commercial SiO_2 sample are presented in Fig. 1. The peaks around −110, −101 and −91 ppm correspond to Q^4 (four Si-O-Si linkages), Q^3 (three Si-O-Si + one Si-OH linkages) and Q^2 (two Si-O-Si + two OH linkages) Si environments, respectively. The assignments are substantiated by ^{29}Si NMR spectrum of neat SiO_2, which contains three sets of peaks centered around −112, −101 and −91 ppm representing similar Si environments in the bare support [28,29]. The second set of peaks around −68 and −58 pm were assigned to the linker Si (originated from triethoxy chloropropyl silane). The presence of the two peaks indicates the presence of two different types of linkages. The peak at −68 ppm is assigned to the Si having three –O-Si linkages and a propyl imidazole group and the peak at −58 ppm is assigned to the Si having two –O-Si linkages, one ethoxy group and a propyl imidazole group [28,30].

The ^{13}C CP-MAS NMR spectrum of Si-Imid sample is given in Fig. 1. Two peaks around 123 and 139 ppm correspond to the C nuclei of the imidazole ring [30]. The peaks around 100, 24 and 54 ppm are assigned to the three C nuclei of the propyl group [28,30]. Although ^{29}Si MAS NMR data indicated the possibility of having two different types of linkages using triethoxy chloropropyl silane, ^{13}C NMR spectrum does not differentiate these two linkages. These multinuclear CP-MAS NMR studies prove that the anchoring of imidazole group to the SiO_2 surface is through the propyl silane linker. Recently, we used ^{15}N labeled imidazole and prepared Si-Imid and characterized it using ^{15}N CP-MAS NMR to prove the structure of this catalyst [28]. This is further substantiated by the elemental analyses (C, H and N) of the resultant material. From the elemental analyses it has been concluded that the loading of imidazole was approximately 69.5 mg (1.02 mmol for 5 g of silica)

3.2. IR and UV-Vis spectral studies

FT-IR and diffuse reflectance UV-Vis spectra of Si-Imid material were recorded and are given in Fig. 2. The IR spectrum of Imid-SiO_2 shows the characteristic bands for imidazole moiety besides the bands corresponding to the propyl group and SiO_2. The bands observed in between 2800 and 2950 cm^{-1} are assigned to the C-H stretching vibrations of the propyl group present in Si-Imid. The 1460 cm^{-1} band is from the stretching of C = N bond of the imidazole ring [28,31]. Solid-state UV-Vis spectra of pure imidazole gave a band around 204 nm which correspond to the π-σ^* transition of the C = N bond [32]. The presence of a band at 204 nm for Si-Imid proves the presence of imidazole in it. These IR and UV-Vis spectra along with the NMR spectra prove the structure of Si-Imid.

3.3. Catalytic studies

After confirming the structure of Si-Imid, by spectroscopic characterization, we tested these materials for the synthesis of cyclic carbonates from epoxides and CO_2. Initially, we used epicholorohydrin as the substrate, and the reaction was performed at 403 K with a CO_2 pressure of 0.6 MPa. After 4 h of reaction time, the conversion reached 98% with 88% selectivity for the cyclic carbonate with a TOF of 24 $mol_{cc}\ kg_{cat}^{-1}\ h^{-1}$ (Table 1). The only observed by-product is the ring-opened product of the epoxide. We found that Si-Imid prepared by both methods (methods 1 and 2) have similar activities (Table 1). Hence, Si-Imid