Journal of CO_2 Utilization 22 (2017) 44–52

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Benzyl substituted imidazolium ionic liquids as efficient solvent-free catalysts for the cycloaddition of CO_2 with epoxides: Experimental and Theoretic study

Tengfei Wang[a,b], Danning Zheng[b], Yuan Ma[a,b], Jiayi Guo[b], Zhipeng He[a,b], Bin Ma[c], Lianhuan Liu[c], Tiegang Ren[a,b,*], Li Wang[b,*], Jinglai Zhang[b,*]

[a] Engineering Laboratory for Flame Retardant and Functional Materials of Henan Province, Henan University, Kaifeng, Henan 475004, PR China
[b] College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China
[c] Minsheng College, Henan University, Kaifeng, Henan 475004, PR China

ARTICLE INFO

Keywords:
Ionic liquid
Epoxides
CO_2
Cyclic carbonate
Benzyl

ABSTRACT

A series of low-cost and easily prepared benzyl substituted imidazolium ionic liquids are firstly synthesized and employed as catalyst for the cycloaddition of carbon dioxide with epoxides without any solvent and co-catalyst. The synthesized imidazolium ionic liquids are characterized by ^{1}H NMR, HRMS, and MS. The influence of different substituted groups in cation and reaction parameters on catalytic activity is investigated. The highest conversion yield of cyclic carbonate (94.89%) could be achieved with slight amount of catalyst (0.25 mol%) under 130 °C and 2.0 MPa during 4 h. Meanwhile, the mechanisms of cycloaddition of carbon dioxide with epoxides catalyzed by four benzyl substituted ionic liquids with different substituted groups are investigated by theoretical calculations. The role of hydrogen bond and other noncovalent interactions played in catalytic process is further uncovered to deeply understand the difference of various catalysts from atomistic level.

1. Introduction

Carbon dioxide (CO_2) is the most famous greenhouse gas, which has aroused serious environmental problems [1]. However, it is also an abundant, cheap, and nontoxic C1 resource. The chemical fixation and resource utilization of CO_2 is beneficial for not only improving global environment but also alleviating energy crisis. Some achievements have been reported including the synthesis of urea, methanol, carbon monoxide, salicylic acid, cyclic carbonate, and polycarbonates from CO_2 [2–4]. One of the most efficient methods is to produce the five-membered cyclic carbonates by coupling reaction of epoxides and CO_2 [5,6] due to the cheap reactants and low by-product [7]. Moreover, cyclic carbonates has been widely used as polar aprotic solvents, intermediates, fuel additives, and electrolytes in lithium-ion batteries [8,9].

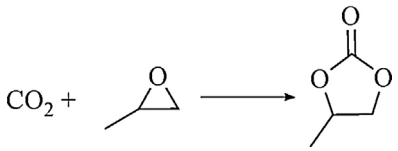
How to activate CO_2 in the highest oxidation state is the main road block to employ it as raw materials. In recent years, a variety of catalysts and catalytic systems have been designed and synthesized for the title reaction (Scheme 1). The typical catalysts include metal oxides [10], metal-salen complexes [11], metal organic frameworks (MOFs) [12], metalloporphyrins [13], other metal-modified catalysts [14], ionic liquids (ILs) [15,16], and organic functionalized polymers [17]. Ionic liquids stand out from various catalysts because of some unique characteristics, such as inexpensive, negligible volatility, great solubility, and easy separation [18,19].

Many ionic liquids have been developed including imidazolium salts [20,21], quaternary ammonium salts [22], quaternary phosphonium salts [23,24], pyridinium salts [25], guanidinium salts [26,27], urea based ILs [28–31], and others [32,33]. However, there are some common shortcomings deserved to be overcome, such as, unsatisfactory catalytic performance, harsh reaction conditions, and requirement for toxic solvent or metal salt as co-catalyst, which seriously restricts their large scale application. Imidazolium salts are one of the most popular ILs those have been widely explored [34–36]. As early as 1982, the first imidazolium salts was synthesized by Wilkes [37]. In 2001, Peng employed it as the catalyst for the coupling reaction of CO_2 with propylene oxide (PO) [38]. It is the first example to utilize a single catalyst for the title reaction. Later, Zhang et al. synthesized the hydroxyl-functionalized imidazolium salts, which could efficiently promote the fixation of CO_2 than the room-temperature imidazolium salts [39]. Other task specified imidazolium salts have been developed in succession.

Besides catalytic efficiency, preparation process and production cost are also important items to refine the performance of catalyst. It is

* Corresponding authors at: College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China.
E-mail addresses: rtg@henu.edu.cn (T. Ren), chemwangl@henu.edu.cn (L. Wang), zhangjinglai@henu.edu.cn (J. Zhang).

http://dx.doi.org/10.1016/j.jcou.2017.09.009
Received 22 May 2017; Received in revised form 12 September 2017; Accepted 12 September 2017
Available online 20 September 2017



Scheme 1. Cycloaddition of CO_2 with propylene oxide to prepare propylene carbonate.

expected that to explore a new room temperature IL that is easy to be obtained with higher or comparable catalytic performance as compared with the existed ILs. Benzyl group has the high activity, which has been widely utilized as substituted group in literatures [40]. Moreover, it would be easily incorporated in the preparation of imidazolium ionic liquid via N-alkylation reaction since the larger activity of alkylation reagents would lead to the milder reaction conditions, higher production yield, and simpler post-processing [41,42]. In this study, eight kinds of benzyl substituted imidazolium ionic liquids (See Scheme 2) are synthesized via N-alkylation reaction of 1-methylimidazole with substituted benzyl chloride as alkylation reagents. Compared with other imidazolium ILs reported in literatures [43,44], these benzyl substituted imidazolium ILs would be synthesized in the milder reaction condition with higher yield (> 85%). Moreover, their post-processing is simpler. Subsequently, the synthesized ILs are employed to catalyze the cycloaddition of CO_2 with epoxides without any solvent and co-catalyst with the aim to explore the effect of substituted group in cation. Furthermore, the optimal reaction parameters on catalytic activity are confirmed. Finally, the mechanism is investigated by density functional theory (DFT). The role of hydrogen bond and other noncovalent interactions played in catalytic process is elucidated by noncovalent interaction (NCI) and atoms in molecules (AIM) analysis, which is favorable for uncovering the essential factor to control the catalytic performance from the microscopic viewpoint. It is expected that more efficient ILs would be explored for the chemical fixation of CO_2 with epoxides. Moreover, they are easy to be synthesized in a benign condition with high product yield.

2. Experimental

2.1. Physical measurement and materials

Mass spectra (MS) were determined with an Agilent 1100LC–MS mass spectrometer. Infrared (IR) spectra of obtained products within 400–4000 cm^{-1} were recorded with a Nicolet 170 SXFT-IR spectrometer (mixed with KBr and pressed into pellets). Nuclear magnetic resonance (^1H NMR) spectra in DMSO-d_6 solvent were recorded with an INOVA-400 spectrometer in the presence of tetramethylsilane as an internal standard. High resolution mass spectra were measured in Agilent 1290 infinity LC with 6224 TOF MSD system. The melting point was tested by means of a differential scanning calorimeter (Mettler Toledo DSC851e) in the temperature range from 25 °C to 200 °C and the thermal decomposition temperature was analyzed with a thermal gravimetric analyzer (Mettler Toledo TGA/SDTA851e). GC analyses were performed on Agilent GC–7890 B using a flame ionization detector.

All of the chemicals and solvents were analytical purity grade and used without further purification.

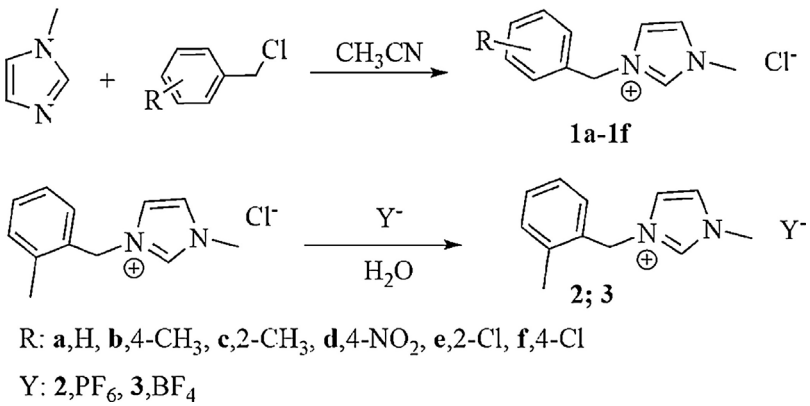
2.2. Preparation and characterization of benzyl substituted imidazolium ILs

Six kinds of benzyl substituted imidazolium ILs with Cl^- as anion were synthesized according to the literature [45,46], then two different kinds of anion (PF- 6and BF- 4) were chosen to replace Cl^- using **1c** as substrate to investigate the influence of anion on the catalytic performance. A typical procedure for preparation of 3-benzyl-1-methylimidazolium chloride ([BzMIM]Cl) (**1a**) is as follows: In dark conditions, 1.23 g (0.15 mol) 1-methylimidazole (99%) was dissolved in 15 mL of dry acetonitrile, then 40 mL acetonitrile solution that contained 0.01 mol benzyl chloride (99%) was dropwised into the above solution slowly. The obtained mixture was heated at 35 °C for 20 h with constant stirring under N_2 atmosphere. Afterward, the solvent was removed, and the obtained viscous liquid was washed three times (15 mL × 3) with dry ethyl acetate followed by washing three times (15 mL × 3) with dry diethyl ether. Then, they are dried at 50 °C under vacuum for 12 h to obtain colorless liquid **1a** 1.96 g. yield: 94.23%. ^1H NMR (400 MHz, DMSO-d_6) δ: 9.79 (s, 1H, −CH), 8.02 (d, J = 1.9 Hz, 1H, −CH), 7.88 (d, J = 1.9 Hz, 1H, −CH), 7.58-7.34 (m, 5H, −Ph), 5.57 (s, 2H, −Ph-CH_2), 3.91 (s, 3H, $-CH_3$). MS (ESI) m/z: 172.97 [$BzMIM^+$]; 381.17 [$(BzMIM^+)_2Cl]^+$.

Other substituted imidazolium ILs were prepared with the similar procedure to **1a.** 1-methyl-3-*p*-methylbenzylimidazolium chloride ([*p*-MBzMIM]Cl) (**1b**): colorless liquid 1.91 g, yield: 85.82%. ^1H NMR (400 MHz, DMSO-d_6) δ: 9.74 (s, J = 1.8 Hz, 1H, −CH), 7.96 (d, J = 1.8 Hz, 1H, −CH), 7.83 (d, J = 1.7 Hz, 1H, −CH), 7.40 (d, J = 8.0 Hz, 2H, −Ph), 7.17 (d, J = 7.8 Hz, 2H, −Ph), 5.48 (s, 2H, −Ph-CH_2), 3.87 (s, 3H, $-CH_3$), 2.25 (s, 3H, $-CH_3$). MS (ESI) m/z: 187.02 [*p*-$MBzMIM^+$]; 409.24 [(*p*-$MBzMIM^+)_2Cl]^+$. HR-MS (QTOF) calcd. for $C_{12}H_{15}N_2$ (m/z): 187.1221, found 187.1235.

1-methyl-3-*o*-methylbenzylimidazolium chloride ([*o*-MBzMIM]Cl) (**1c**): white solid 1.84 g, yield: 82.60%, mp = 111 °C. ^1H NMR (400 MHz, DMSO-d_6) δ: 9.36 (s, J = 1.7 Hz, 1H, −CH), 7.81 (d, J = 1.8 Hz, 1H, −CH), 7.78 (d, J = 1.8 Hz, 1H, −CH), 7.26 (m, 4H, −Ph), 5.50 (s, 2H, −Ph-CH_2), 3.89 (s, 3H, $-CH_3$), 2.32 (s, 3H, $-CH_3$). MS (ESI) m/z: 187.02 [*o*-$MBzMIM^+$]; 409.22 [(*o*-$MBzMIM^+)_2Cl]^+$. HR-MS (QTOF) calcd. for $C_{12}H_{15}N_2$ (m/z): 187.1195, found 187.1235.

1-methyl-3-*p*-nitrobenzylimidazolium chloride ([*p*-NBzMIM]Cl) (**1d**): light yellow solid 2.28 g, yield: 90.4%, mp = 175 °C. ^1H NMR (400 MHz, DMSO-d_6) δ: 9.52 (s, J = 1.7 Hz, 1H, −CH), 8.28 (d, J = 8.4 Hz, 2H, −Ph), 7.91 (s, 1H, −CH), 7.81 (s, 1H, −CH), 7.72 (d, 2H, J = 8.4 Hz, −Ph), 5.69 (s, 2H, −Ph-CH_2), 3.89 (s, 3H, $-CH_3$). MS (ESI) m/z: 217.98 [*p*-$NBzMIM^+$]; 471.09[(*p*-$NBzMIM^+)_2Cl]^+$. HR-MS



R: **a**,H, **b**,4-CH_3, **c**,2-CH_3, **d**,4-NO_2, **e**,2-Cl, **f**,4-Cl

Y: **2**,PF_6, **3**,BF_4

Scheme 2. Synthesis of benzyl substituted imidazolium ionic liquids.