Applied Catalysis A, General 547 (2017) 265–273

Contents lists available at ScienceDirect

Applied Catalysis A, General

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

Research paper

Dialkylpyrazolium ionic liquids as novel catalyst for efficient fixation of CO_2 with metal- and solvent-free

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ARTICLE INFO

Keywords:
dialkylpyrazolium ionic liquids
CO_2
cycloaddition reaction
structure-activity relationship
DFT

ABSTRACT

The efficient fixation of CO_2 without co-catalyst and solvent under metal-free condition is still an urgent topic in sustainable chemistry. In this work, a series of dialkylpyrazolium ionic liquids are employed to promote the cycloaddition of CO_2 and PO to produce PC. They would be easily synthesized by a simple one-pot reaction. The effect of alkyl chain length in cation and different anion is explored. Diethylpyrazolium iodide presents the excellent catalytic activity with the product yield of 96% and selectivity of 99% in a benign condition. Moreover, the catalyst could be reused for at least five times without significant loss of catalytic activity. An intensive structure-activity research testifies that the cycloaddition of CO_2 with PO is activated by a synergistic effect from both cation and anion of ILs. To confirm it, the detailed mechanism is investigated by density functional theory associated with the non-covalent interactions and atoms in molecule analysis. Besides the electrostatic interaction between cation of ionic liquid and PO, the noncovalent interaction, especially for hydrogen bond, plays a vital role in promoting the reaction.

1. Introduction

With the rapid development of economy and industrialization process, the fossil fuels are gradually depletion. Carbon dioxide (CO_2) is inexpensive, nontoxic, abundant, and renewable C1 resource in the world. Many efforts have been made to convert CO_2 to useful chemical products including methane [1], carboxylic acid [2], hydrocarbon [3], and cyclic carbonate [4]. The cyclic carbonate has been widely applied in numerous regions, such as electrolytes of Li ion batteries [5], aprotic polar solvents [6], degreasing agents [7], and valuable monomers of polycarbonates and polyurethanes [8]. Up to date, the cycloaddition of CO_2 with epoxides is regarded as one of the most efficient methods to synthesize cyclic carbonate because of the 100% atom utilization and negligible side product. However, the thermo stability and kinetic inertness of CO_2 greatly impede its large scale application [9]. Although numerous catalysts have been developed, such as, modified molecular sieves [10], metal oxide [11], transition metal complexes [12] and ionic liquids (ILs) [13], they confront some common shortcomings including the requirement of co-catalyst and organic solvent, harsh reaction condition, and others [14,15]. It is still an urgent problem to develop single-component catalyst to activate the chemical fixation of CO_2 with high efficiency.

Recently, ionic liquids have become a hotspot in catalytic region because of their special structure and properties [16]. Moreover, they are also an excellent solvent. Many ionic liquids have been employed as effective catalysts with metal- and solvent-free to activate the cycloaddition of CO_2 with epoxides [17]. Imidazolium ionic liquids, as one of the most popular catalysts, have attracted extensive experimental and theoretical attentions [18]. As their structural isomer, fewer investigations have been focused on pyrazolium ionic liquids. In 1983, dimethylpyrazolium iodide (DMPzI) was firstly synthesized by Claramunt et al. [19]. Later, Enrique et al. have synthesized dibutylpyrazolium iodide (DBPzI) by microwave radiation heating [20]. After that, Huynh et al. have synthesized diethylpyrazolium bromide (DEPzBr) and used it to prepare N-heterocyclic carbene complexes [21]. However, their catalytic activity for the conversion of CO_2 has never been investigated.

In this work, they are firstly employed to accelerate the cycloaddition of CO_2 with epoxides. In addition, other twelve pyrazolium ionic liquids are also synthesized to explore the influence of different alkyl chain length and anions on the catalytic performance. Moreover, the effect of catalyst loading, initial CO_2 pressure, reaction temperature,

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http://dx.doi.org/10.1016/j.apcata.2017.09.009
Received 19 July 2017; Received in revised form 4 September 2017; Accepted 6 September 2017

and reaction time is studied to confirm the optimal reaction condition. The reusability and generality of diethylpyrazolium iodide (DEPzI) is also considered. Finally, the reaction mechanism is elucidated by density functional theory (DFT) to uncover the difference of various catalysts from the micro viewpoints. It is expected that pyrazolium ionic liquids would become a new focus in catalytic field after imidazolium ionic liquids. Combination of theoretical and experimental studies would open an express pathway to search for efficient and single-component ionic liquids to promote the chemical fixation of CO_2 in a proper condition.

2. Experimental section

2.1. Instruments and reagents

Fourier transform infrared (FT-IR) spectra were collected on Bruker Vertex 70 spectrometer (KBr disks). HR-MS was determined with Agilent 1290 Infinity LC with 6224 TOF MSD. MS was determined by Bruker AmaZon SL (ESI) mass spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker Avance III HD spectrometer with the presence of tetramethylsilane as an internal standard. The melting point was tested by using a differential scanning calorimeter (Mettler Toledo DSC851e) in the temperature range from 0 °C to 200 °C and the thermal decomposition temperature was analyzed with a thermal gravimetric analyzer (Mettler Toledo TGA/SDTA851e). Elemental analyses were performed on a Vario EL cube elemental analyzer. GC analyses were performed on Agilent GC–7890 B using a flame ionization detector.

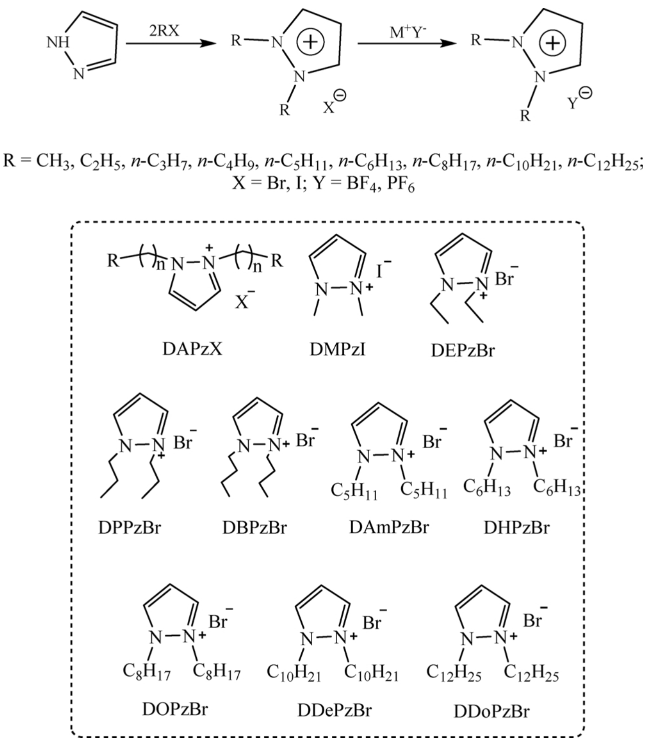
The pyrazole and halohydrocarbon were purchased from Macklin Biochemical Co., Ltd. Propylene oxide (PO), styrene oxide, epoxy chloropropane, and ethylene oxide were purchased from Aladdin Co. Other commonly used chemical regents were produced by Sinopharm Chemical Reagent Co., Ltd. CO_2 (99.9% purity) were purchased from Kaifeng Xinri Gas Co. All reactants were used directly as received without any further purification.

2.2. Preparation of pyrazolium ionic liquids

These dialkylpyrazolium ionic liquids were prepared according to the literature [21] with some revision. The typical synthesis procedure of dialkylpyrazolium ILs is shown in Scheme 1. 1,2-Diethylpyrazolium Iodide (DEPzI): In a three-necked bottle, pyrazole (10 mmol) and powdered KOH (10 mmol) were added into 10 mL CH_3CN and the mixture was stirred at ambient temperature for 1 h. Then ethyl iodide (24 mmol) was added to reactants and the reaction was continued for 24 h under reflux conditions. After the reaction, the volatiles were removed under reduced pressure. CH_2Cl_2 was added to the residue and the resulting suspension was filtered. The solvent of the filtrate was removed by vacuum distillation, and the resulting residue was subsequently washed with ethyl acetate to give a yellow solid. After removing the moisture by cyclohexane reflux, the pure DEPzI was obtained: 1.162 g, yield 46%, m.p: 140.3 °C. *T*m (decomposition temperature of 10% weight loss): 201.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.48–8.40 (d, J = 3.0 Hz, 2H, Py-H), 6.79 (t, J = 3.0 Hz, 1H, Py-H), 4.86-4.79 (q, J = 7.3 Hz, 4H, $-NCH_2$), 1.69 (t, J = 7.3 Hz, 6H, $-CH_3$). ^{13}C NMR (100 MHz, D_2O): δ 135.82 (s, N-CH), 107.43 (s, CH), 45.40 (s, N-CH_2), 13.40 (s, $-CH_3$). Anal. Calcd for $C_7H_{13}N_2I$: C, 33.33; H, 5.159; N, 11.11. found: C, 33.66; H, 5.375; N, 10.80. MS (ESI): *m/z* 125.14 [$C_7H_{13}N_2{}^+$]; 127.04 [I^-].

Other dialkylpyrazolium iodide and bromide were synthesized with the identical procedure for DEPzI.

1,2-Dimethylpyrazolium Iodide (DMPzI). White solid (51%); m.p: 194.0 °C. (lit[19]: 186–187 °C). *T*m: 201.4 °C. ^1H NMR (400 MHz, D_2O): δ 8.02 (d, J = 2.9 Hz, 2H, Py-H), 6.60 (td, J = 3.0 Hz, 1H, Py-H), 3.99 (s, J = 1.2 Hz, 6H, N-CH_3). ^{13}C NMR (100 MHz, D_2O): δ 137.42 (s, N-CH), 107.00 (s, CH), 36.44 (s, $-CH_3$). Anal. Calcd for $C_5H_9N_2I$: C, 26.79; H, 4.018; N, 12.50. found: C, 26.35; H, 3.848; N, 12.29. MS (ESI): *m/z* 97.30 [$C_5H_9N_2{}^+$].



R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$;
X = Br, I; Y = BF_4, PF_6

Scheme 1. Synthetic route and structures of the dialkylpyrazolium ionic liquids (DAPzILs).

1,2-Dipropylpyrazolium Iodide (DPPzI). Yellow solid (43%); m.p: 83.7 °C. *T*m: 199.6 °C. ^1H NMR (400 MHz, D_2O): δ 8.07 (d, J = 3.0 Hz, 2H, Py-H), 6.62 (t, J = 3.0 Hz, 1H, Py-H), 4.27 (t, J = 7.3 Hz, 4H, N-CH_2), 1.79 (m, J = 7.4 Hz, 4H, $-CH_2$-), 0.80 (t, J = 7.4 Hz, 6H, $-CH_3$). ^{13}C NMR (100 MHz, D_2O): δ 136.87 (s, N-CH), 107.28 (s, CH), 51.35 (s, N-CH_2), 21.98 (s, $-CH_2$-), 9.81 (s, $-CH_3$). Anal. Calcd for $C_9H_{17}N_2I$: C, 38.57; H, 6.071; N, 10.00. found: C, 38.58; H, 6.316; N, 10.03. MS (ESI): *m/z* 153.07 [$C_9H_{17}N_2{}^+$].

1,2-Dibutylpyrazolium Iodide (DBPzI). Yellow solid (42%); m.p: 71.4 °C. *T*m: 195.8 °C. ^1H NMR (400 MHz, D_2O): δ 8.11 (d, J = 2.9 Hz, 2H, Py-H), 6.67 (t, J = 3.0 Hz, 1H, Py-H), 4.35 (t, J = 7.4 Hz, 4H, N-CH_2), 1.80 (m, J = 7.5 Hz, 4H, $-CH_2$-), 1.27 (m, J = 7.4 Hz, 4H, $-CH_2$-), 0.84 (t, J = 7.4 Hz, 6H,-CH_3). ^{13}C NMR (100 MHz, D_2O): δ 136.73 (s, N-CH), 107.29 (s, CH), 49.76 (s, N-CH_2), 30.27 (s, $-CH_2$-), 18.84 (s, $-CH_2$-), 12.65 (s, $-CH_3$). Anal. Calcd for $C_{11}H_{21}N_2I$: C, 42.86; H, 6.818; N, 9.09. found: C, 42.93; H, 6.807; N, 8.94. MS (ESI): *m/z* 181.06 [$C_{11}H_{21}N_2{}^+$].

1,2-Diamylpyrazolium Iodide (DAmPzI). Yellow solid (33%); m.p: 75.7 °C. *T*m: 195.0 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 2.9 Hz, 2H, Py-H), 6.78 (t, J = 2.9 Hz, 1H, Py-H), 4.72 (t, J = 7.5 Hz, 4H, N-CH_2), 1.96 (m, J = 7.4 Hz, 4H, $-CH_2$-), 1.41 (m, J = 6.1, 3.3, 2.6 Hz, 8H, $-CH_2$-), 0.88 (t, 6H, $-CH_3$). HR-MS (QTOF) calcd. for $C_{13}H_{25}N_2I$ (*m/z*): 209.2018, found: 209.1985.

1,2-Diethylpyrazolium Bromide (DEPzBr). Yellow solid (47%); ^1H NMR (400 MHz, D_2O): δ 8.10 (d, J = 3.0 Hz, 2H, Py-H), 6.67 (t, J = 3.0 Hz, 1H, Py-H), 4.37 (q, J = 7.3 Hz, 4H, N-CH_2), 1.46 (t, J = 7.2 Hz, 6H, $-CH_3$). MS (ESI): *m/z* 125.14 [$C_7H_{13}N_2{}^+$], 81.80 [Br^-].

1,2-Dipropylpyrazolium Bromide (DPPzBr). Yellow solid (43%); ^1H NMR (400 MHz, D_2O): δ 8.07 (d, J = 3.0 Hz, 2H, Py-H), 6.62 (t, J = 3.0 Hz, 1H, Py-H), 4.27 (t, J = 7.3 Hz, 4H, N-CH_2), 1.79 (q, J = 7.4 Hz, 4H, $-CH_2$-), 0.80 (t, J = 7.4 Hz, 6H, $-CH_3$). MS (ESI): *m/z* 153.07 [$C_9H_{17}N_2{}^+$].

1,2-Dibutylpyrazolium Bromide (DBPzBr). Yellow solid (42%); ^1H