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Editor's choice paper

Efficient solvent-free fixation of CO_2 into cyclic carbonates catalyzed by Bi(III) porphyrin/TBAI at atmospheric pressure

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ABSTRACT

A series of Bi (III) porphyrin complexes were synthesized and tested as catalysts for chemical fixation of carbon dioxide (CO_2) and epoxides under solvent-free conditions in the presence of tetrabutylammonium iodide (TBAI) as co-catalyst. The influences of various factors (catalyst systems, catalyst amount, pressure, time, and temperature) on the catalytic activities have been studied systematically. The catalytic performances were strongly influenced by the substitute of porphyrin framework and axial group X^-. 2a/TBAI was screened as the most active catalyst system under the optimized conditions (90 °C, 1 h, 2 MPa). Notably, a very high turnover frequency (TOF) value (37,900 h^{-1}) for catalyst 2a was achieved via adjusting reaction factors. This binary catalytic system also exhibited good activities (up to 98%) and selectivities (>99%) for the cycloaddition reaction of many epoxides, including diepoxides, with CO_2 into corresponding cyclic carbonates at atmospheric pressure (0.1 MPa) within 6 h. Especially, the glycidyl methacrylate, which is known to have the self-polymerization tendency at higher temperature, could be converted into its corresponding cyclic carbonate selectively with high yield of 94.8% with 2a/TBAI as catalyst at room temperature and 0.1 MPa. In spite of the homogeneous property of the catalytic system, 2a/TBAI, could maintain the high performance under atmospheric pressure for 60 h, or even longer. Moreover, kinetic studies gave out an inferred mechanism.

1. Introduction

CO_2, as an abundant, inexpensive, nontoxic, and nonflammable carbon resource which is produced from the metabolism of living organisms and industrial manufacture, is an important resource because it is environment-benign and easy to handle on an industrial scale [1–5]. The chemical fixation of CO_2 into industrially useful materials is an attractive method because there are many possibilities for CO_2 to be used as a safe and cheap C_1 building block in organic synthesis [6,7]. One of the most meaningful and environment-friendly ways for this procedure is the cyclic carbonates synthesis via the coupling reaction of epoxides with CO_2. The cyclic carbonates are useful intermediates in organic synthesis, aprotic polar solvents and raw materials for plastics [8–10].

Within the last decades, many catalysts, such as metal complexes [11–14], metalloporphyrins complexes [15–19], metal oxides [20–22], molecular sieves [23], ion-exchange resins [24], quaternary ammonium salts [25,26], metal-organic frameworks [27,28], Lewis acids or bases [29–32], nanoparticles [33], ionic liquids [34–37], and so on, have been developed for this reaction and met the requirements of green sustainable technology. Metal complex catalysts (*e.g.*, Zn, Ni, Rh, Ir, Fe, Cu, Re, Al, Co, Cr, Pb, et al.) are popularly used for the coupling reaction of epoxides with CO_2 [38–47]. As biomimetic catalysts, metalloporphyrins could be used as an intermediate of oxygen carrier for biological systems, and have been widely used as catalysts for various reactions [48]. The first homogeneous porphyrin catalysts for the copolymerization of CO_2 and cyclohexene oxide were aluminium porphyrin complexes, which were reported by Takeda and Inoue in 1978 [49].

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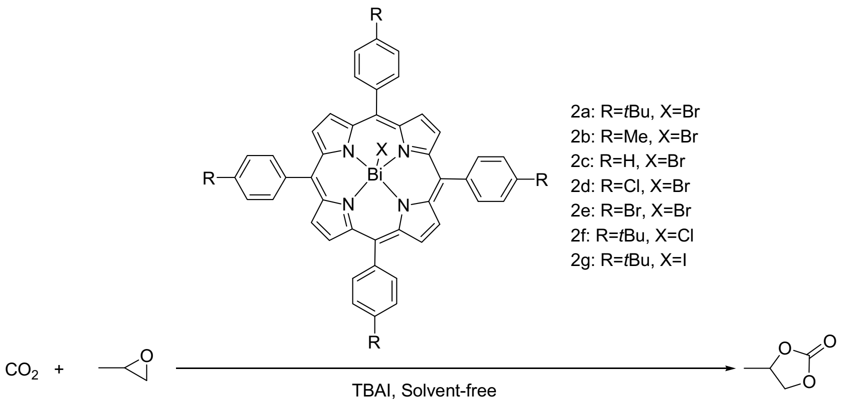

Scheme 1. Coupling reaction of CO_2 and PO to PC catalyzed by bismuth porphyrins in the presence of TBAI as co-catalyst.

From then on, various metal porphyrin catalysts have been developed, including Mg, Al, Cr, Co, Mn, Fe, Zn, Cu, Ru and Sn [50–59]. Recently, Ema synthesized a bifunctional Mg porphyrin catalyst [60,61] and Qin designed a non-toxic aluminum porphyrin catalyst [62–64], both could obtain high TOF values for the coupling reaction between CO_2 and epoxides, demonstrating that metalloporphyrin complexes are promising catalysts for this coupling reaction. The possible reason might be that the porphyrin framework can be carefully designed, *i.e.*, the coordination site can be highly functionalized, thereby providing a way to further enhance the catalytic activity of such complexes. Most recently, Jing and co-workers [65] developed a series of bifunctional porphyrinatozinc-based ionic liquids, which showed satisfying activities as homogeneous catalysts in the cycloaddition reaction of epoxides and CO_2. So, as a kind of biomimetic catalysts, the design and detailed research of metal porphyrin catalysts are still attractive.

Bismuth is known to be nontoxic and noncarcinogenic, and the compounds of bismuth could be used as reaction reagents, oxidizing agents, catalysts, medicine and so on [66,67]. However, compared to the use of metalloporphyrin complexes, the use of bismuth-centre complexes [68–74], especially bismuthporphyrin complexes for chemical fixation of CO_2 is rare. Therefore, in present study, a series of bismuth porphyrin complexes were designed and synthesized as biomimetic environmentally-benign catalysts to catalyze the cycloaddition of CO_2 and epoxides in the presence of TBAI with the maximum TOF of 37,900 h^{-1} (Scheme 1). The catalytic performance had been systematically investigated under various reaction conditions. Many cyclic carbonates, other than propylene carbonate (PC), could be obtained under atmospheric pressure (0.1 MPa). Furthermore, a mechanism was proposed on the basis of the kinetic studies.

2. Experimental section

2.1. Chemicals and analytical methods

Pyrrole bought from Alfa Aesar Chem was distilled over CaH_2 under nitrogen for 5 h before being used. Benzaldehyde and derivatives obtained from Alfa Aesar Chem was washed with H_2SO_4, 10% $NaHCO_3$ and water, dried over $CaCl_2$, and distilled under nitrogen. Dichloromethane, propionic acid and glacial acetic acid were purchased from Tianjin Kemel Co. LTD (China). CH_2Cl_2 was washed successively with concentrated H_2SO_4, water and dried over $CaCl_2$, and distilled over CaH_2 under nitrogen. Propylene oxide bought from Alfa Aesar Chem was distilled over CaH_2 and $Ca(OH)_2$ before being used. Carbon dioxide was purchased from Wuhan Steel Co. (99.99%, mass fraction). Other materials were obtained from J&K Acros Co. and used without further purification.

NMR experiments were performed on a Bruker Al–400 MHz instrument using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. UV experiments were recorded on a PE Lambda 35 UV spectrophotometer. Elemental analysis was conducted on a PE 2400 series II CHNS/O elemental analyzer.

2.2. Preparation of Bi (III) porphyrin complexes [75]

All the porphyrin ligands 1a-1e were synthesized, purified and characterized using the literature procedure (Scheme 2) [76–78]. The Bi (III) porphyrin complexes were synthesized using a modified literature procedure (Scheme 2) [79,80]. In a typical reaction, the Bi (III) porphyrin complexes were obtained by metallation of porphyrin ligands 1a–1e (1.0 mmol) with BiX_3 (1.05 mmol) in tetrahydrofuran (THF) (500 ml). The crystalline product was washed with THF and dried. The product was purified by silica gel column chromatography with dichloromethane as eluent.

2.2.1. 2a

^1H NMR ($CDCl_3$, δ, ppm): 8.10 (d, J = 7.4 Hz, 4H), 8.02 (s, 4H), 7.44 (m, J = 26.3, 6.9 Hz, 16H), 1.33 (d, J = 49.5 Hz, 36H). ^{13}C NMR ($CDCl_3$, δ, ppm): 206.88, 203.00, 175.51, 170.14, 168.48, 164.85, 160.68, 133.84, 130.17, 128.90, 98.36, 89.78, 51.59, 30.90, 29.69, 20.67. Selected IR peaks (KBr, cm^{-1}) υ: 2961, 1603, 1481, 1405, 1362, 1276, 1262, 1108, 987, 750. Anal. calcd for $C_{60}H_{60}N_4BiBr$: C, 64.00; H, 5.37; N, 4.98%. Found: C, 63.97; H, 5.39; N, 5.01%.

2.2.2. 2b

^1H NMR ($CDCl_3$, δ, ppm): 8.52 (s, 8H), 7.83 (s, 16H), 2.80 (s, 12H). ^{13}C NMR ($CDCl_3$, δ, ppm): 206.83, 185.14, 146.15, 140.60, 138.96, 137.23, 134.52, 129.29, 127.79, 127.41, 122.53, 51.60, 30.91, 21.65, 20.69. Selected IR peaks (KBr, cm^{-1}) υ: 2913, 1502, 1470, 1384, 1218, 1180, 1108, 982, 965, 757. Anal. calcd for $C_{48}H_{36}N_4BiBr$: C, 60.20; H, 3.79; N, 5.85%. Found: C, 60.17; H, 3.76; N, 5.88%.

2.2.3. 2c

^1H NMR ($CDCl_3$, δ, ppm): 8.86 (s, 4H), 8.24 (d, J = 6.3 Hz, 4H), 7.88 (m, J = 84.9, 21.1 Hz, 20H). ^{13}C NMR ($CDCl_3$, δ, ppm): 206.96, 154.90, 147.89, 134.55, 126.67, 124.26, 120.13, 119.48, 99.99, 51.59, 34.85, 30.90, 29.68, 20.68. Selected IR peaks (KBr, cm^{-1}) υ: 3172, 1484, 1441, 1270, 1228, 1180, 1042, 1001, 984, 748. Anal. calcd for $C_{44}H_{28}N_4BiBr$: C, 58.61; H, 3.13; N, 6.21%. Found: C, 57.18; H, 3.07; N, 6.38%.