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Efficient solvent-free fixation of CO_2 catalyzed by new recyclable bifunctional metal complexes

Jing Peng[a,b], Hai-Jian Yang[b,*], Sheng Wang[b], Binru Ban[b], Zidong Wei[a], Bo Lei[b], Cun-Yue Guo[c,*]

[a] The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, PR China

[b] Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, Key Laboratory of Analytical Chemistry of the State Ethnic Affairs Commission, National Demonstration Center for Experimental Ethnopharmacology Education, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan, 430074, PR China

[c] School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing, 100049, PR China

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ABSTRACT

A series of metal complexes containing a metal ion (Zn, Cu, Pb, Ni, Co) and two quaternary phosphonium salt units anchored on the ligands were designed and synthesized as efficient single-component bifunctional catalyst for the solvent-free coupling reaction of CO_2 and epoxides without any co-catalysts. The effects of various reaction variables on the catalytic activity were investigated systematically and the optimized reaction conditions were screened as (130 °C, 1 MPa and 5 h). The order of the catalytic activity for these single-component bifunctional metal complexes was found to be Zn-PPBCl (96%) > Co-PPBCl (90%) ≈ Ni-PPBCl (90%) > Pb-PPBCl (86%) > Cu-PPBCl (15%). Notably, a high turnover frequency (TOF) value (1230 h^{-1}) for bifunctional catalyst Zn-PPBCl was achieved *via* adjusting reaction variables. Moreover, this series of catalysts can also catalyze the coupling reaction at atmospheric pressure, and most of them showed high conversion of epoxide (propylene carbonate (PC) yield > 90%) within 7 h. The catalysts are also applicable to a variety of epoxides and good catalytic performances were achieved for producing the corresponding cyclic carbonates in most cases. Furthermore, the catalyst can be easily recycled and reused for at least five times without dramatic activity loss after simple filtration and drying. Finally, kinetic studies were carried out preliminarily for four metal (Zn, Co, Ni, Pb) catalysts and the formation activation energies (E_a) of cyclic carbonate were obtained. The apparent activation energy E_a catalyzed by Zn-PPBCl is only 37.6 kJ/mol, while the E_a (Pb-PPBCl) is 70.0 kJ/mol, E_a (Ni-PPBCl) is 65.6 kJ/mol, and E_a (Co-PPBCl) is 43.1 kJ/mol. The sequence of E_a agrees well with the catalytic activity. Based on the kinetic studies and experimental results, an inferred mechanism was deduced.

1. Introduction

As a renewable C1 source for the synthesis of many industrially important chemicals, carbon dioxide (CO_2) has the advantage of being economical, abundant, nonflammable, non-toxic and capable of replacing fossil fuel sources [1–3]. Cycloaddition of CO_2 and epoxide is a 100% atom economical reaction and one of the most promising applications for chemical utilization of CO_2 as a carbon source in the synthesis of carbonates [4–6]. Among diverse possible transformations, the cyclic carbonates synthesis from CO_2 and epoxides has attracted great interest both industrially and academically [7–10]. Cyclic carbonates are valuable synthetic products with various applications, such as polar aprotic solvents, lithium batteries electrolytes, fuel additives and chemical manufacture intermediates, and so forth [11–13]. Among almost all processes of CO_2 transformations, a large energy input is always required, so highly reactive catalysts are necessary to facilitate the reaction [14,15].

Within the last decades, several kinds of catalytic systems, such as metal complexes [16–22], porphyrins [23,24], metal oxides [25], ionic liquids [26–29], metal-organic frameworks [30,31], organocatalysts [32–39] and immobilized catalysts [40–43] etc., have been studied for the cycloaddition of CO_2 and epoxides, which met the requirements of green sustainable technology. The metal complexes catalyst have been most widely employed due to their unique properties, such as tunable activity *via* adjusting the substituents of ligands, a wide variety choice of metal ions center, stability against air and moisture, and so forth [44–46]. Recently, He et al. developed $Zn(O)_4$-type complexes as efficient catalysts in the presence of TBAI for the coupling reaction

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* Corresponding authors.
E-mail addresses: yanghaijian@vip.sina.com (H.-J. Yang), cyguo@ucas.ac.cn (C.-Y. Guo).

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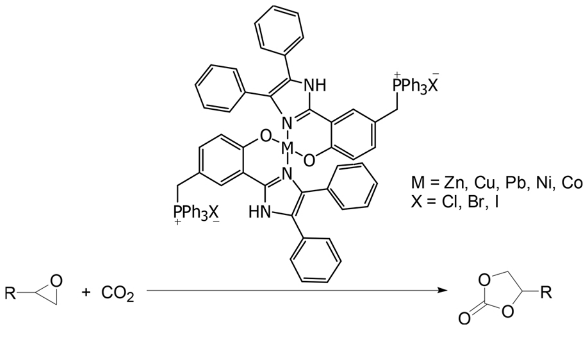
between epoxides and CO_2 with a TOF of 22 000 h^{-1} [47]. Except zinc complex, North et al. synthesized chromium and aluminium salphen complexes combining with TBAB for this reaction [48]. Wani et al. used di-nuclear Cu(II), Co(II) and Ni(II) complexes along with TBAI for the cycloaddition under mild condition and with low catalyst loading [49]. Wang et al. prepared aluminium complexes derived from a hexadentate salen-type Schiff base as catalyst with TBAB as co-catalyst for the synthesis of cyclic carbonates under atmosphere pressure [50]. Bimetallic Fe(III) thioether-triphenolate complexes in combination with TBAB, reported by Capacchione et al., can also played as an excellent catalytic system, with a TOF value of 5200 h^{-1}[51]. From the foregoing, although various metal catalyst systems for the coupling reaction of CO_2 and epoxides have been studied voluminously, in which a co-catalyst is still needed to open the ring of epoxide. It is difficult to explore the mechanism and catalyst recyclability with binary system. So, many multifunctional catalysts with both Lewis acidic and basic portion in one molecule have been developed. Comparing with the binary catalyst systems, multi-functional metal complexes with two or more catalytic sites in one catalyst molecule exhibited higher catalytic activity without any co-catalyst [52–55].

To catalyze the cycloaddition of CO_2 and epoxide, it is well-known that Lewis acid-base bifunctionality is the key for the catalyst from the point of mechanistic considerations view [56–58]. Generally, in view of the function for CO_2 and epoxide activation, a metal complex to build the bifunctional catalyst should have both a Lewis acid (metal) centre and a Lewis base (an anion X^- as nucleophile) group [59]. Previously we reported a series of metal complexes as effective binary catalysts for the conversion of CO_2 and various epoxides into cyclic carbonates [60–63]. Therefore, in order to create bifunctional analogues of these complexes, a series of new bifunctional metal (Zn, Cu, Pb, Ni, Co) complexes were designed and synthesized for the coupling reaction of CO_2 and epoxide in present work (Scheme Scheme 1). The systematical investigation of catalytic performances for these bifunctional catalysts gave out the optimal catalytic conditions. The catalytic performances for the coupling reactions of CO_2 and various epoxides to cyclic carbonates have been achieved under atmospheric pressure (0.1 MPa). Additionally, the catalyst reusability was also been detected. The rate constants for the reactions catalyzed by bifunctional metal complexes were obtained as a function of process temperature in the range of 373–403 K, as well as the reactions activation energies deduced from the Arrhenius plots. Finally, an inferred mechanism was presented.

2. Experimental section

2.1. Chemicals and analytical methods

The materials' informations are listed in Table S1. All the chemicals were used as received except for the epoxides, which were purified by distillation from CaH_2 before utilization. Complexes Zn-BCl and Zn-BH were synthesized following our reported paper and used for comparision of catalysis [60]. The general procedure for the cycloaddition of CO_2 to epoxides, copies of all spectra of synthesized complexes and carbonate products are provided in the Supporting Information.



Scheme 1. Cycloaddition of CO_2 to epoxides with bifunctional metal complexes as catalysts.

A Bruker Al-400 MHz instrument were used for NMR spectra test using TMS as an internal standard. Cross polarization magic angle spinning (CP-MAS) solid state 13C NMR spectra were recorded with a Bruker Avance 600 WB spectrometer. A Perkin-Elmer 2000 FT-IR spectrometer were used for IR spectra record. Elemental analysis was conducted on a PE 2400 series II CHNS/O elemental analyzer. X-ray diffraction studies were performed on a Bruker-APEX diffractometer equipped with a CCD area detector, MoKa-radiation ($\lambda = 0.71073$ Å), and a graphite monochromator. Melting point was obtained from X-4-type digital micro-melting point apparatus.

2.2. Synthesis of PPBX and X-ray crystallographic studies

The ligand's precursors PX and PPX (X = Cl, Br, I) were prepared and characterized according to the procedures reported by Ji et al. (Scheme Scheme 2) [52,55,59].

Ligand PPBX: 9.51 mmol of PPX (X = Cl, Br, I), 9.51 mmol (1 equivalent, 2 g) of benzil, and ammonium acetate (20 equivalent, 14.6 g) were dissolved in 30 mL glacial acetic acid and refluxed for 3.5 h. Then, an excess of de-ionised water was poured into the reaction system to obtain a white precipitant. After filtration and being washed with water, the resulting crude product was dissolved in CH_2Cl_2 and dried over $MgSO_4$. The solution, after filtration, was collected and evaporated to obtain a powder. After recrystallision from CH_2Cl_2-pentane, PPBX was obtained as a white crystalline solid in 31% yield.

The structure of PPBCl was further confirmed with single crystal X-ray crystallography (Fig. 1). Sigle crystal of PPBCl•$3H_2O$ could be obtained by slow evaporation of concentrated methanol solution. Crystallographic details are: $C_{40}H_{38}ClN_2O_4P$, $M_r = 677.14$, monoclinic, $P2_1/c$, $a = 13.6605(16)$ Å, $b = 21.537(3)$ Å, $c = 12.5616(15)$ Å, $\beta = 104.884(2)^\circ$, $V = 3571.8(7)$ Å^3, $Z = 4$, $\rho = 1.259$ mg•M^{-3}, $\mu = 0.195\ mm^{-1}$, $\lambda = 0.71073$ Å, $T = 296(2)$ K, $F(000) = 1424$, crystal size = 0.10 × 0.10 × 0.10 mm, $\theta(min) = 1.54^\circ$, $\theta(max) = 27.00^\circ$, 29,537 reflections collected, 7790 reflections that are unique ($R_{int} = 0.0638$), GoF = 1.022, $R_1 = 0.0560$ and $wR_2 = 0.1391$ [$I > 2\sigma(I)$], $R_1 = 0.1051$ and $wR_2 = 0.1688$ (all indices), min/max residual density = -0.467/0.606 (e Å^{-3}). Completeness to $\theta(27.00^\circ) = 99.9\%$. The reference number of CCDC is 1,430,040.

2.3. Synthesis of metal complexes M-PPBX

The general synthesis procedure of bifunctional complexes (M-PPBX) was shown in Scheme Scheme 2. Details of these complexes were shown in supporting information.

3. Results and discussion

3.1. Effect of reaction parameters on the cycloaddition

First, to optimize the yield of the cyclic carbonate and evaluate the catalytic performances of our bifunctional metal complexes, the reaction conditions including the CO_2 pressure, time, temperature and the catalyst loading were investigated. The cycloaddition reaction between CO_2 and propylene oxide (PO) catalyzed by Zn-PPBCl was examined systematically as a model reaction system (Fig. 2). Since the diffusion may affect the kinetics of reactions in the mass transfer accompanied by the cycloaddition of CO_2 and epoxide, an optimum CO_2 pressure ranges for the maximum yield of PC must exist [64]. The pressure effect investigation was carried out in the range of 0.5–5.0 MPa. As shown in Fig. 2a, the PC yield increased sharply when the CO_2 pressure increased from 0.5–1.0 MPa, but then decreased at higher pressure (1.0–5.0 MPa). This phenomenon has also been reported by many other scientists [65–67]. Based on their reports, it could be explained that in the low-pressure region, higher CO_2 pressure could increase the CO_2