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Cycloaddition of CO_2 to Epoxides Catalyzed by Polyaniline Salts

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Abstract: The catalytic activity of polyaniline-HX (X = I, Br, Cl) (PANI-HI, PANI-HBr, PANI-HCl) for the cycloaddition of CO_2 to propylene oxide (PO) to produce propylene carbonate (PC) was studied for the first time. It was shown that all the PANI salts were active for the reaction, and PANI-HI was most active and selective. On the basis of the preliminary results, the effect of the reaction conditions on the cycloadditions of CO_2 to propylene oxide and epichlorohydrin was further investigated by using PANI-HI as the catalyst. The results indicated that the optimized temperature was around 115 °C. The maxima occurred in yield versus pressure curves at about 5 MPa for both substrates. Complete conversion was achieved in 3 h for epichlorohydrin and 6 h for propylene oxide at 115 °C and 5 MPa. With propylene oxide as the substrate, the reusability of PANI-HI was evaluated and no loss of catalytic activity was detectable after the catalyst had been reused five times. The catalyst was characterized by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), which provided further evidence for the high stability of the catalyst. We believe that the catalyst has great potential for industrial applications because it has some unusual advantages, such as its easy preparation, high activity, selectivity, stability, low cost, and simple separation from products.

Keywords: carbon dioxide · cycloaddition reaction · epoxides · heterogeneous catalysis · polymers

Introduction

Great efforts have been made towards the fixation of CO_2 during the past two decades. This is partly due to the fact that CO_2 can be used as an C1 building block in organic synthesis.[1] Another important impetus is the global warming problem, which is mainly caused by CO_2. Atom efficient cycloaddition of CO_2 to epoxides to produce cyclic carbonates is one of the most successful examples of CO_2 fixation to produce the carbonates which are excellent aprotic polar solvents, pharmaceutical and fine chemical intermediates, precursors for polycarbonate materials, and so on.[2] It is not surprising that these kinds of reactions have been studied extensively.

For the coupling of CO_2 and epoxides, homogeneous catalysts, including tetraethylammonium bromide and potassium iodide, are commonly utilized in current industrial processes. In addition, a lot of homogeneous catalysts have been reported, such as ionic liquids,[3] transition metal complexes,[4] quaternary ammonium and phosphoniums salts,[5] and alkali metal salts.[6] Homogeneous catalysts are undesirably dissolved in the products, thus some procedures are required to separate the products from the catalysts. In order to facilitate the separation of the catalysts from the products, many solid catalysts have been developed, including metal oxide,[7] modified SiO_2,[8] lanthanide oxychloride,[9] insoluble ion-exchange resins,[10] and gold nanoparticles supported on ion-exchange resins.[11] However, most catalysts cannot meet the current industrial demands because of some drawbacks, such as the need for a cosolvent or cocatalyst, their low activity, and their high cost.

In recent years, functional polymers have been used as catalysts and catalyst supports. They are attractive for technological applications and manufacture processes with simplified product recovery. Polyaniline (PANI) is one of the most useful conducting polymers due to its facile synthesis, environmental stability, and simple acid/base doping/dedoping chemistry.[12] It has been extensively investigated for many applications, such as antistatic and anticorrosion coatings, chemical sensors, and electrodes for light-emitting

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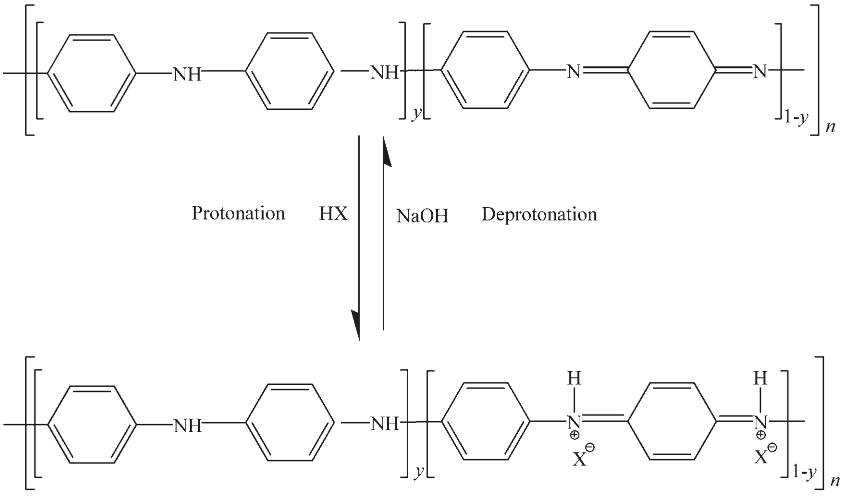
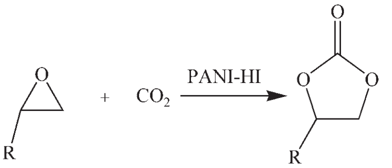


Scheme 2. Structure of polyaniline and its acid/base doping/undoping process.

diodes, capacitors, and batteries.[12] Furthermore, because of its easy preparation, recyclability, environmental stability, low cost, and nonsolubility in most of the organic solvents and water, PANI has attracted much attention as efficient heterogeneous catalysts. For example, PANI doped with metal complexes or heteropoly acid has been used as a catalyst in the preparation of amino acid derivatives,[13] alkene epoxidation,[14] aerobic oxidation of alcohols to aldehydes and ketones,[15] dehydration of alcohols,[16] synthesis of methyl tertiary butylether,[17] hydrogenation of 2-ethylanthraquinone,[18] Suzuki reaction, and asymmetric dihydroxylation of olefins.[19] PANI doped with inorganic acids (H_2SO_4, HNO_3) has been used to catalyze esterification[20] and transesterification[21] reactions as solid acid catalysts.

It is of great importance to develop highly efficient heterogeneous catalysts for the coupling of CO_2 and epoxides. In this work, we discovered that PANI salts could be used as heterogeneous catalysts for the coupling of CO_2 with epoxides (Scheme 1) to produce cyclic carbonates without any organic additives under mild conditions. Especially, PANI-HI was very active and stable, inexpensive, easy to prepare, and easily separable from products. As far as we know, this is the first report on the cycloaddition of CO_2 to epoxides catalyzed by PANI-based catalysts.



Scheme 1. Cycloaddition of CO_2 to epoxides. In this work R = $-CH_3$, CH_2Cl.

Results and Discussion

As shown in Scheme 2, PANI contains benzenoid and quinonoid units. According to the ratio of the two units, the intrinsic redox state of the polymer can vary from the fully oxidized ($y=0$) to the fully reduced ($y=1$).[22] The unprotonated and 50% intrinsically oxidized polymer has been termed as an emeraldine base ($y=0.5$), in which the number of reduced units and oxidized units is equal.[22] Different PANI salts can be obtained by protonating an emeraldine base with different acids. The counter anions are well-dispersed in PANI salts because the reduced units and oxidized units distribute alternatively on the backbone of the emeraldine base[21] and the protonation occurs preferentially at the imine repeating units.[22b] So the active sites are well-dispersed when PANI salts are used as catalysts.

To select a more active catalyst, the effect of anions (I^-, Br^-, Cl^-) of polyaniline salts on the coupling of CO_2 and propylene oxide was studied by performing the reaction with the same amount of the catalysts at 115 °C and 5 MPa with a reaction time of 6 h (Table 1). The yield of PC was only 6% when unprotonated emeraldine base was used as the catalyst, while the yield greatly increased after protonating the emeraldine base by halide acids. It is also shown that the yield of PC strongly depended on the anions of polyaniline salts. The order of activity of the catalysts was PANI-HI > PANI-HBr > PANI-HCl. For all the experiments with different catalysts, no byproduct was detected. PANI-HI was further characterized because it was the most active.

Table 1. Effect of counter anions on PC yield. Reaction conditions: 115 °C, propylene oxide (17.4 mmol), catalyst (0.2 g), 5 MPa CO_2, 6 h.

Catalyst	Yield [%] of PC
emeraldine base	6.0
PANI-HCl	31.2
PANI-HBr	81.0
PANI-HI	99.1

Figure 1 illustrates the dependence of the PC yield on reaction temperature at a CO_2 pressure of 5 MPa with a reaction time of 6 h. It is clear that the catalytic activity of the catalyst was sensitive to reaction temperature. The yield of PC increased with the reaction temperature up to 115 °C.

Dependence of the product yield on reaction time at 115 °C and a CO_2 pressure of 5 MPa is shown in Figure 2. It indicates that the yield increased with reaction time, and propylene oxide could be converted completely within 6 h.

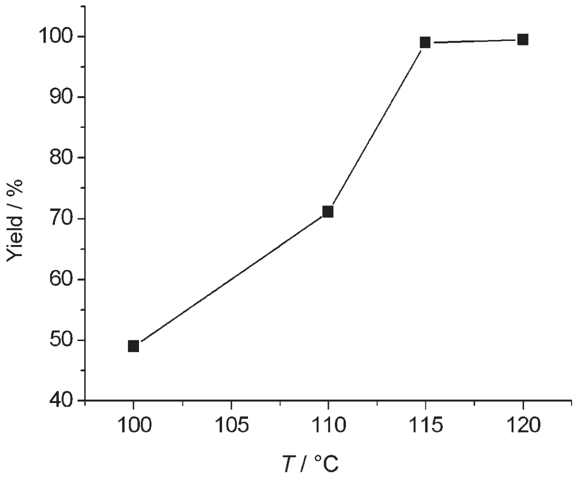


Figure 1. Dependence of PC yield on temperature at 5 MPa of CO_2 pressure. Reaction conditions: propylene oxide (17.4 mmol), catalyst PANI-HI (0.2 g), 6 h.

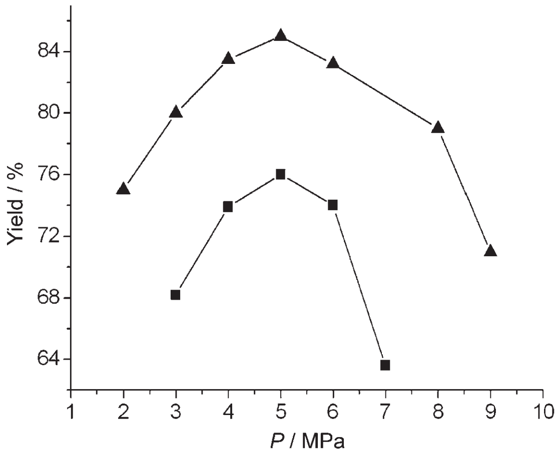


Figure 3. Dependence of product yield on CO_2 pressure at 115 °C. ▲ (Chloromethyl)ethylene carbonate, ■ propylene carbonate. Reaction conditions: epoxides (17.4 mmol), catalyst PANI-HI (0.2 g), 4 h for propylene oxide and 2 h for epichlorohydrin.

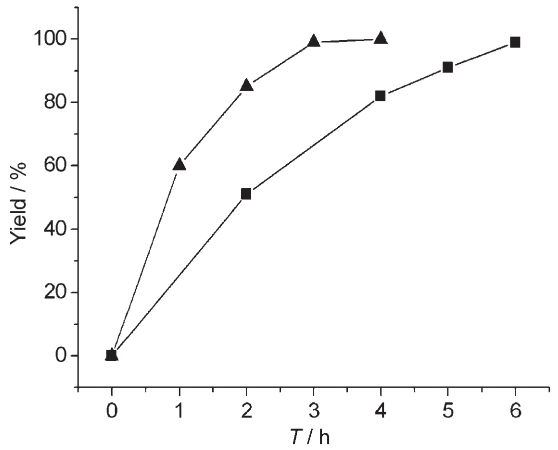


Figure 2. Dependence of product yield on reaction time at 115 °C and 5 MPa of CO_2 pressure. ▲ (Chloromethyl)ethylene carbonate, ■ propylene carbonate. Reaction conditions: epoxides (17.4 mmol), catalyst PANI-HI (0.2 g).

The coupling of CO_2 and epichlorohydrin was also conducted under the same conditions, and the reaction could be finished in 3 h, as shown in Figure 2. This demonstrated that the epichlorohydrin is more reactive than propylene epoxide when PANI-HI was used as catalyst. The possible reason for the faster reaction rate of epichlorohydrin is the presence of the electron-withdrawing chloromethyl group, which results in easy ring opening of epichlorohydrin by nucleophilic attack.

CO_2 pressure usually has a significant effect on the reaction rate.[6,10,24] Therefore, it can be used as a tunable parameter to optimize the reaction efficiency. In this work, the effect of CO_2 pressure on the yields of cyclic carbonates was studied at 115 °C with PANI-HI as the catalyst, and the reaction times for propylene oxide and epichlorohydrin were 4 and 2 h, respectively. As shown in Figure 3, the maximum yield was achieved at about 5 MPa for both substrates. This can be explained qualitatively by the effect of pressure on the concentrations of CO_2 and epoxides in the two phases. The partition behavior of substrate between phases has been shown previously to affect reaction rate in a biphasic system.[25] In this work, we observed the phase behavior of CO_2-propylene oxide and CO_2-epichlorohydrin systems by using the view cell reported previously.[26] It was demonstrated that there were two phases in the system under all the experimental conditions studied. The upper phase was the CO_2-rich phase and the bottom phase was the epoxide-rich phase. The reactions took place mainly in the liquid phase because the catalyst was dispersed in this phase. The change in reaction rate was related to the partition behavior of the substrate,[25] and the increase in CO_2 pressure had two opposite effects on the reactions. First, the solubility of CO_2 in the epoxides increases with increasing pressure, which favored the reaction considering that CO_2 was a reactant. At the higher pressures, however, more epoxides were in the CO_2-rich phase and the concentration of epoxides in the liquid phase was too low, which reduced the reaction rate. At lower CO_2 pressure, the first factor was dominant because the concentration of CO_2 in the liquid phase was low. The second factor became dominant as the pressure of CO_2 became high enough. Therefore, a maximum appeared in each pressure versus yield curve.

Two series of experiments were carried out to examine the recyclability of the catalyst when using PO as the substrate at 115 °C and 5 MPa, with the reaction time of 2 and 6 h, respectively. In each cycle, PANI-HI as a solid catalyst was recovered by filtration, followed by rinsing with acetone and drying, and reused as the catalyst for the next run. The yields of PC for the five repeated runs are shown in Figure 4. There was no detectable decrease of the yield of PC product in the two series of experiments, indicating that the catalyst was very stable. The excellent stability was also supported by the results of thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Figure 5

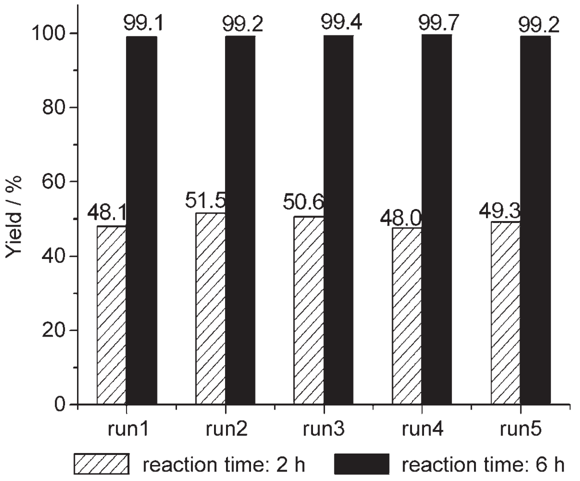


Figure 4. Yields of PC in the five repeated runs for the two series of experiments at 115 °C and 5 MPa with reaction times of 2 and 6 h, respectively.

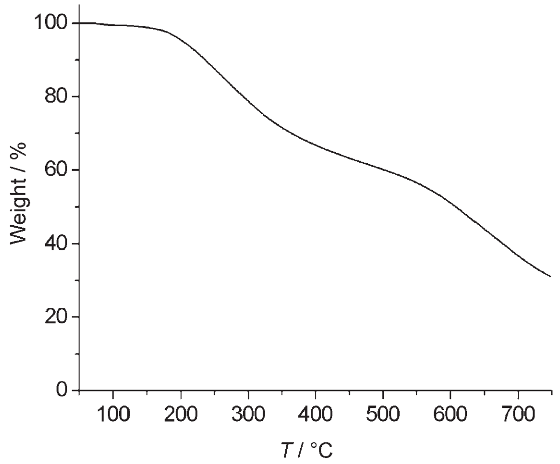


Figure 5. Thermogram of PANI-HI.

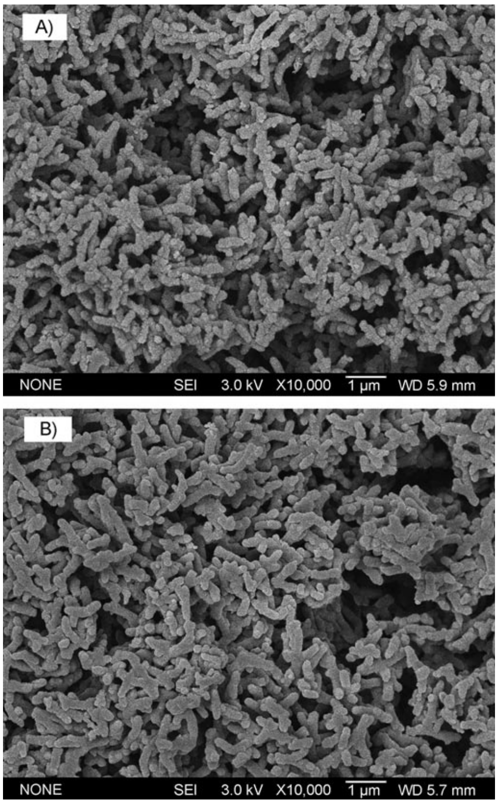
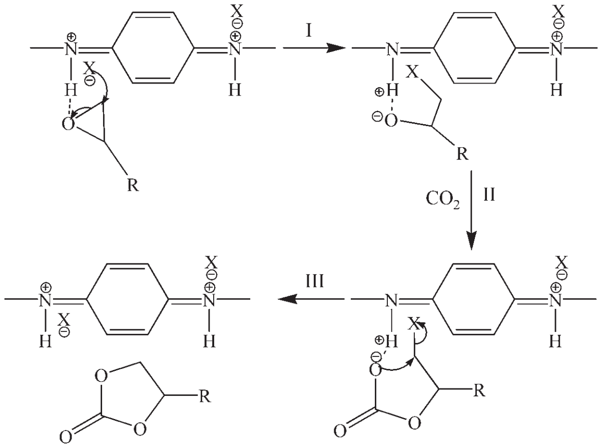


Figure 6. SEM images of the PANI-HI catalyst before (A) and after (B) it had been used five times.



Scheme 3. Cycloaddition mechanism of CO_2 to epoxides.

gives the thermogram of PANI-HI. It is observed that the weight loss of the catalyst was 0.65 % at about 100 °C. This could be attributed to the desorption of trapped water molecules in the polymer matrix.[23] Removal of the dopants began at 190 °C, which is much higher than the reaction temperature (115 °C) in our catalytic experiments. The SEM images of unused and used PANI-HI are given in Figure 6A and B, respectively. The figure shows that the morphology of the catalyst did not change noticeably after it had been used five times.

As for the catalytic mechanism of the coupling reaction between epoxides and CO_2, it is widely recognized that three steps are involved when halogen-containing catalysts are used;[6] these are: ring opening of epoxides by nucleophilic attack of an anion at the least-hindered carbon (step I), insertion of CO_2 (step II), and subsequent intramolecular cyclization resulting in the cyclic carbonate and the regeneration of the catalyst (step III; Scheme 3). However, the dominant step of the reactions depends on the properties of the catalysts. In order to get evidence for studying which step was dominant when PANI salts were used as the catalysts, elemental analysis was performed for the PANI-HX prepared in this work and the results are listed in Table 2. The degree of protonation in PANI-HCl (4.5 mmol g^{-1}) was considerably higher than that in PANI-HBr (3.1 mmol g^{-1}) and PANI-HI (3.0 mmol g^{-1}), but the catalytic activity of PANI-HCl was much lower (Table 1). In addition, the activity of PANI-HI was higher than PANI-HBr, although the protonating degree was nearly the same.

Table 2. Compositions of the PANI-HX salts.

	C [%]	N [%]	H [%]	X [%][a]
PANI-HI	47.69	9.17	3.21	39.93 (3.1 $\mathrm{mmol\,g^{-1}}$)
PANI-HBr	60.27	11.31	4.42	24.00 (3.0 $\mathrm{mmol\,g^{-1}}$)
PANI-HCl	66.37	12.79	4.78	16.06 (4.5 $\mathrm{mmol\,g^{-1}}$)

[a] X = Halogen.

The catalytic activity of the catalysts was in the order PANI-HI > PANI-HBr > PANI-HCl. The nucleophilicity of the anions is in the order $Cl^{-1} > Br^{-1} > I^{-1}$, while the leaving ability follows the order $I^{-1} > Br^{-1} > Cl^{-1}$. Therefore, it can be deduced that the leaving ability is dominant for the activity.

Conclusion

The catalytic performance of PANI-HX ($X = Cl^-$, Br^-, I^-) for the cycloaddition of CO_2 to epoxides has been studied for the first time. It has been discovered that PANI-HX can be used as heterogeneous catalysts for the cycloaddition of CO_2 to propylene oxide. The order of activity of the catalysts is PANI-HI > PANI-HBr > PANI-HCl, which indicates that the leaving ability of the anions in the PANI salts is dominant for the activity. Further study by using PANI-HI as the catalyst has demonstrated that catalytic activity is sensitive to temperatures below 115 °C. At 115 °C, the yields for the coupling of CO_2 with propylene oxide and epichlorohydrin increase with increasing pressure as the pressure is lower than 5 MPa, and the yields decrease as the pressure is increased further. Under optimized conditions, complete conversion can be achieved in 6 h for propylene oxide and 3 h for epichlorohydrin. PANI-HI also has shown excellent recyclability. The heterogeneous catalyst is inexpensive, very active, selective, stable, and can be easily separated from the products. These characteristics make it a valuable catalyst with great potential for industrial applications.

Experimental Section

Materials: Analytical grade aniline was purchased from the Beijing Shiying Chemical Company and was purified by distillation under reduced pressure before use. Ammonium persulfate obtained from Yili Fine Chemicals Company was used as received. Hydroiodic acid (45 %, Sinopharm Chemical Reagent Company), hydrobromic acid (40 %, Yili Fine Chemical Company), and hydrochloric acid (36–38 %, Beijing Chemical Plant) were diluted to a desired concentration with distilled water. Analytical grade propylene oxide and epichlorohydrin were provided by Beijing Chemical Reagent Company and used as received. CO_2 (99.995 %) was supplied by Beijing Analytical Instrument Factory.

Preparation and characterization of the catalysts: Nanofibrous PANI-HCl was synthesized via the oxidative polymerization of aniline as reported by Kner et al.[27] In the experiment, aniline (5.96 g, 64 mmol) and ammonium persulfate (14.60 g, 64 mmol) were separately dissolved in HCl aqueous solution (200 mL, 1 M) at 0 °C. Then the two solutions were mixed in a 1000 mL beaker under rapid stirring for 30 s and the mixture was kept still for 6 h at 0 °C. The solid nanofibres were filtered out and then washed with distilled water. The as-synthesized PANI-HCl was undoped by treatment with excess NaOH aqueous solution (1 M) for 1 h with stirring at room temperature in order to obtain emeraldine base, which was filtered out and washed with distilled water until the filtrate reached pH 7, and it was then washed with ethanol and acetone. After drying at 40 °C for 12 h under a vacuum, the emeraldine base was grounded into powder.

Different PANI salts (PANI-HCl, PANI-HBr, PANI-HI) were prepared by protonating emeraldine base with the corresponding halide acid (HCl, HBr, HI). Emeraldine base (1.5 g) was charged into halide acid aqueous solution (150 mL, 0.5 M) and stirred for 12 h at ambient temperature. Light was blocked by black paper when using hydroiodic acid and hydrobromic acid as the protonating agents. The PANI salts were separated by filtration and washed with distilled water and acetone until the filtrate appeared colorless. After drying at 40 °C under vacuum for 12 h, the PANI salts were grounded into powder and stored in desiccator for use.

Thermogravimetric analysis (TGA) of PANI-HI was performed on Perkin–Elmer 7 Series Thermal Analysis System at a heating rate of 20 °C $\mathrm{min^{-1}}$. The morphology of the catalyst was investigated by means of a scanning electron microscope (SEM, JEOL JSM 6700F). The compositions of the PANI salts were determined by using a Flash EA1112 analyzer.

Reaction of CO_2 and epoxides: All the reaction experiments were performed in a stainless steel reactor of 6 mL with a magnetic stirrer. In a typical experiment, catalyst (0.2 g) and epoxide (17.4 mmol) were charged into the reactor, and the reactor was placed in the constant temperature air bath. After thermal equilibrium had been reached, CO_2 was charged to the desired pressure, and the pressure was kept constant during the reaction. After a suitable reaction time, the reactor was cooled down, and the gases were vented slowly at 0 °C. *n*-Pentanol (5 mL) as the solvent and acetophenone (0.4 g) as the internal standard were added. After the catalyst precipitated, the liquid phase was analyzed by GC (Agilent 4890 D) equipped with a flame-ionized detector. The purity and structure of the products obtained by using some typical experimental conditions were also checked by NMR spectroscopy and GCMS methods, and no byproduct was detected. In the catalyst recycling experiments, the product and the catalyst were separated by filtration and the solid catalyst was reused after washing with acetone and drying.

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