

Pd/C as a high efficient and reusable catalyst for cycloaddition of CO₂ to epoxides



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ABSTRACT

Pd/C was found to be an excellent catalyst in the coupling reaction of carbon dioxide and epoxides with tetrabutylammonium iodide (TBAI) as cocatalyst and the corresponding cyclic carbonates were obtained in good yields and high selectivities. 3-Chloropropylene carbonate was synthesized under extremely mild conditions of room temperature and atmosphere. The proposed mechanism was also calculated and confirmed by DFT. The palladium catalyst could be simply recycled and reused for 5 times without significant loss of activity.

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1. Introduction

The development of efficiently chemical fixation of carbon dioxide has received much attention recently since CO₂ is a cheap, nontoxic, and abundant C1 building block [1–6]. A promising methodology in this area is the cycloaddition of epoxide and carbon dioxide to afford cyclic carbonates [7–9]. Various catalyst systems for the synthesis of cyclic carbonates have been successfully developed in recent years, such as metal salts [10–19], metal complexes [20–23], organometallic compounds [24,25], ionic liquids [26–31] and organic bases [32]. However, those homogeneous catalysts suffer from drawbacks of high toxicity, expensive fabrication, usage of organic solvent and difficulty of reutilization. Hence, the exploration of efficiently heterogeneous catalysts for coupling carbon dioxide with epoxides is really desired.

As one of the most common heterogeneous palladium catalysts, palladium on activated carbon (Pd/C) has been applied to hydrogenation [33–36] and various cross-coupling reactions [37,38], in which the palladium shows high activity because

activated carbon has an extremely large surface area (800–1200 m²/g) and allows palladium to disperse uniformly on the solid support. In this paper, we report Pd/C catalyses the cycloaddition of CO₂ to epoxides in conjunction with TBAI under solvent-free conditions (Scheme 1).

2. Experimental

2.1. Materials

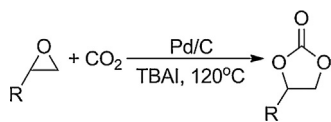
Propylene oxide, other epoxides, tetrabutylammonium fluoride (TBAF), tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI) and 5% Pd/C (wetted with ca. 50% water, 2.65% exactly measured by atomic absorption spectroscopy) were obtained from Sinopharm Chemical Reagent Co., Ltd. Phenyltrimethylammonium tribromide (PTAT) was ordered from Aladdin. DMAP was purchased from Aldrich. The propylene oxide (PO) was purified and dried over CaH₂ before use, while all other chemicals were used as-received without further purification.

2.2. Characterizations

¹H NMR spectra were recorded on a Varian AM-300 spectrometer using trimethylsilane (TMS) as an internal standard. GC

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Scheme 1. Pd/C-catalyzed cycloaddition of CO₂ to epoxides.

analyses of cyclic carbonates were carried out on a Varian CP-3800 gas chromatograph equipped with FID detectors.

2.3. Typical procedure for cycloaddition of CO₂ to epoxides

A 100 ml stainless steel autoclave equipped with a magnetic stir bar was charged with known amounts of 5% Pd/C (0.1 g), cocatalyst (0.1 mmol) and epoxide (25 mmol). The reactor was purged and pressurized with CO₂ to 2.0 MPa. Then it was merged into an oil bath that was heated and stirred at 120 °C. After a proper time, the reactor was quickly cooled down to 0 °C in ice-water and then carefully vented. The yield of cyclic carbonate was determined by subtraction method or by ¹H NMR spectroscopy.

The Pd/C catalyst was simply separated by filtration, washed with CH₂Cl₂ (3 ml) for five times, then reused directly to the next run with another portion of TBAI cocatalyst.

3. Results and discussion

In our lab, although metalloporphyrins, metallocene types, ionic liquids, metallocene and Lewis base/acid catalyst systems have been developed [25,39–45], the pure metal catalyst is rarely reported till now. The Pd/C was firstly applied to the coupling reaction of carbon dioxide and epoxides in the presence of Lewis bases. As well known that this reaction needs the Lewis acid and Lewis base catalyst work together, the Pd/C like metallic compounds cannot alone initiate the reaction but activates only epoxides. The Lewis base activates CO₂ to make the reaction take place smoothly.

3.1. Effect of catalyst concentration on cycloaddition of PO and CO₂

In Table 1, we applied Pd/C and TBAI to the synthesis of cyclic carbonate. The cycloaddition reaction did not happen using Pd/C as the only catalyst (Table 1, entry 1). TBAI could catalyze this reaction by itself (Table 1, entry 2); the addition of Pd/C significantly accelerated this coupling reaction from 38.8 to 98.8% (Table 1, entry 2 vs 3). This experimental result indicates the mechanistic understanding that the reaction must involve Lewis acid and base centers. The metal palladium provides a good Lewis acidic center and the co-catalyst TBAI simultaneously supplies the required Lewis basic center for this reaction.

Table 1
Effect of catalyst concentration in the coupling reaction of CO₂ and PO.^a

| Entry | Pd/C (mg) | TBAI (mmol) | Time (h) | Selectivity of PC ^b (%) | Yield ^b (%) |
|-------|-----------|-------------|----------|------------------------------------|------------------------|
| 1 | 100 | – | 8 | – | None |
| 2 | – | 0.1 | 8 | >99 | 38.8 |
| 3 | 100 | 0.1 | 8 | >99 | 98.8 |
| 4 | 50 | 0.1 | 8 | >99 | 50.8 |
| 5 | 100 | 0.05 | 8 | >99 | 63.1 |

^a Reaction condition: 5% Pd/C, cocatalyst TBAI, PO (25 mmol), CO₂ pressure (2.0 MPa), T (120 °C).

^b Isolated yield, the selectivity determined by GC.

Table 2
Cocatalyst effect in the coupling reaction of CO₂ and PO.^a

| Entry | Cocatalyst | CO ₂ pressure (MPa) | Time (h) | Selectivity of PC ^b (%) | Yield ^b (%) |
|-------|------------|--------------------------------|----------|------------------------------------|------------------------|
| 1 | TBAF | 2.0 | 8 | 57.6 | 7.6 ^c |
| 2 | TBAC | 2.0 | 8 | >99 | 60.8 |
| 3 | TBAB | 2.0 | 8 | >99 | 75.9 |
| 4 | TBAI | 2.0 | 8 | >99 | 98.8 |
| | | 2.0 | 8 | >99 | 98.6 ^d |
| 5 | PTAT | 2.0 | 8 | >99 | 91.6 |
| 6 | DMAP | 2.0 | 8 | >99 | 5.8 |
| 7 | DBU | 2.0 | 8 | >99 | 1.7 |
| 8 | TBAI | 2.0 | 48 | >99 | 25.0 ^e |
| 9 | TBAI | 2.0 | 48 | >99 | 10.7 ^{e,f} |

DMAP: 4-dimethyl aminopyridine; DBU: 1,8-diaza bicyclo[5.4.0]undec-7-ene.

^a Reaction condition: 5% Pd/C (100 mg, 0.1 mol%), cocatalyst (0.1 mmol), epoxide (25 mmol), T (120 °C).

^b Isolated yield, the selectivity determined by GC.

^c 1,2-Propanediol was obtained in 5.6% yield.

^d 0.45 ml H₂O (0.025 mol) was added, $n_{(H_2O)}/n_{(PO)} = 1:1$.

^e Room temperature.

^f Using of TBAI as catalyst only.

3.2. Effect of various cocatalysts on cycloaddition of PO and CO₂

Various cocatalysts were screened in the coupling reaction of CO₂ and PO (Table 2). Firstly, different quaternary ammonium salts were investigated. The order of their catalytic activity is TBAI > PTAT > TBAB > TBAC > TBAF, which is consistent with the nucleophilicity of anions and their leaving group tendencies (Table 2, entries 1–5). Furthermore, when using Lewis bases of tertiary amines DMAP and DBU as cocatalysts, the PC yields were only 5.8% and 1.7% (Table 2, entries 6 and 7), respectively. The possible reason we propose is that the coordination ability of nitrogen atom in Lewis bases is much stronger than that of oxygen atom in PO. Consequently, the metal palladium as Lewis acid center dominantly prefers to be coordinated by DMAP or DBU rather than PO. It is worth indicating that the reaction can take place even under room temperature. Up to 25.0% yield was achieved within 48 h at 25 °C using Pd/C-TBAI catalyst system (Table 2, entry 8). In addition, 1,2-propanediol was not obtained in the final product, when 25 mmol H₂O was introduced into the reaction ($n_{(H_2O)}$: $n_{(PO)} = 1:1$, Table 1, entry 4). This result is totally different than that using SalenCr(III) complex as catalyst reported by Hansen et al. [46] and demonstrates that the selectivity of heterogeneous catalyst Pd/C is very high. Only using TBAF as cocatalyst, it gave 5.6% 1,2-propanediol due to the strong hydrolysis of fluorine anion (Table 2, entry 1).

3.3. Effect of temperature on cycloaddition of PO and CO₂

To optimize reaction conditions for the Pd/C-TBAI catalyst system, the effects of various reaction parameters were considered and investigated. The influence of temperature on this reaction is exhibited in Fig. 1. It is obvious that the propylene carbonate (PC) yield increased up to 98.8% at 120 °C under 2.0 MPa CO₂ pressure over 8 h. When the temperature was higher than 120 °C, the yield of PC decreased slightly due to the decomposition of cocatalyst (see Supporting information). Therefore, the optimal temperature for the coupling reaction of PO and CO₂ is 120 °C.

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