

Highly Efficient Catalytic Cyclic Carbonate Formation by Pyridyl Salicylimines

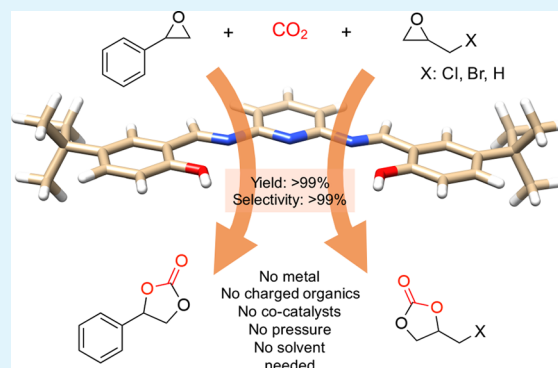
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Supporting Information

ABSTRACT: Cyclic carbonates as industrial commodities offer a viable nonredox carbon dioxide fixation, and suitable heterogeneous catalysts are vital for their widespread implementation. Here, we report a highly efficient heterogeneous catalyst for CO₂ addition to epoxides based on a newly identified active catalytic pocket consisting of pyridine, imine, and phenol moieties. The polymeric, metal-free catalyst derived from this active site converts less-reactive styrene oxide under atmospheric pressure in quantitative yield and selectivity to the corresponding carbonate. The catalyst does not need additives, solvents, metals, or co-catalysts, can be reused at least 10 cycles without the loss of activity, and scaled up easily to a kilogram scale. Density functional theory calculations reveal that the nucleophilicity of pyridine base gets stronger due to the conjugated imines and H-bonding from phenol accelerates the reaction forward by stabilizing the intermediate.

KEYWORDS: carbon dioxide, chemical fixation, cycloaddition, organocatalyst, heterogeneous



INTRODUCTION

Greenhouse gas carbon dioxide (CO₂) is an appealing C₁ synthon, renewable, and nontoxic resource,^{1–7} and its direct incorporation into organic molecules would be highly desirable in finding ways to reduce CO₂ concentration in the atmosphere.⁸ In principle, a CO₂ fixation route could go the redox (reduction) or the nonredox (no electron transfer) pathways; the latter is more likely to be implemented as a means to fight global warming because providing electrons would require higher energy input. Even then, a major obstacle is the activation of thermodynamically and kinetically stable CO₂. Therefore, reactive reagents such as strong organic bases and metal catalysts are often used to activate CO₂.^{9,10}

Commercially important cyclic carbonates¹¹ are very efficient atom-economical nonredox products with wide applications such as in the synthesis of durable polycarbonates and their use as green electrolytes in batteries.¹² To date, a number of homogeneous^{13–15} and heterogeneous catalysts^{16–18} have been shown to achieve appreciable performance in terms of conversion yields. For example, efficient catalytic systems involving ammonium salts,^{19–22} ionic liquids,^{23–27} transition metal complexes,^{28–30} functional polymers,^{31–39} and metal–organic frameworks^{40–43} were studied. However, production of cyclic carbonates in satisfactory yields often requires high pressures (>5 atm) and additives such as cationic salts as co-catalysts and promoters. Compared with the homogeneous counterparts, heterogeneous systems enable rapid catalyst recovery for large-scale operations, with the amount of waste kept at minimum, and prevent polymerization into polycar-

bonates or homopolymers of epoxides by sterically hindering chain extension along with electronic factors.¹ Particularly, heterogeneous catalysts such as Cu metal–organic frameworks,^{44,45} cobalt–salen-conjugated microporous polymers,⁴⁶ amine-functionalized graphene oxide⁴⁷ showed considerable activity for the production of cyclic carbonate under atmospheric conditions, but still the use of ammonium-based co-catalyst additive for achieving high yields is a serious setback for potential industrial applications. Another challenge is the metal (or in some cases acid) leaching of catalysts. Molten salts are also used, despite the elevated temperature requirements,^{9,21} leading to high energy demand. In all of the cases, it seems that cyclic carbonate formation requires a Lewis acidic salt. To the best of our knowledge, there have not been any attempts to provide a catalytic system that is solely based on neutral components and also show high catalytic activity.

In this work, we designed and synthesized a unique, neutral catalytic site based on pyridyl salicylimines, a multifunctional platform that includes optimal basicity and hydrogen bonding. The new catalysts show unprecedented catalytic activity, surpassing well-known catalysts even for difficult substrates like styrene oxide. Our theoretical assessments reveal a six-membered ring formation that makes use of the basicity of pyridine–imine pair and the H-bonded stabilization by phenols.

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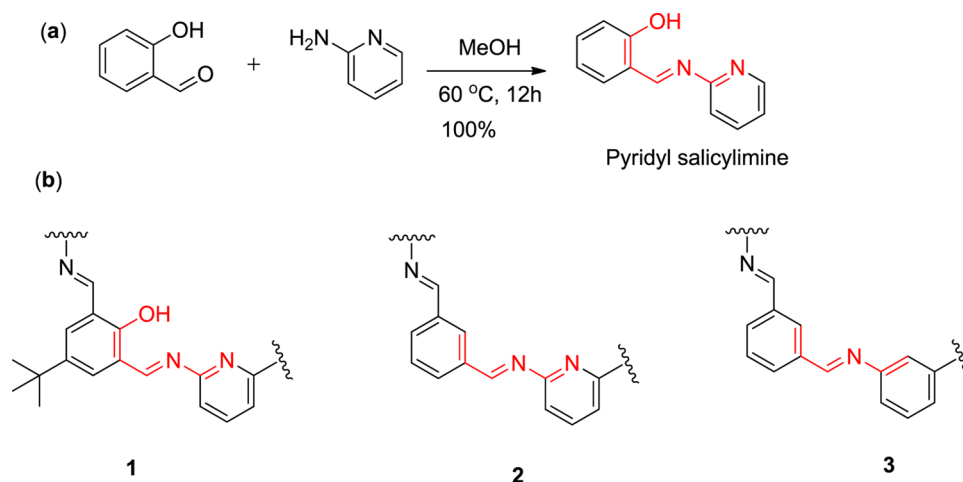


Figure 1. Catalyst synthesis. (a) Synthesis of the multifunctional active site, pyridyl salicylimine as a model compound and homogeneous catalyst. (b) Polymeric heterogeneous catalysts 1–3.

RESULTS AND DISCUSSION

Catalyst Design and Synthesis. Our designs led to a multifunctional moiety that has pyridine, imine, and phenol groups (Figure 1). The pyridyl salicylimine model compound was then synthesized from the commercially available salicylaldehyde and 2-amino-pyridine in a simple Schiff base addition reaction. ^1H NMR confirmed protons of imine (9.42 ppm) and phenol (13.44 ppm) (Figure S1).

The polymeric organocatalyst **1** was prepared similarly by the representative condensation reaction of 4-*tert*-butyl-2,6-diformylphenol and 2,6-diaminopyridine using methanol as the solvent under catalyst-free conditions (Figure 1). The precipitate was filtered and washed repeatedly with methanol, tetrahydrofuran, and acetone. The solid was dried under vacuum at 80 °C for overnight. Owing to the internal H bonds, **1** is highly hydrophobic, is insoluble in organic solvents, and remains as an air-stable catalyst for at least a month.

The formation of **1** was confirmed by solid-state cross-polarization magic angle spinning ^{13}C NMR spectra. The presence of peak at 164.45 ppm confirms the imine linkages, peaks at 148.6, 136.1, 126.2, and 116.2 correspond to aromatic carbons of pyridine and phenol moieties, and the tertiary butyl group was found at 40.8 and 37.9 ppm (Figure S2a). Fourier transform infrared (FT-IR) spectroscopy further confirms the typical imine linkage with the characteristic band at 1610 cm^{-1} , aromatic $\text{C}=\text{C}$ at 1562 cm^{-1} , and hydroxyl band around 3270 cm^{-1} (Figure S2b). The thermal stability of **1** was investigated under nitrogen using thermogravimetric analysis (TGA) and found that it is stable up to 350 °C (Figure S2c). The specific Brunauer–Emmett–Teller (BET) surface area of **1** was measured at 77 K and as expected, a low BET value of $18\text{ m}^2/\text{g}$ was observed (Figure S3). The low BET value indicates that the polymer packs well through hydrogen bonding yielding little or no empty volume. The scanning electron microscopy image displays a spherical beadlike morphology and appears to have slightly rough surfaces (Figure S2d). The powder X-ray diffraction pattern exhibits amorphous nature of **1** (Figure S4). Catalysts **2** and **3** were also characterized using FT-IR and TGA (Figures S5 and S6).

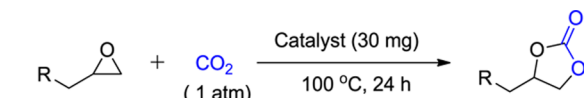
Catalyst Optimization. To find the most suitable conditions for cyclic carbonate formation, cycloaddition reaction of CO_2 and epichlorohydrin was chosen as a probe reaction (Table 1) because almost all of the literature examples

Table 1. Optimization of Reaction Conditions for the Cycloaddition of Epichlorohydrin and CO_2 ^a

entry	catalyst	catalyst loading (mg)	temperature (°C)	time (h)	conversion ^b (%)
1	pyridyl salicylimine	30	100	24	84
2	1	30	100	24	99
3	2	30	100	24	91
4	3	30	100	24	05
5	1	20	100	24	84
6	1	40	100	24	99
7	1	30	28	24	03
8	1	30	40	24	05
9	1	30	60	24	31
10	1	30	80	24	72
11	1	30	100	4	12
12	1	30	100	8	26
13	1	30	100	12	60
14	1	30	100	16	74
15	1	30	100	20	91
16 ^c	1	30	100	24	05
17 ^d	1	30	100	24	04

^aReaction conditions: catalyst, epichlorohydrin (5 mmol), and CO_2 (1 atm). ^bConversions were determined by using ^1H NMR. ^cUsing Al complex of catalyst **1**. ^dUsing Co complex of catalyst **1**.

have commonly used them to demonstrate their activity. The reaction was carried out at 100 °C by purging with atmospheric pressure CO_2 under solvent-free and co-catalyst-free conditions. Catalyst **1** demonstrates excellent activity when compared to the model compound and the control polymers **2** and **3** (Table 1). The lack of the phenol group in catalyst **2** only lowered the conversion to 91% while being active, proving the secondary role of the phenolic moiety in providing H-bonded stabilization for the oxygen of epoxide and carbon dioxide. The disappearance of pyridine group in catalyst **3**, however, fatally disrupted the catalytic activity, leading to a very low conversion yield of 5%. These results indicate the importance of the local environment (3N system) and the

Table 2. Cycloaddition Reaction of CO₂ with Various Epoxides Catalyzed by 1^a


Entry	Epoxides	Products	Conversion (%) ^b	Selectivity (%) ^b
1			99	99
2			99	99
3 ^c			99	99
4			99	99
5			96	99

^aReaction conditions: substrate (5 mmol), catalyst 1 (30 mg), CO₂ (1 bar), and temperature (100 °C). ^bDetermined by using ¹H NMR. ^cCarried out in glass-lined autoclave reactor because of the volatility of the epoxide.

central role of pyridine N (breakage of conjugation). Without pyridine, there is no driving force to activate the epoxide. Thus, the observed catalytic activity of 1 could be attributed mainly due to the incorporation of conjugated 3N system in the polymeric structure, closer proximity of the catalytic sites rendering the activation of both substrates and CO₂ simultaneously. Polymeric catalyst enriching the local concentration of CO₂ near the catalytic centers then leads to a high catalytic performance. Remarkably, this new heterogeneous catalytic site did not require high pressure, any external nucleophilic co-catalyst, or metals to promote the reaction.

For further optimization and obtaining the best catalytic activity, the cycloaddition reaction of epichlorohydrin and CO₂ was conducted under different reaction parameters such as catalyst loading, temperature, and reaction time (Table 1). Quantitative conversion of epichlorohydrin to cyclic carbonate was achieved with 30 mg of catalyst loading (6% w/w with respect to the substrate), which was decreased to 84% with the catalyst loading of 20 mg and there was no significant change when it was increased to 40 mg (Table 1). The loading is minimal when compared to other known catalytic systems where no co-catalyst was used (Table S1). Increasing the reaction temperature from room temperature to 100 °C had a pronounced positive effect on the yield of the cyclic carbonate (Table 1). It was also observed that the formation of cyclic carbonate proceeded slowly in the initial reaction time (Figure S9).^{16,32} We believe that CO₂ dissolution is enhanced by the presence of cyclic carbonates, leading to more availability of the substrates.

Metal complexes are well known to be highly active for cyclic carbonate formations.¹⁴ Particularly, heterogeneous metal salophen structures⁴⁶ are considered to be very effective. They feature salicylimine constructs but no pyridines. This

prompted us to investigate addition of a metal center to coordinate to the active site. Therefore, we prepared an aluminum complex of catalyst 1 and characterized extensively (Figures S7 and S8). Even though Al–1 complex showed improved porosity with a BET specific surface area of 159 m²/g (Ar, 87 K), it fatally inhibited the activity of the catalyst in the cycloaddition probe reaction (Table 1). Similar to aluminum, cobalt is reputed one of the most effective metals for the cycloaddition reaction of epoxide and CO₂.^{15,46} Thus, we also prepared cobalt complex of catalyst 1 and studied the catalytic activity. However, there was no improvement and the result was the similar catalytic activity as aluminum (Table 1). We attribute this deleterious effect to the strong binding between metal ions and the catalytic pocket, leading to the elimination of reactivity for the pyridyl salicylimine system.

Substrate Scope. Industrially, the most challenging cyclic carbonate formation is from styrene oxide derivatives^{11,15,48} because of the lower reactivity of the epoxide by the resonance stabilization of the intermediates. To understand the scope of the catalytic activity, we tested representative epoxides with varying electronic and steric effects (Table 2). Changing chloride to bromide resulted no loss in activity. The commercially important propylene oxide also showed a near quantitative conversion. More importantly, styrene oxide was converted with 99% yield and selectivity. It is important to note that styrene oxide was not previously reported with these high yields under ambient conditions without additives or high pressures. The catalytic pocket that is designed in this study eliminates the need for co-catalysts, metals, or high pressures that are commonly employed for difficult transformations like styrene oxide to styrene carbonate (Table S1). Fluorinated styrene oxide, an even lesser active epoxide, also gave very high yields and near-perfect selectivity. Considering the substrate

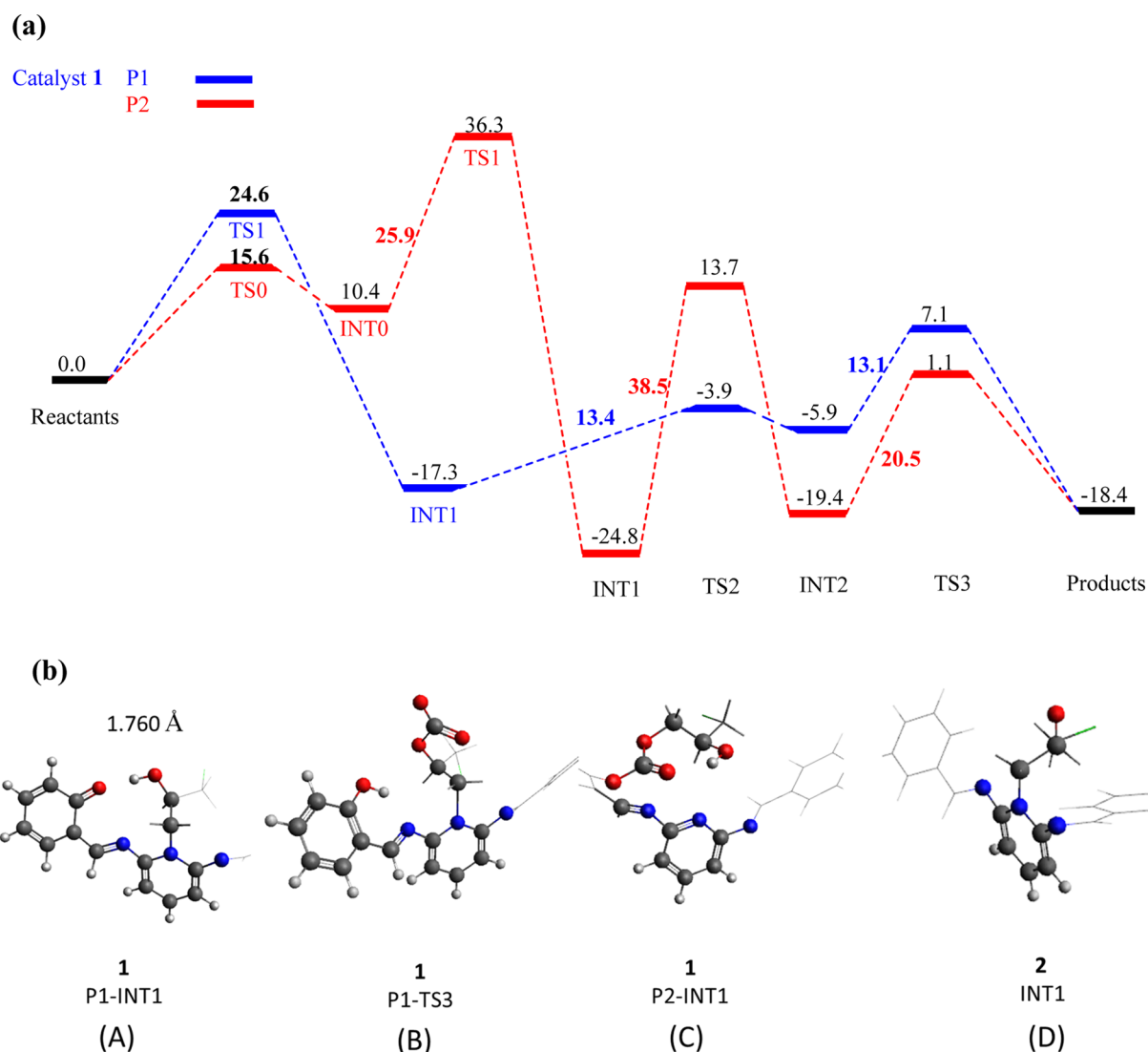


Figure 2. Theoretical calculations of the plausible mechanisms. (a) The calculated relative electronic energies (kcal/mol) following P1, N-epoxide pathway (blue), and P2 carbonate (OH + CO₂) pathway (red). (b) The selected geometries of the stationary states (A–C) for catalyst 1 and INT1 of catalyst 2 was presented as (D) for comparison.

tolerance, catalyst 1 shows great promise with the newly identified catalytic pocket made of pyridyl salicylimines.

Theoretical Calculations. To find the most feasible pathway and intuitive insights behind this catalytic protocol, we performed the density functional theory (DFT) of B3LYP/6-31+Gs with the dispersion correction of Grimme (D3) as implemented in the Q-CHEM quantum chemistry package.⁴⁹ The calculation models of catalyst and their geometries in the stationary phase were presented in the Supporting Information (Figures S10 and S11). The activation energy required for the noncatalyzed cycloaddition reaction of epoxide to produce cyclic carbonate is found to be around 55–57 kcal/mol, which unambiguously depicts the need for the catalyst. In the presence of catalyst 1, either pyridine nitrogen activates the epoxide followed by the addition of CO₂ (path 1 or P1) or phenolic hydroxyl interacts with CO₂ to form the carbonate species and thereby opens the epoxide and propagates the formation of cyclic carbonate (path 2 or P2) (Figure 2). All of the calculations were done in the presence of air and following the stepwise bimolecular reaction.

In P1, the aromatic nitrogen atom on catalyst 1 interacts with the β -carbon of the epoxide via its lone pair of electrons (it should be noted here that the lone pairs of resonant imine Ns in the side arms also contributed for the increased nucleophilicity of pyridine N (N_{py})), resulting in the ring-opening of epoxides with 24.6 kcal/mol (TS1). The resonant 3N system played a crucial role in lowering the activation energy compared to the pristine pyridine (38.3 kcal/mol). Furthermore, proton from the phenolic hydroxyl group migrates to the epoxide oxygen with partial negative charge and transforms to its stable intermediate (−17.3 kcal/mol) (Figure 2a), and this is consistent with the reported proton abstraction mechanisms.^{50–52} The formation of the H-bond stabilized INT1 after ring opening of epoxide, which is considered as the rate-determining step of the cycloaddition reaction, and thereby explains the slower initial reaction rate. Subsequently, the thermodynamically stable CO₂ was coupled with epoxide oxygen as the migrated proton goes back to recover hydroxide group toward TS2 with the activation energy of 13.4 kcal/mol. Then INT2 goes through the ring-closing reaction of S_N2 type nucleophilic substitution reaction (Figure

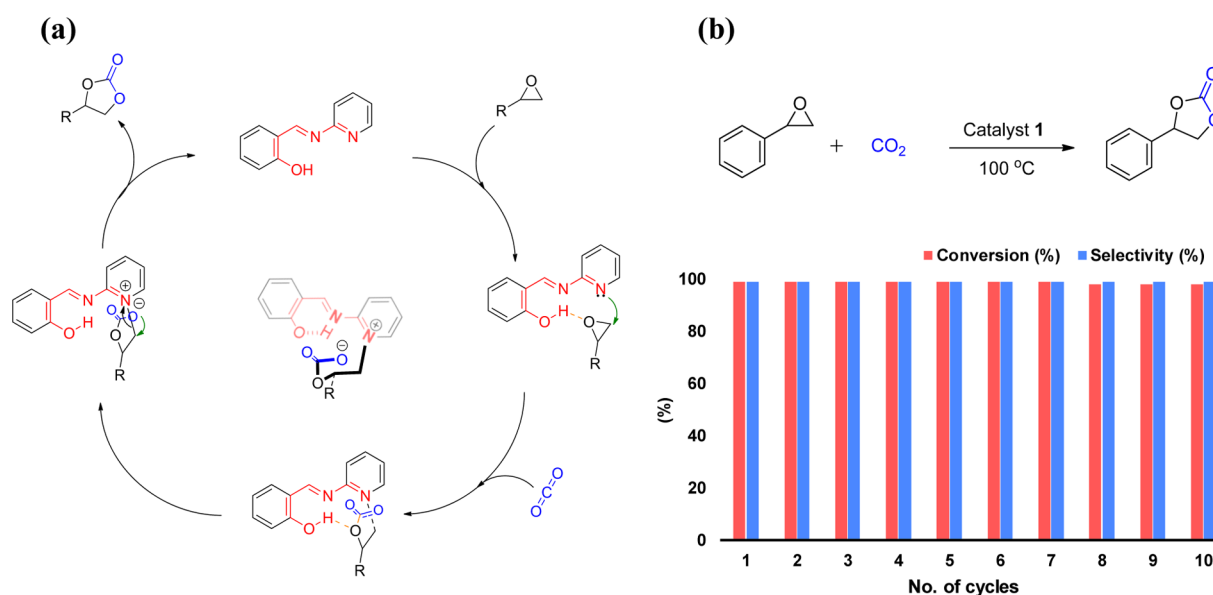


Figure 3. Probable mechanism and recyclability studies. (a) A proposed mechanism for the coupling reaction of an epoxide with CO₂ by catalyst 1. (b) Recycling of the catalyst in the coupling reaction of styrene oxide and CO₂ under optimized reaction conditions.

2b) with the activation energy of 13.1 kcal/mol (TS3, Figure 2b), which results in the product formation. From the thermodynamic viewpoint, the stability of INT1 makes the equilibrium shift toward forward direction. Therefore, large portions of reactants existing in the form of INT1 will convert into the products.

To investigate the role of phenolic OH, we studied the other possible pathway P2 considering the chance for the formation of carbonate by the interaction of acidic phenolic OH and CO₂ (Figure 2a, red line). Though the carbonate formation (TS0) occurs with the moderate activation energy of 15.6 kcal/mol, the subsequent activation energy required for the ring-opening of epoxide is still high with 25.9 kcal/mol. Following which, a huge energy barrier was associated with the highly stabilized intermediate (INT1) by the migration of proton from carbonate to epoxide (Figure 2b), with the strong H-bond interaction in TS2 and also with the formation of cyclic carbonate (TS3). Thus, by comparing the two pathways, nitrogen-assisted ring opening of epoxide followed by the cycloaddition of CO₂ is the most feasible pathway for this catalytic system.

Mechanism and Recyclability. In the light of the experimental results and DFT calculations, a suitable catalytic cycle of catalyst 1 is proposed (Figure 3a). We suggest three transition states and two intermediates for the cycloaddition reaction of epoxide and CO₂ (Figure S11b). The notable catalytic activity was believed to have originated from the resonant 3N system and the ring opening of epoxide by the basic N_{py} is the rate-determining step. The H-bond stabilizes the intermediate, and the partial negative charge on the epoxide oxygen leads to the coupling of CO₂. The mechanism is then followed by a S_N2 fashion ring closure providing the desired cyclic carbonate and setting the catalyst free for other cycles. We have further shown that the catalyst can be recycled and reused without any significant change in the catalytic activity or structural deterioration (Figure 3b).

CONCLUSIONS

In summary, we developed a new active catalytic site bearing resonant 3N system and phenolic hydroxyl groups for the cycloaddition reaction of epoxide and CO₂. The simple and easy-to-handle polymeric organocatalyst 1 can effectively function under ambient pressure, free of co-catalyst, metal, or solvents, and shows near quantitative yields with different epoxides to produce cyclic carbonates. On the basis of the experimental evidence and DFT calculations, a suitable catalytic cycle has been proposed. The heterogeneous catalyst was recycled for multiple successive runs without the loss of catalytic activity. We believe that the newly identified catalyst active site offers effective tandem transformations especially for those that require simultaneous activation of two substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b00485.

Materials and methods, characterization of catalysts, DFT studies, comparison of catalytic activity, and characterization of products (PDF)

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Notes

The authors declare no competing financial interest.

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