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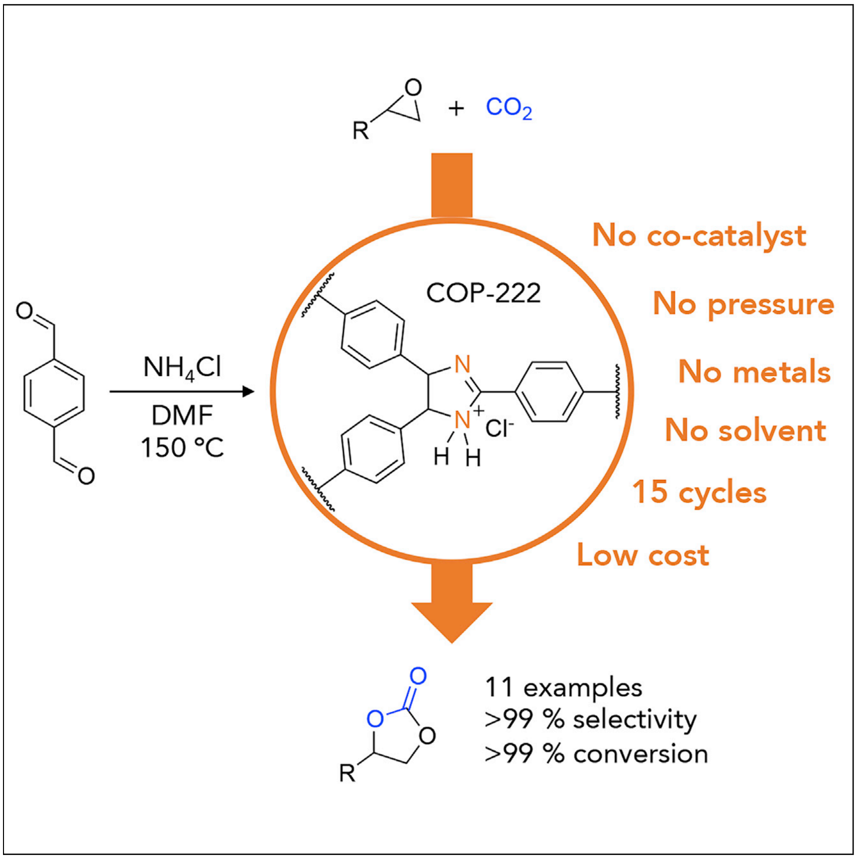
Catalytic Non-redox Carbon Dioxide Fixation in Cyclic Carbonates



Yavuz and colleagues introduced a highly active catalyst for non-redox fixation of CO_2 into cyclic carbonates, a versatile product family with potential use in green polymers and solvents. The metal-free, heterogeneous imidazolinium network structure is easily made, scaled up, recycled, and inexpensive and provides quantitative selectivity and conversion yields over a wide substrate scope of epoxides.

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HIGHLIGHTS

A direct synthetic pathway to the elusive imidazoline-based network polymer

Quantitative and selective cycloaddition of CO_2 to epoxides at ambient conditions

Wide substrate scope, low-cost, heterogeneous, recyclable, and metal-free catalyst

A comprehensive simulation of speciation explaining the cycloaddition mechanism

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Catalytic Non-redox Carbon Dioxide Fixation in Cyclic Carbonates

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SUMMARY

If cycloaddition of CO_2 to epoxides is to become a viable non-redox CO_2 fixation path, it is crucial that researchers develop an active, stable, selective, metal-free, reusable, and cost-effective catalyst. To this end, we report here a new catalyst that is based on imidazolinium functionality and is synthesized from an unprecedented, one-pot reaction of the widely available monomers terephthalaldehyde and ammonium chloride. We show that this covalent organic polymer (COP)-222 exhibits quantitative conversion and selectivity for a range of substrates under ambient conditions and without the need for co-catalysts, metals, solvent, or pressure. COP-222 is recyclable and has been demonstrated to retain complete retention of activity for over 15 cycles. Moreover, it is scalable to at least a kilogram scale. We determined the reaction mechanism by using quantum mechanics (density functional theory), showing that it involves nucleophilic-attack-driven epoxide ring opening (ND-ERO). This contrasts with the commonly assumed mechanism involving the concerted addition of chemisorbed CO_2.

INTRODUCTION

The rising atmospheric CO_2 levels[1] call for suitable conversion methods, those that do not produce more CO_2 than sequestering.[2–5] It is rather difficult since CO_2 is a very stable molecule.[6] Despite the high kinetic stability, CO_2 is an inexpensive feedstock for production of valuable chemicals. Unfortunately, catalysts with dramatically reduced activation barriers are essential to increase efficiency.[7,8] Conventional approaches make use of high-energy redox processes to produce methanol, methane, ethanol, or ethylene.[9] In contrast, non-redox reactions of CO_2 such as cyclic carbonate formation present significant advantages. Specifically, non-redox reactions can be conducted under ambient conditions, they are kinetically and thermally favorable, and the reaction rates can be tuned easily by designing suitable catalysts.

Indeed, the synthesis of cyclic carbonates through the cycloaddition of CO_2 to epoxides is a small scale but particularly effective way of chemically fixing CO_2 since cyclic carbonates are of widespread utility.[10–12] For example, they are precursors for synthesis of polycarbonates that are used as electrolytes, aprotic polar solvents, and intermediates in fine chemical production, such as dialkyl carbonates, glycols, carbamates, and pyrimidines.[13–15] Because of their importance, many catalysts have been developed for cyclic carbonate formation, including ionic liquids,[16–18] metal complexes,[15,19] functional polymers,[20–22] ammonium and phosphonium salts,[23,24] metal-organic frameworks (MOFs),[8,25,26] hydrogen-bonding catalysts,[7,27,28] and supported catalysts.[29,30] Homogeneous, organometallic catalysts have often proved effective with well-defined mechanisms and notable catalytic activity,[10,11] but the added cost of separations and purification of metallic species

The Bigger Picture

To stop global warming, we must introduce a variety of CO_2 reuse pathways. Redox chemistry is not trivial; reduction of CO_2 back to methane requires up to 8 electrons per molecule, leading to heavy energy demand. Non-redox paths have low energy needs and could provide a quick relief. A promising non-redox CO_2 product, cyclic carbonate is a versatile building block for green plastics and solvents. Although studies date back as early as 1969, no industrially viable process has since been introduced, mainly because of the lack of an effective catalyst for direct addition of CO_2 to the epoxides. Conceptually, the ideal catalyst should (1) be free of metals; (2) be free of co-catalysts; (3) be free of high pressure requirements; (4) provide quantitative selectivity to cyclic carbonate (5) provide a wide substrate scope, including very hard substrates; (6) provide reusability; and (7) be inexpensive. The imidazolinium catalyst that we developed herein addresses all 7 qualities and offers rapid implementation for CO_2 reclamation.

makes them unattractive. Heterogeneous catalysts are more advantageous in terms of scalability, rapid catalyst recovery, and reusability. For example, Farha and coworkers reported zirconium-based MOFs as catalysts and tetrabutylammonium bromide (TBAB) as a co-catalyst for CO_2 fixation into styrene oxide and achieved quantitative conversion under mild reaction conditions.[31] More recently, Byun and Zhang reported a facile route for imidazolium ionic liquids with heterogeneous property that enabled the selective formation of cyclic carbonates (up to 99%) under ambient reaction conditions.[32] We also previously reported a pyridyl salicylimine polymeric catalyst that showed quantitative conversion without the need for additives or co-catalysts for conversion of even hard substrates such as styryl epoxide.[33] See Table S1 for a list of selected catalysts and their comparisons in catalytic activities.

Despite these remarkable advances, most literature reports demand the use of co-catalysts, harsh reaction conditions (e.g., high pressure), and multi-step synthesis of rare metal-based catalysts, leading to high energy requirements and high costs.[34] To date, very few catalytic systems have shown considerable activity under ambient conditions, and they remain far from being feasible for successful industrial applications. This necessitates the design of new catalysts that combine structural versatility with suitable functionalities, amenability, and durability[35] for cycloaddition reactions of CO_2 with epoxides.[36]

In order to develop a commercially attractive and environmentally benign metal-free heterogeneous catalyst, we examined low-priced and non-toxic starting materials. To achieve this challenging task, we limited the steps to synthesize the catalysts, avoided the use of specialty chemicals, and focused on inert reaction conditions. In a serendipitous discovery, we achieved a thermally robust heterogeneous catalyst with inbuilt basic and quaternary ammonium centers that paved the way toward a sustainable catalyst. We use a one-pot reaction of terephthalaldehyde and ammonium chloride, to form an imidazolinium network polymer that shows excellent chemical fixation of CO_2 without the need for co-catalysts, a solvent, or extreme conditions. The reactions proceed with great substrate tolerance and no obvious catalyst deactivation was observed over 15 cycles. In order to understand the reaction mechanisms underlying this dramatically improved catalyst, we carried out quantum mechanics (QM) calculations (density functional theory [DFT]) to obtain the reaction barriers for the various possible reaction pathways. These DFT studies showed the key role played by the quaternary ammonium center and its chloride counter anion. Indeed, our QM predicted rate constants lead to kinetics (including products and intermediate concentrations) in excellent agreement with experiments, validating the new nucleophilic attack-driven epoxide ring opening (ND-ERO) mechanism.

RESULTS AND DISCUSSION

Developing catalysts for cyclic carbonate production that work at atmospheric pressure conditions is crucial to provide a negative emissions technology (NET) for industrial implementations. This requires a well-designed heterogeneous catalyst that is robust, easily synthesized, scalable, cost effective, rapidly recovered, and recyclable. Based on our previous experience, we considered cyclic amine systems to provide a solution since these structures have highly modular properties and can be built stepwise, providing tunable structures. Consequently, we examined reactions of aliphatic aldehydes with ammonia. In particular, we examined a commonly reported procedure to form an aldehyde ammonia trimer.[37,38] We speculated that the one-pot reaction of terephthalaldehyde and ammonium chloride salt would form a new porous material containing cyclic amines.

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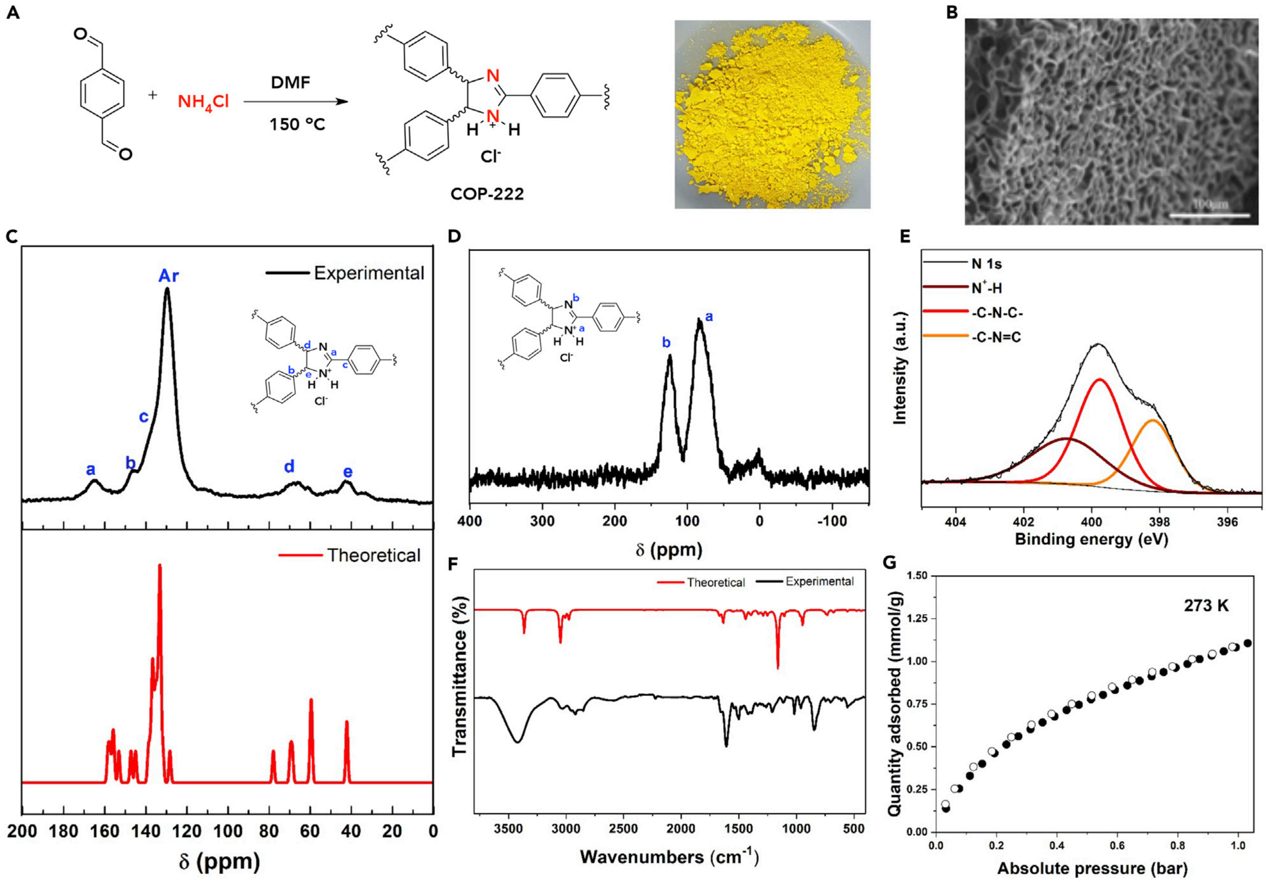


Figure 1. Synthesis and Characterization of COP-222

(A) One-step, one-pot synthesis from commercially available substrates.

(B) SEM micrograph of the as-synthesized network polymer. The scale bar represents 100 μm.

(C) Theoretical and experimental ^{13}C-NMR.

(D) ^{15}N-NMR with ^{15}N-enriched COP-222.

(E) XPS (N-1s) data.

(F) Theoretical and experimental FTIR spectra.

(G) CO_2 (273 K) uptake isotherm, filled symbols show adsorption and empty symbols represent desorption.

Therefore, we investigated the reaction of terephthalaldehyde with ammonium chloride salt in the presence of dimethylformamide (DMF) solvent and heated the reaction mixture to 150°C for 24 h. We obtained a yellow precipitate (covalent organic polymer [COP-222], the code is only for indexing purposes, no chemical information is intended) that was collected and washed repeatedly with water, methanol, tetrahydrofuran (THF), and acetone (Figure 1A). The yellow solid was dried under vacuum at 100°C overnight and characterized with a series of analyses. The morphology of the developed material was examined by SEM analysis (Figure 1B) and appears to have rough surfaces with macropores. The solid-state cross-polarization magic-angle spinning (CP-MAS) ^{13}C NMR spectra shows an aromatic (aryl) signal at 129.61 ppm that was accompanied by two distinct peaks in the region of 43.02 and 68.89 ppm and one around 166.59 ppm. This shows clearly that the cyclic ammonia trimer was not formed (Figure 1C). This prompted us to further elucidate the structure by examining the ^{15}N CP-MAS NMR (Figure 1D). In a symmetrical trimer, one would expect a single peak for ^{15}N. We observed two separate peaks (83.72 and 124.18 ppm), revealing that there are two chemically dissimilar nitrogens.

Quaternary ammonium nitrogens are usually observed at 20–80 ppm and imines at 130–300 ppm, while secondary amines show up at 10–90 ppm.[39,40] These findings led to us to postulate an imidazolinium construct (Figure 1). Revisiting the ^{13}C-NMR, we then confirmed that the peaks at 43.02 and 68.89 ppm can be ascribed to the carbon (d, e) and the peak at 166.59 ppm corresponds to -C=N- imine carbon (a) in the imidazolyl ring (Figure 1A). These signals match well with the theoretical ^{13}C-NMR spectra for an imidazolinium ring system (Figure 1C), and the observed chemical shift patterns are in line with similar structures reported in the literature.[41,42] Furthermore, X-ray photoelectron spectroscopy (XPS) showed strong N-1s signals located at 399.78. We deconvoluted the N-1s spectrum for COP-222 into three peaks at 398.28, 399.78, and 400.78 corresponding to imine, pyrrolic, and quaternary ammonium nitrogens, respectively. The XPS spectra for C, O, and Cl are given in the Supplemental Information (Figure S1). The chemical connectivity and the presence of the imidazoline ring were also confirmed by the stretching bands observed at 1,618 cm^{-1} (-C=N-) and a broad peak around 3,400 cm^{-1} (-NH_4^+-) in Fourier transform infrared spectroscopy (FTIR) spectra (Figure 1F).

First, we studied the porosity of our COP-222 network polymer by the nitrogen adsorption-desorption isotherms measured at 77 K leading to a Brunauer-Emmett-Teller (BET) surface area of 21 m^2/g (Figure S2). This unexpected low surface area might be due to the well-packed polymer through the hydrogen bonding, which leads to a low diffusive volume. We then investigated the affinity of COP-222 toward CO_2 and carried out uptake measurements at 273, 298, and 323 K (Figures 1G and S2). The CO_2 uptake of 1.08 mmol/g at 273 K is appreciable, and isosteric heat of adsorption (Qst) was found to be in the order of 27–30 kJ/mol, reflecting an expected physisorptive nature. In order to confirm the chemical composition, elemental analysis was performed showing that COP-222 possess a high nitrogen content of 11.36%, which is close to the expected value of 12.13% (Figure S3). We also analyzed the powder X-ray Diffraction (XRD) of COP-222 and found a characteristic spectrum of an amorphous solid (Figure S3). Thermogravimetric analysis shows that COP-222 is thermally stable up to 250°C (Figure S4). Acidic and basic sites of COP-222 were screened using temperature-programmed desorption (TPD) with CO_2 and NH_3 gases. In CO_2-TPD, the peaks at 107°C and 209.9°C represent the basic sites that may be derived from imine and pyrrolic nitrogens (Figure S5A). A broad NH_3 desorption peak appeared at 102.6°C in the NH_3-TPD profile (Figure S5B) representing quaternary ammonium acidic sites. Co-existence of both acidic and basic sites confirm its potential as a cycloaddition catalyst.

The imidazolinium structure features two key functionalities for an effective catalyst in cycloaddition of CO_2 to epoxides:[33] a quaternary amine and a basic amine. This is why we investigated its utility in non-redox CO_2 fixation. To test its activity, we chose the reaction of epichlorohydrin since it is very reactive and is used in almost all reports dealing with CO_2 cycloaddition to epoxides (Figure 2).[43] Industrially, however, epichlorohydrin is not too important. In a typical experiment, we subjected epichlorohydrin (5 mmol) to our catalysts (30 mg) under solvent-free conditions at 100°C by purging with atmospheric pressure CO_2. Owing to the presence of imidazolinium centers, COP-222 demonstrated excellent catalytic activity (>99% conversion) compared with control structures (Figure 2B). Among those, COP-1 is a nitrogen-rich porous COP[44] while others are commercially available molecules: 2-imidazolidinone, ammonia acetaldehyde trimer, and imidazole. Despite being heterogeneous, COP-222 accomplished quantitative conversion and stoichiometric selectivity. This remarkable catalytic activity shows that the high N content combined with bifunctional sites is critical. This also explains why other heterogeneous catalysts always

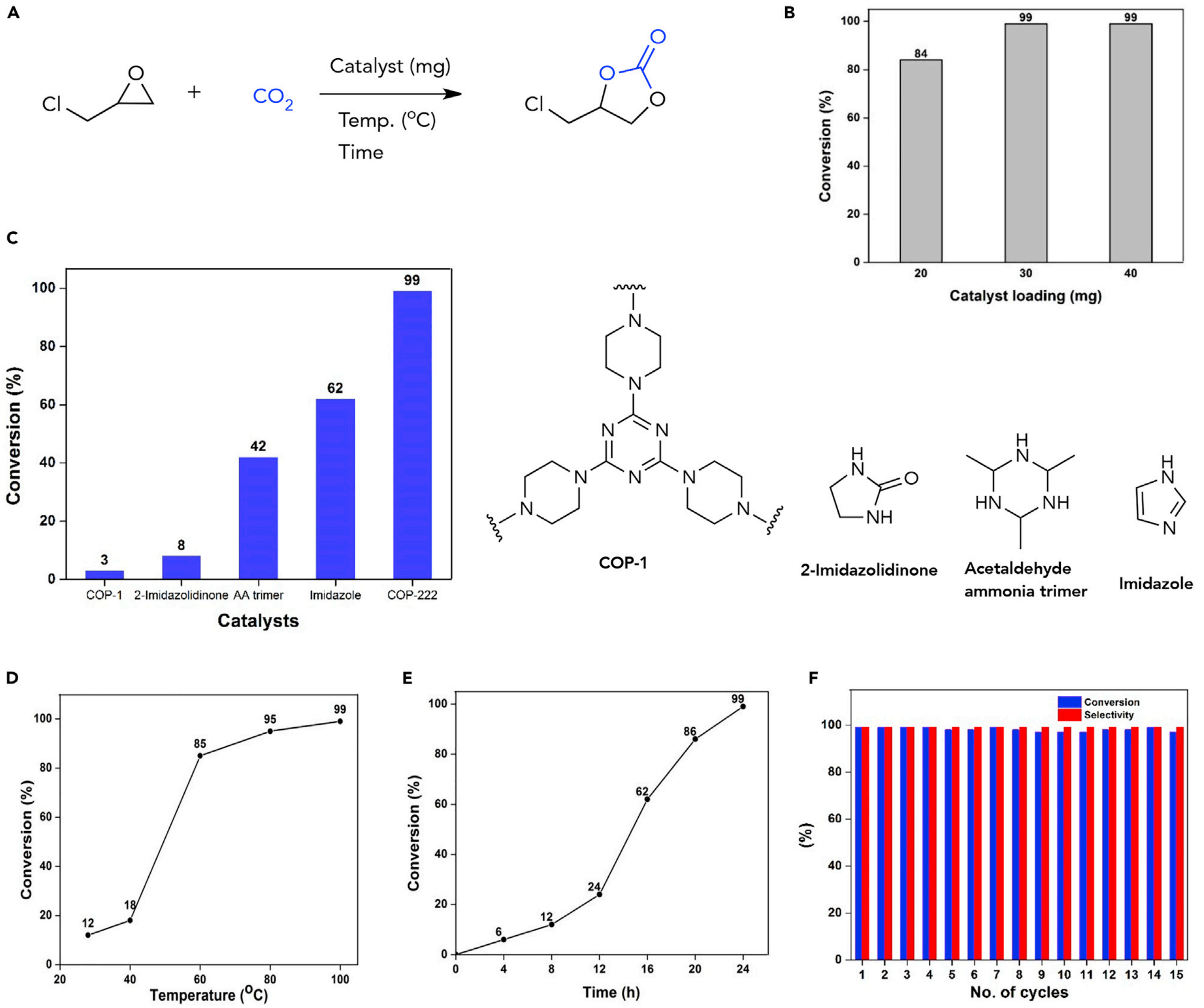


Figure 2. Optimization of Catalyst Activity

(A) Cycloaddition of CO_2 to epichlorohydrin was used to optimize catalytic activity.

(B) Screening of control structures for the cycloaddition reaction.

(C) Screening of catalyst loading.

(D) Screening of temperature.

(E) Conversion with respect to time.

(F) Recyclability of COP-222 for 15 cycles. Each cycle was set up using the recovered catalyst. Reaction conditions: catalyst, epichlorohydrin (5 mmol), and CO_2 (1 atm). Conversions were determined by using ^1H NMR.

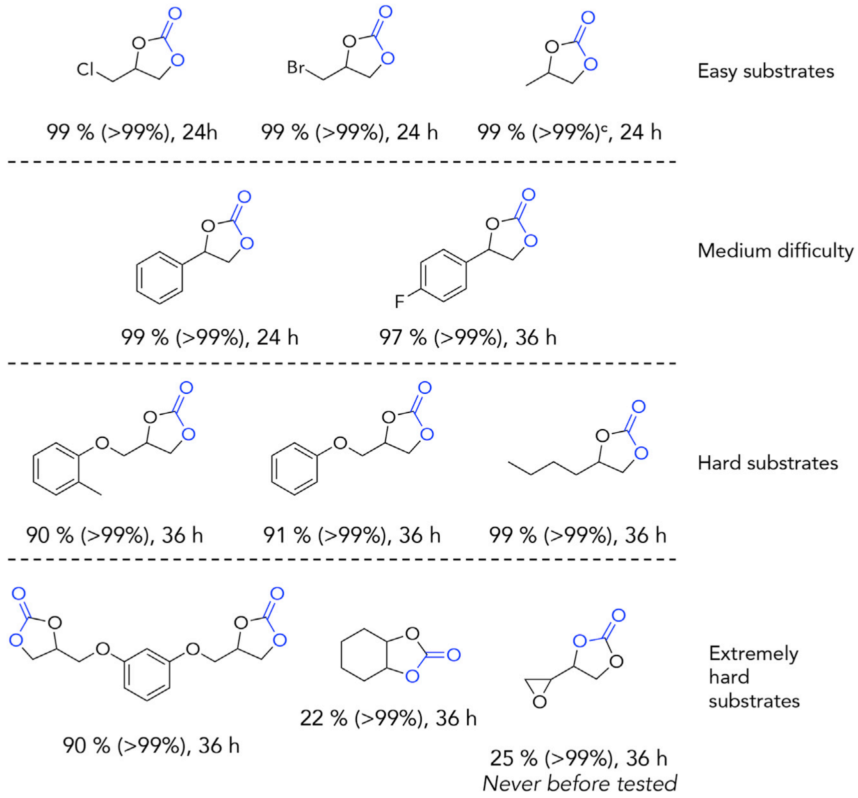
need a co-catalyst (in many cases TBAB) even though they have basic nitrogen sites. Porosity seems to be less important as the reaction is rather slow and diffusion hindrance is not the bottle neck. This is also reflected in the need for an induction time (Figure 2D), as is common for biphasic systems where intermediate species need to build up to proceed further.

In order to optimize catalytic activity, we screened various reaction parameters such as catalyst loading, temperature, and time. Decreasing catalyst loading to 20 mg did not improve reaction yield (84%), and increasing it to 40 mg led to no significant change (Figure 2C). At temperatures higher than 60°C, COP-222 worked well and resulted in good to excellent yields (Figure 2D). The influence of reaction time in the formation of cyclic carbonate is crucial, which increases with increasing time, reaching a maximum at 24 h (Figure 2E). The steeper increase in yield after initial reactions could be due to the enhanced solubility of CO_2 in the cyclic carbonate-rich reaction medium.[33,45] Since rapid separation of the catalyst from the reaction mixture and recyclability are the main reasons for developing heterogeneous catalytic systems, we examined the cyclability of COP-222 using epichlorohydrin as a substrate under optimized reaction conditions and found that the catalyst can be recycled at least 15 times without any loss in its activity (Figure 2F). We also monitored for potential chloride leaching using ion chromatography and found no detectable presence in the catalytic reactions. In addition, we used ammonium bromide and iodide in making COP-222 variations. These derivatives did not improve the catalytic activity, nor the synthesis procedure. Since chloride is found to be more active in cycloaddition reactions, and also commonly available, we focused our attention to the chloride version.

For widespread industrial use, the catalysts need to show effective cyclic carbonate formation from challenging epoxides such as styryl or hexyl epoxides.[33] To access synthetically useful cyclic carbonates, we turned our attention to explore the scope of epoxide substrates (Scheme 1). Simple aliphatic epoxides that are similar to the benchmark substrate, epichlorohydrin, also yielded quantitative conversion and selectivity. Styrene oxide and derivatives are commonly known as challenging substrates because of their low reactivity.[14] COP-222 was very effective, converting styryl substrates quantitatively to the corresponding cyclic carbonates. We then investigated hard substrates such as hexyl- and phenoxy-substituted epoxides, where we also found high conversion yields and selectivity. It is important to note that there are only a few previous literature reports showing appreciable conversions of hexyl epoxide.

In order to determine the limits of our catalyst, we tested the cycloaddition of CO_2 to extremely hard substrates (Scheme 1). Cyclohexene oxide and resorcinol diglycidyl ether are both sterically and electronically challenging. We found that COP-222 shows great performance in converting both with quantitative selectivity and high conversion yields. In the literature, cyclohexene oxide has been rarely studied, except a calcium-polyethylene glycol catalyst[46] and a squaramide organocatalyst.[27] However, those studies require either high pressure (20–30 bar) CO_2 or a co-catalyst. Finally, we took on a completely new epoxide, never before tested for cyclic carbonate formation. The bis epoxide 1,3-butadiene diepoxide presents a unique challenge since the adjacent ring strains and their proximity could lead to unconventional products, including extended ring formation. In repetitive tests, we achieved, as a single product, a five-membered cyclic carbonate while the other epoxide is untouched. This new functional asymmetry opens new directions for this commercial monomer. With all the substrate scope and conversion yields, it should be noted that the catalytic performance of COP-222 is outright superior to all previously reported heterogeneous catalysts[8,34,47] and even better than most homogeneous systems.[48–50]

The mechanism of the cycloaddition of CO_2 to epoxides is commonly believed to be a multi-component ordeal, where epoxide is preferentially activated on a Lewis acid site and CO_2 is provided by a base through chemisorption.[8,51] In order to validate the accepted mechanism, we performed DFT calculations as described in the Supplemental Information. The calculation models of the catalyst, intermediate energy profiles, and their predicted geometries in the stationary phase are presented in the Supplemental Information. The DFT calculations find a ND-ERO mechanism (Figure 3). The ND-ERO catalytic cycle begins with (1) coordination of the epoxide to an



Scheme 1. Cycloaddition Reaction of CO_2 with Various Epoxides Catalyzed by COP-222

Conversion yields for the corresponding catalytic reactions[a] are given in percentages.[b] The selectivities are reported in parentheses.

[a] Reaction conditions: substrate (5 mmol), COP-222 (30 mg), CO_2 (1 atm) and temperature (100°C).

[b] Determined by using ^{1}H-NMR.

[c] Carried out in glass lined autoclave reactor because of the volatility of the epoxide.

ammonium proton (step 1), (2) the nucleophilic chloride ion then opens the epoxide ring via a S_N2-type mechanism (step 2), (3) subsequently, the oxyanion is stabilized by the ammonium proton until the oxyanion can attack the carbon of a nearby coordinated carbon dioxide (step 3), and (4) the new oxyanion then undergoes another S_N2-type reaction, closing the 5-membered carbonate ring (step 4).[52] In addition to the above quite plausible pathway, we also assessed side reactions for potential involvement. For example, we find that the chemical binding of CO_2 to the imine nitrogen (Lewis base) is not favorable (Figure 3) requiring +6 kcal/mol energy. Another possible side reaction is the release of 2-chloropropanol after the epoxide ring opening. Once again, the energy differences were far lower than the adduct (-10.7 versus -21.4 kcal/mol), leading to the completion of the catalytic cycle. We observed the same after the CO_2 addition to the alkoxide. The free carbonic acid intermediate produced half the enthalpic change compared to the coordinated version. Finally, we calculated the energy requirement to release the HCl molecule from COP-222. This is particularly important since the cyclability and product purity would otherwise be adversely affected. The decomposition of COP-222 into neutral base and HCl was energetically uphill, in the order of a staggering +19.9 kcal/mol. This confirms our experimental observations of a stable catalyst.

Imidazoles are often reported to be active for cycloaddition catalysis.[16] For comparisons, we calculated the neutral imidazole equivalent of COP-222 and found that the

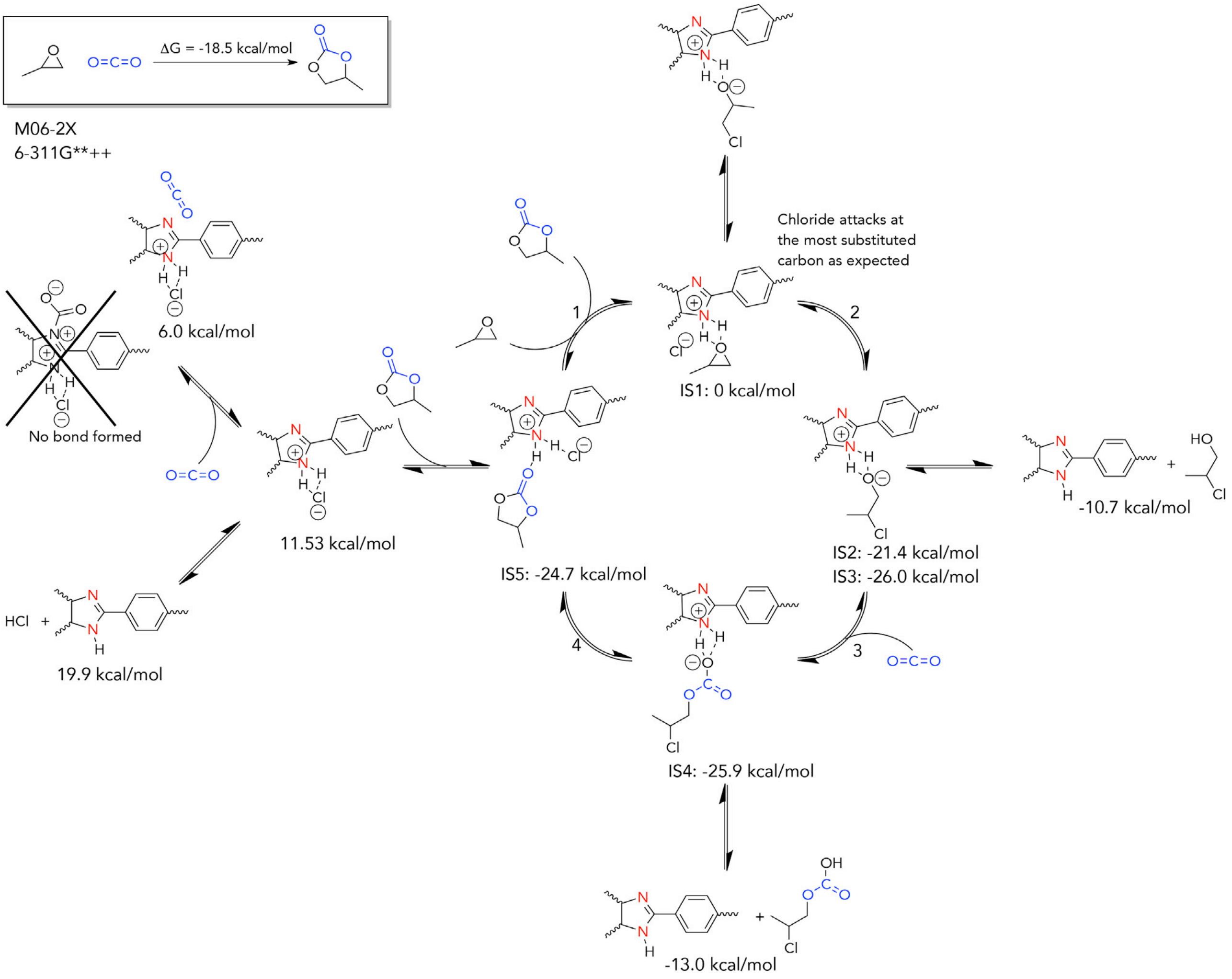


Figure 3. The Nucleophilic Attack-Driven Epoxide Ring Opening (ND-ERO) Reaction Mechanism

Reaction mechanism for the COP-222 catalyst derived from quantum mechanics, including free energy reaction barriers.

zwitterionic product is >25 kcal/mol uphill from the reactants with a barrier of ~40 kcal/mol (Figure S23, calculated with M06-2X/6-311G and implicit solvation). In comparison, the initial catalytic step for COP-222 has a barrier of ~20 kcal/mol and is downhill by 21 kcal/mol. Similarly, non-aromatic imidazolium was found to be unstable and form the aromatic imidazolium cation (Figure S24). The aromatic imidazolium, however, is also unable to activate an epoxide as there is no site for the epoxide oxygen to coordinate to, rendering the chloride attack entropically unfavorable.

EXPERIMENTAL PROCEDURES

General Synthetic Procedure for COP-222

A 20 mL sample vial was charged with terephthaldehyde (7.45 mmol), ammonium chloride (29.82 mmol), and 15 mL DMF. The sample vial was closed with the screw cap and covered with a Teflon tape. The mixture was then allowed to heat at 150°C (in the rate of 2°C/min) for 48 h. The yellow precipitate was collected, filtered, and then washed repeatedly with water, methanol, and acetone and chloroform. The resulting powder was dried at 100°C under vacuum overnight.

General Procedure for the Synthesis of Cyclic Carbonates

In a typical reaction, a well-dried Schlenk tube equipped with a magnetic stirring bar was charged with catalyst (30 mg) and epoxides (5 mmol). The Schlenk tube was purged and pressurized with CO_2 (1 atm), placed in a preheated oil bath, and stirred for 24 h at 100°C. Upon completion of the reaction, the tube was cooled to room temperature. The reaction mixture was filtered off and washed thoroughly with chloroform to ensure complete removal of the product. The collected filtrate was evaporated under reduced pressure and the samples were analyzed by ^{1}H NMR spectroscopy. The recovered catalyst was dried at 100°C under vacuum and reused for further cycles.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr.2019.10.009.

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AUTHOR CONTRIBUTIONS

S.S. and D.K. synthesized and characterized the catalyst and carried out catalytic experiments. J.O. and W.A.G. carried out DFT calculations and explained the mechanism. T.S.N. studied the new butadiene oxide substrate. W.M.H.S. carried out the cyclic experiments. B.K. performed all solid-state NMRs. C.T.Y. conceived the project and wrote the manuscript with contributions from all authors.

DECLARATION OF INTERESTS

KAIST has filed a provisional patent application (KR #10-2019-0060197) related to the catalysts reported in this manuscript.

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