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Authors	Mousumi Garai, Vepa Rozyyev and Cafer T. Yavuz
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ORCID® iDs	Mousumi Garai - https://orcid.org/0000-0003-0807-4402; Vepa Rozyyev - https://orcid.org/0000-0002-4340-1985; Cafer T. Yavuz - https://orcid.org/0000-0003-0580-3331

Zwitterion π–conjugated nanoporous polymer based on guanidinium and β-ketoenol as a heterogeneous organo-catalyst for chemical fixation of CO_2 into cyclic carbonates

Mousumi Garai*, Vepa Rozyyev, Cafer T. Yavuz

Address: Graduate School of Energy, Environment, Water and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

Email: mousumi@kaist.ac.kr

* Corresponding author

Abstract

The chemical fixation of CO_2 with epoxides to cyclic carbonate is an attractive 100% atom economic reaction. It is a safe and green alternative to the route from diols and toxic phosgene. In this manuscript, we present a new zwitterionic π–conjugated nanoporous catalyst (Covalent Organic Polymer, COP-213) based on guanidinium and β-ketoenol functionality, that is synthesized from triaminoguanidinium halide (TGCl) and β-ketoenols via ampoule method at 120°C. The catalyst is characterized by NMR, FTIR-ATR, PXRD, TGA, and for surface area (BET) and CO_2 uptake. It shows quantitative conversion and selectivity in chemical fixation of CO_2 to epoxides under ambient conditions and without the need for co-catalysts, metals, solvent, or pressure. The catalyst can be recycled at least three times without loss of reactivity.

Keywords

carbon dioxide; cyclic carbonate; catalysis; chemical fixation; guanidinium; β-ketoenol; nanoporous

Findings

Carbon dioxide (CO_2) is one of the dominant anthropogenic greenhouse-gasses and the main culprit for global warming and climate change, hence CO_2 chemistry (capture and conversion) has appealed worldwide as the most important and top priority for the scientific community [1-7]. Recently, the CO_2 concentration increased to 415 ppm in the atmosphere and continue increasing.

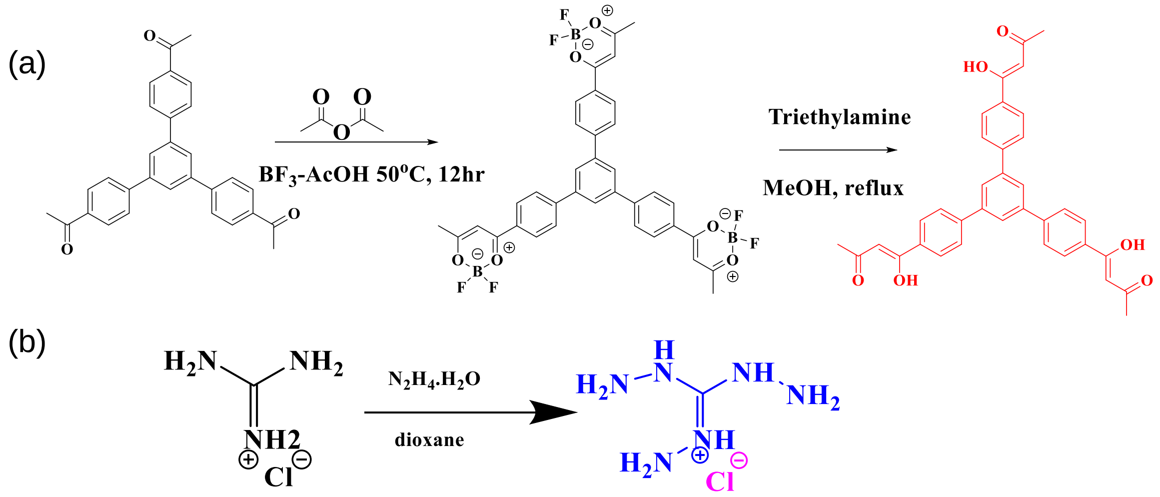
On the other hand, CO_2, an abundant, nontoxic, cheap and nonflammable carbon source, which is formed from living organisms and in industrial processes, is a significant resource and can be easily handled at an industrial level. Chemical fixation of CO_2 is a growing interest in the development of the eco-friendly processes, as CO_2 can be used as a cheap and safe building block in organic synthesis [8]. Among them, one of the most promising methodologies is the synthesis of five-membered cyclic carbonates via the cycloaddition reaction of CO_2 to epoxides [9-14]. These cyclic carbonates are important as precursors of raw materials in the production of plastics, pharmaceutical chemical intermediates, aprotic polar solvents and biomedical applications [15-17]. Recently, numerous catalyst systems, such as ammonium and phosphonium salts, ionic liquids, cyclic amidines and guanidines, porous organic polymers, metal-organic frameworks (MOFs), have been developed for this conversion [18-33]. Generally, homogeneous catalysts show effective catalytic activity with well-defined mechanisms but main drawbacks are the need for separations and the purification of products. Heterogeneous catalysts are more beneficial in terms of scalability, rapid catalyst recovery, and reusability. But the leading heterogeneous catalysts are found to be restricted due to poor stability and low activity in the harsh reaction conditions. Some of the promising recent reports include the work by Byun et al. [34] that shows an imidazolium ionic liquid catalyst that facilitated the selective formation of cyclic carbonates under ambient reaction conditions. Recently, we [35] have investigated a new type of pyridyl salicylimine polymeric catalyst that exhibits good conversion without any co-catalysts. Zhang et al. [36] showed the importance of guanidine based organo-catalyst in the field of CO_2 fixation. Therefore, it is still a challenging field to explore heterogeneous catalysts with excellent stability and activity under mild conditions for the non-redox chemical fixation of CO_2.

Guanidine-based functional motifs in the form of neutral (guanidine), cationic (guanidinium), and anionic (guanidinate) units have shown wide use in chemistry such as in crystal engineering and asymmetric catalysis. These guanidine groups exist not only in enzymes and proteins but also in many natural drugs products. The guanidinium salts promote the reactions by using ion-pair interactions and hydrogen bonding to accelerate reaction rates. The strong basicity owing to resonance stabilization of the corresponding conjugate and ease for structural modification offer guanidine derivates significant value in organic synthesis, especially in the field of CO_2 conversion.

In terms of framework building, dynamic covalent chemistry assists self-assembly of reactive building blocks into structurally complex yet robust materials, such as covalent organic frameworks (COFs), covalent organic polymers (COPs) and porous organic polymers (POPs) [37-44]. In literature, boronic acid self-condensation, aldehyde/amine condensation (Schiff base reaction), polycondensation with aromatic diols, and nitroso dimerization mainly show this dynamic mechanism. Among them, the π–conjugated COPs can be designed by Schiff base reaction formation of imine bonds that exhibit similar dynamic covalent chemistry.

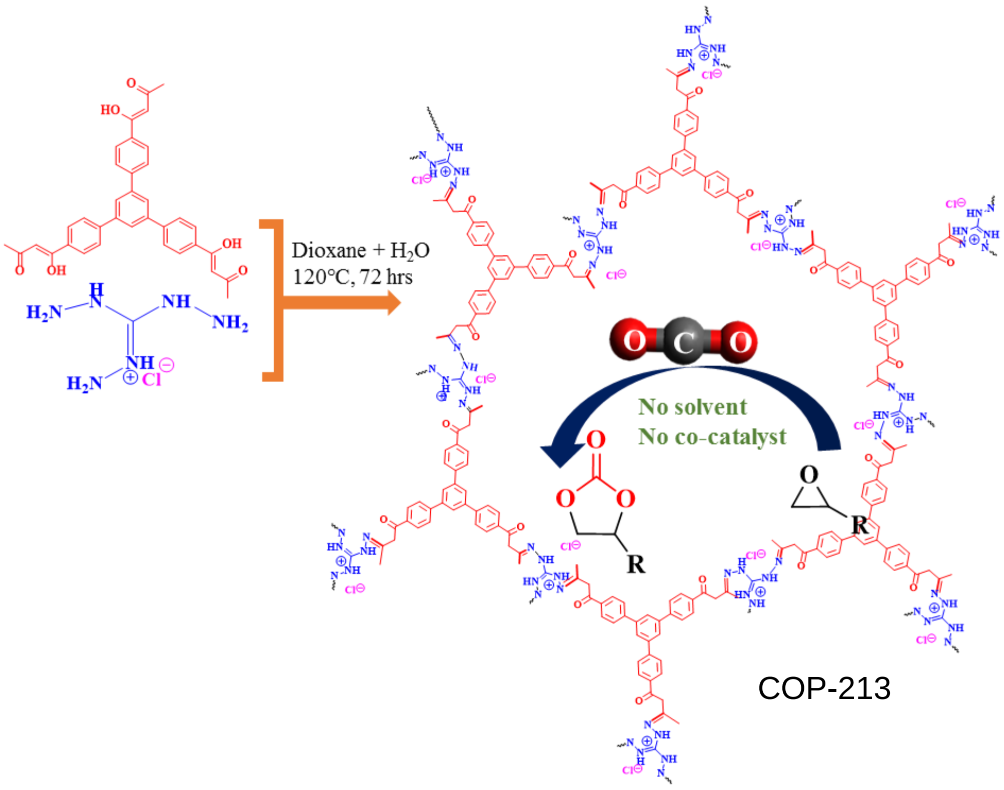
Herein, a unique zwitterionic active site on guanidinium- β-keto-enol based π–conjugated nanoporous polymers (COP-213) have been designed and synthesized that show good activity and selectivity in cyclic carbonate formation without the participation of co-catalysts or solvents, and under mild condition. The structure of the materials has been analysed in detail and proved by FTIR-ATR, PXRD, TGA, and surface area (BET) and CO_2 uptake. To the best of our knowledge, guanidine and β-keto-enol based nanoporous organic polymer-catalyzed transformation of CO_2 is not yet reported.

The design for a cycloaddition catalyst necessitates a quaternary ammonium center and polar/heterocyclic backbone that is stable enough for the reactive conditions. One way to achieve this goal is to include multiple modes of connectivity and nucleophilic units. Hydrazone formation through a β-keto-enol and hydrazine reaction would yield a promising architecture. Our catalyst (COP-213), therefore, consists of these multifunctional moieties, the β-keto-enol and zwitterionic guanidium units shown in Scheme 1. To prepare β-keto-enol, we revised a synthetic strategy that was reported earlier [45-46] but applying to the triphenyl benzene core. This also marks the first time the tris β-keto-enol derivative of the triphenyl benzene was synthesized.



Scheme 1: Synthesis of monomers: (a) C3 symmetric β-ketoenol unit, and (b) triaminoguanidinium halide (TGCl).

In order to incorporate guanidinium units within the polymers, we have prepared triaminoguanidinium halide (TGCl) from well-known procedures [47] and reacted with C3 symmetric β-ketoenol at 120°C in the presence of dioxane: H_2O mixture (2: 0.6 mL) (Scheme 2). The resulting yellow colour powder was filtered and washed with dioxane and water several times. After that, materials were purified by Soxhlet extraction (THF and DCM solvent over 24 hrs) and dried under vacuum at 100 °C for 12 hrs.



Scheme 2: Schematic representation of nanoporous organocatalyst COP-213 for chemical fixation of CO_2 and epoxides to cyclic carbonates.

The polymer catalyst (COP-213) was examined first by FTIR-ATR spectra. It revealed characteristic C=C stretching frequency at 1555 cm^{-1}, carbonyl stretching frequency at 1610 cm^{-1} and C−N stretching frequency at 1280 cm^{-1}, while characteristic primary amine stretching frequency (1679 cm^{-1}) of the precursors was absent (Figure 1a). The morphology analysis was then studied by scanning electron microscopy image to show the nanoporous nature of polymers. The powder X-ray diffraction pattern showed largely amorphous feature of COP-213 (Figure 1b). Permanent porosity of COP-213 was verified using N_2 adsorption/desorption isotherms of the activated samples at 77K, The Brunauer−Emmett−Teller (BET) the surface area of COP-213 was found to be 1.8 m^2 /g. The low BET value indicates that strong hydrogen bonding of polymers networks. However, it shows good CO_2 uptake performance with the values of 1.12 mmol/g (25.27 cm^3 /g) at 298K (Figure 1c). A moderate BET surface area of 126 m^2/g is calculated based on CO_2 as a probe molecule. The thermal stability of COP-213 was studied under nitrogen atmosphere showed that it is stable up to 350°C (Figure 1d).

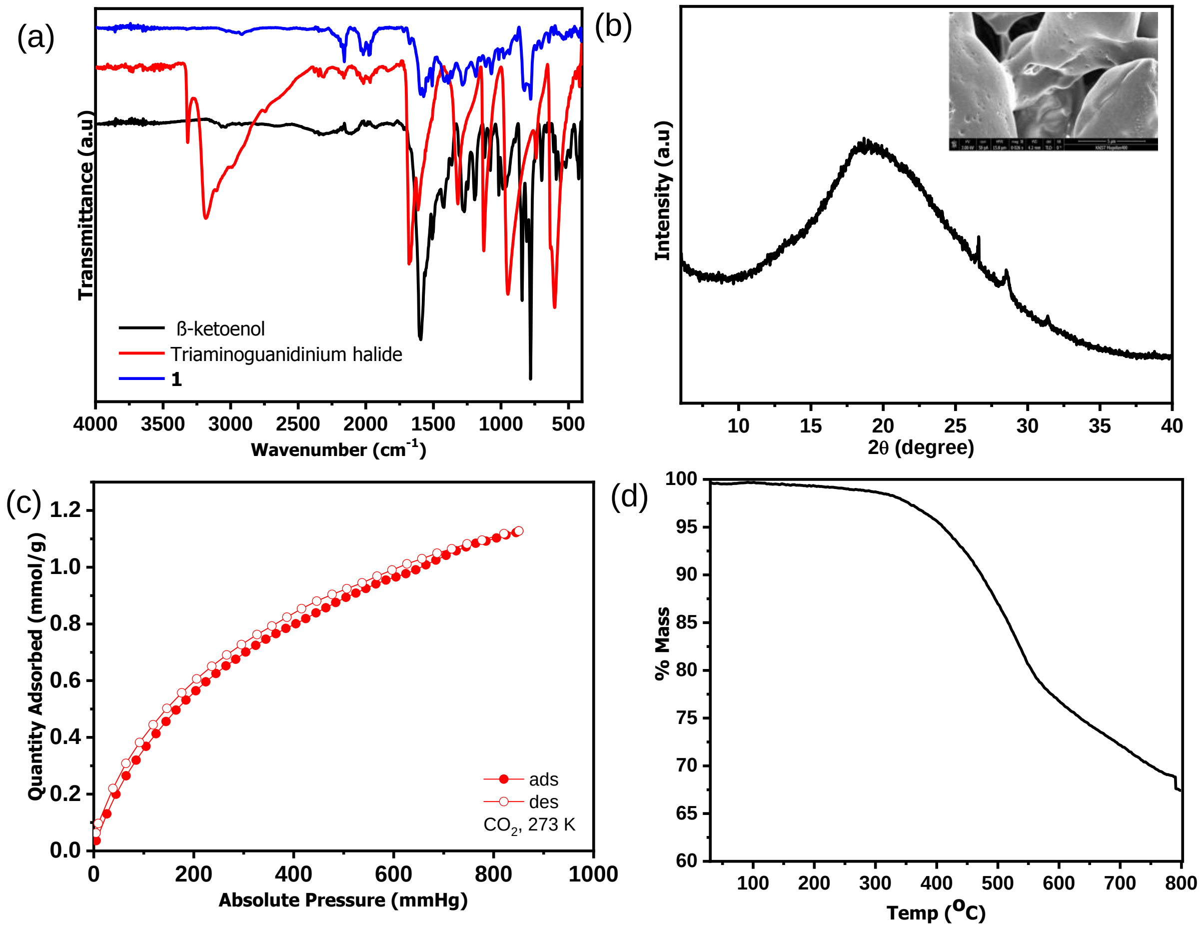


Figure 1: Characterization of COP-213: (a) FTIR-ATR spectra, (b) PXRD data (inserted box shows SEM image of the nanoporous polymer), (c) CO_2 uptake at 273 K, and (d) Thermal analysis.

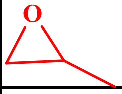
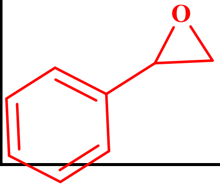
To optimize the catalytic activity for chemical fixation of CO_2, epichlorohydrin was selected as a model reaction according to literature reports. A typical experiment for catalytic cycloaddition of CO_2 to the epoxide was as follows:

epichlorohydrin (5 mmol) and catalysts (30 mg) under solvent-free conditions were charged into a reactor that connects with a CO_2 cylinder under atmospheric pressure. The reactor vessel was placed into an oil bath at 100 °C and kept under stirring. After the given time, the reaction mixture was cooled to room temperature. Conversion and selectivity were measured by a 300 MHz ^1H NMR analysis. The catalyst COP-213 shows excellent catalytic activity (>99% conversion) after 48 hrs.

The remarkable catalytic activity of polymer COP-213 for the cycloaddition of CO_2 to epoxides allowed us to obtain structural facts on the grafting of guanidinium moieties. Both cation and anion parts of the guanidinium unit are expected to have a significant effect on catalytic activities. Selection of the halide ion is also crucial because counter anion needs to show a nucleophilicity to activate the epoxide ring and then have good leaving ability. Among them, chloride ions show the highest activity through a S_N2 mechanism. It is proposed that the epoxide is activated along with the electron deficient guanidinium unit of polymer. On the other hand, the bulkiness of the guanidinium ion influences the electrostatic interaction between the cations and anions, which limits the counter anion to be more nucleophilic.

Various factors including time, loading of catalyst and substrate variations were investigated to find the optimal reaction condition and evaluate the catalytic performance. The dependence of product yield and selectivity on reaction time was studied under identical conditions shown in Table 1. The yield of cyclic carbonate increased rapidly in the initial time and stayed steady after 48 hrs. The effect of varying catalyst loading was investigated for different catalyst amount at 100 °C and atmospheric CO_2 pressure for 24 hrs. Minimum catalyst loading shows negligible yield. However, increased loading realized a significant enhancement in activity, and a steady increment was observed at 30 mg catalyst loading (Figure 2b). To monitor industrial viability, the substrate scope was also examined. Aliphatic propylene oxide shows good conversion and selectivity. The hard substrate styrene oxide led to a low conversion but high selectivity in cyclic carbonates. We studied the reusability of COP-213 using model substrate under optimized reaction conditions and found that the catalyst can be reused at least 3 times with minimum loss in its activity (Figure 2c).

Table1: Screening of substrates for the cycloaddition reaction.

	Substrates (5 mmol)	**CO_2 (bar)**	**Temperature (^{0}C)**	**Time (hrs)**	**Conversion (%)**	**Selectivity (%)**
1		1	100	4	10	>99
				8	32	>99
				12	64	>99
				24	91	>99
				48	99	>99
2		1	100	48	99	>99
3		1	100	48	53	>99

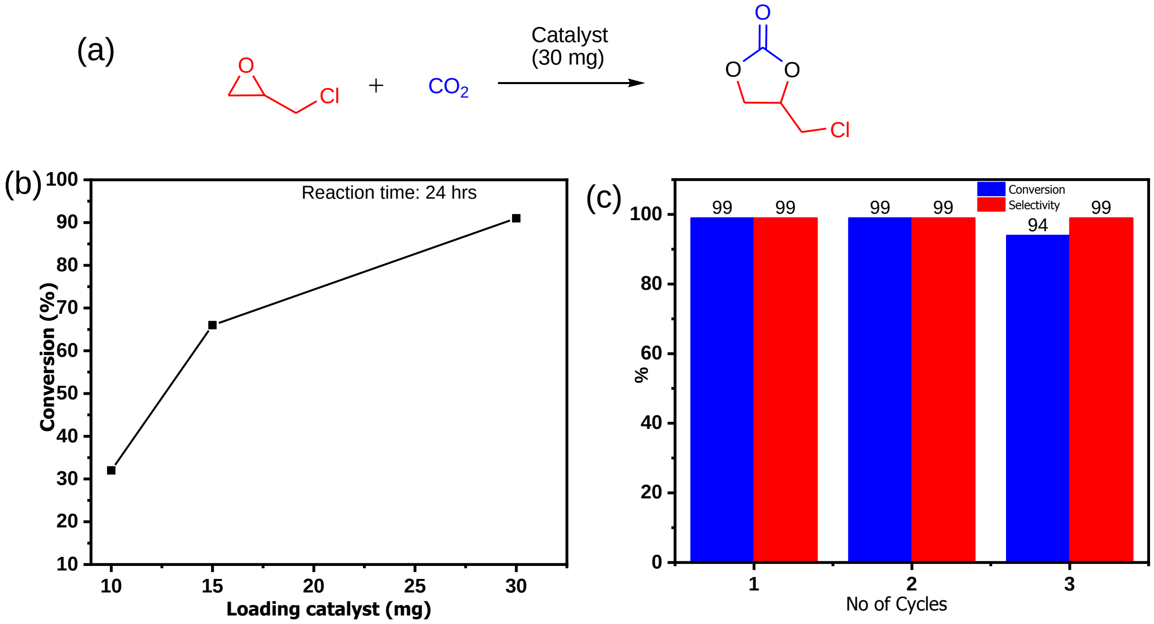
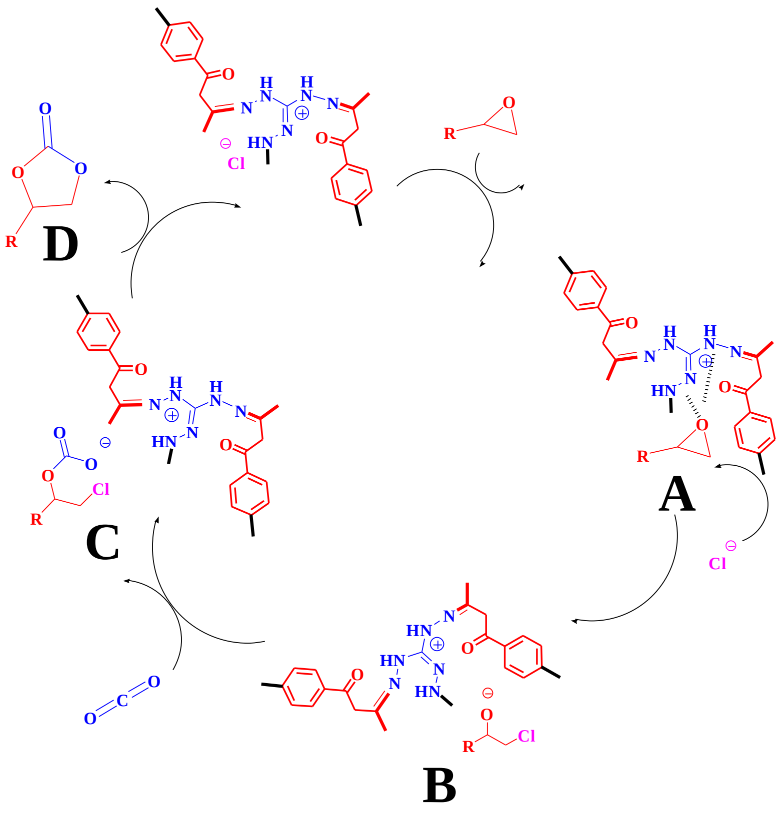


Figure 2: Optimization of catalyst activity: (a) Cycloaddition of CO_2 to epichlorohydrin was used as a model reaction to optimize catalytic activity, (b) screening of the catalyst loading, and (c) reusability of **COP-213**.

Based on the literature examples [48-52], a plausible mechanism is shown in Scheme 3. First, the epoxide is activated through the interaction with the guanidinium cation of zwitterion π–conjugated porous polymer. Simultaneously, the nucleophilic attack of the halogen counter-anion on the epoxide furnishes the ring-opened intermediate B. Next, a CO_2 molecule coordinates to the polymers and is attacked by the alkoxy anion formed during the epoxide ring opening, resulting in the formation of intermediate C. Finally, the cyclic carbonate D is produced by an S_N^2 type intramolecular elimination, at the same time regenerating the catalyst for another cycle.



Scheme 3: A plausible mechanism for the catalytic cycloaddition of CO_2 to epoxides.

In conclusion, a novel π–conjugated zwitterionic nanoporous polymer, based on β-keto-enol and guanidinium units has been synthesized and characterized successfully. The synthesized organo-catalyst exhibit high activity and selectivity for cycloaddition reaction of CO_2 to epoxide without co-catalyst under a solvent-free condition in atmospheric pressure. The conversion of CO_2 to various cyclic carbonates takes place effectively using this nanoporous catalyst because of the “electrophile–nucleophile” synergistic effect for epoxide ring-opening. It is expected that guanidine-based polymers could significantly impact the development of heterogeneous catalysis through rational design, and play an important role in CO_2 capture and utilization to value-added chemicals in industry.

Supporting Information

Materials and methods, characterization of organo-catalysts, and products.

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