Catalytic Non-redox Carbon Dioxide Fixation in Cyclic Carbonates

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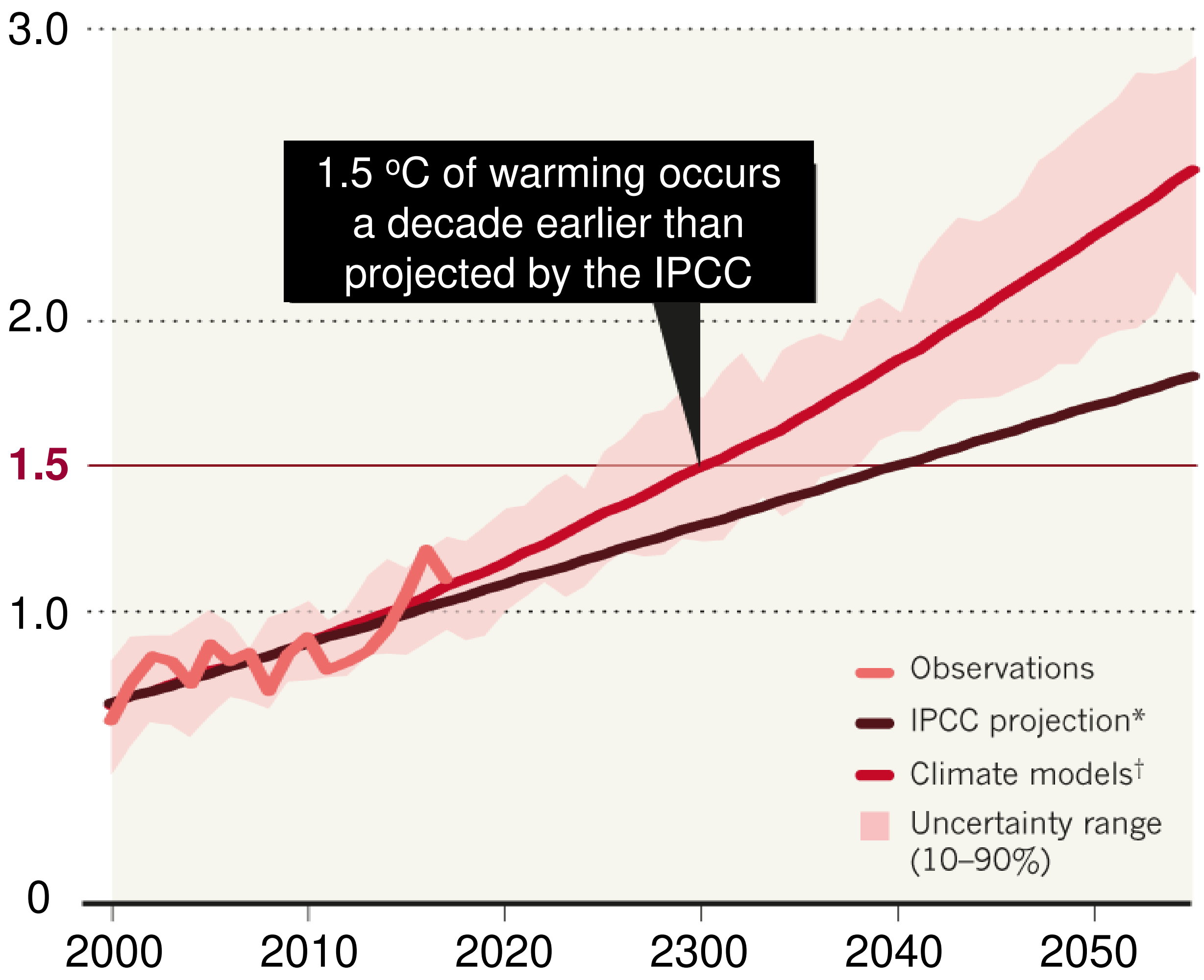
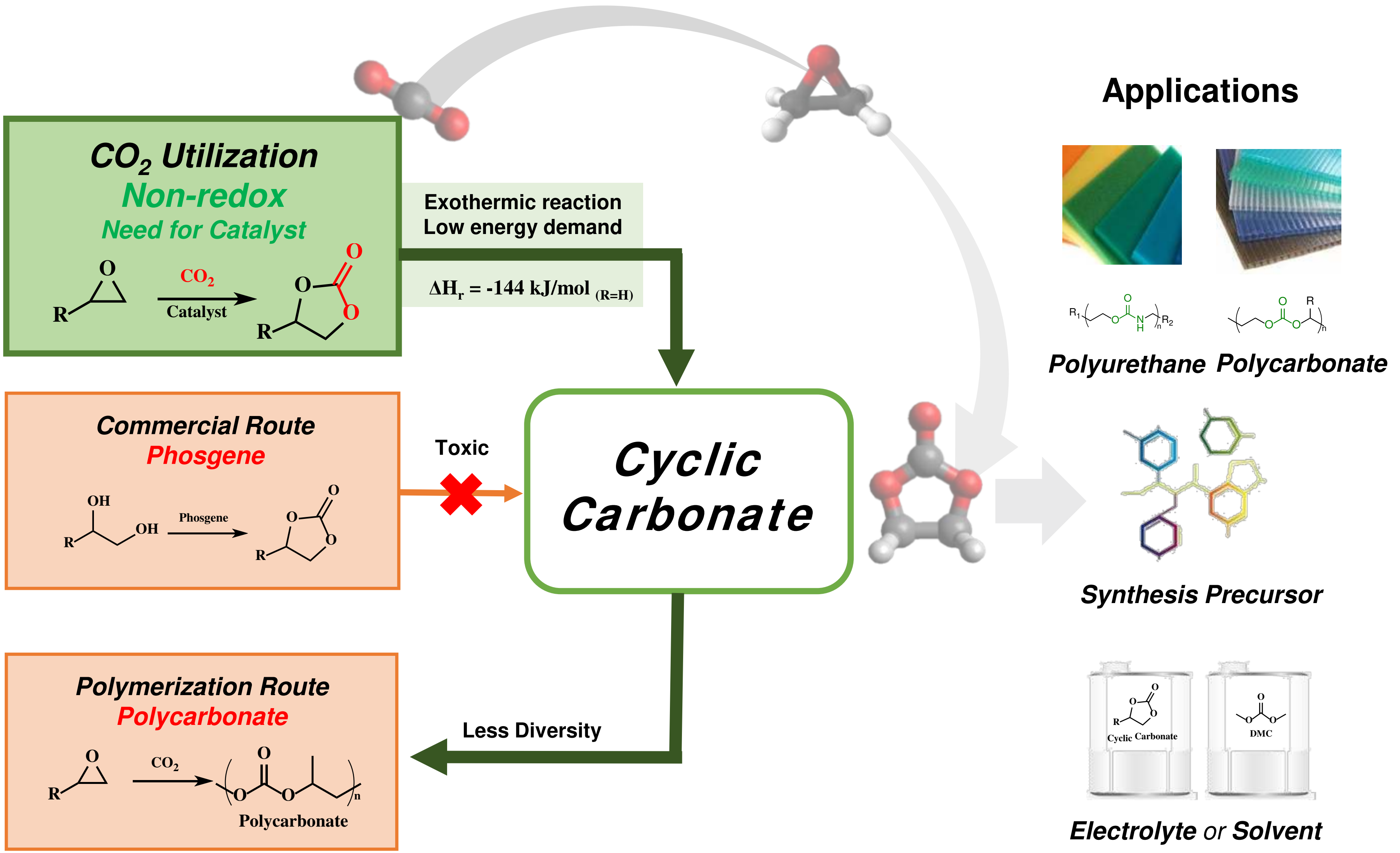
Accelerated Warming



Nature **564**, 30-32 (2018)

Non-redox CO_2 Utilization



State of the Art in Heterogeneous Catalyst

Current Heterogeneous System

- ❖ Low Reactivity, Selectivity
- ❖ Deactivation

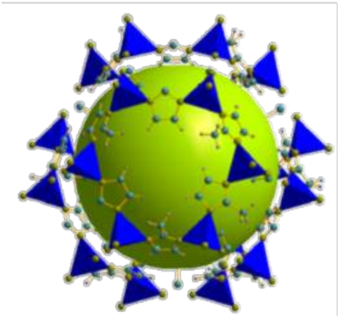
Needs

High Pressure	Narrow Substrate
Co-catalyst	Solvent

⬇

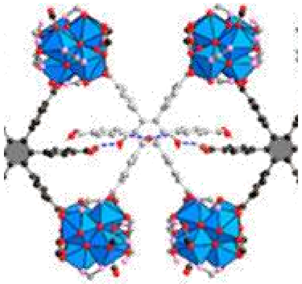
Improvements

Atmospheric Pressure	Challenging Substrate
Additive-Free Condition	Recyclability



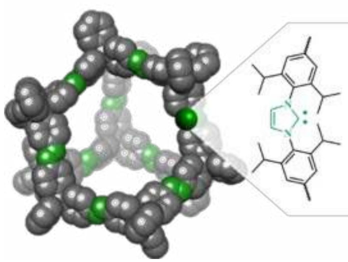
ZIF-8

ACS Catalysis 2012 *2* (1), 180-183



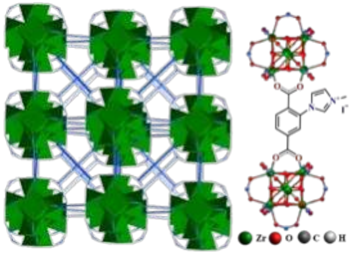
MOF-892

ACS Appl. Mater. Interfaces, 2018, 10 (1), 733–744



Nanoporous NHC

Chem. Mater. 2015, 27, 19, 6818-6826



Imidazole-MOF

Chem. Commun., 2018, 54, 342

Novel Imidazolinium-based COP-222

Imidazolinium-based Covalent Organic Polymer (COP)-222

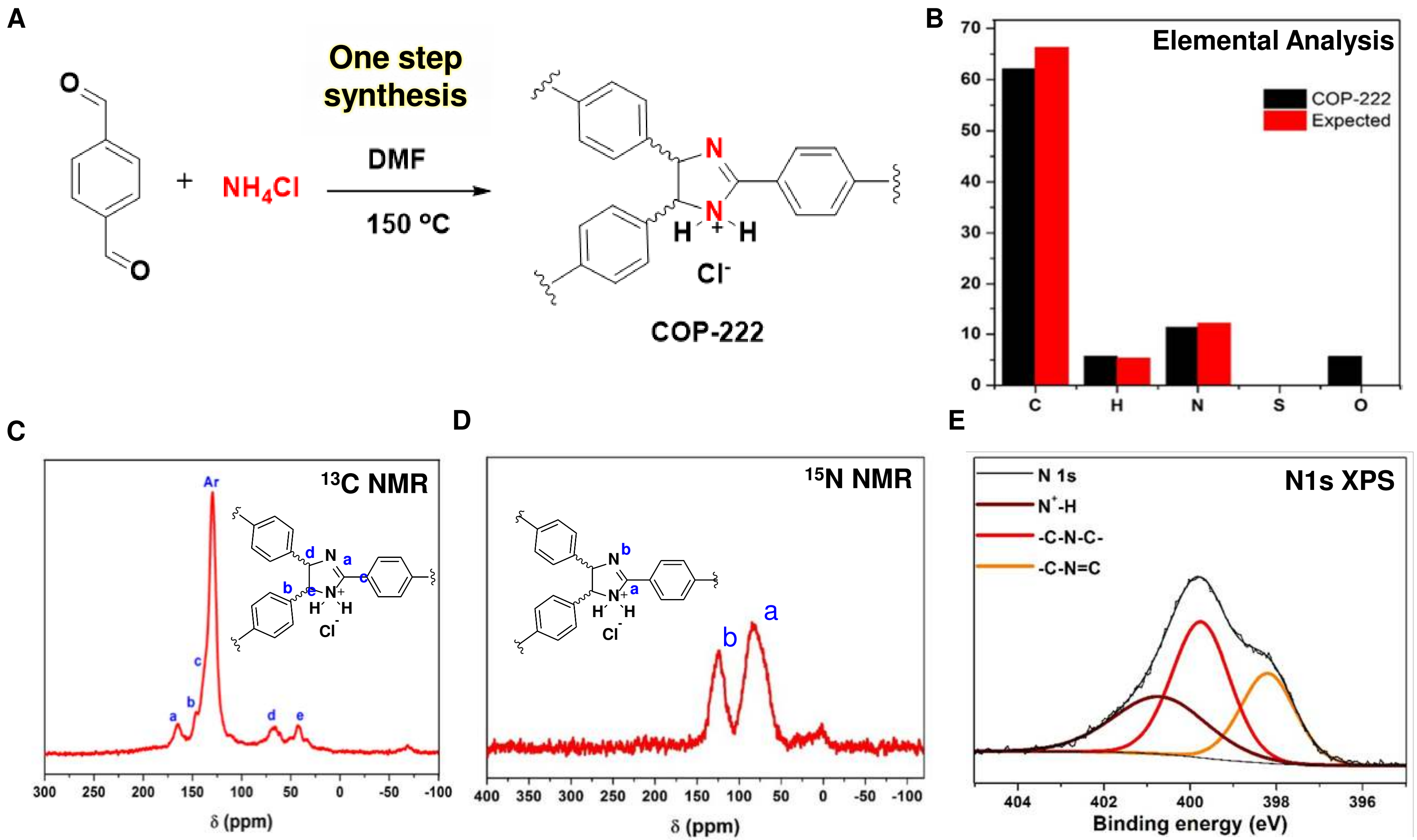


Figure 1. Synthesis and imidazolinium characterization of COP-222 (A) One-step, one-pot synthesis from commercially available substrates. (B) Elemental analysis (C,N,H,O) with expected imidazolinium structure (C) Experimental ^{13}C-NMR. (D) ^{15}N-NMR with ^{15}N-enriched COP-222. (E) XPS (N-1s) data.

Physicochemical Property of COP-222

XRD, SEM, BET, CO_2 Isotherm, and TPD Analysis

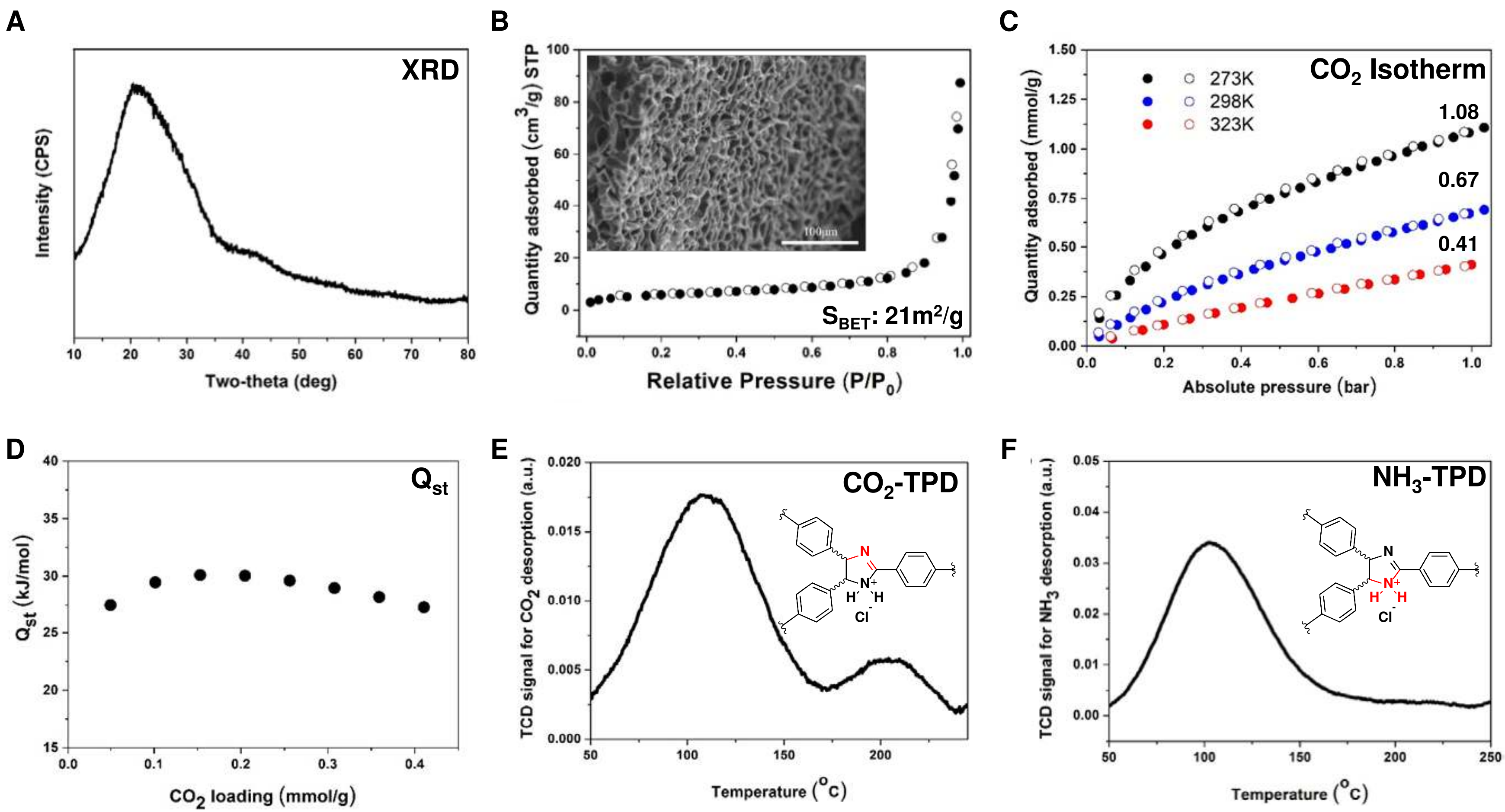


Figure 2. Physicochemical characterization of COP-222 (A) XRD pattern reflects amorphous nature. (B) N_2 adsorption-desorption isotherm at 77K indicates non-porous architecture. Inset displays scanning electron microscopy image of COP-222 (C) CO_2 adsorption isotherm at different temperature: 273, 298, and 323K. (D) Isosteric heat of adsorption (Q_{st}) data of COP-222 using Clausius-Clapeyron equation. Temperature programmed desorption profiles of COP-222 (E) CO_2-TPD curve (F) NH_3-TPD curve.

Optimization of Catalytic Activity

Cycloaddition Reaction of CO_2 with Epoxides

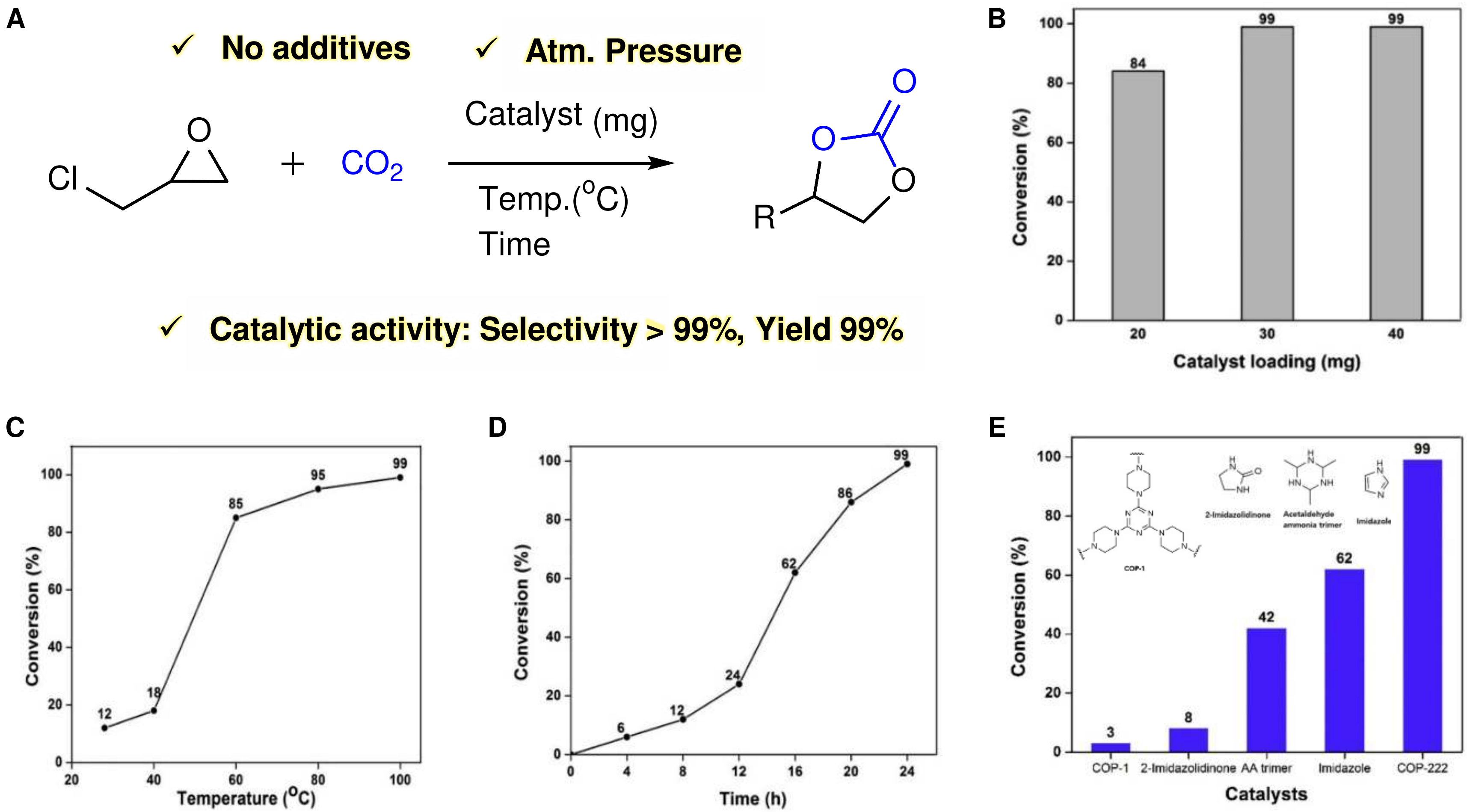


Figure 3. Optimization of catalyst activity (A) Cycloaddition of CO_2 to epichlorohydrin was used to optimize catalytic activity. (B) Screening of catalyst loading. (C) Screening of temperature.(D) Conversion with respect to time. (E) Screening of control structures for the cycloaddition reaction. Reaction conditions: catalyst, epichlorohydrin (5mmol), and CO_2 (1atm).Conversions were determined by using ^{1}H NMR.

Substrate Scope and Recyclability

✓ **Wide substrate scope** ✓ **Recyclable (at least 15)**

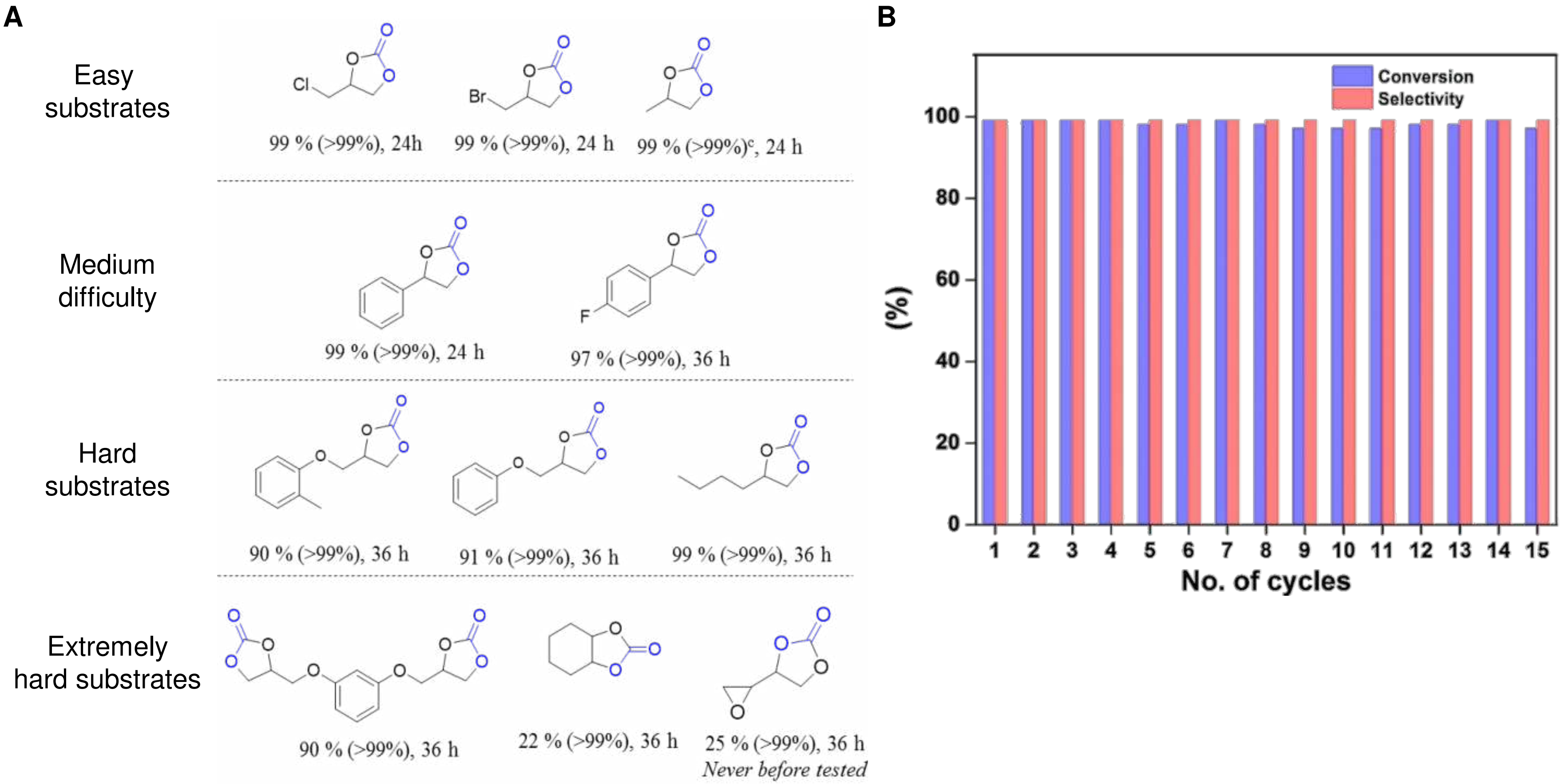


Figure 4. (A) Cycloaddition reaction of CO_2 with various epoxides catalyzed by COP-222. Conversion yields for the corresponding catalytic reactions are given in percentages. The selectivities are reported in parentheses (B) Recyclability of COP-222 for 15 cycles. Each cycle was set up using the recovered catalyst and epichlorohydrine. [a]Reaction conditions: substrate (5 mmol), COP-222 (30 mg), CO_2 (1atm) and temperature (100^{o}C). [b]Determined by using 1H-NMR.

ND-ERO Reaction Mechanism

Nucleophillic attack-driven Epoxide Ring Opening (ND-ERO) Mechanism

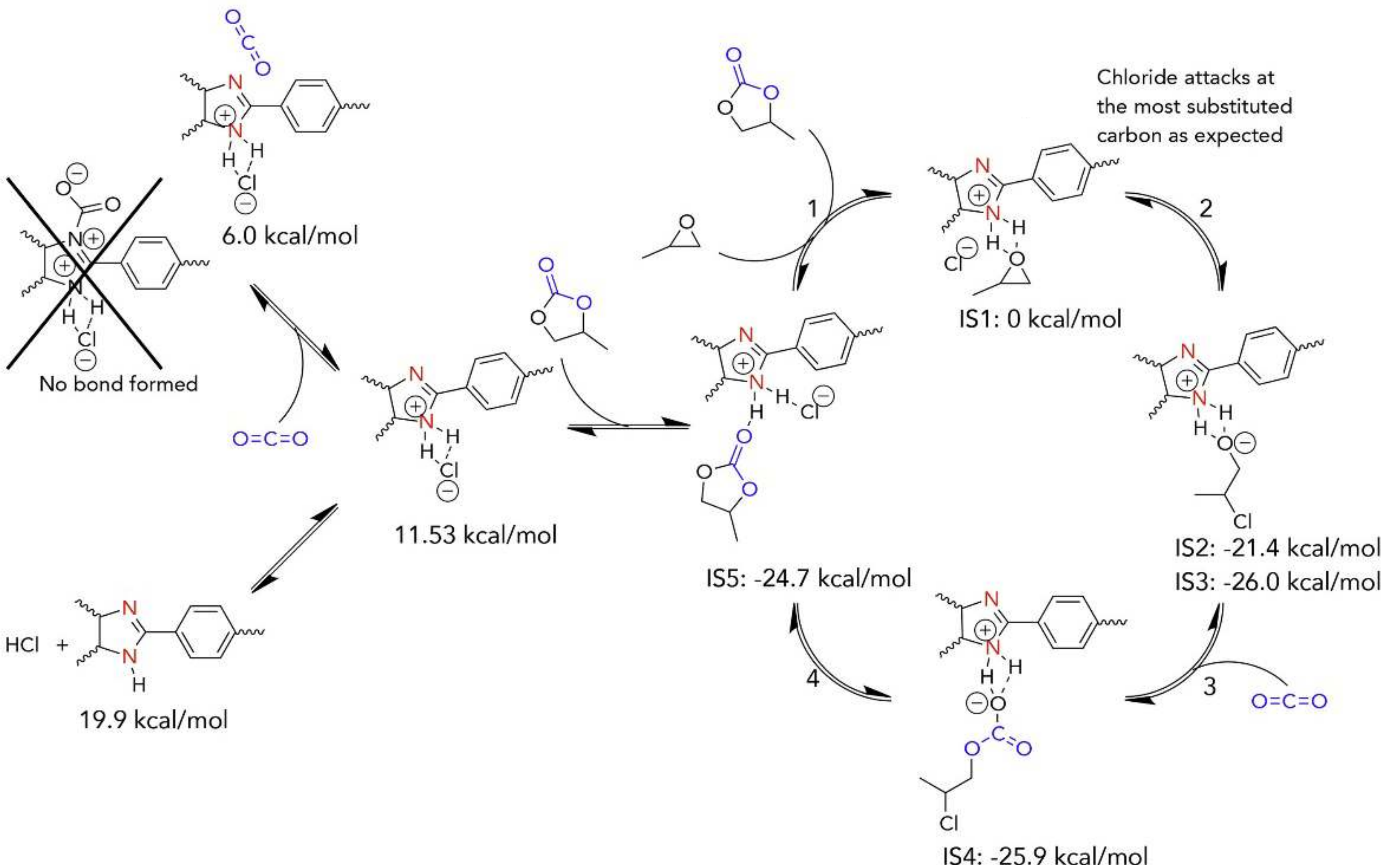
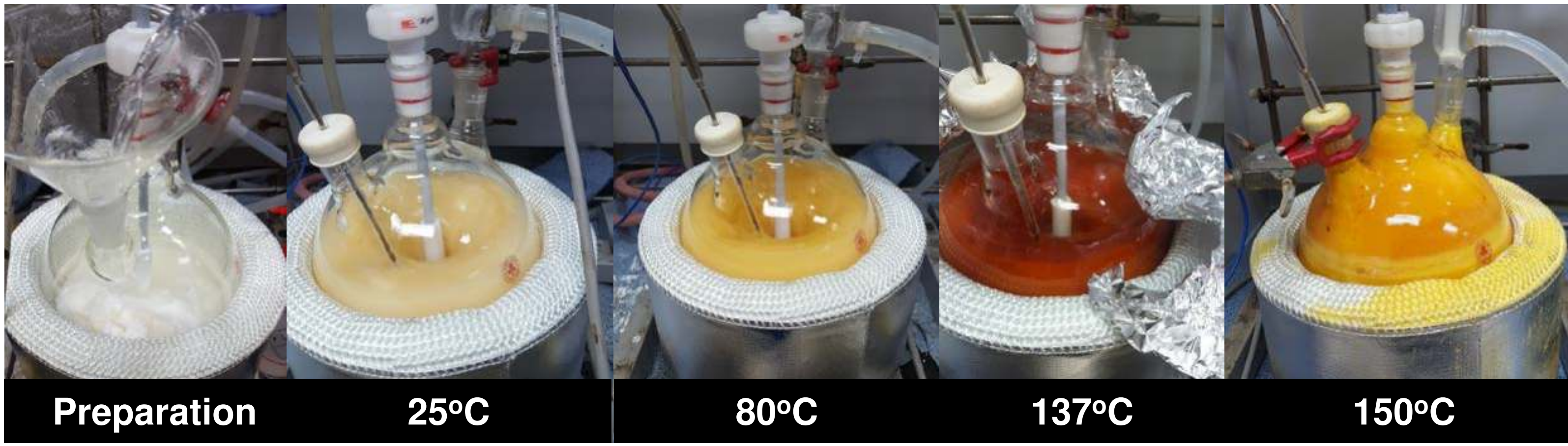


Figure 5. The Nucleophilic Attack-Driven Epoxide Ring Opening (ND-ERO) Reaction Mechanism Reaction mechanism for the COP-222 catalyst derived from quantum mechanics, including free energy reaction barriers.

Scalability and Cost

Bench-scale Testing (1.5L)



141$ / kg

Figure 6. Scale-up for COP-222 synthesis with terephthalaldehyde (200g) and ammonium chloride (320g) in dimethylformamide (1.5L)

Conclusions

The imidazolinium catalyst that we developed herein addresses all 7 qualities and offers rapid implementation for CO_2 reclamation.
(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**.

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Article

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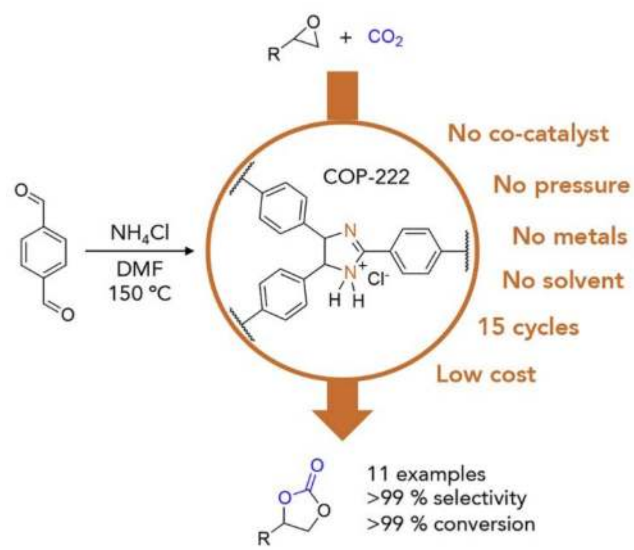

Thank you for your listening!