FMRI REHSS 2016-A Metal-Metalloporphyrin Framework Featuring Lewis-acid Centers for CO_2 Chemical Transformation

Clarice Su[1], Jesse Hope[2], Wen-Yang Gao[3], Shengqian Ma[3]

1. C. Leon King High School; 2. Tampa Bay Tech High School; 3 Department of Chemistry, University of South Florida

Abstract

The chemical transformation of inexpensive, abundant, and sustainable carbon dioxide (CO_2) into useful chemicals paves an avenue to reduce greenhouse gas emission. Herein, a porous metal-metalloporphyrin framework, MMPF-10, was utilized as a heterogeneous Lewis-acid catalyst for CO_2 cycloaddition reaction with aziridine. MMPF-10 was fabricated by a octatopic porphyrinic ligand and in situ generated $Cu_2(CO_2)_4$ paddlewheel clusters, which exhibits unsaturated Cu(II) centers in the accessible channels. The reactions between different substituted aziridines and CO_2 were performed to examine how the side chains influence the reaction yield.

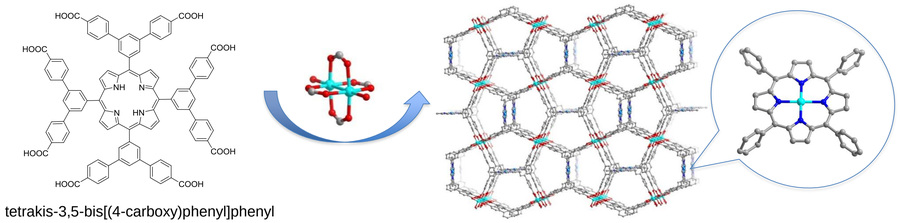
Background

The high levels of carbon dioxide in the atmosphere has become a major contributor to climate change in the past decade, and many pathways have been investigated to capture this carbon dioxide and store it elsewhere. One such possibility investigated is the chemical conversion of carbon dioxide, a C1 source and a readily available waste, with aziridine to produce oxazolidinone, an antibacterial compound used in pharmaceutical products. This CO_2 cycloaddition reaction has already been investigated with different catalysts, but in this study, we explored a porous metal–metalloporphyrin framework, MMPF-10, as the catalyst and tetra-*n*-butylammonium bromide (TBAB) as the co-catalyst.

MMPFs are a class of materials composed of metal-containing secondary building units and metalloporphyrin ligands that form a coordination network. MMPFs are a sub-class of Metal-Organic Frameworks (MOFs), which are highly porous materials with centers of metals ions or clusters connected by organic linkers. MMPF-10 used in this study has copper paddlewheel cluster nodes connected with a octatopic porphyrin ligand. MMPF-10 has already been shown to be an effective catalyst in the coupling reaction of carbon dioxide to aziridine, and in this study, we show the effect of the aziridine side chain (methyl-, propyl-, benzyl-) on the product yield of oxazolidinone.

Objective

To determine whether the side group on the aziridine substrate (methylamine, propylamine, and benzylamine) has an effect on the product yield of oxazolidinone from the coupling reaction between carbon dioxide and aziridine.



tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine (tbcppp)

Figure 1. The porphyrin ligand of tbcppp and copper paddlewheel cluster used in building MMPF-10. The porphyrin core was metallated by Cu(II) during the synthesis of MMPF-10. Atom Colors: C=Gray, O=Red, N=Blue, Cu=Turquoise.

Approach

Synthetic procedures of aziridine substrates

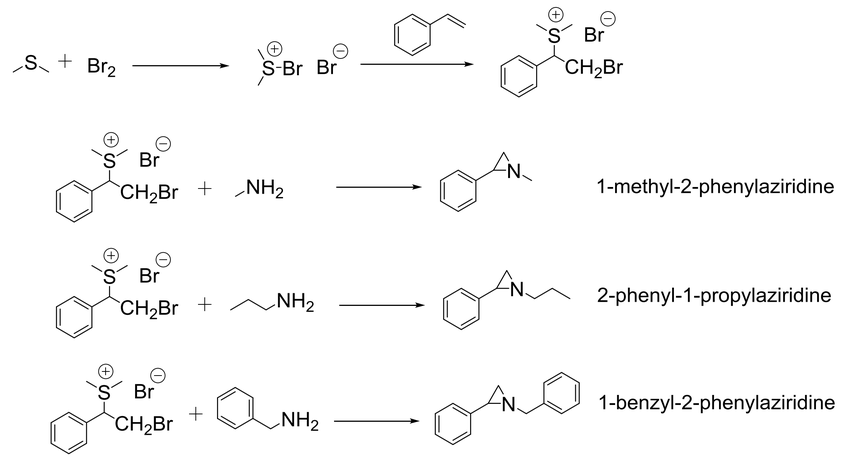
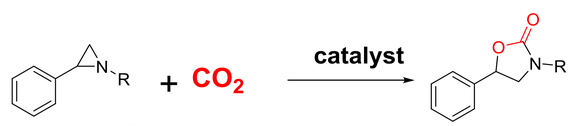


Figure 2. Schematic representation of synthetic details of different substituted aziridines for CO_2 cycloaddition reaction.

CO_2 cycloaddition reaction with aziridine to form 2-oxazolidinone

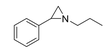
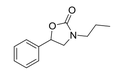
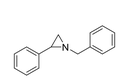
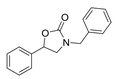


R = methyl, propyl, and benzyl groups

Figure 3. Schematic representation of CO_2 cycloaddition reaction with aziridines.

To determine the yield of oxazolidinone from the fixation of carbon dioxide to aziridine, 1.0 mmol of aziridine was placed in a pressurized chamber along with 0.0125 mmol of catalyst MMPF-10 and 0.0125 mmol of co-catalyst TBAB. These compounds were then dissolved in 0.5 mL of 2-proponal and carbon dioxide gas was pumped in at 2.5 MPa at room temperature. After ten minutes, the chamber was sealed and placed in an oil bath at 50 ºC for two hours while the mixture inside was kept stirring. Finally, the mixture was removed and cooled in an ice bath. Through NMR spectroscopy, the yield of oxazolidinone was determined. This procedure was repeated for all three aziridines: methylaziridine, propylaziridine, and benzylaziridine.

Table 1. CO_2 cycloaddition reactions with different substituted aziridines.

Entry	Substrate	Product	Yield (%)
1			57.5
2			33.0
3			19.0

All reactions were performed with 0.0125 mmol MMPF-10 catalyst, 0.0125 mmol TBAB as the coc-atalyst, and 0.5 mL 2-proponal as the solvent under CO2 pressure of 2.5 MPa at 50 ºC for two hours.

Conclusions

MMPF-10 cooperated with TBAB and proved to be an efficient catalyst system for CO_2 chemical transformation with different substituted aziridines into 2-oxazolidinones. Furthermore, an impressive decrease in the yield of 2-oxazolidinone was observed with an increase of the molecular size of the aziridine substrate. The lower yield of MMPF-10 could be ascribed to not only the intrinsic activity of the substrate, but also the limited diffusion of the large substrate into the narrow channels of MMPF-10, hence displaying size-selective catalysis.

Referenced Resources

(1) Gao, W.-Y.; Chrzanowski, M.; Ma, S. *Chem. Soc. Rev.*, 2014, *43*, 5841-5866.
(2) Gao, W.-Y.; Chen, Y.; Niu, Y.; Williams, K.; Cash. L.; Perez, P. J.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S. *Angew. Chem. Int. Ed.*, 2014, *53*, 2615-2619.

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