

# CO<sub>2</sub> Fixation Using Aluminum Catalysts

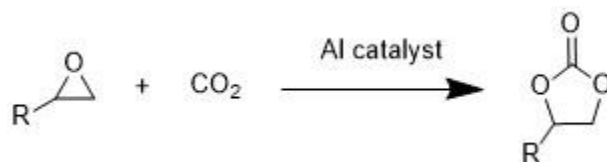
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The burning of fossil fuels such as coal and oil releases carbon dioxide, a greenhouse gas, into the atmosphere. The abundance of CO<sub>2</sub> provides an ideal opportunity to utilize it as a carbon source in chemical reactions. Catalysts have been developed to transform carbon dioxide into more usable chemicals, such as cyclic carbonates, which can further be used as polar aprotic solvents, raw materials for the synthesis of polycarbonates, electrolytes in secondary lithium-ion batteries, etc.<sup>1</sup> A common CO<sub>2</sub> fixation reaction involves reacting CO<sub>2</sub> with an epoxide and, using a metal-catalyst, forming a cyclic carbonate (Fig. 1). The metal center of the catalyst serves as a Lewis acid capable of activating the epoxide. The presence of a counteranion, often a halide, opens up the epoxide ring, enabling CO<sub>2</sub> insertion.<sup>1-3</sup>

While many metals have been utilized in the catalysts for such reactions, the use of naturally abundant aluminum, which is the most abundant metal in the Earth's crust, lowers the cost of the catalyst, given comparable ligand design. Al has long been utilized in catalysts for synthetic reactions, including the use of AlCl<sub>3</sub> in Friedel-Crafts acylation and alkylation reactions discovered in the late nineteenth century and the use of AlEt<sub>3</sub> in Ziegler's Aufbau reaction discovered in the mid-twentieth century.<sup>4</sup> Recently, there has been a surge in the use of aluminum catalysts due to its low toxicity compared to other commonly used metals in these systems, such as cobalt or zinc. Additionally, utilizing a metal with high Lewis acidity like aluminum makes it ideal for activating the cyclic ether in these CO<sub>2</sub> fixation reactions.<sup>1-3</sup>

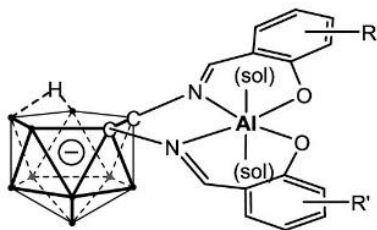


**Figure 1.** General scheme for five-membered cyclic carbonate synthesis.

With the aim of developing an effective catalytic system to convert epoxides into five-membered cyclic carbonates, the Mahalingam group at the Indian Institute of Science synthesized a catalyst comprised of guanidine hydrochloride grafted onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (referred to as Al-Gh) using a three-step process. The product of each step, AlO(OH),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Al-Gh, was confirmed using powder X-ray diffraction. Furthermore, N<sub>2</sub> absorption/desorption isotherms of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al-Gh found that the surface area of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was almost eight-times larger than that of the Al-Gh catalyst, thus indicating that guanidine hydrochloride occupies the pores of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Additionally, high CO<sub>2</sub> uptake by Al-Gh was confirmed by obtaining CO<sub>2</sub> absorption/desorption isotherms of both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al-Gh.<sup>2</sup>

Additional studies were conducted concerning the conversion of CO<sub>2</sub> and a model epoxide, epichlorohydrin, into a five-membered cyclic carbonate using Al-Gh. The ideal temperature, catalyst loading, and necessity of the free amine groups and counteranion of guanidine hydrochloride were determined. These reactions were carried out at atmospheric pressure, 85°C, and without the use of additives. Overall, the synthesis of a new, bifunctional aluminum catalyst coupled with relatively mild reaction conditions allowed for high % conversion of epoxides and CO<sub>2</sub> to five-membered cyclic carbonates.<sup>2</sup>

Using the same general scheme for synthesizing five-membered cyclic carbonates (Fig. 1), the Xiao group at Hangzhou Normal University in Zhejiang, China recently developed *o*-carborane-supported salen ligands and subsequently formed the analogous aluminum solvento catalysts (Fig. 2). Previous reports on the catalytic activity of salen-type ligands in aluminum complexes for epoxide/CO<sub>2</sub> reactions, such as that by Yao et al., and on the stability and bulkiness of *o*-carborane ligands led to the development of this stable aluminum catalyst.<sup>3,5</sup> The structures of these complexes were confirmed using single-crystal X-ray diffraction. The large % conversion of various epoxides and CO<sub>2</sub> into five-membered cyclic carbonates at 1 bar pressure and 50°C confirmed the catalytic activity of the synthesized aluminum catalysts. Subsequent DFT studies shed light on the binding of epoxides on both sides of the aluminum center, possible transition states, and overall spontaneity of the reaction, as modeled by propylene oxide.<sup>3</sup>

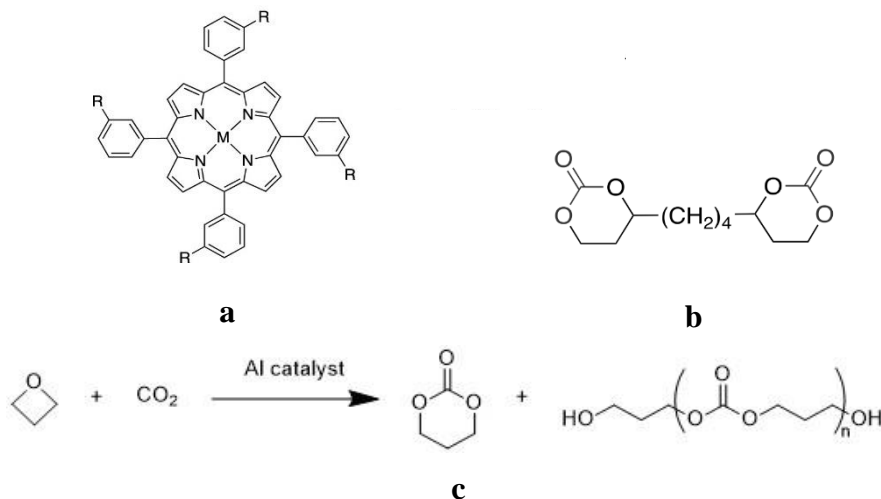


**Figure 2.** Al catalyst with *o*-carborane-supported salen ligand (R = H, 3,5-<sup>t</sup>Bu, 4-OMe, or 5-<sup>t</sup>Bu and sol = MeOH).<sup>3</sup>

Lastly, the recent development of a new aluminum metalloporphyrin catalyst (Fig. 3a) by the Ema group at Okayama University in Tsushima, Okayama, Japan via a previously published route for the analogous Mg and Zn complexes<sup>6</sup> proposes a new way to synthesize six-membered cyclic carbonates from oxetanes and CO<sub>2</sub> (Fig. 3c).<sup>1</sup> By varying the reaction conditions, including CO<sub>2</sub> pressure and type of tetrabutylammonium salts (TBAX where X = I, Br, Cl, or OMe), either more trimethylene carbonate (TMC) complexes or poly(trimethylene carbonate) complexes were produced, with more TMC being made with greater CO<sub>2</sub> pressure and using TBAI as the additive. Furthermore, the cross-linking polymerization utilizing the Fig. 3b structure is a prime example of the formation of copolymers from cyclic carbonates.<sup>1</sup>

The syntheses of new aluminum-based catalysts for the conversion of epoxides or oxetanes into five- or six-membered cyclic carbonates via CO<sub>2</sub> fixation enables the utilization of CO<sub>2</sub>, given

its abundance in the atmosphere. These new advances, utilizing mild conditions and new ligands, allows for a decrease in the amount of energy being put into the system, and therefore less CO<sub>2</sub> being created inadvertently. Additionally, the research done by the Ema group allowed for production of cross-linked polymers which can be further used in industrial applications.



**Figure 3.** **a)** Aluminum metalloporphyrin catalyst structure. **b)** 4,4'-(butane-1,4-diyl)bis(1,3-dioxan-2-one) structure. **c)** General scheme for six-membered cyclic carbonate synthesis.<sup>1</sup>

## References

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