# Carbon Dioxide Activation Center 2022 - HIGHLIGHTS

**About the Center**

The Carbon Dioxide Activation Center (CADIAC) was established in 2015 at Aarhus University with Prof. Troels Skrydstrup as the Center leader, in collaboration with external scientists from the Leibniz Institute of Catalysis in Rostock, and the University of Michigan. The goal of the research center is to explore new methods for the activation of carbon dioxide eventually providing sustainable solutions for the exploitation of this molecule as a valuable reagent to high-value chemicals of industrial importance, and in the aid of pharmaceutical development programs. The highlights of the published work from CADIAC for the year 2021 and start of 2022 are described below. As in the other years of the Center's existence once again the CADIAC publication record has been excellent with numerous publications in the *Journal of the American Chemical Society* and *Angewandte Chemie International Edition* representing the top chemistry journals. (See discussion on page 2 of the report). Gratifyingly, the foundation of CADIAC has paved the way for the establishment of a new center on $CO_2$ capture and conversion funded by the Novo Nordisk Foundation which will increase and support CADIAC activities participating in the development of key solutions for the creation of a sustainable society.

**Highly Active and Chemoselective Electrocatalyst for $CO_2$ Conversion to CO**

To date, metal-nitrogen co-decorated carbon (M-NC) materials, featured with atomically dispersed metal cations, are developing into interesting heterogeneous catalysts for $CO_2$ reduction. CADIAC scientists at Aarhus in collaboration with chemists in China have recently published in *Angewandte Chemie International Edition* on a novel nitrogen-stabilized low-valence Zn-based single atom catalyst displaying excellent performance for electrochemical $CO_2$-to-CO conversion in aqueous medium. This catalyst exhibits a remarkable near 100% CO selectivity at a small overpotential (310 mV). From an industrial perspective, the Zn-NC catalyst achieves a remarkable current density of 1 A $cm^2$ with high CO selectivity using a flow-cell reactor. Overall, this work reveals the relationship among coordination number, valence state, and catalytic performance, serving as guidelines for designing and developing atomically dispersed active sites for electrocatalytic $CO_2$ reduction at industrially relevant activity.

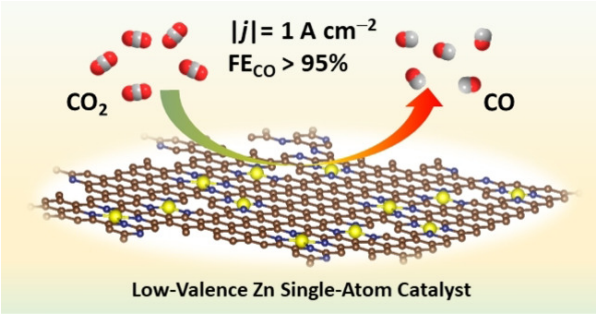


**Figure 1:** A nitrogen-anchored low-valence Zn single-atom catalyst, containing coordinately unsaturated Zn-$N_3$ active sites, boosting electrochemical $CO_2$ reduction to industrial application levels.

**A Novel Approach to Carbon Capture and Utilization for the Synthesis of Formate**

A team of CADIAC chemists in Aarhus reported in the *Journal of Materials Chemistry A* an interesting study on the structure–activity relationship of six different bismuth(III) coordination polymers for the electrochemical reduction of $CO_2$ to formate. Bismuth is an appealing metal for applications in such electrochemical reductions because of its moderate price. Whereas most of the bismuth-based coordination polymers readily degrade in the bicarbonate electrolyte, one phenolate based polymer displayed high activity even after 30 min of bulk electrolysis. Overall, it was concluded that a less expensive linker and simple precursor synthesis would provide the cheapest possible $CO_2$ conversion. With the demonstrated high bismuth mass activity of 200 A $g^{-1}$, these materials have potential for being used as materials for scaling-up the electrolyzers.

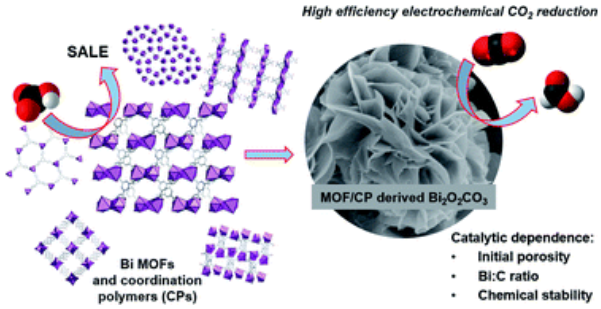


**Figure 2:** Bismuth-based coordination polymers applied to the electrochemical reduction of $CO_2$ to formate.

**From $^{13}CO_2$ to $^{13}CO$ to Carbon Labeling of Pharmaceutically Relevant Aliphatic Carboxylates**

Many commercial drugs, as well as upcoming pharmaceutically active compounds in the pipeline, display aliphatic carboxylic acids or derivatives thereof as key structural entities. Synthetic methods for rapidly accessing isotopologues of such compounds are highly relevant for undertaking critical pharmacological studies. CADIAC chemists have in 2021 disclosed in the *Journal of the American Chemical Society* a direct synthetic route allowing for full carbon isotope replacement via a nickel-mediated alkoxycarbonylation. Employing a nickel(II) pincer complex ([($N_2$N)Ni–Cl]) in combination with carbon-13 labeled CO (originating from $^{13}CO_2$), alkyl iodide, sodium methoxide, photocatalyst, and blue LED light, it was possible to generate the corresponding isotopically labeled aliphatic methyl carboxylates in good yields. Furthermore, the developed methodology was applied to the carbon isotope substitution of several pharmaceutically active compounds, whereby complete carbon-13 labeling was successfully accomplished. Particularly interesting is the good functional group tolerance of the chemistry developed. This chemistry has relevance for drug development programs.

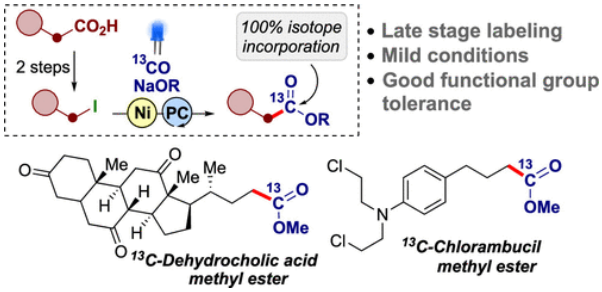


**Figure 3:** A novel methodology for introducing carbon-13 into pharmaceutically relevant compounds from $^{13}CO_2$.

**References**

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[2] Frank, S.; Grape, E. S.; Bøjesen, E. D.; Larsen, R.; Lamagni, P.; Catalano, J.; Inge, A. K.; Lock, N. Exploring the influence of atomic level structure, porosity, and stability of bismuth(III) coordination polymers on electrocatalytic $CO_2$ reduction. *J. Mater. Chem. A* **2021**, *9*, 26298–26310.

[3] Ton, S. J.; Neumann, K. T.; Nørby, P.; Skrydstrup, T. Nickel-Mediated Alkoxycarbonylation for Complete Carbon Isotope Replacement. *J. Am. Chem. Soc.* **2021**, *143*, 17816–17824.