Carbon Dioxide Activation Center 2021 - 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 2020 and start of 2021 are described below. It should be pointed out that the CADIAC publication record over the last 6 years has been outstanding with many publications in the *Journal of the American Chemical Society* and *Angewandte Chemie International Edition*. (See discussion on page 2 of the report). Furthermore, considerable additional funding has also been secured by CADIAC scientists to ensure that we have an active participation in developing viable solutions for a sustainable society.

Blood Porphyrin for the Catalytic Conversion of CO_2

Electrochemical CO_2 reduction to valuable chemicals represents a green and sustainable approach to close the anthropogenic carbon cycle, but has been impeded by the low efficiency and high cost of electrocatalysts. In an interdisciplinary effort between CADIAC teams in Aarhus and Rostock, CADIAC scientists have now completed a study on the use of a cost-effective hybrid catalyst consisting of hemin [chloroprotoporphyrin IX iron(III)], a product recovered from bovine blood, and adsorbed onto commercial Vulcan carbon.[1] Upon heat treatment this material shows significantly improved activity and selectivity for CO_2 reduction in water to carbon monoxide. Interestingly, the heat treatment leads to the decomposition of the iron porphyrin ring, restructuring to form atomic Fe sites. The optimized hybrid catalyst then allows a near-unity selectivity for reduction of CO_2 to CO at a small overpotential of 310 mV. The insight into the transformation of adsorbed Fe complexes into single Fe atoms upon heat treatment provides a guidance for the development of single atom catalysts. Particularly interesting with this method is that a waste product (bovine blood) is used to convert another waste product (CO_2) to a useful compound.

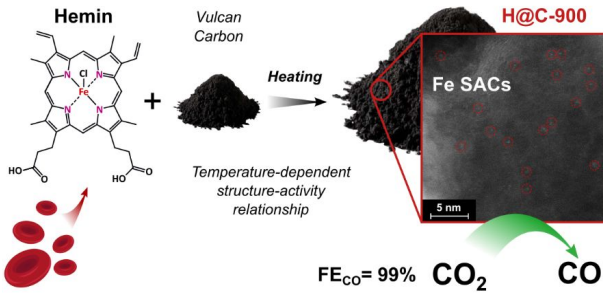

Figure 1: The conversion of bovine blood to a useful catalyst for CO_2 conversion.

A Novel Approach to CCU for the Synthesis of Formate

In a study published in *Chemical Science*,[2] CADIAC scientists at the LIKAT report a novel amino acid based reaction system for CO_2 capture and utilization (CCU) to produce formates in the presence of the naturally occurring amino acid L-lysine. Utilizing a specific ruthenium-based catalyst system, hydrogenation of absorbed carbon dioxide occurs with high activity and excellent productivity. Noteworthy, following the CCU concept, CO_2 can be captured from ambient air in the form of carbamates and converted directly to formates in one pot with high turnover numbers. This protocol opens new potential for transforming captured CO_2 from ambient air to C1-related products.

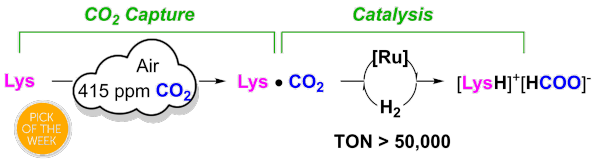

Figure 2: An example of a carbon capture and utilization methodology applying amino acids for the selective reduction of CO_2 to formate.

Applying CO_2 for Carbon Labelling of Carboxamides

Carbon isotope labelling methodologies are widely used by the pharmaceutical and agrochemical industry for understanding the metabolic profile of new active compounds. In a recent article in *Chemistry, A European Journal*, a team of CADIAC chemists reported on a novel carbon-13 isotope labelling technique for a series of pharmaceutically relevant small molecules and biopharmaceuticals bearing aliphatic carboxamides.[3] Key to the success of this novel isotope labeling technique is the observation that ^{13}C-labeled Ni^{II}-acyl complexes, formed from a ^{13}CO insertion step with Ni^{II}-alkyl intermediates, rapidly react in less than one minute with a specific disulfide to quantitatively form an activated ester. Two different CO releasing molecules can be used, both synthesized using ^{13}C-labeled carbon dioxide, allowing for the stoichiometric addition of isotopically labelled carbon monoxide. Subsequent one-pot acylation of a series of structurally diverse amines provides the desired ^{13}C-labeled carboxamides in good yields. Further optimization of the reaction parameters, opens up the possibility for carbon-11 labelling as well, which could also allow Positron Emission Tomography studies. Particularly noteworthy, is the adaptation of this isotope labelling strategy to the synthesis of the ^{13}C-labeled biomolecules liraglutide and insulin degludec, both representing important antidiabetic drugs from Novo Nordisk.

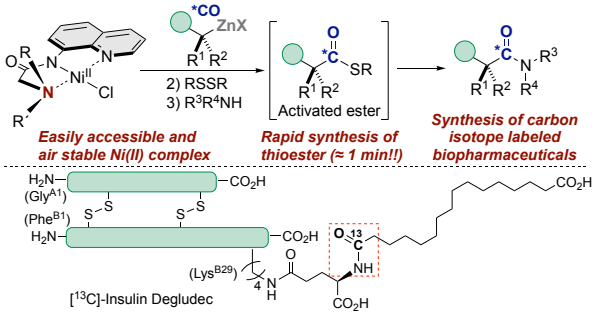

Figure 3: Applying Ni-complexes for specific carbon isotope labelling of carboxyamides in pharmaceutically relevant molecules.

References

[1] Miola, M.; Li, S.; Hu, X.-M.; Ceccato, M.; Surkus, A.-E.; Welter, E.; Pedersen, S. U.; Junge, H.; Skrydstrup, T.; Beller, M.; Daasbjerg, K. Highly scalable conversion of blood protoporphyrin to an efficient electrocatalyst for the CO_2-to-CO reduction, *Adv. Mater. Interfaces* **2021**, manuscript accepted for publication.

[2] Wei, D.; Junge, H.; Beller, M. An amino acid based system for CO_2 capture and catalytic utilization to produce formats, *Chem. Sci.* **2021**, DOI: 10.1039/D1SC00467K.

[3] Pedersen, S., Donslund, A. S., Mikkelsen, J., Bakholm, O., Papp, F., Jensen, K., Gustafsson, M., Skrydstrup, T. Rapid Nickel(II)-Mediated Thiocarbonylation as a Direct Route to Isotopically Labeled Aliphatic Carboxamides. *Chem. Eur. J.* **2021**, DOI: 10.1002/chem.202005261.