Carbon Dioxide Activation Center 2020 - 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 2019 and start of 2020 are described below. It should be pointed out that the CADIAC publication record over the last 5 years has been outstanding with many publications in the *Journal of the American Chemical Society* and *Angewandte Chemie International Edition*. (See discussion on page X of the report).

Bismuth-Based Metal-Organic Framework (MOF) as Precursor to Active Catalysts

The research groups of Nina Lock, Xinming Hu and Kim Daasbjerg recently published a paper in *Advanced Functional Materials*.[1] CADIAC scientists have demonstrated that a bismuth-based metal-organic framework (MOF) can be used as starting material to form a selective CO_2-to-formate converting electrocatalyst. The active material consists of bismuth nanoparticles embedded in a porous organic matrix. By using a microporous MOF as starting material, the catalytic bismuth sites are highly accessible, leading to a very high activity per mass load of bismuth in the catalyst. The material is outperforming most other nanostructured bismuth materials. This study is one of the most detailed to date combining electrochemical screening with in-depth structural studies, revealing the mechanism of the transformation from the MOF into the active catalyst at reducing potentials.

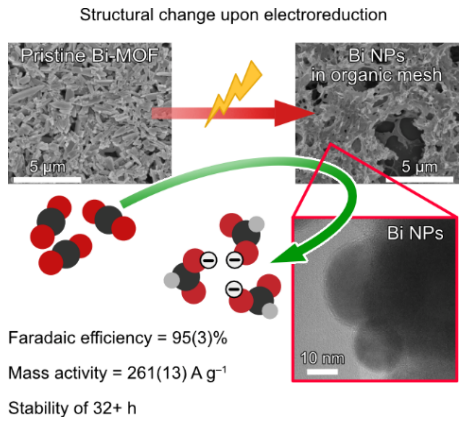

Figure 1: A bismuth-based metal-organic framework trans-forms into an active catalyst for selective CO_2-to-formate conversion.

Applying CO_2 for Carbon Labeling of β-Amino Acids

In a study published in the *Journal of the American Chemical Society*,[2] CADIAC scientists report on a new late-stage carbon isotope-labeling technique, exploiting $^{13}CO_2$ as the origin of the isotope label. β-Amino acids are a class of structural motifs, which have received much interest in the construction of bioactive peptides. Techniques for the rapid carbon isotope labeling can be useful in drug development programs for pharmacokinetic studies. In this work, a series of ^{13}C-labeled acyl nickellacycles have been efficiently prepared via the carbonylation of 4-membered azametallacycles with stoichiometric ^{13}C-labeled carbon monoxide generated from $^{13}CO_2$, and their reactivity has been studied. Subjecting these organometallic scaffolds to a variety of nucleophiles allowed for the isolation of ^{13}C-labeled β-amino acids and derivatives thereof, as well as β-amino ketones. The utility of the metallacycles was demonstrated by the rapid synthesis of a ^{13}C-labeled variant of the blockbuster anti-diabetic drug sitagliptin. We envision that these air-stable Ni-acyl complexes will provide new opportunities for the selective incorporation of carbon isotopes into bioactive molecules.

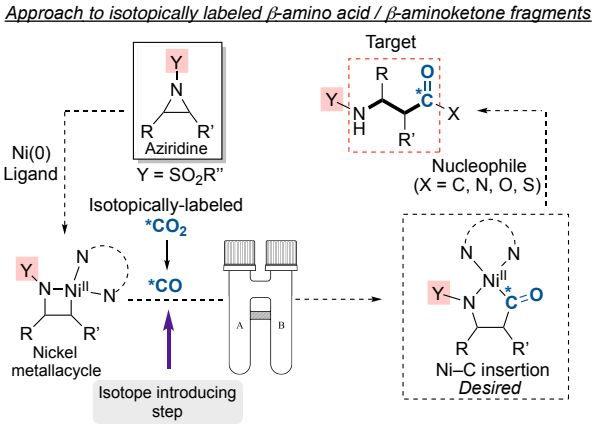

Figure 2: An approach to the carbon isotope-labeling of β-amino acids applying nickel metallacycles.

Controlling CO_2 Reduction with New Catalysts

In a recent article from CADIAC in the *Journal of the American Chemical Society*,[3] the research groups of Kim Daasbjerg, Troels Skrydstrup, and Mu-Hyun Baik (Korean Advanced Institute of Science and Technology) collaborated to design a range of engineered catalysts for the reduction of CO_2. The reduction products can be tuned to either produce preferentially carbon monoxide or formic acid depending on small structural changes to the ligand surrounding the manganese metal center. Interestingly, the designed catalysts are also among the most active molecular catalysts for the conversion of CO_2 to formic acid. This study highlights the importance of an interdisciplinary collaboration combining chemical synthesis, electrochemical techniques and calculations to design and understand the catalyst activity.

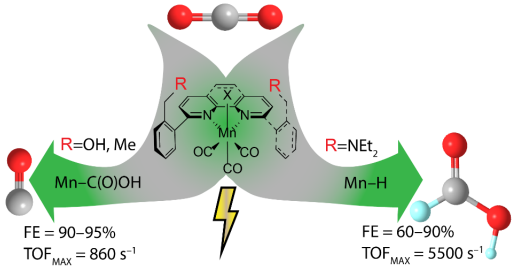

Figure 3: Controlled CO_2 reduction to either CO or formic acid depending on the catalyst design.

References

[1] Lamagni, P.; Miola, M.; Catalano, J.; Hvid, M. S.; Mamakhel, M. A. H.; Christensen, M.; Madsen, M. R.; Jeppesen, H. S.; Hu, X.-M.; Daasbjerg, K.; Skrydstrup, T.; Lock, N. *Adv. Funct. Mater.* **2020**, doi:10.1002/adfm.201910408.

[2] Ravn, A. K.; Vilstrup, M. B. T.; Nørby, P.; Nielsen, D. U.; Daasbjerg, K.; Skrydstrup, T. *J. Am. Chem. Soc.* **2019**, *141*, 11821.

[3] Rønne, M. H.; Cho, D.; Madsen, M. R.; Jakobsen, J. B.; Eom, S.; Escoudé, É.; Hammershøj, H. C. D.; Nielsen, D. U.; Pedersen, S. U.; Baik, M.-H.; Skrydstrup, T.; Daasbjerg, K. *J. Am. Chem. Soc.* **2020**, *142*, 4265.