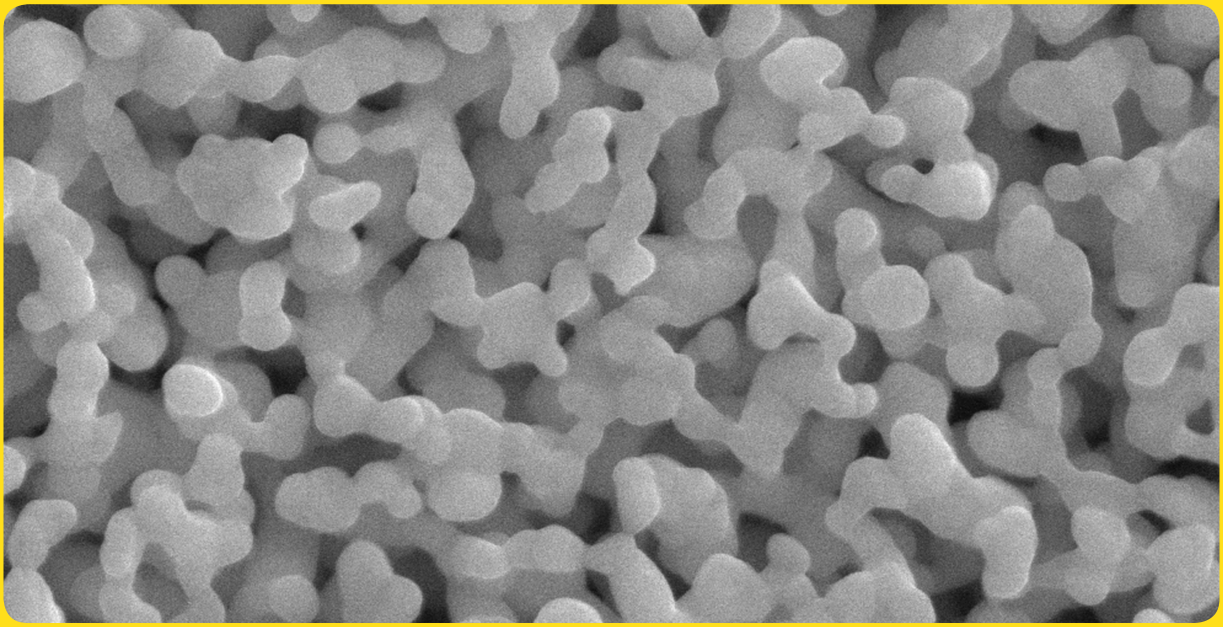
Center for Catalytic Science & Technology

Departments of Chemical & Biomolecular Engineering and Chemistry & Biochemistry



CCST Spring 2014 Highlights

The faculty and students of the Center for Catalytic Science and Technology have made a number of remarkable discoveries in the year 2013. This short publication highlights a number of these discoveries that we think are of general interest to the industrial catalysis community and to those interested in advancing the frontiers of catalysis science.

The discoveries span two novel and selective electrocatalysts for the selective reduction of CO_2 into CO (see Jiao and Rosenthal), new insights into the site requirements for efficient ammonia decomposition by innovative computational techniques (Vlachos), a new type of covalent 3D framework material with good basic catalysis properties (Yan) and others. This is but a small sample of all the ongoing work at the CCST and reflects the vitality and creativity of the CCST research groups, a hallmark of the center's culture that help us attract some of the best graduate students and postdoctoral fellows in the country. We invite you to visit our website or to call us to find out more about current research activities and potential collaborations with CCST faculty.

Raul F. Lobo
CCST Director

Efficient electrocatalyst for carbon dioxide reduction

• Feng Jiao
Chemical & Biomolecular Engineering

CO_2 capture and sequestration topic is an important technology for the reaction of anthropogenic green house gas emissions. A wide range of approaches have been proposed, while the efficiency and selectivity are always the challenge. In the CCST, we are actively pursuing the idea of converting CO_2 to CO, an important feedstock for producing synthetic fuels via the Fischer-Tropsch process and or producing methanols. We recently discovered a nanoporous silver catalyst, able to electrochemically convert carbon dioxide into carbon monoxide very selectively and efficiently (Figure 1). The catalyst fabrication is straightforward and scalable; suitable for a large scale manufacturing. By tuning the synthetic conditions, we could control the properties of the resulting nanoporous catalyst for optimal performance. The porous structure* creates an extremely large surface area for catalytic reaction and the curved internal surface generates a large number of highly active step sites for CO_2 conversion, resulting in an exceptional activity that is much higher than that of the polycrystalline counterpart at a moderate overpotential of < 500 mV. Such a remarkable activity for CO_2 electroreduction has been achieved with a CO Faradaic efficiency of 92%. The significance of this novel catalyst relies on the unique capability to lower the activation energy of carbon dioxide reduction by stabilizing the reactions intermediates on its highly curved internal surface, resulting in the highest carbon dioxide to carbon monoxide reaction rate and energy efficiency ever achieved. This work has been published in Nature Communications and has been widely reported in media outlets.

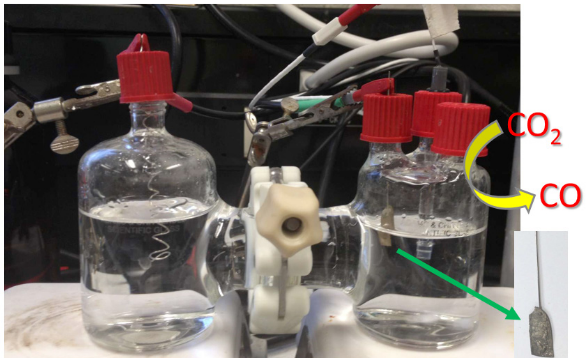


Figure 1. An electrochemical reactor for CO_2 reduction to CO.

1. Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen & F. Jiao. A selective and efficient electrocatalyst for carbon dioxidereduction. Nat. Commun. 5:3242 doi: 10.1038/ncomms4242 (2014)

* Front cover image

In silico prediction of bimetallic catalysts

• Dion Vlachos
Chemical & Biomolecular Engineering

The in silico prediction of active and selective catalysts has been a long standing goal of the catalysis community. First-principles microkinetic models have recently set the foundations for the discovery of active and selective catalysts and in particular of core-shell nanostructures whose properties are not an interpolation of those of the parent metals and are often superior to single metal catalysts.

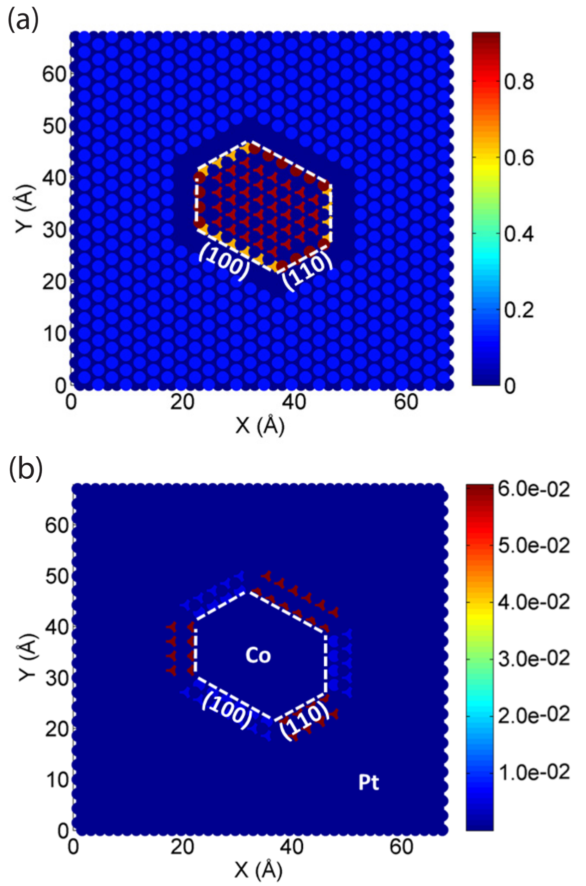


Figure 2. (a) Map of N local coverage at maximum activity during temperature programmed desorption of Co clusters on a Pt(111) terrace. (b): Map of average association rate in the temperature range 600-720 K (events per second per site for each site type). The white dashed lines indicate the edges of the hexagonal Co cluster on Pt(111). (110) and (100) steps are marked. N segregates on the most strongly adsorbing metal (Co) and spills over to interfacial sites along and across steps to readily desorb to the gas-phase. (110) steps are the most active sites followed by (100) steps and potentially sites along steps, with the rest of the catalyst serving as a reservoir of N.

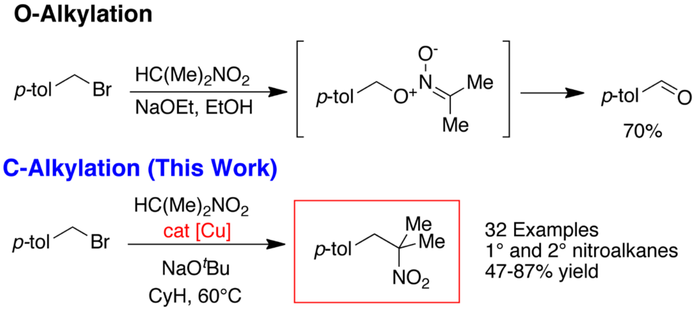
Yet, these models lack site specificity and microstructure information. We have introduced first-principles kinetic Monte Carlo simulations to understand the active site, site cooperativity, and the effect of loading of the second metal and the overlayer microstructure on catalyst performance. The results have clearly shown, for the ammonia decomposition as a test reaction, that ideal monolayer bimetallics are poor catalysts. Instead, *incomplete* monolayers are essential for high activity by creating active sites at the interface between the two metals (Figure 2b). Multiple active sites are discovered, and the activity of a site alone cannot explain catalyst performance; that is, the coverages at these sites (Figure 2a) are also important. As a result, a simplistic single binding energy descriptor on ideal catalysts fails to describe reactivity. The model results are in quantitative agreement with experimental data and rationalize the paradox of Co/Pt binding nitrogen (N) more weakly than Ni/Pt but being a less effective catalyst than Ni/Pt in ammonia decomposition. The success of the model holds the promise that we can not only predict important bimetallics but also quantitatively rank them and identify the optimal loading of the shell.

1. D. A. Hansgen, D. G. Vlachos, and J. G. Chen, First Principles-Based Bimetallic Catalyst Prediction: An Application to the Ammonia Decomposition Reaction. Nature Chem. 2(5), 484-489, (2010).
2. W. Guo, M. Stamatakis, and D. G. Vlachos, Design Principles of Heteroepitaxial Bimetallic Catalysts. ACS Catal. 3(10), 2248-2255, (2013). DOI:10.1021/cs4005166.
3. W. Guo, and D. G. Vlachos, On factors controlling activity of submonolayer bimetallic catalysts: Nitrogen desorption. J. Chem. Phys. 140(1), 7, (2014). DOI:10.1063/1.4855235.

Transition Metal Catalyzed Methods for Preparing Nitroalkanes and Alkyl Amines

• Donald Watson
Chemistry & Biochemistry

The Watson Group has been awarded a $1.47M grant to develop new catalytic reactions of nitroalkanes. Nitroalkanes are extremely versatile and important building blocks in the synthesis of complex organic compounds, including pharmaceutical agents and other biologically active molecules. While nitroalkanes participate in a wide range of reaction, the simple alkylation of nitroalkanes using alkyl halides has remained an unmet challenge in synthetic chemistry for more than a century. Recently, the Watson group developed a novel copper catalyst capable of alkylating nitroalkanes using benzyl bromides. For the first time, this new reaction allows for the alkylation of nitroalkanes under mild, synthetically useful conditions. This grant will allow the Watson group to continue to investigate this important new catalytic process, as well as several additional new catalytic reactions of nitroalkanes. This work is expected to greatly expand the utility of nitroalkanes in synthesis, and the preparation of complex organic molecules that can be derived from them.

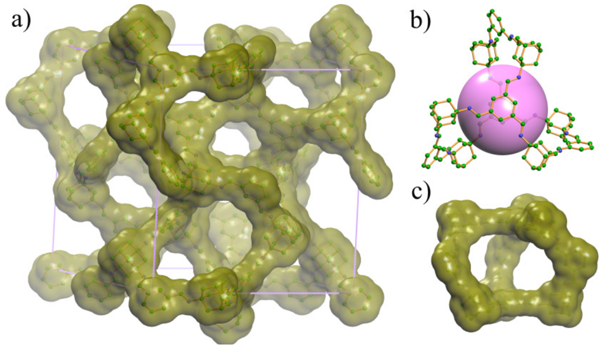


1. P.G. Hildner, A.A.S. Gietter, D. Cui and D.A. Watson, Benzylation of Nitroalkanes Using Copper-Catalyzed Thermal Redox Catalysis: Toward the Facile C-Alkylation of Nitroalkanes, J. Am. Chem. Soc., 2012, 134 :9942–9945 DOI: 10.1021/ja304561c.

3D microporous base-functionalized covalent organic frameworks (COFs)

• Yushan Yan
Chemical & Biomolecular Engineering

The design and synthesis of 3D covalent organic frameworks (COFs) have been a challenge and the demonstrated applications of 3D COFs have so far been limited to gas adsorption. The Yan's group has recently designed and synthesized two new 3D microporous base-functionalized COFs, termed BF-COF-1 and BF-COF-2, by the use of a tetrahedral alkyl amine, (1,3,5,7-tetraaminoadamantane) combined with 1,3,5-triformylbenzene (TFB) or triformylphloroglucinol (TFP). Both BF-COFs showed remarkable conversion (96% for BF-COF-1 and 98% for BF-COF-2), high size selectivity, and good recyclability in base-catalyzed Knoevenagel condensation reactions. This study suggests that porous functionalized 3D COFs could be a promising new class of shape-selective catalysts.

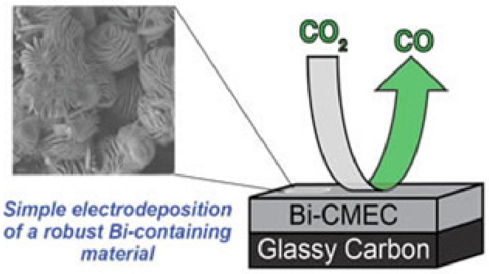


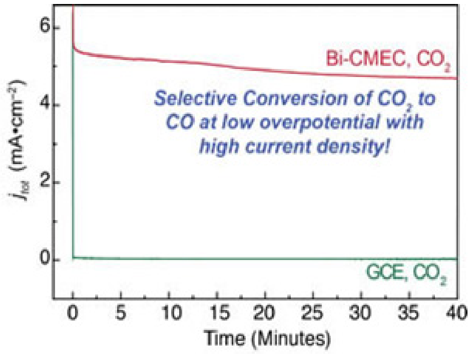
1. Q. R. Fang, S. Gu, J. Zheng, Z. B. Zhuang, S. L. Qiu, Y. S. Yan, 3D Microporous Base-Functionalized Covalent Organic Frameworks for Size-Selective Catalysis, Angew. Chem. Int. Ed., 2014, DOI: 10.1002/ange.201310500

New and Effective Carbon Monoxide Evolving Catalyst

• Joel Rosenthal
Chemistry & Biochemistry

Rosenthal's group is taking advantage of new methods to control the selectivity and efficiency of catalytic processes using novel homogeneous complexes and heterogeneous materials. In addition to studying photoactive compounds that display a notable multielectron photochemistry for solar light harvesting and small-molecule activation, Rosenthal's lab has also developed an inexpensive and environmentally benign bismuth based catalyst for reduction of CO_2 to a fuel. This platform drives the selective conversion of CO_2 to CO with exceptionally high-energy efficiency, the magnitude of which has historically only been observed using expensive materials containing noble metals such as gold and silver. The development of this inexpensive Bismuth-Carbon Monoxide Evolving Catalyst (Bi-CMEC) represents a potentially transformative advance to the fields of electrocatalysis, molecular energy conversion and renewable energy storage. Rosenthal's group communicated their Bi-CMEC invention in 2013 in the Journal of the American Chemical Society.[1] The development of this catalyst system was highlighted by Chemical and Engineering News among others. Rosenthal's lab has filed a patent for the Bi-CMEC invention, which is currently being incorporated into a high efficiency reactor for production of CO from CO_2 waste streams. Rosenthal's recent achievements in catalysis, CO_2 activation and molecular energy conversion have been recognized through a Camille and Henry Dreyfus Environmental Chemistry Fellowship, an Alfred P. Sloan Research Fellowship and an NSF-CAREER award.





1. DiMeglio, John L.; Rosenthal, Joel. "Selective Conversion of CO_2 to CO with High Efficiency Using an Inexpensive Bismuth-Based Electrocatalyst", J. Am. Chem. Soc. 2013 135, 8798-8801.

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UPDATE

Save the Date

2014 CCST Research Review

October ~~22~~ 15, 2014 (3:00 pm - 6:00 pm)
October ~~23~~ 16, 2014 (8:00 am - 3:30 pm)