EFRC: CENTER FOR UNDERSTANDING AND CONTROL OF ACID GAS-INDUCED EVOLUTION OF MATERIALS FOR ENERGY (UNCAGE-ME)

UPDATED: OCTOBER 2016

AWARDS: $11.6M (August 2014 – July 2018)

WEBSITES: http://science.energy.gov/bes/efrc/centers/uncage-me/; http://efrc.gatech.edu/

TEAM: **Georgia Institute of Technology (Lead):** Krista Walton (Director), Michael Filler, Phillip First, Christopher Jones, Ryan Lively, Sankar Nair, Thomas Orlando, David Sholl; **Lehigh University**: Jonas Baltrusaitis, Israel Wachs; **Oak Ridge National Laboratory**: Sheng Dai, Gernot Rother, Tjerk Straatsma, Bobby Sumpter, Zili Wu; **Pennsylvania State University**: Susan Sinnott; **University of Alabama**: David Dixon; **University of Florida**: Sergey Vasenkov; **University of Wisconsin**: JR Schmidt; **Washington University in St. Louis**: Sophia Hayes

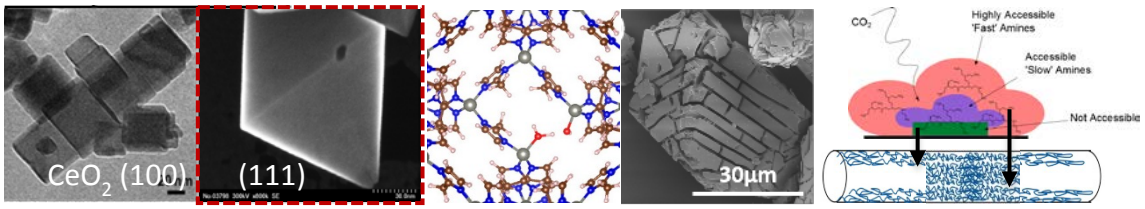
SCIENTIFIC MISSION AND APPROACH

UNCAGE-ME seeks to provide a fundamental understanding of acid gas interactions with solid materials through integrated studies of the interaction of key acid gases (CO_2, NO_2, NO, SO_2, H_2S) with a broad range of materials. The center combines the application of *in situ* molecular spectroscopic studies with complimentary modeling techniques to develop a deep knowledge base with a broad class of materials that will ultimately accelerate materials discovery for large-scale energy applications. The center conducts research in three major thrust areas:

1) **Model Metal Oxides**: Develops a molecular level understanding of the surface chemistry of acid gas interactions with model sorbents and catalysts and their structural evolution.
2) **Ordered Porous Materials**: Explores the effects of local defects, linkers and metal centers of metal-organic frameworks to tune adsorption interactions and determine structural features that control (in)stability.
3) **Disordered Porous Materials**: Seeks to build on knowledge base of model oxide and ordered porous systems to understand heterogeneous systems and to develop a body of knowledge relating support structure/polymer/heteroatom/defects to interaction and stability in the presence of acid gases.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Demonstrated the influence of synthesis methods of state-of-the-art supported metal oxide catalysts for selective catalytic reduction of NO by NH_3: characterizations revealed that unique defect sites were introduced for one synthetic method over the other and resulted in increased catalytic activity.
- Computational characterization of ZIF-8 MOFs found that defects and vacancies provide the starting points for material degradation upon acid gas exposure, which is consistent with observations from model oxide studies.
- Demonstrated the ability to tune kinetic water stability in MOF-74 through proper combination of metal sites while still maintaining high CO_2 adsorption capacities under flue gas conditions.
- Identified distinct differences in the stability of porous organic cages towards SO_2 exposure depending on the chirality of cage linkers and demonstrated stability through use of racemic mixtures.
- Investigations of polymer morphology in aminopolymer-silica composites yielded insights into sorbent efficacy that provide guidelines for the design of sorbent systems with improved kinetics and efficiency for CO_2 capture.



UNCAGE-ME research, from left: ceria nanocrystals with well-defined surface facets provide a model system to study acid gas interactions; defects in ZIF-8 are the starting point of acid gas degradation; grain boundaries in porous organic cages accelerate degradation; insights into polymer morphology of aminopolymer-oxide composite sorbents provide guidelines for designing sorbents with improved kinetic performance as well as CO_2 capture efficiency.

IMPACT

- Several EFRC PIs have won national awards including Hayes (2015 ACS Saint Louis Award), Jones (2016 AIChE Andreas Acrivos Award for Professional Progress in Chemical Engineering), Wachs (2015 Lee Hsun Lecture Award of the Chinese Academy of Sciences), and Walton (2015 ACS Women Chemists' Committee Rising Star Award and 2016 AIChE FRI/John G. Kunesh Award for Outstanding Contributions to Separations Technologies)
- Penn State (Sinnott) has developed molecular models and new force field parameters for the COMB3 potential that allows for molecular modeling of titanium carbide-derived carbons. These parameters were distributed to the community via the LAMMPS website. (http://lammps.sandia.gov/)
- Georgia Tech (Lively/Sholl) published a perspective article in *J. Phys. Chem. Letters* (reference in the list below) and produced a short YouTube video (with help from Walton) for the American Chemical Society to describe their findings (https://www.youtube.com/watch?v=1BS2oKeE9aM). This video was also highlighted in the science blog "The Leap" (http://www.scilogs.com/the-leap/researchers-get-fancy-with-an-iggy-azalea-inspired-journal-submission/).
- EFRC PI Filler established a new podcast called Nanovation, a forum to address the big questions, challenges, and opportunities of nanotechnology. Sixteen episodes are currently available at http://www.fillerlab.com/nanovation/.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of Oct 2016, UNCAGE-ME had published 41 peer-reviewed publications cited over 150 times. The following is a selection of impactful papers:

- Holewinski, A.; Sakwa-Novak, M. A.; Jones, C. W. Linking CO_2 Sorption Performance to Polymer Morphology in Aminopolymer/Silica Composites through Neutron Scattering. *Journal of the American Chemical Society* **137**, 11749-11759, doi:10.1021/jacs.5b06823 (2015). [**12 citations**]
- Jiao, Y. *et al.* Tuning the Kinetic Water Stability and Adsorption Interactions of Mg-MOF-74 by Partial Substitution with Co or Ni. *Industrial & Engineering Chemistry Research* **54**, 12408-12414, doi:10.1021/acs.iecr.5b03843 (2015). [**11 citations**]
- Sholl, D. S.; Lively, R. P. Defects in Metal-Organic Frameworks - Challenge or Opportunity? *The Journal of Physical Chemistry Letters* **6**, 3437-3444, doi:10.1021/acs.jpclett.5b01135 (2015). [**22 citations**]
- Tumuluri, U. *et al.* Surface Structure Dependence of SO_2 Interaction with Ceria Nanocrystals with Well-Defined Surface Facets *Journal of Physical Chemistry C* **119**, 28895-28905, doi:10.1021/acs.jpcc.5b07946 (2015). [**3 citations**]
- Zhang, C. *et al.* Computational Characterization of Defects in Metal-Organic Frameworks: Spontaneous and Water-induced Point Defects in ZIF-8 *The Journal of Physical Chemistry Letters* **7**, 459-464, doi:10.1021/acs.jpclett.5b02683 (2016). [**8 citation**]
- He, Y. *et al.* Influence of Synthesis Method on Selective Catalytic Reduction (SCR) of NO by NH_3 with V_2O_5-WO_3/TiO_2 Catalysts *Applied Catalysis B* **193**, 141-150, doi:10.1016/j.apcatb.2016.04.022 (2016) [**2 citations**]
- Zhu, G. *et al.* Engineering Porous Organic Cage Crystals with Increased Acid Gas Resistance *Chemistry- A European Journal* **22**, 10743-10747, doi:10.1002/chem.201601659 (2016). [**0 citations**]