The Center for Understanding & Control of Acid Gas-Induced Evolution of Materials for Energy

Mission Statement: To develop a deep knowledge base in the characterization, prediction, and control of acid-gas interactions with a broad class of materials to accelerate materials discovery for large-scale energy applications.

UNCAGE-ME’s core research model is to use a variety of in-situ experimental tools coupled with complimentary modeling techniques to improve the performance of materials in acid gas environments and to advance materials discovery.

http://efrc.gatech.edu

Major Challenges:
(1) Mechanisms of acid gas interactions with complex materials are poorly understood
(2) Ability to predict or prolong lifetimes of functional materials is limited
Scientific Organization of UNCAGE-ME

1. **Model Metal Oxides**: Surface chemistry of acid gas interactions with model sorbents and catalysts and their structural evolution. (Lead: Zili Wu, ORNL)

2. **Ordered Porous Materials**: Effects of local defects, linkers and metal centers of MOFs to tune adsorption interactions and determine structural features that control (in)stability. (Lead: David Sholl, GT)

3. **Disordered Porous Materials**: 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. (Lead: Chris Jones, GT)

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**Highlight 1: Mechanisms of acid gas interactions with complex materials: how dangling bonds and surface oxygens impact degradation and reactivity**

Dangling bonds and metal vacancies in MOFs and surface defects in metal oxides lead to increased reactivity with acidic species (sulfuric acid, sulfurous acid, nitric oxide).

For ZIF-8, small concentrations of defects lead to protonation of N in the imidazole ring, resulting in cleavage of Zn-N bonds and degradation of structure upon exposure to humid SO$_2$.

Dangling ligands in MIL-125 form from breaking 2 Ti-O bonds by reaction with: (i) 2 water molecules and (ii) a water and a H$_2$SO$_3$ molecule. Adding –NH$_2$ functional group to BDC ligand prevents the formation of these dangling bonds and stabilizes the MOF.


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Preparation of VO\textsubscript{x}-WO\textsubscript{x}/TiO\textsubscript{2} catalysts using co-precipitation method creates additional O=VO\textsubscript{3} and O=WO\textsubscript{4} sites anchored to defects in the TiO\textsubscript{2} support.

Selective catalytic reduction (SCR) experiments: N\textsubscript{2} evolution results indicate 1V5WTi(C) is most active for SCR.

Co-precipitated 1V5WTi(C) and impregnated 1V5WTi(I) catalysts possess the same composition and surface area, but the co-precipitated catalyst displays higher activity for SCR of NO, forming \(~50\%\) more N\textsubscript{2} than the impregnated catalyst reflecting the presence of more reactive surface ammonia species on the co-precipitated catalyst.

He, Y. et al., *Applied Catalysis B: Environmental*, 2016, 188, 123.\ He, Y. et al., *Applied Catalysis B: Environmental*, 2016, 193, 141.
Highlight 2: Creating sulfur tolerant sorbents and catalysts through control of crystal facets and grain boundaries

Crystal facets dictate surface basicity and accessibility to acid species, which control propagation of degradation from the surface throughout the particle.

The mechanism for degradation appears to follow a shrinking-core model, with surface imidazolates being replaced by hydroxyls. Computational investigations support this and suggest that the reaction is more favorable on the \{110\} facet than the \{100\} facet due to steric constraints.

Pang, SH et al., Chemistry of Materials, 2016, 28, 6960.

Structure and binding strength of adsorbed species from \(\text{SO}_2\) depend on shape of \(\text{CeO}_2\) nanocrystals.
* Rods have the most surface defects (greatest amount of oxygen); most unstable
* Octahedra ceria is most stable and desorbs \(\text{SO}_2\) most readily at low temperature

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CC3-based porous organic cages (POCs) were studied for stability against SO$_2$ contamination. Distinct differences in the stability of CC3 cages were observed depending on the chirality of the diamine linkers. Confocal microscopy suggests this is due to decreased packing defects in the racemic crystals.

Impactful Capabilities Developed by UNCAGE-ME

**New Hazardous Gas Laboratory at GT**

**New Computational Capabilities:**

**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/).

**Alabama (Dixon)** has developed computational approaches for the prediction of Lewis acid gas interactions with metal oxide nanoclusters and ZIFs/MOFs. The electronic structure methods include density functional theory and correlated molecular orbital theory at the coupled cluster CCSD(T) level.
Overview of Activities to Promote Synergy and Collaboration

1. Callaway Gardens
   Student/Postdoc Retreat (10/16)
   Team building exercises
   (ziplining/obstacle course); Poster sessions; Evening presentation by
   David Sholl

2. Team building in Escape Rooms at the All Hands Meeting (3/17) in Atlanta

3. Research Enhancement Visits (year round)
   Students/postdocs visit collaborator labs for 1-4 weeks
Schedule of Oral Presentations

1. Zili Wu (ORNL) “Role of Surface Structure and Dopants on the Interaction Between Acid Gases and Metal Oxide Catalysts”
   – Session C. Catalysis, Tue 8:50 - 9:10 am

2. Ryan P. Lively (GT) “Engineering Nanoporous Materials with Increased Acid Gas Resistance”
   – Session G. Separation Science, Tue 8:30 - 8:50 am

3. Bobby G. Sumpter (ORNL) “Linking Morphology and Interfacial Interactions to Acid Gas Uptake”
   – Session G. Separation Science, Tue 9:10 - 9:30 am

4. Robert M. Marti (WUSTL); Joshua D. Howe(GT), “Understanding Structure and Dynamics of CO2 Adsorbed in Open-Site Metal-Organic Frameworks” Competition
   – Session G. Separation Science, Tues 9:50-10:10am
Schedule of Poster Presentations

   – Session I. Synthesis Science, Mon 5:00-6:30pm
   – Session J. Materials and Chemistry by Design, Mon 5:00-6:30pm
   – Session I. Synthesis Science, Tue 3:30-5:00pm
   – Session I. Synthesis Science, Tue 3:30-5:00pm
   – Session J. Materials and Chemistry by Design, Tue 3:30-5:00pm