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Title: Some General Themes in Catalysis at LANL

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Some General Themes in Catalysis at LANL

- Storage and release of energy within chemical bonds (e.g. H₂ storage in and release from covalent bonds, N₂ functionalization, CO₂ functionalization, H₂ oxidation/evolution, O₂ reduction/evolution).
- Can we control the chemistry of reactive substrates to effect energy relevant transformations in non-traditional media (e.g. can we promote C-C couplings, dehydrations, or hydrogenations in water under relatively mild conditions)?
- Can we supplant precious metal or rare earth catalysts to effect these transformations, by using earth abundant metals/elements instead? Can we use organocatalysis and circumvent the use of metals completely?
- Can we improve upon existing rare earth catalyst systems (e.g. in rare earth oxides pertinent to fluid cracking or polymerization) and reduce amounts required for catalytic efficacy?

Some Recent Examples from LANL

A. Upgrading of (Non-Food Based) Biomass Derived Molecules into Fuels

switchgrass

wood residue

Catalysis

High Energy Density
 C_8-C_{15} Fuels

Carbohydrates can be accessed from non-food based biomass sources such as woody residues and switchgrass. After extracted from the plant source, our goal is to upgrade these classes of molecules into useful fuels.

Converting Sugars and Derivatives into Hydrocarbons

**“Method of Carbon Chain Extension using Novel Aldol Reaction”,
US patent application 20110040110, filed August 17th, 2009.**

**“Compounds and Methods For the Production of Long Chain Hydrocarbons From Biological Sources”,
1st US Provisional Patent (Application No. 61/534,496), filed September 14th, 2011; 2nd Provisional Patent
(Application No. 61/669,775), filed July 10th, 2012.**

We have also demonstrated the production of hydrocarbons directly from oligosaccharides:

**“One Step Conversion of Oligomeric Starch or Cellulose to Single C₁₀ or C₁₁ Carbon Chains Furans and their
Conversion to Fuel Hydrocarbons”, US provisional patent application 61/669,980, filed July 10th, 2012.**

N₂ Functionalization Chemistry

The industrial production of ammonia (NH₃) from dinitrogen (N₂) and hydrogen (H₂) is integral to U.S. and world-wide food supplies

- Responsible for *ca.* 50% of the nitrogen in our bodies
- 10⁸ tons/year of NH₃ is produced
- > 1% of the world's total energy output is consumed by this *single process*

While the reaction is thermodynamically favorable ($\Delta H^0 = -45.2 \text{ kJ mol}^{-1} \text{ NH}_3$), the large activation barrier ($E_A = 420 \text{ kJ mol}^{-1}$) is responsible for the energy-intensive reaction conditions ($\sim 500^\circ \text{C}$ and $\sim 200 \text{ atm}$)

Impact of catalysis under mild conditions: Meaningful decrease in the collateral effects of energy generation

Approach

- Develop an Fe-based catalyst (Global scale considerations)
- Cooperative weakening of the N-N bond in order to decrease the number of intermediates (and possible decomposition pathways)
- Develop an Fe(0)/Fe(III) reduction cycle

N-N bond: 1.21, 1.22 Å (2 molecules/unit cell)
free N₂: 1.10 Å
 $\nu_{\text{NN}} = 1501 \text{ cm}^{-1}$, free N₂: 2331 cm⁻¹

John Gordon, Neil Henson, Fran Rein, Nathan Smythe, *et.al.*

Conversion of CO₂ into MeOH

- Current research (Stephan *et al.*, Denning *et al.*) shows conversion of CO₂ to MeOH non-catalytically at RT with frustrated Lewis pairs (FLPs).
- FLPs destroyed on MeOH release on H₂O addition.
- Our goal – develop air/water/acid tolerant FLPs to bind CO₂ to facilitate ***catalytic*** conversion of CO₂ to MeOH.

Andy Sutton, Nathan Smythe, *et al.*

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Base Metal Hydrogenations

Cobalt catalyst hydrogenates alkenes, ketones, and aldehydes

- Maintains activity in the presence of water:

Susan Hanson, et. al.

Non-Precious Metal Oxygen Reduction Catalysts for Fuel Cells

Catalyst SEM: Layered-graphene sheet marked with green arrow; FeCo-containing nanoparticle shown with red arrow.

- Pt-based fuel cell catalysts currently representing *ca.* 25% of the entire fuel cell system cost
- Graphene-rich polyaniline-derived catalysts, e.g. PANI-FeCo-C, combining for the first time: (a) high activity (close to that of Pt); (b) high stability; (c) excellent selectivity (O₂ reduction to H₂O not H₂O₂); and (d) low cost – **a major progress in polymer electrolyte fuel cell technology**

Thin Rare Earth Oxide (REO) Films for Critical Material Needs

Challenge/Motivation

- Improve understanding of f-electron contributions to physical and chemical properties of rare earth oxides (REO)-Materials Genome
- Materials optimization through control of microstructure in thin film REO catalyst materials (Nd, Pr, Ce, La)

Goal/Deliverable

- Predict and control REO properties using advanced modeling, spectroscopy, and synthesis
- Optimized REO thin film catalysts that reduce dependence on rare earth elements

Approach:

- High quality epitaxial thin films of REO using polymer assisted deposition technique
- Leverage our actinide oxide successes in synthesis, structure-property control, and theory
- Band gap, XRD, TEM, electronic structure measurements (ARPES), XAFS and XANES, including *in-situ* measurements, to advance theory and materials design

Control of UO_2 oxidation via substrate choice
(*in-situ* XRD studies).

- Synthesis and Characterization: Bauer, Holesinger, Jia, McCleskey, Scott
- Theory: Martin
- Electronic Structure: Joyce, Durakiewicz
- EXAFS/XANES: Conradson, Kozimor