Argonne NATIONAL LABORATORY

2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

3.3.1.11. Selective Deoxygenation Catalysts

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Bio-Oil Technology Area Review

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U.S. DEPARTMENT OF ENERGY

Goal/Objective Statement

- Develop and demonstrate catalysts synthesized by Atomic Layer Deposition for long-lived service in deoxygenation of biomass pyrolysis oil.
- FOA – none
- Effective and long-lived catalysts are essential to all pathways

Project Quad Chart Overview

Timeline

- Project Start date: Sept 30, 2012
- Project end date: Sept. 30 2014
- 25%

Barriers

- Barriers addressed
  - Tt-G

Budget

Total project funding (DOE & cost share) = $860K
Funding received in FY 2011 (DOE & cost share)
Funding in FY 2012 – 0
Funding for FY 2013 – $260K
ARRA Funding – N/A
Years the project has been funded & average annual funding – 1 year @ $260K

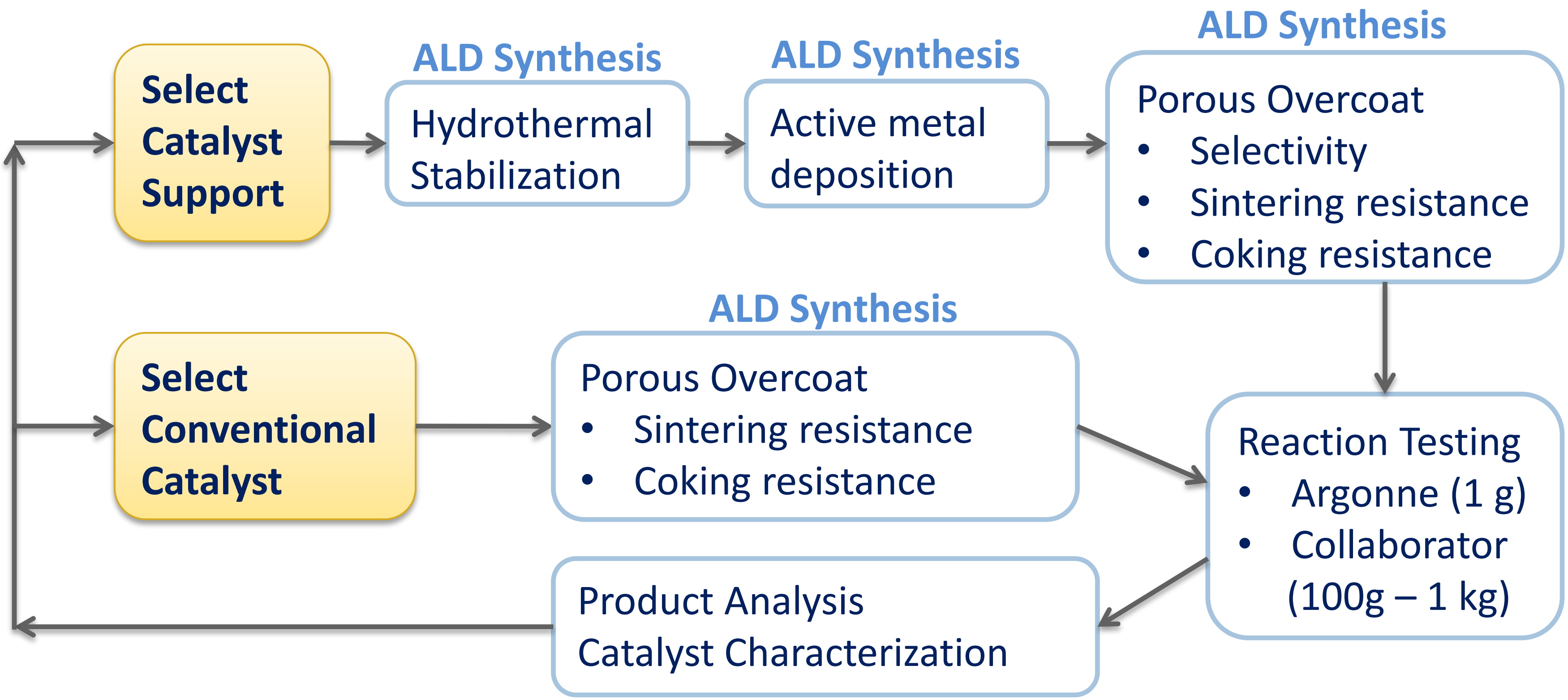
Partners & Roles

- Catalyst synthesis and testing are in-house for the early stages of the project. Close collaboration with the IACT EFRC at Argonne.
- Pyrolysis oil samples will be obtained by request or purchase from NREL and/or R. Brown (ISU)

Project Overview

- This project addresses technical barrier Tt-G using the unique capabilities of atomic layer deposition (ALD) to synthesize catalysts.

- Catalyst Development Flowchart :

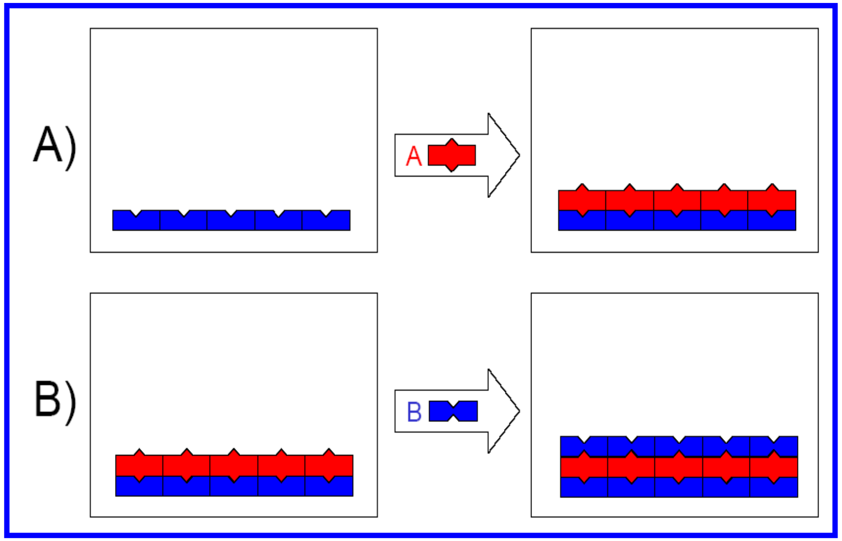


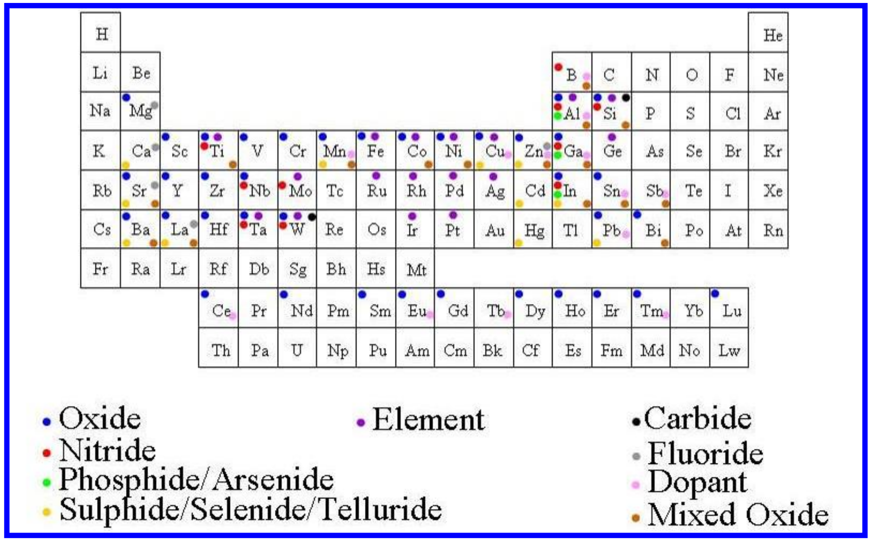
1a - Approach

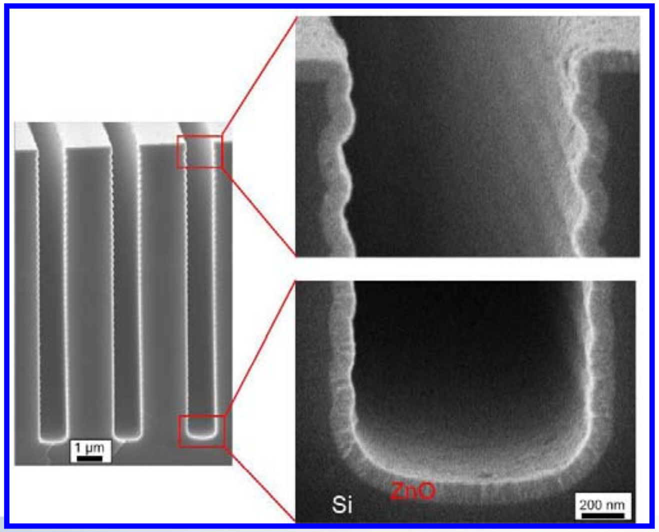
- The general strategy for Atomic Layer Deposition catalyst development is based on following advances made in previous work from the IACT(Institute for Atom-Efficient Chemical Transformations) EFRC and the Elam ALD group :
  - ALD substrate modification for stabilization in hydrothermal environments, ACS Catalysis, (**1**), 1234-1245 (2011)
  - ALD overcoats to prevent sintering and coking, Science, **335**, 1205 (2012)
  - ALD to control nanoparticle composition (bimetallic, core-shell), Chemistry of Materials, **24** (18), 3525–3533, (2012)
  - ALD for fine control over nanoparticle size, ACS Catalysis, **1** (6), 665-673 (2011)
  - ALD for size- and shape-selective catalysts, Nature Chemistry, **4**, 1030-1036 (2012)

1b - Introduction to Atomic Layer Deposition (ALD)

- Layer-by-layer thin film coating method
- Atomic level control over thickness and composition
- Precise coatings on 3-D objects







1c - ALD Catalyst Synthesis

Catalyst Active Metal

Example: palladium

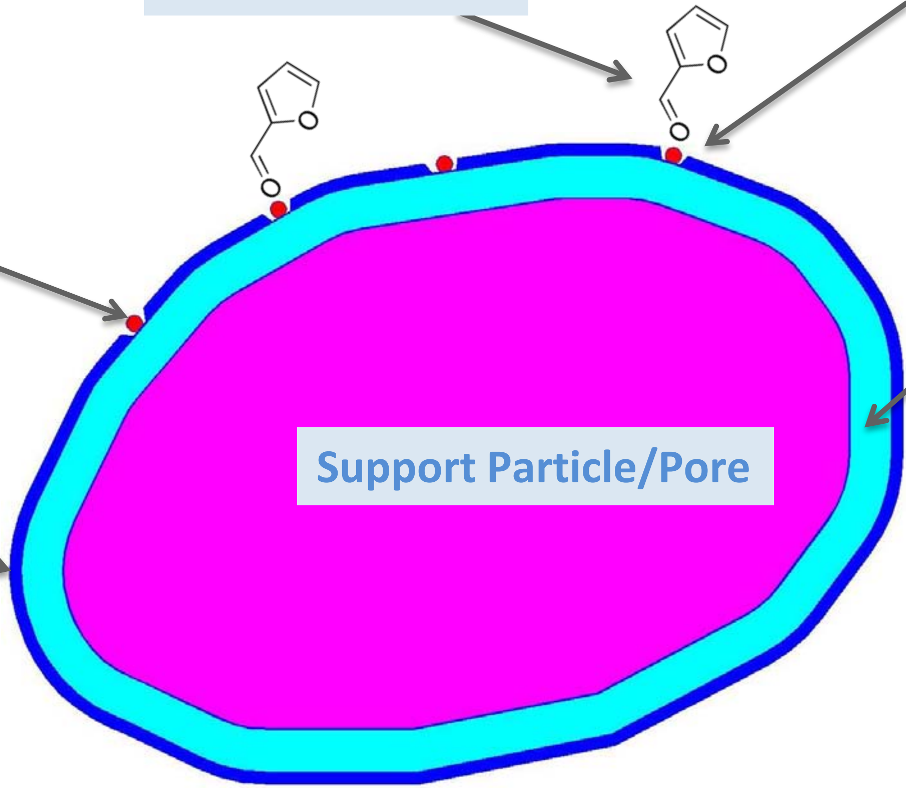
ALD:
Pd(hfac)2/
Formaldehyde

Catalyst Overcoat

Example: alumina

ALD:
Trimethyl aluminum/
Water

Biomass reactant



Conformational control of reactant adsorption

Substrate Overcoat

Example: niobia

ALD:
Niobium ethoxide/
Water

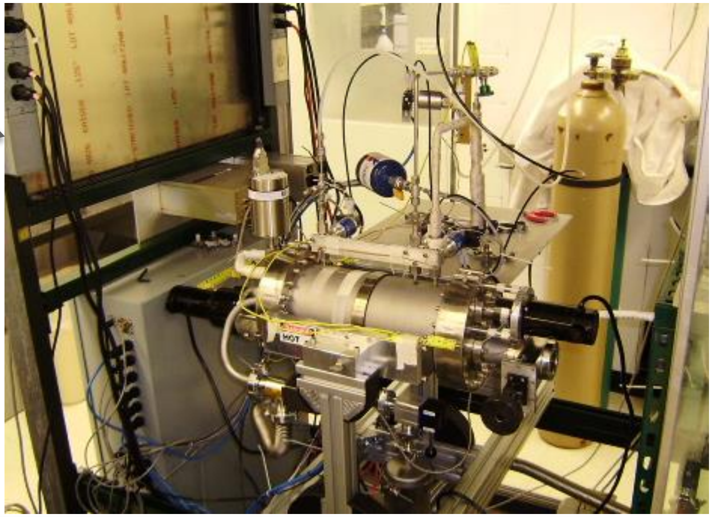
ALD Overcoat Materials: alumina, niobia, zirconia, magnesia, ceria, titania.

ALD Active Catalyst Metals: Pd, Pt, Ru, Ir, Mo, Ni, Co.

2 - Technical Accomplishments/ Progress/Results

Recap of Existing ALD Synthesis Tools

- Research ALD reactor
  - 3 g powder, static tray
  - heated stage for variable temperature deposition
  - ALD, H_2 reduction, calcination, in situ growth monitoring
- 100 g powder, rotating drum
- FTIR in-situ diagnostic
  - ALD chemistry
  - Surface acidity, metal sites
- XRF for pre- and post-test analysis of ALD catalyst composition.



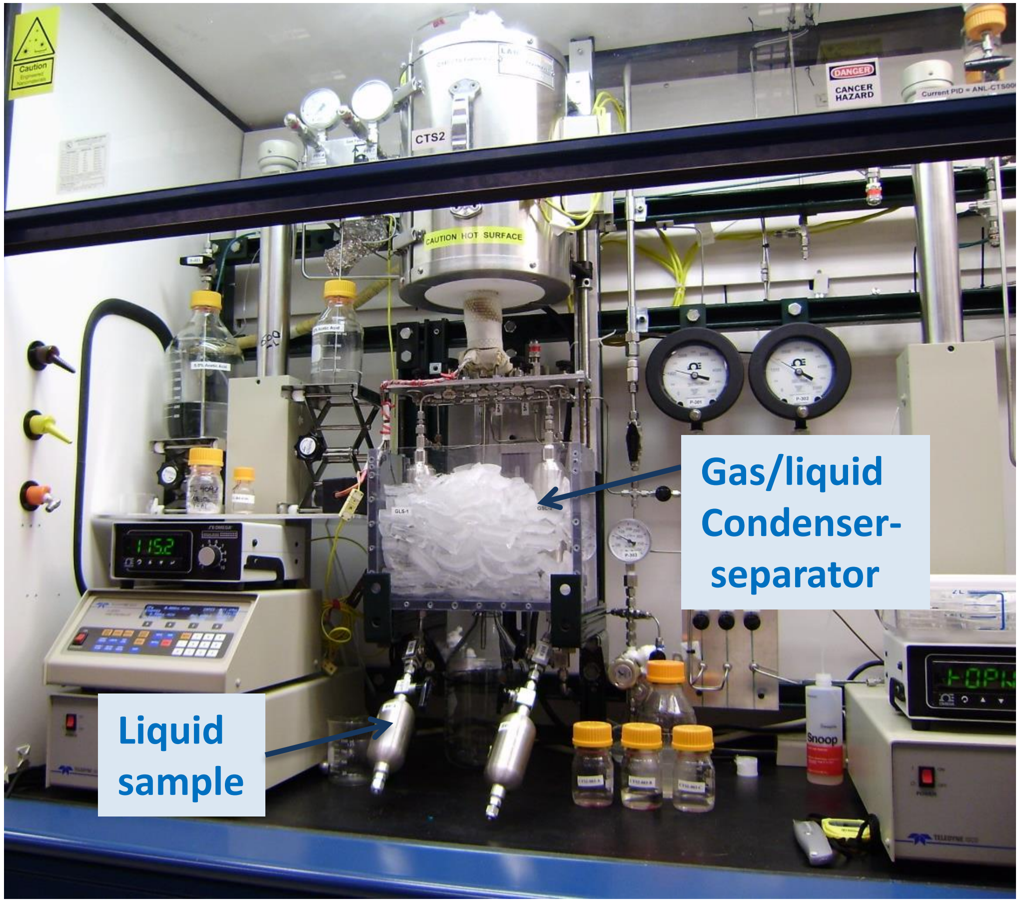
2 – Constructed and Commissioned High Pressure Hydrogenation Test Unit

New System Construction

- 12/12 -Completed design
- 2/13 Procured syringe pump, high pressure MFC
- 3/13 Completed construction, obtained safety approval
- 4/13 Initiated testing

System Features:

- 500-3000 psig H_2 (4-200 sccm)
- Temperature 100-350^{o}C
- 0.25-5 ml/min reactant feed with dual syringe pump for extended testing



2 – Reaction Product Analysis

GC and GCMS

- 3/13 - Procured HP 6890 GCMS dedicated to the project
- 4/13 Installed columns and developed methods for acetic acid, furfural, guaiacol and associated deoxygenated compounds
- 4/13 - Started analysis of reaction tested acetic acid
- 3/13 Installed existing HP5890 GC for online gas analysis

HPLC

- Existing unit is available to analyze pyrolysis oil

NMR

- NMR analysis (by functional group) for pyrolysis oils

2 – Initial Catalyst Development Plan and First Results

Initial Survey of ALD Catalysts

- We are using the work of G.Huber and D.Elliot on acetic acid, furfural and guaiacol as the starting point.

- Catalyst testing started on 4/12/13. Our first series of catalysts are based on niobia coated supports following our previous work that niobia stabilizes SBA-15 in hydrothermal environments.
  - Catalyst JL-R4-4098 Niobia blank. Synthesized and tested 4/12/13-4/13/13. No reactions products observed up to 210^{o}C.
  - Catalyst JL-R4-4111 Niobia with active metal 1. Tested on 4/17-4/18. Initial activity to ethanol was observed at 180^{o}C followed by rapid deactivation.
  - Catalyst JL-R4-4113. Niobia with active metal 1 with overcoat. Testing week of 4/22/13. Initial activity followed by rapid deactivation.
  - Catalsyt JL-R4-4118. Niobia with active metal 2. Tested 4/26-4/30. High activity and selectivity to ethanol. Secondary activity to ethyl acetate.

2 – Catalyst Characterization

- Our research reactor has in-situ FTIR for evaluating ALD chemistries, measuring surface acidity (via pyridine chemisorption) and characterizing catalytic metal sites (via CO chemisorption).
- Pyridine chemisorption has been shown to probe of surface acidity and will be used to study ALD support materials and overcoat materials.
- Surface area analysis before and after hydrothermal exposure will identify deactivation due to the hydrothermal exposure itself.

3 – Relevance

Tt-G "There is a need for hydrotreating and hydrocracking catalysts that are highly selective to the desired end product, robust with respect to the bio-oil (pyrolysis oil) impurities, and have high conversion rates and long lifetimes. The development of robust catalysts for upgrading and hydrotreating bio-oils to produce liquid transportation fuels is vital for the success of these processes"

- **ALD has been demonstrated to create catalysts that resist sintering and coking and provide greater selectivity. These strategies will be used to design catalysts that avoid polymerization (coking) in pyrolysis oil hydroprocessing thus extending catalyst life.**

4 – Critical Success Factors

1. Successful performance of ALD catalysts using pyrolysis oil for 500+ hours on stream
   - Demonstrate selectivity control by ALD overcoating
   - Demonstrate ALD catalyst lifetime enhancement using pyrolysis oil

2. Evaluate cost for ALD catalyst production at scale
   - Synthesize 100 grams batches
   - Measure energy and chemical precursor consumption
   - Extrapolate to scale quantities, compare with existing catalysts

5 - Future Work

- Present-9/14: ALD synthesize and rapidly screen 2-3 catalysts per week to identify high performance catalysts. Perform lifetime testing of high performers.
- 7/13: Begin scale-up of promising catalysts using 100g reactor.
- 7/13: Initiate pyrolysis oil testing using promising catalysts.

Summary

- Long-lived catalysts are essential for the success of biomass pyrolysis oil to fuels technology.
  - ALD provides unique synthetic capabilities and yields catalysts with extended lifetime and improved selectivity.
  - Demonstrated long catalyst lifetime on pyrolysis oil, and scalable ALD catalyst manufacturing are necessary to establish viability.
- A continuous feed high pressure hydrogenation test unit was built to enable rapid screening of ALD catalysts.
  - HP6890 GCMS for liquid analysis, HP5890 GC for online gas phase analysis.
  - 4/12: ALD catalyst testing started.
  - 4/26: ALD catalyst identified showing high acetic acid to ethanol conversion and secondary conversion to ethyl acetate.
- Future Work: Screen to identify promising ALD catalysts using model systems and pyrolysis oils. Begin 100 g scale ALD catalyst synthesis and testing (compare to 1 g scale)