### Improved Catalyst Selectivity and Longevity Using Atomic Layer Deposition

WBS 2.1.10.1 Argonne National Laboratory, Forge Nano, Honeywell UOP May 2018 – June 2019

Christopher L. Marshall, Chemical Sciences and Engineering Division, Argonne National Laboratory

U.S. DOE Advanced Manufacturing Office Program Review Meeting Washington, D.C. June 12, 2019

## **Overview**

Project Title: Improved Catalyst Selectivity and Longevity Using Atomic Layer Deposition

#### Timeline:

Project Start Date:	05/01/2018
Budget Period End Date:	04/30/2020
Project End Date:	04/30/2020

#### Project Budget and Costs:

Budget	DOE Share	Cost Share	Total	Cost Share %
Overall Budget	\$1,600,000	\$512,320	\$2,112,320	24.3%
Approved Budget (BP-1&2)	\$1,600,000	\$512,320	\$2,112,320	24.3%
Costs as of 3/31/19	\$666,306	\$210,286	\$882,284	23.8%

#### **Barriers and Challenges:**

- Catalysts lose effectiveness due to sintering of metals
- Manufacturers normally address this activity by increasing the catalyst temperature
- Eventually the catalyst must be removed and replaced

#### AMO MYPP Connection:

- Developing an advanced propylene manufacturing catalyst that outperforms conventional market-leading catalysts
  - Higher activity and better selectivity at reduced temperatures
- Supporting AMO goal
  - Reducing the life-cycle energy consumption required to manufacture light olefins by 50% in 10 years.

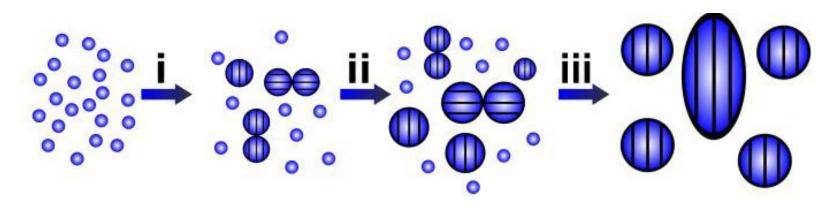
#### Project Team and Roles:

- Argonne National Laboratory
  - Project Management
  - Catalyst Evaluation
    - Activity and Selectivity
- Forge Nano
  - Catalyst overcoating and scale Up
- Honeywell UOP
  - Catalyst Synthesis, Process
    Verification, Life Cycle Analysis

# **Project Objectives**

## **Sintering (Aging)**

- Loss of active surface area from the prolonged exposure to high temperatures.
- Commercial catalysts lose surface area and hence activity via a process called sintering.
- In most cases the remedy for sintering is:
  - Increase reactor temperature (energy inefficient)
  - Remove spent catalyst and replace with new material.
    (expensive and leads to loss in productivity)



## **Project Objectives**

ANL and its partners Honeywell UOP (UOP) and Forge Nano (FN) are applying protective layers using Atomic Layer Deposition (ALD) to inhibit metal sintering of commercial Pt-based PDH catalysts to extend usable lifetime.

- Improve the efficiency of the catalytic reaction to reduce the energy required for the process.
- Larger energy savings would result from an improvement in selectivity.
  - Undesirable chemical byproducts that require high energy consumption processes for separation and removal from the product stream.
- Activity and selectivity are both degraded by sintering. This presentation does not contain any proprietary, confidential, or otherwise restricted information.

# **Technical Innovation 1**

### **Improved Catalyst Selectivity and Longevity**:

- Catalyst deactivation costs the chemical industry billions of dollars in lost revenue
- Imperfect selectivity in catalytic transformations engenders the use of large, costly separation processes to remove unwanted impurities.

### <u>The use of ALD to inhibit metal sintering</u> will avoid these issues and generate several <u>benefits:</u>

- Improved catalyst lifetime >100% due to a reduction in deactivation rate.
- Higher catalytic reaction selectivity and reduced energy required
- Validation and acceptance of atomic layer deposition as a scalable catalyst manufacturing technique.

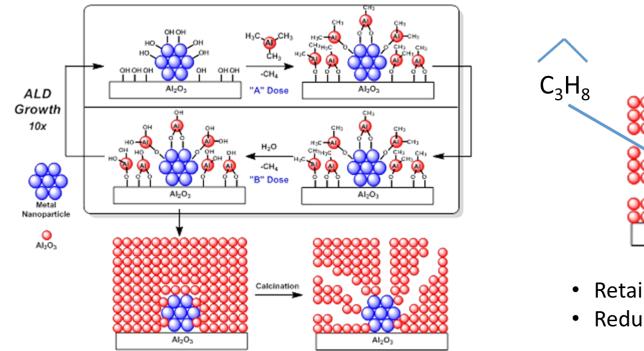
### <u>BES sponsored Energy Frontier Science</u> <u>Center (EFRC)</u>

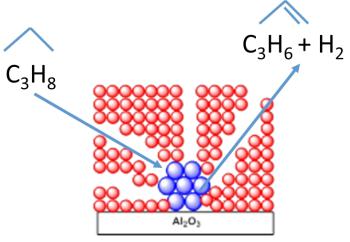


# **Technical Innovation 2**

### Improved Catalyst Selectivity and Longevity :

- ALD overcoating prevents sintering of the active catalytic metal.
- ALD overcoating improves the selectivity to olefin
  - avoiding coke formation.
- New technology from FN could make ALD useful for large volume applications such as catalyst manufacturing.



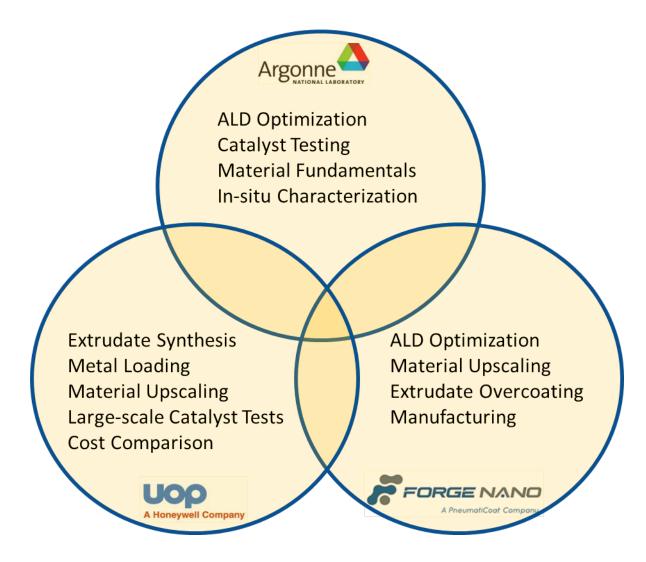


- Retain/Improve Productivity
- Reduced Metal Sintering

# **Technical Approach 1**

- Test the ALD overcoating
  - Several metal oxides (Al<sub>2</sub>O<sub>3</sub> TiO<sub>2</sub>) and metal oxide loadings
  - Different surface areas.
  - Improved catalyst
    - Longevity, selectivity
- Potential project risks and unknowns
  - Ability to scale up ALD to the volumes required for use in the refining and chemical industry.
  - Understanding of the fundamental impact of ALD based Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> overcoating on catalyst performance in the formed materials under study.
  - Changeover costs in the market, necessitating drop-in ready catalysts

## **Technical Approach & Project Roles**



## **Results and Accomplishments**

### Demonstrated

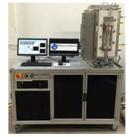
- Overcoating applied to wide variety of catalysts
  - including %Pt and surface areas
- Al<sub>2</sub>O<sub>3</sub> overcoats optimized
  - Works effectively at all SA levels tested
  - Little to no effect on catalyst selectivity
- Calcination opens active sites
- Overcoating covers some of the active Pt sites
- Steaming used to simulate long term deactivation.

### Milestones

- Two-year project spanning 3FY began in 2018.
- Lab-scale synthesis of base catalysts and determination of penetration depth of ALD precursors into the formed materials using TiO<sub>2</sub> overcoatings (2018).
- Understanding of catalytic effectiveness of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> ALD overcoating and down selection of process variables (2019).
- Scaled-up production of selected ALD overcoated catalysts in large quantities. Performance validation of the scaled-up coatings and techno-economic analysis of scaled-up process (2020).

# Transition

- Technical readiness (TR) level
  - Start (May 2018)
    - TR3 Research to Prove Feasibility
  - Project end (April 2020)
    - TR6 Technology Development
- Patent filing underway
- Intellectual property licensing will be explored.



Develop infiltration strategies and optimize process conditions & coating loadings at the 1g scale

Make instrumentation modifications to enable chemistry on extrudates at scale



Scale to: 1 kg batches