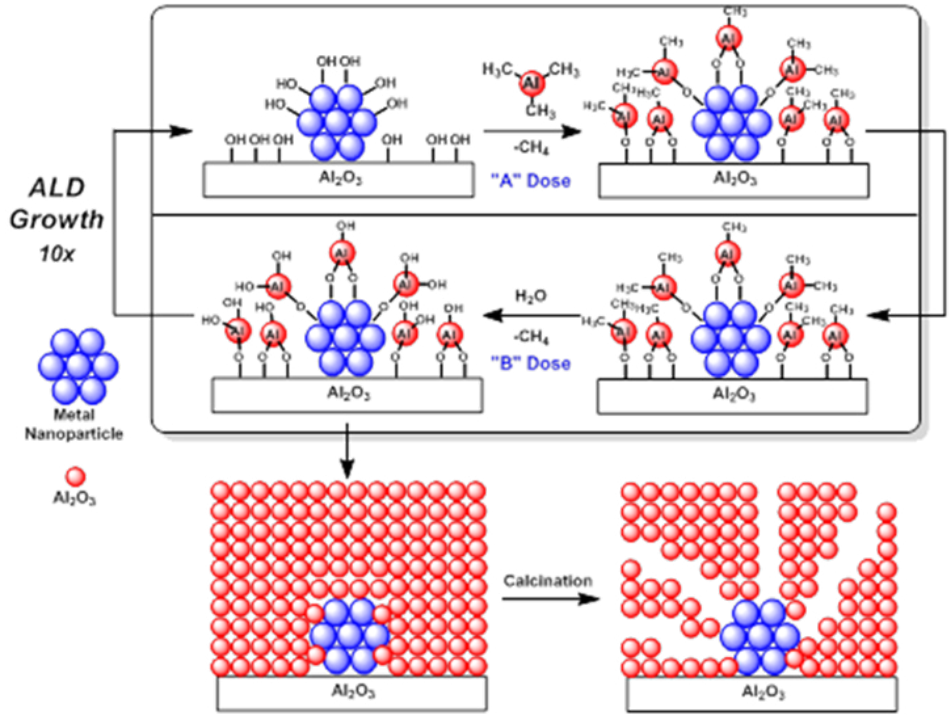
U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY & RENEWABLE ENERGY

Improved Catalyst Selectivity and Longevity Using Atomic Layer Deposition



Overview of the ALD overcoating that will prevent sintering and coke formation on catalysts used in the production of propylene from propene.
Photo credit Argonne National Laboratory.

Many important industrial scale chemical reactions rely on catalysts and require high temperatures to achieve commercially viable product yields. However, catalysts deactivate over time and lose surface area due to thermal degradation (sintering), fouling, and poisoning. Decreased catalytic activity often results in lower selectivity and a higher presence of unwanted chemical byproducts that must be removed from the process stream using energy-intensive separation processes. In many cases, the remedy for sintering of metals on the catalyst surface is to raise the reactor temperature and thus increase energy consumption, or to remove and replace the spent catalyst, which is expensive and leads to loss in productivity.

This project seeks to overcome catalyst degradation issues via the use of an overcoating technology that deposits protective layers around the catalysts and preserves catalyst integrity under reaction conditions. The Atomic Layer Deposition (ALD) overcoating technique will apply one or more protective layers to the catalyst to inhibit metal sintering. Channels can be introduced into the ALD layers to provide reactants with access to the catalyst's active particles to improve reaction selectivity. This project will apply the overcoating technology to platinum-based heterogeneous catalysts used in the propane dehydrogenation (PDH) to propylene. On-purpose propylene is a rapidly growing market as an essential chemical for plastics manufacturing. An improvement in the efficiency of catalytic reaction will reduce the energy required for the process, and improved selectivity will generate even larger savings.

Benefits for Our Industry and Our Nation

Catalyst deactivation costs the chemical industry billions of dollars in lost revenue due to reduced product yields over time and the embedded cost and energy associated with the replacement or regeneration of spent catalysts. Also, imperfect selectivity in catalytic transformations engenders the use of large, costly separation processes to remove unwanted impurities. The use of ALD to inhibit metal sintering will avoid these issues and generate several benefits:

- Improved catalyst lifetime by more than 100% due to a reduction in deactivation rate
- Higher catalytic reaction selectivity and reduced energy required for the following separation process currently consuming 140 TBtu/yr
- Increased validation and acceptance of atomic layer deposition as a scalable catalyst manufacturing technique yielding a leading U.S. position in a developing advanced manufacturing technique

Applications in Our Nation's Industry

This ALD overcoating technology will have broad applicability in the petrochemical and fine chemical industries, which rely on heterogenous catalysts for most of their industrial processes. Techniques developed from this process will be broadly applicable to other high volume/value applications in other industries such as petroleum refining, petrochemical production, automobile exhaust treatment, and many other processes requiring chemical reactions.

Project Description

The project objective is to facilitate the design of catalysts with higher selectivity and greater longevity for alkane dehydrogenation, thus reducing the energy required for the overall process.

ALD will be used to apply one or more protective layers on commercial platinum-based PDH catalysts to inhibit metal sintering. Overcoating via ALD allows for precise control over the thickness, composition, and porosity of the protective layers, thus preserving catalytic activity to the greatest extent while improving catalyst stability and selectivity. The project team will apply overcoatings with different shell thicknesses and compositions.

Shell materials of interest for investigation include aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2). Known methods of varying the pore dimensions will be employed. Al_2O_3 and TiO_2 demonstrated the ability to stabilize catalysts during previously funded EFRC work. This project will advance the knowledge and application of Al_2O_3 and TiO_2 based ALD overcoating methods in high temperature catalytic transformations.

The ALD-coated PDH catalysts will be tested for propane conversion, propylene selectivity, and sintering resistance in a range of conditions, and then successful concepts will be scaled up for in-house pilot-line testing.

Barriers

- 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_2O_3 and TiO_2 overcoating on catalyst performance in the formed materials under study
- Changeover costs in the market, necessitating drop-in ready catalysts

Pathways

The project will first synthesize small quantities of overcoated Pt/Al_2O_3 catalysts with different shell thicknesses. Shell materials having different acid-base properties than Al_2O_3 (e.g. TiO_2) will then be studied followed by known methods of varying the dimension of the pores, using different thermal processing temperatures and deposition sequences. In addition to studying the individual oxide overcoating materials, the project team will investigate ALD using various mixes of the top-performers. Evaluating and characterizing these coatings will enable the project team to optimize the materials and support subsequent scale-up efforts.

Following the laboratory validation, the top candidate materials will undergo production runs in larger quantities. Samples from these scaled-up batches will be tested for on-stream characterization, and the remaining materials will be pilot tested and validated to ensure that their benefits have also scaled up. A techno-economic analysis of the scaled-up process will be conducted on the top candidate catalyst formulation.

Milestones

This two-year project began in 2018.

- Lab-scale synthesis of base catalysts and determination of penetration depth of ALD precursors into the formed materials using TiO_2 overcoatings (Completed)
- Understanding of catalytic effectiveness of Al_2O_3 and TiO_2 ALD overcoating and down selection of process variables (Completed)
- Scaled-up production of selected ALD overcoated catalysts and performance validation of the scaled-up coatings and techno-economic analysis of scaled-up process (2020)

Technology Transition

Argonne National Laboratory has partnered with Forge Nano and Honeywell UOP to determine if the ALD coating process can be scaled to commercial levels and if the scaled-up materials behave like their laboratory analogues. The team will also investigate the costs of the new materials compared to current commercial catalysts.

Following successful completion of this project, Forge Nano will further develop and demonstrate particle-coating technologies at its Colorado facility. Honeywell UOP is a catalyst supplier with a long-term manufacturing presence along the U.S. Gulf Coast and will pursue sales avenues through typical UOP offerings.

Project Partners

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