

Using Atomic Layer Deposition to Improve Catalyst Performance and Longevity

It is estimated that 95% of all commercially produced chemical products involve one or more catalysts at some stage in their manufacturing process, enabling an estimated global economic impact of ~\$15 trillion per year.¹ Heterogeneous catalysts are vital for petroleum refining, plastics manufacturing, food and biofuel production and many more core chemical manufacturing processes. Thermal degradation or sintering of the active material cause catalyst performance to decrease and deactivate over time, a major cost driver for chemical manufacturing. Billions in lost revenue every year is attributed to catalyst deactivation associated with reduced product yields and higher energy usage associated with regenerating or replacing spent catalysts. Atomic-level control over the catalyst composition and structure will create high-performance catalysts that cannot be achieved with conventional synthesis methods. ALD provides an opportunity to surface engineer active catalyst sites to provide inherent stability, selectivity and performance.⁵ Atomic layer deposition (ALD) has been demonstrated as cost effective and dramatically improves catalyst performance in a wide variety of applications.

ALD Improves Catalyst Materials

ALD coatings provide selectivity and lifetime enhancements to catalysts which provides greater performance. The stabilizing nature of ALD coatings reduce metal catalyst leaching or sintering that would otherwise reduce reaction surface area and performance.

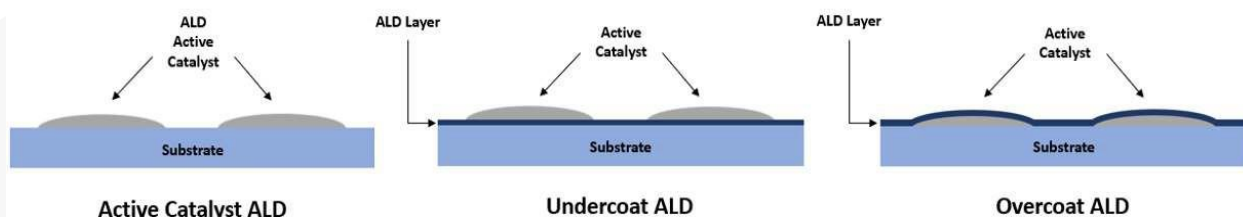
Effects of ALD on catalysts benefit:

- Minimized metal nanoparticle leaching¹
- Higher overall catalytic activity²
- Reduced thermal degradation³
- Decreased active site sintering³
- >100% Increased catalyst lifetime due to decreased deactivation⁴
- Greater selectivity between chemical reactions⁴

There are three ALD methods that are often used in catalyst applications:

- 1) ALD of the active catalyst on high-surface area supports
- 2) ALD of an undercoat for catalyst selectivity and increased lifetime
- 3) ALD of an overcoat to limit thermal degradation and increase selectivity

ALD Catalyst Toolbox



Active Catalyst ALD

ALD has been found to be useful in depositing catalyst materials such as Pd, Pt, Ni, Rh, Fe, Ir and Ru onto ultra-high surface area base supports. The high surface energy of the catalyst materials allows small "islands" to form on the base support, creating a high dispersion of active material while maintaining ultra-low loading for reduced material costs. Unlike wet chemical synthesis techniques, ALD can penetrate ultra-high aspect ratio pores in catalyst supports and

achieve uniform deposition.⁶ In addition, ALD can be controlled for near surface deposition for the manufacturing of eggshell structured catalyst.

Undercoat ALD

Using ALD to create an interface layer underneath the active catalyst will also help sustain longer lifetime and thermal stability. By depositing a thin film onto a high surface area substrate without adversely affecting pore size or morphology, ALD can be used to modify surface acidity/basicity and prevent dissolution of the active catalyst into the substrate material.⁵ In one example, ALD- modified substrates demonstrated improved catalytic activity, lifetime and selectivity for oxidative dehydrogenation of propane compared to bulk silica or alumina substrates.⁷

Overcoat ALD

ALD is also effective for depositing uniform films as a protective overcoat onto the catalyst while additionally improving catalytic performance. Depositing thin oxide films such as Al_2O_3 , TiO_2 , NbO_x , NiO , ZrO_2 or Co_3O_4 protects catalyst integrity during high temperature reaction conditions while inhibiting metal degradation, sintering, and leaching.^{1,4,5} In one example, alumina ALD overcoat layers preserved and enhanced catalytic activity of Pd nanoparticles while preventing sintering up to 500°C .⁸

For specific catalyst performance data, please contact Staci Moulton at SMoulton@forgenano.com.

About Forge Nano

Forge Nano is a leading materials science company harnessing the power of Atomic Armor, the company's proprietary ALD nanocoating technology, to accelerate manufacturing innovation, transform product performance and achieve a more sustainable future for a range of industries around the world. Atomic Armor produces superior coatings that can unlock a material's performance at the atomic level and deliver custom solutions from small-scale R&D and laboratory work to large-scale, high-volume production lines. A range of materials can be enhanced through Atomic Armor, including batteries, medical devices, catalysts, propellants and 3D additives. Forge Nano has received major support and signed meaningful partnerships with Volkswagen, LG Technology Ventures, Mitsui Kinzoku, Air Liquide and Sumitomo Corporation of Americas, largely as a result of the company's innovation in the Lithium-ion battery industry and successful track record of improving product performance and safety while reducing cost.

Forge Nano's Capabilities

- **>20 in-house ALD systems for coating of wafers, powders and objects**
 - Including research, pilot and commercial scale systems capable of processing anywhere from 1.0 g to 30,000 kg powder or extrudates per day
 - Fast deposition times up to 30nm per minute for rapid Al₂O₃ ALD coating solutions
- **The world's most knowledgeable and experienced team for ALD onto a range of materials**
 - PhD scientists, certified Professional Engineers, career scientists
 - 20+ years' experience designing and building powder ALD systems

Working with Forge Nano

Forge Nano assists customers daily with both R&D and commercialization of ALD-enabled materials. For R&D, we offer research services for proofs of concept and also sell our R&D equipment globally. For commercialization, we offer joint development of products, production equipment and IP licensing.

References

1. O'Neill, Brandon J., et al. "Catalyst Design with Atomic Layer Deposition." ACS Catalysis, vol. 5, no. 3, 2015, pp. 1804–1825., doi:10.1021/cs501862h.
2. Shekhar, Mayank, et al. "Size and Support Effects for the Water–Gas Shift Catalysis over Gold Nanoparticles Supported on Model Al₂O₃ and TiO₂." Journal of the American Chemical Society, vol. 134, no. 10, 2012, pp. 4700–4708., doi:10.1021/ja210083d.
3. Zhang, Xingguang, et al. "Heterogeneously Catalyzed Hydrothermal Processing of C₅–C₆ Sugars." Chemical Reviews, vol. 116, no. 19, 2016, pp. 12328–12368., doi:10.1021/acs.chemrev.6b00311.
4. Marshall, Chris. "Improved Catalyst Selectivity and Longevity Using Atomic Layer Deposition." U.S. DOE Advanced Manufacturing Office Program Review Meeting, Argonne National Lab, 2019
5. Singh, Joseph A., et al. "Nanoengineering Heterogeneous Catalysts by Atomic Layer Deposition." Annual Review of Chemical and Biomolecular Engineering, vol. 8, no. 1, 2017, pp. 41–62., doi:10.1146/annurev-chembioeng-060816-101547.
6. George, Steven M. "Atomic Layer Deposition: An Overview." Chemical Reviews, vol. 110, no. 1, 2010, pp. 111–131., doi:10.1021/cr900056b.
7. Sereda, Grigoriy, et al. "Effect of Atomic Layer Deposition Support Thickness on Structural Properties and Oxidative Dehydrogenation of Propane on Alumina- and Titania- Supported Vanadia." Catalysis Letters, vol. 142, no. 4, 2012, pp. 399–407., doi:10.1007/s10562-012-0780-x.
8. Feng, Hao, et al. "Alumina Over-Coating on Pd Nanoparticle Catalysts by Atomic Layer Deposition: Enhanced Stability and Reactivity." Catalysis Letters