

Enhanced Catalyst Durability for the Oxidative Production of Biobased Chemicals

Cooperative Research and Development Final Report

CRADA Number: CRD-19-00827

NREL Technical Contact: Wilson McNeary

NREL is a national laboratory of the U.S. Department of Energy Office of Energy Efficiency & Renewable Energy Operated by the Alliance for Sustainable Energy, LLC **Technical Report** NREL/TP-5100-84759 December 2022

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Cooperative Research and Development Final Report

Report Date: December 6, 2022

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the CRADA final report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Forge Nano; Johnson Matthey PLC

CRADA Number: CRD-19-00827

<u>CRADA Title</u>: Enhanced Catalyst Durability for the Oxidative Production of Biobased Chemicals

Responsible Technical Contact at Alliance/National Renewable Energy Laboratory (NREL):

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Sponsoring DOE Program Office(s): Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies Office (BETO)

Joint Work Statement Funding Table showing DOE commitment:

| Estimated Costs | NREL Shared Resources a/k/a Government In-Kind | | | |
|-------------------------|---|--|--|--|
| Year 1 | \$335,000.00 | | | |
| Year 2, Modification #1 | \$.00 | | | |
| Year 3, Modification #2 | \$.00 | | | |
| Year 4, Modification #3 | \$.00 | | | |
| TOTALS | \$335,000.00 | | | |

Total funds were received at in Year 1 in a single payment at the beginning of the project.

Executive Summary of CRADA Work:

This CRADA will facilitate technology maturation for NREL-developed atomic layer deposition (ALD) coated catalyst materials that are tailored for durability during the oxidative production of biobased chemicals. This project will address optimizing process parameters for scaling aluminum oxide (Al₂O₃) ALD coated catalysts, demonstrating ALD coated catalyst performance for biomass oxidation, and validating economic models that project significant cost benefits for ALD-enhanced catalyst manufacturing for energy-related technology. Critical information will be collected to elevate the Technology Readiness Level and increase our competitiveness for cooperative R&D agreements and licensing. Success of this work will be crosscutting as it can facilitate advanced catalyst development for both renewable and conventional processes.

CRADA benefit to DOE, Participant, and US Taxpayer:

Development of more durable catalysts for the production of biobased chemicals will accelerate the shift towards cleaner commodity chemical supply chains based on renewable feedstocks.

Summary of Research Results:

Task 1: Rigorously validate leaching and sintering resistance of ALD-coated Pd/TiO₂ catalysts.

A suite of uncoated Pd and Pt catalysts were delivered to NREL, along with two ALD coated Pd catalysts. The ALD coatings are denoted by number of cycles and type of coating (e.g., $10cTiO_2$ indicates 10 cycles of TiO₂ ALD were applied). *In these initial tests, the catalysts were reduced ex situ at 200 °C under H₂ for 2 h before testing.* The oxidation of 1,6-hexanediol in batch reactors was used as probe reaction for initial catalyst screening (**Fig. 1**). The catalysts were separately subjected to a 15-h leaching test in 5% gluconic acid to screen leaching resistance. ICP-OES was used to measure elemental content of the liquid effluent from the leaching test (**Figs 2 and 3**).

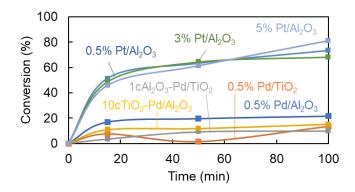


Fig. 1. Conversion of 1,6-hexanediol in batch reactions. Reaction conditions: 0.1 M 1,6-hexanediol, S/M = 500, 15 mL, 1000 rpm, 100°C, 40 bar dry air.

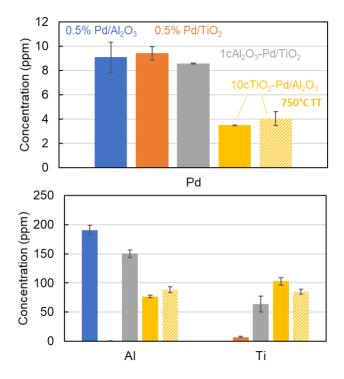


Fig. 2. Concentrations of Pd, AI, and Ti in the aqueous product of gluconic acid leaching test of Pd catalysts. Conditions: 5 wt% gluconic acid in water, 100 mg catalyst, 20 mL, 800 rpm, 100°C, 10 bar dry air, 15 h.

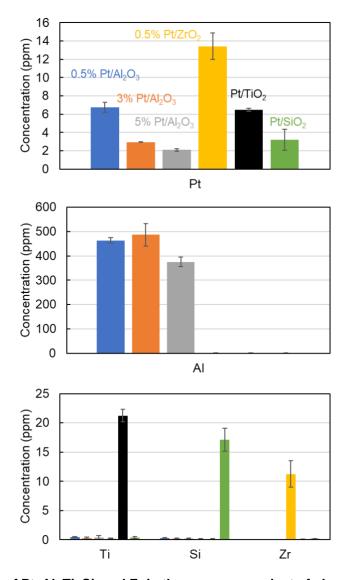


Fig. 3. Concentrations of Pt, Al, Ti, Si, and Zr in the aqueous product of gluconic acid leaching test of Pt catalysts. Conditions: 5 wt% gluconic acid in water, 100 mg catalyst, 20 mL, 800 rpm, 100°C, 10 bar dry air, 15 h.

Fig. 1 shows that Pt was significantly more active towards 1,6-hexanediol oxidation than Pd. A TiO₂ ALD coating on the Pd/Al₂O₃ catalyst slightly depressed the performance of that base catalyst, likely by blocking catalyst sites. **Fig. 2** shows the leaching results for uncoated and ALD coated Pd catalysts. The 10cTiO₂ ALD coating on Pd/Al₂O₃ decreased both Pd and Al leaching by > 2x. The ALD coated catalysts leached significant amounts of (> 100 ppm) their coating metal species, which suggests that the coatings themselves are prone to degradation in this environment. A high temperature calcination (750°C TT) on the 10cTiO₂-Pd/Al₂O₃ did not significantly alter leaching of the ALD coating, active metal, or support. Thus, crystallizing the TiO₂ ALD layer will not prevent leaching of the coating. **Fig. 3** shows the leaching results for uncoated Pt catalysts. Pt was found to be least stable supported on ZrO₂. The TiO₂, SiO₂, and ZrO₂ catalysts leached considerably less of their constituent metals than did Al₂O₃ supported catalysts, as they were by far the most active and preliminary evidence suggested that Al leaching can be mitigated with TiO₂ ALD coatings.

Batches of 3% and 5% Pt/Al₂O₃ catalysts were coated with 5cTiO₂ at the 4 g scale and tested for 1,6-hexanediol oxidation. *From this point forward, all catalysts tested were in their as-delivered state and not pre-reduced due to their use an oxidizing environment.*

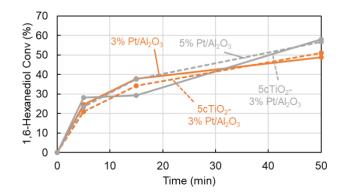


Fig. 4. Conversion of 1,6-hexanediol in batch reactions with uncoated and ALD-coated catalysts. Reaction conditions: 100 °C, 40 bar dry air, 1000 rpm, substrate/metal molar ratio (S/M) = 500, 15 mL of 0.1 M 1,6-hexanediol.

Table 1. Dispersion as determined by CO chemisorption, rate of 1,6-hexanediol consumption, and turnover frequency (TOF) for uncoated and ALD-coated catalysts. Rate and TOF were calculated at 5 min of reaction time.

| | Dispersion (%) | Rate (mmol1,6-HDgcat-1 s-1) | TOF (s-1) |
|--------------------|----------------|--------------------------------|--------------|
| 3% Pt/Al2O3 | 54.6 | 0.09 | 1.06 |
| 5% Pt/Al2O3 | 41.7 | 0.13 | 1.27 |
| 5cTiO2-3% Pt/Al2O3 | 43.0 | 0.06 | 0.85 |
| 5cTiO2-5% Pt/Al2O3 | 34.3 | 0.10 | 1.11 |

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Fig. 4 displays the conversion profiles of uncoated and ALD-coated Pt catalysts. Since each catalyst was run with S/M = 500, differences in Pt loading have already been accounted for in these results. The conversion values at most recorded time points were marginally lower for the catalysts coated with 5 cycles of TiO₂ ALD (dashed lines) relative to their uncoated base catalysts (solid lines). Likewise, the calculated rate and TOF values for uncoated catalysts in **Table 1** were slightly depressed after ALD coating. This behavior was likely due to partial coverage of active sites by the ALD layers, a hypothesis further supported by the loss in dispersion values seen for each catalyst following ALD. In the use of ALD for heterogeneous catalyst coating, ALD growth is thought to nucleate initially on metal oxide supports; however, some metal site coverage is common and to be expected as ALD cycles increase. It appears that the 5 cycles of TiO₂ used in this work caused only minor depression of the reaction rate and did not significantly alter the conversion profiles of these catalysts. Given these positive results, and additional set of both catalysts were synthesized with 10 cycles of TiO₂ and their leaching resistance tested in gluconic acid leaching tests.

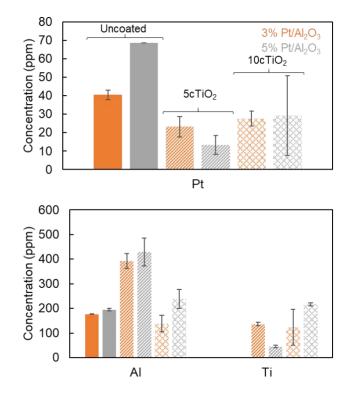


Fig. 5. Concentrations of Pt, Al, and Ti in the aqueous product of gluconic acid leaching tests. Base catalyst type is denoted by color and number of ALD cycles applied is denoted by crosshatching of the bars. Leaching test conditions: 100 °C, 10 bar dry air, 800 rpm, 100 mg catalyst, 20 mL of 5 wt% gluconic acid in water, 15 h.

Fig. 5 displays the concentrations of active metal (Pt) and support and coating ions (Al and Ti, respectively) in aqueous solution after a 15 h gluconic acid leaching test with 3% Pt/Al₂O₃ and 5% Pt/Al₂O₃ base catalysts, both uncoated and ALD coated. These results are normalized by catalyst mass loaded into the reactor, *not* Pt loading. The 5cTiO₂ coating was found to substantially decrease Pt leaching in both uncoated catalysts—by 43% in the case of 3% Pt/Al₂O₃ and 81% in the case of 5% Pt/Al₂O₃. The 10cTiO₂ catalysts nominally having twice the thickness of ALD coating as 5cTiO₂ indicate that the thicker coating does not necessarily provide better protection for Pt active metal against leaching. However, Al leaching is reduced in 10cTiO₂ catalysts relative to 5cTiO₂, suggesting that the alumina support is sensitized by the water dosing during the initial stages of the ALD process, and 10 cycles may provide enough coverage of the support to counteract this effect. From these results, the 10cTiO₂-3% Pt/Al₂O₃ catalyst was downselected for scaled ALD synthesis at 25 g to compare performance at the 4 g scale. The 25 g scale was chosen rather than the 1 kg scale to preserve materials and lower project costs given the long synthesis time (> 2 weeks) that would be necessary to apply 10 cycles of TiO₂ ALD to 1 kg of a substrate with ~100 m²/g of surface area.

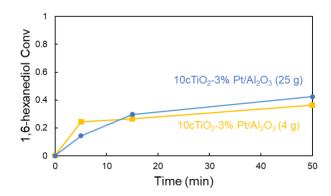
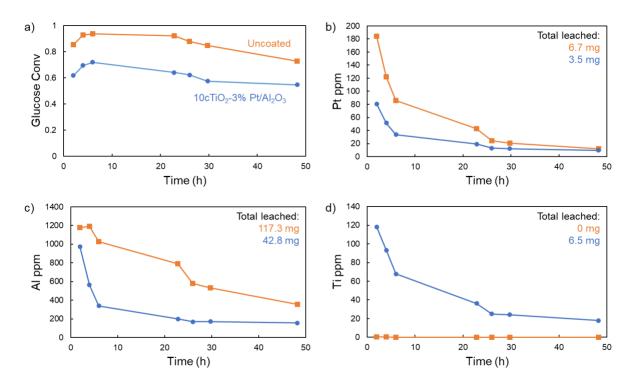


Fig. 6. Conversion of 1,6-hexanediol in batch reactions with 4-g and 25-g batches of $10cTiO_2-3\%$ Pt/Al₂O₃. Reaction conditions: 100 °C, 40 bar zero air, 1000 rpm, substrate/metal molar ratio (S/M) = 500, 15 mL of 0.1 M 1,6-hexanediol.

Table 2. Concentrations of Pt, Al, and Ti in the aqueous product of gluconic acid leaching tests. Leaching test conditions: 100 °C, 10 bar zero air, 800 rpm, 100 mg catalyst, 20 mL of 5 wt% gluconic acid in water, 15 h.

| | Pt content (ppm) | Al content (ppm) | Ti content (ppm) |
|--|---------------------|---------------------|---------------------|
| 10cTiO ₂ -3% Pt/Al ₂ O ₃ (4 g batch) | 27.5 ± 4.1 | 138.3 ± 33.3 | 122.9 ± 73.1 |
| 10cTiO ₂ -3% Pt/Al ₂ O ₃ (25 g batch) | 58.9 ± 3.8 | 386.3 ± 31.1 | 135.6 ± 14.5 |

Fig. 6 and Table 2 display the results of the 25-g batch of 10cTiO₂-3% Pt/Al₂O₃ in the batch oxidation of 1,6-hexanediol and 15 h gluconic acid leaching tests, respectively, versus the performance of a previously-reported 4 g batch of this ALD catalyst in those same tests. The performance of 25-g catalyst in batch oxidation was similar overall to its 4 g counterpart. However, the 25-g catalyst exhibited slightly higher conversion beyond 15 minutes of reaction. Previously, we have shown that 1,6-hexanediol conversion is suppressed by thicker ALD coatings. These results indicate that the ALD layer on the 25-g catalyst may be thinner than the one deposited on the 4-g catalyst. Significant differences were observed in the leaching test results. The 25-g catalyst leached almost twice as much Pt and nearly 2.5 times more Al over the course of the same test. The leaching of Ti for both catalysts was statistically indistinguishable. The increased leaching of Pt and Al from the 25-g catalyst suggests that greater amounts of the underlying 3% Pt/Al₂O₃ catalyst were exposed to the liquid environment during the test than in the case of the 4-g catalyst. These results are consistent with the results from batch oxidation and point to a thinner coating deposited on the 25-g batch of 10cTiO₂-3% Pt/Al₂O₃. Since ALD is a surface-mediated process, slight differences in substrate surface area from run to run may affect the overall amount of coating deposited; additionally, scaling up to a large reactor system for the synthesis of the 25-g batch may have affected mass transport of the ALD precursor to the catalyst surface. Regardless, the ALD coating on the 25-g batch of 10cTiO₂-3% Pt/Al₂O₃ was still expected to provide a degree of leaching resistance in the continuous oxidation of glucose vs. uncoated 3% Pt/Al₂O₃, and a 48 h time on stream experiment was set up to test this. Please note that all further discussions of 10cTiO₂-3% Pt/Al₂O₃ refer to the 25-g batch.



Task 2: Demonstrate superior sustained performance for gluconic acid production with ALD-coated catalysts.

Fig. 7. Performance of uncoated and 25-g 10cTiO₂-3% Pt/Al₂O₃ catalysts over continuous glucose oxidation: a) glucose conversion; b) Pt leached in effluent; c) Al leached; d) Ti leached. Elemental leaching totals were calculated based on the ppm of metal and mass of total liquid sample collected at each data point. Reaction conditions: 125 °C, 500 psig, 300 sccm zero air, 0.5 g catalyst, 0.07 mL/min of 5% glucose in water.

Continuous glucose oxidation to gluconic acid was conducted in a trickle bed reactor set to 125 °C and 500 psig with zero air flowing at 300 sccm for the duration of the experiment. Liquid effluent from the reactor was analyzed by LC-FID and ICP-OES. **Fig. 7** provides all reactivity and leaching data collected over 48 h glucose oxidation with uncoated 3% Pt/Al₂O₃ and 10cTiO₂-3% Pt/Al₂O₃ catalysts. In absolute terms, the 10cTiO₂-3% Pt/Al₂O₃ exhibited lower glucose conversion than uncoated throughout the experiment. As seen previously in 1,6-hexandiol batch oxidation, ALD coatings are expected to partially block Pt sites and suppress activity in type of oxidation reactions. Both catalysts exhibited similar trends over the course of the reaction—an initial break-in period, steady-state performance from 8-22 h, and gradual decline in performance beyond 22 h. At longer times beyond 30 hours, the 10cTiO₂-3% Pt/Al₂O₃ appeared qualitatively more stable than uncoated, implying that a second steady-state may have been reached for the ALD coated catalyst, while the uncoated would suffer continuous performance loss at the observed rate beyond 48 h. Overall, the uncoated catalyst lost around 15% of its initial conversion over the test, while the 10cTiO₂-3% Pt/Al₂O₃ lost 11%.

The most marked differences in performance between the two catalysts were observed in the amounts of Pt, Ti, and Al leached into the reactor effluent. For both Pt and Al, the catalysts exhibited high leaching at the beginning of the run that gradually decreased; however, the starting value and rate of decrease were much lower for 10cTiO₂-3% Pt/Al₂O₃, which indicates that the

ALD layer helped to suppress leaching of the catalyst and support. Overall, the total leaching of Pt and Al were reduced by 48% and 68%, respectively, in the 10cTiO₂-3% Pt/Al₂O₃. Some Ti leaching was observed in the case of 10cTiO₂-3% Pt/Al₂O₃ due to the presence of the TiO₂ coating; however, at 6.5 mg, leaching from the ALD coating was much less widespread than leaching from the Al₂O₃ support. Due to difficulties physically separating the catalysts from the quartz sand in the catalyst bed, data on retained surface area and dispersion of the catalysts after glucose oxidation was not collected. However, the data on leaching behavior of both catalysts does confirm our hypothesis that ALD coatings can provide significant protection from the oxidizing, aqueous, and low pH environment of catalytic glucose oxidation.

Task 3: Refine techno-economic models for ALD-coated Pd/TiO₂ manufacturing and biogluconic acid production.

We performed a cost-benefit analysis for the 10cTiO₂ coating that compares the expected savings due to reduced leaching with the increased cost of the ALD-coated catalyst relative to an uncoated material. This analysis used the CatCost catalyst cost estimation tool as well as 10cTiO₂-specific economic information provided by Forge Nano. The CatCost-determined costs are lifetime catalyst costs, considering both the cost to purchase the material initially and the value of the spent catalyst that can be credited at end-of-life to reduce lifetime cost. For this analysis, we simply subtracted the estimated spent catalyst value from the catalyst purchase cost to determine the lifetime cost.

The reduced leaching observed for 10cTiO₂-3% Pt/Al₂O₃ vs. the uncoated catalyst is expected to improve the economics increasing the amount of platinum recoverable at the end of the catalyst's life, thus increasing the spent catalyst value and lowering lifetime catalyst cost. Since the exact relationship between initial leaching rates (in ppm/h) and final observed losses in use of Pt (which are typically in the range 2–4%) is unknown, we simply assumed that a baseline rate of Pt loss in use (4%) assumed for uncoated catalyst was reduced by the experimentally observed leaching reduction for 10cTiO₂-3% Pt/Al₂O₃ (48%, yielding a loss in use value of 2.08%). Focusing just on the leaching reduction and assuming a low ALD coating cost of \$12.08, it appears that the improvement in Pt losses would pay for the cost of ALD coating, but only just (Table 3, scenarios A and B). However, this analysis leaves out the substantially lower initial activity observed for coated vs. uncoated catalyst. Including this via an assumed activity reduction of 25% (all production costs and spent catalyst value are simply multiplied by the ratio of uncoated vs. coated activity) reveals that the ALD coated catalyst has a much higher lifetime cost than that of the uncoated catalyst (scenario C). In further analysis, we determined that the thin margin of improvement generated by the reduced leaching only allows for about a 1% reduction in activity to keep the coated catalyst economic, so performance would have to be optimized. In a final analysis, we looked at the improvement in activity stability that was observed for the coated vs. uncoated catalyst (11% activity loss for coated vs. 15% for uncoated). Assuming leaching and initial activity are unchanged, if final activity were improved by 10%, this would also be just barely sufficient to pay for ALD coating.

Table 3. Four scenarios showing different catalyst costs (including synthesis cost and ALD coating cost, which together comprise total purchase cost, along with spent catalyst value, which is subtracted from total purchase cost to give lifetime cost). Scenarios B, C, and D include differences relative to scenario A, the baseline.

| Scenario inputs | | | | Catalyst costs in \$/kg uncoated catalyst, with difference from baseline (scenario A) | | | | | |
|--------------------------|----------|----------------|------------------|---|----------------|------------------|----------------------------|----------------------|---------------|
| Catalyst | Scenario | Pt Loss in Use | Initial Activity | Final Activity | Synthesis Cost | ALD Coating Cost | Total Purchase Cost | Spent Catalyst Value | Lifetime Cost |
| 3% Pt/Al2O3 | А | 4% | 100% | 100% | 828.44 | - | 828.44 | 701.19 | 127.24 |
| 10cTiO2-3% Pt/Al2O3 | В | 2.08% | 100% | 100% | 828.44 | 12.08 | 840.52 | 715.34 | 125.18 |
| (difference to baseline) | | | | | - | (+12.08) | (+12.08) | (+14.15) | (-2.07) |
| 10cTiO2-3% Pt/Al2O3 | С | 2.08% | 75% | 100% | 1,104.58 | 16.11 | 1,120.69 | 953.78 | 166.90 |
| (difference to baseline) | | | | | (+276.15) | (+16.11) | (+292.25) | (+252.59) | (+39.66) |
| 10cTiO2-3% Pt/Al2O3 | D | 4% | 100% | 110% | 753.12 | 10.98 | 764.11 | 637.45 | 126.66 |
| (difference to baseline) | | | | | (-75.31) | (+10.98) | (-64.33) | (-63.74) | (-0.59) |

In sum, the economics of ALD coating in this catalyst system are marginal. We have assumed very favorable ALD coating costs at the low end of typical estimates by Forge Nano. For an ALD-coated catalyst to succeed commercially, it would need substantially larger margins of improvement that are confirmed upon scale-up and longer-term testing. Our previous results with hydrogenation and hydrodeoxygenation reactions in which partial coverage of the Pt by the TiO₂ layer and creation of Pt-TiO₂ interface sites can produce significant activity improvements, rather than losses, offer a much clearer path to commercial viability.

Task 4: Engage in industry outreach for advancing market penetration and identifying potential partners for follow-on efforts.

Fig. 8 displays the ALD technical brochure developed from this and previous BETO-funded ALD projects. **Table 4** shows the primary takeaways from a series of industrial interviews with stakeholders in the catalysis community. A recurring point in many of these discussions was the tradeoff between ALD-induced performance enhancements and the cost of an ALD coating. It was suggested that high-value catalysts, such as Rh, may provide the most economically favorable platform for ALD coatings, as even modest reductions in Rh loading or lifetime would have substantial impacts on overall catalyst cost that far outweigh the additional cost of adding an ALD layer. Additionally, these interviews suggest that further advancement of ALD catalysts should focus on engineered catalyst forms, such as pellets, in order to increase relevance to industry.

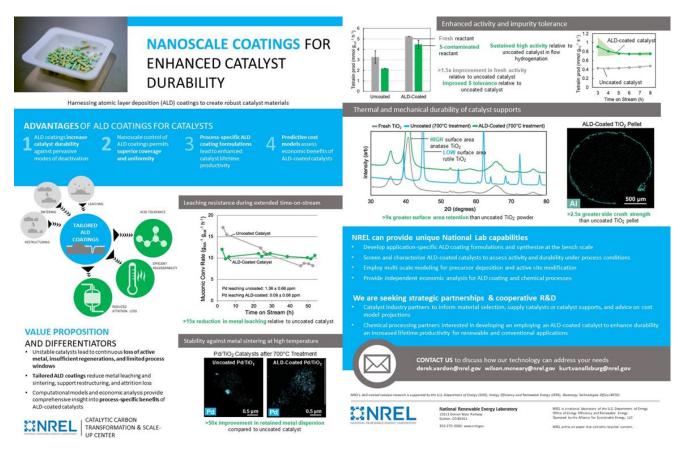


Fig 8. ALD catalyst technical brochure developed for industrial outreach. Full PDF available upon request.

Interviewee Affiliation **Primary Takeaways** Karl Albrecht Archer Daniels Midland Reaction selectivity in glucose oxidation is a major (ADM) challenge with conventional heterogeneous catalysts. ALD would have to be compatible with pelletized Csupported catalysts and produce substantial selectivity/durability benefits to be attractive. Cost of ALD process is a major barrier to any interest from ADM. Chris Nicholas C2P Sciences Primary challenge in catalysis is the transition away from hydrocarbon processing towards bio-based feedstocks with high levels of oxygenates and aqueous phase processing. ALD could be a viable option in addressing deficiencies with crush strength of hydrothermally-stable supports (e.g., SiO2). High-value catalysts may be the best place to maximize economic incentive of durability benefits of ALD. Must show that ALD is scalable and find the balance between preferred performance and price point. Matthew Greaney Clariant Major challenges in catalysis include reliable assessing catalyst lifetime, raw material costs, and improving catalyst selectivity. Value-add of ALD will be maximized on high-value catalysts like those utilizing Rh. Clariant would be most interested in demonstrated ALD improvements on thermal stability of catalysts for gasphase reactions; condensed phase is not as relevant for industry. Joe Powell Shell Major challenges in catalysis include catalyst stability in aqueous systems and electrocatalyst durability (e.g. electrolysis). If Pt could be replaced by an earth abundant metal with ALD coating (and achieve higher activity/selectivity and cost parity), this would be a significant improvement. Ralph Gillespe Lanzatech One of the most significant long-term challenges in catalysis is stability/deactivation, but this depends on the system. Overall, aqueous phase heterogeneous catalysts are a minority. Whether ALD would be useful to a catalyst user depends on how disruptive using a modified catalyst would be to their process (e.g., reactor changeover, new capital investment) Rh catalysts may be an area to make an impact with ALD, but would have to also demonstrate high conversion/selectivity.

Table 4. ALD Catalysis industrial interview participants, affiliations, and primary takeaways.

Conclusions

In conclusion, we have demonstrated that TiO₂ ALD coatings can be used to mitigate active metal and support leaching in the oxidation of glucose; however, an attendant decrease in overall catalyst activity is observed due to blockage of the Pt sites. Further cost-benefit analysis shows that, in this case, the cost of the ALD coating may outweigh its benefits in terms of leaching resistance because of this decrease in catalyst activity. Informational interviews with industry experts suggested that the ideal niche for ALD in catalysis would consist of (1) a high-value catalyst, such as Rh, in which preservation of the active metal is of primary economic importance or (2) a high-value product that can be selectively produced at higher rates with application of an ALD coating. We recommend that future efforts in this space be directed towards reaction chemistries in which an ALD coating might be expected to synergistically promote the catalytic metal (e.g., hydrogenation, hydrodeoxygenation) and allow for lower metal loading. While extending the catalyst lifetime with ALD should remain a goal, it must be pursued while also promoting catalyst activity and/or selectivity.

Subject Inventions Listing:

None

<u>ROI #</u>:

None