

ALD Applications

Room Ybor Salons I-IV - Session AA1-TuA

ALD for Catalysts and Fuel Cells

Moderators: Hao Van Bui, Phenikaa University, Chang-Yong Nam, Brookhaven National Laboratory

1:30pm AA1-TuA-1 Copper's Cosy Blanket: A Comparison of Non-Selective and Area-Selective ZnO deposition on Catalyst Stability, Kalani Ostermeijer, Ruud van Ommen, Evgeny Pidko, Delft University of Technology, Netherlands

In the past few decades, valorizing CO₂ has drawn significant interest as it offers a more carbon neutral pathway to chemicals and fuels. However, CO₂ reduction has proven to be problematic due to its thermodynamic and kinetic constraints. Heterogeneous thermo-catalysts can improve the kinetics, thus play a critical role in the push for the industrialization of sustainable chemicals and fuels. Methanol is considered a promising product thanks to being a key chemical building block. Currently, the commercial Cu/ZnO/Al₂O₃ catalyst requires harsh conditions (50-100 bar H₂ and 200-300 °C). After prolonged exposure to temperatures above 200 °C, sintering of the dispersed active phase is observed. This was shown to worsen in the presence of water vapor, which is produced in high amounts during the hydrogenation process. Therefore, protecting Cu nanoparticles from thermal and hydrothermal sintering is key to enhancing the operating productivity and efficiency of the methanol production process.

In this work we aim to protect Cu nanoparticles by forming a ZnO overlayer on top of a Cu/SiO₂ catalyst using both non-selective and area-selective atomic layer deposition. ZnO was deposited using diethyl zinc and ethanol under atmospheric pressure in a fluidized bed reactor at 100 °C. To induce area-selectivity, the Cu/SiO₂ catalyst was treated with trimethoxypropylsilanes using air-free wet synthesis techniques, passivating surface silanol groups. All catalysts were characterized using temperature programmed desorption, elemental analysis, electron microscopy (focused ion beam scanning electron microscopy and transmission electron microscopy), and x-ray photoelectron spectroscopy, and their stability was assessed in a fixed-bed reactor under industrially relevant conditions (250 °C and 50 bar). Herein, we explore how tailoring the metal oxide interface using targeted ZnO deposition can alter the stability of Cu/ZnO based methanol hydrogenation catalysts, improving the rational design of catalysts via ALD.

This work is part of the Advanced Research Center for Chemical Building Blocks, ARC CBBC, which is co-founded and co-financed by the Dutch Research Council (NWO) and the Netherlands Ministry of Economic Affairs and Climate Policy

1:45pm AA1-TuA-2 Effect of Buffer Layers on Cobalt-Based Thin-Film Catalysts for Fischer–Tropsch Synthesis, Muhammad Hamid Raza, Avela Kunene, Helmholtz-Zentrum Berlin (HZB), Germany; Lucia M. Toscani, Department of Interface Design, HZB, Germany; Alexander Steigert, Helmholtz-Zentrum Berlin (HZB), Germany; Athanasios Skaltsogiannis, Department of Interface Design, HZB, Germany; Ali Shan Malik, Helmholtz-Zentrum Berlin (HZB), Germany; Catalina E. Jiménez, Department Interface Design, HZB, Germany; Marcus Bär, Department of Interface Design and Energy Materials In-Situ Laboratory Berlin (EMIL), HZB, Berlin. Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (HI ERN), Berlin. Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen., Germany; Rutger Schlatmann, Daniel Amkreutz, Helmholtz-Zentrum Berlin (HZB), Germany

In Fischer-Tropsch synthesis, *hcp*-Co⁰ nanoparticles show higher CO dissociation activity and enhanced C_s selectivity than the *fcc*-Co⁰ nanoparticles due to the presence of more numerous and more active B_s sites.¹ As such, thin film catalysis offers opportunities to tailor catalysts properties by design that are pre-adapted to specific crystallographic morphology for their targeted application. Fischer-Tropsch synthesis (FTS) benefits from thin film catalysts, by selectively tailoring the catalytically most active phase *i.e.*, *hcp*-Co⁰. This streamlined catalyst design enhances catalytic activity and selectivity toward the desired end products.² Varying deposition conditions and metal-support interactions affect the reducibility and crystallographic morphology of the FTS active phase. Herein, cobalt-based thin film FT catalysts are synthesized with varying chemical structures and crystallographic phases, including metallic and metal oxides phases, onto various supports and buffer layers (Al₂O₃, SiO₂, ZrO₂, CeO₂, Si_xN_y, Si_xC_y, TiO₂). Key properties such as film morphology and stability, as well as metal/metal oxide-support interactions (MSI) in terms of support-induced reducibility and morphological evolution of the cobalt films are investigated

in thin films catalyst systems. Phase changes are systematically studied under *in-situ* FTS-relevant oxidation–reduction conditions using synchrotron grazing incident X-ray diffraction. Indeed, as-deposited metallic cobalt shows higher stability than its oxide counterpart, the *spinel*-Co₃O₄, under FT-relevant reduction conditions. A semi-quantitative analysis of the diffraction data indicates that the relative *fcc*-to-*hcp* ratio depends on the nature of the buffer layer, with samples supported on CeO₂, TiO₂ and Al₂O₃ - SiO₂ exhibiting the lowest apparent *fcc*/*hcp* ratio. These well-defined cobalt-based (Co, Co_xO_y) thin film catalysts offer a promising alternative for enhancing FT performance. Clear structure–property correlations will be presented to guide the rational design of advanced FT catalyst systems.

1 Liu, J.-X., Wang, P., Xu, W. & Hensen, E. J. M. Particle Size and Crystal Phase Effects in Fischer-Tropsch Catalysts. *Engineering* **3**, 467-476 (2017).

2 Kunene, A. *et al.* Thin-Film Catalysis Innovations in Fischer–Tropsch Synthesis for Enhanced Activity. *Industrial & Engineering Chemistry Research* **64**, 22939-22948 (2025).

2:00pm AA1-TuA-3 Preparing Well-defined CO₂-Conversion Catalysts using Atomic Layer Deposition, Doga Özerk, Evgeny Pidko, J. Ruud van Ommen, TU Delft, Netherlands

CO₂ hydrogenation to methanol is attractive, as methanol serves both as a base chemical and an energy carrier. However, due to the thermodynamic stability and low reactivity of CO₂, its conversion remains highly challenging and requires the use of efficient catalysts. Conventional catalyst synthesis methods, such as wet chemistry, often lack control over the structural and morphological properties of the materials, typically yielding catalysts with broad particle size distributions and mixed compositions. In contrast, ALD provides atomic-level precision in catalyst design, enabling the synthesis of catalysts with well-defined compositions, controlled particle sizes, and tailored active sites. This work focuses on the development of Cu and Pd-based catalysts via ALD for CO₂ hydrogenation. Copper-based catalysts have been widely studied for this reaction due to their excellent hydrogen dissociation capability and cost-effectiveness compared to noble metals. However, Cu-based catalysts often suffer from nanoparticle sintering under reaction conditions, leading to catalyst deactivation through the loss of active sites and disruption of the synergistic interactions between Cu and other components in the catalyst. Pd-based catalysts have been traditionally used as Reverse Water Gas Shift catalysts, however their full potential for methanol synthesis remains underexplored. Recent studies report high methanol selectivities, yet no comprehensive mechanistic investigation has revealed the origin of this performance or established clear structure-activity relationships, due to inadequate control over Pd dispersion in conventional synthesis methods. The goal of this study is to achieve precise control over Cu and Pd dispersion and particle size at the atomic level to enhance activity and selectivity.

Cu and Pd-ALD catalysts are synthesized using Cu(hfac)₂ + H₂O and Pd(hfac)₂ + CH₂O as precursors in an atmospheric-pressure fluidized bed ALD system operating at 250 °C, with N₂ as the carrier gas. Pulse and purge times, as well as the number of ALD cycles, are varied to tune the catalyst properties. TiO₂, Al₂O₃, and CeO₂ nanoparticles (particle size: ~25 nm) are used as supports.

We will report the Cu and Pd particle size distributions on various metal oxide supports and their correlations with ALD parameters. The effect of particle size on catalytic activity and selectivity for methanol synthesis will be evaluated. The ALD-prepared catalysts will be compared to counterparts synthesized via wet impregnation. Differences in morphology, particle size, surface area and crystallinity will be discussed to elucidate structure-performance relationships.

2:15pm AA1-TuA-4 Palladium Nanostructures by ALD for Electrocatalysis: From Single Atoms to Nanoparticles, Raul Zazpe, Jhonatan Rodriguez-Pereira, Jan Macak, Uni Pardubice, Czechia

This presentation is focused on the ALD growth of Pd nanostructures – from single atoms, through atomic clusters up to nanoparticles – that are deposited on various substrates and demonstrate an excellent electrocatalytic performance [1-3] for the hydrogen evolution reaction (HER).

In fact, Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance for various catalytic applications [4]. Due to their scarcity, efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique to facilitate lowering of loading mass on a support of interest [5-7].

Due to the governing surface energy variations between noble metals and support surfaces, the growth initiates as single atoms, continues through

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atomic clusters to nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP's dominates over the individual NP size increase, thus developing thin films of relatively higher thickness.

For electrocatalytic applications, it is important to choose the right substrates. Among the available ones, carbon papers (CP) and titania nanotube (TNT) layers are best choices considering their physio-chemical properties, availability, vast literature, and low costs incurred using these as support substrates in electrocatalysis and photocatalysis.

The presentation will introduce and describe the synthesis of Palladium nanostructures – starting from single atoms, through NPs to solid films by ALD on CP substrates [1] and TNT layers with high aspect ratios [2] and QCM crystals [3]. It will also include the corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

References:

- [1] B. Bawab et al., Chem. Eng. Journal 482 (2024) 148959.
- [2] B. Bawab et al., Electrochim. Acta 429 (2022) 141044.
- [3] C. Schott et al., ACS Catalysis 15 (2025) 9035
- [4] Huang, Z. F. et al. Advanced Energy Materials 7 (2017) 1700544.
- [5] Yoo, J. E. et al. Electrochem. commun. 86 (2018) 6
- [6] Anitha, V. C. et al. J. Catal. 365 (2018) 86.
- [7] Dvorak, F. et al. Appl. Mater. Today 14 (2019) 1.

2:30pm AA1-TuA-5 Controlling the Wettability and Durability of PEM Electrolysers with Plasma-Enhanced ALD of Niobium Nitride, Athina Tzavara-Roussi, Volkert van Steijn, Ruud van Ommen, Delft University of Technology, Netherlands

Green hydrogen has emerged as an effective energy storage medium, capable of buffering excess electricity generated from intermittent renewable sources. Proton exchange membrane (PEM) water electrolyzers is a key technology for green hydrogen production as they offer higher efficiency, compact design and rapid response to fluctuating energy input. However, their large-scale deployment requires reducing reliance on critical raw materials while maintaining their durability.

The porous transport layer (PTL) plays a crucial role on the anodic side of PEM electrolyzers. This titanium-based layer is responsible for the transport of water to the catalytic sites and the discharge of oxygen gas to the flow plates, as well as providing an electrically conductive pathway for electrons. However, the PTL faces two critical challenges that impact the performance and cost. The first challenge is the progressive growth of an oxide layer on the surface of titanium, which significantly reduces its electrical conductivity. Commercially the platinization of the titanium substrate is commonly applied to mitigate this issue, but further increases the manufacturing costs. The second challenge lies in the counter-current transport of liquid water and oxygen as dissolved gas and bubbles. This leads to the accumulation of oxygen gas within the pores of the PTL, which increases mass transport losses. This limitation becomes more pronounced at higher current densities due to higher gas production, which is otherwise advantageous for lowering the unit cost of hydrogen production.

In this work, we demonstrate the plasma-enhanced atomic layer deposition (PE-ALD) of niobium nitrides to fabricate a functional coating on the PTL surface. Niobium is an attractive candidate to replace noble metals and as nitride it can promote electron transfer to reduce ohmic losses by protecting the titanium substrate from oxidation and simultaneously being highly conductive itself. The niobium nitride coating additionally provides hydrophilicity to facilitate the water imbibition throughout the PTL, while accelerating the removal of oxygen bubbles to decrease mass transport losses. We investigate how the elemental composition, the morphology and the thickness of the niobium nitride coating influence its conductivity and hydrophilicity. Ultimately, the impact of the PTL coating on the performance and stability of a 4cm² PEM cell is evaluated.

This project receives a Dutch National Growth Fund contribution from the programme NXTGEN HIGHTECH.

2:45pm AA1-TuA-6 ALD Imparts Efficiency Improvements in Proton Exchange Membrane Water Electrolysers, Arrelaine Dameron, Sara Harris, Dane Lindblad, Forge Nano; Alexandra Oliveira, Mott Corporation; JingJing Jin, Lucas Cohen, Zhexi Lin, Columbia University; Alexander Papandrew, Mott Corporation; Daniel Esposito, Columbia University; Matthew Weimer, Forge Nano

Green hydrogen (H₂) offers a pathway to decarbonizing ammonia, methanol, and other chemical manufacturing processes, but widespread

adoption requires achieving cost parity with hydrogen produced via steam methane reforming. Improving the electrical efficiency and achievable current density of proton-exchange membrane water electrolyzers (PEMWEs) is therefore essential for lowering the cost of green hydrogen. In this work, we use atomic layer deposition (ALD) to engineer two critical PEMWE stack components, enabling high-current-density operation at elevated cell potentials to directly enhance system efficiency and reduce cost.

A major limitation to high-efficiency PEMWE operation is the significant ohmic loss across the Nafion membrane, which becomes dominant at current densities above ~2 A cm⁻². Nafion is also a per- and polyfluoroalkyl substance (PFAS), raising environmental and regulatory concerns. To address these challenges, we developed zero-gap electrolyzers that employ PFAS-free, proton-conducting silicon oxide membranes fabricated via ALD. Although pristine SiO₂ exhibits proton conductivity 2–3 orders of magnitude lower than Nafion, phosphorus doping substantially enhances H⁺ transport. As a result, thin (<50 nm) PO_x-doped SiO₂ membranes achieve area-specific resistances more than 10× lower than Nafion-117, while their dense structure simultaneously suppresses hydrogen crossover to acceptable levels at pressures up to ~100 bar.

A second barrier to efficient operation is the corrosion and passivation of titanium porous transport layers (PTLs) under high-potential, acidic conditions. This degradation increases interfacial contact resistance and drives voltage decay. Conventional mitigation relies on micrometer-thick noble-metal coatings (Au, Ir, Pt) applied by electrodeposition or PVD, which significantly increases system cost. Here, we investigate ultrathin ALD-deposited iridium coatings (10–20 nm) on titanium sinter PTLs. These ALD Ir coatings exhibit lower interfacial contact resistance than comparable Pt layers due to their high conductivity in both metallic and oxide states. When implemented in PEMWE cells, they support stable operation at 3 A cm⁻² and <1.9 V for 1000 hours with no detectable voltage degradation.

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