Tuesday Afternoon, June 30, 2020

ALD Applications
Room Van Rysselberghe - Session AA-TuA
ALD for Catalysis I & II

Moderators: Stacey F. Bent, Stanford University, Rong Chen, Huazhong University of Science and Technology

1:00pm **AA-TuA-1 Design of Advanced Photocatalytic Materials by Atomic Layer Deposition (ALD)**, ***Syreina Alsayegh***, *M Bechelany, F Zaviska, G Lesage,* Institut Européen des Membranes, France; *A Razzouk, J Stephan,* Lebanese University, Lebanon

Due to the increasing contamination of our natural water resources by a wide range of organic micropollutant (OMPs), there is a need for developing new energy-efficient advanced oxidation processes for the treatment of water contaminated by such refractory pollutants.

Photocatalysis has attracted much attention, due to its ability to degrade toxic organic compounds in wastewater into environmental friendly compounds such as CO_2 and water**.**

Among the various photocatalytic materials, titanium dioxide (TiO_2) has been widely used due to its high photocatalytic efficiency, high stability and low toxicity. However, fast charge recombination and the narrow absorption range in the UV spectrum; limit its photocatalytic efficiency under visible-light irradiation.

In this work TiO_2 nanofibers were synthesized by electrospinning method. In order to improve the photocatalytic activity under visible light, a developed process based on atomic layer deposition (ALD) was used to grow boron nitride (BN) and palladium (Pd) on these fibers. The morphological, structural and optical properties of all fibers were investigated by several characterization techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The influence of chemical and physical properties on the photocatalytic degradation of acetaminophen has been investigated. The results indicate that acetaminophen is stable and difficult to be photodegraded in the absence of photocatalyst. After 4h of visible light irradiation, acetaminophen has been degraded up to 90% in the presence of TiO_2-BN-Pd nanofibers, compared to only 20% degradation with pure TiO_2.

Based on these promising results, the development of ceramic nanofiltration membranes coated with these highly photocatalytic materials will be investigated. In parallel, a better understanding of the photocatalytic oxidation pathways (based on by-product analysis) coupled with toxicity tests (Vibrio Fisheri, Microtox) will be studied.

1:30pm **AA-TuA-3 Atomic Layer Deposition of Manganese Oxide Ultra-Fine Clusters on Titanium Dioxide Nanoparticles for Photocatalytic Hydrogen Production: Experiments & Simulations**, ***Saeed Saedy***, *R Verma,* Delft University of Technology, Netherlands; *S Rhatigan,* University College Cork, Ireland; *J Liu,* Delft University of Technology, Ireland; *M Nolan,* University College Cork, Ireland; *R van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is an attractive method to synthesize advanced functional nanomaterials e.g. photocatalyst: materials that use light to drive chemical reactions. ALD enables depositing uniform nanoparticles (NPs) on the support with controlled size, shape, and morphology. We have deposited manganese oxide (MnO_x) ultra-fine clusters on titanium dioxide ($TiO\text{-}_2$) NPs by means a fluidized bed ALD reactor. Bis(ethylcyclopentadienyl)manganese ($[(C_2H_5)C_5H_4]_2Mn$) and water were used for ALD of MnO_x clusters at 150°C. The microstructure and surface chemistry of ALD synthesized MnO_x/TiO_2 samples were examined using different methods including TEM, XPS, and XRD. The MnO_x/TiO_2 samples were employed as photocatalyst for solar production of H_2. In addition, we have performed first principles studies of models of MnO_x-modified TiO_2. We present detailed results on first principles modelling the metal precursor step in ALD of MnO_x on TiO_2 substrates.

TEM images of the samples revealed ultra-fine MnO_x clusters uniformly dispersed over TiO_2. Powder XRD was not able to detect any reflection corresponding to crystalline manganese oxide; indicating highly dispersed MnO_x. The surface chemistry study of ALD synthesized MnO_x/TiO_2 samples using XPS revealed that the majority of manganese exists in Mn^{2+} form. Such oxidation state could be attributed to mild synthesis temperature employed. This makes it possible to easily obtain the higher oxidation states (i.e. Mn^{3+} and Mn^{4+}) with further post-treatment of samples. In this way a good balance between different oxidation states of manganese, that are crucial for enhanced photocatalytic activity, could be obtained. Density functional theory (DFT) results show that a range of manganese oxidation states can co-exist, along with oxygen vacancies and that the modification of TiO_2 with MnO_x can enhance electron hole separation and trapping. Co-existence of Mn^{2+}, Mn^{3+}, and Mn^{4+} in heterojunction of MnO_x/TiO_2 facilitate charge separation and electron-hole trapping, resulting in superior H_2 productivity. The low temperature nature of ALD synthesis makes it possible to obtain good balance between these diverse oxidation states in final product; whilst the conventional wet chemistry methods require high temperature calcination step to remove the residues of precursors and solvent, which results in higher oxidation state of products as well as resulting in large particles.

1:45pm **AA-TuA-4 In situ Electrochemical APXPS Analysis of ALD Grown Cu Catalyst for CO_2 Reduction**, *H Ali-Löytty, L Palmolahti, M Hannula,* ***Jesse Saari***, Tampere University, Finland; *K Lahtonen,* Tampere University, Finlan; *H Wang, M Soldemo, A Nilsson,* Stockholm University, Sweden; *M Valden,* Tampere University, Finland

The grand challenge in artificial photosynthesis is to produce liquid solar fuels from water and carbon dioxide. Unfortunately, current materials solutions for a photocatalytic (PEC) solar fuel reactor lack efficiency, selectivity towards liquid fuel products, and long-term stability. Cu based catalysts are so far the most promising materials for the carbon dioxide reduction reaction (CO_2RR), whereas the selectivity of Cu catalyst towards liquid products is strongly affected by the exact chemical composition and structure. Recently, Eilert et al. suggested, based on in situ electrochemical APXPS measurements on Cu foil, that the high activity of oxide-derived copper towards CO_2RR stems from subsurface oxygen that was proposed to increase the CO binding energy and thus enhance the production of methanol and multicarbon products [1]. This contradicts the alternative hypothesis that assigns the activity to Cu_2O on the surface, albeit no copper oxide should be stable at reductive CO_2RR conditions.

In this work, ALD grown Cu oxide thin film was analyzed in situ by electrochemical APXPS at the HIPPIE beamline, MAX IV Laboratory. The results show similar oxygen species on reduced ALD Cu oxide thin film to what was assigned to subsurface oxygen in Ref. [1]. Therefore, the ALD grown Cu oxide thin film combined with ALD TiO_2 [2–4] forms a promising catalyst coating for photocathodes in solar fuel cells to produce methanol and multicarbon products from carbon dioxide, water, and sunlight.

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[3] M. Hannula, H. Ali-Löytty, K. Lahtonen, J. Saari, A. Tukiainen, M. Valden, Highly efficient charge separation in model Z-scheme $TiO_2/TiSi_2/Si$ photoanode by micropatterned titanium silicide interlayer, Acta Mater. 174 (2019) 237–245.

[4] H. Ali-Löytty, M. Hannula, J. Saari, L. Palmolahti, B.D. Bhuskute, R. Ulkuniemi, T. Nyyssönen, K. Lahtonen, M. Valden, Diversity of TiO_2: Controlling the Molecular and Electronic Structure of Atomic-Layer-Deposited Black TiO_2, ACS Appl. Mater. Interfaces. 11 (2019) 2758–2762.

2:45pm **AA-TuA-8 Atmospheric-Pressure Atomic Layer Deposited Bimetallic MCu/CeO_2 Catalysts for Enhanced Removal of CO from Fuel-Cell Hydrogen by Preferential Oxidation**, *E Farmani Gheshlaghi, A Irandoust,* ***Fatemeh Gashoul***, *A Khodadadi, Y Mortazavi,* University of Tehran, Iran

Atomic layer deposition has recently been successfully used for uniform deposition of catalyst reactive species on supports with remarkable dispersion, intimate contact and stability. The hydrogen produced for PEM–fuel cells usually contains about 1% CO, which electrically poisons the fuel-cell. The CO can be removed at low temperatures by PROX.

Atomic layer deposition was used to deposit 2.3% Cu and either 0.3% Ni or 0.8% Ru on CeO_2 and the resulting bimetallic catalysts were used in preferential oxidation of CO in H_2-rich feed (PROX).

$Cu(acac)_2$ was reacted with CeO_2–OH groups at 210 °C for 75 min and the produced Hacac was monitored in a gas-cell in FTIR, followed by purging by Ar and subsequently introduction of zero-Air for oxidizing the remaining acac species at 350 °C for 30 min. The number of CeO_2–OH groups was determined by Grignard reaction. The self-limiting deposition of (acac)Cu-O-CeO_2 was confirmed by monitoring Hacac FTIR peak at 1626 cm^{-1}. The sharp decay of CO_2 produced in the oxidation step of remaining acac ligand was a further proof for self-limited deposition. The Catalyst average particle sizes are in the range of 8.7-13.4 nm. 2.3wt% Cu was deposited on ceria by ALD with a remarkable dispersion of 93% when 0.3wt% Ni was ALD deposited on the CuO/CeO_2 the dispersion is still very high at 84%, while the dispersion of the same $NiCu/CeO_2$ catalyst prepared by the conventional method of impregnation is much lower at 66%. $NiCu/CeO_2$ catalyst prepared by ALD reduces about 80-90 ^oC lower than the one prepared by impregnation, indicating higher oxygen mobility required for the PROX.

The CO conversion of catalysts in PROX is shown in Fig3 .The lowest T_{50} and T_{90}, (i.e. temperatures at 50 and 90% CO conversion, respectively) were observed for $RuCu/CeO_2$. The $NiCu/CeO_2$ catalyst prepared by ALD showed much higher activity corresponding to lower T_{50} and T_{90} than the one prepared by impregnation. This catalyst showed a bifunctional synergy of chemisorption and activation of CO on Cu species and mars van krevelen oxidation using surface bimetallic nickel-copper oxide [1, 2]. In conclusion, the $NiCu/CeO_2$ and $RuCu/CeO_2$ catalysts prepared by self-limiting ALD method showed a remarkably high dispersion and activity in PROX.

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2. Fiorenza, R., C. Crisafulli, and S. Scire, *H2 purification through preferential oxidation of CO over ceria supported bimetallic Au-based catalysts.* international journal of hydrogen energy, 2016. **41**(42): p. 19390-19398.

3:30pm **AA-TuA-11 ALD Fabrication of BN Membranes: Environmental Applications***, **Catherine Marichy,*** CNRS, France*; W Hao, C Journet, V Salles,* UNiv Lyon 1, France **INVITED**

Boron nitride (BN) structures are very attractive materials with applications in various areas such as in energy[1] and environmental domains[2]. In particular, BN nanotubes (BNNT) have proven to be suited for conversion of osmotic energy. Use of nanotubes arrays or membrane would thus allow osmotic power harvesting under salinity gradients. BN nanostructures like foams and nanotubes have also revealed to be promising for water purification. ALD technique is an effective approach for surface modification and fabrication of complex nanostructured materials[3]. Recently, based on the polymer derived ceramics route, we developed a two-step ALD process[4] that enables using polymer template and fabricating various BN nanostructures.

Herein, the potential of ALD combined with PDCs for BN membranes will be discussed and exemplified. Highly stable boron nitride nanotube (BNNT) mats are fabricated, from low cost unwoven template, using the 2-step ALD of BN. The obtained membranes display high quality BNNTs, superhydrophocity and stability over a month in air and various pH conditions. Thin material containing several thousands of BN tubes, are also prepared, from a commercially available membrane. In particular, using a double inversion of a polymer membrane combining ALD and PDC vapor infiltration, good quality and large surface boron nitride membranes are successfully elaborated with fine control of the through porosity in term of shape (from annular to cylindrical pores) and size (from few tens to hundreds nanometers)[5]. The ALD fabricated BN materials are characterized in term of morphology and structure using TEM, SEM, EDS, XPS and Raman. Particular attention is given to their use and performances in water treatment.

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5. Marichy, C. *et al.* Fabrication of BN membranes containing high density of cylindrical pores using an elegant approach. *RSC Adv***7**, 20709–20715 (2017).

4:15pm **AA-TuA-14 Highly Stable and Active Catalyst for Dry Reforming of Methane via Molecular Layer Deposition Approach***, **Piyush Ingale,** C Guan, R Kraehnert, R Naumann d'Alnoncourt, A Thomas,* Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

Nickel based catalysts are typically used for the production of synthesis gas by reforming reaction [1]. Dry reforming of methane (DRM) is an attractive reaction for production of synthesis gas by reduction of carbon dioxide. However, Ni nanoparticles (NPs) used in DRM reaction suffer from severe coking and sintering at high temperature which leads to decreased activity of the catalyst [2]. The challenge is to synthesize a catalyst with a high Ni loading and dispersion that is stable under reaction conditions.

Molecular Layer Deposition (MLD) is a novel technique, which is a variant of atomic layer deposition. Organic compound replaces H_2O as ALD reactant to form purely organic or hybrid inorganic-organic layers [3]. In our study, we deposited thin hybrid inorganic-organic layers of alucone on NiO/SiO_2 catalyst via alternative reaction of trimethylaluminium and ethylene glycol at 150°C in a fixed bed reactor [4]. The growth behavior of alucone layers on NiO/SiO_2 powder was studied by in-situ mass-gravimetric study. The synthesized catalytic materials were analyzed by N_2 sorption, XPS, XRD, HRTEM and XRF. The reference and MLD modified catalysts were tested for activity and stability during dry reforming of methane at different temperatures (500°C-800°C). Deactivation of a Ni/SiO_2 reference catalyst was prevented by forming a defined porous net-like over-layer by decomposition of sacrificial organic part of alucone, which prevented the sintering and detachment of Ni nanoparticles by filamentous carbon.

References

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4:30pm **AA-TuA-15 Using ALD to Probe Support and Promoter Effects for Syngas Conversion Catalysts***, S Nathan, A Asundi,* Stanford University*; A Hoffman, A Boubnov, S Bare,* SLAC National Accelerator Laboratory*; **Stacey F. Bent,*** Stanford University

With the intensifying global need for alternative energy and fuels, there is strong interest in the development of efficient catalysts that can drive the chemical conversion of renewable resources into useful products. One promising pathway is to catalytically convert synthesis gas (syngas, CO + H_2) to oxygenates. However, a commercial catalyst that converts syngas to desirable products such as ethanol and other higher oxygenates has not yet been developed due to the many kinetically favorable side reactions that shift selectivity away from the desired products. We study the conversion of syngas to synthetic liquid fuels and high-value chemicals using supported metal, heterogeneous catalysts. Two different examples will be described in which atomic layer deposition (ALD) is used to precisely-modify the catalysts to probe support and promoter effects. First, the promotion of rhodium-based catalysts, which have intrinsic selectivity towards desirable higher oxygenate production, is explored using metal oxides deposited by ALD to modify Rh nanoparticles with monolayer-precise amounts of MoO_3. We show that the promoted catalysts exhibit an increase in both activity and oxygenate selectivity relative to unpromoted Rh nanoparticles, and that this is the result of formation of a novel catalyst structure. The second system is cobalt-based catalysts. Recently, interest has risen in Co_2C catalysts for oxygenate production. We will describe how introducing a ZnO promoting overlayer on Co/SiO_2 by ALD significantly enhances oxygenate selectivity by enabling Co_2C formation during syngas reaction. By exploring several different metal oxide supports, we will show that the composition of the support surface strongly controls whether ZnO-promoted Co can transform into the catalytically-selective Co_2C. Synchrotron-based studies provide insight into the mechanisms by which the support and promoters change reactivity, while density functional theory (DFT) calculations reveal the reaction pathways on the ALD-modified catalyst surfaces. The outlook for atomic scale surface modification using ALD to synthesize and study catalytic materials will be discussed.

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