

# Monday Afternoon, July 17, 2017

## Emerging Materials

### Room Plaza E - Session EM+AA-MoA

#### Organic-Inorganic Hybrid Materials & MLD (1:30-3:30 pm)/Catalysis and Fuel Cells II (4:00-5:30 pm)

Moderators: Sang In Lee, Synos Foundation, Yongfeng Mei, Fudan University, China, Ville Miikkulainen, University of Helsinki

##### 1:30pm EM+AA-MoA-1 Unique Inorganic-Organic Hybrid Materials by ALD/MLD as Enablers of Next-generation Applications?, *Maarit Karppinen*, Aalto University, Finland **INVITED**

The combined ALD/MLD approach has the capacity to yield unique functional hybrid materials, consisting of finely-tuned combinations of inorganic and organic components and possessing a property palette that may reach properties even beyond those directly derived from the component inorganics and organics. These materials are formed through different bonding schemes and may be amorphous or crystalline, isotropic or organized into different superlattice structures. Our recent works<sup>[1-9]</sup> have demonstrated e.g. exciting coordination-network or MOF-type crystal structures, attractive heat and Li-ion conduction properties, and various luminescence phenomena, relevant to next-generation applications in e.g. flexible heat harvesters, photoconverters, microbatteries, sensors or catalysts.

1. T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, Efficiently suppressed thermal conductivity in ZnO thin films via periodic introduction of organic layers, *J. Mater. Chem. A* **2**, 12150 (2014).
2. J.-P. Niemelä, A. Giri, P.E. Hopkins & M. Karppinen, Ultra-low thermal conductivity in TiO<sub>2</sub>:C superlattices, *J. Mater. Chem. A* **3**, 11527 (2015).
3. Z. Giedraityte, P. Sundberg & M. Karppinen, Flexible inorganic-organic thin-film phosphors by ALD/MLD, *J. Mater. Chem. C* **3**, 12316 (2015).
4. Z. Giedraityte, L.-S. Johansson & M. Karppinen, ALD/MLD fabrication of luminescent Eu-organic hybrid thin films using different aromatic carboxylic acid components with N and O donors, *RSC Adv.* **6**, 103412 (2016).
5. Z. Giedraityte, O. Lopez-Acevedo, L.A. Espinosa Leal, V. Pale, J. Sainio, T.S. Tripathi & M. Karppinen, Three-dimensional uracil network with sodium as a linker, *J. Phys. Chem. C* **120**, 26342 (2016).
6. E. Ahvenniemi & M. Karppinen, Atomic/molecular layer deposition: a direct gas-phase route to crystalline metal-organic framework thin films, *Chem. Commun.* **52**, 1139 (2016).
7. E. Ahvenniemi & M. Karppinen, In-situ atomic/molecular layer-by-layer deposition of inorganic-organic coordination network thin films from gaseous precursors, *Chem. Mater.* **28**, 6260 (2016).
8. M. Nisula & M. Karppinen, Atomic/molecular layer deposition of lithium terephthalate thin films as high rate capability Li-ion battery anodes, *Nano Lett.* **16**, 1276 (2016).
9. M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, Lithium aryloxide thin films with guest-induced structural transformation by ALD/MLD, *Chem. Eur. J.*, in press (2017).

##### 2:00pm EM+AA-MoA-3 Atomic/molecular Layer Deposition of Luminescent Inorganic-Organic Hybrid Erbium Pyridine Dicarboxylate Thin Films, *Lukas Mai*, Ruhr-University Bochum, Germany; *Z Giedraityte*, Aalto University, Finland; *M Schmidt*, *D Rogalla*, *S Scholz*, *A Wieck*, Ruhr-University Bochum, Germany; *M Karppinen*, Aalto University, Finland; *A Devi*, Ruhr-University Bochum, Germany

Erbium containing thin film materials are often used in amplifiers, detectors or LEDs because of the specific luminescence of Er<sup>3+</sup> at ~1500 nm.<sup>1</sup> In fact, the absorption coefficient of Er<sup>3+</sup> ions is too low for practical utilization. In order to enhance the luminescence, either the concentration of the erbium ions can be decreased or an organic molecule, which is sensitizing the Er<sup>3+</sup>, can be used.<sup>2</sup> To introduce a sensing organic molecule into a thin film to produce an inorganic-organic hybrid material, exhibiting a low erbium concentration and a defined stoichiometry, the atomic/molecular layer deposition (ALD/MLD) technique is the method of choice. Here, for a complete reaction, the reactivity of the two precursors toward each other must be sufficient.<sup>3</sup> For the ALD of erbium oxide thin films, tris(N,N'-diisopropyl-2-dimethylamido guanidinato)erbium(III) or [Er(DPDMG)<sub>3</sub>] shows high potential, as the all-nitrogen coordinated complex exhibits a high reactivity toward oxygen functionalities.<sup>4</sup> In addition, it was shown that 3,5-pyridine dicarboxylic acid (3,5-PDA) can be

used organic precursor in an ALD/MLD processes as a sensing ligand for the excitation of europium.<sup>5</sup>

Here, the successful combination of [Er(DPDMG)<sub>3</sub>] and 3,5-PDA in an ALD/MLD process is presented.<sup>6</sup> The usage of the guanidinate precursor resulted in high growth rates compared to common rare earth precursors, such as β-diketonates ([Er(THD)<sub>3</sub>]). Furthermore, we investigated the typical ALD characteristics, including surface saturation for the applied precursors, linearity of thickness vs. cycles and an ALD window between 250 °C and 265 °C, proving a true ALD/MLD process (Figure 1). From Rutherford-Backscattering (RBS) experiments, nearly stoichiometric erbium 3,5-pyridine dicarboxylate ([Er<sub>2</sub>(3,5-PDC)<sub>3</sub>]) was found to be deposited. The thin film structure was confirmed by FT-IR spectroscopy, indicating the reaction between the precursors takes place by deprotonation of 3,5-PDA and subsequent coordination of the nitrogen functionality toward the erbium-ion. From UV-Vis investigation (Figure 2, left), a strong absorption at 270 nm was detected and assigned to the absorption of the organic molecule. Furthermore, by direct excitation of different electronic states of the erbium ions, a sharp photoluminescence emission at 1535 nm arises (Figure 2, right). Here, intensity could be increased with decreasing erbium concentration.

The obtained results show the distinct advantage of using a well-developed inorganic precursor such as [Er(DPDMG)<sub>3</sub>] in combination with different organic molecules for ALD/MLD processes in order to produce novel materials that can be precisely tailored for various applications.

##### 2:15pm EM+AA-MoA-4 Molecular Layer Deposition of Manganese-Ethylene Glycol Hybrid Films, *David Bergman*, *J Baker*, *N Yang*, *C MacIsaac*, *A Strickler*, *M Lilletorup*, *S Bent*, Stanford University

Manganese oxide films have shown potential as earth abundant catalysts for various reactions, including the oxygen evolution and reduction reactions (OER and ORR, respectively), the reduction of hydrogen peroxide, and as a promoter for the Fischer-Tropsch reaction. Because of this, many methods have been developed for depositing manganese-based materials, including incipient wetness impregnation and atomic layer deposition (ALD). However, in recent years, there has been increased effort towards the nanostructuring of materials, driven in part by the desire to increase surface-to-volume ratios, tune reaction site chemistry, and improve catalyst stability. One promising method for depositing nanostructured manganese films is hybrid organic-inorganic molecular layer deposition (MLD). By combining a metal precursor typically associated with atomic layer deposition and an organic counter reactant monomer associated with MLD, films of catalytically relevant materials can be grown with a carbon-based component that can be easily removed, allowing for further nanostructuring.

Here, we discuss the deposition of a hybrid organic-manganese film using MLD and the precursors bis(ethylcyclopentadienyl)manganese and ethylene glycol. As-deposited films are characterized using a combination of spectroscopic ellipsometry (SE), Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS) to verify the self-limiting nature of this layer-by-layer process and the successful reaction of the precursors. Time-resolved SE suggests that the organic component of the films is unstable in air over a time frame that can be controlled through the addition of a blocking layer or through chemical and temperature treatments. Characterization of the stabilized and degraded films with atomic force microscopy, scanning electron microscopy, x-ray reflectivity, and XPS show the extent of organic degradation and removal. Finally, the results of testing the mangancone films for use as a catalyst, including the OER/ORR reaction, will be discussed.

##### 2:30pm EM+AA-MoA-5 Synthesis, Characterization, and Electrochemistry of Molybdenum-1,2-Ethanedithiol Hybrid ALD Films, *Callisto MacIsaac*, *R Closser*, *J Schneider*, *T Hellstern*, *D Bergman*, *S Bent*, Stanford University

Hybrid atomic layer deposition-molecular layer deposition (ALD/MLD) is a self-saturating, layer-by-layer, gaseous technique for depositing thin, conformal thin films that involves both the typical metal-containing precursors used in ALD and the organic linkers of MLD. The combination of ALD and MLD chemistries enables the creation of hybrid materials that incorporate the properties and benefits of the parent materials, with the opportunity to create new electrical, magnetic, and catalytic properties. The exploration of novel gas-phase chemistries and unique new types of inorganic-organic thin films is therefore of interest both for the fundamental chemistry and for potential wide-ranging applications.

One such application is the production of hydrogen, a clean, energy-dense fuel that can be formed by the electrochemical splitting of water. Platinum is considered the ideal catalyst for the hydrogen evolution reaction (HER)

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due to its low overpotential; however, it is costly and scarce. One promising substitute for platinum is MoS<sub>2</sub>, a cheap but highly active and stable alternative whose catalytic properties are well-known. However, the HER activity of crystalline MoS<sub>2</sub> is limited to the exposed edge sites of the MoS<sub>2</sub> sheets, since the basal planes are chemically inert. This has led to the investigation of a variety of novel MoS<sub>2</sub> nanoarchitectures ranging from nanowires, supported nanoparticles, and 3D patterned networks in an effort to increase the number of the active edge sites relative to what is present in MoS<sub>2</sub> sheets. Here, we introduce a novel material that incorporates the -S-Mo-S- chemical moiety of MoS<sub>2</sub>, yet has organic linkers that create a porous matrix for these MoS<sub>2</sub>-like domains, as an alternative HER catalyst. Further, these organic linkers can be removed using sulfurization to introduce catalytically active edge sites.

This work investigates in detail a novel hybrid ALD-MLD process from the precursors Mo(CO)<sub>6</sub> and 1,2-ethanedithiol, with a focus on the film growth behavior and structure. Fourier transform infrared spectroscopy, X-ray diffraction, X-ray reflectivity, Raman spectroscopy, variable angle spectroscopic ellipsometry, and X-ray photoelectric spectroscopy are utilized to characterize the resultant material. This work further details proof-of-concept experiments using the Mo-ethanedithiol hybrid films as a catalyst for HER. The results show that the catalyst is active for HER, with a lower overpotential at 10mA/cm<sup>2</sup> and a higher current density on a geometric basis compared to flat MoS<sub>2</sub>. The study offers insight into the possibility of other organic-inorganic materials with similar properties that can be deposited in an ALD-regime.

**2:45pm EM+AA-MoA-6 Ultrahigh Elastic Strain Energy Storage in Metal-Oxide-Infiltrated Polymer Nanopillars Generated by Infiltration Synthesis, Chang-Yong Nam**, Brookhaven National Laboratory; **K Dusoe**, University of Connecticut; **A Stein, X Ye, K Kisslinger**, Brookhaven National Laboratory; **S Lee**, University of Connecticut

Infiltration synthesis is a type of inorganic-organic hybridization technique derived from atomic layer deposition, where the material precursors infiltrate into polymer medium, generating unique organic-inorganic hybrids. Here, we report the generation of an organic-inorganic hybrid nanostructure having an exceptional ability to store elastic strain energy, whose mechanical modulus of resilience for a given density exceeds what is observed in most engineering materials. Lithographically patterned polymer nanopillars with ~300 nm diameter and 1 μm height from a negative-tone resist SU-8 were subjected to the infiltration synthesis of AlO<sub>x</sub> using trimethylaluminum (TMA) and water as precursors, creating unique composite nanopillars in which an interpenetrating polymer-AlO<sub>x</sub> hybridized matrix extended down to ~50 nm below the surface. We performed the mechanical testing of the produced hybrid nanopillars by using an in-situ nanomechanical testing system based on a scanning electron microscope. The hybrid nanopillars after 16 cycles of AlO<sub>x</sub> infiltration exhibited a high yield strength (500 MPa) which was accompanied by an unusually low Young's modulus (7.5 GPa) in uniaxial nanocompression tests, a unique combination of strength and modulus that has never been observed. The resulting apparent modulus of resilience, a parameter that quantifies the ability of storing elastic energy, was over 16,000 kJ/m<sup>3</sup>, the highest among the known values. Consequently, this is translated into the specific modulus of resilience higher than most engineering materials. The infiltration-synthesized composite nanopillars combine the exceptional, tunable mechanical resilience with the compatibility with lithographic techniques, promising potential applications in micro- and nanoelectromechanical systems which require ultrahigh-elastic components for advanced actuation and sensor devices.

**3:00pm EM+AA-MoA-7 Kinetics of Vapor Phase Infiltration: Fitting Theory to Experimental Measurements, C Leng, Mark Losego**, Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel electrical, chemical, and/or physical properties. These new materials can have applications as chemical barriers, filtration media, or photolithographic hard masks. Here, the focus is to have a better knowledge of the diffusion and reaction kinetics during this vapor phase infiltration process with the goal of understanding how both polymer structure and processing conditions can maximize the depth of inorganic infiltration. In this study, we use the model system of poly(methyl methacrylate) (PMMA) films exposed to trimethylaluminum (TMA) gaseous precursors. A basic kinetics model has been developed to describe the diffusion and reaction processes in VPI and has been fit to experimental

data. From spectroscopic ellipsometry we are able to track total infiltration based upon film swelling and changes in refractive index. At a process temperature of 60°C, films are found to initially swell with the square root of time, suggesting that kinetics are dominated by Fickian-like diffusion behavior. A maximum film swelling of 60% is measured at any exposure time exceeding 1000 minutes. Using these swelling curves as a proxy for infiltration amount, we calculate effective diffusion coefficients for TMA in PMMA at 60° C to be on the order of 10<sup>-15</sup> cm<sup>2</sup>/s, with faster diffusion in PMMA films of lower molecular weight. At higher temperatures (160° C), swelling is less significant, but refractive indices of infiltrated films increase by 2% to 3%. We interpret the decrease in swelling as a result of faster chain relaxation when processing above the glass transition temperature of the polymer. To determine whether polymer films infiltrated and swollen below T<sub>g</sub> can also undergo similar polymer relaxation behaviors, a systematic study of post-annealing was carried out at 150° C. In these instances, the amount of swelling decreases by approximately half and refractive index increases but to a lesser degree than those from the initial high process temperatures. The results of this study will be put in context with other ongoing research in the field to help build a phenomenological model that can be used to better design vapor phase processing schemes to form organic-inorganic hybrid materials.

**3:15pm EM+AA-MoA-8 Vapor Phase Infiltration for Doping Conducting Polymers, W Wang, F Yang, CIC nanoGUNE, Spain; C Chen, Y Qin, Chinese Academy of Sciences, China; Mato Knez, CIC nanoGUNE, Spain**

Vapor phase infiltration is a top-down strategy that is based on the ALD process and allows fabrication of organic-inorganic hybrid materials by incorporation of metal organic precursors into polymeric substrates. The growth of inorganic clusters or particles in the subsurface area of a polymer allows modifying some of the physical properties of the polymer greatly. While related earlier work investigated the improvement of mechanical properties of polymers applying the infiltration route, here we describe a novel approach, namely a single precursor infiltration process to dope polyaniline (PANI) or the polythiophene P3HT. The infiltration was performed with various precursors typically used in ALD processes. The conductivities were assessed with four-point probe measurements and showed significant enhancement by up to 6 orders of magnitude, confirming the efficiency of the infiltration process. Furthermore, we found that the thermal and temporal stability of the thus doped polymers were significantly enhanced in comparison to their traditionally wet-chemically doped counterparts. For example, conductivities of infiltration-doped PANI outperform the conductivity of HCl-doped PANI if exposed to elevated temperatures (150 °C) in vacuum. In the case of P3HT, the infiltration-doped polymer maintains the gained conductivity even after exposure to ambient conditions for more than 30 days. The chemical changes resulting from the infiltration of the two polymers were characterized by FTIR and Raman spectroscopy and will be discussed. SEM micrographs showed that the morphologies of the samples did not alter after the infiltration process, being one of the most important arguments for doping conductive polymers in the presented way.

**4:00pm EM+AA-MoA-11 Catalysts Modified by ALD for Harsh Biomass Conversion Processes, Steven Christensen, K Hurst, M Griffin, D Vardon, National Renewable Energy Laboratory**

Black liquor, fast pyrolysis, and bio-coke are terms that denote some of the challenges encountered from the feedstock, processes, and unwanted products of catalytic biomass conversion that ALD techniques can address. Catalysts developed for the petroleum industry often deactivate and degrade when applied to biomass applications. Furthermore, biomass can offer chemicals and fuels that cannot be derived from petroleum feedstock and therefore new catalyst formulations and properties are required. Research of catalytic materials for biomass conversion at the National Renewable Energy Laboratory is using ALD to reduce metal leaching, improve de-oxygenation catalysis, and tailor catalysts with novel properties. An overview of the challenges for biomass processing and strategies for how ALD catalysts can be designed to solve these problems will be presented. The production of bio-nylon precursors and catalytic fast pyrolysis of bio-oil will be used as examples. Advanced catalysts from ALD look to have an exciting future to help enable new technologies for this industry.

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4:15pm EM+AA-MoA-12 Effects of Alumina Incorporation by Particle Atomic Layer Deposition on Sintering and Microstructure of Yttria-Stabilized Zirconia (8YSZ), *Christopher Bartel, R O'Toole, M Kodas, A Drake, A Horrell, University of Colorado - Boulder; R Hall, ALDNanoSolutions, Inc.; C Musgrave, A Weimer, University of Colorado - Boulder*

Yttria-stabilized cubic zirconia (YSZ) is the most-common electrolyte material for solid oxide fuel cells (SOFC) due to its reasonable oxygen-ion conductivity and chemical stability across a wide range of environments. To achieve suitable ionic conductivity, YSZ electrolytes must be near theoretical density; this necessitates high sintering temperatures, often exceeding 1450 °C. This high sintering temperature limits the viability of low-cost one-step sintering during manufacturing and thus increases the cost of SOFC fabrication. Previous researchers have successfully lowered the required YSZ sintering temperature through incorporation of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) particles with the YSZ. While this technique has proven to be successful in reducing the sintering temperature, the presence of particulate  $\text{Al}_2\text{O}_3$  inclusions in densified parts reduces the homogeneity of the electrolyte which may have deleterious effects on operation. In this work, we report on the use of atomic layer deposition (ALD) to precisely and conformally coat individual YSZ particles with the desired amount of  $\text{Al}_2\text{O}_3$ . Constant-rate-of-heating (CRH) experiments were conducted using a horizontal push-rod dilatometer to extract the activation energy of sintering in the initial stage and also gain mechanistic insights into the active diffusion mechanisms as a function of ALD film thickness. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to characterize the as-deposited thin  $\text{Al}_2\text{O}_3$  films and the effects of the  $\text{Al}_2\text{O}_3$  films on grain growth and microstructure during densification.  $\text{Al}_2\text{O}_3$  incorporation by ALD is shown to have unique phenomenological effects on the densification of YSZ as compared with conventional  $\text{Al}_2\text{O}_3$  incorporation using particle-based approaches.

4:30pm EM+AA-MoA-13 Low-Temperature ALD Cobalt Sulfide for High-Efficient Hydrogen Evolution Textiles, *Donghyun Kim, J Park, H Kim, Yonsei University, Republic of Korea*

Hydrogen energy is promising energy source, because it is sustainable and renewable green energy alternatives for fossil fuels and coal. The key component for producing hydrogen in water is the catalyst for hydrogen evolution reaction (HER).

To increase HER efficiency, maximizing surface area for reaction is important factor. Complex structure is widely used to meet this requirement. For example, conducting substrate based on nanowire, nickel foam, or carbon nanotube would serve as electron transfer template. However, these conventional substrates for HER limit its applicable area such as flexible devices. To overcome the limit, conducting textile could be adequate substrate for HER. Textile is intensively used as form of fabric, and it can be applied from clothes to massive energy storage system.

Up to now, the noble metal including Pt is considered as the best electrocatalyst for HER with low overpotential, tafel slope and high exchange current density. However, the noble metal is extremely expensive so that catalyst based on earth-abundant materials with high-efficiency are required. Transition metal chalcogenides (TMCs) have attracted attention owing to its superior catalytic properties. Due to the electron configuration of TMCs, outermost  $d$  orbitals of TMCs make electron transfer easy. Especially, metallic TMCs including cobalt sulfide, vanadium sulfide, 1T-molybdenum sulfide shows superb electrochemical properties due to their high conductivity which promotes transport of electrons.

In this study, the cobalt sulfide ( $\text{CoS}_x$ ) was synthesized using atomic layer deposition (ALD). ALD is the self-limited process based on surface reaction so that the  $\text{CoS}_x$  could be deposited with excellent uniformity, precisely controlled thickness in large area. The characteristics of deposited ALD  $\text{CoS}_x$  were analyzed using XPS and XRD. The morphology and thickness of the film were observed using SEM and AFM and finally, the electrocatalyst based on cobalt sulfide could be synthesized. It showed low tafel slope (~41 mV/dec) comparable to the value of Pt, and low overpotential. Also, conducting textiles could be utilized as template for HER catalyst due to the low-temperature process of ALD. As the result, the ALD  $\text{CoS}_x$  can be considered as the promising electrocatalyst for HER as promising candidate for replacement of Pt.

4:45pm EM+AA-MoA-14 Atomic Layer Deposition of Platinum: An Avenue to the Scalable Synthesis of Ultra-low-loading Fuel Cell Catalysts?, *A Goulas, Delft IMP B.V., Netherlands; F Grillo, A Dokania, Delft University of Technology, Netherlands; D Valdesueiro, Delft IMP B.V., Netherlands; H Van Bui, Delft University of Technology, Netherlands; Bart van Limp, Delft IMP B.V., Netherlands; J Mouljin, J van Ommen, Delft University of Technology, Netherlands*

We present an approach for tailoring the growth of platinum nanostructures on commercially-available carbon black powder (Vulcan XC72) based on atomic layer deposition (ALD) in an atmospheric-pressure fluidized bed reactor. By varying the number of ALD cycles, the metal loading could be effectively controlled in the 2 – 10 wt.% range. The expansion of the ALD processing window into lower deposition temperatures, enables us to steer the Pt growth towards highly-dispersed nanoparticles with narrow size distributions.

Although one does not simply control the NP size by the number of ALD cycles, here, by using atmospheric-pressure ALD in a fluidized bed reactor we could use the temperature as another knob to tailor the size distribution. In particular, by employing low deposition temperatures we could achieve narrow size distributions while maximizing the inter-particle distance.

5:00pm EM+AA-MoA-15 Pd-Ag Bimetallic Nanograin-Decorated Nylon Nanofibers: Efficient Catalytic Reduction of 4-Nitrophenol, *K Ranjith, A Celebioglu, Bilkent University, Turkey; H Eren, Delft University of Technology, Netherlands; N Biyikli, Utah State University; Tamer Uyar, Bilkent University, Turkey*

Reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride catalyzed by both monometallic and bimetallic nanostructures through hydrogenation process is of utmost interest. By constructing the bimetallic functionality on a support or template has attracted much attention over the points of catalytic interaction and stability. We demonstrate an effective synthesis process of creating the Pd-Ag bimetallic functionality on the Nylon nanofibers by combining the atomic layer deposition (ALD) of Pd nano grains followed by the solution chemical reduction of Ag ions to form the Pd-Ag bimetallic nanograin alloys. Through the ALD process, the size, density and monodispersivity of the Pd nanoparticles were controlled and reflected as nucleation sites for the loading of Ag ion with controllable ratio. The evolution of the catalytic activity through the reduction of 4-nitrophenol to 4-aminophenol improved on constructing the bimetallic functionality which betters the selectivity of p-nitrophenol adsorbate to the catalytic surface as predicted by Brønsted–Evans–Polanyi (BEP) relation. Different composition ratio of the Ag ion with the bimetallic functionality with ALD Pd nano grains initiates the understanding of the electronic and geometric effect exhibited by the role of Ag ion at the Pd interface. Additionally, Pd nanograins act as nucleation platform for the Ag ion loading, which reveal the absence of sole decoration of Ag ions on the nylon fiber surface. The reduction rate was significantly higher for the Pd-Ag bimetallic alloys loaded nylon fibers relative to the Ag and Pd decorated Nylon fibers which evidence the electronic promotion of Pd ions through the Ag ion which results in the improved catalytic behavior. This observation attributes to the simultaneous effect of (i) enhancive surface area for the interaction through the template form, (ii) supportive high interactive crystallographic facets for the catalytic reduction, and composition of the bimetallic nanostructures. The template based catalyst shows the use of recoverable and reusable performance without obvious loss on catalyst and activity after 3 consecutive cycles.

5:15pm EM+AA-MoA-16 Size-Selective Catalysts with an Ultra-Thin Porous Shell Prepared by Molecular Layer Deposition, *Zeyu Shang, X Liang, Missouri University of Science and Technology*

Heterogeneous catalysts are widely used due to many advantages, including the ease of separating the catalysts by filtration after reaction. However, heterogeneous catalysts usually cannot selectively convert specific molecules in a reactant mixture to only desired products. Size-selective catalysis is an important concept for improving the selectivity of heterogeneous catalysts. In most previous studies, unsupported and nonporous substrates supported metallic nanoparticles were encapsulated in relatively thick porous structures to realize the size-selectivity of heterogeneous catalysts by the size discrimination effect of the porous shell. However, the catalytic activity of the catalysts greatly decreased due to mass transfer limitations brought by relatively thick shells and the contact areas between the porous shells and active sites. In our study, we deposited an ultra-thin porous oxide shell on high surface area substrate-supported Pt nanoparticle catalysts, using molecular layer deposition

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(MLD), followed by oxidation to remove the organic components in hybrid organic/inorganic MLD films. The encapsulated catalyst showed very high selectivity in catalyzing hydrogenation reactions of n-hexene over cis-cyclooctene. However, there was a decrease of the catalytic activity due to contact areas between the porous shell and metallic nanoparticles. To reduce the contact areas, we introduced gaps between the Pt nanoparticles and porous shells using a sacrificial layer of self-assembled monolayers (SAMs) on the Pt nanoparticles, before the deposition of a MLD layer. This novel nanostructured catalyst showed much higher activity, as compared to the catalyst that had been directly coated with the MLD layer.

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