

Nanomaterials

Room Hau - Session NM-MoE

Nanocatalysis

Moderators: Ryan Richards, Colorado School of Mines, USA, Brian Trewyn, Colorado School of Mines, USA

6:00pm NM-MoE2 Electrocatalysis - Ensemble versus Single Nanoparticle Investigations, Kristina Tschulik, Ruhr-Univ. Bochum, Germany INVITED
Nanomaterials play a crucial role in catalysis thanks to their large surface-to-volume ratio and the possibility to adjust their electronic structure, i.e. reactivity. As it provides several promising routes to sustainable energy, electrocatalysis is a strongly expanding research topic to date. It provides a route to both, the production of sustainable fuels by water electrolysis or CO₂ reduction, and to their environmentally friendly utilization in hydrogen or alcohol fuel cells. The fact that these reactions occur at the solid liquid interface and that electronic and ionic charge carriers are involved, make the characterization of nano-electrocatalysts a challenging task. The overlapping effects of altered mass transport at nanoparticle modified surfaces and of changed electronic connection add to the changes in reaction kinetics. Hence, it is difficult to directly extract kinetic information from experimental data.

To overcome the obstacles of poor electronic conductivity and slow diffusional mass transport, nanomaterials are typically mixed with a conductive binder and thick films of this mixture are immobilized on rotating disc electrodes for electrocatalysis studies. However, this conventional procedure fails if porous films result or the influence of the binder material is not known. Thus, new methods for binder-free electrocatalyst characterization are being developed to enable fast and reliable electrochemical characterization of new catalyst materials. Two new approaches are presented that facilitate binder-free testing of electrocatalysts either using (sub-)monolayer films of nanomaterials [1] or single nanoparticle impact studies. In the first case, ensembles of nanoparticles on an electrode are produced [1], while the latter approach utilizes the Brownian motion based impacts of nanoparticles at an electrode to study their [2] electrocatalytic performance [2]. Both methodologies avoid thick films and convection. Hence, conductivity effects are minimized, while changes in the mass transport of reactants can be quantified using numerical simulations of the diffusional processes at nanoparticle modified electrodes. Accounting for these overlapping effects, the experimental electrochemical response during electrochemical reduction of CO₂, O₂ or H⁺, can be deconvoluted to reveal the true kinetic performance of novel catalysts. These methods may thus enable a more rational design and testing of new catalyst materials in the future.

References:

[1] C.C.M Neumann, E. Laborda, K. Tschulik, K.R. Ward, R.G. Compton, *Nano Res.* 6 (2013), 511.

[2] X. Li, C. Batchelor-McAuley, S.A.I. Whitby, K. Tschulik, L. Shao, R.G. Compton, *Angew. Chem.*, 55, (2016) 4296.

6:40pm NM-MoE4 Formation and Migration of a Au-CO Complex in Gold-assisted Catalysis, Monica McEntee, University of Virginia, USA; J. Wang, Oak Ridge National Laboratory, USA; W. Tang, M. Neurock, University of Virginia, USA; A.P. Baddorf, P. Maksymovych, Oak Ridge National Laboratory, USA; J.T. Yates, Jr., University of Virginia, USA

Fabrication of highly active, stable and selective nanocatalysts requires an understanding of the mechanisms that control charge transfer and the activation of adsorbate interactions at specific surface sites. Here I report on the nature of low coordinated Au sites (likely to be on Au nanoparticles) by creating nano-pits on a Au (111) single crystal surface using scanning tunneling microscopy (STM). At room temperature, CO molecules adsorb on Au atoms and form Au-CO complexes, which allow for Au atom extraction from dislocation sites of the herringbone reconstruction. These complexes migrate and form Au clusters on elbows and edges of the Au surface. In conjunction with STM, transmission infrared (IR) spectroscopy and density functional theory (DFT) calculations were used to understand this new mechanistic motif. The mechanism for the Au atom extraction involves electron transfer from CO to Au forming positive charge on CO that creates stronger bonding with Au atoms of lower coordination number. Nanocatalysts involving Au nanoparticles with an abundance of low coordinated Au sites likely exhibit similar properties and these studies could foster future enhanced catalysts.

7:00pm NM-MoE5 Advanced Nanostructures as Electrocatalysts for Energy Applications, Vojislav Stamenkovic, Argonne National Laboratory, USA

Electrocatalysis is a subclass of heterogeneous catalysis that is aimed towards increase of the electrochemical reaction rates that are taking place at the surfaces. Real-world electrocatalysts are usually based on precious metals in the form of nanoparticles due to their high surface-to-volume ratio, which enables better utilization of employed materials. Ability to tailor nanostructure of an electrocatalyst is critical in order to tune their electrocatalytic properties. Over the last decade, that has mainly been achieved through implementation of fundamental studies performed on well-defined extended surfaces with distinct single crystalline and polycrystalline structures. Based on these studies, it has been demonstrated that performance of an electrocatalyst could be significantly changed through the control of size, composition, morphology and architecture of employed nanomaterials. This presentation will outline the most important in development of an efficient electrocatalyst: 1) electrochemical properties of well-defined surfaces, 2) synthesis and characterization of different electrocatalysts, and 3) correlation between physical properties (size, shape, composition and morphology) and electrochemical behavior (activity and durability). In addition, a novel research platform in the development of functional nanomaterials for energy conversion and storage applications such as fuel cells electrolyzers and batteries will also be presented.

Besides activity, our results have demonstrated that durability of an electrocatalyst can also be tailored by manipulating the catalyst structure. For instance, in order to address this issue a core-shell electrocatalyst where an Au core was coated by a multilayered MPt₃ shell was developed. Such core-shell Au/MPt₃ electrocatalysts showed negligible activity loss after 60,000 cycles between 0.6 – 1.1 V (vs. RHE). In the most recent example, an entire gold core was replaced by Ni core which was coated by gold and then encapsulated by Pt-bimetallic shell, creating a core-interlayer-shell structure with unique electrochemical properties. In addition, a highly functional hollow type multimetallic structures will be discussed as efficient electrocatalysts for oxygen reduction, hydrogen oxidation and evolution reactions.

Common ground for all systems relies on distinguished approach that includes collection of fundamental knowledge from well-defined highly crystalline systems and connects them to the real world nanomaterials.

References:

[1] Stamenkovic et al. *Science* 315 (2007) 493.

[2] Stamenkovic et al. *Nature Mat.* 6 (2007) 241.

[3] Chen et al. *Science* 343 (2014) 1339.

[4] Kang et al. *Nano Letters* 14(2014) 6361.

7:40pm NM-MoE7 Metal Nanoparticles Intercalated in Mesoporous Silica as Robust Catalyst Platforms, Ryan Richards, S. Gage, Y. Ji, M. Menart, M. Davidson, S. Pylpenko, B. Trewyn, Colorado School of Mines, USA

Metal nanoparticles have been in the research spotlight for decades for their activity as efficient and highly selective heterogeneous catalysts. Similar to many nanoscale metal particles, the catalytic activity of for example Pd and Au NPs also depends on particle size. At high temperatures however the particles often undergo aggregation and sintering resulting in an increase in particle size and a corresponding loss in activity. In order impart robustness to Pd and Au NPs catalysts, supporting NPs on another material is a common approach. Amongst support materials, silica is attractive for its relative chemical inertness and thermal stability. Here, we present a sol-gel process by which we intercalated Pd and Au into the wall framework of mesoporous silica yielding a catalytic material termed PdMS or GMS here (Pd or Au in the walls of mesoporous silica). The PdMS material has been shown to be stable (maintaining both porous silica framework and Pd nanoparticle size) at temperatures as high as 650 °C making them attractive for high temperature processes.

8:00pm NM-MoE8 Development of Noble-metal Free and Durable Nanoporous Catalysts for Exhaust-Gas Conversion, Takeshi Fujita, Tohoku University, Japan

Precious metals (Pt and Pd) are typical materials for heterogeneous exhaust-gas catalysts in automotive systems. During a catalytic reaction in conventional nanoparticulate systems, such as Pt, active nanoparticles (typically less than 5 nm) aggregate, resulting in a significant reduction of performance. In addition, their limited resources and high market-driven

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prices are principal issues in realizing the path toward a more sustainable society.

Herein, we developed an earth-abundant nanoporous NiCuMnO catalyst by leaching Mn from a CuNiMn precursor. The developed catalyst was catalytically active and durable for NO reduction and CO oxidation. During catalytic reactions, the nanostructure self-transformed into a more active nanostructure; in particular, the Cu/CuO regions derived from the nanostructure were very active, and further significant coarsening was not observed without the loss of activity, as these regions were tangled with a stable nanoporous NiMnO network. The self-transformed nanostructure successfully completed a long-term durability test for NO reduction at 400 °C for 10 days. The *in situ* TEM under NO reduction clearly provided evidence for the instant reaction-induced self-transformation of the nanostructure. This result demonstrates an important implication of this work: even when nanoporous alloys are coarsened to significantly greater than 100 nm, as long as the metal phase is entangled and sustained within a stable nanoporous network of oxides, geometrically necessary surface defects can be retained as catalytically active sites and further enhanced catalytic performance exhibited because of the metal-oxide interfaces (i.e. perimeter); thus, catalytic activity can be retained with durability.

Although the nanoporous NiCuMnO catalyst requires more improvement at low temperatures, the temperature of the catalyst bed in an automobile system is typically higher than 400 °C, where nanoparticles become significantly unstable. Production of the nanoporous catalysts can be easily scaled up, and they may be a rational alternative to traditional precious-metal catalysts for automotive systems in the near future [1].

References

[1] T. Fujita *et al.*, *Adv. Func. Mater.* **26** (2016) 1609-1616.

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