

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-TuM

### Nanochemistry in Heterogeneous Catalysis

**Moderator:** Matthew Marcinkowski, Pacific Northwest National Laboratory

8:00am **HC+SS-TuM1 Probing Oxide Supported Single Rh Atoms as Model Catalysts for CO Oxidation**, *Alex C. Schilling, E.C.H. Sykes*, Tufts University

In recent years, single atom active sites have become a central topic in the creation of new catalysts with a focus on supported Rh atoms as a means of activating C-H bonds and catalyzing the water-gas shift reaction. These heterogeneous catalysts can operate at the single atom limit, decreasing the amount of precious metal on the support and thereby the price of the catalyst. However, debate still exists in the literature over the nature of the active sites and their mechanism of operation. We have taken a reductionist model study approach towards understanding these issues in well-defined single atom systems. Using surface-sensitive techniques, such as Temperature Programmed Desorption (TPD) and Reflection Absorption Infrared Spectroscopy (RAIRS), we assess the ability of single Rh atoms to oxidize CO. Experiments show that this system has the potential to convert the majority of Rh adsorbed CO to CO<sub>2</sub> at relatively low temperature. At low coverages of Rh (0.5-6%) preliminary experiments show two distinct desorption states for CO<sub>2</sub> at 325 K and 462 K. These TPD peaks account for 85% of all CO desorption from the Rh sites. The other 15% desorbs from Rh as CO at the same temperatures. Further work on this system will give insight into the nature of the active Rh sites, their interaction with both CO and support oxide, as well as the reaction mechanism.

8:20am **HC+SS-TuM2 Methanol Partial Oxidation Mechanisms on a Single-site Catalyst Pt<sub>1</sub>/ZnO(10-10): A First-principles Study**, *Tao Jiang*, University of Central Florida; *T.B. Rawal*, Oak Ridge National Laboratory; *D. Le, T.S. Rahman*, University of Central Florida

The rational design of single metal atoms anchored on non-metallic surface has the great potential to offer catalysts with high activity and selectivity [1]. Towards this goal, we have carried out density functional theory based calculations of the catalytic behavior of singly dispersed Pt atoms on ZnO, Pt<sub>1</sub>/ZnO(10-10), as a model system for methanol partial oxidation. We find that methanol adsorption is favored at the surface Zn site whereas oxygen prefers to adsorb at the Pt-Zn site. The adsorption of reaction intermediates CO, CO<sub>2</sub>, and H<sub>2</sub> are favored at the Pt site, whereas H<sub>2</sub>O prefers to sit at the Zn site. Secondly, along the reaction pathways for methanol dehydrogenation, we will illustrate that the O-H bond scission from methanol is slightly exothermic ( $\Delta E = -13$  meV). The resultant methoxy then preferentially adsorbs at the Pt-Zn site, where C-H bond of methoxy can be easily activated. The dissociation of methoxy (CH<sub>3</sub>O' → CH<sub>2</sub>O+H) is exothermic ( $\Delta E = -0.42$  eV) and that of formaldehyde (CH<sub>2</sub>O → CHO+H) is endothermic ( $\Delta E = +0.16$  eV). The results suggest that Pt<sub>1</sub>/ZnO(10-10) is a potential single-atom catalyst for methanol oxidation. We will compare our findings with those for the related system Pd<sub>1</sub>/ZnO(10-10) [1] and available experimental observations to evaluate their relative advantages for methanol partial oxidation.

[1] T. B. Rawal, S. R. Acharya, S. Hong, D. Le, Y. Tang, F. F. Tao, and T. S. Rahman, submitted (2018).

The work is partially supported by DOE grants DE-FG02-07ER15842

8:40am **HC+SS-TuM3 Imaging the Ordering of Weakly Adsorbed CO<sub>2</sub> Molecules on Rutile Titania using Ambient Pressure Microscopy and Spectroscopy**, *Rebecca Hamlyn*<sup>1</sup>, Brookhaven National Lab; *J.A. Rodriguez, S. Senanayake, M. Mahapatra, F. Xu, D. Grinter, S. Luo, P. Liu, R. Palomino, I. Waluyo, S. Kattel, D.J. Stacchiola*, Brookhaven National Laboratory

Recently, great effort has been devoted to the capture, activation and conversion of carbon dioxide (CO<sub>2</sub>), a ubiquitous greenhouse gas and by-product of many chemical processes. The high stability and non-polar nature of CO<sub>2</sub> leads to weak bonding with well-defined surfaces of metals and oxides. The interactions of CO<sub>2</sub> involve intermolecular forces with noncovalent bonding (van der Waals), and often a surface needs to be functionalized to create polar sites that can "capture" or bind CO<sub>2</sub>. Images from ambient pressure scanning tunneling microscopy show that a substantial amount of CO<sub>2</sub> can reside on a TiO<sub>2</sub>(110) surface at room temperature as a consequence of weak bonding interactions with the

substrate. Furthermore, the adsorbates exhibit a disorder-order transition on this surface, despite the lack of a strong interaction that may serve to impose its substrate periodicity on the adsorbed film. This phenomena is of interest to many areas of the surface science and chemistry community wherein condensation of van der Waals gases such as CH<sub>4</sub>, N<sub>2</sub>, or CO<sub>2</sub>.

We have employed microscopic imaging under *in situ* conditions, soft X-ray spectroscopy and theory to decipher the unique ordering behavior seen for CO<sub>2</sub> on TiO<sub>2</sub>(110).

9:00am **HC+SS-TuM4 Using Sn Atomic Layer Deposition to Tune the Coking Resistance of Size-selected Pt Model Catalysts**, *Timothy Gorey*<sup>2</sup>, *E. Baxter, A. Cass, S. Anderson*, University of Utah; *B. Zandkarimi, A. Alexandrova*, University of California at Los Angeles

Size-selected cluster catalysts are powerful tools that enable us to probe and characterize specific catalytic reaction mechanisms controlled by the particle's size. By combining deposition of atomically-selected Pt clusters, with ALD to selectively add Sn atoms to the clusters, we obtain Pt-Sn alloy clusters with exactly known numbers of Pt atoms, and a narrow distribution of Sn atoms. In addition to being a powerful experimental tool, having size-selected model catalysts with well-defined compositions allow detailed theoretical simulations, providing insight into cluster structure, and the mechanistic origins of the size and alloying effects observed experimentally. It is found that tin alloying has a large and beneficial effect on both the branching between intact ethylene desorption vs. dehydrogenation/carbon deposition, and on the thermal stability of the clusters at temperatures to 700 K. Theoretical predictions for the structures and electronic properties of the thermally accessible ensemble of isomers are used to rationalize the observed effects in detail.

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9:20am **HC+SS-TuM5 Synergistic Effects of Pd and PdO Domains on Thin Film TbO<sub>x</sub>(111)/Pt(111)**, *Christopher Lee*<sup>3</sup>, *J.F. Weaver*, University of Florida

Among the rare earth oxides (REOs), the terbium oxides exhibit favorable properties in selective oxidation catalysis due to the flexibility in the storage and release of oxygen within the lattice. Of particular note is the ease of structural rearrangement into well-ordered intermediates between the Tb<sub>2</sub>O<sub>3</sub> and TbO<sub>2</sub> stoichiometries, providing a novel, dynamic surface interface for the promotion of oxidation reactions. We investigated the stabilization and reactivity of metallic Pd domains grown on top of ultrathin c-Tb<sub>2</sub>O<sub>3</sub>(111)/Pt(111) films in ultrahigh vacuum (UHV) and subsequently oxidized by plasma-generated gaseous atomic oxygen. XPS shows that while both the film and metallic domains are almost fully oxidized to both TbO<sub>2</sub> and PdO by atomic oxygen, subsequent annealing to ~600 K can significantly reduce the TbO<sub>x</sub> supporting film while leaving the PdO largely unreduced. Our results provide evidence that the presence of Pd structures on the TbO<sub>x</sub> surface greatly promotes the thermal reduction of TbO<sub>2</sub>. Further annealing of the system at ~900 K results in PdO decomposition and agglomeration of metallic Pd domains as evidenced by the diminution of the XPS Pd 3d peaks.

The oxidation/reduction behavior of the Pd/TbO<sub>x</sub>(111) system has enabled the study of oxidative reactions on three characteristic interfaces: PdO on TbO<sub>2</sub>(111), PdO on Tb<sub>n</sub>O<sub>2n-m</sub>(111), and Pd on c-Tb<sub>2</sub>O<sub>3</sub>(111). TPD and TPRS experiments show that adsorbed CO and C<sub>3</sub>H<sub>8</sub> only react with the stabilized PdO domains, with C<sub>3</sub>H<sub>8</sub> desorption at ~200 K being characteristic of adsorbed propane  $\sigma$ -complexes observed previously on PdO(101) surfaces. Continual reduction of PdO with adsorbed CO and C<sub>3</sub>H<sub>8</sub> also show that when thermal reduction is limited to ~600 K, the underlying TbO<sub>x</sub> support will continually replenish the reduced PdO domains with oxygen. This is also noted by the substantially higher conversion of adsorbed CO to CO<sub>2</sub> compared with that seen on pure PdO(101) as conversion would be less limited if reactive oxygen is supplied from both PdO and the TbO<sub>x</sub> support. This behavior suggests a strong synergy between the surface Pd/PdO domains and the underlying TbO<sub>x</sub> film, such as a Mars-van Krevelen interaction in which TbO<sub>x</sub> readily transfers O-atoms to Pd and thereby sustains oxidation chemistry.

<sup>1</sup> Heterogeneous Catalysis Graduate Student Presentation Award Finalist

Tuesday Morning, October 23, 2018

<sup>2</sup> Heterogeneous Catalysis Graduate Student Presentation Award Finalist

<sup>3</sup> Heterogeneous Catalysis Graduate Student Presentation Award Finalist

# Tuesday Morning, October 23, 2018

9:40am **HC+SS-TuM6 Copper Vapor Adsorption Calorimetry on  $\text{HfCa}_2\text{Nb}_3\text{O}_{10}$ (001) Nanosheets: Energetics and Adsorbate Structure, Wei Zhang<sup>1</sup>, J.E. Eichler, University of Washington; R. Uppuluri, T.E. Mallouk, The Pennsylvania State University; C.T. Campbell, University of Washington**  
The metal/oxide interface is essential to many current and prospective technologies, including oxide-supported metal catalysts, fuel cells, photocatalysis, and nanoscale electronic contacts, so understanding the chemical bonding strength at such interfaces is of great interest. These strengths have been measured on single-crystal oxide films of a single metal element by metal vapor adsorption calorimetry in ultrahigh vacuum (UHV), but never before on mixed oxides of two or more metal elements, yet mixed oxides are often used as supports in catalysis with considerable improvement on various aspects of catalyst performance. The preparation of atomically-smooth single-crystal mixed-oxide films in well-defined composition that would be applicable in our adsorption calorimetry is very challenging. Mallouk et. al. have reported a class of lamellar  $\text{HfCa}_2\text{Nb}_3\text{O}_{10}$ (001) nanosheets which can be deposited in a layer-by-layer fashion on flat substrates using Langmuir-Blodgett (LB) techniques to make thin and well-ordered mixed-oxide films. These nanosheets can extend laterally for long distances (>1  $\mu\text{m}$ ) indicating that they have very high surface area with homogeneous surface sites and a huge ratio of terrace sites to sheet-edge sites. Furthermore, when used as supports for transition metal oxide (or hydroxide) nanoparticles, they display unusual stability against sintering. Here, we apply the surface chemistry techniques derived for single-crystal oxide films to the much more complex perovskite mixed-oxide films by investigating the adsorption of Cu atoms on the  $\text{HfCa}_2\text{Nb}_3\text{O}_{10}$ (001) nanosheets (~6.3 nm thick) at both 300 K and low temperature (<150 K). Cu atoms show an initial heat of 186 kJ/mol at 300 K, which is close to the DFT value for Cu monomers. The heat of adsorption then increases quickly to the heat of sublimation of bulk Cu(s) (337 kJ/mol). Low-energy He<sup>+</sup> ion scattering spectroscopy (LEIS) allows us to investigate the morphology and the number density of Cu particles. The possible chemical reactions between the Cu atoms and the  $\text{HfCa}_2\text{Nb}_3\text{O}_{10}$ (001) nanosheets during adsorption are elucidated using X-ray photoelectron spectroscopy (XPS).

11:00am **HC+SS-TuM10 Adsorption and Adhesion of Ni on MgO(100) at 300 and 100 K by Calorimetry, Zhongtian Mao, W. Zhao, Z. Almualem, C.T. Campbell, University of Washington**

Metal nanoparticles anchored on the surface of oxide support form the basis of modern heterogeneous catalysts used for clean energy, pollution prevention and industrial-scale chemical production. Since the catalytic activity, selectivity and long-term stability of supported nanoparticles correlate with metal chemical potential which in turn decreases strongly with the metal/oxide interface adhesion energy,  $E_{\text{adh}}$ , it is crucial to understand how the properties of both metal and oxide control  $E_{\text{adh}}$ . Adhesion energies of metal nanoparticles to clean oxide surfaces were previously measured in ultra-high vacuum using either single-crystal adsorption calorimetry (SCAC) or particle-shape measurements by electron microscopy or grazing-incidence X-ray scattering. The results reveal a trend that  $E_{\text{adh}}$  on a given oxide surface increases linearly from metal to metal with increasing metal oxophilicity, defined as the magnitude of the heat of formation of the most stable oxide from gas-phase metal atoms.<sup>1</sup> The oxophilicity of Ni is so high that it is predicted by this trend to have 50% higher adhesion than any of the other metals that have been studied on MgO(100) (i.e., Pb, Ag, Au, Pd Cu and Pt). We report here calorimetric heats of adsorption of Ni gas onto MgO(100) which validate this prediction and thus prove the predictive ability of this trend. Oxide-supported Ni nanoparticles are widely used as industrial catalysts, so these results are of interest in catalysis research. The adsorption of Ni vapor onto MgO(100) films grown on Mo(100) is studied at 300 and 100 K using single crystal adsorption calorimetry. The Ni particle morphology is investigated using He<sup>+</sup> low-energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS). Combining the heat of adsorption and this information on Ni particle morphology also allows the adhesion energy of Ni(solid) to MgO(100) to be found. The initial heat of adsorption at 300 K is 276.5 kJ/mol, 35.7 % lower than the saturation heat at high coverage (equal to the bulk heat of Ni sublimation). This initial heat corresponds to making Ni cluster that are ~0.53 nm in diameter. We also report the chemical potential of Ni versus particle size on MgO(100).

[1] Hemmingson, S. L.; Campbell, C. T. ACS Nano 2017, 11, 1196–1203.

11:20am **HC+SS-TuM11 In situ Microscopy of Oxide Growth and Transformation under Reaction Conditions, Jan Ingo Flege, University of Bremen, Germany**  
**INVITED**

Current research in heterogeneous catalysis aims to provide a deeper understanding of all the components in a real catalytic system, which depending on the conditions typically comprises both metals and oxides in nanoparticulate form. Significant progress has been achieved by studying carefully devised model systems that facilitate detailed investigation of the structure and chemistry of the individual constituents in controlled environments. While traditional approaches have focused on the role of oxide-supported metal nanoparticles, in the so-called inverse configuration a nanosized metal oxide is supported on a transition metal, thereby allowing us to assess the properties of the nanoscale metal oxide and its defect chemistry as well as to gain complementary access to the oxide-metal interface.

In this presentation, we will focus on the epitaxial growth of ultrathin metal oxide films and nanostructures on transition metals, with a special emphasis on rare-earth oxides. These materials have attracted considerable attention owing to their rich chemistry and enhanced reducibility in proximity to transition metals. We will demonstrate that real-time monitoring of their synthesis under vacuum conditions as well as their structural and chemical modifications on the nanometer scale in reactive gaseous environments is possible using low-energy electron microscopy and related methods [1]. Primary examples will address reversible structural transformations in ruthenium, platinum, and copper supported cerium oxide inverse model catalysts [2-5] upon thermal and chemical reduction, e.g., from  $\text{CeO}_2$  via the cubic  $\text{Ce}_2\text{O}_3$  phase to hexagonal  $\text{Ce}_2\text{O}_3$ , concomitant with partial dissolution of the cerium oxide particles and considerable dispersion of metallic cerium on the substrate, resulting in irreversible morphological changes. Similar sesquioxide and dioxide phases are present directly after deposition of praseodymium oxide on the Ru(0001) surface [6, 7], illustrating an intrinsic nanoscale complexity and the importance of the oxide-metal interface.

[1] J. I. Flege and D. C. Grinter, Prog. Surf. Sci. (2018), in press. DOI: 10.1016/j.progsurf.2018.02.001

[2] D. C. Grinter, S. D. Senanayake, and J. I. Flege, Appl. Catal., B 197, 286 (2016).

[3] J. Höcker et al., Adv. Mater. Interfaces 2, 1500314 (2015).

[4] J. Höcker, J.-O. Krispeneit, Th. Schmidt, J. Falta, and J. I. Flege, Nanoscale 9, 9352 (2017).

[5] M. Sauerbrey, G. Gasperi, P. Luches, J. Falta, S. Valeri, J. I. Flege, Top. Catal. 60, 513 (2017).

[6] J. Höcker et al., Phys. Chem. Chem. Phys. 19, 3480 (2017).

[7] J. I. Flege et al., Ultramicroscopy 183, 61 (2017).

## Author Index

**Bold page numbers indicate presenter**

— A —

Alexandrova, A.: HC+SS-TuM4, 1

Almualem, Z.: HC+SS-TuM10, 2

Anderson, S.: HC+SS-TuM4, 1

— B —

Baxter, E.: HC+SS-TuM4, 1

— C —

Campbell, C.T.: HC+SS-TuM10, 2; HC+SS-TuM6, 2

Cass, A.: HC+SS-TuM4, 1

— E —

Eichler, J.E.: HC+SS-TuM6, 2

— F —

Flege, J.I.: HC+SS-TuM11, 2

— G —

Gorey, T.: HC+SS-TuM4, 1

Grinter, D.: HC+SS-TuM3, 1

— H —

Hamlyn, R.: HC+SS-TuM3, 1

— J —

Jiang, T.: HC+SS-TuM2, 1

— K —

Kattel, S.: HC+SS-TuM3, 1

— L —

Le, D.: HC+SS-TuM2, 1

Lee, C.: HC+SS-TuM5, 1

Liu, P.: HC+SS-TuM3, 1

Luo, S.: HC+SS-TuM3, 1

— M —

Mahapatra, M.: HC+SS-TuM3, 1

Mallouk, T.E.: HC+SS-TuM6, 2

Mao, Z.: HC+SS-TuM10, 2

— P —

Palomino, R.: HC+SS-TuM3, 1

— R —

Rahman, T.S.: HC+SS-TuM2, 1

Rawal, T.B.: HC+SS-TuM2, 1

Rodriguez, J.A.: HC+SS-TuM3, 1

— S —

Schilling, A.C.: HC+SS-TuM1, 1

Senanayake, S.: HC+SS-TuM3, 1

Stacchiola, D.J.: HC+SS-TuM3, 1

Sykes, E.C.H.: HC+SS-TuM1, 1

— U —

Uppuluri, R.: HC+SS-TuM6, 2

— W —

Waluyo, I.: HC+SS-TuM3, 1

Weaver, J.F.: HC+SS-TuM5, 1

— X —

Xu, F.: HC+SS-TuM3, 1

— Z —

Zandkarimi, B.: HC+SS-TuM4, 1

Zhang, W.: HC+SS-TuM6, 2

Zhao, W.: HC+SS-TuM10, 2