Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 103A - Session HC+SS-ThA

Advances in Theoretical Models and Simulations of Heterogeneously-catalyzed Reactions

Moderator: Donna Chen, University of South Carolina

2:20pm **HC+SS-ThA1 Theoretical Pathways to Predict (meta-)stability of Gas Phase Metal Oxide Clusters: Beyond the Static Mono-Structure Description***, Saswata Bhattacharya,* Indian Institute of Technology Delhi, India*; L.M. Ghiringhelli,* Fritz-Haber-Institut der Max-Planck-Gesellschaft*; N. Marom,* Tulane University

This talk is driven by the vision of computational design of cluster-based nanocatalysts. The discovery of the extraordinary activity in catalysis exhibited by small metal-oxide clusters has stimulated considerable research interest. However, in heterogeneous catalysis, materials property changes under operational environment (e.g. temperature (T) and pressure (p) in an atmosphere of reactive molecules). Therefore, a solid theoretical understanding at a realistic (T, p) is essential in order to address the underlying phenomena. In this talk, I shall first introduce a robust methodological approach that integrates various levels of theories combined into one multi-scale simulation to address this problem[1]. I shall show one application of this methodology in addressing (T, p) dependence of the composition, structure, and stability of metal oxide clusters in a reactive atmosphere at thermodynamic equilibrium using a model system that is relevant for many practical applications: free metal (Mg) clusters in an oxygen atmosphere[2].

More recently, I have extended this development in designing clusters with desired properties. The novelty of this implementation is that it goes beyond the interpretation of experimental observations and addresses the challenging “inverse problem” of computationally designing clusters with target properties. The methodology is applied and thoroughly benchmarked on $(TiO_2)_n$ clusters [n=2, 3,...., 10, 15, 20][3]. All the results are duly validated using the highest level of theories currently achievable within Density Functional Theory (DFT).

References:

[1] S. Bhattacharya, S. Levchenko, L. Ghiringhelli, M. Scheffler, New J. Phys. 16, 123016 (2014).

[2] S. Bhattacharya, S. Levchenko, L. Ghiringhelli, M. Scheffler, Phys. Rev. Lett. 111, 135501 (2013).

[3] S. Bhattacharya, B. Sonin, C. Jumonville, L. Ghiringhelli, N. Marom, Phys. Rev. B 91, 241115 (R), (2015).

2:40pm **HC+SS-ThA2 Role of Oxygen at the Surface and Subsurface during Catalytic Oxidation by Silver***, Sharani Roy,* University of Tennessee

Catalytic oxidation by the silver surface is used in several important industrial processes, such as epoxidation of ethylene to form polyethylene or partial oxidation of methane to form methanol. To understand the mechanisms of catalytic oxidation at the molecular level, it is essential to understand the interactions of atomic oxygen with the silver surface. We present a detailed theoretical study of oxygen adsorbed on the surface and subsurface of silver based on density functional theory and molecular dynamics simulations. Our ultimate goal is to develop a conceptual model of reactivity of surface oxygen and subsurface oxygen in catalytic oxidation by the silver surface. While the detailed quantum chemical calculations serve to accurately model the ground-state potential energy landscape of the oxygen-silver system, molecular dynamics simulates the motion of oxygen on the surface and subsurface at realistic laboratory or catalytic temperatures. We focus on several important phenomena, including surface-site preference, coverage dependence, and temperature dependence of oxygen adsorption at the surface and subsurface. We also investigate the changes in the surface structure of silver induced by the presence of oxygen. Due to the differences in structure, interatomic spacing, and binding sites of the (111) and (110) faces of the silver crystal, the adsorption properties of atomic oxygen vary for the two surfaces. Our study determines some fundamental differences in silver-oxygen interactions on the two surfaces, and provides qualitative insight on how the choice of surface can affect the participation of surface and subsurface oxygen in catalytic oxidation by silver. Future work will explore the interactions of surface oxygen and subsurface oxygen with reactant molecules such as methane or ethylene.

3:00pm **HC+SS-ThA3 Using Theory and Computation to Understand Plasma Enhanced Dry Reforming on Nickel Catalysts***, George Schatz,* Northwestern University **INVITED**

Dry reforming is a process wherein CH_4 and CO_2 react to give synthesis gas and/or liquid fuels. Dry reforming is normally done under high temperature and pressure conditions, with a Ni catalyst, however it has recently been discovered that if a plasma is also present near the catalyst, then it is possible to get this reaction to go under modest conditions close to room temperature and atmospheric pressure. The role of the plasma in this process is poorly understood. In this talk I will describe several electronic structure studies that my group is doing which are designed to describe the processes involved in plasma enhanced dry reforming, including both the role of the plasma, and the gas-surface chemistry that occurs in the presence of plasma species. The plasma is known to fragment the reacting gases, especially CH_4, so we will study the interaction of methane fragments with various Ni surfaces, to show how this enhances chemisorption, surface dissociation, and subsequent reaction with species already on the surface. A highlight of this work involves the reaction of subsurface hydrogen with adsorbed CO_2 to give CO, water and other products. We have also studied the influence and ions and electrons on surface chemistry.

4:00pm **HC+SS-ThA6 The Impact of Structure on the Catalytic Behavior of Cu_2O Supported Pt Atoms***, Andrew Therrien*[*]*,* Tufts University Department of Chemistry*; E.C.H. Sykes,* Tufts University

Single site catalysts composed of individual atoms on various oxide supports have been a major research focus in recent years. Such catalysts exhibit novel reactivity with the benefit of 100% atom efficiency and a dramatic reduction in the precious metal loading. However, despite several experimental examples of efficient single atom catalysts, there is much debate regarding the structure and catalytic mechanisms of such catalysts and debate over whether single atoms or nanoparticles are the active species. Given the complexity of heterogeneous catalysts and the size scale of the active sites, there is a need for a surface science and microscopy approach to understand the structure and reactivity of atomically dispersed atoms on oxides.

We have studied the structure and reactivity of individual Pt atoms supported on oxidized Cu using scanning tunneling microscopy (STM) and temperature programmed reaction (TPR). We first elucidated the structure of the support, a previously observed but unsolved Cu_2O overlayer on Cu, by density functional theory (DFT) and comparison of simulated STM images with experimental STM. We discovered that the oxide surface is inert towards CO oxidation, while the single Pt atom decorated surface is efficient for low-temperature CO oxidation. This system is also capable of water activation. Our combination of TPR and STM studies suggest that single Pt atoms supported on the oxide are indeed catalytically active and may be a good catalyst for the water-gas shift reaction.

4:20pm **HC+SS-ThA7 Energetics of Water Dissociative Adsorption on NiO(111)-2x2***, Wei Zhao,* University of Washington*; M. Bajdich,* Stanford University*; S. Carey,* University of Washington*; M. Hoffmann, A. Vojvodic, J. Nørskov,* Stanford University*; C.T. Campbell,* University of Washington

The energetics of the reactions of water with metal oxide surfaces are of tremendous interest for catalysis and electrocatalysis, yet the energy for the dissociative adsorption of water was only previously known on one well-defined oxide surface, $Fe_3O_4(111)$.[1] Here we report the first calorimetric measurement of the heat of reaction for the dissociative adsorption of water on NiO(111)-2x2 as a function of coverage, showing that the heat of dissociative adsorption decreases with coverage from 177 kJ/mol to 119 kJ/mol in the first 0.25 ML of coverage. These measurements provide an important benchmark for validating computational estimates of adsorption energies of molecular fragments on correlated metal-oxide such as NiO and for oxide surface chemistry in general, which is more challenging in this respect than for metal or wide-gap semiconductor surfaces. We also present DFT calculations of the energetics of this reaction, and compare it to the calorimetric results.

[1] P. Dementyev, K.-H. Dostert, F. Ivars-Barceló, C.P. O'Brien, F. Mirabella, S. Schauermann, X. Li, J. Paier, J. Sauer, H.-J. Freund, Water Interaction with Iron Oxides, Angewandte Chemie International Edition, 54 (2015) 13942-13946.

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[*] **Morton S. Traum Award Finalist**

4:40pm **HC+SS-ThA8 Challenges in the First-Principles Description of Reactions in Electrocatalysis*, Axel Groß,*** Ulm University, Germany **INVITED**

In spite of its technological relevance in the energy conversion and storage, our knowledge about the microscopic structure of electrochemical electrode-electrolyte interfaces and electrical double layers is still rather limited. The theoretical description of these interfaces from first principles is hampered by three facts. i) In electrochemistry, structures and properties of the electrode-electrolyte interfaces are governed by the electrode potential which adds considerable complexity to the theoretical treatment since charged surfaces have to be considered. ii) The theoretical treatment of processes at solid-liquid interfaces includes a proper description of the liquid which requires to determine free energies instead of just total energies. This means that computationally expensive statistical averages have to be performed. iii) Electronic structure methods based on density functional theory (DFT) combine numerical efficiency with a satisfactory accuracy. However, there are severe shortcomings of the DFT description of liquids, in particular water, using current functionals.

Despite these obstacles, there has already significant progress been made in the first-principles modeling of electrochemical electrode-electrolyte interfaces. In this contribution, I will in particular focus on how the electrochemical environment can be appropriately taken into account using numerically efficient schemes. In the presence of an aqueous electrolyte, metal electrodes are in general covered by either cations or anions. Based on the concept of the computational hydrogen electrode, the equilibrium coverage of Pt(111) with hydrogen (1,2) and halides (3) as a function of the electrode potential has been derived showing that halide and hydrogen adsorption is competitive, in agreement with experimental findings. The presence of the aqueous electrolyte has been taken into account modeling water layers either implicitly through a polarizable medium (2) or explicitly in ab initio molecular dynamics runs (3). To obtain a proper description of the water-water and the water-metal interaction, it turns out that the consideration of dispersion corrections is essential (4). The importance of the electrochemical environment in electrocatalytic processes will be demonstrated using the methanol electrooxidation on Pt(111) (5) as an example.

References

(1) S. Sakong, M. Naderian, K. Mathew, R. G. Hennig, and A. Gross, J. Chem. Phys. **142**, 234107 (2015).

(2) T. Roman and A. Gross, Catal. Today. **202**, 183 (2013).

(3) F. Gossenberger, T. Roman, and A. Gross, Surf. Sci. **631**, 17 (2015).

(4) K. Konigold and A. Gross, J. Comput. Chem. **33**, 695(2012).

(5) S. Sakong and A. Gross, submitted.

5:20pm **HC+SS-ThA10 Beyond the 2D Lattice Gas and 2D Ideal Gas Models for Adsorbates: The Hindered Translator / Hindered Rotor Model*, Liney Arnadottir,*** *L.H. Sprowl,* Oregon State University*; C.T. Campbell,* University of Washington

With the recent explosion in computational catalysis and related microkinetic modeling, the need for a fast yet accurate way to predict equilibrium and rate constants for surface reactions has become more important. In such calculations, adsorbates are usually treated within either the 2D lattice gas or 2D ideal gas approximation to estimate their partition functions and entropies. Here we present a fast new method to estimate the partition functions and entropies of adsorbates that is much more accurate than those approximations, and recognizes the true oscillating nature of the adsorbate's potential energy for motions parallel to the surface. As with previous approaches, it uses the harmonic oscillator (HO) approximation for most of the modes of motion of the adsorbate. However, it uses hindered translator and hindered rotor models for the three adsorbate modes associated with motions parallel to the surface, and evaluates these using an approach based on a method that has proven accurate in modeling the internal hindered rotations of gas molecules. The translational and rotational contributions to the entropy of a hindered translator / hindered rotor calculated with this new method are, in general, very closely approximated (to within <0.25R error per mode) by the corresponding harmonic oscillator (i.e., 2D lattice gas) entropy when kT is less than the barrier. When kT exceeds the barrier, the hindered translator / hindered rotor model is closely approximated (to within 0.1 R) by the entropy of an ideal 2D gas. The harmonic oscillator / lattice gas model severely overestimates the entropy when kT greatly exceeds the barrier. The cutoff between the temperature ranges of applicability of these simple two approximations is very sharp but with our combined hindered rotor/hindered translator approach the whole temperature range is covered with the same approach.

5:40pm **HC+SS-ThA11 Methanol Partial Oxidation Catalyzed by Singly-dispersed Pd on ZnO(101¯0)*, Takat B. Rawal*[*]*,*** *S.R. Acharya, S. Hong, T.S. Rahman,* University of Central Florida

Heterogeneous catalysis by singly-dispersed metal atoms on non-metallic surfaces offers great potential for maximizing the efficiency of metal atoms, and optimizing their activity and selectivity. Herein, we present results from our *ab-initio* density functional theory (DFT) calculations for methanol partial oxidation (MPO), an industrially important reaction for the production of H_2, on Pd_1/ZnO(101¯0). To begin with we find that the Pd atom prefers to adsorb at the oxygen vacancy site i.e. the anion vacancy is responsible for stabilizing singly-dispersed Pd atom on ZnO(101¯0). We discuss the adsorption characteristics of a set of gas molecules (CH3OH, O_2, CO, CO_2, H_2O, H_2), and the potential energy profile including activation barriers for the reaction processes associated with MPO on Pd_1/ZnO(101¯0), and compare them with those on Pd16Zn16 nanoparticle and pristine ZnO(101¯0). We find that the singly dispersed Pd sites offer a high activity towards the formation of CO_2 and H_2 over that of CO and H_2O. We trace this reactivity to the electronic structure of the single Pd site as modified by its local environment which in turn facilitates a strong binding of CO to the Pd site, thereby increasing the CO desorption barrier and stabilizing O_2 on ZnO(101¯0), which is essential for further oxidation steps. With activation energy barriers and pre-exponential factors calculated from DFT, for a large set of reaction intermediates, we perform kinetic Monte Carlo simulations to determine the turn over frequencies and rate limiting steps in the formation of CO_2 and H_2 on Pd1/ZnO(101¯0), under ambient conditions.

Work supported in part by DOE grant DE-FG02-07ER15842.

6:00pm **HC+SS-ThA12 Simulations of Surface Induced Dissociation, Soft Landing, and Reactive Landing in Collisions of Protonated Peptide Ions with Organic Surfaces*, William Hase,*** *S. Pratihar,* Texas Tech University

Chemical dynamics simulations have been performed to explore the atomistic dynamics of collisions of protonated peptide ions, peptide-H^+, with organic surfaces. Overall, the results of the simulations are in quite good agreement with experiment. The simulations have investigated the energy transfer and fragmentation dynamics for peptide-H^+ surface-induced dissociation (SID), peptide-H^+ physisorption on the surface, soft landing (SL), and peptide-H^+ reaction with the surface, reactive landing (RL). The primary structure of biological ions is determined by SID, as well as information regarding the ions' fragmentation pathways and energetics. SID occurs by two mechanisms. One is a traditional mechanism in which peptide-H^+ is vibrationally excited by its collision with the surface and then dissociates in accord with the statistical, RRKM unimolecular rate theory after it rebounds off the surface. For the other mechanism, the ion *shatters* via a non-statistical mechanism as it collides with the surface. The simulations have also provided important dynamical insight regarding SL and RL of biological ions on surfaces. SL and RL have a broad range of important applications including preparation of protein and peptide microarrays. The simulations indicate that SL occurs via multiple mechanisms consisting of peptide-H^+ physisorption on and penetration in the surface. An important RL mechanism is intact deposition of peptide-H^+ on the surface.

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[*] **National Student Award Finalist**

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