

Surface Science Division

Room 203C - Session SS+HC-MoA

Theory and Modeling of Surfaces and Reactions

Moderators: Liney Arnadottir, Oregon State University, Petra Reinke, University of Virginia

1:20pm **SS+HC-MoA-1 Elucidating the Chemical Nature of Single-Site Catalysts from First Principles**, *A Hensley*, Washington State University; *A Therrien*, Tufts University; *R Zhang*, Washington State University; *A Schilling*, Tufts University; *K Groden*, Washington State University; *C Sykes*, Tufts University; *Jean-Sabin McEwen*, Washington State University **INVITED** Automotive catalysis is more complicated than most applications of catalysts, because of the complex and dynamic changes in the exhaust gas environment. The ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable [1]. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions [2]. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we have studied low-temperature CO oxidation on Pt single-site catalysts supported on the "29" Cu surface oxide. The "29" Cu surface oxide is a high coverage chiral structure. Through the use of scanning tunneling microscopy (STM), CO temperature programmed desorption (TPD), and density functional theory (DFT) techniques, we determined that an accurate model for the "29" Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings [3, 4]. Furthermore, the state of the Pt single atoms before, during, and after reaction is determined through a combination of theoretical and experimental techniques. It is found that the Pt dosed to the "29" Cu oxide surface forms well dispersed single atom sites which are metallic in nature [5]. During catalysis, CO₂ forms from the combination of an oxygen from the "29" Cu oxide surface with the CO adsorbed on the Pt single atoms.

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2. Ding, K., A. Gulec, A.M. Johnson, N.M. Schweitzer, G.D. Stucky, L.D. Marks, and P.C. Stair, *Science*, 2015. **350**(6257): p. 189-192.
3. Therrien, A.J., R. Zhang, F.R. Lucci, M.D. Marcinkowski, A.J.R. Hensley, J.-S. McEwen, and E.C.H. Sykes, *Journal of Physical Chemistry C*, 2016. **120**: p. 10879-10886.
4. Hensley, A.J.R., A.J. Therrien, R. Zhang, M.D. Marcinkowski, F.R. Lucci, E.C.H. Sykes, and J.-S. McEwen, *Journal of Physical Chemistry C*, 2016. **120**: p. 25387-25394.
5. Therrien, A.J., A.J.R. Hensley, M.D. Marcinkowski, R. Zhang, F.R. Lucci, B. Coughlin, A.C. Schilling, J.-S. McEwen, and E.C.H. Sykes, *Nature Catalysis*, 2018. **1**: p. 192-198.

2:00pm **SS+HC-MoA-3 Unravelling the Complex Features in STM Images of O/Ag(110) System**, *Takat B. Rawal*, University of Central Florida; *M Smerieri*, IMEM-CNR, UOS Genova, Italy; *J Pal*, University of Genova, Italy; *S Hong*, Brewton-Parker College; *M Alatalo*, University of Oulu, Finland; *L Savio*, *L Vattuone*, University of Genova, Italy; *T Rahman*, University of Central Florida; *M Rocca*, University of Genova, Italy

Elucidating the various structures involving oxygen adsorption on silver surfaces is a key issue in understanding the industrially relevant Ag oxidation process. Recently it was demonstrated that atomic oxygen can cause the extraction of substrate atoms off metal surfaces. In particular for Ag(110), the excavation process takes place already when O₂ is dosed at 175 K leading, at low coverage, to the formation of single Ag vacancies [1], which can serve as reactive sites. Vacancy creation proceeds thereby via the formation of O-Ag-O complexes, which involve a local reconstruction of the surface and ignite the disruption of the Ag substrate. Here, we present details of such processes and of the various structures formed by the O adatoms at very low coverage, for some of which the energetics had already been reported in ref. [2]. To this purpose we performed scanning tunnelling microscopy experiments and density functional theory calculations. A variety of features such as isolated grey dots, sombreros,

shallow grey and white structures oriented along [001] and [1-10], grey stripes, and lozenges were identified and assigned to the O adatoms in different configurations. Most of the oxygen ends up either in "zig-zag chain" or in pinned, "lozenge" shaped structures. The former interact strongly with the STM tip and are easily disrupted, giving rise to highly mobile, sombrero shaped, isolated O adatoms. Around 200 K, not only Ag vacancies are mobile with anisotropic migration rates and can merge at larger coverage into complex features, but also the mobile Ag atoms are trapped by O adatoms leading finally to the O-Ag chains oriented along [001] forming the well-known added row reconstruction.

[1] J. Pal, T. B. Rawal, M. Smerieri, S. Hong, M. Alatalo, L. Savio, L. Vattuone, T. S. Rahman, and M. Rocca, *Phys. Rev. Lett.*, **118**, 226101 (2017).

[2] T. B. Rawal, S. Hong, A. Pulkkinen, M. Alatalo, and T. S. Rahman, *Phys. Rev. B*, **92**, 035444 (2015).

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2:20pm **SS+HC-MoA-4 First Principles Investigations on CO₂ Adsorption and Dissociation on Cu_{cluster} / Cu(111) Surfaces: Influence of Co-adsorbed CO Molecule**, *Allan Abraham Padama*, University of the Philippines Los Baños, Philippines; *H Nakanishi*, *H Kasai*, National Institute of Technology, Akashi College, Japan; *J Ocon*, University of the Philippines Diliman, Philippines

Cheap Cu surfaces play important role in the synthesis of methanol and in reverse water gas shift reactions, in which, the interaction of the surfaces with carbon dioxide (CO₂) is an important process. Recent developments revealed the stable structures of Cu clusters on Cu(111) (Cu_{cluster} / Cu(111)) that is activated by CO adsorption [*Science* 351 (6272), 475-478]. Interestingly, it is found that the surface facilitates water dissociation. In connection to these, we see the importance of studying the adsorption and dissociation of CO₂ on this system which could provide additional insights to the use of Cu-based surfaces as catalyst in various reactions.

In this work, we performed first principles calculations based on density functional theory (DFT) to investigate the adsorption and dissociation of CO₂ on Cu_{cluster} / Cu(111), with and without the presence of co-adsorbed CO molecules. We modeled the system with three Cu atoms as cluster, which was experimentally identified as among the stable clusters on the Cu(111). The adsorption energy of CO₂ on Cu_{cluster} / Cu(111) is ~0.25 eV, comparable to the obtained adsorption energy of CO₂ on flat Cu(111). We found that the cluster and the presence of CO do not influence the dissociation of CO₂. An activation energy of ~1.6 eV accompanies the dissociation when it takes near the cluster which is similar to the barrier on pristine Cu(111). The dissociation barriers on the cluster region are ~1.0 – 1.2 eV, lower than on Cu(111), and it appears that co-adsorbed CO molecules do not significantly affect the dissociation process. CO₂ that dissociates directly on the cluster is only accompanied by ~0.6 eV activation barrier, but further diffusion of the adsorbed species away from the cluster increases the barrier. The geometric and electronic properties analyses that support the obtained results will be presented in the symposium.

2:40pm **SS+HC-MoA-5 Step-Spacing Distributions Revisited: New Motivations from Curved Crystals and Other Systems**, *Theodore L. Einstein*, University of Maryland, College Park

Recent experiments on curved crystals of noble and late transition metals (Ortega and Juurlink groups) have renewed interest in terrace width distributions (TWD) for vicinal surfaces. We first summarize refinements of TWD analysis that are absent from the standard reviews. Rather than by Gaussians, TWDs are better described by a single-parameter distribution with a power-law rise and a Gaussian decay, thereby including effects evident for weak step repulsion: skewness and peak shifts down from the mean spacing. Curved crystals allow analysis of several spacings with the same substrate, so that one can check the scaling with the mean width. This is important since such scaling confirms well-established theory. Failure to scale also can provide significant insights. Complicating factors can include step touching (local double-height steps), oscillatory step interactions mediated by metallic (but not topological) surface states, short-range corrections to the inverse-square step repulsion, and the offset between adjacent layers of almost all surfaces. We discuss how to deal with these issues. Many of the curved-crystal experiments involve in-plane misoriented (zig-zag) steps. There are formulas to describe the stiffness but not yet the strength of the elastic interstep repulsion. Some theory results are available for these orientations; more are needed. Other intriguing results have been reported for spacings of spiral steps around a dislocation.

Monday Afternoon, October 22, 2018

3:00pm **SS+HC-MoA-6 Small Molecule Activation Using Computational Catalysis and Machine Learning**, *Yousung Jung*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Electrochemical activation of small molecules (CO₂, N₂, etc) towards value-added products is an efficient and sustainable way to address energy problems and global climate changes. In this talk, I will discuss some of our recent efforts to understand and design new materials towards electrochemical catalysis using density functional calculations [1-4]. In addition, solid state materials are often complex, but can also be potentially highly tunable if there is a way to accurately extrapolate the large set of existing data for a new discovery, an area in which machine learning can help significantly accelerate the discovery process with improved accuracy. At the end of this talk, thus, I will briefly describe some of our initial efforts to use machine learning for chemical science [5-7] that can contribute greatly to creating solutions to catalysis and materials problems, in general.

[1] "Single-Atom Catalysts for CO₂ Electroreduction with Significant Activity and Selectivity Improvements", S. Back, J. Lim, N. Kim, Y. Kim, and Y. Jung, *Chem Sci* 8 1090-1096 (2017)

[2] "TiC and TiN Supported Single Atom Catalysts for Dramatic Improvements in CO₂ Electrochemical Reduction to CH₄", S. Back and Y. Jung, *ACS Energy Lett* 2, 969-975 (2017)

[3] "On the active sites of Au and Ag nanoparticle catalysts for CO₂ electroreduction to CO", S. Back, M. Yeom, and Y. Jung, *ACS Catal* 5, 5089-5096 (2015)

[4] "Selective Heterogeneous CO₂ Electroreduction to Methanol", S. Back, H. Kim, and Y. Jung, *ACS Catal* 5, 965-971 (2015)

[5] "Actively learning with non-ab initio input features toward efficient CO₂ reduction catalyst", J. Noh, S. Back, J. Kim, and Y. Jung, *Chem Sci* (2018) (accepted)

[6] "A Local Electronic Descriptor for Machine-Learned Density Functional Theory at GGA Level", H. Ji and Y. Jung, *J Chem Phys* (under revision)

[7] "Artificial neural network for the configuration problem in solids", H. Ji and Y. Jung, *J Chem Phys* 146, 064103 (2017)

3:40pm **SS+HC-MoA-8 Elucidating Mechanisms of Alkanol Catalysis on SrTiO₃ Perovskite Surfaces using Density Functional Theory**, *Robert Chapleski*, S Roy, University of Tennessee Knoxville

Targeted at understanding observed differences in reaction dynamics for various alkyl alcohols on catalytic SrTiO₃ surfaces, we describe the results of our computational study of isopropanol adsorption and catalysis on SrTiO₃ (100). Using the PBE density functional with a Hubbard-U correction to initially probe the potential energy surface of adsorption, we have found a minimum-energy orientation for isopropanol adsorbed on the surface in good agreement with recent sum-frequency generation experiments. Continuing with this minimum, we followed multiple competing pathways and determined necessary transition states and intermediates in order to describe the kinetics and thermodynamics of these reactions. Armed with these results, we elucidate recent experimental findings favoring the formation of the dehydrogenation product acetone over the dehydration product propylene. Finally, we probed the adsorption potential energy surfaces of products in order to describe the contributions of product orientation and lateral surface diffusion to overall reaction dynamics. Our future work will consider different SrTiO₃ surfaces such as (111) and (110), as well as different alkanol adsorbates such as ethanol. Overall, these studies provide insight into the fundamental aspects of catalysis of this class of reagents on perovskite surfaces.

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