Surface Science Division
Room A220-221 - Session SS+HC-MoA

CO2, CO, Water, and Small Molecule Chemistry at Surfaces

Moderators: Donna Chen, University of South Carolina, Omur E. Dagdeviren, Yale University

1:40pm **SS+HC-MoA-1 Calculations of the Electrochemical Reduction of CO2 and the Competing Hydrogen Evolution Reaction***, **Hannes Jónsson**,* University of Iceland, Iceland **INVITED**

Calculations of electrochemical CO2 reduction to formate, alcohols and hydrocarbons will be presented. The mechanism for the formation of the various products is established, the rate evaluated and comparison made with experimental measurements. The rate of the main side reaction, the hydrogen evolution reaction, is also estimated. The calculations are based on a detailed atomistic model of the electrical double layer (metal slab and water layer) and density functional theory calculations to evaluate not only the free energy of intermediates as a function of applied voltage but also the activation energy for each elementary step, both Heyrovsky and Tafel reactions [1]. Comparison is also made with calculations using an implicit solvation model [2]. A range of close packed metal surfaces are compared, including Cu, Ag, Au, Ni, Fe, Rh, Ir and Pt. The resuls are in remarkably good agreement with the reported experimental measurements. A two parameter descriptor is established that can help identify improved catalysts for CO2 electrochemical reduction.

[1] J. Hussain, H. Jónsson and E. Skúlason, ACS Catalysis 8, 5240 (2018).

[2] M. Van den Bossche, E. Skúlason, C. Rose-Petruck and H. Jónsson, J. Phys. Chem. C 123, 4116 (2019).

2:20pm **SS+HC-MoA-3 CO-$_2$ Adsorption on the O-Cu(100) Surface Studied by STM and DFT***, S Tjung, Q Zhang, J Repicky, S Yuk,* The Ohio State University*; X Nie,* Dalian University of Technology*; **Seth Shields**,* The Ohio State University*; N Santagata,* University of Memphis*; A Asthagiri, J Gupta,* The Ohio State University

Copper oxide catalysts are promising candidates for reducing CO_2 into useful fuels, such as ethanol, but the mechanism remains obscure. Studying the O-Cu(100) surface, which represents the initial transition of the oxidation of copper to copper oxide, and the adsorption process of CO_2 has the potential to elucidate the CO_2 reduction mechanism.

We performed a DFT/STM theoretical and experimental probe of the properties of CO--$_2$ -adsorption on the O-Cu(100) surface.- The Cu(100) surface was repeatedly sputtered with Ar^+ and annealed at 550°C in an ultra-high vacuum chamber, and subsequent Auger spectroscopy revealed the lack of surface contamination. The O-Cu(100) surface was obtained by exposing the Cu(100) face to 10^{-6} mbar of oxygen for 5 minutes at 300°C. The sample was then cooled and transferred into an attached low temperature (5K) ultra-high vacuum (10^{-11} mbar) STM chamber.

The atomic resolution STM revealed the $(2\sqrt{2}\times \sqrt{2})$ R45°O-Cu(100) reconstruction, in good agreement with the DFT calculations. The reconstruction consists of an O-Cu-O row structure separated by missing Cu rows. Additionally, there are two equivalent domains which result from nucleation along the [001] and [010] directions of the Cu(100). Differential conductance spectroscopy reveals an increase in the work function of the O-Cu(100) surface, and two additional unoccupied states generated by the oxygen atoms, in agreement with the DFT calculations.

CO-$_2$was adsorbed onto the O-Cu(100) surface via *in situ* dosing in the STM. The CO_2 adsorbed exclusively between two oxygen atoms in the missing row reconstruction, which has the largest predicted adsorption energy. The lack of point defects on the surface indicates that the CO-$_2$ does not dissociate, and the CO-$_2$ molecules are easily disturbed by the tip under all tunneling conditions, which is consistent with the theoretically predicted low diffusion barrier.

This work acknowledges funding from the NSF (1809837).

2:40pm **SS+HC-MoA-4 Employing Carbon Monoxide and Carbon Dioxide Plasmas to Improve the Gas Sensing Performance of Tin(IV) Oxide***, **Kimberly Hiyoto**, E Fisher,* Colorado State University

Metal oxide semiconductors are commonly researched materials for solid-state gas sensors; however, several limitations (i.e., operating temperatures of ≥300 °C and poor selectivity) impede wide-spread commercialization of these devices. Plasma processing offers a desirable alternative route to traditional methods, such as doping, because of the tunability of treatment parameters and the ability to modify the surface of the material while maintaining bulk properties. Previous work using plasma modification to enhance tin dioxide (SnO_2) gas sensor performance has mainly focused on oxygen or oxygen/argon plasma systems because these systems are thought to etch oxygen from the SnO_2 lattice creating oxygen vacancies that can lead to lower operating temperatures and improved sensor selectivity. Thus, further work needs to be done with other precursor gases to determine an effective strategy for fabricating improved gas sensors.

Here, we present carbon monoxide (CO) and carbon dioxide (CO_2) plasma-treated SnO_2 nanoparticle gas sensors treated at various applied rf powers. After plasma processing, the sensors demonstrate higher response to CO, ethanol, and benzene at lower operating temperatures compared to untreated SnO_2. In addition, the response and recovery behavior of the treated and untreated sensors were also evaluated as a metric for improved performance. To elucidate how plasma modification resulted in these changes, optical emission spectroscopy measured during plasma treatment and material characterization post plasma processing (X-ray photoelectron spectroscopy and X-ray powder diffraction) will also be discussed. All of these data work toward better understanding the relationship between surface chemistry and gas sensing performance, ultimately to develop a targeted approach to designing improved gas sensors.

3:00pm **SS+HC-MoA-5 The Role of Steps in the Dissociation of CO_2 on Cu***, **Johan Gustafson**, B Hagman,* Lund University, Sweden*; A Posada-Borbón, A Schaefer,* Chalmers University of Technology, Sweden*; M Shipilin,* Stockholm University, Sweden*; C Zhang,* Lund University, Sweden*; L Merte,* Malmö University, Sweden*; A Hellman,* Chalmers University of Technology, Sweden*; E Lundgren,* Lund University, Sweden*; H Grönbeck,* Chalmers University of Technology, Sweden **INVITED**

CO_2 chemistry has received significant attention recently, due to the greenhouse effect of CO_2 emissions and the resulting climate change. CO_2 reduction reactions, such as methanol synthesis and reverse water-gas shift, provide routes for recycling of CO_2 and thus limiting the CO_2 emissions. These reactions are commonly performed over Cu-based catalysts, making the interaction of CO_2 and Cu, on the atomic scale, of importance for a fundamental understanding and the development of new and more efficient catalysts.

We have previously studied the dissociative adsorption of CO_2 on Cu(100) using APXPS and DFT. In summary, exposure of the Cu surface to CO_2 in the mbar range at temperatures above room temperature results in dissociation of CO_2 into CO, that desorbs, and O that stays on the surface. The rate of the increase in O coverage, however, was not consistent with what one would expect from adsorption on the flat Cu(100) surface. Instead, we propose a model where the dissociation happen at atomic steps. The steps were found to both lower the activation barrier for the dissociation and separate the products, such that the probability for recombination is lowered.

As an obvious follow-up of this study, we have studied the dissociative adsorption of CO_2 on Cu(911), which exposes five atoms wide (100) terraces separated by monatomic steps. In contrast to what we expected, the O coverage did not increase significantly faster on this stepped surface. Our preliminary analysis suggests that diffusion of O from one step to another reduces the effect of the steps separating O and CO, but also that the steps facilitate O diffusion to the subsurface region and possibly stabilisation of CO_2 or CO_3 species on the surface.

In this presentation we will report how we conclude that the steps control the dissociation and, especially, the present status of the studies of Cu(911).

4:00pm **SS+HC-MoA-8 Surface Temperature Dependence of Methane Dissociation on Ni(997)***, **Daniel Tinney**, E High, L Joseph, A Utz,* Tufts University

Commercial steam reforming reactors operate at temperatures of 1000K or higher, and methane dissociation on the Ni catalyst is generally believed to be the rate-limiting step in this industrially important process. Despite the commercial importance of this reaction, nearly all studies probing the dynamics of methane dissociation have focused on surface temperatures of 600K or lower. Here, we use energy and vibrationally state selected methane molecules in a supersonic molecular beam to quantify the impact of surface temperature on methane activation over a wide range of surface temperatures. Our use of methane molecules with a precisely defined energy highlights provides a clear view of how surface temperature impacts reactivity.

Vibrationally state-resolved reactivity measurements reveal details of fundamental processes that impact reactivity in the field of heterogeneous catalysis. Non-statistical, mode-specific, and bond-selective enhancements observed for methane and its isotopologues on transition metal surfaces provide insights into energy flow during reactions. Reactive gas molecules with strictly-defined energy in well-defined energetic coordinates used in state-selective experiments have also proven to be valuable probes of how surface atom motion affects overall reactivity. For this work, vibrationally state-resolved data was collected via infrared (IR) laser excitation of the anti-symmetric stretch of supersonically-expanded methane (CH_4) gas molecules impinging on a lightly-stepped Ni(997) surface. Measurements on the single crystal were investigated over a broad range of surface temperatures ($82 K \le T_S \le 1000 K$) while utilizing varying incident energies (E_i = 20 kJ/mol to >140 kJ/mol). A comparison with prior data on Ni(111) surface reveals the role that steps may play in methane activation.

4:20pm **SS+HC-MoA-9 Promotion and Inhibition of Methane Dissociation by Carbon on Ni Single Crystal Surfaces***, **Arthur Utz**, E High, D Tinney,* Tufts University

State-resolved beam-surface scattering measurements, when coupled with molecular beam reactivity modulation measurements, permit real-time measurement of methane dissociation on Ni(111) and Ni(997) surfaces. At surface temperatures above 550K, methyl reaction products dehydrogenate to C atoms, and H atoms recombine and desorb, leaving C atoms behind. At higher surface temperatures, C atoms begin to aggregate on the surface and also absorb into the Ni subsurface region. We monitor how the presence of these C atoms on and beneath the surface impacts methane dissociation probability.

4:40pm **SS+HC-MoA-10 Two-Dimensional Polymorphism as a Result of Non-Equilibrium Self-Assembly***, **Angela Silski**[1], J Petersen,* University of Notre Dame*; R Brown,* Clarkson University*; S Kandel,* University of Notre Dame

The challenge in the field of molecular self-assembly is that the outcome of these processes is not easily predicted a priori, rather, results of self-assembly processes are often rationalized after the fact. In this study, a systemic approach to self-assembly is taken; the chemical structure of the starting molecule is iteratively changed (adding, removing or substituting particular functional groups) and the resulting self-assembled structure is observed via scanning tunneling microscopy. The focus of this study is on the functional groups that can form directional interactions (hydrogen- and halogen-bonds). We observe a metastable cyclic pentamer for isatin (1H-indole-2,3-dione) with density functional theory providing support for a cyclic structure stabilized by both NH· · ·O and CH· · ·O hydrogen bonds between neighboring molecules. The CH· · ·O hydrogen bond is made between the 7-position proton acting as the hydrogen bond donor and the 3-position carbonyl as the hydrogen bond acceptor, and calculations indicate that the isatin pentamer structure is 17 kJ/mol more stable than the dimer on the per molecule basis. To probe the importance of the CH···O hydrogen bond in stabilizing the isatin pentamer, we compare to isatin derivatives: we replace the 3-position carbonyl with a methyl group (3-methyl 2-oxindole), the 7-position proton with a fluorine (7-fluoroisatin), systematically move the location of the hydrogen bond donor/acceptor by one position, (phthalimide), and remove of the primary hydrogen bond donor (1,2-indandione and 1,3-indandione). We show that cyclic pentamer formation is either altered or precluded as a result of these substitutions. To our surprise, substituting the 6-position with a bromine (6-bromoisatin) which is a position remote to the positions of the hydrogen-bond contacts, does not result in the formation of cyclic pentamers on the surface. A monolayer of 6-bromoisatin consists of almost entirely “zipper” dimer structures. Additionally, the importance of CH···O bonding in forming isatin pentamers is supported by electrospray ionization mass spectrometry (ESI-MS) measurements, which include a magic-number isatin pentamer peak. A mass spectrum of 6-bromoisatin also shows a relatively intense pentamer peak, whereas the other derivative molecules show little clustering under the same conditions. This work is significant in understanding the role that the position of the hydrogen- and halogen-bond donor/acceptor groups has on the resulting 2D supramolecular assemblies.

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

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