

Surface Science Division

Room 203C - Session SS+HC+NS+PS-TuM

Controlling Mechanisms of Surface Chemical Reactions

Moderators: Bruce D. Kay, Pacific Northwest National Laboratory, Arthur Utz, Tufts University

8:00am **SS+HC+NS+PS-TuM-1 Bond Making and Bond Breaking at Wet and Dry Surfaces**, *Angelos Michaelides*, University College London, UK **INVITED**
The making and breaking of chemical bonds at the surfaces of crystalline materials is key to an almost endless list of physical phenomena and technological processes. Increasingly computer simulation techniques are playing an important role in helping to understand such processes, acting as a complement and guide to experiments. In this talk I will discuss recent simulation work in which we are working at: (i) obtaining fundamental physical insight of chemical reactions at the surfaces of transition metal alloys; and (ii) understanding and improving the accuracy of electronic structure simulations of surface chemical processes.

8:40am **SS+HC+NS+PS-TuM-3 Stability and Reactivity of Isolated Rh₁ Atoms on Fe₃O₄(001)**, *Gareth Parkinson*, TU Wien, Austria

In this talk I will address the thermal and chemical stability of Rh adatoms adsorbed on Fe₃O₄(001), and discuss the reactivity of these species with a view to single-atom catalysis. Using a combination of atomic-scale imaging, spectroscopies and DFT-based calculations, I will show that Rh adatoms adsorb in a bulk-continuation cation site at room temperature on Fe₃O₄(001), where they remain stable upon CO adsorption and can catalyze CO oxidation via a reaction with the support at 500 K. However, at this temperature Rh begins to incorporate within the support lattice, and the higher coordination environment significantly modifies the reactivity. In addition, I will show that Rh₁ species efficiently dissociate water, leading to H spillover of H onto the support, and that Rh₁ diffusion is induced upon adsorption of O₂ and NO.

9:00am **SS+HC+NS+PS-TuM-4 The Mechanism of Glaser Coupling Reactions on Ag(111) and Cu(111) Surfaces: a Case for Halogen Substituted Terminal Alkyne**, *T Wang, H Lv*, University of Science and Technology of China, China; *L Feng*, University of Science and Technology of China; *J Huang, X Wu*, University of Science and Technology of China, China; *Junfa Zhu*, National Synchrotron Radiation Laboratory and Department of Chemical Physics, University of Science and Technology of China, China

Ullman and Glaser homo-couplings are the two most well-developed on-surface coupling reactions, which have been successfully employed to fabricate one-dimensional and two-dimensional nanostructures on metal surfaces. The mechanism towards surface-confined Ullman coupling has been well-established. However, the mechanism of surface-confined Glaser coupling has been poorly understood. In this presentation, we report our recent studies on the surface-confined Glaser coupling reactions on Ag(111) and Cu(111) using 1,1'-biphenyl,4-bromo-4'-ethynyl (BPBE) as the precursor molecule. By direct observations of alkynyl-Ag-alkynyl and alkynyl-Cu-alkynyl type organometallic intermediates on Ag(111) and Cu(111), respectively, we have proposed a reaction pathway initiated by single-molecule dehydrogenation, similar as the mechanism of on-surface Ullman coupling. The reaction processes were further explored by density functional theory based transition state calculations. Interestingly, the dehydrogenation of terminal alkyne is revealed as a H adatom-related process on Ag(111) while a Cu adatom-related process on Cu(111). After the release of interstitial metal adatoms in the organometallic intermediates, the final C-C coupling occurs easily on Ag(111), but shows extremely low efficiency on Cu(111) due to the too strong interaction between ethynylene and the Cu(111) substrate. In addition, we have demonstrated that Glaser reaction of the molecule is prior to Ullman reaction on Ag(111), which provides a promising approach of stepwise fabrication of sp-hybrid nanostructures. *This work is supported by the National Natural Science Foundation of China (21773222, 21473178) and the National Key R&D Program of China (2017YFA0403402).*

9:20am **SS+HC+NS+PS-TuM-5 Sulfur-driven Switching of the Ullmann Coupling on Au(111)**, *Jonathan Rodríguez-Fernández, S Schmidt, J Lauritsen*, Aarhus University, Denmark

Ullmann coupling reaction has been attracted great interest in the last decades due to the advantage to build 1D-2D nanostructures from bottom-up fabrication like graphene nanoribbons, polymer, etc[1]. This reaction, it

is used to generate covalent molecular linked coupling, C-C, by different halogen molecule precursors. The reaction is activated by the substrate, where the precursors will be dehalogenated. Thus, the substrate plays an important role in the success of the reactions. There are several challenges, one of them is the scaling-up production of high quality nanostructures, where defects or co-adsorbates can reduce the success of this process. It has been reported two cases, where the Ullmann coupling reaction is partially inhibited[2,3]. Here, we reported for the first time the reactivation of the reaction after inhibited on Au(111) by molecular gases[4].

In this work we describe a variable temperature Scanning tunneling microscopy (VT-STM) study that allows us to identify the switch on and off of the Ullmann coupling reaction of this molecule (2,8-Dibromodibenzothiophene) on Au(111). After low temperature deposition on pristine Au(111), the results show that surprisingly Ullmann coupling mechanism happens even at 100 K. We speculate that the modification of the herringbone reconstruction due to the strong interaction between S and Au atoms can facilitate the lifting of the Au adatoms inducing the reaction even at low temperature. On the other hand, when we firstly dose sulfur atoms on the pristine gold crystal by H₂S vapor and subsequently depositing DBDBT molecules, the Ullmann coupling reaction has been completely inhibited due to the formation of S-Au complexes, which is blocking the activation of the reaction due to the gold adatoms on the terrace and step-edges are not available. Dysprosium and Iodine atoms have reported similar partial inhibition on silver and copper, respectively. However, we are able to reactivate the reaction by removing the sulfur atoms from the substrate by exposing the sample to H₂ (gas). STM images show again the Ullmann coupling reaction has been switched on. This result shows the importance of co-adsorbates on the substrate and also emphasizes the strong interaction between substrate adatoms (terraces and step edges) and the molecule precursors during the dehalogenation reaction.

[1]M. Lackinger, Chem. Commun. 53 (2017) 7872-7885.

[2]A. R. Lahrood, et. al. Chem. Commun. 51 (2015) 13301-13304.

[3]B. Cirera, J. Björk, R. Otero, J.M. Gallego, R. Miranda, D. Ecija, J. Phys. Chem. C. 121 (2017) 8033-8041.

[4]J. Rodríguez-Fernández, S.B. Schmidt, J.V. Lauritsen, Chem. Commun. 54 (2018) 3621-3624.

9:40am **SS+HC+NS+PS-TuM-6 The Step Sites of Ultrathin ZnO Promote Methanol Oxidation to Formaldehyde**, *Xingyi Deng, D Sorescu, J Lee*, National Energy Technology Laboratory

We investigated the adsorption and oxidation of methanol on ultrathin ZnO layers supported on Au(111) using temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) calculations. In the TPRS experiments, we found that only molecular methanol-¹⁸O desorbed from the planar ZnO bilayer surface at T = 220 K and 260 K following adsorption of methanol-¹⁸O at T = 100 K, whereas a partial oxidation product, formaldehyde-¹⁸O (~95% selectivity), and a small amount of carbon dioxide (C¹⁸O¹⁸O) were produced at T = 580 K at the bilayer-trilayer step sites. Computational modeling based on the DFT calculations identified the adsorption configurations of methanol on the planar ZnO surface and at the step sites, as well as the reaction pathways to gaseous formaldehyde. The most stable adsorption configuration was found to be a methanol molecule adsorbed at the bilayer-trilayer step sites with its C-O axis parallel to the upper terrace edge, forming a bond between its O atom and a Zn site on the lower terrace, and also a hydrogen bond between its H atom in the OH group and a lattice O anion at the upper terrace edge. Starting from the most stable adsorption configuration at the step sites, formation of gaseous formaldehyde was shown to take place preferentially via a methoxy (CH₃O(ad)) intermediate, following the pathways CH₃OH(ad) → CH₃O(ad) + H(ad) → CH₂O(g) + 2H(ad) with an overall barrier of 19.0 kcal/mol. Formation of CO₂ was kinetically hindered due to a much larger barrier of ~ 38 kcal/mol to produce a lattice O-bonded formaldehyde (H₂COO_{lattice}(ad)), the proposed precursor leading to CO₂. These computational results suggesting the preference to produce gaseous formaldehyde from methanol oxidation at the step sites agreed well with the high selectivity toward formaldehyde observed in the TPRS experiments.

11:00am **SS+HC+NS+PS-TuM-10 Investigation of Configuration Change in Water Clusters on a Bilayer ZnO Surface**, *Junseok Lee, D Sorescu, X Deng*, National Energy Technology Laboratory

Adsorption of water on the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying

water-oxide interfaces. In many cases, the water molecules form hydrogen bonded clusters or extended networks on surfaces. On a bilayer ZnO/Au(111) surface, two types of cyclic triangular water clusters are found to be formed at a specific Moire domain. By using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, the behavior of the water clusters on the bilayer ZnO surface have been further interrogated. The configurations of the two types of cyclic water clusters can be converted to each other by the excitation from the STM tip at a threshold energy. In addition, another pathway for the cluster configuration change was identified at a higher electron energy where the cyclic water clusters could be turned into non-cyclic clusters reversibly. The physical origin of the configuration changes will be discussed.

11:20am **SS+HC+NS+PS-TuM-11 Oxygen Reduction Reaction on Fullerene, Yosuke Kikuchi, J Nakamura, The University of Electro-Communications (UEC-Tokyo), Japan**

It has been reported that nitrogen-doped graphene exhibits high oxygen reduction reaction (ORR) activity, while pristine graphene does not [1]. This is because that doped-nitrogen atoms provide extra electrons to graphene, leading to the stabilization of the reaction intermediates on graphene surface. On the other hand, if curvature can be given to graphene, the chemical bond nature between carbon atoms varies from pure sp^2 to sp^3 -like sp^2 , and then the reactivity of graphene surface is expected to increase. In this study, we evaluated the ORR activity of fullerene as an example of carbon materials with a curvature.

We investigated the ORR activity of fullerene (C_{60}) using first-principles calculations based on the density functional theory. Electrocatalytic activities were evaluated on the basis of the computational hydrogen electrode model proposed by Nørskov *et al.* [3] We evaluated the energetics of reaction intermediates in terms of free energy of adsorption. In general, the ORR mainly proceeds in two pathways: For the two-electron pathway ($2e^-$), oxygen molecule (O_2) is reduced to hydrogen peroxide (H_2O_2), and for the direct four-electron pathway ($4e^-$), the final product is water (H_2O). H_2O_2 for the $2e^-$ pathway might corrode a carbon-based electrocatalyst material itself, causing to low durability. Therefore, we also played up the selectivity for the $4e^-$ pathway.

It was found that the fullerene molecule has ORR activity with extremely high selectivity for the four-electron pathway, even if the nitrogen atom is not doped. On the other hand, nitrogen-doped fullerene hardly shows the ORR activity, because the reaction intermediates are overstabilized by nitrogen-doping to fullerene; the maximum electrode potentials show negative values for both the direct four-electron and two-electron pathways.

[1] K. R. Lee, K. U. Lee, J. W. Lee, B. T. Ahn, S. I. Woo, *Electrochem. Commun.* 12, 1052 (2010)

[2] S. Ni, Z. Li, J. Yang, *Nanoscale*, 4, 1184 (2012)

[3] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, *J. Phys. Chem. B* 108, 17886 (2004)

11:40am **SS+HC+NS+PS-TuM-12 Surface Structure and Reactivity of Ni-Cu Single-Atom Alloys, Dipna Patel, C Sykes, Tufts University**

Ni is one of the most extensively used industrial catalytic metals. Utilized for steam reforming of hydrocarbons, Ni atom ensembles detrimentally catalyze the formation of graphitic carbon which leads to coking and deactivation of the catalyst. By alloying Ni into Cu, a catalytically less active host metal, our single-atom alloy approach has the potential to greatly enhance catalytic selectivity and reduce poisoning, analogous to other systems such as Pt-Cu and Pd-Cu. First, we report characterization of the atomic-scale surface structure and local geometry of low coverages of Ni deposited on a Cu(111) single crystal, using scanning tunneling microscopy. Near room temperature, Ni preferentially alloys into the Cu host by forming Ni rich brims along ascending step edges. Next, temperature programmed desorption studies reveal that CO binds more weakly to single Ni atoms in Cu compared to larger Ni ensembles in Ni(111) which is promising for catalytic applications in which CO poisoning is an issue. This characterization of Ni-Cu surface alloys the catalytic activity and selectivity of the surface to be correlated with the atomic-scale structure of the alloy. Using this approach, the catalytic selectivity and resilience to poisoning can be tuned via both ligand and ensemble effects.

12:00pm **SS+HC+NS+PS-TuM-13 Effective Local Structure for Bottom-up Designed ORR Catalyst Using Pyridinic Nitrogen Containing Molecules, Kotarou Takeyasu, Y Shimoyama, M Furukawa, S Singh, J Nakamura, University of Tsukuba, Japan**

Nitrogen containing carbon materials have been reported to be low-cost and durable catalysts for reactions such as an oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work [1]. Recently, we also have shown that the active site is superseded by pyridinic nitrogen-containing aromatic molecules covering a carbon substrate with high density [2]. That is, bottom-up catalysts composed of pyridinic nitrogen-containing molecules and carbon supports. In the present study, we aim to investigate which local structure for pyridinic nitrogen in a molecule strongly contributes to the ORR activities and to clarify the mechanism.

For this purpose, various nitrogen-containing molecules were prepared, which were 1,10-phenanthroline, 4,7-phenanthroline, 1,7-phenanthroline, benzo[h]quinoline, phenanthridine, acridine, phenazine, quinoxaline, and dipyrrophenazine. The bottom-up catalysts were prepared by simply immersing carbon black (CB) as a support material into a catalyst solution with solvent of nafion. The catalytic performances for oxygen reduction reactions (ORR) of the prepared catalysts were measured by rotating disc method in acidic electrolyte (0.1 M H_2SO_4) at a room temperature. The prepared catalysts were also evaluated by X-ray photoemission spectroscopy (XPS) and density functional calculations.

Among the molecules, 1,10-phenanthroline, quinoxaline, and dipyrrophenazine on CB showed highest activities, whose onset potentials (potentials versus RHE at a current density of 10 mA cm^{-2}) were 0.29 V, 0.28 V, and 0.21 V, respectively. This tendency suggested that an 1,10-phenanthroline type local structure showed high ORR activities because quinoxaline and dipyrrophenazine also contains the same local structure. XPS spectra after the superimposed voltage of 0.2 eV in an ORR condition for 1,10-phenanthroline showed two peaks corresponding to pyridinium N and pyridinic N. This also suggested that N-H...N structure promoted the following ORR reaction. The detail of the effect of the local electronic structure in the adsorbed molecules will be discussed.

References

[1] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, *Science*, 2016, 351, 361-365.

[2] R. Shibuya, T. Kondo, J. Nakamura, *ChemCatChem*, 2018

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