Surface Science Division
Room 25 - Session SS+HC-TuM

Controlling Mechanisms of Surface Chemical Reactions

Moderators: Daniel Killelea, Loyola University Chicago, Andrew Teplyakov, University of Delaware

8:00am SS+HC-TuM-1 Multifunctional Adsorption on Ge(100)-2x1 Surface: The Role of Interadsorbate Interactions, *Tania Sandoval*[1][2], *S Bent,* Stanford University

Adsorption of multifunctional molecules onto semiconductor surfaces provides a pathway to functionalize the surface while leaving unreacted functional groups available for reaction. These hybrid interfaces are important for applications in biosensors, microelectronics, and energy storage. These applications require homogeneous and controllable adsorption of these complex molecules. In this presentation, we will discuss two studies that help elucidate the driving forces governing the overall product distribution during adsorption of multifunctional molecules.

The first example describes the adsorption of homobifunctional pyrazine on the Ge(100)-2x1 surface. Pyrazine ($C_4H_4N_2$) is a six-membered ring molecule with two nitrogen atoms in the para position. The electron-rich nitrogen possesses a lone pair that can easily react with the surface through a dative bond. While benzene is not known to react with germanium, the addition of nitrogen to the aromatic ring opens up additional reaction channels. Previous studies of pyridine (C_5H_5N) on Ge(100) showed that reaction through the nitrogen can yield a mix of adsorption products. Our X-ray photoelectron spectroscopy (XPS) results suggest that pyrazine reacts with Ge(100)-2x1 to form a mix of reaction products. Analysis of the N(1s) and C(1s) spectra indicates that reaction of pyrazine occurs through the N-dative bond and via N=C and C=C cycloaddition reactions. The product distribution was found to be a function of temperature and coverage. This dependence suggests differences in the reaction channels as well as cooperative effects between adsorbate molecules.

The second example describes the adsorption of homotrifunctional 1,2,3-benzenetriol on Ge(100)-2x1 surface. 1,2,3-benzenetriol ($C_6H_6O_3$) is a trihydroxy phenol with three neighboring hydroxyl groups. The proximity between OH-groups promotes intra and inter-molecular hydrogen bonding. XPS and Fourier transform infrared spectroscopy results demonstrated that the reaction occurs through an OH-dissociative pathway. Coverage dependent shows that the extent of surface reactions per molecule decreases as the surface becomes crowded, and we predict this behavior is due to a combination of sterics and intermolecular hydrogen bonding. It has been previously shown that intermolecular hydrogen bonding can lower the reactivity of an OH group and prevent further reactions. Our theoretical analysis confirms that adsorbed molecules will preferentially interact with each other if unreacted OH groups are in close proximity. We expect that these interactions contribute to lowering the saturation coverage, as well as decrease the amount of dissociation events per molecule.

8:20am SS+HC-TuM-2 Steering the Chemical Reactions on Surfaces Toward Targeted Products, *Q Fan, T Wang, Junfa Zhu,* University of Science and Technology of China, China

The bottom-up construction of low-dimensional macromolecular nanostructures directly on a surface is a promising approach for future application in molecular electronics and integrated circuit production. However, challenges still remain in how to control the reaction pathways toward the formation of targeted nanostructures or dimensions. In this presentation, I will report our recent studies on the on-surface synthesis of low dimensional organic nanostructures on different substrate surfaces. These studies were performed under ultra-high vacuum (UHV) conditions using a combination of scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and high-resolution X-ray photoelectron spectroscopy (HR-XPS). Several examples will be shown to demonstrate that by employing different substrate templates,[1-4] special high-dilution synthesis condition[5] or hydrogen bond protection with dedicated precursor molecules on surfaces[6], surface reactions can be driven with different pathways towards the desired products. For example, on Cu(111) and Cu(110), after depositing the same precursor molecule, 4,4''-dibromo-meta-terphenyl (DMTP), at elevated temperatures, Ullmann coupling reaction can proceed via different pathways to form different nanostructures.[1-3] While on the Cu(110)-(2x1)O surface, by controlling the width of the Cu stripes, the spatial confinement effect can steer the reaction of DMTP to form either 1D zigzag organometallic oligomeric chains with different lengths or organometallic macrocycles with different widths.[4] More interestingly, when recently we transplanted the (pseudo-) high dilution method in solution to the conditions of on-surface synthesis in UHV, we found that the reaction of DMTP on Ag(111) can be tailored to specially form cyclic hyperbenzene with high-yield (84%) in contrast to the commonly formed zig-zag open-chain polymers.[5] Except for the presentation of these different structures on surfaces, we will also discuss the principles and mechanisms behind.

References:

(1) Fan, Q.; Wang, C.; et al., *Angew. Chem. Int. Ed.***2013**, *52*, 4668.

(2) Fan, Q.; Wang, C.; et al., *ACS Nano***2014**, *8*, 709.

(3) Dai, J.; Fan, Q.; et al., *Phys. Chem. Chem. Phys.***2016**, *18*, 20627.

(4) Fan, Q.; Dai, J.; et al., *ACS Nano***2016**, *10*, 3747.

(5) Fan, Q.; Wang, T.; et al., *ACS Nano***2017,** DOI: 10.1021/acsnano.7b01870.

(6) Wang, T.; Lv, H.; et al., *Angew. Chem. Int. Ed.* **2017**, *56*, 4762.

8:40am SS+HC-TuM-3 Spectroscopic Characterization of Reaction Pathways over a Pd-Cu(111) Single-Atom Alloy, *C Kruppe, Michael Trenary,* University of Illinois at Chicago **INVITED**

Low coverages of catalytically active metals deposited onto less active metal surfaces can form single atom alloys (SAAs), which often display unique catalytic properties. Such alloys are particularly attractive for selective hydrogenation reactions. It is therefore of interest to probe the surface structure and chemistry of such alloys in the presence of gas phase reactants. We have used polarization dependent reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the in-situ hydrogenation of acetylene to ethylene over a Pd/Cu(111) SAA surface. The coverage and morphology of the deposited Pd is characterized with Auger spectroscopy (AES), temperature programmed desorption (TPD) of H_2 and CO, and PD-RAIRS of CO. After exposing clean Cu(111) and Cu(111) with various Pd coverages to 10 L of CO at 100 K, the RAIR spectra show that the surface is largely unchanged by the presence of less than 0.5 ML of Pd. In the presence of 1×10^{-2} Torr of CO at 300 K, significant CO coverages are only achieved when Pd is present on the surface. The Pd coverage determined from CO peak areas obtained with RAIRS yields a value lower by about a factor of two than the Pd coverage obtained with AES. This is attributed to the presence of both surface and subsurface Pd, with only the former detectable by RAIRS of CO, but both detectable with AES. Surface species and gas phase products of C_2H_2 hydrogenation are monitored between 180 and 500 K on clean Cu(111) and Pd/Cu(111). With a total pressure of 1 Torr and a C_2H_2:H_2 ratio of 1:100, annealing a SAA-Pd/Cu(111) surface to 360 K results in complete conversion of all gas phase C_2H_2 to gas phase ethylene (C_2H_4), without producing any gas phase ethane (C_2H_6). The hydrogenation reaction is accompanied by acetylene coupling reactions that occur both on clean Cu(111) and on Pd-Cu(111).

9:20am SS+HC-TuM-5 Reactivity of Pt and Rh Adatoms, Dimers, and Small Clusters on Fe3O4 (001), *Jan Hulva*[3], TU Wien, Austria*; M Meier,* University of Vienna, Austria*; M Setvin, Z Jakub, R Bliem, M Schmid, U Dieblod,* TU Wien, Austria*; C Franchini,* University of Vienna, Austria*; G Parkinson,* TU Wien, Austria

The rapidly emerging field of "single-atom catalysis" aims to drastically reduce the amount of precious metal required to catalyze chemical reactions by replacing nanoparticles with single-atom active sites. Although there are now many reports of active single-atom catalysts [1], the concept itself remains controversial because it is challenging to characterize real catalysts and determine the reaction mechanism. In our work, we study fundamental properties of supported single metal atoms using a surface science approach. We employ the Fe_3O_4 (001) surface as a model support, because it can stabilize dense arrays of single metal atoms to temperatures as high as 700 K [2,3]. In this contribution, we address the adsorption behavior and reactivity of the Pt and Rh adatoms, dimers, and small

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[1] Morton S. Traum Award Finalist
[2] National Student Award Finalist

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

clusters using a combination of atomically resolved STM and non-contact AFM, high-resolution spectroscopy, and density functional theory. We conclude that Pt adatoms are inactive because CO adsorption results in mobility, and rapid sintering into Pt_2 dimers [5]. Pt dimers, on the other hand, are stable, and highly efficient CO oxidation catalysts. By isotopically labelling the oxide surface with ^{18}O, we unambiguously show that a Mars van Krevelen mechanism is responsible for the catalytic activity. Rh adatoms interact more strongly with the oxide, and do not sinter upon adsorption of CO. As a result, we find that Rh adatoms do catalyze CO oxidation, also via an MvK mechanism.

[1] – Acc. Chem. Res. 46(8), pp.1740-1748.

[2] – Phys.Rev.Lett.108(2012): 216103

[3] – Science 346 (2014): 1215-1218.

[4] – Angew. Chem. Int. Ed. 54.47 (2015): 13999-14002.

[5] – PNAS 113.32 (2016): 8921-8926.

9:40am SS+HC-TuM-6 An AP-XPS Study to Investigate the Reaction Mechanism of the Oxidation of CO on Pt/TiO$_2$ Nanoparticles: A Step Towards Closing both the Pressure and the Materials Gap, *Randima Galhenage, J Bruce, D Ferrah,* University of California Irvine; *I Waluyo, A Hunt,* Brookhaven National Laboratory; *J Hemminger,* University of California Irvine

Platinum supported on oxides, such as TiO_2, are widely studied catalysts to drive oxidation reactions. Even though there are fundamental studies that have been done on single crystal Pt and TiO_2 to understand the reactivity and the mechanism, there lies a sizable knowledge gap due to the complexity of the real catalytic systems compared to the single crystal studies. We studied CO oxidation on a unique model system where Pt nanoparticles (NPs) are deposited on TiO_2 NPs supported on an inert HOPG surface. Our study takes the complexity of the material a step forward. In-operando Ambient Pressure X-ray photoelectron spectroscopy (AP-XPS) was used to study the oxidation states of Pt, Ti, and O during the reaction to understand the role of different oxidation states of the elements on the reaction mechanism. Ex-situ prepared model catalyst which mostly contains a mixture of Pt(4) and Pt(2) were first heated to obtain a mixture of Pt(0) and Pt(2). During the reaction, the TiO_2 remains stoichiometric with no indication of any change in the oxidation state. At 400 K, CO is adsorbed on Pt resulting in a decrease of the Pt(2)/Pt(0) ratio. O1s spectra show the formation of Pt-O bond at 450 K. A rapid decrease of O1s (Pt-O) and a decrease of Pt(2)/Pt(0) ratio were observed simultaneously with CO_2 production at 500 K. In conclusion, we were able to study CO oxidation on a more complex model system of Pt/TiO$_2$ and followed the reaction mechanism. CO first adsorb on Pt and reacts with the oxygen that is dissociated on Pt sites which agree with the existing Langmuir–Hinshelwood (LH) mechanism. Furthermore, we found out that CO gets adsorbed on Pt(2) rather than on Pt(0) when there is a mixture of Pt(2) and Pt(0).

11:00am SS+HC-TuM-10 Oxygen Reduction Reaction of Graphite Decorated by the Pyridinic-Nitrogen Contained Molecules with High Density, *Riku Shibuya, T Kondo,* University of Tsukuba, Japan; *J Nakamura,* University of Tsukuba, Japam

Nitrogen containing carbon materials have been reported to show catalytic activities such as an oxygen reduction reaction (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]. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. Here we report model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule). The DA molecules were deposited on HOPG with different coverage by simply dropping solutions of the DA molecules at room temperature. Scanning tunneling microscopy (STM) measurements revealed that a well-ordered two-dimensional structure of DA monolayer is formed on HOPG surfaces with high densities via π-π interaction, rather than aggregates to form three-dimensional clusters. The nitrogen concentration of the DA-covered HOPG surfaces was estimated to be 0.5~1.5 at.% by XPS. The DA-covered HOPG model catalysts reveled activities of ORR. The specific activity per pyridinic nitrogen atom was estimated to be 0.08 (e sec^{-1} pyriN^{-1}) at 0.3 eV, which is comparable to that for pyridinic nitrogen incorporated graphene sheets (0.07 ~ 0.14 (e sec^{-1} pyriN^{-1}))[1]. The current densities at 0.1, 0.2, and 0.3 V vs RHE were in proportional to the surface coverage of DA molecules, indicating that the

ORR active site was created by DA molecule adsorbed on HOPG. The present studies clearly show that fixing nitrogen-containing aromatic molecules on graphitic carbon materials is one of promising approaches to prepare active ORR carbon catalysts.

References

[1] D.Guo, R.Shibuya, T.Kondo, J.Nakamura, et al., Science, 351 (2016), 361-365.

11:20am SS+HC-TuM-11 Spectroscopic and Computational Studies of Room-Temperature Decomposition of a Chemical Warfare Agent Simulant on Copper Oxide, *Lena Trotochaud,* Lawrence Berkeley National Laboratory; *R Tsyshevsky, S Holdren,* University of Maryland, College Park; *K Fears,* U.S. Naval Research Laboratory; *A Head,* Lawrence Berkeley National Laboratory; *Y Yu,* University of Maryland, College Park; *O Karslioglu,* Lawrence Berkeley National Laboratory; *S Pletincx,* Vrije Universiteit Brussel, Belgium; *B Eichhorn,* University of Maryland, College Park; *J Owrutsky, J Long,* U.S. Naval Research Laboratory; *M Zachariah, M Kuklja,* University of Maryland, College Park; *H Bluhm,* Lawrence Berkeley National Laboratory

Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metal oxides, including CuO_x. Despite decades of work to develop highly effective and versatile filtration materials, little is known about the mechanisms of CWA degradation by material surfaces and filter deactivation/poisoning, in part due to the challenges involved with spectroscopic characterization of filtration material surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present work detailing the mechanism of adsorption and decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant, on polycrystalline copper oxide surfaces. Ambient-pressure XPS enables examination of these surfaces and adsorbed species upon exposure to DMMP and other common atmospheric gases, such as water vapor and NO_x. Multiple decomposition products are observed on CuO_x surfaces, and the oxidation state of the metal appears to influence the mechanistic pathway. Complementary density functional theory (DFT) and *in situ* FTIR studies corroborate our experimental findings and are used to propose likely decomposition pathways. Exposure of the CuO_x surfaces to water vapor or NO_x prior to introducing DMMP affects the decomposition product distribution, but does not appear to significantly inhibit the initial DMMP adsorption.

11:40am SS+HC-TuM-12 Atomic View of Acid Zeolite Chemistry: Surface Chemistry Studies on 2D Silicate Materials, *Jin-Hao Jhang, G Hutchings, C Zhou, U Schwarz, E Altman,* Yale University

Although zeolites have been used in facilitating numerous catalytic reactions for decades, it is still a long-term challenge to understand how surface properties of zeolites promote catalytic reactions. Recently, two-dimensional (2D) silicate materials were discovered and prepared successfully on different substrates, including transition metals and alloy. This achievement makes surface science approaches possible for understanding zeolite chemistry from an atomic view. In this work, we seek to establish that 2D silicates are capable of promoting acid catalyzed reactions in a manner analogous to 3D zeolites. The 2D silicates were prepared on a Pd(111) substrate via physical vapor deposition (PVD) at room temperature followed by annealing at 1000 K in an oxygen background. The probe molecule 2-propylamine reacts through a deammination process and produces propene on the 2D aluminosilicate indicating the existence of acid sites capable of catalysis. In contrast, no propene or other products were detected on the 2D silica surface. We also generated atomic deuterium (D) on both silica and aluminosilicate by a D_2-plasma treatment and a D_2-recombination feature at 540 K assigned to the decomposition of surface OD groups was only observed from the aluminosilicate sample. These findings show the similarity between the 2D aluminosilicate and the acid zeolites which allows us to consider the 2D material as a zeolite model to explore zeolite chemistry.

12:00pm **SS+HC-TuM-13 Establishing Rules for Oriented SURMOF Growth Beyond Template Effects**, *X Yu,* University of Frankfurt, Germany*; J Zhuang,* Guizhou Normal University, P.R. China*; **Andreas Terfort**,* University of Frankfurt, Germany

The surface deposition of metal-organic frameworks (MOFs) opens the opportunity to use these highly designable materials for applications in electronics, data storage, sensing or biointerfaces. Several protocols have been reported to grow or attach MOFs onto a variety of surfaces, but nevertheless, the bandwidth of successfully deposited MOFs is still extremely limited: Besides the archetypical HKUST-1 and ZIF-5, only a family of tetragonal layer systems (with or without pillars) could be grown into well-defined SURMOF layers [1]. Although with some of these systems impressive results for different devices, such as photovoltaic cells, have been reported, the limitation to these classes of MOFs is unsatisfactory.

In this talk, we wish to discuss that the lack of success with other systems is related to the fact that most projects relied solely on the well-established surface-template effects, in which the coordination of surface-bound, functional groups to the metal SBU defines not only the binding mode but the orientation of the whole film. We will show that the rules on the surface differ from the ones in solution by a reduced number of trajectories, which in turn hamper certain reactions [2]. It is also of importance to keep in mind the different surface energies of the crystal surfaces, which can dictate a reorientation of the preformed system by Ostwald ripening during the deposition process [3]. All these processes involve different activation energies, the careful control of which opens the opportunity to grow well-oriented films of MOF systems, which have behaved notoriously difficult up to now.

References

[1] Zhuang, J.-L.; Terfort, A.; Wöll, C. *Coord. Chem. Rev.* 307 (**2016**) 391-424.

[2] Zhuang, J.-L.; Kind, M.; Grytz, C. M.; Farr, F.; Diefenbach,M.; Tussupbayev, S.; Holthausen, M. C.; Terfort, A. *J. Am. Chem. Soc.* 137 (**2015**) 8237-8243.

[3] Yu, X.-J.; Zhuang, J.-L.; Scherr,J.; Abu-Husein,T.; Terfort, A. *Angew. Chem. Int. Ed.* 29 (**2016**) 8348-8352.

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