Surface Science Division
Room 319 - Session SS+AS+TF-MoM
Dynamics and Mechanisms at Surfaces and Interfaces

Moderator: Eric Altman, Yale University

8:20am **SS+AS+TF-MoM-1 Stereodynamics Effects in Grazing-Incidence Fast-Molecule Diffraction***, **Cristina Díaz,*** Universidad Complutense de Madrid, Spain **INVITED**

Grazing-incidence fast-projectile diffraction, measured experimentally for the first time in 2007[1,2], has been proposed both as a complement and an alternative to thermal-energy projectile scattering, which explains the interest that this technique has received in recent years, especially in the case of atomic projectiles (GIFAD)[3,4]. Grazing-incidence fact-molecule diffraction (GIFMD), on the other hand, has received much less attention (mostly theoretical[5,6]), despite the fact that the H_2 molecule:(i) is as easy to generate as atomic H (a widely used projectilein GIFAD experiments); (ii) is lighter than He (another widelyused projectile in GIFAD), which would further reduce surface-phononsinelastic processes; and (iii) can reveal aspects of thesurface landscape that may be relevant in other contexts dueto the internal degrees of freedom (DOFs) and, in the case ofthe ionic surfaces, to the interaction of its quadrupole momentwith the electric field created by the ionic crystal, which is verysensitive to the surface details.Here, we present a theoretical study of grazing-incidence fast-molecule diffraction of H_2 from KCl(001) usinga six-dimensional density functional theory based potential energy surface and a time-dependentwavepacket propagation method. The analysis of the computed diffraction patterns as a function ofthe molecular alignment, and their comparison with the available experimental data, where the initialdistribution of rotational states in the molecule is not known, reveals a puzzling stereo dynamics effectof the diffracted projectiles: Diffracted molecules aligned perpendicular, or quasi perpendicular,to the surface reproduce rather well the experimental diffraction pattern, whereas those moleculealigned parallel to or titled with respect to the surface do not behave as in the experiments. Theseresults call for more detailed investigations of the molecular beam generation process.

1- P. Rousseau, et al., Phys. Rev. Lett., 98, 016104 (2007).

2- A. Schuller et al., Phys. Rev. Lett., 98, 016103 (2007).

3- H. Winter and A. Schuller, Prog. Surf. Sci., 86, 169 (2011).

4- M. Debiossac, P. Pan and P. Roncin, Phys. Chem. Chem. Phys., 23, 7615 (2021).

5- M. del Cueto et al., Phys. Chem. Chem. Phys., 19, 16317 (2017).

6- A. S. Muzas et al., Phys. Rev. B, 96, 205432 (2017).

9:00am **SS+AS+TF-MoM-3 Intermolecular Interactions in Carbonyl Compounds Trigger Surface Reactivity***, **Swetlana Schauermann,** S. Attia, C. Schroeder, M. Schmidt,* Kiel University, Germany

Hydrogenation of carbonyl compounds is an important step in many applications in heterogeneous catalysis. This class of reactions is, however, experimentally highly challenging as it requires the activation of a normally very stable C=O bond. There is an ongoing discussion on an alternative mechanism of C=O bond hydrogenation, which involves keto-enol tautomerization as a first step. In this mechanism, a H atom transfers to oxygen in an intramolecular process to produce a C-O(H) single bond, leaving behind a C=C double bond and forming the enol species. Several theoretical studies predict a significantly lower activation barrier for hydrogenation of the C=C bond in enol as compared to the direct hydrogenation of the C=O bond in ketone for different classes of mono- and dicarbonyl compounds.

In this contribution, we present a mechanistic study on atomistic-level mechanisms of enol formation and stabilization via lateral interactions with co-adsorbed surface species over catalytically active metal surfaces (Pt and Pd).[1, 2] We employ a broad range of carbonyl compounds including acetophenone, acetylpyridine, butanal and ethyl pyruvate, whose adsorption and reactivity behavior were investigated using a combination of infrared reflection absorption spectroscopy (IRAS), scanning tunneling microscopy (STM) and molecular beam techniques. We found that enols can be efficiently formed in different types of carbonyl-containing molecules, however, they require stabilization on the surface via lateral interaction, e.g. by establishing hydrogen bonding between the –OH group of an enol and a carbonyl group of the neighboring adsorbate. Stabilization of formed enols via lateral interactions with the adjustment molecules results in formation of different types of oligomers, including one of more enol molecules. The efficiency of enol formation was found to strongly depend on the chemical structure of the adsorbates and can be affected by e.g. the insertion of the functional groups, such as phenyl or pyridine groups. Also the presence of subsurface hydrogen in Pd was shown to strongly enhance keto-enol tautomerisation in some of the investigated carbonyls. Finally, we provide the first experimental evidence for a low-temperature hydrogenation pathway of carbonyl compounds, which occurs in ketone-enol dimers of acetophenone formed on Pt.[3] In this process, stabilization of enol species via lateral interactions with a neighboring carbonyl is crucial for enabling the target hydrogenation pathway.

1. Attia, S. et al *Angew. Chem. Int. Edit.* **2018,***57*, 16659.
2. Attia, S.et al *ACS Catal.* **2019,***9*, 6882.
3. Attia, S. et al, *J. Phys. Chem. C* **2019,***123* (48), 29271.

9:20am **SS+AS+TF-MoM-4 Velocity Map Images of Subsurface Oxygen Desorbing from Rh(111)***, **Arved Cedric Dorst,** T. Schäfer,* University of Göettingen, Germany*; D. Killelea,* Loyola University Chicago

In heterogeneous catalysis, the reactivity of for example oxidation reactions is often enhanced by transition group metal surfaces as catalysts. After exposure, the oxygen molecules readily dissociate into oxygen atoms on the surface forming characteristic surface reconstruction patterns. However, not only the formation of surface oxygen (O_{surf}) structures but also of subsurface oxygen (O_{sub}) phases is possible, especially when aggressive oxidation agents such as NO_2 or atomic oxygen are used as oxygen source. The O/Rh(111) has been adapted as a benchmark system for O_{sub} formation in the past. In temperature programmed desorption (TPD) experiments, O_{sub} emerges as a narrow desorption feature around 800 K, while O_{surf} forms a subsequent broad desorption feature over several 100 K. Although extensive research has been done on the formed reconstructions of O_{surf}, few is known about the microscopic details of O_{sub} formation.

In the here presented work, velocity map imaging (VMI) was applied to the O/Rh(111) system. We combined TPD and VMI to investigate recombinatively desorbing O_{sub} from Rh(111). This allows a precise assignment of high-resolution velocity distributions of desorption products to certain TPD peaks. We observe a hyperthermal velocity distribution for recombinatively desorbing oxygen from subsurface as well as from surface states. These results provide valuable benchmark data, on which theoretical models describing subsurface oxygen dynamics can be developed and tested.

9:40am **SS+AS+TF-MoM-5 In-Situ Characterization of O_2 Gas-Induced Rearrangement of Near-Surface Composition in Refractory High-Entropy Alloys***, H. Kersell,* Oregon State University*; X. Fan,* University of Tennessee Knoxville*; A. Herman,* Oregon State University*; Z. Lyu,* University of Tennessee Knoxville*; B. Steingrimsson,* Imagars LLC*; P. Liaw,* University of Tennessee Knoxville*; **Gregory S. Herman**,* Oregon State University

Alloy formation enables the enhancement of material properties from electrical and thermal conductivity, to magnetism, chemical reactivity, and mechanical strength and ductility. For example, Ti alloys are lightweight, corrosion resistant, have low Young’s modulus, and possess tunable strength and ductility at high temperatures. Their corrosion resistance and low Young’s modulus make them suitable for biomedical implants, while their light weight, tunable strength, and high working temperatures facilitate use in high-temperature applications. Traditional alloys often contain a principal metal comprising most of the alloy composition, with additional functionality (e.g., oxidation resistance) induced by minority components. In contrast, high-entropy alloys possess multiple principal components, and have recently attracted significant attention for their enhanced tunability and sometimes unexpected physical properties.

Using ambient pressure X-ray photoelectron spectroscopy (AP-XPS), we have probed the initial oxidation of $TiZrHfNb_{0.3}$ refractory high-entropy alloys (RHEAs). Sputter-cleaning the as-cast alloy in ultrahigh vacuum removes adventitious carbon and native oxides, revealing a metallic alloy containing metal carbide species through its bulk. Subsequent vacuum annealing from room temperature (RT) to 100° C enriches the near-surface carbide content. This near-surface carbide enrichment continues with increasing temperature, accompanied by the formation of surface hydrocarbon species. Meanwhile, the relative compositions of Ti, Zr, Hf, and Nb are stable across the same temperature regime in vacuum. Despite their thermal stability, freshly sputter-cleaned, metallic alloy surfaces exposed to 1 mTorr of O_2 gas become enriched by a near-surface layer of

Hf- and Zr- oxides. At the same time, the carbide component is suppressed, and a metal-oxide interface, containing Ti- and Zr- oxides, appears within the XPS probing depth (~8 nm). Subsequent RT oxygen exposure at higher O_2gas pressures induces comparatively minor changes in the surface oxide layer composition.

These results reveal the formation and nature of a thin protective oxide layer at the $TiZrHfNb_{0.3}$ RHEA surface in response to mild oxygen pressures. We present these results in terms of the O_2 pressure/temperature parameter space and discuss implications for the $TiZrHfNb_{0.3}$ RHEA behavior.

10:00am **SS+AS+TF-MoM-6 Surface Faceting and Oxidation in Binary and Ternary Ni-Based Alloys***, **Devin Jessup**, K. Orson, Z. Harris, P. Reinke,* University of Virginia

Future-proofing materials against degradation and failure means designing alloy systems with corrosion resistance built-in, and this is especially important for alloys in extreme environments. Ni-based superalloys are alloyed with Cr, Mo, and W which help form protective layers that are highly corrosion resistant mostly due to chromia (Cr2O3) formation. On polycrystalline alloy surfaces a wide range of crystallographic orientations coexist and are defined by the individual grains. For these often highly stepped or kinked surfaces, a complex surface faceting results from the tendency to minimize the surface free energy leading to an alloy with variable and complex surface topographies. Prior research indicates that different oxide species will nucleate along specific orientations resulting in oxide layer heterogeneity, which can introduce points of failure in the protective layer. Our work focuses on how these differences in surface crystallographic orientation can result in changes in the nucleation and growth of NiO and chromia, whose growth is kinetically controlled under our oxidation conditions.

A Ni11wt%Cr6wt%Mo alloy sample with large grains up to 1 mm offering a wide array of crystallographic orientations was selected for characterization. Scanning Tunnelling Microscopy (STM), Electron Backscatter Diffraction (EBSD), and Scanning Electron Microscopy (SEM) are used to characterize the surface. The native oxide was removed by annealing to 640˚C, and the highly variable surface topography was studied over a range of grains catalogued by EBSD. The alloy shows several unique surface topographies which are controlled by crystallographic orientation. Several examples are included in the supplemental material, which include wave-like facet structures, sharply terminating saw-tooth facets, and flatter “matchstick” structures. These can be correlated with the Miller index of the underlying grain surface on the stereographic triangle. The surface morphology was quantified with respect to facet size, shape, heights, orientation, and spatial distribution. This analysis provided the Miller indices for all well-expressed facets. Grain orientations were matched with their surface structures through a combination of feature matching between SEM and STM imagery and Fast Fourier Transform analysis. Further work will observe oxide nucleation on these facets, and their impact on oxide formation and performance. Understanding these mechanisms will contribute to our understanding of how to design Ni-based alloys for the most stable protective layer.

10:40am **SS+AS+TF-MoM-8 Medard W. Welch Award Talk: Atomistic Simulations to Advance Surface Science***, **Susan Sinnott**[1],* Pennsylvania State University **INVITED**

Computational methods are useful tools in the investigation of atomic and molecular dynamics and associated mechanisms at surfaces and interfaces. Physics-based classical potentials are a class of computational method that is useful for use in classical atomistic simulations of systems made up of thousands to many billions of atoms. These potentials consist of parameterized functions that capture aspects of atomic and molecular interactions within these material systems.

The focus of this presentation is on the third-generation charge-optimized many body (COMB3) potential. COMB3 was developed to enable an atomic-scale description of systems that include combinations of metallic, ionic, and covalent bonding under the same framework. The framework enables the system to determine the charge state of an atom or ion and manifest the physically appropriate type(s) and strength of local bonding as a function of environment correctly and autonomously. The framework further includes a combination of atomic-specific, bond-specific, bond-angle-specific parameters; the former is the same regardless of material, and only new bond-specific and bond-angle-specific parameters are required to extend existing elements to new compounds.

This presentation will provide an overview of the COMB3 potential and illustrate its utility in the study of water-metal surface and nanoparticle interactions, the examination of carbon nanoparticle-metal surface interactions, and the mechanisms associated with the growth of metal films on metallic and oxide substrates.

11:20am **SS+AS+TF-MoM-10 STM Study of Ag Encapsulation of Pd and Pt Islands on Ag(111) at Room Temperature***, **Buddhika Alupothe Gedara**[2], M. Trenary,* University of Illinois - Chicago

PdAg and PtAg bimetallic catalysts are used in many important industrial applications. Therefore, an atomic scale understanding of these catalysts is important for their further development. In this study, the initial stages of submonolayer growth of Pd and Pt islands on Ag(111) at room temperature were investigated using scanning tunneling microscopy (STM). Although Pd (1.7 J m^{-2}) and Pt (2.2 J m^{-2}) have higher surface free energies than Ag (1.1 J m^{-2}) and a similar lattice mismatch (PdAg = 4.8% and PtAg = 4.2%), Pd and Pt show different behavior after deposition on Ag(111) at room temperature. Hexagonal Pd islands are formed on Ag(111) regardless of the coverage. In contrast, Pt shows a high density of small clusters and larger islands indicating less mobility for Pt than Pd on Ag(111). Due to Pd atom place exchange with Ag atoms, Pd-rich brims were observed at the ascending Ag step edges. But, Pt-rich brims were not observed. Because of the absence of Pt-rich brims , removal of Ag atoms created bays at the step edges. Surface Ag atoms migrate to cover both Pd and Pt islands, even at room temperature, creating vacancy pits on the Ag(111) surface. In addition to large vacancy pits, small mobile vacancy pits were observed on Pt/Ag(111). Pd and Pt islands show different moire structures on Ag(111) even though they have almost same lattice mismatch. Migrated Ag atoms nucleate near the center of Pd islands to grow the second layer, whereas, migrated Ag atoms nucleate at the corner of the Pt islands.

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[1] **Medard W. Welch Award Winner**

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

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