

## Surface Science

### Room 120 - Session SS-ThM

#### Celebration of Robert J. Madix and his Contributions to Surface Science (INVITED SESSION)

**Moderators:** Dan Killelea, Loyola University Chicago, Jason Weaver, University of Florida, Linye Árnadóttir, Oregon State University

#### 8:30am SS-ThM-3 Infrared Spectroscopy Studies of Surface Chemical Reactions on Single Atom Alloys, Michael Trenary, University of Illinois - Chicago

INVITED

Low coverages of catalytically active metals deposited onto the surfaces of less active host metals can form single atom alloys (SAAs), which often display unique catalytic properties. The catalytic properties of SAAs are ultimately determined by their surface structure. We have used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) of adsorbed CO to probe the structure of Pd/Cu(111), Pt/Cu(111) and Pd/Ag(111) SAA surfaces. At certain values of the surface temperature and/or CO coverage, CO adsorbs only on Pd or Pt atoms and not on Cu or Ag sites. For low Pd and Pt coverages, only CO adsorbed at atop Pd or Pt sites is detected. At higher Pd or Pt coverages, CO adsorption at bridge sites is observed indicating that metal dimers or other aggregates have formed. Polarization dependent RAIRS was used to study selective hydrogenation reactions of acetylene, propyne, and 1,3-butadiene over a Pd/Cu(111) SAA surface. Reactants and products were monitored in the gas phase with s-polarized spectra, while p-polarized spectra were obtained to identify surface species present during the reaction. In each case, no hydrogenation occurred over the Cu(111) surface, but selective hydrogenation occurred over the Pd/Cu(111) SAA. Full hydrogenation to the saturated alkane did not occur. It is also found that coupling reactions occur to produce a carbonaceous layer on the surface, but that hydrogenation proceeds even in the presence of this layer.

#### 9:00am SS-ThM-5 Vibrationally Hot Precursors as Reactants in the Dissociative Chemisorption of Methane on Ir(111) and Ir(110), Arthur Utz, Tufts University

INVITED

Precursor-mediated reactions can potentially play a key role in the dissociative chemisorption of methane at the high temperatures (> 1000K) typical of steam-reforming reactors. At the average kinetic energies present, reactants can first physically adsorb to the surface as a precursor prior to undergoing subsequent diffusion and reaction (or desorption)<sup>1,2</sup>. High process temperatures also lead to significant populations of vibrationally excited gas-phase reagents and thermally excited lattice motion. This presentation will focus on the unique role that vibrational energy in the incident reactant and surface can play in activating these reactions.<sup>3</sup>

We use beam-surface scattering measurements coupled with infrared laser vibrational-state-selective excitation to prepare methane reactants with well-defined kinetic and vibrational energies. In this work, we study the role of methane's  $\nu_3$  antisymmetric C-H stretching vibration ( $E_{\text{vib}} = 36$  kJ/mol). The prepared molecules impinge on the surface held at a fixed temperature (which dictates the extent of thermal lattice vibration), and we quantify reaction probability as a function of incident kinetic energy, vibrational state, and surface temperature.<sup>2,3</sup> Independent control over these energetic coordinates allows us to unravel their contribution to reactivity. We chose to study the low-index Ir(111) and Ir(110)(1x2) surfaces because their minimum barrier height for dissociation is similar to, or slightly higher than the vibrational energy content of the laser-prepared molecules.

The experiments, when coupled with quasiclassical trajectory calculations, show that vibrational energy in a physisorbed precursor molecule survives long enough to promote reactivity with the same efficacy as reactivity occurring via a direct reaction mechanism. The calculations also point to the pivotal role of surface excitation in providing energetically accessible reaction paths for the physisorbed molecules.

1. J. F. Weaver, A. F. Carlsson, R. J. Madix, The adsorption and reaction of low molecular weight alkanes on metallic single crystal surfaces. *Surf. Sci. Rep.* **50**, 107-199 (2003).

2. E. Dombrowski, E. Peterson, D. DelSesto, A. Utz, Precursor-Mediated Reactivity of Vibrationally Hot Molecules: Methane Activation on Ir(111). *Catalysis Today* **244**, 10-18 (2015).

3. R. Moiraghi *et al.*, Nonthermalized Precursor-Mediated Dissociative Chemisorption at High Catalysis Temperatures. *J. Phys. Chem. Lett.* **11**, 2211-2218 (2020).

4. P. R. Shirhatti *et al.*, Observation of the adsorption and desorption of vibrationally excited molecules on a metal surface. *Nature Chemistry* **10**, 592-598 (2018).

#### 9:30am SS-ThM-7 Modeling of Reaction Mechanisms and Kinetics on Metal Surfaces and the Connection to Experimental Catalysis, Linye Árnadóttir, Oregon State University/PNNL

INVITED

Chemical reactions on surfaces are of central importance for our understanding of catalytic activity in heterogeneous catalysis. Density functional theory calculations and microkinetic modeling are often used to determine reaction mechanisms and kinetics and to model changes in surface coverage and product distribution and for comparison with experiments. With fast-growing computational resources, theoretical studies for reaction mechanisms and microkinetic models have become more commonplace. Traditionally researchers approximate the vibrational frequencies of an adsorbate from an Hessian matrix calculated using a finite difference approach and then use the harmonic oscillator approximation to calculate all modes of motion in the partition function but some of Bob Madix's early work on preexponential factors<sup>[1]</sup> motivated me and C.T. Campbell to propose the hindered translator/rotor model for the three modes of motion parallel to the surface, one for each of the two translations in the directions parallel to the surface and one for rotation about the axis perpendicular to the surface. These methods have since been modified and improved by other scientists and applied to microkinetic modeling by myself and others, inspired by Bob Madix work. Here we will discuss the implementation of these methods and recent DFT and microkinetic models for propane hydrogenation on Pt and Al<sub>2</sub>O<sub>3</sub>-decorated Pt surfaces and as well as complimentary temporal analysis of products (TAP) experiments by our collaborators at INL and ForgeNano, and the many ways Madix influenced our work and effort to bridge the gap between surface science and catalysis.

[1] R.J. Madix, G. Ertl and K. Christmann, Preexponential factors for hydrogen desorption from single crystal metal surfaces, *Chemical Physics Letters*, **62**, 1, 1979

#### 11:00am SS-ThM-13 Crossing the Great Divide Again: Bridging Atomic-Scale Mechanistic Insight from Single-Crystals to Functional Catalysts Using Transient Flow and Spectroscopy., C. O'Connor, Harvard University; E. High, Tufts University; T. Kim, Korea Institute of Energy Research, Republic of Korea; Christian Reece, Harvard University

INVITED

A key aspiration in the rationale design of catalysts is predictive performance (activity, selectivity, and stability) and surface properties (composition and structure) under realistic reaction conditions. This requires an atomic-scale understanding of catalyst reaction systems. Surface science studies on model catalytic systems are the "gold standard" for providing kinetic and mechanistic insight into heterogeneous catalysis. However, transferring this fundamental insight often measured on planar single crystals under ultra-high vacuum (UHV) conditions to applied catalytic reactors using technical catalytic materials at elevated temperatures and pressure can be challenging. Herein, we demonstrate our newly developed transient flow reactor to perform step transient experiments in a packed bed reactor at atmospheric pressure. We examine CO oxidation over palladium-based catalysts as a probe catalytic system to recreate the catalytic performance of planar Pd/Al<sub>2</sub>O<sub>3</sub> in coincident molecular beams experiments under vacuum. We demonstrate that surface science derived kinetics can quantitatively model CO<sub>2</sub> production in our step transient experiments in an atmospheric pressure flow reactor. We establish a continuity of surface species under steady-state reaction conditions and sub-second evolution of surface species for step transient experiments using a custom low-volume Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reactor. This work demonstrates a unique ability to bridge the understanding of the state of the catalyst surface and reaction kinetics from vacuum conditions established using molecular beam experiments to ambient pressure conditions using a transient flow reactor and numerical simulations. Our technique provides a new regime for studying technical catalysts under applied reaction conditions.

11:30am SS-ThM-15 Recent Games in the Surface Chemistry Stadium; Bob helped Build It, and They Came, Charles Sykes, Tufts University

INVITED

One cannot overstate Robert Madix's influence on the modern field of well-defined surface chemistry. His numerous contributions have brought a deep

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understanding of important chemical processes at surfaces. Inspired by Bob's works linking molecular scale processes and well-defined active sites with the rates and selectivity of real catalysts I have strived to collaborate broadly in order to achieve this level of understanding and control. Bob performed fundamental studies with the belief that one day they will inform the design of catalysts. In this talk I will argue we have reached that point and I will discuss a new class of heterogeneous catalysts called *Single-Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.<sup>1-6</sup> These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between atomic-scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. In collaboration with Maria Flytzani-Stephanopoulos these concepts derived from our surface science and theoretical calculations have been used to design *Single-Atom Alloy* nanoparticle catalysts that are shown to perform industrially relevant reactions at realistic reaction conditions. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective hydrogenation and dehydrogenation reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis (Oxford University) and Michaelides (Cambridge University) that predicts reactivity trends for a wide range of *Single-Atom Alloy* combinations for important reaction steps like H-H, C-H, N-H, O-H, and CO<sub>2</sub> activation. Overall, I hope to highlight that this combined surface science, theoretical, and catalyst synthesis and testing approach (that Bob contributed so much to) provides a new and somewhat general method for the a priori design of new heterogeneous catalysts.

## References:

- [1] Kyriakou et al. *Science* **335**, 1209 (2012).
- [2] Marcinkowski et al. *Nature Materials* **12**, 523 (2013).
- [3] Lucci et al. *Nature Communications* **6**, 8550 (2015).
- [4] Liu et al. *JACS* **138**, 6396 (2016).
- [5] Marcinkowski et al. *Nature Chemistry* **10**, 325 (2018).
- [6] Hannagan et al. *Science* **372**, 1444 (2021).

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