

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-WeA

Theory and Dynamics of Heterogeneously Catalyzed Reactions

Moderator: Erin Iski, University of Tulsa

2:20pm **HC+SS-WeA-1 First-Principles Kinetic Monte Carlo Simulation of CO Oxidation on PdO(101): Role of Oxygen Vacancies**, *Minkyu Kim¹, A Asthagiri*, Ohio State University

CO oxidation on transition metal (TM) oxide surfaces has been widely studied both experimentally and theoretically; however, a healthy debate continues on the coupling between changes in oxide phase and surface reactivity. In this study, we investigated CO oxidation over PdO(101) surface, which has been proposed to be important in Pd oxidation catalysis. In contrast to earlier studies of CO oxidation on TM oxide surfaces, we incorporate neighbor effects of oxygen vacancies on all the elementary surface processes. We employ density functional theory (DFT) to map out the kinetics of 50 elementary surface processes. We find that barriers for elementary steps such as O vacancy, O₂ dissociation, and CO₂ formation can be decreased by 20-40% in the presence of O vacancies, while O₂ desorption is increased by 70%. Using the DFT-derived rate constants, we have developed a lattice-based kinetic Monte Carlo (kMC) framework that can simulate CO oxidation under both ultra-high vacuum (UHV) and reaction conditions.

Initially, the kMC simulations were performed under UHV conditions (low CO partial pressure, no O₂ pressure) as a function of increasing surface temperature. As the CO oxidation proceeds and the surface lattice O atom coverage is depleted, the CO oxidation rate decreases rapidly at 400 K; however, the rate sharply increases at temperatures above 450 K. At 450 K, we find a new complex pathway to CO₂ formation that is activated in the presence of O vacancies and is the source of the increased CO oxidation rate despite the depletion of surface oxygen atoms. These kMC results match UHV isothermal experiments under similar conditions. kMC simulations at steady state conditions of low CO and O₂ pressures (P_{CO}: 510⁻⁹ Torr / P_{O₂}: 1.510⁻⁸ Torr), show that the rate-limiting step is O₂ dissociation and this elementary step requires the presence of adjacent oxygen vacancies to be activated at temperatures below 500 K. Without the addition of O vacancy neighbor effects to the kMC model, the PdO(101) surface would be inactive to CO oxidation because surface oxygens cannot be healed by gaseous O₂. In addition, we will discuss kMC simulations under reaction conditions at varying CO/O₂ partial pressures.

2:40pm **HC+SS-WeA-2 Surface Reactivity of Activated CO₂**, *Richard van Lent²*, Leiden University, Netherlands; *A Walsh, M Gleeson*, DIFFER, Netherlands; *L Juurlink*, Leiden University, Netherlands

Catalytically converting CO₂ into renewable fuels is a promising avenue that addresses the current fuel and energy storage challenges. Depending on the process, conversion of CO₂ may involve initial breaking of the OC=O bond. If so, this highly endothermic step is likely rate limiting to the overall process. Ultra-high vacuum (UHV) research on well-defined surfaces can provide fundamental insight into such processes, e.g. how dissociation may be aided by internal energy in CO₂, the metal's identity and the surface structure.

Internal energy has been shown to promote the highly activated dissociative adsorption of CO₂ on Ni(100) [1]. Rovibrationally state-resolved measurements for CH₄ on Ni(100) have shown that excitation of the ν_3 antisymmetric stretch vibration has a promoting effect that approximately equals kinetic energy for Ni(100) surfaces [2,3]. For other metal surfaces and CH₄ vibrations, the relative efficacy of vibrational and kinetic energies varies between 0.4 and 1.4 [2].

To start unravelling how CO₂ dissociates on a surface, we combine standard supersonic molecular beam techniques with high resolution continuous wave (cw) IR laser excitation. We study the effect of ν_3 antisymmetric stretch excitation of CO₂ on dissociative adsorption on a Ni(711) surface.

For excitation, we use a 3.9-4.6 μm single mode optical parametric oscillator (OPO). The OPO is frequency-stabilized by locking onto the derivative of the lamb dip of the specific rovibrational transition of interest.

Frequency-stabilized IR radiation is crossed with a supersonic molecular beam that impinges onto the cleaned Ni(711) surface under UHV conditions. We use methods to determine absolute reactivities for CO₂ molecules with and without laser excitation. We extract rovibrational state-dependent absolute sticking probabilities as a function of kinetic energy. From this data, we determine the relative efficacy of vibrational and kinetic energy in overcoming the large activation barrier to dissociation.

[1] M. P. D'Evelyn, A. V. Hamza, G. E. Gdowski, and R. J. Madix, *Surf. Sci.* **167**, 451 (1986).

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3:00pm **HC+SS-WeA-3 Shining Light on Complexity: State- and Energy-Resolved Studies of Gas-Surface Reaction Dynamics and Mechanism**, *Arthur Utz*, Tufts University **INVITED**

Gas-surface reactions on a metal surface can be far more complex than their net chemical equation would suggest. The heterogeneity of the surface, and its ability to restructure, impact the availability and energetics of reaction sites, energy redistribution processes triggered by the gas-surface collision dictate transition state access, and many coupled chemical processes can influence the reaction's outcome.

The talk will survey the ability to vibrational state selected measurements of gas-surface reactivity to systematically unravel important aspects of this complexity and provide molecular-level mechanistic insights that can guide our understanding and predictions about these processes. The experiments use infrared light to excite a single quantum rotational and vibrational level of the gas-surface reagent molecule and a molecular beam to define its incident kinetic energy. In this way, we are able to make energy-resolved measurements of reactivity while systematically varying the distribution of energy among the system's energetic degrees of freedom. Computational studies by our collaborators inform and guide our interpretation of the data.

Recent results will be featured and examine the impact of a vibrationally excited reagent molecule's symmetry on surface-induced energy redistribution, the quenching lifetime of a vibrationally excited molecule on a metal surface, the role of surface atom motion on reaction energetics, the ability to use these measurements to benchmark DFT electronic structure calculations, and how isolated surface structural features, including steps and adatoms, modify reaction energetics.

4:20pm **HC+SS-WeA-7 Vibration-driven Reaction of CO₂ on Cu Surfaces via Eley-Rideal Type Mechanism**, *Junji Nakamura, J Quan, T Kozarashi, T Mogi, T Imabayashi, K Takeyasu, T Kondo*, University of Tsukuba, Japan

We have long studied the formation of formate (HCOO_a) intermediates as an intermediates of methanol synthesis by hydrogenation of CO₂ on Cu surfaces [1-4]. It has been suggested based on the kinetic analysis for the high pressure bulb experiments that the formate formation proceeds via Eley-Rideal type mechanism, in which CO₂ directly reacts with adsorbed hydrogen atom on Cu. In order to clarify the mechanism and dynamics, we carried out CO₂ molecular beam studies with the translational energy of 1.12-1.97 eV and the nozzle temperature of 800-1100 K. It was found that hot CO₂ in the molecular beam reacts directly with pre-adsorbed hydrogen atoms on cold Cu(111) and Cu(100) surfaces at 120-220 K to form formate adspecies (CO₂ + H_a → HCOO_a). That is, even at the low surface temperatures, formate species is formed rapidly when supplying energy only to CO₂. This indicates that the energy to overcome the reaction barrier comes from the hot CO₂ molecule itself instead of the Cu surface. The vibrational energy of CO₂ was much more effective for the reaction compared to the translational energy; and the reaction rate was independent of the surface temperature. The independence of surface temperature indicates the E-R type mechanism that the CO₂ molecule is not thermally equilibrated with the Cu surfaces but directly reacts with H_a. If the impinging CO₂ molecule chemisorbs on the Cu surfaces before reacting with H_a, the reaction rate should be dependent on the surface temperature, rather than the kinetic and the internal energies of CO₂. We evaluated the barrier distribution factors (*W*) of so-called Luntz equation by analysis of the reaction probability curves, which shows significant efficacy of the vibrational energy on the reaction of CO₂, which has not been observed before. DFT calculations are consistent with the experimental observations [5]. The direct reaction of CO₂ with adsorbed hydrogen atom can be regarded as the first example of vibration-driven bond formation reactions on surfaces.

References

¹ Heterogeneous Catalysis Graduate Student Presentation Award Finalist

² Heterogeneous Catalysis Graduate Student Presentation Award Finalist

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4:40pm **HC+SS-WeA-8 First Principles Reaction Kinetics over Metals, Oxides and Nanoparticles**, *Henrik Grönbeck*, Chalmers University of Technology, Gothenburg, Sweden **INVITED**

A major challenge in heterogeneous catalysis research is the determination of dominating reaction paths and kinetic bottlenecks. One reason for the challenge is the dynamic character of the kinetics, where the active sites may change with reaction conditions. Nevertheless, it is atomic scale information that allow for catalyst development beyond trial-and-error approaches. Kinetic modeling based on first principles calculations have over the past decade grown into an important tool for investigating the importance of different catalyst phases and reaction paths. In this contribution, I will discuss work where we have used density functional theory in combination with kinetic modeling to investigate catalytic reactions over metals, oxides and nanoparticles. The examples cover different aspects of kinetic modeling including determination of adsorbate entropies, importance of attractive adsorbate-adsorbate interactions and the complexity of many types of active sites.

Complete methane oxidation to carbon dioxide and water is used as one example and we have investigated the reaction over metallic Pd(100) and Pd(111) [1] as well as PdO(101) [2]. The reaction paths are shown to be markedly different on the metallic and the oxidized surfaces. We find that the catalytic activity is highly sensitive to adsorbate-adsorbate interactions which for PdO(101) are attractive owing to electronic pairing effects. This effect is crucial and common for oxide surfaces [3].

Reactions over platinum nanoparticles are investigated using a recently developed scaling relation Monte Carlo technique [4]. Taking CO oxidation as a model reaction, we find that the overall activity is determined by complex kinetic couplings. Effects of particle shape as well as internal and external strain will be discussed [5].

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5:20pm **HC+SS-WeA-10 Formation of Pd/Ag Sandwiches, a Stable PdAg Subsurface Alloy, and the Pd Segregation induced by CO and O₂, Studied with STM, Ambient-pressure XPS, and DFT**, *Matthijs van Spronsen*, Lawrence Berkeley National Laboratory; *K Duanmu*, UCLA; *R Madix*, Harvard University; *M Salmeron*, Lawrence Berkeley National Laboratory; *P Sautet*, UCLA; *C Friend*, Harvard University

Efficient chemical production requires the use of materials able to selectively catalyze complex chemical reactions. High selectivity can be obtained by using noble metals. To improve activity, while retaining selectivity, small amounts of an active metal can be added. These species can function as active sites for, e.g., O₂ activation.

A promising alloy for selective hydrogenation is AgPd. The challenge using this material as a catalyst is the larger surface free energy of Pd, compared to Ag. This difference leads to Ag enrichment of the surface, hence, more Pd, both costly and scarce, is needed to ensure that Pd is present in the surface.

Here, the stability of Pd was probed in (sub)surface alloys formed by depositing sub-monolayer amounts of Pd on pure Ag single crystals, in order to evaluate the feasibility of using surface alloys as catalysts. These

surface alloys would use much less Pd, but depend critically on understanding and control of the alloy composition and stability.

Mild annealing (~400 K) under ultra-high vacuum, leads to extensive migration of Ag and the formation of a Ag capping layer on the Pd. These measurements were based on scanning tunneling microscopy and X-ray photoelectron spectroscopy, supported by modeling (density functional theory). The etching, due to the loss of Ag, and the increase in island height, due to the capping, results in three-layer-high islands, covering both the terraces and the steps of the Ag(111) surface. The absence of significant amounts of Pd in the surface was confirmed by the lack of CO adsorption at 120 K.

The exposure of the Ag/Pd/Ag(111) surface alloy to gas atmospheres, either pure CO or O₂ (0.5 & 1 Torr, respectively), reverses the energetics, thus making Pd resurface. This was concluded from large core-level shifts observed in AP XPS measurements. Due to the proximity of Pd to the surface, the required temperature for Pd to segregate was rather low, in fact, for CO it was detected for 300 K. Resurfacing, and subsequent oxidation, of Pd was much slower, requiring cycling the temperature between 300 and 400 K in the O₂ atmosphere, several times. The difference stems from the fact that O₂ needs to be dissociated before it can form strong bonds to Pd, while CO can adsorb directly to Pd. The initial O₂-dissociation activity of the Ag-capped Pd is expected to be rather small.

To conclude, precise understanding of the stability of active metals with a high surface free energy is required to control the composition of surface alloys and its potential as active/selective catalyst.

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