Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 103A - Session HC+SS-ThM

Dynamics of Gas-surface Interactions in Heterogeneous Catalysis

Moderator: Daniel Killelea, Loyola University Chicago

8:00am **HC+SS-ThM1 Adsorption and Hydrogenation of Acrolein on Ru(001)**, ***Dominic Esan***, *Y.D. Ren,* University of Illinois at Chicago; *I.B. Waluyo,* Brookhaven National Laboratory; *M. Trenary,* University of Illinois at Chicago

The partial hydrogenation of α, β-unsaturated aldehyde s is an important step in several synthetic industrial processes especially in the fine chemicals and pharmaceutical industries. Generally, it has been established that the thermodynamics of the catalytic hydrogenation of these unsaturated aldehydes favor the formation of saturated aldehydes via the hydrogenation of the C=C bond while the manipulation of the kinetics of the process may yield the desired unsaturated alcohol product via the hydrogenation of the C=O bond. Most of the studies done on single metal surfaces using acrolein (CH_2=CH=CHO), the smallest of these aldehydes, show that the thermodynamically-preferred product (propanal) is always the favored product. However, bimetallic systems have been shown to possess unique properties, compared to their single metal counterparts, including novel reaction pathways. Thus, our aim is to study acrolein hydrogenation on a bimetallic Pt/Ru(001) system to determine if the presence of the Pt atoms can enhance the selectivity and activity towards the formation of the unsaturated alcohol (2-propenol).

In this initial study, temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) were used to determine if the bare Ru(001) surface is active towards (partial and complete) hydrogenation of acrolein and if it's selective for the desired product (2-propenol). At low coverages, acrolein was found to adsorb on the surface, at 90 K, via the C=O bond and completely decomposes to CO(g) around 460 K. As the coverage increases, adsorption via the C=C bond predominates and most of the acrolein desorbs molecularly or decomposes to CO(g). However, some of the acrolein also self-hydrogenates to yield all the possible hydrogenation products – propanal, 2-propenol, and 1-propanol with TPD peak temperatures at 180, 210, and 280 K respectively – with propanal having the highest yield. Co-adsorption with H_2(g) enhances the adsorption via the C=C bond and the yield of all the products. These results will serve as a guide for the study on the Pt/Ru(001) system.

8:20am **HC+SS-ThM2 Dynamics of Formate Synthesis from CO_2 and Formate Decomposition on Cu Surfaces**, *J. Quan, T. Kozarashi, T. Ogawa, T. Kondo,* ***Junji Nakamura,*** University of Tsukuba, Japan

Much attention has been paid to methanol synthesis by hydrogenation of CO_2 as a promising chemical conversion of CO_2. It has been well-known that Cu-based catalysts show high activity for the methanol synthesis, in which the initial elementary step of CO_2 is formation of formate species by the reaction of CO_2 with surface hydrogen atoms on Cu. Previous kinetic measurements of the formate synthesis by hydrogenation of CO_2 have suggested an Eley-Rideal (E-R) typed mechanism that CO_2 directly attacks a hydrogen atom on Cu surfaces. We have thus tried to prove the E-R typed mechanism by molecular beam experiments assuming that the reaction between incoming CO_2 molecules and Cu surfaces is thermally non-equilibrated. We first prepared hydrogen atoms on cold Cu(111), Cu(110), and Cu(100) kept around 200 K and then hot CO_2 molecular beams were illuminated onto the surfaces with controlling its vibrational and translational energy. It is found that the formate synthesis proceeds significantly without heating Cu samples if vibrational and translational energies are supplied to gaseous CO_2. The results clearly indicate the thermal non-equilibrium dynamics. Possibility of a tunneling mechanism between CO_2 and a hydrogen atom on Cu was discarded because no significant H/D effect was observed on the reaction rate of formate synthesis. On the other hand, we have studied the dynamics of the formate decomposition as a reverse reaction of the formate synthesis. We measured the angular distribution and the translational energy of desorbed CO_2 formed by the decomposition of formate on Cu(110) under a steady state reaction of HCOOH and O_2. The angular distribution showed a sharp collimation, $\cos^6\theta$, perpendicular to the surface. The translational energy of CO_2 was independent of the surface temperature of Cu(110). It is thus found that the formate decomposition is also thermal non-equilibrium dynamics. However, the translational energy was as low as 100 meV, which is much lower than that required for formate synthesis, about 600 meV. The discrepancy will be discussed in the presentation.

8:40am **HC+SS-ThM3 Step-Type Selective Oxidation on Pt Surfaces**, ***Rachael Farber***, Loyola University Chicago; *C. Badan,* Leiden Institute of Chemistry, The Netherlands; *H. Heyrich,* Leiden Institute of Chemistry; *L.B.F. Juurlink,* Leiden Institute of Chemistry, The Netherlands; *D.R. Killelea,* Loyola University Chicago

The development of predictive models of heterogeneously catalyzed systems relies on a sound understanding of the atomic-level details of the interactions of gas-phase species with the metal surface. A key factor in this tapestry is how the surface geometry influences reactivity. Single metal crystals with low Miller indices have often been used to probe the interactions between the reactive adsorbates and catalytic metal substrate. These low index surfaces are more accessible both computationally and experimentally, and have been essential to our current understanding of metal surface-catalyzed chemistry. However, the decreased complexity, because of the absence of active surface defects, can result in incomplete models of actual catalytic systems. Actual catalytic surfaces are believed to possess many defect sites that contribute to the overall reactivity of the catalyst. It has been recently shown that differences in the (110) and (100) step edge greatly influences water structures on the Pt surface. By using highly stepped Pt crystals with (110) and (100) steps, we see that the slight geometric differences between the (110) and (100) step also has profound effects on oxygen adsorption on stepped Pt crystals.

By utilizing highly stepped Pt crystals to study oxygen adsorption, along with ultra-high vacuum (UHV) surface science techniques such as temperature programmed desorption (TPD) and low temperature UHV scanning tunneling microscopy (STM), we are able to further understand O-Pt interactions on a surface that better mimics actual catalytic environments. Pt(553), with (110) step edges, was studied via STM to support the different behavior seen in oxygen adsorption between the (110) and (100) step edges in TPD experiments. The combination of TPD, STM, and variation in crystal step edge geometry allows for a more complete understanding of O_2 adsorption and dissociation on the Pt(553) surface and, more generally, (110) and (100) type step edges on Pt crystals.

9:00am **HC+SS-ThM4 Vibrational Symmetry Effects in the Dissociative Chemisorption of CH_2D_2 on Ni(111)**, ***Arthur Utz***, *N. Chen, E.H. High,* Tufts University

Vibrational state resolved reactivity measurements have established that mode-selective chemistry, in which the reaction probability, S_0, depends on the identity of the reactant's vibrational state, and bond selective chemistry, in which the product identity depends on the reagent's vibrational state, is widespread in the dissociation of methane and its isotopologues on Ni and Pt surfaces. Two factors lead to the observed mode- and bond-selectivity. First, methane's distorted transition state geometry introduces a bias that favors those vibrational motions that best access the transition state geometry. The sudden vector projection (SVP) model of Guo and coworkers predicts selectivity based on this factor. As the methane molecule approaches the surface, the molecule-surface interaction potential can also perturb the molecule's vibrations and lead to vibrational energy redistribution in the entrance channel for the reaction. Reaction path Hamiltonian calculations by Jackson and coworkers, quantum dynamics calculations by Kroes et al., and the vibrational adiabatic predictions of Halonen et al. focus on how this second factor impacts reactivity. In all of these calculations, the incident molecule's vibrational state symmetry can influence the vibrational coupling channels and energy flow pathways for the molecule as it approaches the surface.

This talk will focus on state-resolved experimental measurements of CH_2D_2 dissociation on a 90K Ni(111) surface. Unlike CH_4, the C_{2v} symmetry of the CH_2D_2 molecule results in both the ν_1 symmetric- and ν_6 antisymmetric C-H stretching vibrations being infrared active. Therefore, we can use state-resolved infrared laser excitation of CH_2D_2 in a supersonic molecular beam to measure the reaction probability for these two C-H stretching states as a function of incident translational energy (E_{trans}). By performing the measurements at 90K, we observe a sharp energy threshold for reaction that permits an unusually precise measure of the efficacy of each vibration in promoting reaction. Our choice of excitation transitions further reduces experimental error in comparing the two states' reactivity. Contrary to the predictions of a vibrationally adiabatic model, the two states have nearly identical reaction probability. We will compare these results with recent reaction path Hamiltonian calculations from the Jackson group to explore how the symmetry of these two vibrational states impacts their reactivity.

9:20am **HC+SS-ThM5 Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics***, **Swetlana Schauermann**,* Christian-Albrechts-Universität Kiel, Germany **INVITED**

Atomistic–level understanding of surface processes is a key prerequisite for rational design of new catalytic and functional materials. In our studies, we investigate mechanisms, kinetics and thermodynamics of heterogeneously catalyzed reactions and adsorption processes on nanostructured model supported catalysts by combination of multi-molecular beam techniques, infrared reflection-absorption spectroscopy and single crystal adsorption calorimetry. By employing these methods under well-defined ultra high vacuum conditions, we study mechanistic details of complex multi-pathway surface reactions, such as hydrocarbon transformation in presence of hydrogen or selective hydrogenation of multi-unsaturated hydrocarbons. The ultimate goal of our research is obtaining detailed correlations between reactivity, selectivity and the particular structure of the catalytic surface.

Specifically, it will be shown that selective hydrogenation of the C=O bond in acrolein to form an unsaturated alcohol is possible over Pd(111) with nearly 100 % selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface selective towards propenol formation.

In the second part, a mechanistic picture of interaction of water with model Fe_3O_4(111)/Pt(111) surface will be discussed. A combination of single crystal adsorption calorimetry and infrared spectroscopy was employed to determine the adsorption and dissociation heats of water and identify the surface species. We show that water dissociates readily on iron oxide surfaces forming a dimer-like hydroxyl-water complex and proved that the generally accepted model of water dissociation to two individual OH groups is incorrect.

11:00am **HC+SS-ThM10 CO_2 Hydrogenation on Rhodium: Comparative Study using Field Emission Techniques and 1-D Atom Probe***, **Sten Lambeets**,* Université Libre de Bruxelles, Belgium*; C. Barroo,* Harvard University*; S. Owczarek, N. Gilis,* Université Libre de Bruxelles, Belgium*; N. Kruse,* Washington State University*; T. Visart de Bocarmé,* Université Libre de Bruxelles, Belgium

Valorization of CO_2 into useful products is one way to fulfill current environmental and economic imperatives. This can be done via the selective reduction of CO_2 using heterogeneous catalysts. To get a better understanding of the fundamental processes, we studied the CO_2 adsorption as well as its interaction with H_2 on single nanosized Rh crystals. For this, Field Emission Microscopy (FEM), Field Ion Microscopy (FIM) and 1-D Atom Probe (1DAP) were used. These methods use samples prepared as sharp needles, the extremity of which is imaged with nanoscale (FEM) and even with atomic lateral resolution (FIM).

The structure of the Rh nanocrystals is characterized by FIM, and CO_2 adsorption, dissociation and hydrogenation is studied in FEM mode. The brightness intensity of the FEM pattern depends on the presence and the nature of adsorbates. Probing and analyzing the brightness signal over time allows to qualitatively monitor the variations of surface composition, and thus the presence of surface reactions, during the ongoing processes.

Finally, 1DAP, which corresponds to the combination of a FIM device with mass spectrometry, is used to identify the nature of the different surface species.

The FEM pattern of a clean sample essentially highlights {012} facets. During CO_2 exposure, the brightness of these facets drastically decreases and remains dark, reflecting the CO_2 dissociative adsorption over these facets - leading to the formation of O(ad) species. The presence of O(ad) at the surface induces a new FEM pattern where {113} facets become the most visible. This pattern reflects the formation of subsurface oxygen O(sub) beneath the {113} facets, which is confirmed by comparison with N_2O, O_2 and CO on Rh systems. To study the hydrogenation of CO_2, pure H_2 gas is introduced while the pressure of CO_2 is kept constant. Reaction phenomena, proved by variations in the brightness pattern, were observed from 650 to 734 K.

The adsorption of hydrogen at the surface leads to the formation of H(ad) species reacting with O(ad) to form H_2O(ad). Similar reaction phenomena were also observed with N_2O+H_2/Rh and O_2+H_2/Rh systems in the same temperature range, but not with the CO+H_2/Rh system, proving the role of O(ad) in the mechanism. Our observations allow to identify the reaction as the Reverse Water Gas Shift:

$CO_2(g)+H_2(g)\rightarrow CO(g)+H_2O(g)$

These assumptions are in line with direct local chemical first analyses performed by 1DAP. Rhodium oxides species - RhO^{2+} and RhO_2^{2+} - and CO_2 with its dissociation products, i.e. CO_2^+, CO^+ and O^+ , are detected in the first layers of a (115) facet of the Rh nanoparticle during an exposure to pure CO_2 at 325 K.

11:20am **HC+SS-ThM11 State-resolved Reactivity of Methane on Ir(110)-(1x2)***, **Eric Peterson**, E. Nicotera, E.K. Dombrowski, A.L. Utz,* Tufts University

The rate-limiting step in the steam reforming reaction, in which methane and water react to form hydrogen gas and carbon monoxide (syngas), is the initial cleavage of a C-H bond in the methane molecule. Methane's dissociative chemisorption is highly activated on catalytically active transition metal surfaces. To date, experimental measurements have focused on CH_4 molecules whose internal (vibrational) energy is less, and frequently much less than the threshold energy for reaction. Under those conditions, significant incident translational energy (TE) or energy transfer from the surface is required to activate dissociation, and reactions most often proceed via a direct dissociative chemisorption mechanism. Using a molecular beam in conjunction with an OPO-OPA continuous-wave IR laser, we are able to prepare methane molecules with a sharply defined kinetic energy and 36 kJ/mol of internal vibrational energy, which approaches or even exceeds the threshold energy for dissociative chemisorption. These molecules possess sufficient energy to react via direct or precursor-mediated mechanisms. The direct channel is characterized by an increase in reactivity with increasing TE, and is dominant for molecules with >10 kJ/mol of TE. Molecules with <10 kJ/mol of energy react through precursor-mediated channel, in which reactivity decreases with increasing TE. This low-TE precursor channel is especially interesting in a catalytic context, as most molecules under typical industrial reactor conditions have TEs where trapping, and therefore physisorption probabilities are high.

In studies of CH_4 dissociation on Ir single crystal surfaces, we observe both the precursor and direct channels for reaction. On Ir(111) we observe that 36 kJ/mol of E_{vib} in the n_3 C-H stretch enhances reactivity in both channels at a surface temperature of 1000K. On the corrugated Ir(110)-(1x2) surface, we still observe vibrational-energy enhancement in both channels, but the TE dependence of S_0 differs for the vibrationally hot and ground state CH_4 molecules at T_{surf} = 1000K. Upon lowering T_{surf} to 500K, vibrational ground state molecules no longer have a pronounced precursor-mediated reaction channel, but the vibrationally excited molecules do. We will discuss the origin of these similarities and differences. The observed reactivity of vibrationally hot methane molecules with thermal TE points to the potentially important role that vibrationally hot precursor molecules may play in industrially catalyzed reactors.

11:40am **HC+SS-ThM12 Curved Single Crystals As Tools to Study Structure Dependences in Surface Science and Gas-Surface Reactions Dynamics***, **Ludo Juurlink**,* Leiden University, Netherlands **INVITED**

The surface science approach has benefited for many decades from the availability of flat single crystal samples of high purity and high surface quality. The traditional flat, polished samples provide the user with a single surface structure that dominates over macroscopic length scales. However, a single sample that provides the user with multiple surface structures may provide additional benefits. For example, in attempts to relate chemical reactivity or selectivity to surface structure, having a continuous range of vicinal surfaces in a single sample can speed up scientific research and circumvent experimental difficulties. Also for studies focusing on either short or long-range effects in adsorbates and electronic states that are perturbed by steps, a single sample with a range of surface structures is an excellent tool. Therefore, we have revived the implementation of curved single crystal surfaces in traditional surface science studies and elaborated the implementation toward gas-surface reaction dynamics. Depending on the bulk crystal structure and the directions of the apex and curvature, many different surface structures are available in a single sample. We show how we now use LEED, AES, STM, TPD, RAIRS and supersonic molecular beam techniques to directly relate surface structure to molecular and dissociative adsorption, desorption, and chemical reactions. We exemplify the possibilities by showing recent results from studies that used a cylindrical Ni single crystal, two curved Ag samples, a Co curved sample and two Pt curved single crystal surfaces with various apex directions.

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