Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 24 - Session HC+SA+SS-ThM

Mechanisms and Reaction Pathways in Heterogeneously Catalyzed Reactions

Moderator: David Payne, Imperial College London

8:00am **HC+SA+SS-ThM-1 Effects of Phosphorus and Alkyl Substituents on C-H, C-C, and C-O Bond Rupture within Carboxylic Acids on Ru(0001)**, ***SiWei A. Chang***, *D Flaherty,* University of Illinois at Urbana-Champaign

Transition metal phosphide (TMP) catalysts are selective towards C-O bond rupture during hydrodeoxygenation reactions used to upgrade bio-oil. However, the manner in which bond rupture mechanisms and intrinsic barriers (i.e., C-H, C-C, and C-O bond) differ between transition metals and TMP catalysts are not well understood. In this study, a phosphorus (P) modified Ru(0001) surface is created using sequences of PH_3 adsorption and annealing treatments followed by Auger electron spectroscopy to determine the P:Ru ratio. Synthesized $P_{0.4}$-Ru(0001) surfaces have a (r7xr7) low energy electron diffraction pattern and appear to resemble the (111) facet of bulk Ru_2P materials. The results from temperature programmed desorption of CO and NH_3 demonstrate that the addition of P atoms to Ru(0001) decreases the binding energy of CO and NH_3 by ~12 kJ mol^{-1} compared to Ru, suggesting that P atoms decrease the extent of electron exchange between Ru surfaces and adsorbates (i.e., CO and NH_{-3}).

Results from temperature programmed reaction (TPR) of C_1-C_4 carboxylic acid decomposition on Ru(0001) and $P_{0.4}$-Ru(0001) surfaces indicate that both P atoms and the length of alkyl substituents on carboxylic acids (i.e., R = H, CH_3, CH_2CH_3, and $CH_2CH_2CH_3$) alter the intrinsic activation energy (E_a) of bond ruptures. On both surfaces, TPR and reactive molecular beam scattering (RMBS) results are consistent with carboxylic acid decomposition mechanism, that involves the reaction of carboxylate intermediates to form alkyl surface species with either CO (by C-O bond rupture followed by C-H/C-C bond rupture) or CO_2 (by direct C-H/C-C bond rupture). The addition of P atoms to Ru(0001) increases E_a values for the rupture of all bonds (i.e., C-O, C-H and C-C bonds) by 5-50 kJ mol^{-1} and increases also the ratio of CO to CO_2 production (in the case of formic acid and acetic acid decomposition). In addition, P atoms weaken the linear correlation that exists between E_a for C-C and C-H bond rupture and the homolytic bond dissociation energies (BDE) of the involved bonds (e.g., R-COOH), thereby decreasing the strength of the correlation from near parity on Ru(0001) (i.e., slope m = 1) to moderate changes with BDE on $P_{0.4}$-Ru(0001) (i.e., slope m = 0.2). The RMBS results from formic acid in the presence of P atoms show a higher production of CO than CO_2, which reflects the catalytic consequences of the differences between the C-H and C-O bond rupture energy barriers on $P_{0.40}$-Ru(0001) and those for Ru(0001). Collectively, these results suggest that P atoms alters the production selectivity of CO and CO_2 through a greater increase in the energy barriers of C-O bond relative to C-H/C-C bond rupture.

8:20am **HC+SA+SS-ThM-2 Monitoring Cu(111) Restructuring under Elevated CO Pressures via Polarization Dependent Infrared Spectroscopy**, ***Christopher Kruppe***, *M Trenary,* University of Illinois at Chicago

Recently it was shown that a Cu(111) surface will reconstruct to form nanoclusters when exposed to 0.1 – 100 Torr of CO.[1] We present the use of polarization dependent – reflection absorption infrared spectroscopy (PD-RAIRS) to monitor the Cu(111) restructuring in real time. Under 10 Torr of CO, PD-RAIR spectra display a peak for CO on top of Cu atoms. Scans were taken periodically and displayed new peaks related to CO bound to the nanoclusters that grow over a period of 30 minutes. Spectra obtained at 10 Torr and 300 K show that the creation of the Cu nanoclusters is correlated with an increase in intensity of these C-O vibrational features, which are only visible due to removal of gas phase CO features from the RAIR spectra. Dissociation of H_2O in UHV occurs on the nanoclusters, which is negligible on unreconstructed Cu(111). Previously the splitting of H_2O was thought to be a geometric effect caused by the nanoclusters as under UHV conditions CO does not adsorb on Cu(111) at room temperature. However, after exposing Cu(111) to 10 Torr of CO at room temperature for 30 minutes strong C-O vibrations are observed upon evacuation of the IR cell. In UHV, the H_2O partial pressure is increased in the IR cell to 2×10^{-8} Torr and flowed over the reconstructed Cu(111) crystal. The RAIR spectra indicates there is a reactive CO species that interacts with H_2O to create formaldehyde. This is further confirmed by observing formaldehyde with temperature programmed desorption following H_2O exposure. Auger electron spectroscopy confirms the presence of oxygen on the Cu(111) surface after water exposures in the IR cell. Detailed interpretation of the data requires consideration for the formation of Fe-carbonyls, which can be present in the CO bottle, or produced in the reaction cell. The possibility of Fe as the cause for the CO bound in UHV will be presented.

1. Eren, B.; Zherebetskyy, D.; Patera, L. L.; Wu, C. H.; Bluhm, H.; Africh, C.; Wang, L.-W.; Somorjai, G. A.; Salmeron, M. Activation of Cu(111) Surface by Decomposition into Nanoclusters Driven by CO Adsorption. *Science* **2016**, *351*, 475 LP - 478.

8:40am **HC+SA+SS-ThM-3 Thermal and Plasma Heterogeneous Catalysis Compared: CO_2 and Hydrocarbon Dry Reforming**, *Q Huang, D Zhang,* Center of Interface Dynamics for Sustainability, Chengdu, PR China, China; *E Schuler, M Ronda Lloret, G Rothenberg, N Shiju,* van 't Hoff Institute for Molecular Sciences, Amsterdam, The Netherlands, Netherlands; ***Aart Kleyn***, Center of Interface Dynamics for Sustainability, PR China, China **INVITED**

Endothermic catalytic reactions require operation at elevated temperatures. The heating required is usually obtained by combustion of hydrocarbons and contributes to CO_2 emission. Instead electricity obtained in a sustainable should drive the reaction. In addition, it is desirable that the energy transfer involved is done in a bond specific manner. Plasma excitation and dissociation of molecules can serve this purpose. In plasma, all molecular degrees of freedom are not in equilibrium and dissociation of CO_2 can be realized much more efficiently than in thermodynamic equilibrium. There is a preferential vibrational excitation of CO_2.

In Chengdu we use a plasma chemical reactor with mass spectroscopy, infrared spectroscopy, optical emission spectroscopy and a Langmuir probe to study the characteristics of the plasma, reaction products and the catalyst. In Amsterdam we use a thermal reactor and gas chromatography to study reaction products. The reactions are carried out at pressures of several hundreds of Pa up to atmospheric in Ar buffergas. Catalysts are prepared in the usual way.

The simplest reaction studied in the plasma reactor is the dissociation of CO_2 into CO and O_2. We find energy efficiencies higher than 45%, indicating that the system is not in thermodynamic equilibrium and plasma favors vibrational excitation to translational heating. Adding a catalyst like AgO or NiO on Al_2O_3 does not enhance the yield. However, a purely metallic catalyst does significantly enhance the yield.

Optical emission spectroscopy shows that the radiofrequency (RF) and microwave (MW) plasma behave quite different. In the MW plasma predominantly emission from the C_2 Swann-band is seen, whereas the RF plasma shows mainly chemiluminescence from excited CO. This is due to a different electron excitation mechanism.

In the case of dry reforming of CH_4 with CO_2 in the plasma reactor we find that addition of an oxidic catalyst does not enhance the yield of CO + H_2. In the case of dry reforming of butane (C_4H_{10}) to yield butene (C_4H_8), plasma reforming with or without catalyst does shows only small conversion. Mainly cracking of butane into C_2H_x is seen and polymerization. However, running the same reaction under high temperature conditions in a thermal reactor yields a satisfactory conversion. A Co based catalyst has the best performance.

These studies allow us to obtain mechanistic information on the conversion of simple molecules, pretreated by plasma, on various catalysts. We are exploring to what extend direct Eley-Rideal reactions are relevant in the plasma reactor. This reaction mechanism is very unlikely under thermal conditions.

9:20am **HC+SA+SS-ThM-5 Imaging the Molecular Origins of Symmetry Breaking on Well-defined Surfaces**, ***Amanda Larson***, *R Hannagan, E Sykes,* Tufts University

Understanding the interaction of prochiral reactants with chiral modifiers on surfaces is a key step towards controlling heterogeneous enantioselective catalysis. We have chosen a simple model system composed of interacting chiral propylene oxide and propene molecules on a Cu(111) surface that is amenable to both scanning probe and desorption studies. Low temperature scanning tunneling microscopy (STM) enables an unprecedented level of spatial resolution of the enantioselective molecule-molecule interactions and their dynamics. STM imaging of propylene oxide and propene molecules at 5 K reveals that both molecules, when in isolation on the surface, behave as molecular rotors. Furthermore, the chirality of individual propylene oxide molecules can be discerned from the STM images of the rotating molecule. While propene is achiral in the gas phase it become chiral when bound to surfaces and STM also allows us to distinguish between its surface-bound enantiomers. When studied separately, repulsive forces between both sets of molecules disperse them on the surface at low coverages. However, when co-dosed we observe an attraction between propylene oxide and propene and they form complexes in which their rotation is inhibited. Temperature programmed desorption measurements are used to quantify these chiral modifier-molecule interaction strengths. Finally, the geometry of individual propene and propylene oxide molecules can be determined within the complexes and 1:1 chiral interactions deciphered.

11:00am **HC+SA+SS-ThM-10 A Surface Science Approach for New Heterogeneous Catalyst***, **Ib Chorkendorff**,* Technical University of Denmark, Denmark **INVITED**

First, we shall discuss how surface science and mass-selected nanoparticles can be used to make efficient model systems for heterogeneous catalysts. We shall demonstrate how mass-selected nanoparticles of CuZn alloys can be used to elucidate the dynamics of the methanol synthesis catalysts. The produced nanoparticles will be compared to the conventional CuZnAl at 1 bar for synthesizing methanol from CO_2 and H_2 [1, 2, 3]. The methanol synthesis on CuZn will also be discussed with respect to our recent findings of using alloys of NiGa for methanol synthesis [4]. The use of mass-selected nanoparticles will be further demonstrated for electrochemical Oxygen Reduction Reaction, which is really the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electro-catalysts by alloying Pt with early transition metals [5] or the lanthanides [6]. We have also shown that it is possible to make mass-selected nanoparticles of these alloys with very good activities [7] and PtGd alloys [8]. Finally, we shall also discuss how planar surface science can be used to identify new catalysts for ammonia oxidation. We shall demonstrate how Copper deposited on Ruthenium can enhance the activity substantially and give rational explanations for this enhancement which also can be transferred to high area catalysts used for diesel exhaust treatment [9].

References

1. S. Kuld,....... I. Chorkendorff and J. Sehested, Angew. Chemie 53 (2014) 1.

2. C. Holse,....., I. Chorkendorff,S. Helveg, J. H. Nielsen, J. Chem. Phys. 119 (2015) 2804-2812.

3. S. Kuld,..... I. Chorkendorff,J. Sehested, SCIENCE 352 (2016) 969-974.

4. F. Studt, ..., I. Chorkendorff, and J. K. Nørskov, Nature Chemistry. 6 (2014) 320.

5. J. Greeley, ... I. Chorkendorff, J. K. Nørskov, Nature Chemistry. 1 (2009) 522.

6. M. Escudero-Escribano, ..., I. Chorkendorff, SCIENCE 352 (2016) 73-76.

7. P. Hernandez-Fernandez, ... I. Chorkendorff, Nature Chemistry 6 (2014) 732-8.

8. A. Velázquez-Palenzuela,.....I. Chorkendorff, J. Catal. 328 (2015) 297-307.

9. D. Chakraborty, ..., I. Chorkendorff, Accepted Angew. Chemie. (2017).

11:40am **HC+SA+SS-ThM-12 Chemisorption and Oxidation of H_2 on IrO_2(110)***, **Tao Li**, Z Liang,* University of Florida, Gainesville*; M Kim, A Asthagiri,* The Ohio State University*; J Weaver,* University of Florida, Gainesville

Understanding the interactions of hydrogen with IrO_2 surfaces is central to improving applications of electrocatalysis as well as exploiting the high-reactivity of IrO_2 for promoting methane activation. In this talk, I will discuss our recent investigations of the dissociative chemisorption and oxidation of H_2 on stoichiometric and oxygen-rich IrO_2(110) surfaces. We find that H_2 dissociation is highly facile on s-IrO_2(110), with more than 90% of a saturated H_2 layer dissociating below 225 K during temperature-programmed reaction spectroscopy (TPRS). We observe only H_2O desorption in a broad TPRS peak from about 400 to 780 K after generating low H_2 coverages on s-IrO_2(110) at about 90 K. At high H_2 coverages, we also observe small H_2 desorption peaks at 200 and 530 K which we attribute to molecular and recombinative desorption processes, respectively. We present evidence that H_2 dissociation on IrO_2(110) occurs through a mechanism wherein H_2 σ-complexes adsorbed on the coordinatively-unsaturated (cus) Ir atoms serve as precursors for H_2 dissociation. We show that oxygen atoms adsorbed on the cus-Ir sites, so-called on-top O-atoms, hinder H_2 dissociation on IrO_2(110), while also facilitating H_2O desorption and promoting H-atom transfer from bridging O-atoms to on-top O-atoms. I will also discuss the results of density functional theory calculations of H_2 dissociation and initial steps of H_2O formation on stoichiometric and O-rich IrO_2(110).

Author Index

Bold page numbers indicate presenter

— A —
Asthagiri, A: HC+SA+SS-ThM-12, 2
— C —
Chang, S: HC+SA+SS-ThM-1, **1**
Chorkendorff, I: HC+SA+SS-ThM-10, **2**
— F —
Flaherty, D: HC+SA+SS-ThM-1, 1
— H —
Hannagan, R: HC+SA+SS-ThM-5, 1
Huang, Q: HC+SA+SS-ThM-3, 1
— K —
Kim, M: HC+SA+SS-ThM-12, 2
Kleyn, A: HC+SA+SS-ThM-3, **1**
Kruppe, C: HC+SA+SS-ThM-2, **1**
— L —
Larson, A: HC+SA+SS-ThM-5, **1**
Li, T: HC+SA+SS-ThM-12, **2**
Liang, Z: HC+SA+SS-ThM-12, 2
— R —
Ronda Lloret, M: HC+SA+SS-ThM-3, 1
Rothenberg, G: HC+SA+SS-ThM-3, 1
— S —
Schuler, E: HC+SA+SS-ThM-3, 1
Shiju, N: HC+SA+SS-ThM-3, 1
Sykes, E: HC+SA+SS-ThM-5, 1
— T —
Trenary, M: HC+SA+SS-ThM-2, 1
— W —
Weaver, J: HC+SA+SS-ThM-12, 2
— Z —
Zhang, D: HC+SA+SS-ThM-3, 1