

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-TuA

A Tale of Two Scales: Catalytic Processes and Surface Science

Moderator: Ashleigh Baber, James Madison University

2:20pm **HC+SS-TuA-1** **CO₂ Reduction on the Surface of Cu/TiO₂ NPs Supported on Graphite Studied using Ambient Pressure-XPS and Differential Electrochemical Mass Spectrometer**, *Djawhar Ferrah, A Haines, R Galhenage*, University of California at Irvine; *A Javier*, California Institute of Technology; *J Bruce*, University of California at Irvine; *M Soriaga*, California Institute of Technology; *J Hemminger*, University of California at Irvine

Metal supported on metal oxide (M1/MO) catalyst systems are widely used in industry for the hydrogen production and CO₂/CO conversion to useful fuels. If incontrovertible evidence were founded for the role of the interface in the improvement of catalytic CO₂ hydrogenation efficiency, it would still be an incomplete understanding on the nature of the active sites and associated reaction pathways, namely reactive species adsorption, dissociation and/or activation and intermediate formation stability. The modulation of the reaction selectivity, through the synthesis of catalysts that exhibit specific active sites, is required to design «smart» catalytic systems. Therefore, the investigation of catalytic reactions under real conditions, to illustrate the relation between properties at the atomic level of the surface and reactivity, is needed. In this context, a model catalyst based on Cu/TiO₂ nanoparticles (NPs) supported on graphite (HOPG), have been synthesized and fully characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). Using physical vapor deposition (PVD), a high density of 15 nm TiO₂ NPs are deposited on HOPG and are used to support Cu NPs. TEM studies reveal that most of the TiO₂ NPs have a rutile structure and display mainly (110) vicinal surface, which is favorable for CO₂ adsorption. A formation of thin layer of graphitic carbon at surface of TiO₂ NPs is also reported. Photodeposition of Cu on TiO₂ NPs by irradiating the band gap of TiO₂ in a CuCl₂ solution has been studied. In the present work, two different catalytic aspects for CO₂ reduction on CuO_x/TiO₂ NPs on HOPG systems will be reported: (1) thermocatalytic CO₂ hydrogenation and (2) electrochemical CO₂ hydrogenation. Efforts have been devoted to exploring different surface chemistry effects, as well as the oxidation states of Cu NPs (Cu₂O, Cu, and Cu₂O@Cu) with diameters ranging from 2 to 5 nm and TiO₂ surface encapsulation with thin layer of graphited carbon, on the CO₂ reduction mechanism in the temperature range of 300-550 K using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at the National Synchrotron Light Source II (NSLS-II). Similarly, the CO₂ reduction on CuO_x/TiO₂ NPs on HOPG electrodes in aqueous KHCO₃ has been investigated using a Differential Electrochemical Mass Spectrometer (DEMS) to evaluate the reaction products. Ongoing Infrared reflection-absorption spectroscopy (IRRAS), and AP-XPS experiments on electrochemical CO₂ reduction will be introduced.

2:40pm **HC+SS-TuA-2** **Influence of Bi and Sb on the Structure of Pd-based Catalysts**, *Joo Kang, W Lee, P Vlasak*, The Dow Chemical Company; *A Kirilin*, The Dow Chemical Company, Netherlands; *H Clements, C Menzies, S Yusuf*, The Dow Chemical Company

Oxidative transformation of aldehydes to corresponding esters is a reaction of significant importance. Catalytic oxidative esterification of aldehydes and alcohols in the presence of heterogeneous catalysts is an attractive method for production of esters. Reaction can be carried out in the presence of palladium or platinum often with co-components to improve performance.

The influence of 4d and 5d metal promoters on Pd based catalysts was investigated using a suite of structure probing techniques including x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and X-ray Absorption Spectroscopy (XAS). Results on supported Pd, Pd-Bi and Pd-Sb catalysts allow new insight into active Pd structure and role of the promoters on Pd structure. We present formation of bimetallic phase in both Bi and Sb promoted Pd catalysts and discuss implication on catalytic performance.

3:00pm **HC+SS-TuA-3** **The Molecular Surface Chemistry Approach to Heterogeneous Catalysts**, *Peter Stair*, Northwestern University **INVITED**

The traditional route to solid catalyst materials involves solution phase deposition or liquid-surface reactions. Examples include impregnation, deposition-precipitation, and solution phase grafting of molecular precursors. Atomic Layer Deposition (ALD) is a gas-solid deposition methodology having enormous potential for the synthesis of advanced heterogeneous catalysts with control of composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions. This lecture will provide examples from the laboratories at Northwestern University and Argonne National Laboratory of ALD used to synthesize oxide supports, catalytic oxide overlayers, single-site catalysts, metal nanoparticles, and new porous structures.

4:20pm **HC+SS-TuA-7** **Formation and Stability of Subsurface Oxygen on Ag(111)**, *Marie Turano*, Loyola University Chicago; *S Isbill, S Roy*, University of Tennessee Knoxville; *R Farber*, Loyola University Chicago; *E Iski*, University of Tulsa; *D Killelea*, Loyola University Chicago

A long-standing challenge in the study of heterogeneously catalyzed oxidation reactions on silver surfaces is the determination of what surface species are of greatest chemical importance. This is due to the coexistence of several different types of oxygen on oxidized silver surfaces. A further wrinkle is subsurface oxygen (O_{sub}). O_{sub} are O atoms dissolved into the near surface of a metal, and are expected to alter the surface chemistry and structure, however, these effects have yet to be well characterized. To better understand the interactions of oxidized silver surfaces, synergy between experimental and theoretical studies is necessary. We have studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms using a combination of surface science techniques to determine the resultant surface structure. We observed that once 0.1 ML of O_{sub} has formed, the surface dramatically, and uniformly, reconstructs to a striped structure at the expense of all other surface structures. Furthermore, O_{sub} formation is hindered at temperatures above 500 K. We also observed a coexistence of several surface oxides at intermediate deposition temperatures (475-525K), and the predominance of the p(4x5√3) surface reconstruction at elevated temperatures. Recent DFT-calculated desorption energies of O atoms from Ag(111) agree well with experimentally-derived desorption energies, and provide qualitative insight into the formation and stability of O_{sub} at different oxygen coverages.

4:40pm **HC+SS-TuA-8** **Mechanistic Insights into Catalytic Transfer Hydrogenation and Decarbonylation of Aromatic Aldehydes on P_x-Ru(0001)**, *Abinaya Sampath, D Flaherty*, University of Illinois at Urbana-Champaign

Aromatic aldehydes constitute a significant weight fraction of bio-oil. Transition metal catalysts can hydrogenate these aldehydes using either gaseous H₂ or organic donors to produce valuable chemicals that may replace conventional petroleum derivatives. Here, we study selective decarbonylation of aromatic aldehydes (furfural and benzaldehyde) over Ru(0001) and P_x-Ru(0001) to determine how phosphorus introduces new reaction pathways, such as catalytic transfer hydrogenation (CTH) steps between organic reactants. The catalytic properties of Ru(0001) and P_x-Ru(0001) were probed with temperature programmed reaction (TPR) of furfural, benzaldehyde, and isotopically labeled forms of furfural under ultra-high vacuum conditions with Ru(0001) single crystal. P_x-Ru(0001) is formed by exposing Ru(0001) to 2.5 L of PH₃ at 300 K followed by flash annealing to 1400 K. The treatment produces a surface with an atomic ratio of P: Ru of ~0.4, determined by Auger electron spectroscopy.

On P_{0.4}-Ru(0001), ~68% of furfural adsorbed at 100 K decarbonylates to furan and CO, whereas on Ru(0001), furfural decomposes completely to CO, H₂, and C-atoms. Similarly, benzaldehyde decarbonylates to benzene with a selectivity that is 12-fold greater over P_{0.4}-Ru(0001) than on Ru(0001). Together, these results suggest that, P-modification of Ru(0001) results in selective decarbonylation of aromatic aldehydes. Charge transfer from Ru to P results in reduced electron back donation from Ru to the adsorbates, and causes adsorbates to interact more weakly with P_{0.4}-Ru(0001) than with Ru(0001). These electronic modifications reduce the extent of dissociative reactions leading to selective decarbonylation of aromatic aldehydes, although ensemble effects may also contribute.

TPR of furfural on P_{0.4}-Ru(0001), pre-covered with D* atoms, yields five times more per-hydrogenated furan (C₄H₄O) than mono-deuterated furan (C₄H₃DO), which demonstrates that the CTH does not involve chemisorbed

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H*-atoms. On $P_{0.4}\text{-Ru}(0001)$, TPR of isotopically labeled furfural ($C_4H_3O\text{-CDO}$) forms two furan isotopologues (C_4H_4O , and C_4H_3DO). In addition, C_4H_3DO formed desorbs at a temperature 20 K higher than C_4H_4O , which indicates that intermolecular H-transfer determines the rate of furan formation. The comparisons of labeled furan products show that these critical H-atoms originate from the furfural ring and the carbonyl group of furfural. Hence, $P_{0.4}\text{-Ru}(0001)$ is more selective for decarbonylation of aromatic aldehydes over $\text{Ru}(0001)$, and the addition of phosphorus atoms facilitates CTH steps that do not occur on metallic $\text{Ru}(0001)$.

5:00pm **HC+SS-TuA-9 Hot Electron Flux under Methanol Oxidation on Pt/TiO₂ Catalytic Nanodiode; Intrinsic Relation between Selectivity and Chemicurrent**, *Si Woo Lee*, *S Lee*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *H Lee*, Institute for Basic Science (IBS), Republic of Korea; *W Park*, *Y Jung*, *J Park*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Nonadiabatic electronic excitation in exothermic chemical reactions leads to the flow of energetic electrons with an energy of 1-3 eV which is called "hot electrons". Direct detection of hot electron flow and observation of its role in catalytic reactions are important for understanding metal-oxide heterogeneous catalysis [1, 2]. Using Pt/n-type TiO₂ Schottky nanodiode, we show the production of hot electron flow generated by methanol oxidation (P_{methanol} 4 Torr and P_{oxygen} at 760 Torr) on Pt thin film, and detect as steady-state hot electron current (chemicurrent) which is generated by exothermic chemical reactions on Pt catalyst surface. Under methanol oxidation, methanol can be converted to CO₂ by full oxidation or methyl formate by partial oxidation of methanol. We show that the activation energy of chemicurrent is quite close to that of turnover frequency, indicating that the chemicurrent was originated from the catalytic reaction on Pt thin film. In addition, the dependence of the partial pressure on the chemicurrent was investigated by varying partial pressure of methanol (1-4 Torr). The result shows that the selectivity toward methyl formate formation is well correlated with the chemicurrent. For fundamental understanding of correlation between selectivity and chemicurrent, we carried out the DFT calculation on the thermodynamic energy for each step, and found that the energy gain for partial oxidation reaction was higher than that of the full oxidation reaction, which is responsible for the higher flux of hot electron under methyl formate formation. We discuss the role of metal-oxide interfaces in determining the catalytic selectivity and chemicurrent yield.

Reference

1. Park, J. Y.; Baker, L. R.; Somorjai, G. A., Role of Hot Electrons and Metal-Oxide Interfaces in Surface Chemistry and Catalytic Reactions. *Chem. Rev.* **2015**, *115* (8), 2781-2817.
2. Park, J. Y.; Kim, S. M.; Lee, H.; Nedrygailov, I. I., Hot-Electron-Mediated Surface Chemistry: Toward Electronic Control of Catalytic Activity. *Acc. Chem. Res.* **2015**, *48* (8), 2475-2483.

5:20pm **HC+SS-TuA-10 Online Kinetics Study of Oxidative Coupling of Methane over La₂O₃ for C₂ Activation: What is Behind the Distinguished Light-off Temperatures**, *Yong Yang*, *Z Liu*, *E Vovk*, *X Zhou*, *C Guan*, ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C₂ products (ethane and ethylene). The main difficulties from further investigation of this reaction are due to the nature of its high temperature and reaction exothermicity. In this work, a specially designed online characterization setup is applied for this reaction, which achieved both precise bed temperature control and real time product measurement. The setup combines a micro reactor and realtime mass spectroscopy. The reaction was performed under simulated industrial condition. For the first time, the Arrhenius plots of the major OCM products (CO₂, ethane and ethylene) were obtained, and their temperature dependence as well as the respective activation energy barriers were clearly differentiated, over a recently reported high performance nanorod La₂O₃ catalyst. Different from general expectation, CO₂, the fully oxidized carbon species, dominates all the products in the lower temperature region, and less oxidized C₂ species are only formed at much higher temperatures. Further analysis of the Arrhenius plots indicates that selectivity and apparent activation energy for both CO_x and C₂ products are strongly influenced by the oxygen concentration and temperature. Combined with density functional theory calculations and additional experimental measurements, significant insights are brought to this high temperature reaction of wide interest. Furtheranalysis specially focusing on this temperature region, applying XPS surface studies with *in-situ* high pressure cell and XRD bulk structure with *operando* reactor,

revealed that there are both intermediates and poisoning species formation. With these new experiment results with distinguished lights-off products temperature provide new insights for understanding OCM reaction.

5:40pm **HC+SS-TuA-11 Non-Innocent Solvents, Hydrogen Transfer, Oxygen Dissociation on Nanoparticles during the Direct Synthesis of H₂O₂**, *David W. Flaherty*, University of Illinois, Urbana-Champaign **INVITED**

Direct synthesis of H₂O₂ ($H_2 + O_2 \rightarrow H_2O_2$) could enable on-site, and even *in situ*, H₂O₂ production, which motivates searches for highly selective catalysts and process conditions. H₂O₂ formation rates and selectivities depend sensitively on the addition of other transition metals, adsorption of halides, and solvent identity. The reasons for these changes are not completely understood and are difficult to explain mechanistically.

Rate measurements, X-ray absorption spectroscopy, and computation were conducted for Pd and Pd-based bimetallic clusters to determine the mechanism of this reaction and to understand the reasons why alloying Pd often increases H₂O₂ selectivities. In aqueous alcohols, the change in H₂O₂ and H₂O formation rates with H₂ and O₂ pressures are not consistent with a Langmuirian mechanism, but instead suggest O₂* species react in steps mediated by the solvent. In addition, H₂O₂ formation rates in protic solvents are 10³ larger than those measured in aprotic liquids and large kinetic isotope effects ($k_H/k_D > 7$) strongly suggest that alcohols serve as reactants in the kinetically relevant steps for H₂O₂ formation. In parallel, O-O bonds within chemisorbed intermediates cleave to form H₂O with rates that are less sensitive to the solvent identity. Persistent organic surface residues introduce low barrier reaction pathways to reduce O₂* and increase those for O-O dissociation relative to reaction pathways in pure water. These results show that long-standing observations that H₂O₂ forms in greater yields within alcoholic solvent are not explained by simple differences in the solubility of H₂ in the liquid-phase.

Similar rate laws and solvent requirements indicate that these reactions proceed by the same pathways in the presence of strongly binding halide adsorbates and acids. These modifications change barriers for the formation of H₂O (significantly) with lesser effects on barriers for steps that lead to H₂O₂, and are consistent with electronic modifications of Pd active sites by intra-atomic orbital rehybridization or by charge transfer from Pd atoms, respectively. Overall, this work presents evidence for the mechanism for H₂O₂ formation and explains the roles of solvent identity and surface modification strategies on H₂O₂ selectivities.

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