

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

### Room On Demand - Session HC-Invited On Demand

#### Fundamental Discoveries in Heterogeneous Catalysis Invited On Demand Session

**HC-Invited On Demand-1 Low Temperature Selective Alkane Conversion on IrO<sub>2</sub>(110) Surfaces, Aravind Asthagiri**, The Ohio State University **INVITED**  
Selective alkane conversion to high value fuels or chemicals, such as methanol or ethylene, has drawn increasing interest due to abundance of natural gas. Recently, we reported a combined temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) study of below room temperature ( $T \sim 120$  K) activation of methane on the stoichiometric IrO<sub>2</sub>(110) surface under ultrahigh vacuum (UHV) conditions. Subsequent work also showed that ethane to ethylene selectivity could be increased on IrO<sub>2</sub>(110) by creating some proportion of hydrogenated bridging oxygen (O<sub>br</sub>-H) sites, which limit the oxidative capacity of the surface. This past work suggests that substitution of O<sub>br</sub> sites with inert species may be an avenue to control selectivity between full and partial oxidation. We have used DFT to explore the effects of Cl substitution of O<sub>br</sub>. Chlorine is isoelectronic to O<sub>br</sub>-H and selective Cl substitution of O<sub>br</sub> has been demonstrated on RuO<sub>2</sub>(110) by Over and co-workers. In this work, we apply DFT to explore selective conversion of ethane on Cl-doped IrO<sub>2</sub>(110). We find that the Cl-doped IrO<sub>2</sub>(110) is still facile in converting ethane to ethylene. In contrast, the ethylene selectivity step shows a strong effect due to Cl doping. Specifically, we find that H atom transfer from ethylene to the saturated O<sub>br</sub> sites is unfavorable and therefore Cl doping will promote ethylene desorption over further reaction. Current efforts to develop a microkinetic model to explore ethylene selectivity under both TPRS and reaction conditions will be discussed.

**HC-Invited On Demand-7 Alkali-promoted Copper-based Catalysts for CO<sub>2</sub> Activation, W. Liao**, Stony Brook University; **Ping Liu**, Brookhaven National Laboratory **INVITED**

Alkalis have been reported as a promotor in the heterogeneous catalysis, being able to enhance the activity and selectivity of catalysts. The effective utilization of alkalis in catalyst optimization requires the fundamental understanding of underlying mechanism. This presentation will take potassium (K)-modified Cu<sub>x</sub>O/Cu(111) ( $x \leq 2$ ) model surface as a case study to rationalize the nature of K during the carbon dioxide hydrogenation using combined density functional theory (DFT) calculation and the kinetic Monte-Carlo (KMC) simulation. The result demonstrates the significant tuning of selectivity from carbon monoxide to methanol on going from Cu(111) to K-modified Cu<sub>x</sub>O/Cu(111). The deposited K<sup>+</sup> stabilizes the Cu<sub>x</sub>O thin film under the reducing condition of carbon dioxide hydrogenation. More importantly, our study reveals that K<sup>+</sup> acts as an active center for selective tuning in the binding, an accelerator for charge transfer, and a mediator for the electron tunneling. As a result, the K-modified Cu<sub>x</sub>O/Cu(111) opens a methanediol [H<sub>2</sub>C(OH)<sub>2</sub>]-mediated Formate pathway to facilitate the selective conversion of carbon dioxide to methanol. Our study develops the intrinsic rules of design to tune the catalytic performance using alkali metals.

**HC-Invited On Demand-13 Influence of Water on C-O Hydrogenolysis Catalyzed by Ru/TiO<sub>2</sub>, D. Stuck, A. Mahdavi-Shakib**, University of Maine; **R. Austin**, Barnard College; **L. Grabow**, University of Houston; **B. Frederick, Thomas J. Schwartz**, University of Maine **INVITED**

Several groups have recently shown the importance of metal-TiO<sub>2</sub> interfacial sites for selective activation of oxygen in a variety of reactions, including hydrodeoxygenation of phenolics. Our team has previously shown that TiO<sub>2</sub>-supported catalysts containing small Ru nanoparticles are highly active for the conversion of phenol to benzene, which is consistent with the results from Crossley and coworkers, who have shown the reaction to occur at the Ru-TiO<sub>2</sub> interface. Both observations can be explained by a mechanism wherein surface hydroxyls present on the TiO<sub>2</sub> surface in the immediate vicinity of the Ru nanoparticles are protonated during heterolytic H<sub>2</sub> dissociation, leading to acidic Ti-OH<sub>2</sub><sup>+</sup> surface species. Phenol then adsorbs across the Ru-TiO<sub>2</sub> interface, and the acidic proton from Ti-OH<sub>2</sub><sup>+</sup> facilitates C-O scission, regenerating the Ti-OH moiety and leaving a phenyl ring to be hydrogenated on the Ru surface. This mechanism is predicted to be favorable in the presence of water, and reports from the literature indicate an enhancement in the amount of benzene produced

ranging from 30% to 200%, depending on the fugacity of water in the system. In this work, we seek to clarify the role of water in C-O hydrogenolysis catalyzed by Ru/TiO<sub>2</sub> materials.

We measured reaction orders for phenol hydrogenolysis over Ru nanoparticles supported on two different TiO<sub>2</sub> materials: pure anatase TiO<sub>2</sub> and pure rutile TiO<sub>2</sub>. The phase of water and phenol is verified based on thermodynamic calculations, which show that 85% of the material exists as a vapor. The 15% which exists as a liquid is hypothesized to be trapped in the pore structure of the catalyst, indicating that the reaction should occur in the liquid phase. The reaction is positive-order with respect to water for Ru/rutile and negative-order for Ru/anatase, which correlates with differential heats of irreversible water adsorption on TiO<sub>2</sub> powders that show stronger binding of water to anatase TiO<sub>2</sub> than to rutile TiO<sub>2</sub>. The kinetics are consistent with a rate expression in which water inhibits the reaction by strong binding to Ru-TiO<sub>2</sub> interface sites. Kinetic Monte Carlo results for a catalyst consisting of a Ru nanorod supported on a rutile TiO<sub>2</sub> surface suggest that water-related species are abundant at the Ru-TiO<sub>2</sub> interface at high water pressures, and that as the temperature is lowered these abundant species can lead to the inhibitory effect observed in our kinetics data. The observed reactivity trends are correlated with the surface hydroxyl features of the TiO<sub>2</sub> support, as we have recently observed using FTIR spectroscopy.

**HC-Invited On Demand-19 Reversible Surface Transformation Enables the Revivification of Mixed Metal Hydroxide Water Oxidation Catalysts, C. Kuai, Feng Lin**, Virginia Tech **INVITED**

The electrode-electrolyte interfacial reactivity and stability govern the efficiency and lifetime of electrochemical devices, especially under aggressive reaction conditions such as high temperature, high potential, and corrosive environments. Modulating the metal-oxygen bonding environment at the electrode surface offers an effective path towards enhancing the interfacial reactivity. However, the high interfacial reactivity can trigger undesired interfacial reactions that lead to local structural changes, phase segregation and dissolution, and ultimately the complete degradation of the pre-designed metal-oxygen bonding environment. The rational design of a highly active and stable electrocatalyst is largely hindered by this dilemma. Understanding how the electrocatalyst-electrolyte interface transforms under operating conditions can generate mechanistic insights into identifying the catalytically active motif and establishing methodologies to circumvent the dilemma by repairing the degraded structure. In this presentation, we report that *operando* synchrotron spectroscopic and microscopic analyses suggest that the interfacial degradation can be reversible between catalytic oxidation and reduction potentials. Such reversibility allows us to develop an intermittent reduction methodology to revivify the catalytic activity under operating conditions, enhancing catalyst durability.

**HC-Invited On Demand-25 Designed Metal Release from Complex Metal Oxides, Sara Mason**, University of Iowa **INVITED**

Nanoscale complex metal oxides have transformed how technology is used worldwide. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices. As the number of portable devices is projected to increase, so too will the inadvertent release of complex metal oxide nanomaterials into the environment. This is a pressing problem because the environmental and biological impact of complex metal oxide nanomaterials are most times unknown, since they are subject to transform rapidly with changes in pH and concentration. This brings us to a looming problem that needs to be solved on a global scale. There is a fundamental knowledge gap in developing sustainable nanotechnology because there is not yet a systematic method to predict how the properties of a complex metal oxide will change with changes in chemical environment. We have adapted and developed a method that combines DFT-computed total energies and experimentally adjustable reaction conditions to compute the cation release of complex metal oxides. We focus on the materials found in a Li-ion battery cathode, namely LiCoO<sub>2</sub> (LCO) and compositionally tuned variants with general chemical formula Li(NixMnyCoz)O<sub>2</sub> (NMC). We find that adjusting surface terminations, compositions and pH will change the dissolution properties of this family of materials, and ultimately lead to increased favorability of metal release. We go on to propose a new set of materials, with maintained function, based on non-toxic and abundant metals, thereby reducing the biological impact. We then predict the thermodynamics of metal release to give insight on tailorable properties that can be used to formulate sustainable design principles for future generations of functional complex metal oxide materials.

# On Demand available October 25-November 30, 2021

**HC-Invited On Demand-31 Hydrogenation of CO<sub>2</sub> to Methanol on Metal-Oxide and Metal-Carbide Interfaces, Jose Rodriguez, Brookhaven National Laboratory** **INVITED**

The high thermochemical stability of CO<sub>2</sub> makes very difficult the catalytic conversion of the molecule into alcohols or other hydrocarbon compounds which can be used as fuels or the starting point for the generation of fine chemicals. Pure metals and bimetallic systems used for the CO<sub>2</sub> → CH<sub>3</sub>OH conversion usually bind CO<sub>2</sub> too weakly and, thus, show low catalytic activity. Here, I will discuss a series of recent studies that illustrate the advantages of metal-oxide and metal-carbide interfaces when aiming at the conversion of CO<sub>2</sub> into methanol. CeO<sub>x</sub>/Cu(111), Cu/CeO<sub>x</sub>/TiO<sub>2</sub>(110) and Au/CeO<sub>x</sub>/TiO<sub>2</sub>(110) exhibit an activity for the CO<sub>2</sub> → CH<sub>3</sub>OH conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst. In the Cu-ceria and Au-ceria interfaces, the multifunctional combination of metal and oxide centers leads to complementary chemical properties that open active reaction pathways for methanol synthesis. Efficient catalysts are also generated after depositing Cu and Au on TiC(001). In these cases, strong-metal support interactions modify the electronic properties of the admetals and make them active for the binding of CO<sub>2</sub> and its subsequent transformation into CH<sub>3</sub>OH at the metal-carbide interfaces.

**HC-Invited On Demand-37 Chirality Detection of Surface Desorption Products using Photoelectron Circular Dichroism, J. Wega, Tim Schäfer, G. Westphal, University Göttingen, Germany** **INVITED**

Chirality detection of gas-phase molecules at low concentrations is challenging as the molecular number density is usually too low to perform conventional circular dichroism absorption experiments. In recent years, new spectroscopic methods have been developed to detect chirality in the gas phase. In particular, the angular distribution of photoelectrons after multiphoton laser ionization of chiral molecules using circularly polarized light is highly sensitive to the enantiomeric form of the ionized molecule (multiphoton photoelectron circular dichroism (MP-PECD)). In the talk, I will present the MP-PECD as an analytic tool for chirality detection of the bicyclic monoterpene fenchone desorbing from a Ag(111) crystal. We recorded velocity resolved kinetics of fenchone desorption on Ag(111) using pulsed molecular beams with ion imaging techniques. In addition, we measured temperature-programmed desorption spectra of the same system. Both experiments indicate weak physisorption of fenchone on Ag(111). We combined both experimental techniques with enantiomer-specific detection by recording MP-PECD of desorbing molecules using photoelectron imaging spectroscopy. We can clearly assign the enantiomeric form of the desorption product fenchone in sub-monolayer concentration. The experiment demonstrates the combination of MP-PECD with surface science experiments, paving the way for enantiomer-specific detection of surface reaction products on heterogeneous catalysts for asymmetric synthesis.

## Author Index

### Bold page numbers indicate presenter

— A —

Asthagiri, A.: HC-Invited On Demand-1, **1**

Austin, R.: HC-Invited On Demand-13, **1**

— F —

Frederick, B.: HC-Invited On Demand-13, **1**

— G —

Grabow, L.: HC-Invited On Demand-13, **1**

— K —

Kuai, C.: HC-Invited On Demand-19, **1**

— L —

Liao, W.: HC-Invited On Demand-7, **1**

Lin, F.: HC-Invited On Demand-19, **1**

Liu, P.: HC-Invited On Demand-7, **1**

— M —

Mahdavi-Shakib, A.: HC-Invited On Demand-13, **1**

Mason, S.: HC-Invited On Demand-25, **1**

— R —

Rodriguez, J.: HC-Invited On Demand-31, **2**

— S —

Schäfer, T.: HC-Invited On Demand-37, **2**

Schwartz, T.: HC-Invited On Demand-13, **1**

Stuck, D.: HC-Invited On Demand-13, **1**

— W —

Wega, J.: HC-Invited On Demand-37, **2**

Westphal, G.: HC-Invited On Demand-37, **2**