

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room Ballroom A - Session HC-ThP

### Heterogeneous Catalysis Poster Session

**HC-ThP-2 Facet-Dependent Strong Metal-Support Interaction of Pt Nanoparticles on Morphology Controlled Cu<sub>2</sub>O Under CO Oxidation,** *Seunghwa Hong, D. Kim*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *Y. Song*, Korea Advanced Institute of Science and Technology, Republic of Korea; *K. Kim*, Pohang Accelerator Laboratory (PAL), Republic of Korea; *J. Park*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

The strong metal-support interaction (SMSI), the interaction between metal nanoparticle and metal-oxide support, plays a central part in the catalytic behavior of catalysts, due to synergistic effects on reactivity at the metal-oxide interface. Thus, a fundamental understanding of SMSI in realistic conditions is important to the development of high-performance catalysts. However, direct investigation of SMSI is challenging, due to the structural complexity of the heterogeneous catalysts. Facet-controlled metal-oxide supports, such as Cu<sub>2</sub>O, are excellent candidates for studying the SMSI at the metal and metal-oxide interface, since they possess well-defined surface structure. Furthermore, utilizing operando techniques enables in-depth characterization of the interactions at metal and metal-oxide support interfaces with a molecular level in a realistic environment.

Herein, we investigated facet-dependent SMSI at Pt nanoparticles supported on cubic and octahedral Cu<sub>2</sub>O using surface-sensitive operando techniques. The catalytic measurement revealed facet-dependent CO oxidation activity for Pt/cubic Cu<sub>2</sub>O and Pt/octahedral Cu<sub>2</sub>O catalysts. Furthermore, the results of in-situ ambient pressure X-ray photoelectron spectroscopy and diffuse reflectance FT-IR spectroscopy indicate that the surface changes during the reaction depend on the facet of the support, leading to different catalytic performances. This investigation of the facet-dependent surface changes that significantly influence reactivity provides insight into designing high-performance catalysts via engineering the interface interaction.

**HC-ThP-3 Investigation of Strong metal-support Interaction at the Pt-CoO interface Formed on Pt-Co Bimetallic Nanoparticles,** *Yejin Song, D. Kim, S. Hong*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea; *K. Kim*, Pohang Accelerator Laboratory (PAL), Republic of Korea; *J. Park*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Bimetallic nanoparticles are important catalysts in heterogeneous catalysis; due to the bimetallic synergistic effect, they show higher catalytic performance than monometallic nanoparticles. Pt, a widely used catalyst, is known to alloy well with 3d transition metals (TM, e.g., Ni, Fe, Cu, and Co). In Pt-3d TM bimetallic systems, surface restructuring occurs in a variety of environments. Under oxidation conditions, Co atoms in Pt-Co nanoparticles emerged onto the surface, forming a CoO layer. Moreover, the interface between Pt and CoO enhanced catalytic activity for the Pt-Co bimetallic nanoparticle. This catalytic improvement could be explained by the strong metal-support interaction (SMSI) at the Pt-3d TM oxide interface, from the surface restructuring.

In this study, we investigated the role of the Pt-CoO interface in Pt-Co bimetallic nanoparticles during CO oxidation with surface analysis. Pt-Co nanoparticles of 4 nm were synthesized by the co-reduction method with polyvinylpyrrolidone (PVP) as a capping agent. Pt-Co bimetallic nanoparticles were supported on SiO<sub>2</sub> to be applied to the CO oxidation reaction. Pt-Co bimetallic catalysts exhibited higher catalytic activity than monometallic catalysts. To verify the SMSI effect at the interface of Pt-CoO in Pt-Co bimetallic nanoparticles, operando surface analysis, ambient pressure X-ray photoelectron spectroscopy and in-situ diffuse reflectance infrared Fourier-transform spectroscopy, were used. This study demonstrates that reaction-driven metal-oxide interface is a key factor in boosting catalytic activity.

**HC-ThP-4 Effusive Molecular Beam Study of CH<sub>4</sub> Dissociative Chemisorption on Rh(111): The Remarkable Activity of Step Sites and Extrapolation to Catalytic Rh Films at Temperatures where Tunneling Dominates,** *Xingyu Wang, I. Harrison*, University of Virginia

Effusive molecular beam experiments were used to measure CH<sub>4</sub> dissociative sticking coefficients,  $S(T_B, T_s, J)$  on a Rh(111) crystal, for which the impinging gas temperature,  $T_B$ , and surface temperature,  $T_s$ , could be independently varied, along with the angle of incidence,  $J$ , of the impinging gas. The 500 – 900 K temperature range explored is relevant to heterogeneous catalytic processes such as methane partial oxidation. A dynamically biased precursor mediated microcanonical trapping (PMMT) model of dissociative chemisorption was used to analyze the experimental results. Modelling indicates that the enhanced reactivity of step sites is not promptly poisoned on Rh(111) but rather contributes substantially to the reactivity even as high coverages of carbon accumulate at the surface. Threshold energies for dissociative chemisorption on the terraces and steps sites were optimally modeled as 74.3 kJ/mol and 36.7 kJ/mol. Translations parallel to the surface and rotations were treated as spectator degrees of freedoms. The efficacy of vibrational energy to promote reactivity relative to normal translational energy was  $h_n=0.55$  and one surface oscillator participated in energy exchange within the collisionally formed precursor complexes. A two-channel Arrhenius model restricted to only the thermal dissociative sticking coefficient measured along the direction of surface normal,  $S_n(T_B=T_s)$ , yielded apparent activation energies of 70.6 and 25.5 kJ/mol which could be attributed to terrace and step sites, respectively. PMMT modeling of the step site reactivity on Rh(111) could be extrapolated to replicate the thermal dissociative sticking coefficient of the “defect dominated” Rh film surfaces measured by Ehrlich at temperatures in the 250 -350 K range where much of the elevated kinetic isotope effect (9 to 15) could be attributed to quantum mechanical tunneling through the reactive barrier.

**HC-ThP-5 Adsorption and Decomposition of Zirconium Tetrahydroborate on Pd(111),** *Ravi Ranjan, M. Trenary*, University of Illinois - Chicago

Zirconium tetrahydroborate, Zr(BH<sub>4</sub>)<sub>4</sub>, is a volatile compound that has been widely used as a single-source precursor to grow carbon-free thin films of zirconium diboride by chemical vapor deposition (CVD). However, the basic surface chemistry of this compound that underlies the CVD process is largely unknown. We studied the adsorption and decomposition of Zr(BH<sub>4</sub>)<sub>4</sub> on a Pd(111) surface with reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). Palladium was chosen as the substrate as it is a good dehydrogenation catalyst. The compound was synthesized using literature methods. It was dosed onto the Pd(111) surface using standard gas-handling methods. After exposing Pd(111) at 90 K to Zr(BH<sub>4</sub>)<sub>4</sub>(g), a RAIR spectrum was obtained that closely matched that of the pure compound, indicating that it adsorbs without dissociation at 90 K. However, upon heating to 200 K the RAIR spectrum undergoes dramatic changes indicating that a new surface species is formed that retains B–H bonds, as indicated by a B–H stretch peak at 2540 cm<sup>-1</sup>. This surface species is tentatively identified as either BH<sub>4</sub> or BH<sub>3</sub> and is stable up to 300 K. Both H<sub>2</sub> and B<sub>2</sub>H<sub>6</sub> desorb from the surface at around 175 K as observed with TPD. The decomposition of the BH<sub>x</sub> intermediate is revealed by additional H<sub>2</sub> desorption peaks at 325 K and 425 K. Results obtained with XPS suggest that adsorbing Zr(BH<sub>4</sub>)<sub>4</sub> at low temperature and then annealing does not produce ZrB<sub>2</sub>, but instead leaves only Zr on the surface.

**HC-ThP-6 Preliminary Studies of RhCu Single-Atom Alloys Using Molecular Beams,** *Laurin Joseph, M. Powers, A. Utz*, Tufts University

A new class of heterogeneous catalysts called single-atom alloys (SAAs) combine single, isolated atoms of expensive catalytically active metals alloyed into less expensive base metals. These materials have been shown to have greater selectivity and activity relative to conventional catalysts. To date, detailed surface science studies of these materials have been limited to relatively low-barrier reactions. This work will extend the range of detailed mechanistic studies of these promising new materials to higher barrier reactions, including C-H activation. More specifically, our study focuses on the reaction of methane over a RhCu SAA catalyst. This system has been studied using reflection absorption infrared spectroscopy, temperature programmed desorption, and scanning tunneling microscopy previously.<sup>1,2</sup> Our lab will use supersonic molecular beam experiments to learn more about the energetic barriers and kinetics of this reaction. Presented here will be preliminary findings of these experiments as well as an explanation of the modifications made to our apparatus to make the RhCu surface.

1. Hannagan, R. T. et al. *ChemCatChem***12**, 488–493 (2020).
2. Hannagan, R. T. et al. *Science***372**, 1444–1447 (2021).

## HC-ThP-8 Characterization of a Pt/Cu(111) Single Atom Alloy using CO-RAIRS and CO-TPD, *David Molina, M. Trenary*, University of Illinois - Chicago

A combination of reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD) and Auger electron spectroscopy (AES) were used to characterize a Pt/Cu(111) single metal alloy (SAA). Carbon monoxide was used as a probing molecule to detect Pt sites in diluted alloys, down to 0.1% Pt/Cu(111) concentrations. CO-TPD spectra for known high concentrations of Pt, quantified by the ratio of the 237 MNN Pt and 920 LMM Cu Auger signals, were used for calibration for samples with Pt concentrations below the AES limit of detection. Initial RAIR spectra of CO saturated diluted alloys at 90 K have shown a signal at 2046  $\text{cm}^{-1}$  which is overlapped with the 2078  $\text{cm}^{-1}$  CO stretch on Cu(111) on top sites. Annealing at 180 K, above the desorption temperature of CO from Cu(111), and recoiling to 90 K clearly show the 2046  $\text{cm}^{-1}$  peak. Corresponding TPD spectra have shown desorption of CO at 345 K from the Pt/Cu(111) dilute alloys, in agreement with a previous study of CO desorption from single atom Pt sites on Cu(111). Room temperature RAIR spectra of CO on Pt/Cu(111) alloys with less than 1% Pt concentration have also shown only one vibration at 2046  $\text{cm}^{-1}$ , assigned to CO on top of single Pt atoms. Annealing to 500 K starts diffusion of Pt to the bulk, as previously observed in Pt/Cu alloy studies.

## HC-ThP-9 Surface Chemistry of Acrolein and its Hydrogenation Products on Cu(111) and Single Atom Alloy Pd-Cu(111), *Arephin Islam, D. Molina, M. Trenary*, University of Illinois - Chicago

Adsorption properties and surface chemistry of acrolein and its hydrogenation products propanal, 1-propanol, and 2-propenol on Cu(111) and Pd-Cu(111) single atom alloy surfaces were studied by polarization-dependent reflection absorption infrared spectroscopy (PD-RAIRS) and temperature-programmed desorption (TPD). The experimental RAIR spectra were obtained by adsorbing multilayers of each molecule at 85 K and then annealing the surface up to 200 K to desorb the multilayer and produce the most stable monolayer structure on both surfaces. Each molecule adsorbs weakly to the surface and desorbs without reaction at temperatures below 200 K. Several TPD spectra were collected following adsorption at 85 K using similar coverages as those in the RAIRS experiments. Compared to acrolein and propanal, the two alcohols, 2-propenol and 1-propanol, have notably higher desorption temperatures and display strong hydrogen bonding in the multilayers as revealed by a broadened and redshifted O-H stretch. For acrolein, the out-of-plane bending modes are more intense than the C=O stretch at submonolayer coverage, indicating that the molecular plane is mainly parallel to the surface. In contrast, the opposite intensity trend was observed for multilayer acrolein, suggesting that the C=O bonds are tilted away from the surface. For 1-propanol, annealing the surface to 180 K disrupts the hydrogen bonding to produce unusually narrow peaks. This indicates that 1-propanol forms a highly ordered monolayer and adsorbs as a single conformer at low coverage. For 2-propenol, hydrogen bonding in the multilayer correlates with the observation of the C=C stretch at 1647  $\text{cm}^{-1}$ , which is invisible for the monolayer. This suggests that the C=C bond is parallel to the surface for monolayer coverages of 2-propenol. Similarly, for propanal, the C=O stretch peak at 1735  $\text{cm}^{-1}$  compared to those at 1671 and 1695  $\text{cm}^{-1}$  is very weak for the low coverage. Still, it becomes the most prominent peak for the multilayer, indicating a change in molecular orientation. These results provided further insights into previous studies [1,2] on hydrogenation pathways of acrolein on the Ag(111) and Pd-Ag(111) SAA surface and into the challenges of selectively increasing the yield of the unsaturated alcohol.

References:

- [1] Muir, M., et al., *J Phys. Chem. C* (2020) 124 (44), 24271
- [2] Muir, M., et al., *Phys. Chem. Chem. Phys.* (2020) 22 (43), 25011

## HC-ThP-10 Characterizing the Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst and Nonthermal Plasma Couple via Native OES Diagnostics, *Ryan Chapman, J. Blechle*, Wilkes University

The persistently growing global demand for energy, transportation, and production will inevitably further environmental deterioration by means of hazardous emissions. Minimizing environmental damage thus requires the development of technologies that can mitigate the pollution associated with such anthropogenic sources. The selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) is one of the major breakthrough technologies in the abatement of pollutants from vehicular and industrial emissions, and Ag/Al<sub>2</sub>O<sub>3</sub> has been widely studied as an ideal catalyst for SCR systems due to its selectivity and tolerance to poisoning by SO<sub>2</sub> and water vapor. However, SCR using Ag/Al<sub>2</sub>O<sub>3</sub> exhibits poor efficacy at temperatures below ~250 °C due to diminished activity of the reductant species. A promising means of overcoming these deficiencies is in the synergy between nonthermal plasma (NTP) and Ag/Al<sub>2</sub>O<sub>3</sub> catalysts. Despite the potential of plasma-assisted SCR for pollution abatement as shown in the literature, the chemistry underlying the NTP/catalyst couple must be resolved to optimize the process for commercial use.

In order to further explore these synergies, optical emission spectroscopy (OES) is used to characterize a NTP (N<sub>2</sub>/O<sub>2</sub>/Ar) and Ag/Al<sub>2</sub>O<sub>3</sub> couple on the basis of energy partitioning, densities, and formation/decay kinetics of relevant excited states in the plasma bulk. An inverse proportionality between NO<sup>+</sup> density and vibrational temperature (T<sub>v</sub>) is observed for NTP coupled with Al<sub>2</sub>O<sub>3</sub> surfaces (0-10 wt% loadings in Ag). At high input powers (175-200 W), NO<sup>+</sup> T<sub>v</sub>'s increase only marginally in the presence of 2, 5, and 10 wt% loadings, whereas a marked increase is observed in the presence of 0 wt% Ag/Al<sub>2</sub>O<sub>3</sub>. Even so, NO<sup>+</sup> densities are comparably diminished (relative to the density observed at 25 W) for all systems studied. The catalytic role of Ag species in abating NO<sup>+</sup> is further explored by the decay kinetics of NO<sup>+</sup>. While the initial NO<sup>+</sup> emission intensity decays with time for all NTP's coupled with substrate, the decay rate constants were greatest for bulk NTP coupled with 5 and 10 wt% Ag/Al<sub>2</sub>O<sub>3</sub>. Differing formation and decay behaviors of the excited states are observed with successive plasma treatments, depending on the degree of silver loading. Further investigations, such as plasma pre-treatment of the catalytic surfaces and varying surface analyses provide additional insights into the interconnected plasma-surface system. The combination of these data provide a unique insight into the mechanistic behavior and the role of the system conditions on plasma-enhanced SCR.

## HC-ThP-11 Analysis of Microsilicon and Nanosilicon for Lithium-Ion Battery Anodes, *Aaron Hsi, A. Sheth, C. Chu, A. Suen, S. Annamalai, S. Adibnia, M. Uddin, N. Sangeneni*, Aspiring Scholars Directed Research Program

The abundance and low cost of silicon presents the ideal candidate of silicon anodes as an energy-dense, sustainable alternative to graphite anodes in lithium-ion batteries with a reported theoretical capacity of 4200 mAh/g. However, challenges such as significant volume expansion, rapid pulverization, relatively poor conductivity, and unstable sei layers formed with the use of silicon anodes hinders the practical applications. Microsilicon and nanosilicon demonstrate promise tackling these challenges while utilizing the unique characteristic of silicon due to a larger surface area allowing for greater charge intercalation with the anode material and electrolyte without causing significant volume expansion. We have characterized micro- and nano-silicon with particle size ranges of 50  $\mu\text{m}$ , 20-30 nm, and 150-200 nm through Fourier-Transform Infrared Spectroscopy (FTIR) to evaluate the presence of impurities in our samples and X-Ray Diffraction Spectroscopy (XRD) to determine the crystal structure of our samples. For electrochemical characterization, we utilized cyclic voltammetry (CV) to computationally identify the theoretical capacitance of different micro and nano-silicon-based inks (combinations of carbon black and silicon) deposited on nickel foam electrode material. Likewise we utilized Galvanostatic Charge Discharge (GCD) to identify performance characteristics of the material in battery type conditions identifying energy density, power density, and Coulombic efficiency. Our FTIR analysis indicated nano-silicon of particle sizes ranging from 20-30 nm was more prone to oxygen-related impurity formation due to a strong peak at 1071  $\text{cm}^{-1}$  that corresponds to the asymmetric vibration of Si-O bonds. Through our computational analysis, we found theoretical specific capacitance values of 23.59 F g<sup>-1</sup> of nanosilicon O1 (150-200 nm), 22.04 F g<sup>-1</sup> of nanosilicon O2 (20-30 nm), and 23.3 F g<sup>-1</sup> of Microsilicon. Through testing optimal parameters of various silicon particle sizes we seek to identify the most efficient size of nano-silicon and evaluate its efficiency in an actual model lithium-ion battery utilizing COMSOL software models.

# Thursday Evening, November 10, 2022

**HC-ThP-12 Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages,** *Dan Killelea, E. Jamka, M. Gillum, M. Turano,* Loyola University Chicago; *L. Juurlink,* Leiden University, Netherlands

The interaction of oxygen with the surfaces of catalytically active transition metals has attracted much interest because of the relevance to heterogeneous catalysis. Recently, we have shown that oxygen coverages in excess of 1 ML are achievable using gas-phase atomic oxygen (AO) to dose the metal surfaces. This talk will discuss some recent results comparing the uptake of AO and O<sub>2</sub> on Ag(111) to Rh(111). On Rh(111), subsurface oxygen readily forms from exposure to AO and the surface phases are dependent on the exposure temperature. We also discovered that subsurface O emerges at defects and alongside surface phase transitions. Finally, the uptake of oxygen on Ag(111) is discussed; unlike Rh(111), where little surface reconstruction occurs, Ag(111) undergoes several phase transformations as the oxygen coverage is increased. These results using AO demonstrate that UHV compatible dosing can prepare the same surfaces resulting high pressure O<sub>2</sub> exposures, allowing for quantitative and structural analysis of the oxidized surfaces.

**HC-ThP-13 Density Functional Theory Computed Descriptors for Heterogeneous Catalysis of CO<sub>2</sub> Sorbent Amines,** *Joshua Gabriel,* Argonne National Laboratory, USA

Integrating carbon capture and conversion is a promising direction towards a decarbonized future for industries that are heavily dependent on carbon-based raw materials. Progress has been made in achieving the electrocatalytic reduction of carbon dioxide to carbon monoxide from CO<sub>2</sub> captured in a monoethanolamine solution on silver catalysts. In this work, we use density functional theory calculations to test a hypothesis that the coverage of alkali cation controls the relative binding strength of proposed species of reactants, byproducts, and products, and hence the reaction product selectivity. Our results support the hypothesis that the alkali cation affects the relative binding strength of species for CO<sub>2</sub> reduction and hydrogen evolution, with increased coverage favoring CO<sub>2</sub> reduction. This discovery provides a useful computational descriptor to better understand the process conditions that can control product selectivity in heterogeneous catalysis.

**HC-ThP-14 Reactivity of Primary and Secondary Butanol Isomers on TiO<sub>2</sub>/Au(111),** *Haley Frankovich, L. Garber, A. Galgano, C. Grant, E. Schell, J. Yoo, C. Rogers, J. Carmany, A. Baber,* James Madison University

Biofuels can be used to reduce global dependence on fossil fuels while contributing to a carbon neutral cycle. Biobutanol has low volatility and multiple transportation options which make it an attractive alternative fuel. Understanding the fundamental thermal catalysis processes of butanol over heterogeneous model catalysts can aid in the design of more efficient catalysts. Butanol isomers give rise to products including isobutyraldehyde, 2-butanone, butyraldehyde, isobutene, and butene, all of which have applications ranging from gasoline additives to bioplastics. For the partial oxidation of butanol isomers, TiO<sub>2</sub>/Au(111) inverse model catalysts are promising due to their ability to catalyze redox reactions of C<sub>1</sub> – C<sub>3</sub> alcohols. Titania coverage effects were not reported for methanol or 2-propanol, but lower TiO<sub>2</sub> coverages in the presence of excess oxygen enhance selectivity of the partial oxidation of ethanol. To better understand how butanol breaks down in heterogeneous catalytic processes, temperature programmed desorption (TPD) is used to investigate its reaction. In this study, the reactivity of butanol isomers, specifically 1-butanol, 2-butanol, and isobutanol, on TiO<sub>2</sub>/Au(111) was investigated. TPD was used to detect products and atomic force microscopy (AFM) highlighted the morphology of the surface. At low coverages of TiO<sub>2</sub>, only 2-butanol showed expected oxidation reactivity, while, 1-BuOH exhibited low reactivity and formed reduced products, and isobutanol produced the recombinative product. At higher coverages of TiO<sub>2</sub>/Au(111), 2-butanol formed both oxidized and reduced products, 1-butanol only formed reduced products, isobutanol produced oxidation, reduced, and recombinative products. The selectivity of the reaction was not altered during successive desorption experiments, indicating that the model catalyst was stable without reoxidation between experiments. AFM images show that the Au(111) crystal has ~0.13 ML and 0.27 ML of TiO<sub>2</sub> with predominantly 1D wire-like nanoparticles. Higher coverages of TiO<sub>2</sub> result in more particles distributed across the surface indicating that the reactivity was influenced by butanol proximity to TiO<sub>2</sub> nanoparticle rather than differences in size or shape.

**HC-ThP-16 Synthesis and Characterization of Mixed-Ligand Monolayers on Silver Nanoparticles,** *X. Wang, William Hemmingson, D. Green,* University of Virginia, USA

Functionalized silver nanoparticles (AgNPs) are high-value materials that have a wide variety of uses including drug delivery and catalysis. To achieve these functions, a self-assembled monolayer (SAM) of ligands is synthesized on the surface of the particle. For a mixture of ligands, it is essential to study how the ligands arrange on the surface since that can affect the properties of the system. In this study, thiolated ligands with varying chain lengths and headgroups consisting of a carboxylic acid or methyl group were synthesized and subsequently characterized using matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-MS). Based on the known fragmentation pattern of AgNPs, the nearest neighbor distribution of the ligands can be determined. However, it was discovered that the fragmentation of AgNPs with carboxylic acid ligands is inconsistent at pH 7. Thus, a sodium salt solution should be added to the sample to promote cationization, which facilitates detection in MALDI-MS. Further, basic (pH=9) or acidic (pH=1) solutions have a higher yield of charged fragments than a pH-neutral sample. However, there is evidence that, under either of these conditions, the fragmentation pattern changes, and that change must be accounted for during analysis. Ultimately, this ongoing study will aid in understanding the functioning mechanisms of high-value AgNPs.

**HC-ThP-17 Morphological Studies of TiO<sub>2</sub> Nanoparticles on Au(111),** *Erin Schell, J. Yoo, A. Baber,* James Madison University

TiO<sub>2</sub> nanoparticles (NPs) supported on Au(111) form an inverse model catalyst that is active for alcohol oxidation and reduction. To fully understand the influence that the nanoparticle size and structure have on alcohol reactivity, TiO<sub>2</sub>/Au(111) catalysts were synthesized and characterized. TiO<sub>2</sub>NPs were deposited on Au(111) in an O<sub>2</sub> background under ultrahigh vacuum (UHV) conditions. The reactivity of the TiO<sub>2</sub>/Au(111) was tested using butanol temperature programmed reaction spectroscopy (TPRS). Two TiO<sub>2</sub> deposition times were studied, resulting in TiO<sub>2</sub> coverages of 0.13 ML and 0.27 ML, as determined by atomic force microscopy (AFM). In addition to quantifying TiO<sub>2</sub> coverages, the morphology and distribution of TiO<sub>2</sub> NPs were observed with AFM. To obtain the clearest images possible, the TiO<sub>2</sub>/Au(111) samples were briefly annealed with a H<sub>2</sub> flame to clean contaminants from the surface. While a brief H<sub>2</sub> flame anneal does not affect the TiO<sub>2</sub> morphology, longer flame anneals cause large changes in the morphology consistent with the formation of a mixed metal oxide. With longer TiO<sub>2</sub> deposition time, the TiO<sub>2</sub> coverage increased, but particle size remained the same. Interestingly, the higher coverage of TiO<sub>2</sub> resulted in more consistent reactivity with butanol isomers, whereas the smaller coverage of TiO<sub>2</sub> NPs showed low reactivity. AFM images suggest that the difference in reactivity is likely due to the lower number of particles rather than to differences in the size and shape of TiO<sub>2</sub>NPs. These results help to inform the design of more active catalysts for alcohol partial oxidation.

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