

# Fundamentals of Catalysis and Chemical Transformations

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## Objectives

Our objective is to achieve a detailed understanding of how oxygenates adsorb, transform and react with one another and other functionalities on highly uniform model catalysts. The hypothesis is that this approach may lead to general methods for design of improved catalysts. A related objective is to elucidate the role of site geometry, oxygen availability, confinement, and metal support interactions in controlling selectivity in reactions catalyzed on oxides surfaces and supported metal particles.

## Technical Barriers

The conversion of biomass is limited by a need for new, stable and more selective catalysts. Success in our project may lead to a general understanding of catalytic oxygenate transformations that may lead to improved catalysts.

## Abstract

The overarching goal of this proposal is to learn how oxygenated molecules, relevant to the conversion of biomass, interact and react in fluid phases and at the surfaces of heterogeneous catalysts. We tailor new catalysts by original synthetic methods, probe their structures by a wide array of techniques before, during and after their use in catalytic reactors, examine their surface species during reaction using *operando* and flow pyrolysis techniques, determine their actual catalytic performance and computationally model the molecular and interfacial interactions that explain their behavior. We focus on oxide catalysis, especially  $\text{CeO}_2$ ; catalysis by Au, especially with respect to structure and

stabilization of supported Au and Au based catalysts; and reaction pathways of model lignin molecules tethered to  $\text{SiO}_2$  surfaces. Our work combines computational methods to aid interpretation of experimental measurements and to create detailed models of reaction pathways.

## Progress Report

### Surface chemistry on monolithic $\text{CeO}_2$

Highly oriented films of  $\text{CeO}_2(111)$  and  $\text{CeO}_2(100)$  have been used as model surfaces to typify the surface chemistry of oxygenates on reducible oxides. Recently we have focused on the comparison of these two surface structures to explore the role of site geometry upon the surface chemical transformations. We have explored adsorption and evolution of methanol and water and find that the increased ease of vacancy formation on the (100) surface compared to the (111) surface plays a role in altering the selectivity for decomposition compared to desorption. Another focus area is the effect of structure on the transformations of the oxygenates, especially small alcohols and aldehydes.

We have examined the surface intermediates that form as a function of temperature, coverage and oxidation state of the surface on these two surfaces. Temperature-dependent adsorption and reaction of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) on a fully oxidized and a highly reduced thin-film  $\text{CeO}_2(111)$  surfaces have been investigated using a combination of reflection-absorption IR spectroscopy (RAIRS) and periodic density functional theory (DFT+U) calculations. On the fully oxidized surface, acetaldehyde adsorbs weakly through its carbonyl O interacting with a lattice  $\text{Ce}^{4+}$  cation in the  $\eta^1\text{-O}$  configuration. This state desorbs at 210 K without reaction. On the highly reduced surface, new vibrational signatures appear below 220 K due to a dimer state formed from the coupling of the carbonyl O and the acyl C of two acetaldehyde molecules. This dimer decomposed above 400 K to produce enolate ( $\text{CH}_2\text{CHO}^-$ ). Calculated activation barriers for the coupling of acetaldehyde, the decomposition of the dimer state, and the recombinative desorption of enolate and H as acetaldehyde, agree with TPD for acetaldehyde adsorbed on reduced  $\text{CeO}_2(111)$ . The results demonstrate that surface oxygen vacancies play a crucial role in stabilizing and activating acetaldehyde for coupling reactions.

Acetaldehyde adsorption on  $\text{CeO}_2(100)$  is stronger than on the (111) surface and desorption extends through a larger T range from 200 K to above 400 K. In addition to the parent molecule, above 400 K additional products are observed. Total decomposition to CO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are the principal pathways with a small amount of dehydration to

produce acetylene at 700 K. In addition, a notable product is the small amount of crotonaldehyde that is evident at 430 K, a result of the aldol condensation coupling reaction between two acetaldehyde molecules. The adsorption and reaction on  $\text{CeO}_2(100)$  is consistent with trends previously observed for the other oxygenates. Specifically, stronger adsorption results from a greater number of coordination vacancies around the Ce cation on  $\text{CeO}_2(100)$  compared to  $\text{CeO}_2(111)$ . The CO and  $\text{CO}_2$  products result from dehydrogenation of the adsorbed acetaldehyde by the basic O anions. The water desorption results from the relative ease with which the H reacts with the surface O.

### Studies on shaped nanocrystals

Oriented single crystals have limited surface area and the UHV environment is challenging for probing catalytic pathways. To bridge this gap we have initiated studies of reactions chemisorption and reactions studies on shaped nanoparticles that have well defined surface structures including cubes that terminate on {100} surfaces, octahedra that terminate on {111} and rods that terminate on a mixture of defective but low index terminations. Using these nanoshapes we have probed structure dependence in chemisorption and reaction rates.

Adsorption and desorption of a probe molecule, methanol, were followed by *in situ* IR and Raman spectroscopy to probe surface species and mass spectrometry to probe temperature dependent evolution of desorption products. Upon methanol adsorption, on-top, bridging and three-coordinate methoxy species are formed on rods and cubes while only on-top methoxy is present on the octahedra. The distribution of the methoxy species is believed to be determined by the coordination status of surface Ce cations and the amount of defect sites on the three nanoshapes. During the TPD the methoxy species are gradually dehydrogenated into  $\text{H}_2$  and CO *via* formate intermediates. Formyl is also evident on the rods. Methoxy is more reactive on the rods, resulting in desorption of  $\text{H}_2$  and CO at lower temperature ( $< 583$  K) than on cubes and octahedra. Higher than stoichiometric H/CO ratio is observed in the methanol-TPD products, attributed to retention of some amount of formate and carbonate on the ceria nanoshapes as revealed by *in situ* IR. A small amount of methanol and formaldehyde desorbs below 423 K from the three surfaces due to the disproportionation of methoxy. UV Raman and IR results indicate that the ceria nanoshapes are slightly reduced at room temperature by methanol adsorption, and become more reduced during methanol desorption. The degree of reduction is dependent on the surface structure of the nanoshapes.

Shaped  $\text{CeO}_2$  nanoparticles have also been used to explore the effect of surface structure upon the surface chemistry and catalytic selectivity for the ethanol selective oxidation reaction.  $\text{CeO}_2$  octahedra, cubes and rods were synthesized using previously published methods. Adsorption

and desorption behavior on these nanoshapes was determined by a combination of temperature programmed desorption (TPD) and *in situ* DRIFTS. Activity and selectivity were measured in steady state and in temperature programmed surface reaction (TPSR). Shape dependent differences are observed in surface adsorbates, their transformation temperatures and the selectivity for dehydration, dehydrogenation and decomposition. Ethoxide and acetate are the primary surface species present under both TPD and TPSR conditions for all shapes. Different rates of  $\alpha$ - and  $\beta$ -CH bond scission on the different shapes are responsible for different product selectivity. Structure dependent, reductive vacancy formation and availability of reactant  $\text{O}_2$  combine to control surface H which in turn plays a role in controlling product selectivity

### Au catalysts, clusters and bimetallic catalysts

We have explored various salts as supports, including phosphates and sulfates, that may stabilize Au catalysts for gas phase reactions such as CO oxidation. Au catalysts containing  $\text{BaSO}_4$  nanocrystals (5–8 nm) were prepared by *in situ* growth method using amphiphilic sulfonate (SDBS) as the sulfate source, leading to new, highly stable, nonreducible but “active” Au catalyst supports that may be preferable to the typical reducible oxides for low-temperature CO oxidation. The results suggest a unique interaction between Au nanoparticles and nanosized  $\text{BaSO}_4$  supports. We have also explored another strategy for stabilizing ultra-small gold clusters under thermal treatment. By this strategy, thiolated gold clusters ( $\text{Au}_{25}$ ,  $\text{Au}_{144}$ ), after removal of the protecting thiolate ligands by thermal treatment, can be stabilized onto heterostructured mesoporous supports. The essence of this strategy lies in use of the heterostructured binary oxide supports ( $\text{M}_x\text{O}_y\text{-mSiO}_2$ ) synthesized through a combination of a transition-metal oxide and an ordered mesoporous silica. Monodispersed Au clusters can be readily absorbed into the pores of this heterostructured oxide. The size of the clusters is maintained after removing the thiolate ligands by thermal treatment in air, making this method superior to *in vacuo* treatment. Small gold clusters supported on these heterostructured mesoporous supports were found to be active for CO oxidation.

We have developed a synthetic methodology to create supported, nanoscale AuCuPd ternary alloy nanoparticles through the diffusion of  $\text{Cu}^0$  and  $\text{Pd}^0$  atoms in an organic solvent using hexadecylamine as a reductant and ligand stabilizer. Subjecting the AuCuPd catalyst to reductive or oxidative pretreatment conditions greatly affected the catalytic activity for the oxidation of CO. *In situ* XRD and EXAFS indicated that oxidizing the catalyst to 300 °C produced a AuPd alloy core that was separated from CuO and a small amount of PdO. Oxidation at 500 °C resulted in the segregation of PdO and CuO to form a decorated Au rich particle. Forming a PdO and CuO rich surface on the AuPd

or Au-rich core decreased  $O_{ads}$  spill over from Cu to Au or Pd sites and hindered access to the Au active sites resulting in decreased catalytic activity. Reducing the catalyst under  $H_2$  formed a AuCuPd alloy with a Cu rich surface and formed the most active catalyst. It is likely that Cu, a base metal, helped to lower the activation energy through the activation  $O_2$  that could migrate to Au or Pd sites. However, AuCu/SiO<sub>2</sub> demonstrated an opposite structure-activity relationship. Reduced AuCu alloy was the least active catalyst and improved after it was oxidized to form a Au-CuO hybrid particle.

Au<sub>15</sub>(SR)<sub>13</sub> is the smallest, stable thiolated gold nanocluster experimentally identified so far and its elusive structure may hold the key to the origin of the nucleus in the formation of thiolated gold nanoclusters. By an extensive exploration of possible isomers by DFT, we arrive at a novel structure for Au<sub>15</sub>(SR)<sub>13</sub> with high stability and whose optical-absorption features match experiment. This structure features a cyclic [Au(I)-SR] pentamer interlocked with one staple trimer motif protecting the tetrahedral Au<sub>4</sub> nucleus, together with another trimer motif. This structure suggests that Au<sub>15</sub>(SR)<sub>13</sub> is a transitional composition from the [Au(I)-SR]<sub>x</sub> polymer (Au<sub>10</sub>(SR)<sub>10</sub>) to larger Au<sub>n</sub>(SR)<sub>m</sub> clusters that have only the staple motifs; and that the nucleation process starts from the Au<sub>4</sub> core. We have also explored the interaction between gold nanoclusters and a fully hydroxylated surface, Mg(OH)<sub>2</sub> basal plane, by using a DFT-enabled local basin-hopping technique for global-minimum search. We find strong interaction of Au clusters with the surface -OH via a short bond between edge Au atoms and O atoms of the OH groups. We expect that this strong interaction is ubiquitous on hydroxylated support surfaces and helps the gold clusters against sintering, thereby contributing to their CO-oxidation activity at low temperatures.

## Future Directions

Additional DFT computations will be performed to understand better how surface site geometry affects the rates of  $\alpha$ - and  $\beta$ -CH bond scission, and how this alters product selectivity. Probe molecules will be chosen to examine substituent group effects on the CH bond cleavage of the adsorbed reactants. Adsorption of various ‘test’ gases (pyridine, acetonitrile, CO, CO<sub>2</sub>...) on the CeO<sub>2</sub> nanoshapes will be used to quantify how structure affects acid-base parameters and bonding interactions. We will examine increasingly more complicated oxygenates such as polyols to understanding how adjacent hydroxyls compete for sites. Experimental studies of reaction selectivity and surface intermediates on the CeO<sub>2</sub> shapes will be supplemented with computer simulations to build a detailed understanding of the reaction pathways. Following a similar approach, work will continue on characterizing ketonization of acids, especially acetic acid, on the ceria nanoshapes. We will initiate studies of Au clusters deposited on CeO<sub>2</sub> nanoshapes with the

goal of creating highly uniform model catalysts that have known support structure and identically sized Au particles. The stability and temperature dependent evolution of these catalysts will be studied microscopically, and their reactivity/selectivity will be characterized and compared to the CeO<sub>2</sub> and Au reactivities to elucidate metal-support effects on the model surfaces.

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