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# BESH2014 Fundamentals of Catalysis and Chemical Transformations

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## Program Scope

The overarching goal of this project is to understand how to control reaction selectivity through tuning cooperativity in multi-functional catalysts. The vision of our research is that by fundamentally understanding the catalytic sites and mechanistic pathways, we will be enabled to precisely assemble closely interacting components into a catalyst to achieve the desired level of selectivity and activity. Specifically, we aim to elucidate the role of site geometry, surface and bulk composition, acid-base and redox sites, confinement, and metal support interactions in controlling selectivity in reactions catalyzed by oxides surfaces and supported metal particles. Our approach has been based on model catalysts with increasing complexity and model reactions with rich pathways. The model catalysts range from thin films and single crystal in ultra-high vacuum (UHV) surface science study to oxide nanocrystals with controlled surface facets and compositions, and supported metals with defined architectures. This allows us to bridge the materials and pressure gaps between UHV and reactor based methods. The reactions are the transformation of model oxygenates and hydrocarbons with controlled reactivity and selectivity. The surface chemistry, reaction kinetics and catalytic properties are studied by a collection of state-of-the-art operando and in situ methods including the neutron scattering methods at ORNL. The experimental work combines computational methods to aid interpretation of the experimental measurements and to create detailed models of reaction pathways.

## FY 2016 Highlights

### Surface structural effect of oxide catalysts

We have observed many cases where molecules react differently on CeO<sub>2</sub>(111) and CeO<sub>2</sub>(100). In general, the CeO<sub>2</sub>(100) surface has been more reactive than CeO<sub>2</sub>(111) as indicated by a stronger adsorption energy for molecules such as water, CO<sub>2</sub>, alcohols and aldehydes. However, the reactions on CeO<sub>2</sub>(100) are generally less selective and organic molecules tend to fully decompose in CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O.

*SO<sub>2</sub> Adsorption:* CeO<sub>2</sub> has been shown to have a high affinity for the adsorption of SO<sub>2</sub>. This can be detrimental as in the poisoning of automotive exhaust catalysts but could also possibly be exploited by utilizing ceria to traps SO<sub>2</sub> in effluent streams. Previous studies have shown that SO<sub>2</sub> adsorbs on fully oxidized CeO<sub>2</sub>(111) as sulfite, SO<sub>3</sub><sup>2-</sup>. This species is non-reactive and eventually desorbs as SO<sub>2</sub> at elevated temperatures. On partially reduced CeO<sub>2-x</sub>(111) the SO<sub>2</sub> adsorbs as sulfite at low temperatures but decomposes into O<sup>2-</sup> and S<sup>2-</sup> creating a sulfide and re-oxidizing Ce<sup>3+</sup> to Ce<sup>4+</sup>.

We hypothesized that the increased reactivity of CeO<sub>2</sub>(100) might result in sulfate (SO<sub>4</sub><sup>2-</sup>) following SO<sub>2</sub> exposure and possibly different decomposition paths with S<sup>0</sup> as a product. Surprisingly, considering the differences observed for other molecules on CeO<sub>2</sub>(111) and CeO<sub>2</sub>(100), the adsorption of SO<sub>2</sub> on these two surfaces was virtually identical in terms of the species formed on the surfaces and their stabilities. SO<sub>3</sub><sup>2-</sup> was the only species observed on the fully oxidized surfaces. The sulfite decomposed into sulfide on the reduced surfaces.

*Density Functional Theory (DFT) of Ethanol Reaction:* In addition to our experimental efforts, we used computational methods to gain insights into chemical conversion on ceria surfaces at the atomic level. Specifically, we employed DFT, where the surfaces were modeled as semi-infinite, two-dimensional slabs applying periodic boundary conditions. We studied ethanol reactions on the (111) and (100) ceria surfaces

starting from ethoxy, the experimentally determined dominant surface species. Ethylene and acetaldehyde can be produced in a single step through simultaneous  $\beta$ -scission and oxygen-carbon bond cleavage and  $\alpha$ -scission, respectively. Alternatively, ethylene and acetaldehyde can be formed through a common radical intermediate that is product of a  $\beta$ -scission reaction. The kinetically and thermodynamically preferred pathway on both surfaces, however, is the single step acetaldehyde formation via  $\alpha$ -scission. We observed that intermediate and transition state structures are stabilized on the (100) surface compared to the (111) surface. To assess pathway contributions, we computed transition state rate constants and carried out kinetic analysis. Our results are consistent with temperature programmed surface reaction and steady-state experiments, where acetaldehyde was found as the main product and evidence was presented that ethylene formation at higher temperature originates from changes in adsorbate and surface structure.

## Surface composition effect of oxide catalysts

Adsorption and reaction of oxygenates and hydrocarbon can be controlled not only by the surface structure of oxides such as  $\text{CeO}_2$  with different facets (mentioned above), but also by the surface composition of oxides such as binary oxides including perovskites and mixed oxides.

*Alcohol Reactions over Perovskite Particles:* The wide tunability of the A and B cations in  $\text{ABO}_3$  perovskites provides an opportunity in tuning not only the redox property but also the acid-base property. We aim to understand how the coupling of the acid-base and redox properties of perovskite oxides is controlling the reactivity and selectivity in alcohol conversion. In an on-going effort, we tested  $\text{ABO}_3$  where A = Ba, Sr, Zn and B = Ti and Zr for isopropanol conversion because they differ in reducibility and acid-base property. The dehydration vs. dehydrogenation of isopropanol was used as a model reaction to understand the acid-base catalysis by these perovskites. In situ infrared and microcalorimetry were used to characterize both qualitatively and quantitatively the surface acid-base and redox sites. The type, strength and amount of acid-base sites were found to vary with the A and B cations in the perovskites. Reactivity test of isopropanol is currently underway to correlate the acid-base property to the reaction activity and selectivity.

*Ambient pressure X-ray photoelectron spectroscopy of alcohol on perovskite thin film:* Methanol and ethanol oxidation on doped  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3(001)$  thin film have been studied using ambient pressure X-ray photoelectron spectroscopy.  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3(001)$  was grown on single crystal Nb-doped  $\text{SrTiO}_3(001)$  by pulse laser deposition. In order to investigate the so-called “pressure gap” that may occur between reactions studied under vacuum conditions and at pressure approaching atmospheric pressure, experiments were conducted at nominally  $10^{-5}$  torr and at 0.1 torr between  $250^\circ\text{C}$  and  $350^\circ\text{C}$ . Results using methanol or ethanol as the reactant are generally the same, i.e., only methoxy/ethoxy on the surface at lower pressures, a mixture of methoxy/ethoxy and formate/acetate at higher pressure in the absence of  $\text{O}_2$ , and exclusively formate/acetate on the surface when  $\text{O}_2$  was present. The only significant difference between methanol and ethanol was a greater tendency for ethanol to form the carboxylate in the absence of  $\text{O}_2$ . At the higher pressure the Mn 2p spectra indicated that the alcohol partially reduced  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  and there was also an indication in the O 1s spectra that O was removed from the surface. These observations indicated that methanol was being oxidized through reaction with the surface.

*Hydrocarbon oxidation over mixed oxides:* Catalytic synergism often occurs when two oxides are intimately mixed such as in solid solution mode. We synthesized a  $\text{Mn}_{0.5}\text{Ce}_{0.5}\text{O}_x$  solid solution that shows exceptional catalytic performance in the low temperature, heterogeneous oxidation of cyclohexane ( $100^\circ\text{C}$ , conversion: 17.7%, selectivity for KA oils [K: cyclohexanone, A: cyclohexanol]: 81%) with molecular oxygen as the oxidant. It is significantly superior to the results of current technology ( $140\text{--}160^\circ\text{C}$ , conversion: 3–5%). Detailed investigation indicates several unique characteristics of the  $\text{Mn}_{0.5}\text{Ce}_{0.5}\text{O}_x$  solid solution: (1) A high proportion (44.1%) of active oxygen species on the surface to promote O–O/C–H bond activation; (2) the introduction of 50 mol% Mn4p ions into ceria matrix for the formation of maximum solid solution phases that can lower the energy for oxygen vacancy formation and benefit the rapid migration of oxygen vacancies from

the bulk to the surface, thus continuing the activation of gas oxygen molecules; (3) a mesoporous structure for fast mass transfer/diffusion, and rich porosity to expose any more active sites ready for interaction with cyclohexane/O<sub>2</sub>. We expect that the Mn<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>x</sub> solid solution will provide a strategy for oxidation of cyclohexane and other hydrocarbons under mild conditions.

## Supported Metal nanoparticles

Catalysis of oxides can be drastically tuned or changed when metal nanoparticles are attached on the surface. More complication is the introduced metal–support interaction where the perimeter sites between metal and oxide seem to be important for catalysis. We have explored ways how to tune the interface structure to tune the catalysis of supported metal nanoparticles.

*Interface engineering via surface structure of oxide:* The strong support effect is known for metal catalysis, especially known for gold catalysis. Instead of the changing the composition of the support, we investigated how the surface structure of an oxide (CeO<sub>2</sub>) can affect the catalysis of gold nanoparticles. The different CeO<sub>2</sub> nanostructures can impact the size, morphology, and interface structures of Au catalysts through the metal–support interaction. Yet a detailed and atomistic view of the interface in Au–CeO<sub>2</sub> catalytic system is still missing. Recently we have performed aberration-corrected high angle annular dark field scanning transmission electron microscopy imaging on Au–CeO<sub>2</sub> nanostructures with well-defined shapes. With atoms clearly resolved, the size, morphology, and atomic interface structures of the Au–CeO<sub>2</sub> catalysts before and after the water-gas shift (WGS) reaction were systematically analyzed. It was found that the oxidation state of the ceria substrate plays a major role for both Au–CeO<sub>2</sub> systems, with larger adhesion for Au under oxidative condition. Under oxidative condition, Au particles with SK layers are present on the Au–CeO<sub>2</sub> nanocubes. The SK layers vanish and there is a morphological change of the Au particles after the WGS reaction, which is attributed to reduction of the Au–CeO<sub>2</sub> (100) interface. In contrast, the Au–CeO<sub>2</sub> nanorods contain regular Au particles and some rafts under oxidative conditions. After the WGS reaction, the Au atoms in the rafts migrate to the particles. The Au particles on the CeO<sub>2</sub> nanorods are almost uncharged before and after the WGS reaction. The loss of strong adhesion of Au to the support CeO<sub>2</sub> (the SK layer and the rafts) is partly responsible for the decrease of the activities in the WGS reaction.

*Construction of hierarchical interfaces:* Decreasing the size of metal nanoparticles is a general approach to enhance the catalytic activity. But it comes with the price of instability of small metal particles. One-dimensional (1D) metal nanowires, small in diameter and expose high percentage of active sites, are more stable than the nanoparticle counterparts. Further increase of their activity can involve the engineering of the interfaces. We demonstrated in constructing catalytic active hierarchical interfaces in 1D nanostructure as exemplified by the synthesis of TiO<sub>2</sub>-supported PtFe–FeO<sub>x</sub> nanowires (NWs). The hierarchical interface, constituting atomic level interactions between PtFe and FeO<sub>x</sub> within each NW and the interactions between NWs and support (TiO<sub>2</sub>), enables CO oxidation with 100% conversion at room temperature. We identify the role of the two interfaces by probing the CO oxidation reaction with isotopic labeling experiments. Both the oxygen atoms (Os) in FeO<sub>x</sub> and TiO<sub>2</sub> participate in the initial CO oxidation, facilitating the reaction through a redox pathway. Moreover, the intact 1D structure leads to the high stability of the catalyst. After 30 h in the reaction stream, the PtFe–FeO<sub>x</sub>/TiO<sub>2</sub> catalyst exhibits no activity decay. Our results provide a general approach and new insights into the construction of hierarchical interfaces for advanced catalysis.

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