

Fundamental Studies of the Steam Reforming of Alcohols on Pd/ZnO and Co/ZnO Catalysts

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array of surface sensitive spectroscopic probes (HREELS, XPS, LEED, AES, TPD, AFM) is being used to characterize surface structures and adsorbed intermediates at the molecular level. In addition to determining the mechanisms of alcohol steam reforming reactions, this project is also providing fundamental insights that will be useful in designing a wide range of supported metals catalysts.

Progress Report

Structure-activity relationships for supported Co catalysts

XPS and TPD studies of the reaction of ethanol on Co films and CoO particles supported on non-reducible YSZ(100) (see Figure 1 for representative TPD data) show that the activation energy for the dehydrogenation of adsorbed ethoxide to produce acetaldehyde, which is a key intermediate in ethanol steam reforming (ESR), is a function of the oxidation state of the cobalt. The activation energy varies from 86 kJ/mol on O₂-dosed Co/YSZ(100) to 126 kJ/mol CoO/YSZ(100). These results along with those obtained from Co foils implicate Co²⁺ as the active site for dehydrogenation of ethoxide to produce acetaldehyde, and indicate that the most active surface for this reaction consists of either a two-dimensional oxide layer on metallic cobalt or an oxygen covered metallic cobalt surface. Studies of the reaction of ethanol on model Co/ZnO(0001) and Co/CeO₂(100) catalysts also show that partially oxidized cobalt films or particles that contain both Co⁰ and Co²⁺ are

Objectives

The overall goal of this project was to provide fundamental insight into the factors that control the activity and selectivity of supported metal catalysts for the steam reforming of alcohols to produce hydrogen. Specific goals were to determine how metal-support interactions, including transfer of oxygen from reducible oxides to the metal, affect catalyst reactivity and stability, and to determine the mechanism by which alloying affects the selectivity of group VIII metal-based catalysts.

Abstract

In this project we are studying the relationships between the structure and reactivity of ZnO-supported Pd, Pt, and Co alcohol steam reforming catalysts and determining the origins of their unique reactivity and high selectivity for producing H₂ and CO₂. In addition to identifying the relevant reaction pathways and intermediates, we are investigating how alloying Pd and Pt with Zn significantly alters the selectivity for methanol steam reforming and how interactions at the Co-ZnO interface influence the extent of oxidation of the Co and its reactivity. A surface science approach using model single crystal catalysts (e.g. Pd/ZnO(0001), Zn/Pd(111), Co(0001) and Co/ZnO(0001)) and an

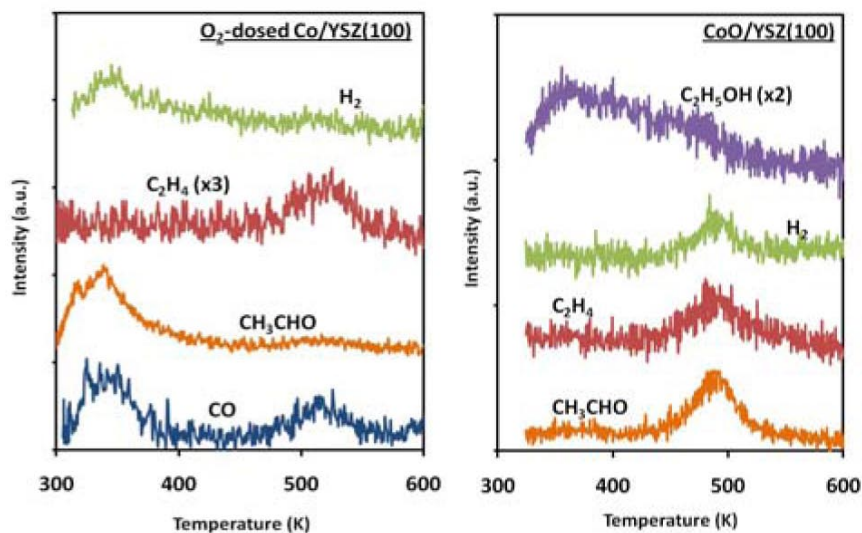


FIGURE 1. Ethanol TPD spectra obtained from O₂ pre-dosed Co/YSZ(100) and CoO/YSZ(100).

the most active for the dehydrogenation of adsorbed ethoxide species to produce acetaldehyde. For these systems, however, the Co can be maintained in a partially oxidized state via reaction with the reducible support.

The results obtained in our studies provide considerable insight into how the support influences the overall activity of Co-based SRE catalysts. In particular, they indicate that the high activity observed for Co on reducible supports is due to the fact that these supports facilitate the oxidative dehydrogenation of ethoxide to acetaldehyde by providing the oxygen required for this reaction. This pathway results in reduction of the support which is then reoxidized via reaction with water in a subsequent step. This pathway is shown schematically in Figure 2 for a Co/CeO₂/YSZ(100) model catalyst. Our results also show that in addition to promoting this reaction, the facile transfer of oxygen from the support to the Co plays a role in removing carbon deposits and thereby helping to maintain activity.

PtZn alloy catalysts for alcohol steam reforming

In the previous 3-year grant cycle we investigated the mechanism by which alloying Pd with a small amount of Zn dramatically alters the selectivity of Pd-based methanol steam reforming catalysts. Our study showed that Zn formed two-dimensional ordered surface phases which had electronic properties significantly different than that of bulk Pd. These electronic effects were found to alter the activation energies for C-H bond cleavage thereby stabilizing adsorbed aldehyde intermediates, and to decrease the adsorption energy for

CO. During the current grant cycle we have returned to the issue of alloying with Zn and have expanded our previous studies with Pd to include Pt. The goal here was to determine if the insights obtained for the Pd-Zn system are general and applicable to other group VIII metals. Pt/ZnO catalysts have high activity and selectively for methanol and ethanol steam reforming and PtZn alloys have been proposed as catalysts for both oxygen reduction and fuel oxidation in PEM fuel cells, and for the hydrogenation of aldehydes to produce α,β -unsaturated alcohols. Thus, this system is also technologically relevant.

Structural Characterization: We have collaborated with Bruce Koel's group at Princeton to determine the structure of near surface PtZn alloys formed by vapor deposition of Zn onto Pt(111) followed by annealing. Our group has collected detailed LEED, AES, and XPS data for Zn-modified Pt(111) surfaces, while Koel's group has performed an in-depth low energy ion scattering spectroscopy (LEIS) study. Our combined data show that Zn adlayers on Pt(111) substitute into the surface layer upon annealing above 600 K which is consistent with previous studies by Rodriguez. Ordered surface phases are not observed, however, and the Zn distributes itself into the first 2-3 atomic layers with the Zn concentration in the outermost layer being relatively low.

CO bonding on Zn-modified Pt(111): The heat of adsorption of CO was measured and used to assess how Zn addition affects the surface electronic properties. Consistent with our previous studies of PdZn, alloying Pt with Zn was found to decrease the heat of adsorption of CO. In a

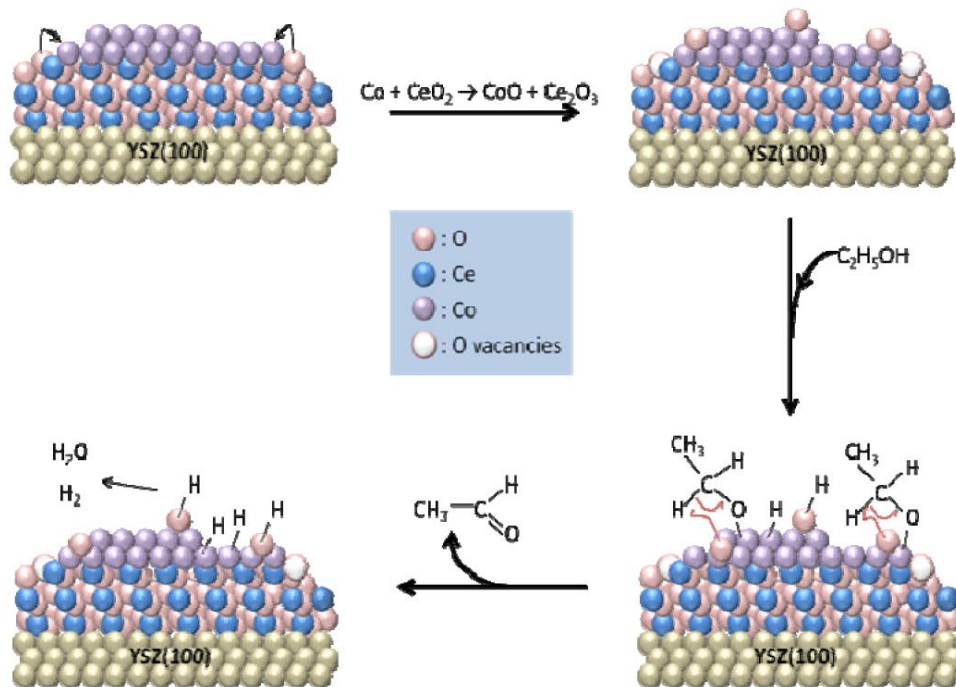


FIGURE 2. Pathway for the dehydrogenation of ethanol to produce acetaldehyde on Co/CeO₂/YSZ(100).

somewhat surprising result, however, just the opposite trend was observed for a Pt(111) surface decorated with Zn adatoms (Zn/Pt(111)) where the CO desorption temperature increased relative to that on clean Pt(111). HREELS data indicate that at temperatures above 200 K, CO does not adsorb on the Zn adatoms on this surface. Thus, different perturbations of the surface electronic properties are observed for Zn adatoms and those incorporated into the surface layer.

Reactivity of PtZn/Pt(111) surfaces towards oxygenates:

CH₃OH was found to adsorb only molecularly on Pt(111) (some reaction does occur at defect sites). In contrast on PtZn/Pt(111) it undergoes dissociative adsorption to form methoxide groups which decompose to CO and H at temperatures below 300 K. Since the Zn concentration in the outmost layer of the PtZn/Pt(111) surface is less than 5% of a monolayer, we attribute this enhanced reactivity for O-H bond scission to an electronic effect rather than reaction at the isolated Zn sites. These results further demonstrate the large effect that alloying with small amounts of Zn has on the reactivity of group VIII metals.

Much more interesting chemistry was observed for reaction of oxygenates on Pt(111) surfaces decorated with Zn adatoms. We have used TPD and HREELS to map out the reactivity of the surface towards methanol as a function of the Zn coverage. Several interesting trends were observed. First the Zn adatoms provide sites for O-H bond scission in adsorbed methanol to form methoxide groups which appear to reside on both Zn and Pt sites. Those adsorbed on the Zn adatoms undergo dehydrogenation near 300 K to produce adsorbed formaldehyde, while those on the Pt sites decompose completely to CO and H₂. These reaction pathways are summarized in Figure 3. We are currently

using TPD and HREELS to study the adsorption and reaction of ethanol and acetaldehyde on the Zn-modified Pt(111) surfaces. Our preliminary results for these molecules suggest that at least under some conditions the Zn adatoms provide sites for C-O bond cleavage in adsorbed aldehydes. This result suggests that the Pt-alloy catalysts may also have some activity for the deoxygenating of both aldehydes and polyols which might be useful in the production of fuels and chemicals from cellulosic biomass.

While the Zn-adatom surfaces used here are not likely to be representative of those in real Pt/ZnO alcohol steam reforming catalysts it is noteworthy that high activity for PdZn and PtZn alloys for alcohol steam reforming is only observed for catalysts that contain Zn in excess of the stable 50:50 alloy composition. This is consistent with our hypothesis that the presence of Zn adatoms on the alloy surface is required for high reforming activity.

Publication acknowledging the DOE grant or contract

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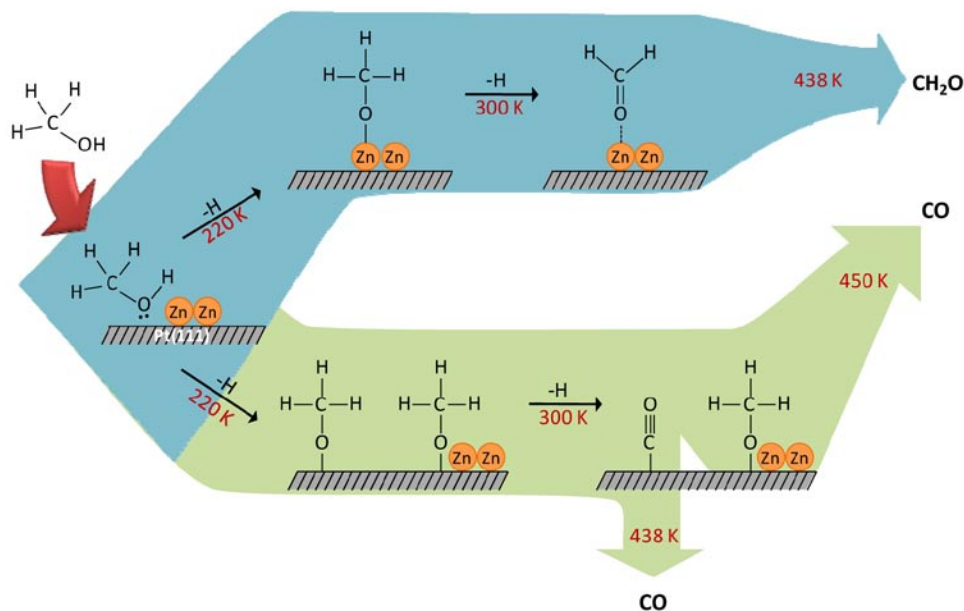


FIGURE 3. Pathways for the reaction of methanol on Zn-modified Pt(111) surfaces.

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