Effect of Zn alloying on the reactivity of Pd catalysts

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Introduction
Methanol and other alcohols are potential bio-renewable sources of hydrogen. The use of alcohols, however, as a source of H₂ or for H₂ storage requires stable reforming catalysts that have high activity at low temperatures. One such catalyst that has received much attention for steam reforming of CH₃OH (SRM) [CH₃OH + H₂O → CO₂ + 3H₂] is Pd supported on ZnO. Pd/ZnO catalysts have unusually high selectivity for the production of CO₂ and H₂ from methanol (> 95%) and ethanol (> 60%), in spite of the fact that bulk Pd exhibits nearly 100% selectivity for the dehydrogenation of CH₃OH and CH₃CHO to CO and H₂ under typical steam reforming conditions [1-3]. The dramatic change in the selectivity of Pd for SRM and SRE upon supporting it on ZnO has been attributed at least in part to the formation of a PdZn alloy under reaction conditions [4]. However, a mechanistic understanding of why the PdZn alloy exhibits such different reactivity compared to pure Pd is still lacking.

In order to elucidate how alloying with Zn affects the reactivity of Pd and provide insight into the reaction mechanism for the SRM on PdZn, the structure and reactivity of model catalysts consisting of submonolayer amounts of Zn supported on a Pd(111) single crystal have been investigated. Temperature programmed desorption (TPD) data for the reaction of CH₃OH, CH₃O, CH₃CHO, CH₃H₂O, HCOOH and H₂O on Pd(111) as a function of Zn coverage as well as results of a high resolution electron energy loss spectroscopy (HREELS) study of the bonding configurations of these species on Zn/Pd(111) surfaces will be presented.

Materials and Methods
Experiments were carried out in an ultra high vacuum (UHV) chamber equipped with a quadrupole mass spectrometer for TPD studies and a Kesmodel LK-2000 HREEL spectrometer. Zn was deposited on the single crystal substrate using an evaporative metal source and a quartz crystal film thickness monitor was used to determine absolute coverages.

Results and Discussion
The adsorption of alcohols and aldehydes on Zn/Pd(111) as a function of Zn coverage have demonstrated that Zn is very effective in poisoning the activity of the Pd(111) surface for both the dissociative adsorption of methanol and ethanol as well as the subsequent dehydrogenation of adsorbed alkoxide intermediates. The extent of the dehydrogenation of these species during TPD dropped by roughly 50% with the addition of just 0.1 ML of Zn and was nearly absent for Zn coverages above 0.5 ML. These experimental results are consistent with DFT calculations of Chen at al. [5] which report the activation energy for the dehydrogenation of adsorbed methoxide and formaldehyde groups to be significantly higher on PdZn(111) than on Pd(111).

Submonolayer amounts of Zn were also found to increase the propensity for adsorbed HCOOH to decompose to CO₂ rather than CO. Figure 1a compares the amounts of CO and CO₂ produced following the adsorption of a saturation dose of HCOOH on Zn/Pd(111) for various Zn coverages and 1b presents this data in terms of the CO₂/CO selectivity obtained.

As the figures above show, the addition of just 0.03 ML of Zn causes a significant increase in the amount of CO₂ produced from HCOOH along with a slight decrease in CO production, causing the CO₂/CO selectivity to increase to 81% from 52%. Overall, the stabilization of CH₃O as well as the decomposition of HCOOH to CO₂ on PdZn allow us to predict a reaction mechanism for the SRM in which the Zn-stabilized CH₃H₂O would remain on the surface at sufficiently high temperatures to react with hydroxyl groups to produce formate, eventually decomposing to CO₂.

Significance
The results obtained in this study provide evidence of the dramatic effect on reactivity that low coverages of Zn has on Pd(111) and proposes a reaction mechanism for the SRM on the PdZn alloy surface.

References