

Support Crystal Plane Effects in the Steam Reforming of Alcohols on Pd/ZnO and Co/ZnO

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Introduction

The steam reforming of alcohols, particularly methanol and ethanol, presents a promising method of producing hydrogen. Due to its high activity at relatively low temperatures, Pd/ZnO has received attention as a methanol steam reforming (MSR) catalyst to produce H_2 at very high CO_2 selectivity.¹ Pd supported on most other materials dehydrogenates methanol to CO. Similarly, Co catalyzed ethanol steam reforming (ESR) exhibits very good activity and selectivity toward H_2 when supported by ZnO, although the distinction between ZnO and other supports is not as pronounced as with the Pd/ZnO catalyzed MSR.²

The activation of the MSR pathway on Pd/ZnO has been attributed to the formation of PdZn alloys when reduced at high temperatures.¹ While the incorporation of Zn into the Pd surface clearly alters the reaction energetics,³ it is not known if ZnO contributes a secondary effect. To assist in understanding the role of ZnO in the steam reforming of alcohols, we investigated the decomposition of methanol and ethanol on Pd and Co supported by ZnO single crystals. As part of a larger study to understand the role of ZnO, we focused on examining differences in catalyst reactivity of Pd and Co toward alcohol decomposition when supported on ZnO(0001) and ZnO(10 $\bar{1}$ 0) single crystal substrates. In this talk, we report how changing the surface structure of ZnO influences alloy formation as well as the activity of the metal-support interface.

Materials and Methods

Experiments were performed in an ultrahigh vacuum chamber in which metals (Pd, Co) were vapor deposited on ZnO(0001) and ZnO(10 $\bar{1}$ 0). Structural characterization was performed with XPS and CO TPD experiments. Methanol and ethanol TPD experiments were performed to examine alcohol decomposition. Samples were progressively annealed to 800 K to examine morphological effects and to attempt to form PdZn (or CoZn) alloys.

Results and Discussion

CO TPD experiments revealed a slight weakening of CO on Pd/ZnO(0001) relative to that on Pd/Zn(10 $\bar{1}$ 0) in their freshly deposited film-like states which suggests an electronic interaction between Pd and ZnO(0001). Upon annealing at 650 K, Pd/ZnO(0001) exhibited significant favoring of weakly adsorbed. Additionally, the more strongly bound CO was found to desorb at lower temperatures. These observations are not explained by geometric arguments alone and suggest the formation of a PdZn on Pd/ZnO(0001). The considerably smaller CO TPD peak shifts on Pd/ZnO(10 $\bar{1}$ 0) indicate that PdZn alloy formation is less facile than on ZnO(0001).

Methanol TPD experiments revealed an even more pronounced difference between the two ZnO supports. Prior to high temperature annealing, both Pd/ZnO(0001) and Pd/ZnO(10 $\bar{1}$ 0) exhibited methanol TPD spectra characteristic of methanol decomposition on low index Pd single crystals. This may result from a combination of adsorbate-adsorbate repulsion and lack of dehydrogenation activity on defect sites. Annealing Pd/ZnO(10 $\bar{1}$ 0) at high temperatures led to modest increases in the CO yield as a fraction of saturation CO coverage, consistent with the increase in Pd particle size. In contrast, annealing Pd/ZnO(0001) at 700 K and above led to marked increases in CO yield from methanol decomposition. At these temperatures, saturation CO coverage was achieved from methanol decomposition (Figure 1).

Annealing the Pd/ZnO surfaces at 700 K induces significant agglomeration, which exposes the ZnO substrate. The resulting interfacial sites on Pd/ZnO(0001) are highly active, while those on Pd/ZnO(10 $\bar{1}$ 0) are inactive. We propose that methanol dehydrogenation intermediates react rapidly at the Pd-ZnO(0001) interface before diffusing to more favorable Pd adsorption sites. The differences in activity between the ZnO supports may be attributed to the highly defected ZnO(0001) surface and comparatively defect free ZnO(10 $\bar{1}$ 0) surface.⁴

Significance

These results, in concert with the high surface area Pd/ZnO catalyst work of our collaborators at PNNL, demonstrate a dependence of the ZnO structure on Pd catalyst activity. Further work on high surface area catalysts may lead to further improvements in selectivity.

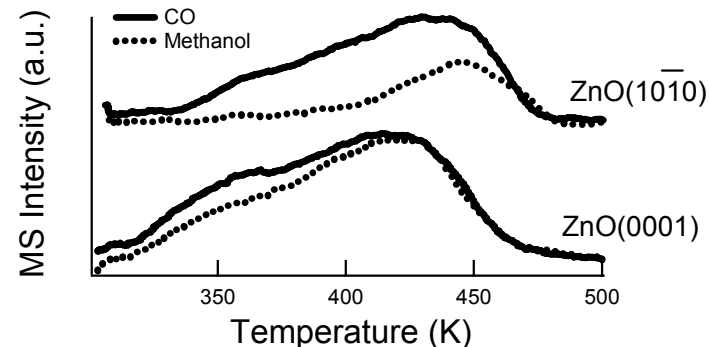


Figure 1. Comparison of CO desorption spectra resulting from CO TPD (solid) and methanol TPD (dotted) experiments on 1 ML Pd/ZnO. Labels identify substrate crystal plane. Samples annealed at 800 K.

References

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