Mechanistic Studies of the Steam Reforming of Methanol on Pd/ZnO 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 H_2 or for H_2 storage requires stable reforming catalysts that have high activity at low temperatures. One such catalyst that has received much attention for steam reforming of CH_3OH (SRM) [$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$] is Pd supported on ZnO. Pd/ZnO catalysts have unusually high selectivity (>95%) for the production of CO_2 and H_2 from methanol, in spite of the fact that bulk Pd exhibits nearly 100% selectivity for the dehydrogenation of CH_3OH to CO and H_2 under typical SRM conditions [1,2]. Iwasa and others have demonstrated that partial alloying of the Pd with Zn is required to obtain a highly selective Pd/ZnO SRM catalyst [3]. While the importance of alloy formation has been established, the mechanism by which Zn alters the selectivity to produce CO_2 rather than CO is not understood. Iwasa *et al*. have proposed, however, that the dramatic change in selectivity upon Zn addition may result from the destabilization of η^2-CH_2O intermediates in which the carbonyl group is parallel to the surface and bonding is by both the C and O atoms in favor of η^1-CH_2O in which the carbonyl is perpendicular to the surface and only the oxygen interacts with the metal [4]. Presumably this later species is more resistant to dehydrogenation and reacts with hydroxyl groups to produce CO_2 and H_2.

In order to elucidate how alloying with Zn affects the CH_3OH dehydrogenation activity of Pd, the structure and reactivity of model catalysts consisting of submonolayer amounts of Zn supported on a Pd(111) single crystal have been investigated. In this talk we will present temperature programmed desorption (TPD) data for the reaction of methanol 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 CO, CH_2O, and CH_3OH on Zn/Pd(111) surfaces. TPD data for the reaction of methanol on Pd supported on ZnO(0001) single crystal surfaces will also 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 and Pd were deposited on the single crystal substrates using evaporative metal sources and a quartz crystal film thickness monitor was used to determine absolute coverages.

Results and Discussion

Methanol TPD data as a function of Zn coverage demonstrated that Zn is very effective in poisoning the activity of the Pd(111) surface for both the dissociative adsorption of CH_3OH and the subsequent dehydrogenation of adsorbed methoxide intermediates. For Zn coverages as low as 0.1 ML the amount of CO produced during a CH_3OH TPD experiment was less than 4 % of that produced on clean Pd(111).

Submonolayer amounts of Zn were also found to alter the bonding configuration of aldehydes on the Zn/Pd(111) surface. This is demonstrated by the HREELS data in Figure 1 which displays the vibrational spectrum of formaldehyde adsorbed on both clean Pd(111) and 0.25 ML Zn/Pd(111). The η^2–CH_2O and η^1–CH_2O species can be distinguished by their distinctive vibrational bands at 1450 cm^{-1} and 1655 cm^{-1}, respectively

Note that on clean Pd(111) only the peak at 1450 cm^{-1} is observed indicating an η^2 bonding configuration. In contrast for the O.25 ML Zn/Pd(111) surface both the 1450 and 1655 cm^{-1} peaks are observed demonstrating the presence of both η^2–CH_2O and η^1–CH_2O species on this surface.

Figure 1 also provides information about the bonding sites of the CO on the surface. The peak at 1860 cm^{-1} corresponds to CO in threefold sites while that at 2070 cm^{-1} is CO in on top sites. Note that the preferred CO bonding configuration changes form threefold to on top upon the introduction of Zn.

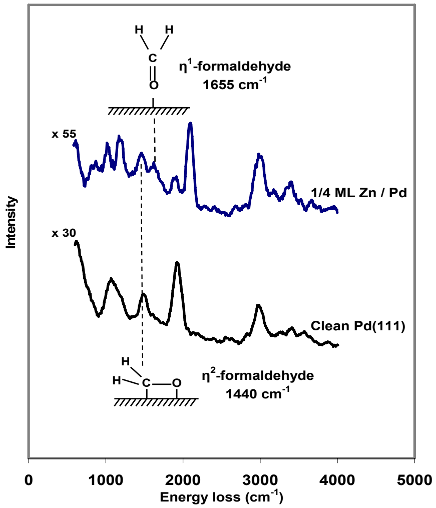

Fig. 1. HREEL spectrum of CH_3OH adsorbed on Pd(111) and 0.25 ML Zn/Pd(111) at 200 K.

Significance

The results obtained in this study provides fundamental insight into how Zn alters the reactivity of Pd for the dehydrogenation of CH_3OH and this insight is useful in elucidating the mechanism of the steam reforming of methanol on Pd/ZnO catalysts.

References

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