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A Comparative Study of CO Adsorption and CO Oxidation on Model Silica Supported and Single Crystal Pd Catalysts
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Introduction: Understanding the basic phenomena of heterogeneous catalytic processes is a crucial step toward developing new, highly active and selective catalytic materials. Toward this end many studies utilize analytical techniques which combine an ultrahigh vacuum (UHV) environment and metal single crystals to model the more realistic catalysts. Whether studies performed on metal single crystal catalysts under UHV conditions can be correlated with data obtained on high surface area supported metal catalysts under industrial catalytic conditions is a valid question. Recently several efforts have been made toward bridging the so-called pressure and material gaps. Combined elevated pressure reactor - UHV surface analytical systems have been used to study catalytic reactions for more than a decade and in many cases excellent agreements have been found among data acquired in very different pressure regimes [1]. Generally oxide-supported metal catalysts have been modelled with metal oxide, e.g. ZnO or MgO, single crystals onto which the metal of catalytic interest is deposited. However, these model oxide systems are much less than ideal due to charging when probed with particle beams and to non-uniform heating. Recently model supported metal catalysts have been prepared and characterized by a variety of surface analytical techniques in our laboratories. Adsorption and catalytic studies have shown that these materials model very accurately the corresponding high surface area supported metal catalyst.
Here we report results on the adsorption and oxidation of CO on model silica supported Pd catalysts as well as results for single crystal Pd catalysts. Infrared reflection-absorption spectroscopy (IRAS) was used to demonstrate the correspondence between the adsorption properties of the model silica supported Pd catalysts and Pd single crystals. The catalytic behavior of the model supported and single crystal Pd catalysts has also been investigated with respect to the oxidation of CO by O₂.

**Experimental:** Both the adsorption and catalytic studies were carried out in a combined elevated pressure IR cell - UHV surface analysis system. The experimental details of the CO adsorption and CO oxidation studies have been described elsewhere [2]. The Pd/silica catalysts were prepared by evaporating Pd onto a silica thin film supported on a Mo(110) substrate [3]. The detailed characterization of these model supported catalysts has been reported elsewhere [4].

**Results and Discussion:** IR spectra of adsorbed CO on model silica supported Pd catalysts are displayed in Figure 1 for Pd coverages of 1.0, 7.0 and 15 ML. The Pd overlayers on the thin silica films were annealed to 900K prior to the CO adsorption experiments. This thermal treatment has been shown to produce small metal particles in the range 30 to 500 Å, with larger particles being formed for the higher palladium coverages. The IR spectra of adsorbed CO on model Pd/SiO₂ catalysts with different Pd coverages show three distinct absorption features corresponding to CO adsorbed onto three-fold hollow (1880 cm⁻¹), bridging (1990 cm⁻¹) and a-top (2110 cm⁻¹) configurations. At θₚd=1.0 ML the dominant absorption feature corresponds to CO adsorbed onto an a-top position, while the peaks originating from three-fold hollow and bridging CO are broad, suggesting a non-homogeneous distribution of these adsorption sites. Increasing the Pd coverage to 7.0 ML and then to 15 ML results in the sharpening of the absorption features and the dominance of the peak originating from CO adsorbed in the bridging positions. These results demonstrate that the larger particles have well-defined crystal orientations whereas the smaller particles have a wide distribution of adsorption sites. A comparison of the IR spectra of equilibrated CO overlayers obtained from the Pd₁₅ ML/SiO₂ sample and the Pd(100) and Pd(111)
Figure 1. IRAS spectra for CO on Pd(111), Pd(100) and silica-supported palladium.

Figure 2. Infrared reflection absorption spectra for CO adsorption on silica-supported palladium. The silica film (100 Å) was supported on a Mo(110).

Single crystals reveals striking similarities. As Figure 2 shows, the stretching frequencies of adsorbed CO on the model Pd/SiO₂ catalyst are identical to the combined features observed for Pd(100) and Pd(111). The agreement among the IR spectra of the model supported catalysts and the metal single crystals suggests that the metal particles formed on the thin SiO₂ film have facets consisting primarily of (100) and (111) orientation. This is anticipated in that the formation of metal particles with low Miller indices is thermodynamically favored.

The oxidation of CO on these model systems has been studied as well. Figure 3 shows the dependencies of specific CO₂ formation rates on the reaction temperature. The specific activities of the single crystal and the supported catalysts for CO oxidation are essentially identical. The apparent activation
energies for the relatively large particles ($\theta_{Pd}>2$ ML) are similar (~27 kcal/mol), but somewhat lower (~25 kcal/mol) for the smaller particles (0.6, 0.3 ML). The apparent activation energies for each of the three Pd single crystals with different orientations are similar but distinctive [29.4±0.3 kcal/mol for Pd(100), 28.1±0.4 kcal/mol for Pd(111) and 30.7±0.5 kcal/mol for Pd(110)]. An excellent correspondence is found among the results obtained for the model silica supported Pd catalysts and the Pd single crystals for the oxidation of CO.

In summary, our results on the adsorption and oxidation of CO on model silica supported Pd catalysts and Pd single crystals show remarkable agreement. The utilization of the model supported catalysts and combined elevated pressure reactor-UHV surface analytical systems can aid significantly in bridging the pressure and material gaps between the idealized environments and materials of
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References:


   
   (b) J. Szanyi and D. W. Goodman, in preparation.
