

An *in situ* Investigation of CO Oxidation on Pd(110) by Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS)

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Introduction

CO oxidation on various catalysts has been extensively studied for many years [1-6]; however research at the molecular level using metal single crystals is less extensive and more recent [2, 4-6]. In the latter case only a few studies have used *in situ* infrared spectroscopy [6]. In the present study, polarization modulation infrared reflection adsorption spectroscopy (PM-IRAS) [7] has been used to monitor *in situ* CO oxidation over Pd(110) at elevated pressures (up to 90 Torr) and temperatures. Various compositions of CO/O₂ mixtures showed that the rate or turnover frequency (TOF) of CO oxidation reaches an unprecedented value at relatively low CO/O₂ ratios. The dramatic change in the surface composition under these high reactivity conditions is reflected in the PM-IRAS CO adsorption data that show a switch from metallic Pd sites to oxidized-Pd sites with the rapid rise in reactivity. Additional investigations by AES and PM-IRAS show that at the point of the rapid rate increase, the surface is covered by a thin oxide film rather than bulk oxide.

Materials and Methods

A clean Pd(110) surface was prepared by multiple cycles of Ar⁺ sputtering at room temperature followed by an anneal at 1100 K. Surface cleanliness was checked by AES and LEED. The sample preparation was carried out in an ultrahigh vacuum (UHV) analysis chamber and the reaction studies performed in an elevated-pressure reaction cell. All CO oxidation reactions were at 525 K unless otherwise stated.

Results and Discussion

Plots of temperature and/or pressure versus reaction time acquired during various CO oxidation reactions at less than stoichiometric CO/O₂ ratios on Pd(110) show similar behavior, i.e. a gradual decrease in the total pressure followed by an abrupt pressure drop over a 10 second time period. Concurrent with the rapid pressure drop, the reaction temperature increases by ~30 K above the steady-state reaction temperature. The TOF at the point of the rapid rate rise is estimated to be >2000. *In situ* PM-IRAS data indicate that prior to the rapid increase in rate and temperature, the surface is predominantly covered by CO_{ads} (features at 2072 and 1985 cm⁻¹); at the rapid rate rise point, no CO_{ads} was apparent on the surface. Upon cooling the surface to ~450 K, features at 2140 cm⁻¹ appear, consistent with the formation of an oxidized Pd surface [4]. Ancillary CO adsorption data at low temperature on a pre-oxidized Pd(110) surface show that reaction with O₂ at 10 Torr and 525 K for less than 1 min forms an oxide film less than 1-2 monolayers. Based on these results the surface following reaction that gives rise to the 2140 cm⁻¹ CO feature discussed above is believed to be O_{ads} rather than bulk oxide. Indeed reaction with CO showed this O-Pd film to be reduced rapidly at room temperature.

Significance

This study shows the power of an *in situ* vibrational technique such as PM-IRAS to address the

nature of a catalytic surface under working conditions. New results are reported with respect to the surface composition during the oxidation of CO over Pd at relatively high O₂/CO ratios. Specifically a surface consisting primarily of adsorbed oxygen is shown to give rise to exceptional high reactivities for this important technological reaction.

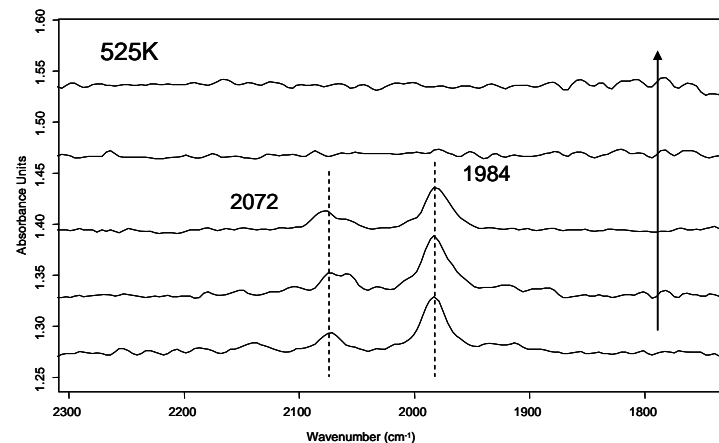


Figure 1. PM-IRAS data collected *in situ* under CO oxidation conditions at 525 K in the sequence indicated by the arrow. The collection time for each spectrum was 10 second. P_{CO} = 14 Torr and P_{O₂} = 50 Torr at the onset of reaction.

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