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Hydrogen-induced low temperature CO displacement from the Pt(111) surface

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A new low temperature displacement mechanism for CO on the Pt(111) surface has been observed in the presence of high pressures of hydrogen (0.001 to 0.1 Torr H_2). Temperature-programmed fluorescence yield near-edge spectroscopy (TP FYNES) was used to continuously monitor the CO coverage as a function of temperature both with and without hydrogen. For hydrogen pressures above 0.01 Torr, removal of CO begins at 130 K (E_d = 10.6 kcal/mol) instead of near the desorption temperature of 400 K (E_d = 26 kcal/mol). The large decrease in CO desorption energy appears to be caused by substantial repulsive interactions in the compressed monolayer induced by coadsorbed hydrogen. The new low temperature CO desorption channel appears to be caused by displacement of the compressed CO adlayer by coadsorbed hydrogen. In addition, the desorption activation energy for the main desorption channel of CO near 400 K is lowered by ~ 1 kcal/mol for hydrogen pressures in the 0.001 to 0.1 Torr range. These new results clearly emphasize the importance of in-situ methods capable of performing kinetic experiments at high pressures on well characterized adsorbed monolayers on single crystal surfaces. High coverages of coadsorbed hydrogen resulting from substantial overpressures may substantially modify desorption activation energies and thus coverages and kinetic pathways available even for strongly chemisorbed species. These phenomena may play an important role in surface reactions which occur at high pressure.

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The study of the interactions of CO and H_2 on transition metals has received considerable attention because of the importance of these molecules in Fischer–Tropsch and methanation chemistry. CO adsorption alone on Pt(111) has received a great deal of study [1–5]. CO is adsorbed molecularly on Pt(111) with an activation energy for desorption of 31 kcal/mol at low coverage [1–4]. This activation energy decreases sharply above $\theta_{CO} = 0.50$ ML where compression of the adlayer begins and repulsive interactions become important [1]. The activation energy for desorption continues to decrease as θ_{CO} increases, approaching the heat of sublimation as the CO adlayer adopts a closest-packed structure [1]. Coadsorption studies of CO and H_2 are of particular interest because of the repulsive nature of the interactions between these adsorbed species, and because of the tendency for these coadsorbed species to form islands [6]. Thermal energy atom scattering (TEAS) experiments performed by Bernasek et al. [7] on a Pt(111) surface precovered with $\theta_{CO} = 0.22$ ML show that CO forms islands with a local density of $\theta_{CO} = 0.50$ ML on the hydrogen-saturated surface at 180 K. Considering only nearest-neighbor interactions, the authors propose an energy window of 6–8 kcal/mol for the CO–H nearest-neighbor repulsion energy. Further studies on this system [8] showed that the presence of coadsorbed hydrogen lowered the temperature of the onset of CO mobility from 160 to ~ 130 K. The islanding of CO induced by coadsorbed hydrogen has also been studied by infrared reflection absorption spectroscopy [9]. These studies confirm the results of Bernasek et al. [7] and suggest an optimum temperature of 150 K for the growth of large islands. In the presence of coadsorbed hydrogen, the number of bridge bonded species was found to increase at the expense of the more tightly bound on-top molecules. Evidence is also presented for a weak direct interaction between the coadsorbed species [9].

Coadsorption experiments in UHV have provided a great deal of useful information on the interactions of these adsorbed species, yet some effects or intermediates may exist only under high pressures of the reactant gases. A new low temperature displacement mechanism for CO on Pt(111) in the presence of high pressures of hydrogen (0.001 to 0.1 Torr H_2) is clearly present in this data. Temperature-programmed fluorescence yield near-edge spectroscopy (TP FYNES) was used to continuously monitor the CO coverage as a function of temperature both with and without hydrogen. Fluorescence yield near-edge spectroscopy (FYNES) is a photon-in/photon-out method which allows near-edge X-ray absorption fine structure (NEXAFS) spectra to be obtained in-situ under high pressures of reactive gases [10]. The in-situ capability of FYNES to monitor the π resonance of chemisorbed CO as a function of temperature at various pressures of hydrogen was used in order to obtain the surface CO concentration as a function of temperature in the presence of substantial hydrogen overpressures.

The experiments were performed at the U1 beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. The details of the experimental apparatus have been described in detail previously [10]. Briefly, the apparatus consists of a multilevel UHV analysis chamber with a reaction chamber on top which can be isolated from the main chamber by means of a gate-valve. The Pt(111) crystal was given a saturation exposure of CO at $T < 100$ K in the main chamber and then raised to the reaction chamber where the FYNES spectra was recorded at normal incidence in order to locate the energy position of the π resonance. The photon energies were calibrated using the strong carbon absorption feature at 291 eV in the incoming beam due to carbon deposited on the beam-line optics. The π resonance was measured at 288.2 eV. Control experiments were performed to insure that the energy of the π resonance was invariant with hydrogen pressure, CO coverage, or surface temperature below the desorption temperature. Uptake experiments for CO on Pt(111) [11] show that the intensity of the CO π resonance is linearly dependent on surface CO coverage. Differentiation of the TP FYNES data for the experiment performed in vacuum shows agreement with previous thermal desorption experiments [1–4] providing additional evidence that the CO π resonance is linearly dependent on surface coverage.

A typical TP FYNES experiment involved giv-

ing the Pt crystal a saturation exposure of CO at low temperature (< 100 K). The monochromator was then positioned to provide an incident photon energy of 288.2 eV which is the energy of the CO π resonance for chemisorbed CO on Pt(111). The fluorescence yield intensity resulting from the CO π resonance transition was measured as a function of time while the temperature of the Pt crystal was ramped at a rate of 1 K/s. In this manner, the concentration of adsorbed CO could be measured as a function of temperature in the presence of hydrogen. The experiment was performed for several different pressures of hydrogen flowing through the chamber, and in vacuum. Special precautions were taken to ensure that the hydrogen was free of impurities [12].

Fig. 1 shows the TP FYNES data for vacuum and for three different hydrogen pressures (0.001, 0.01, and 0.1 Torr). Since the CO π intensity measured by fluorescence yield is proportional to coverage, the data are presented as CO coverage versus temperature, where the saturation CO coverage is 9.6×10^{14} molecules/cm^2 [13]. The vacuum experiment shows a sharp drop in the CO coverage beginning at 340 K, falling to zero by 480 K. This corresponds to the thermal desorption of CO from clean Pt(111) [1–4]. The inflection point corresponding to the maximum desorption rate occurs at 399 K. This is in agreement with previous TPD results [1–5], after accounting for the difference in heating rate. In the presence of 0.001 Torr hydrogen, the surface CO concentration remains constant until approximately 250 K and then begins to decrease with the point of maximum slope occurring at 389 K, 10 K lower than in the vacuum case. When the hydrogen pressure is increased to 0.01 Torr, the CO coverage decreases beginning at 130 K and continuing to 200 K, with an inflection point at 168 K, corresponding to the maximum rate of desorption for this low temperature displacement channel. At this hydrogen pressure, one fourth of the adlayer is lost through this low temperature channel lowering the surface CO coverage from $\theta_{CO} = 0.64$ ML to 0.5 ML. As the temperature increases, the CO coverage remains constant at $\theta_{CO} = 0.5$ ML until 275 K where it begins to decrease with an inflection point occurring at 386 K, 13 K lower than for the vacuum desorption case. When the hydrogen pressure is increased to 0.1 Torr, the thermal conductivity of the room-temperature hydrogen gas causes the temperature of the sample

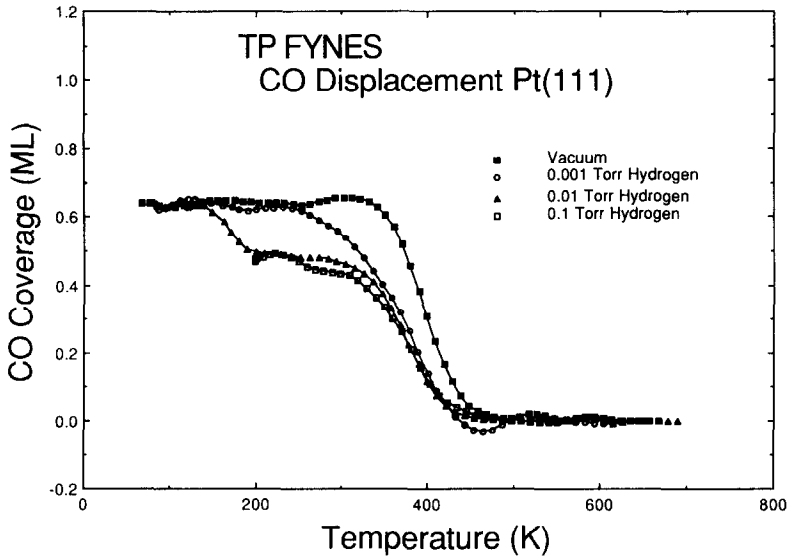

Fig. 1. Series of temperature-programmed fluorescence yield near-edge spectroscopy (TP FYNES) experiments illustrating the effect of hydrogen pressure on CO removal from the Pt(111) surface. Note the new CO removal process which is beginning at 130 K for hydrogen pressure above 10^{-2} Torr.

to increase to 200 K. Thus, the displacement of 0.14 ML of CO occurs during H_2 introduction and the starting coverage is $\theta_{CO} = 0.5$ ML. This curve for 0.1 Torr H_2 exhibits an inflection point at 386 K, as in the 0.01 Torr hydrogen case.

CO is more strongly chemisorbed on the Pt surface than hydrogen. The heat of adsorption for CO is 31 kcal/mol [1] compared to 19 kcal/mol for hydrogen on Pt(111) [14] in the limit of zero coverage. Nevertheless, the decrease in activation energy for CO removal in the presence of hydrogen at temperatures below the normal desorption temperature for CO from Pt(111) might be predicted based on simple energetic arguments. The heat of desorption of CO is strongly dependent on the surface coverage [1]. Hydrogen will displace more weakly bound CO under conditions where repulsive interactions in the adsorbed layer (CO(a)–CO(a), CO(a)–H(a)) reduce the desorption energy for CO to a value smaller than the heat of adsorption for hydrogen. We can approximate the activation energy for this hydrogen-induced low temperature CO desorption process with the method of Redhead [16]. Assuming a pre-exponential factor of 10^{13} s^{-1} and a reaction order of 1, we estimate that the activation energy for this process is 10.6 kcal/mol. The amount of CO displaced, from $\theta_{CO} = 0.64$ ML to 0.5 ML, corresponds to the amount present in the compressed layer. Thus, it appears that the displacement of CO by hydrogen at this low temperature corresponds to the removal of this compressed CO layer.

Based on the predominance of nearest-neighbor interactions, and using the 6–8 kcal/mol value for the CO–H repulsion energy estimated by Bernasek et al. [7], the lowering of the activation energy for desorption (displacement) from 26 to 10.6 kcal/mol suggests that two to three hydrogen atoms are involved in the displacement of each CO molecule. The displacement of the compressed CO layer occurs at 130 K. This also corresponds to the temperature for the hydrogen-induced onset of CO mobility reported by Lenz et al. [8]. Based on several structural studies in agreement with the results presented here, a CO coverage of 0.5 ML seems to have special stability in the presence of hydrogen. Lower coverages coalesce to form 0.5 ML local coverages in the presence of hydrogen [9], and higher coverages are removed at 130 K to form an overlayer containing 0.50 ML of CO. Taken together this data strongly supports our contention that the low temperature displacement process on Pt(111) is caused by destabilization of the compressed CO monolayer in the presence of hydrogen pressures above 0.01 Torr.

The low temperature displacement channel is not observed at 0.001 Torr hydrogen pressure but is seen at 0.01 Torr hydrogen. This pressure dependence of the appearance of the low temperature displacement mechanism can be understood based on surface coverage considerations. Changing the hydrogen pressure by a factor of 10 can change the hydrogen surface coverage up to a factor of 10. At the lower pressure (0.001 Torr), the surface concentration of hydrogen is evidently not high enough to cause the repulsive interactions necessary to keep the islands of compressed CO.

The temperature of the main desorption channel also shifts slightly to lower temperature in the presence of hydrogen in the 10^{-3} to 10^{-1} Torr range. From the position of the inflection point, we estimate that the activation energy for desorption has been reduced by 1 kcal/mol. Recent steady-state displacement experiments on the Pt(111) surface indicated that substantial further destabilization of CO coverages below 0.5 ML result from H_2 pressures above 10^{-1} Torr [18]. The small shift to lower desorption energy in the 10^{-3} to 10^{-1} Torr range may be due to increased population of the less strongly bound bridge-bonded CO at the expense of the on-top bonded CO molecules. This has been seen previously for coadsorbed CO and hydrogen [9] where large exposures of hydrogen caused the formation of islands of high local CO coverage with increased amounts of bridge-bonded CO relative to on-top CO. The 1 kcal/mol decrease is in good agreement with the energy difference reported for the two states of CO. An alternative explanation for the decrease in the activation energy for the desorption channel is a direct interaction between the coadsorbed hydrogen and CO [9].

The observation of a new displacement channel has been seen on the Ni(100) surface [12,16] as well as on the Pt(111) surface [17]. The displacement of CO on the Ni(100) surface preferentially

depletes the low temperature shoulder seen in the TPD spectrum [12,16]. This low temperature shoulder is associated with compressed CO having large repulsive interactions. The displacement process on both the Ni(100) and Pt(111) surfaces appears to remove the compressed repulsive CO from the surface. These observations on Pt(111) and Ni(100) indicate that displacement of a compressed CO adlayer may be a general result.

These results illustrate the importance of in-situ methods capable of performing kinetic experiments on well characterized adsorbed monolayers on single crystal surfaces. High coverages of coadsorbed species resulting from high pressures of the coadsorbate substantially modify surface coverages of chemisorbed species, may affect desorption activation energies, and may provide new kinetic pathways available for adsorbed species. These observations play an important role in understanding surface reactions which occur at high pressure.

In summary, we report the appearance of a new low temperature channel for displacement of CO from Pt(111) which is induced by high pressures of hydrogen. This process has an estimated activation energy of 10.6 kcal/mol. We believe that this low temperature process corresponds to removal of the compressed CO adlayer that forms above $\theta_{CO} > 0.5$ ML, which is weakly adsorbed and displaced by competing dissociative adsorption of hydrogen to form coadsorbed H(a). Repulsive interactions between H(a) and CO(a) keep the islands of compressed CO at $\theta_{CO} = 0.64$ ML until the overall CO coverage decreases to 0.5 ML. For $\theta_{CO} < 0.5$ ML, the activation energy for desorption is also lowered by ~ 1 kcal/mol in the 10^{-3} to 10^{-1} Torr H_2 pressure range. A CO coverage of 0.5 ML seems to have special stability in the presence of hydrogen based on these results and other coadsorption studies. FYNES has proven to be very useful for probing the interactions between coadsorbed species in-situ, and for making coverage measurements on a rapid time scale under high pressure conditions.

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