steady-state emission dissymmetry measurements, consider a sample that contains 10 mM of $Tb(dpa)_3^{3-}$ as the racemic probe luminophore and 10 μM of $Ru(phen)_3^{2+}$ quencher (for which η_Q is unknown). With use of the data given in Table I for this system, eq 35a may be evaluated to yield $\bar{g}_{em}(\lambda' = 543.7\text{ nm}) = -2.64 \times 10^{-2}\eta_Q$. The detection limit on the magnitude of $\bar{g}_{em}$ (for Tb* emission at 543.7 nm) is approximately 10^{-4}, and therefore, $|\eta_Q|$ values as small as 0.004 may be determined. This lower limit of $|\eta_Q|$ corresponds to 0.4% enantiomeric (or optical) purity, and in a 10 μM concentration of $Ru(phen)_3^{2+}$ quencher, it corresponds to a 0.04 μM *difference* in the concentrations of the Λ and Δ enantiomers. Applications of enantioselective quenching measurements to the determination of enantiomeric purities will be presented in greater detail in a future report.

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Registry No. $Tb(dpa)_3^{3-}$, 38682-37-0; $Eu(dpa)_3^{3-}$, 38721-36-7; $Ru(phen)_3^{2+}$, 22873-66-1; $Ru(bpy)_3^{2+}$, 15158-62-0; $Co(phen)_3^{3+}$, 18581-79-8; $Co(en)_3^{3+}$, 14878-41-2.

Displacement of CO Chemisorbed on Metals by Hydrogen

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Contribution from the Exxon Research and Engineering Company, Clinton Township, Annandale, New Jersey 08801. Received July 5, 1988

Abstract: Chemisorbed CO can be displaced from both the Ni(100) and Pt(111) surfaces by hydrogen in a temperature range where thermally activated desorption is substantially slower. This result is unexpected since hydrogen is adsorbed more weakly than CO on both the Pt and Ni surfaces. This paper describes a series of experiments that clearly establish that *displacement* occurs on these two surfaces. *Displacement* of a strongly adsorbed species by a more weakly adsorbed species is a different process than surface *exchange* where one isotopic form of an adsorbed species is exchanged by another. The kinetic results presented here indicated that the displacement reaction is thermally activated and that the thermal activation barrier is substantially smaller than the thermal activation energy required for CO desorption in the absence of hydrogen. The first-order dependence on surface CO coverage suggests that a single adsorbed CO molecule is involved in the rate-limiting step. The positive order (about 0.5) observed in hydrogen pressure suggests that the atomic hydrogen coverage plays a role in the rate-limiting step. No isotope effect is observed with deuterium substitution. He, Ne, Ar, N_2, and CH_4 do not cause displacement under the conditions studied (up to 10^{-3} Torr). Adsorbed hydrogen is rapidly displaced by CO as expected since hydrogen is more weakly adsorbed than CO. The reaction energetics and probabilities observed are consistent with substantial weakening of adsorbed CO by high coverages of coadsorbed hydrogen.

Carbon monoxide has been studied extensively on both the Ni(100)[1-4] and Pt(111)[5-9] surfaces. CO is adsorbed in terminal and bridge sites on both surfaces; heats of CO adsorption are 30 kcal/mol on the Ni(100) surface[4] and 31 kcal/mol on the Pt(111) surface at low coverages.[6-9] Increasing repulsive interactions between adsorbed CO molecules results in decreasing heats of adsorption with increasing CO coverage on both surfaces. Hydrogen has a heat of adsorption of 23 kcal/mol on the Ni(100) surface[10,11] and about 19 kcal/mol on the Pt(111) surface.[12] The interaction between coadsorbed hydrogen and CO is quite complex on the Ni(100) surface.[13-16] CO adsorbed on a hydrogen-presaturated surface desorbs at about 210 K, about 100 K lower than CO desorption from the clean surfaces; this suggests that a weakened CO–Ni interaction can occur in the presence of a large amount of coadsorbed hydrogen. A recent detailed study of coadsorbed CO and hydrogen on the Pt(111) surfaces indicates that only small repulsive interactions are observed at high coverage. This repulsion results in the formation of CO islands in the presence of hydrogen even for low CO coverages.[17]

Several authors have characterized isotopic exchange of CO and adsorbed atomic hydrogen on metal surfaces.[18,19] Several mechanisms have been proposed to rationalize isotopic exchange which involves weakly adsorbed surface intermediates induced by high adsorbed coverages or resonant energy transfer between incoming molecules and adsorbed molecules. Exchange mechanisms are generally not appropriate for the displacement reactions discussed in this paper.

These experiments were performed in a UHV system described in detail previously[18] equipped with facilities for multiple-mass temperature-programmed desorption, Auger electron spectroscopy

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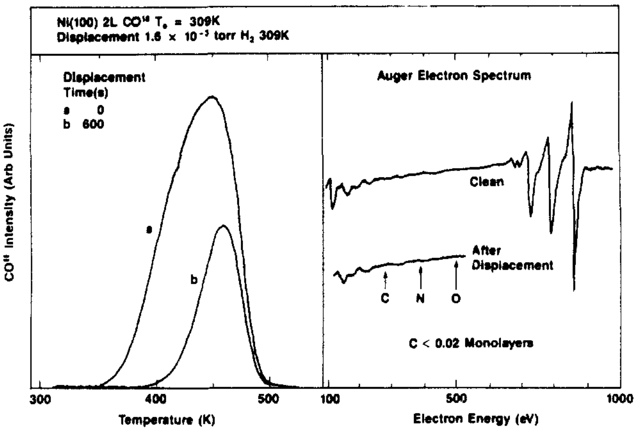

Figure 1. The CO desorption spectra in the left panel illustrates CO displacement by hydrogen. The upper spectrum is a reference taken after a 2-L exposure to CO at 309 K. The lower spectrum was taken after exposing the CO covered surface to 1.6 × 10^{-3} Torr of H_2 for 600 s. The Auger spectra in the right-hand panel illustrate the cleanliness of the sample before and after the displacement experiment.

(AES), and low-energy electron diffraction. Transient fluorescence yield near edge spectroscopy (FYNES) measurements were performed in this same system by adding a fluorescence yield (FY) detector system and entrance window assembly so that CO coverages can be directly determined in the presence of the displacing hydrogen gas. In situ CO coverages were determined during the FYNES experiments by measuring the intensity of the π resonance of CO at 284.5 eV at normal incidence after suitable control experiments were performed to ensure that the CO π intensity is directly proportional to CO coverage. The details of this FYNES experiment are being published separately.[19]

The data presented in Figure 1 illustrate the key aspects of a typical TPD displacement experiment. After the Ni(100) surface was exposed to 2 L of $C^{18}O$ at 309 K the reference $C^{18}O$ spectrum (0 time) shown in the left panel was obtained. After a second 2-L exposure at 309 K, the surface was exposed to 1.6 × 10^{-3} Torr of hydrogen for 600 s. During the hydrogen exposure 65% of the $C^{18}O$ was removed from the surface as shown by the second spectrum in the left panel. This spectrum was taken after a 4-min evacuation period to remove the gas-phase hydrogen from the system. Relative coverages were determined by comparing the integrated area with the reference spectrum obtained from a saturated surface at the same temperature. The Auger spectrum in the right panel illustrates that the surface was initially clean. After displacement, the surface remains clean. Only undisplaced CO and hydrogen remain on the surface. The CO desorption spectra from a series of displacement experiments at 309 K are shown in the left panel of Figure 2. The rate of displacement was determined by running a series of displacement reactions for different time periods and plotting the CO coverage as a function of displacement time. The right panel presents all the data from several series of displacement experiments at 309, 320, and 330 K. The increasing rate with increasing temperature indicates that the process is thermally activated. Note that the hydrogen displacement initially removes the low-temperature portion of the CO desorption peak. A transition in the CO displacement rate occurs in the same coverage range, suggesting that the first-order displacement reaction may depend on the energies or structure of the adsorbed CO overlayer. The thermal activation energies observed are about 8 ± 2 kcal/mol in the high-coverage region (the initial rate) and 12 ± 1 kcal/mol in the low-coverage region (less than 0.3 to 0.4 monolayer of CO).[20]

The TPD displacement experiments with the Pt(111) surface are illustrated in Figure 3. In this case the results are more complex since slow thermal desorption occurs in the temperature range where displacement rates can be easily observed for hydrogen pressures of 2 × 10^{-2} Torr. The lower right hand panel in Figure 3 illustrates a series of TPD spectra taken as a function of time to measure the rate of thermal desorption at 309 K. The first-order thermal desorption rate is indicated by the upper line in the upper panel. A series of TPD spectra taken following hydrogen exposure at 2 × 10^{-2} Torr are shown in the lower left hand panel of Figure 3. Adsorbed CO is removed about 5 times faster in the presence of hydrogen than in the absence of hydrogen, illustrating that displacement is occurring. Auger spectra and thermal desorption spectra taken following displacement indicate that only hydrogen and undisplaced CO remain on the surface following displacement. The apparent displacement rate has been approximately corrected for a thermal desorption contribution by assuming that the thermal desorption rate observed at each displacement temperature remains constant. A series of corrected displacement rates are shown in Figure 4 for 308, 318, 328, and

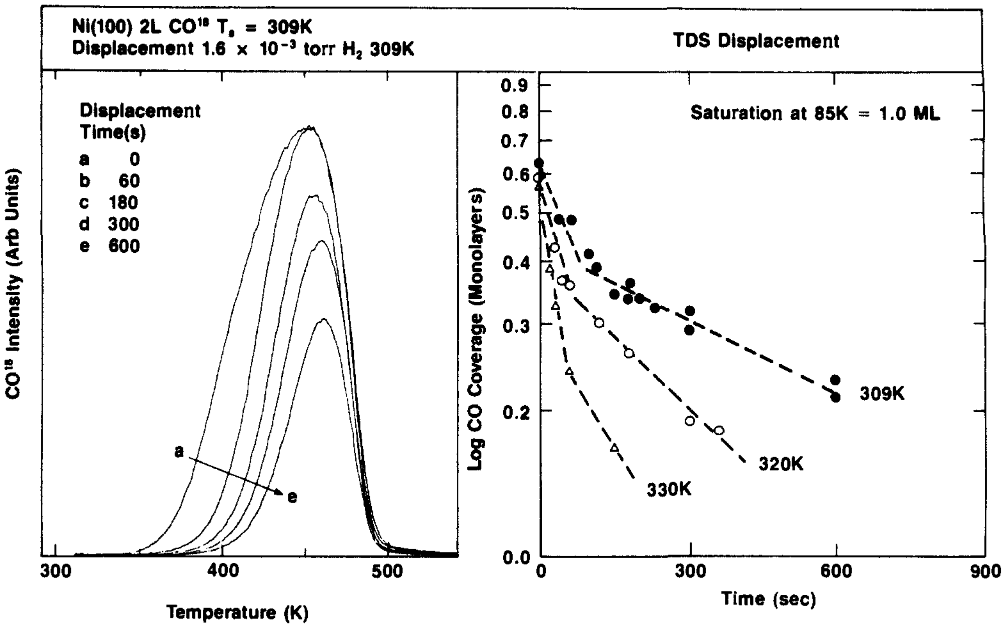

Figure 2. A representative series of CO TDS spectra following displacement by 1.6 × 10^{-3} Torr of H_2 for the indicated time periods. The right panel presents the logarithm of CO coverage versus displacement time. The two linear regions observed suggest that CO displacement is first order in CO coverage.

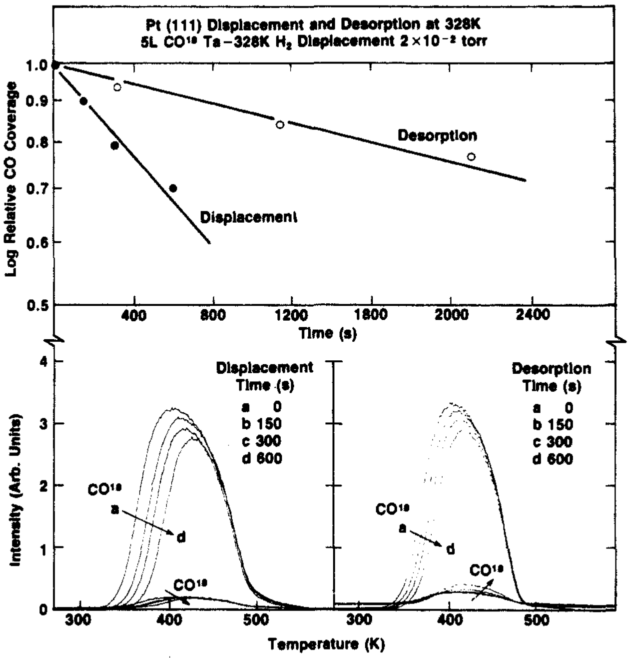

Figure 3. A representative series of CO TDS spectra from the Pt(111) surface illustrating CO thermal desorption at 309 K (lower right panel) and CO displacement by hydrogen at 309 K (lower left panel). The rates of desorption and displacement are compared directly in the semilog plot in the upper panel.

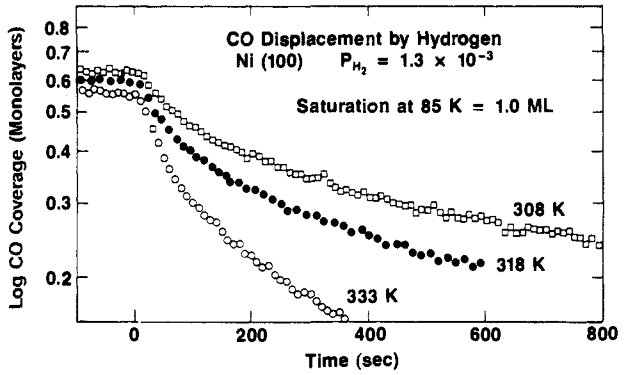

Figure 4. A set of in situ displacement experiments for the Ni(100) surface at 1.3 × 10^{-3} Torr of hydrogen pressure. These surface transients were determined with fluorescence yield near edge spectroscopy as a real time monitor of the CO displacement rate.

338 K. The approximate "corrected" displacement rate increases with increasing temperature, suggesting that the process is thermally activated. The data suggest that the displacement reaction is approximately first order in CO coverage since the corrected semilog plots are linear. However, caution must be exercised since the number of data points is fairly small and the correction for thermal desorption is substantial. Analysis of these data suggest that thermal activation energy for displacement is in the 15 to 20 kcal/mol range. Experiments at lower hydrogen pressure indicate that the displacement rate decreases with decreasing hydrogen pressure, indicating a positive order in hydrogen pressure. The approximate reaction probabilities at 10^{-2} Torr are 10^{-8} per incident H_2 molecule.

A set of real time in situ FYNES displacement experiments is illustrated in Figure 4 for a hydrogen pressure of 1.3 × 10^{-3} Torr on the Ni(100) surface. The details of this new method have been previously presented.[18] Reiterating briefly the intensity of carbon monoxide's π resonance at a 248.5 eV photon energy and normal incidence has been established as an accurate measure of the CO surface coverage. The displacement rates obtained indicate a first-order displacement rate in surface CO coverage with a break in the rate with decreasing CO coverage. Thermal activation energies obtained from these data indicate that the activation energy at high coverage is 7 ± 2 kcal/mol and the low coverage activation energy is 10 ± 2 kcal/mol. Note that the CO coverages reported here are on an absolute scale relative to a 85 K saturated surface since the FYNES technique can easily be used to establish absolute coverage scales.

The observation that CO adsorbed on two very different surfaces like Ni(100) and Pt(111) can be displaced by hydrogen suggests that the displacement process may be quite general. The observation that the kinetics on these two surfaces is quite similar further suggests that the displacement mechanism may even be similar. The reaction appears to be first order in CO coverage on both surfaces, indicating that a single CO may be involved in the rate-limiting step. The order in hydrogen partial pressure is positive on both surfaces, indicating that hydrogen participates in the rate-limiting step. The kinetic results on the Ni(100) surface suggest that the rate-limiting step depends on the surface atomic hydrogen coverage. The thermal activation energies observed for CO displacement are substantially smaller that the respective CO desorption energies from the clean metal surfaces.

The energetics and low reaction probabilities observed for these displacement reactions are consistent with a substantial weakening of the metal–CO bond in the presence of very high coverages of coadsorbed hydrogen. Several mechanistic experiments in progress may yield further information about the reaction mechanism. In order to account for the observed energetics the bond must be weakened substantially (~10–20 kcal/mol). However, only a small fraction of the adsorbed CO need to be affected to account for the relatively slow displacement rates observed (<10^{-2} monolayer/s). In this scenario, a CO molecule with a weakened surface bond would be thermally desorbed from the surface. The number of "weakened" CO molecules might depend on the steady state coverage of hydrogen atoms (ca. half order in P_{H_2}). On the Ni(100) surface, low temperature TPD and EELS results[3] indicate that coadsorbed hydrogen can substantially weaken the metal–CO bond; however, on the Pt(111) surface only small CO–H interactions have been observed.[17]

Registry No. CO, 630-08-0; Ni, 7440-02-0; Pt, 7440-06-4; H, 1333-74-0.