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Abstract. CO adsorbed on Pd{110} at half monolayer coverage and 300 K produces a weak $c(2 \times 2)$ structure, with an intense IR absorption band at 1914 cm^{-1}. Subsequent adsorption of NO causes a complete attenuation of this band, which is substituted by a sharp band appearing at 2060 cm^{-1}. This novel transformation is attributed to site transfer of the CO adsorbate from bridge sites, which are occupied by CO even at monolayer coverage, to linear sites, induced by NO in the adlayer. As NO is first adsorbed onto the surface, the CO band switches to 1937 cm^{-1}; this band is then also attenuated by further NO adsorption, when the 2060 cm^{-1} band develops. In contrast, adsorbed NO is relatively unperturbed by co-adsorbed CO. The site transfer is attributed to repulsive interactions between bridged NO and CO molecules sharing a surface Pd atom, and mutually attractive interactions between bridged NO and linearly adsorbed CO on neighbouring sites.

1. Introduction

Group VIII transition metals are active catalysts for NO reduction and thus are important in pollution control processes for combustion products. Of particular importance in these processes is the reaction of NO with CO. The details of the interaction between these molecules on transition metal surfaces are not well known or understood. Reflection–absorption infrared spectroscopy (RAIRS) can reveal details of the state of adsorbates, sites and details of interactions between adsorbed molecules. However, there have been relatively few high-resolution RAIRS studies of mixed molecular adsorption systems. Separately, CO and NO have been found to adsorb molecularly on Pd{110} [1]. A two-fold bridge site is the most stable site for both species on this surface, both at low coverages and at saturation. In this paper some new facts concerning the effect of CO and NO on each other on the Pd{110} surface are presented. In particular NO causes CO to occupy a type of site which it does not normally occupy on Pd{110}.

2. Experimental

Experiments were carried out in a newly constructed UHV chamber with an infra-red cell which is interfaced to a Mattson Cygnus 100 Fourier-transform spectrometer. The equipment possesses LEED, Auger, TDMS and crystal cleaning facilities. The system routinely reaches a pressure of 1×10^{-10} Torr. A detailed description of the instrument, built by VSW Scientific Instruments, is presented elsewhere [2].
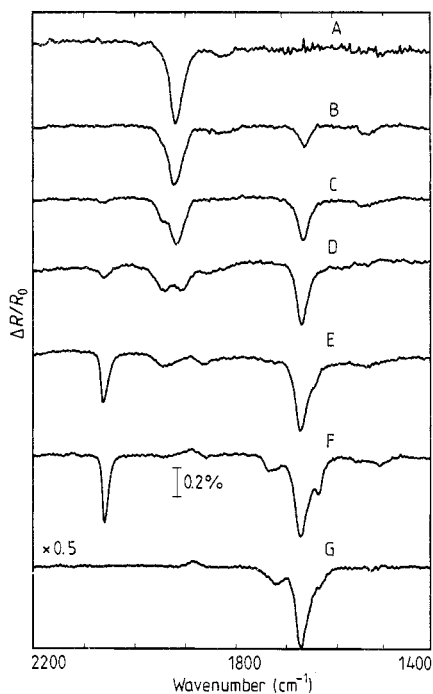
Figure 1. RAIRS spectra of NO–CO–Pd{110} at 300 K. A, 2.0 L CO; B, 1.0 L NO–2.0 L CO; C, 1.5 L NO–2.0 L CO; D, 2.0 L NO–2.0 L CO; E, 3.5 L NO–2.0 L CO; F, 5.5 L NO–2.0 L CO; G, 1×10^{-7} mbar NO.
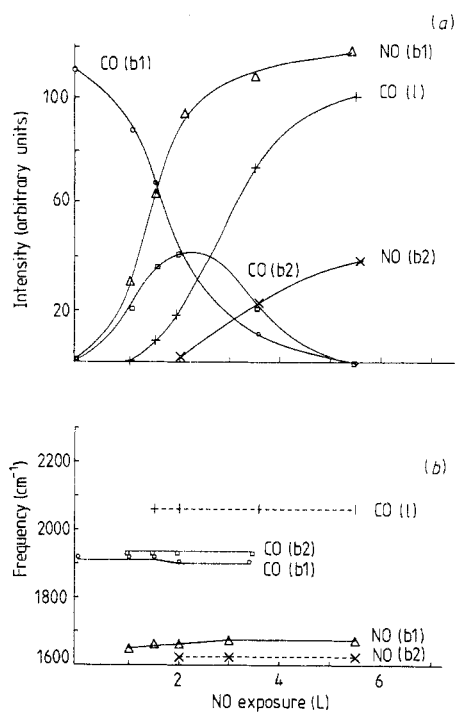
Figure 2. (*a*) Relative intensities as a function of NO exposure; (*b*) band frequencies as a function of NO exposure.

All RAIRS spectra are presented as ratios of single-beam spectra with the adsorbate present to that of the clean surface. Spectra were recorded at 4 cm^{-1} resolution with 100 scans co-added (accumulation time of 56 s). A narrow band mercury–cadmium telluride (MCT) detector, which allowed a spectral range of 4000–670 cm^{-1} to be accessed, was used and only plane polarised light detected.

3. Results

An IR spectrum obtained from CO on Pd{110} at 300 K after an exposure of 2 Langmuir (1 L $\equiv 10^{-6}$ Torr s), which produces a diffuse c(2 × 2) structure, is shown in figure 1, curve A. The strong band at 1914 cm^{-1} (hereafter CO(b1)), assigned to the ν_{CO} stretch of a bridge-bonded structure, has a full width at half-maximum, $\omega_{1/2}$, of 28 cm^{-1}. The weak band at 1825 cm^{-1} is tentatively attributed to adsorption at defect sites, or at multicentre sites.

The influence of successive doses of NO on the structure of the pre-adsorbed c(2 × 2)-CO are demonstrated by the spectra B–F shown in figure 1. For comparison, spectrum G is obtained from the *clean* Pd{110} surface in an ambient pressure of 1×10^{-7} mbar NO. Up to 1 L NO exposure on the c(2 × 2)-CO surface there is little effect on the CO band: a small high-frequency shoulder denotes the appearance of a new band at
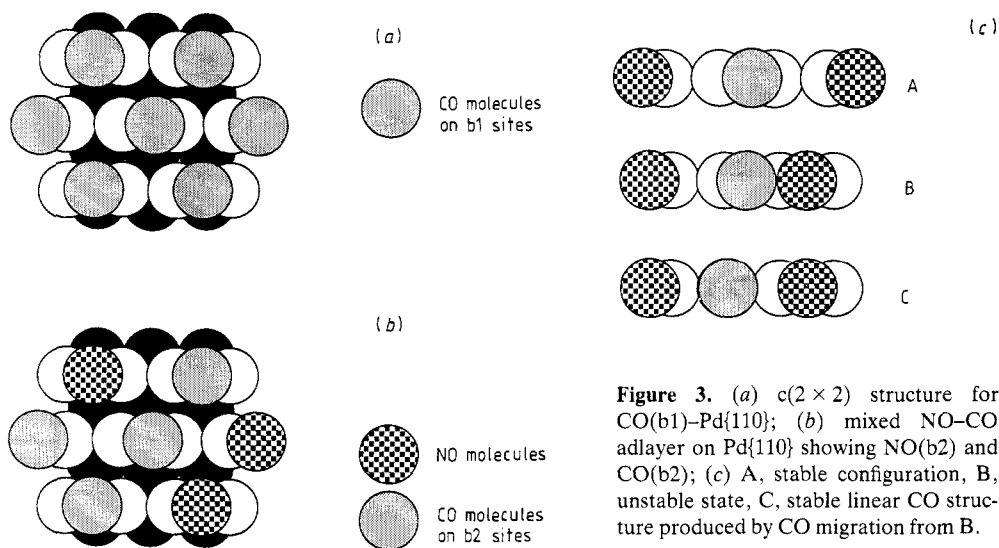
Figure 3. (*a*) c(2 × 2) structure for CO(b1)–Pd{110}; (*b*) mixed NO–CO adlayer on Pd{110} showing NO(b2) and CO(b2); (*c*) A, stable configuration, B, unstable state, C, stable linear CO structure produced by CO migration from B.

1937 cm^{-1} (hereafter CO(b2)) which develops to maximum intensity at an NO exposure of 2.0 L. Concomitant with its growth, the 1914 cm^{-1} band is attenuated and undergoes a small downward frequency shift as it does so, and, from 1.5 L NO exposure onwards, a new band appears at 2060 cm^{-1} (designated CO(l)). This band continues to grow with little change in frequency. After 5.5 L NO exposure it is the only CO band of any significant intensity left on the surface.

As the CO(b1) state is converted through CO(b2) to the CO(l) state, the main NO band develops at 1650 cm^{-1}, assigned to a bridge-bonded species (NO(b1)). There is also a minor band at 1525 cm^{-1}, which could be assigned to a bent or tilted species, or to NO at a multicentre site. The main NO band still dominates after 5.5 L NO exposure, with a small shift to 1661 cm^{-1}, and a medium intensity band appears at 1725 cm^{-1}, attributed to a linearly bonded NO species. These features are all present in the NO–Pd{110} spectrum G in figure 1. However, one feature of the spectrum has no analogue in the NO–Pd{110} spectrum: the sharp band at 1625 cm^{-1} (NO(b2)). This band grows in as the CO(l) band develops intensity, and appears to be directly linked to it. Gentle heating of the surface results in attenuation of *both* NO(b2) and CO(l) bands, confirming this.

The CO(l) band at 2061 cm^{-1} is significantly sharper ($\omega_{1/2} = 13$ cm^{-1}) than the original band at 1914 cm^{-1}, and in this respect is reminiscent of the 1990 cm^{-1} band observed at full monolayer CO coverage on Pd{110} ($\omega_{1/2} = 13$ cm^{-1}). Its sharpness suggests a homogeneous well ordered environment.

4. Discussion

To facilitate discussing the surface processes, the intensities and frequencies of the principle bands are plotted as a function of NO exposure in figure 2 and suggested adsorbate structures are given in figure 3. The c(2 × 2) LEED pattern has been assigned to a CO bridge structure as shown in figure 3(*a*). The LEED pattern is fairly diffuse and

the CO exposure is such as to cover only one-fourth to one-third of the surface with the double-spaced structure; the CO is distributed into imperfect, small islands.

The band intensity and frequency variations with NO exposure in figure 2 suggest the following co-adsorption behaviour.

(i) Low exposures to NO cause the appearance of new bands not observed at higher coverages when CO is adsorbed on Pd{110}, and the attenuation of features characteristic of CO–Pd{110}. We conclude that NO adsorption does not proceed solely into separate islands or domains, with compression of adsorbed CO into local high-density domains, but that at least part of the NO is intermingled with the CO domains. Initially, the effect is to perturb the bridged site from b1 to b2. NO adsorption into the CO domains also decreases the CO–CO dipole coupling in the b1 state. This is demonstrated by the small downward shift in frequency of CO(b1) during NO adsorption. The mixed CO–NO structure is illustrated in figure 3(*b*).

(ii) At higher NO exposures the CO(b1) and (b2) states both become unstable with respect to CO(l), and site-switching occurs. This is schematically illustrated in figure 3(*c*); as the NO coverage is increased, bridged NO and CO species would bond-share with surface Pd atoms (line 2); this is unstable and the structure therefore switches to that shown in line 3 of figure 3(*c*). The sharpness and symmetrical shape of the CO(l) band suggest a homogeneous local environment with co-adsorbed NO, such as that shown. The NO depicted in this structure is associated with the NO(b2) band at 1615 cm^{-1}, which is also a sharp band.

(iii) The major part of the NO structure at high NO + CO coverages is relatively unperturbed with respect to NO–Pd{110}, as shown by comparing spectra F and G in figure 1. This suggests a two-phase system, with islands of the mixed CO–NO phase (figure 3(*b*)) in equilibrium with islands of NO.

The interaction between NO and CO which produces the stabilisation of the linear species of CO (and the destabilisation of the bridged species) and the perturbed bridged NO species, NO(b2), may be rationalised in the following way. When NO or CO is bridge-bonded, the π orbitals (defined here as the p orbitals whose charge axis is perpendicuar to the molecular axis) make a greater contribution to metal bonding than ⁺he σ orbitals (defined here as the s orbitals and the p orbital parallel to the molecular axis). The opposite is true for linear, on-top bonding. This is borne out in Fenske–Hall calculations [3] for CO and NO interacting with small Pd and Ni clusters. Our calculations also show that the π orbitals of NO make a relatively larger contribution to the metal bonding than do the π orbitals of CO. This is expected because the energy levels for NO, particularly the $2\pi^*$ levels, are lower than those for CO. Experimentally this is verified by photo-emission and inverse photo-emission spectra for CO and NO adsorbed on Ni [4].

At saturation coverage of CO the surface stoichiometry is 1 : 1, CO : Pd. Each surface Pd atom is therefore bond-sharing to two bridged CO molecules. Because there is a net negative charge on each CO molecule, the dipole field mutually destablises adjacent CO molecules. However, where there is direct competition to form bridge bonds by CO and NO to the same Pd atom, the Pd–N orbitals, being lower in energy, will be more substantially filled than the Pd–C orbitals, and the CO would be more substantially destabilised. In addition, linearly bonded CO, which is dominantly σ-bonded, may be expected to involve a net charge flow to the substrate: this state is therefore stabilised by the dipole field of the neighbouring bridge-bonded NO. This is mutual stabilisation:

experimentally, this is manifest though a shift in the NO frequency from 1660 cm^{-1} to 1615 cm^{-1} (the b2 NO state).

The interaction of a p–π orbital of N or C with a surface atom in the bridge structure reduces the metal density of states near the Fermi level both because the bonding interaction lowers some levels and because the electron repulsion terms from the added electron density in the bond to the surface atom raises some levels above the Fermi level. This decreased density of states reduces the ability of a surface atom to form a second bridge bond. The effect of N is greater than the effect of C because the N has greater electron charge in the p–π bond to the metal.

5. Conclusion

The effect of NO and CO on each other for the Pd{110} system examined here is distinctly different from effects found on Pt, Rh or Ru. Whereas for NO–CO–Pd{110} linear CO all desorbs on warming to 340 K to leave only NO on the surface, Pt(111) CO causes the NO to desorb at a lower temperature [5] and in thermal desorption work with Pt(111) and Pt(110) CO causes adsorbed NO to shift from one desorption state to another [6]. RAIRS spectra of CO–NO–Pt(100) show that CO and NO cause small shifts in the infrared frequencies of the pre-adsorbed species and NO causes CO to be more tightly held [7]. On Rh NO dissociates on heating, while no direct evidence for NO dissociation on Pd{110} was found [8, 9]. On Ru(001) CO causes a change in the ratio of bridged to linear NO states, which have similar binding energies [10]. For Pd{110} NO destablises the main bonding mode of CO (a bridge state) and stabilises a linear CO state which becomes the only stable state. With only CO present the linear state is negligibly occupied even at saturation coverage (CO:Pd = 1:1). The rationale given here for the destabilisation effect on Pd does not apply to Pt and Ru because on those metals the linear CO state is the most stable state even on the clean surface.

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