

## Phase Separation in Mixed K–NO Chemisorbed Layers on Co{10 $\bar{1}$ 0}

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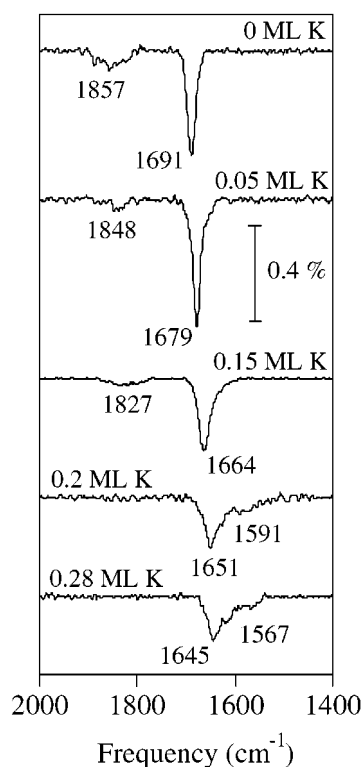
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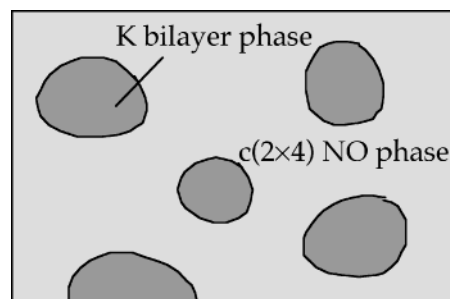
The action of alkali metals and their oxides as promoters for many catalytic reactions has been known for almost a century.<sup>1</sup> Alkali promotion of carbon monoxide reactivity has received particular attention<sup>2,3</sup> and a range of spectroscopic, calorimetric, and structural techniques have been used to examine the effect.<sup>2–7</sup> The adsorption heat is increased by up to a factor of 2.5 with coadsorbed K.<sup>6</sup> The strength of this interaction stabilizes formation of a mixed adlayer at all coverages. The interaction of NO with coadsorbed K has also received some attention, on Ag, Pt, and Rh surfaces, with general agreement that the dissociation rate of NO is promoted by coadsorbed K.<sup>8</sup> Here we report the results of a detailed reflection–absorption infrared (RAIR) spectroscopy study of the coadsorption of NO and K on Co{10 $\bar{1}$ 0}, in which we find that at high NO coverages there is complete phase separation between NO and K on the surface, in contradiction to all expectations. The NO–K interaction is more repulsive than the NO–NO interaction under these conditions, with important implications for the bonding of NO to metal surfaces.<sup>9</sup>

The ultrahigh vacuum experimental system interfaced with an FTIR spectrometer, and general procedure, have been described previously.<sup>5,10</sup> Potassium was deposited from a well outgassed SAES getter source onto a Co{10 $\bar{1}$ 0} crystal which was maintained at 300 K. The RAIR spectra were recorded over a spectral range of 800–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> (100 scans coadded) with the crystal at 100 K.

When NO is adsorbed on a clean Co{10 $\bar{1}$ 0} surface at 100 K, non-dissociative adsorption takes place, with three different adsorption sites occupied at low coverages.<sup>10</sup> These are a 3-fold coordinate site, with N–O stretching frequency at 1443 cm<sup>-1</sup>, a bridging site (1643 cm<sup>-1</sup>), and an atop site (1797 cm<sup>-1</sup>). However, as the coverage increases to saturation at 0.5 monolayers (ML), the bridge-bonded species becomes dominant, with the band shifted up to 1690 cm<sup>-1</sup>, and a sharp *c*(2 × 4) LEED pattern is formed. With 0.33 ML K or more no NO was taken up by the surface, but with lower precoverages the NO uptake is significant. In the presence of preadsorbed K, at low NO coverages we find a very marked influence on the adsorption state of NO,<sup>11</sup> but at saturation the spectrum is dominated by a single band due to bridge-bonded NO, at ~1660 cm<sup>-1</sup>, shown in Figure 1. This band is within the range of frequencies for NO adsorbed on a K-free surface. As on the K-free surface,<sup>10</sup> a sharp *c*(2 × 4) LEED pattern is formed at NO saturation; its appearance during NO exposure coincides with the development of the band at ~1660 cm<sup>-1</sup>. We



**Figure 1.** RAIR spectra for saturation exposures of NO on Co{10 $\bar{1}$ 0} at 100 K with various preadsorbed K coverages.



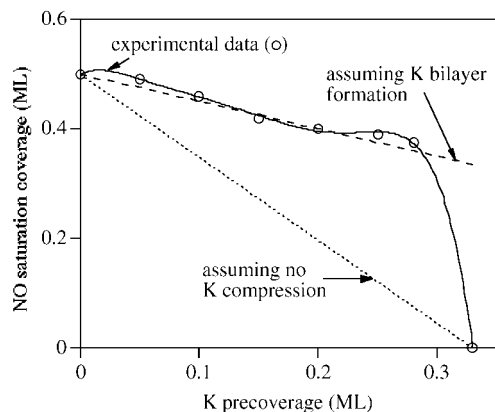
**Figure 2.** Schematic representation for a phase separation between NO and K adsorbates.

note that the small band at ~1850 cm<sup>-1</sup> (Figure 1) is also observed on K-free Co{10 $\bar{1}$ 0} at 100 K after saturation with NO, and has been attributed to coadsorption with a small amount of the dissociation products of NO, particularly O adatoms.<sup>10</sup> As we show in detail elsewhere,<sup>11</sup> K has no significant influence on the rate of NO dissociation on this surface.

The frequency of the dominant NO band shifts upward *uniformly* as the amount of preadsorbed K decreases, all the way to zero precoverage. K has a minimal influence on this band. However, a new band is clearly observed as a sideband on the dominant band for K coverages above 0.15 ML, at 1591 to 1567 cm<sup>-1</sup>. We discuss this sideband later.

At this stage we tentatively conclude that at saturation NO coverage there is a *complete* phase separation between NO and K domains, as schematically illustrated in Figure 2. The frequency range of the bridge band and the *c*(2 × 4) LEED pattern are both clear signatures for NO adsorption on clean Co{10 $\bar{1}$ 0} at 100 K. The frequency shift observed as a function of K precoverage (Figure 1) is attributable to decreased dipole coupling as the area of the surface covered by NO is decreased. The effective area of the surface blocked by preadsorbed K from NO adsorption can

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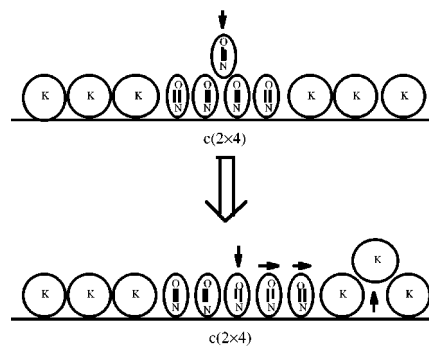
**Figure 3.** The dependence of the saturation NO coverage, in ML, on the K precoverage.

be semiquantitatively estimated by using the integral areas of the infrared bands as a measure of relative coverages, and the band intensity at NO saturation on the clean surface, when the coverage is 0.5 ML, to yield the absolute coverage. The NO saturation coverage determined in this way is shown as a function of K precoverage in Figure 3.

We see that the NO coverage only falls from 0.5 to 0.4 ML with  $\Theta_K = 0.28$  ML, and then abruptly to zero at  $\Theta_K = 0.33$  ML. The linear fall anticipated from a straightforward K blocking model (dotted line, Figure 3) is not a relevant description of the behavior. The implication, shown by the dashed line, is that the K adlayer is compressed by the growing NO-rich areas into islands in which the local K coverage reaches  $\sim 1.1$  ML. Thus, for all K precoverages, NO saturation squeezes the K adatoms into islands where the local coverage is twice that required to saturate the first K layer, reported as 0.58 ML.<sup>12</sup> This is a unique and surprising result.

At a K precoverage of 0.33 ML (or higher) NO adsorption is totally precluded. We ascribe this to a kinetic, and not a thermodynamic, factor. At this coverage the K adlayer has been described as a distributed vacancy structure which is relatively homogeneous.<sup>12</sup> The trapping probability for gaseous NO into a precursor state<sup>13</sup> onto this structure must be very low. On the other hand, when the K coverage is only slightly lower, 0.28 ML, a large NO uptake ( $\sim 0.38$  ML) is readily achieved. Clearly, once NO chemisorption takes place into vacant double (bridge) sites, further adsorption can take place by: (i) efficient trapping into an extrinsic precursor state over the filled NO sites, (ii) empty site generation within the NO island by forcing the K layer into a bilayer structure, and (iii) transition of the precursor into the chemisorbed state. This process is schematically illustrated in Figure 4.

At first sight the energetics of the bilayer formation process indicated in Figure 4 may appear to preclude it from happening. The process is, however, driven by the exothermicity of the transfer from physisorbed to chemisorbed NO, for which we estimate an energy change  $\leq 100$  kJ mol<sup>-1</sup>. The transfer of K adatoms from first layer to second layer is only slightly endothermic, provided that the first layer is close to saturation. Thus,



**Figure 4.** A schematic representation of the formation of a K bilayer with K precoverages less than 0.33 ML.

second layer desorption takes place at  $\sim 300$  K,<sup>12</sup> and desorption from the saturated first layer starts at  $\sim 400$  K, suggesting an energy change of  $\leq 40$  kJ mol<sup>-1</sup> for the transfer of K from first to second layer. Overall, the process is exothermic by  $\sim -60$  kJ mol<sup>-1</sup>. The process is thermodynamically feasible, since associated entropy changes are negligible.

The sideband appearing at 1591–1567 cm<sup>-1</sup> (Figure 1) can now be assigned to NO molecules adsorbed at the NO/K boundary, the interaction causing a downward shift in the N–O stretch frequency. In turn, this assignment provides a means of obtaining a rough estimate of the K island dimensions (Figure 2). Assuming the islands to be circular, density  $n$  cm<sup>-2</sup>, radius  $r$ , and a local K coverage in the islands of  $\Theta_K^L$ , then the K coverage averaged over the whole surface is  $\Theta_K = n\pi r^2\Theta_K^L$  and the amount of NO at the boundaries averaged over the whole surface is  $\Theta_{NO}^{boun} = 2\pi r n d N_o$ , where  $d$  is the effective NO molecular diameter ( $\sim 0.3$  nm) and  $N_o$  is the surface density of Co atoms ( $9.71 \times 10^{14}$  cm<sup>-2</sup>).  $\Theta_{NO}^{boun}$  may be estimated from the relative integrated intensities of the  $\sim 1550$  and the  $\sim 1660$  cm<sup>-1</sup> bands. This yields, for  $0.2 \leq \Theta_K \leq 0.28$  ML,  $6 \times 10^{12} \geq n \geq 5 \times 10^{12}$  islands cm<sup>-2</sup>, and  $1.1 \leq r \leq 1.4$  nm. These islands should therefore be readily imaged by AFM or STM techniques. We note that CO and NO chemisorption cause localized magnetic quenching of surface Co or Ni atoms,<sup>14</sup> but K has little effect on these local magnetic moments.<sup>15</sup> A locally resolving magnetic imaging technique should also therefore be capable of resolving the K islands.

Very surprisingly, the result demonstrates that there is no enhancement in the NO adsorption heat in the mixed NO/K phase compared with the pure NO phase. This contrasts very sharply, for example, with the very large calorimetrically measured increase in CO adsorption heat on Ni{100} in the presence of K<sup>6</sup> and the detailed understanding of this phenomenon achieved by DFT calculations.<sup>16</sup> Further calculations, for NO/K coadsorption, should reveal key differences between NO and CO chemisorption.

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