Bonding and thermal stability of CO on potassium-doped Co(1010)

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Abstract. Adsorption of CO upon a Co{10$\bar{1}$0}-supported potassium c(2 × 2) overlayer results in the formation of a co-adsorbed layer of K:CO stoichiometry 1:1. The CO remains molecular with its bond axis along or close to the surface normal in the c(2 × 2)(K + CO) monolayer. A model resembling an ionic K/CO 'surface compound' is suggested on the basis of ARUPS and TDS data for this structure.

Despite extensive use of cobalt as a Fischer–Tropsch catalyst, few adsorption studies of well characterised single-crystal surfaces have been reported. As part of a programme of study of H_2 and CO adsorption and surface reactions on cobalt metallic and bimetallic surfaces, we have examined the interaction of CO and K on Co{10$\bar{1}$0}. The experiments were performed in a VG Scientific ADES-400 electron spectrometer. The sample was cleaned by prolonged argon-ion bombardment and annealing at 650 K. The adsorption/desorption behaviour of CO on the Co{1010}(1 × 1) surface was in accord with previous reports [1, 2]. Potassium was evaporated from a well degassed line-of-sight SAES getters source.

Potassium adsorption at 300 K was characterised by LEED AES and secondary-electron-yield measurements. Close to completion of the first K atomic layer, indicated by a clear point of inflection in both the potassium LMM and substrate Auger signal versus deposition time plots, a c(2 × 2) overlayer ($\theta_K = 0.5$ ML) was formed.

The aforementioned c(2 × 2) overlayer was utilised for CO co-adsorption experiments. Adsorption of CO to saturation coverage resulted in formation of a c(2 × 2) monolayer. The overlayer-induced LEED beams were intense and sharp. No ordered or disordered intermediate phases were observed during CO uptake. Utilising the absolute K coverage of 0.5 ML, the ratio of the integrated area of the potassium ($2p_{3/2}$) and oxygen (1s) core levels, corrected for analyser transmission and cross section effects, indicated a K:CO stoichiometry of 1:1. TDS spectra from the c(2 × 2)(K + CO) overlayer indicated a shift of the CO desorption peak maximum to higher temperature and a large decrease in the peak width with respect to that of CO on clean Co{10$\bar{1}$0}. In agreement with the large body of literature available on K/CO co-adsorption studies, CO is found to be more strongly bound to a K-doped surface.

ARUPS measurements ($h\nu = 21.22$ and 40.82 eV) reveal that CO retains its molecular integrity in the presence of potassium. No significant thermally induced dissociation
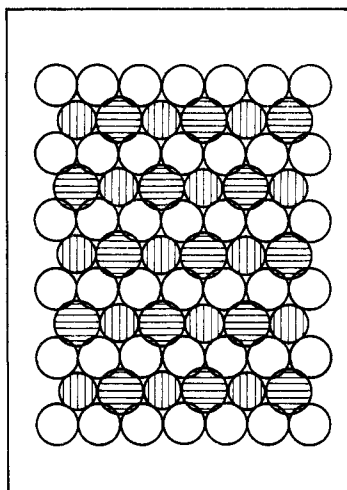
Figure 1. A possible model of the c(2 × 2)(K + CO) overlayer. Large hatched spheres represent potassium adatoms drawn at their ionic radius. Shifting of the c(2 × 2) CO or K sublattice in the [0001] direction towards the close-packed Co rows maintains the c(2 × 2) periodicity and yields other possible overlayer models. Unambiguous determination of the bonding sites of K and CO requires a full structural study, for example by LEED.

($T < 650$ K) was observed. A comparison of the intensity variation from the CO 4σ-orbital at normal emission ($h\nu = 40.82$ eV) as a function of angle of incidence of the photon beam for both the CO-saturated clean surface ((2×1) glide line phase) and the co-adsorbed monolayer indicated a strong suppression of emission for predominantly s-polarised light. This behaviour is in keeping with a CO species chemisorbed with its bond axis along or close to the surface normal, retaining a C_2 rotation axis as an effective symmetry element despite the presence of co-adsorbed potassium. Potassium-induced changes in the CO bonding, including a shift to higher binding energy of 0.5 eV of the 4σ-level and an intense CO-related emission at a binding energy of 6.4 eV in He I spectra (corresponding spectra of CO on clean Co$\{10\bar{1}0\}$ indicate only weak emission at 6.4 eV due to the tail of the overlapping $5\sigma/1\pi$-emissions) have also been observed.

The results summarised here, along with data for lower potassium coverage, show that although there is a strong local K/CO interaction stabilising CO on the surface, no significant dissociation occurs under ultra-high-vacuum conditions. Although it is not possible to draw unambiguous conclusions regarding the exact nature of the K/CO interaction, we do propose a tentative model of the K/CO overlayer. The model illustrated in figure 1 is in keeping with the 1:1 stoichiometry, LEED observations and the conclusion that CO molecules are upright. Clearly, the density of the proposed overlayer requires that the effective radius of the potassium adatom is substantially reduced from its metallic value, implying charge transfer from potassium (4s) to CO ($2\pi^*$) and also implying anisotropic direct interactions between the CO π-levels and the pre-adsorbed K. The proposed model resembles an ionic 'surface compound', as recently suggested by Pirug and Bonzel (see [3] and references therein) for the K/CO system on Pt$\{111\}$ at high K coverages.

References

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