

Structural analyses of Cs + CO coadsorbed on Ru(0001)

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(Received 26 October 1994)

Adsorption of CO onto a Ru(0001) surface precovered with Cs (coverage 0.25) leads to the formation of two distinct (2×2) -Cs-CO phases with one and two CO molecules in the unit cell. Structural analysis by means of low-energy electron diffraction reveals that the Cs atoms remain in on-top positions, while the CO molecules are located in threefold sites, contrary to the occupation of on-top sites if adsorbed alone. This effect of site switching is attributed to the enhanced electron density of the Ru substrate leading to more pronounced back donation in bonding the CO molecules.

Coadsorption of alkali-metal atoms and carbon monoxide on transition-metal surfaces is considered to model the promoter action of related systems in heterogeneous catalysis and has hence been widely investigated in the past.¹ Bonding of CO is discussed in terms of a donor-acceptor mechanism in analogy to carbonyl compounds, in which the highest occupied orbital of the ligand (5σ) coupled to empty states of the metal, while back donation of electronic charge from the metal into the empty $2\pi^*$ orbital strengthens the M-CO bond but simultaneously weakens the C-O bond.² The bond of adsorbed alkali-metal (AM) atoms is strongly polarized with the negative charge pushed toward the substrate metal.^{3,4} According to a simple electrostatic model (which is corroborated by corresponding quantum-mechanical calculations^{5,6}), the presence of a neighboring adsorbed AM atom enhances the back-donation effect. Evidence for such a mechanism stems from application of various surface spectroscopic techniques,⁷⁻⁹ while the stabilization of the surface bond of both species was demonstrated by thermal-desorption spectroscopy¹⁰ (TDS) and even more directly in recent calorimetric measurements.¹¹ In the latter study, it was concluded that part of the energy gain is due to direct electrostatic interaction between the AM atoms and the CO molecules—a view that was supported theoretically by an electrostatic model¹² as well as experimentally in investigations on the Ru-Cs vibration by high-resolution electron-energy-loss spectroscopy (HREELS).¹³

The frequently observed pronounced redshift of the C-O stretch vibration is usually attributed to the enhanced back donation,^{1,10,14,15} although also direct interaction associated with the formation of surface compounds has been suggested.¹⁶ Since the frequency of the C-O vibration is strongly affected by the symmetry of the adsorption site, a change of this site has, however, to be taken into account as an additional complication. Obviously, detailed structural information is needed in order to reach a coherent picture of this important type of coadsorption systems. We present here the first complete structural analyses exemplified with Cs and CO coadsorbed on a Ru(0001) surface,³³ employing the technique of low-energy electron diffraction (LEED).

It turns out that the coadsorbates are intimately mixed and are both bonded to the substrate, which, in part, also mediates the mutual interactions. Most remarkably, in

the presence of the Cs atoms the CO molecules switch their adsorption sites from on top to threefold coordination, presumably as a consequence of the enhanced back donation.

The experiments were conducted in a UHV chamber at a base pressure of 6×10^{-11} mbar equipped with facilities for TDS, Auger electron spectroscopy, and for measuring work-function changes. Details about the experimental setup and sample preparation can be found in Ref. 17. LEED intensity curves were measured at a sample temperature of 50 K at normal incidence. In the experiments to be described, a Cs- (2×2) overlayer was formed by evaporation of Cs from a commercial dispenser source (SAES Getters, Inc.), which was subsequently exposed to CO. The CO coverages were determined by the integrated TD signal and calibrated with the TDS data determined from the optimum CO- $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure, which was assumed to have a coverage of $\frac{1}{3}$; the coverage Θ is defined as the ratio of the number of adsorbate particles to top-layer Ru atoms.

The pronounced interaction between Cs and CO is demonstrated by comparison of the CO-TD spectra for a saturated CO overlayer on Ru(0001) ($T = 300$ K) and the Cs-TD spectrum for a Cs- (2×2) covered Ru(0001) surface with the data from the mixed Cs-CO phase ($\Theta_{\text{Cs}} = 0.25$, $\Theta_{\text{CO}} = 0.50$).¹⁸ Apart from thermal stabilization of *both* species, the most striking feature is the coincident desorption of Cs and CO at about 700 K reflecting a strong Cs-CO interaction. Similar effects were reported for related systems such as K-CO-Ru(0001) (Ref. 7) or K-CO-Cu(110).¹⁶ An “auto-catalytic” reaction process may account for this effect: With the release of CO from the surface, the cause of the stabilization of Cs also ceases (and vice versa), leading to the simultaneous desorption of Cs and CO. The high-temperature tail of the Cs-TD spectrum is not affected because at those temperatures all CO molecules have already gone. This phenomenon demonstrates that both kinds of adsorbates are intimately intermixed rather than present in separate domains.

From the saturation coverage of CO for the mixed Cs-CO phase of 0.5 and the persistence of the (2×2) structure observed in LEED throughout CO deposition, it follows that the (2×2) unit cell may contain up to two CO molecules. This raises the question whether it is possible to prepare an ordered Cs-CO- (2×2) structure containing

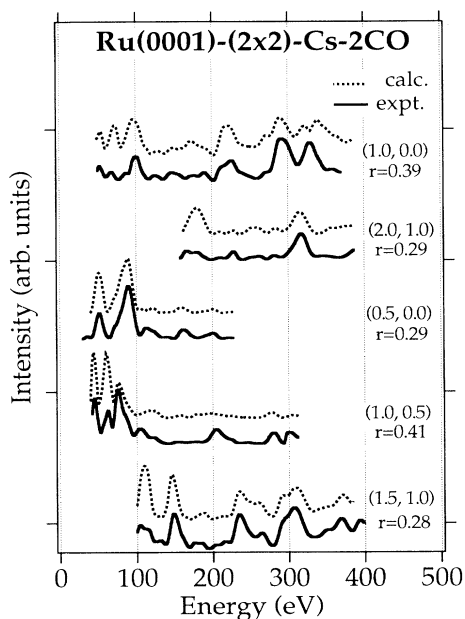


FIG. 1. Comparison between the experimental (solid curves) and calculated (dashed curves) LEED I/V spectra from a representative selection of beams. The Pendry r factor for each individual beam is indicated.

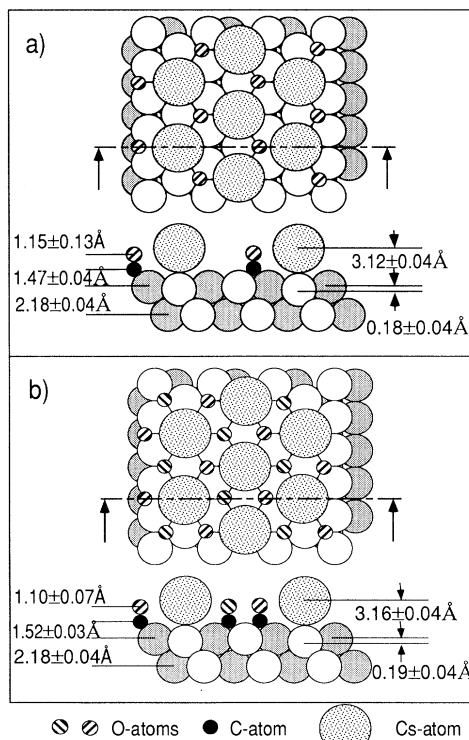


FIG. 2. Structural models and parameters for the best-fit arrangement of the (a) Cs-1CO-Ru(0001)-(2 \times 2) and (b) Cs-2CO-Ru(0001)-(2 \times 2) phase. The best agreement between experiment and theory is reached for Cs atoms in on-top positions and the CO molecules in threefold sites (hcp for the Cs-1CO phase: $r_{DE}=0.36$, $r_P=0.39$; and hcp+fcc for the Cs-2CO phase: $r_{DE}=0.36$, $r_P=0.37$).

increase in ionicity of the Cs atoms overcompensates the dipole moment with opposite sign introduced by the CO molecules. HREELS experiments with Cs adsorbed on Ru(0001) revealed that the Ru-Cs vibration is accessible in the spectra at low coverages, but becomes screened in the Cs-(2 \times 2) phase in which the adlayer is metallic due to pronounced Cs-Cs interactions. Subsequent admission of CO, however, causes the Ru-Cs electron loss to reappear because of the buffering effect under discussion.¹³

If compared with a pure CO adlayer, the energy of the C-O stretching vibration in the Cs-CO coadsorption phases is drastically lowered, from 252 to 203 meV,¹³ which is in line with similar observations with related systems.^{1,14,15} In contrast to previous general practice, a conclusive assignment of the C-O vibration to a certain type of adsorption site is questionable.²⁷ However, if this band is shifted under the influence of a coadsorbate, it is usually assumed that such an effect is not due to a change of the geometry of the adsorption site, but solely reflects the alteration of the local electronic properties. This definitely does not hold for the present system, in which the CO molecules are displaced from on-top to threefold sites by the presence of alkali-metal atoms. Surface sites with higher coordination (bridge or threefold, etc.) are generally characterized by lower values for the C-O vibration energy, reflecting a higher degree of back donation of electronic charge into the $2\pi^*$ orbitals. σ donation, on the other hand, is favored by adsorption in on-top positions, and hence the competition between both effects will be decisive for the energetically lowest adsorption geometry. If the degree of back donation is enhanced by the presence of coadsorbed alkali-metal atoms, a switching from on top to higher-coordinated adsorption sites becomes plausible, just as found for the present system.

It is expected that this conclusion should be of more general relevance, and there are indeed several examples supporting this idea: With CO adsorbed on Pt(111), HREELS data suggested that the presence of K suppressed the population of on-top sites while the relative occupation of bridge (or even threefold?) sites increased.²⁸ With adsorption of N_2 , σ coupling is known to be more important than with adsorption of CO,²⁹ and consequently in the system N_2 /Ru(0001) again on-top positions are occupied.³⁰ Chemisorbed O atoms have the opposite effect than alkali-metal atoms on the electronic properties of a surface, i.e., they are expected to enhance the σ -donor contribution. On the O(2 \times 2)-precovered Ru(0001) surface, subsequently adsorbed N_2 molecules might occupy either on-top or fcc-threefold sites, but they are only located in on-top positions as concluded from a recent LEED analysis.³¹ More dramatically, with a (2 \times 1)-O adlayer adsorbed on Ru(0001) it was recently found that additional uptake of CO even causes a rearrangement of the O adatoms, by which sterically favorable on-top sites are created onto which the CO molecules are bound.³²

In conclusion, the geometries of both the Cs-1CO-(2 \times 2) and Cs-2CO-(2 \times 2)-Ru(0001) phases are characterized by on-top adsorption of the Cs atoms and by threefold coordination of the CO molecules to the substrate.

only one CO molecule in the unit cell. The LEED structure analyses, described below, indeed provide evidence for the additional existence of such a low CO-coverage phase. The latter is formed by exposure to 25 L of CO, while the Cs-2CO-(2×2) phase was obtained by saturation of the Cs-(2×2)-covered sample at 300 K with about 200 L exposure. In passing, we note that electron-stimulated decomposition of CO has not been observed for these mixed Cs-CO phases in contrast to observations of the pure CO-($\sqrt{3}\times\sqrt{3}$) phase.

The operation of strong attractive interactions between coadsorbed CO and Cs is also reflected by the following experiment: For coverages $\Theta_{\text{Cs}} < 0.17$ adsorbed Cs forms liquidlike structures, which are characterized by ringlike features in the LEED pattern rather than superstructures with long-range order.¹⁷ If a surface covered with $\Theta_{\text{Cs}} < 0.12$ is subsequently exposed to CO, again a well-ordered 2×2 phase is formed. This is reflected by the pronounced increase of intensity at the (1/2,0) spot position with CO exposure¹⁸ leading to I/V curves, which are similar to those of the perfect Cs-CO-(2×2) phase. Obviously, the addition of CO causes formation of islands from the mixed Cs-CO phase due to strong electrostatic Cs-CO attractions overcompensating the Cs-Cs dipole-dipole repulsions.

The dynamical LEED-intensity calculations were carried out using a real and reciprocal space-symmetrized code,¹⁹ employing up to nine spin-averaged phase shifts for Ru, C, O, and Cs. The atomic-scattering matrices were corrected for the effects of dynamical and static disorder using a constant Debye temperature of 450 K for Ru and CO, and of 80 K for Cs. The agreement between experimental and theoretical I/V data was quantified by the r_{DE} factor introduced by Kleinle *et al.*²⁰ and by Pendry's r factor r_P .²¹ The structural analyses were performed in two stages. First, a wide-range grid search over the Cs-Ru layer spacing and the C-Ru layer spacing was carried out for various Cs and CO adsorption sites; at this stage, the C-O bondlength was set to be 1.15 Å. Several local r -factor minima were found and served then as starting geometries for structural refinement using a nonlinear least-square optimization procedure with respect to both r_P and r_{DE} .^{22,23}

For the structural analyses of both Cs-CO-(2×2) phases, a total number of 450 data points, giving a cumulative energy range of 2300 eV in three integer and eight fractional-order beams, was used for comparison with the experiment. Cs was allowed to occupy different high-symmetry sites, namely hcp, fcc, on-top, and bridge sites. A saturated Cs($\sqrt{3}\times\sqrt{3}$) adlayer was found to virtually completely inhibit CO adsorption, while in the present case with the more open Cs(2×2) layer, the thermal stability of adsorbed CO was even enhanced with respect to that on a pure Ru(0001) surface. It is hence obvious that CO adsorbs on the Ru substrate *between* the Cs atoms, rather than *on* the latter. The CO molecules were placed in those high-symmetry adsorption sites, which were left for steric reasons.

In the pure Cs-(2×2) phase, the adsorbed Cs atoms are located in on-top sites which, assisted by a slight buckling of the substrate, provide better mutual screening than

threefold sites, which would be preferred in the absence of such interactions between the adsorbates, and which are actually also occupied with the Cs-($\sqrt{3}\times\sqrt{3}$)R30° phase.¹⁷ Obviously, for Cs atoms the energetic differences between different adsorption sites are very small so that site switching may readily occur. This conclusion is corroborated by calculations for the related system K/Al(111).⁴

CO adsorbed on Ru(0001) forms, on the other hand, a ($\sqrt{3}\times\sqrt{3}$)R30° structure with coverage $\theta_{\text{CO}} = 0.33$ where again on-top sites are occupied. If these are to be maintained in the Cs+CO coadsorbate phases, the Cs atoms would necessarily have to be displaced from their on-top positions onto threefold sites. Corresponding LEED calculations reveal, however, only very poor agreement with experiment and r factors > 0.6 . It turns out that the actual structures are characterized by site switching of the adsorbed CO molecules rather than of the Cs atoms: The best agreement between experiment and theory is reached for Cs atoms in on-top positions and the CO molecules in threefold sites (hcp for the Cs-1CO phase: $r_{\text{DE}} = 0.36$, $r_P = 0.39$, and hcp+fcc for the Cs-2CO phase: $r_{\text{DE}} = 0.36$, $r_P = 0.37$). A selection of representative I/V curves corresponding to the best-fit structure of the Cs-2CO phase is shown in Fig. 1. Hard-sphere models of the optimum structures including the best-fit structural parameters are displayed in Fig. 2. The Ru-Cs layer spacing with 3.14 ± 0.04 Å is equal to the value found for the pure Cs-(2×2) system: 3.15 ± 0.08 Å. The C-O bond length in the Cs-1CO phase (1.15 ± 0.13) might have slightly increased if compared with the pure CO-($\sqrt{3}\times\sqrt{3}$) phase (1.10 ± 0.07 Å).²⁴ However, the uncertainty of 0.13 Å is too large to allow firm conclusions on such an effect. For the high-coverage phase, the C-O bond length apparently shortens again resulting in the same C-O bond distance as with the pure CO-($\sqrt{3}\times\sqrt{3}$) surface.²⁴ An increase in C-O bond length by 0.12 Å as claimed for a similar system, CO-Na-Pt(111) (Ref. 25) can clearly be ruled out for the high-coverage Cs-CO phase.

With the Cs-2CO-2×2 phase, the two CO molecules within the unit cell exhibit only rather small mutual separation of 3.0 Å. Detailed analysis of the structural parameters of polynuclear carbonyl cluster compounds revealed that such a value indeed marks the closest distance between two parallel CO ligands.²⁶

The structural properties derived here offer a natural explanation to other observations made with the same or related systems and corroborate some previously drawn conclusions: Coadsorption of Cs and CO initiates partial transfer of electronic charge (mediated through the Ru substrate) from Cs to CO by which effect a "saltlike" configuration is reached. The electrostatic attractive interaction is governed by the Madelung energy¹² leading to the observed island formation even at low total Cs coverages as well as to strengthening of the adsorption bond of both components as reflected by TDS and calorimetric¹¹ data. The CO molecules, by buffering the Cs-Cs interactions, cause the Cs adlayer to change its electronic character from metallic to ionic: The observed decrease of the work function upon exposing a Cs-(2×2)-Ru(0001) surface to CO (Ref. 18) indicates that the

The adsorption site for CO hence changes from on top for the pure CO- $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure to hcp and fcc sites under the influence of coadsorbed alkali-metal atoms. This effect is attributed to the dominance of π back donation over σ donation in CO bonding under the altered situation of increased electronic charge density at the substrate surface. The effective electron transfer from Cs to CO mediated by the Ru substrate causes the forma-

tion of a saltlike mixed lattice in which strong lateral interactions between Cs and CO are essentially electrostatic in nature. This effect accounts for the pronounced stabilization of the coadsorption layer as well as for the growth of islands at low coverages.

The authors are grateful to K. Jacobi for fruitful discussions.

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