



Coadsorption of Cs with O and CO on Ru(0001): relation between structural and electronic properties

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Abstract

We have studied structural, electronic and energetical aspects of ordered overlayers which were prepared by depositing Cs and CO on the (2×2) -O-precovered Ru(0001) surface. This ternary system may serve as a model system to study the Cs promoted CO oxidation reaction over Ru(0001). The electronic properties of the Cs subsystem, in particular the delocalized character of the Cs-6s state, are only little affected by the (2×2) -O overlayer, while the addition of CO leads to a demetallization of the Cs overlayer. The ternary system reveals two metastable configurations (besides a stable one) which are produced at low sample temperatures. In the first one, Cs and CO have changed their adsorption sites if compared to the stable ternary (2×2) -O+Cs+CO phase, i.e. Cs sits in hcp and CO in on-top position. Our studies emphasize the importance of the threefold hollow position of CO to strengthen the back bonding of CO. The surface structure of the second metastable (ternary) arrangement is still elusive. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since most of the heterogeneously catalyzed reactions proceed via the so-called *Langmuir-Hinshelwood mechanism*, i.e., the reactants have to adsorb on the catalyst's surface prior to the actual reaction step, the investigation of coadsorption systems is a promising starting point to advance our understanding of the microscopic mechanisms involved in such reactions [1]. A prototypical reaction in surface chemistry is the CO oxidation reaction over platinum-group metal surfaces. While molecular oxygen adsorbs dissociatively, CO adsorbs molecularly. The actual catalytic step in the CO oxidation reaction is the dissociation of the strongly bonded oxygen molecule, creating an atomic oxygen species adsorbed on the metal surface. The activation barrier for the catalyzed CO oxidation reaction is then essentially given by the O–metal bonding. Unfortunately, high dissociation probability of oxygen goes hand in hand with a strong metal–O bonding. Therefore, the highest activity for CO oxidation has been found for Pd and Pt, for which the metal–O bonding is not very strong and still the dissociative sticking coefficient for molecular oxygen is moderately high.

However, even if a metal surface is not very active in terms of a particular reaction, its activity can be markedly improved by using additives and promoters. Among the most prominent promoters are the alkali metals which serve as electronic modifiers [2]. For instance, it has been observed that under UHV conditions the Ru(0001) surface is not active at all in oxidizing CO. However, small quantities of Cs, which were added to the surface, increased the reaction probability by several orders of magnitude [3,27]. Fig. 1 shows the CO₂ flux leaving the surface when a (2 × 2)–Cs + CO covered Ru(0001) surface is exposed to molecular oxygen [3]. A dramatic increase in the reactivity of Ru(0001) was also found when the CO oxidation reaction takes place under oxidizing conditions which are able to maintain a (1 × 1)–O overlayer at the surface [4,28]. In this high O coverage phase, oxygen is notably less strongly bound (by about 0.8 eV) [5] than in the low O coverage (2 × 2) phase and therefore may explain the experimentally observed high activity. It turned out from preliminary molecular beam experiments that the Cs precovered surface is even more active than the (1 × 1)–O-precovered surface towards CO oxidation [27].

Accordingly, the CO oxidation over Ru(0001) offers the unique and interesting opportunity to follow structural and electronic properties upon tuning the surface from the non-active into the active state by simply adding Cs atoms to the Ru(0001) surface. The primary goal of this project is to unravel the particular mechanisms of the surface reaction and how the promoter enters this scenario. Some recent progress toward this goal will be discussed in the following.

2. Results and discussion

We report on the atomic geometries and how structural parameters change when the three species Cs, CO, and O are brought together onto the Ru(0001)

surface. The structural results are compared with those of the corresponding binary and single adsorption systems in order to gain a deeper insight into the interactions involved in the ternary system. Besides the atomic geometries, we investigated the electronic properties of this ternary and the associated binary systems. We employed the *metastable deexcitation spectroscopy* (MDS), a technique which is very sensitive to s-electron density and which mainly probes the electronic structure of the outermost surface layer since the deexcitation process takes place 5–10 Å in front of the surface. This allows us to monitor the electronic changes of the Cs subsystem upon coadsorption of O and CO. The experimental findings are substantiated and supplemented by results obtained from *density functional theory* (DFT) calculations using the supercell approach. The calculation scheme allows for the relaxation of both the electrons and atoms. The optimum structures found by DFT calculations are compared with those found by *low energy electron diffraction* (LEED) crystallography. For technical details concerning our MDS [6,7] and LEED [8] experiments and our ab-initio calculations [9,29] the reader is referred to recent publications.

The single and binary systems, i.e., O-Ru(0001) [5,10,11,30], CO-Ru(0001) [12,31], Cs-Ru(0001) [8], Cs-O-Ru(0001) [11,13–16], CO+O-Ru(0001) [17,18], and Cs-CO-Ru(0001) [19] have already been investigated and the corresponding surface structures were determined by quantitative LEED [5,8,10–19,30] and DFT calculations [9]. We found that the ternary system O+Cs+CO is able to form an

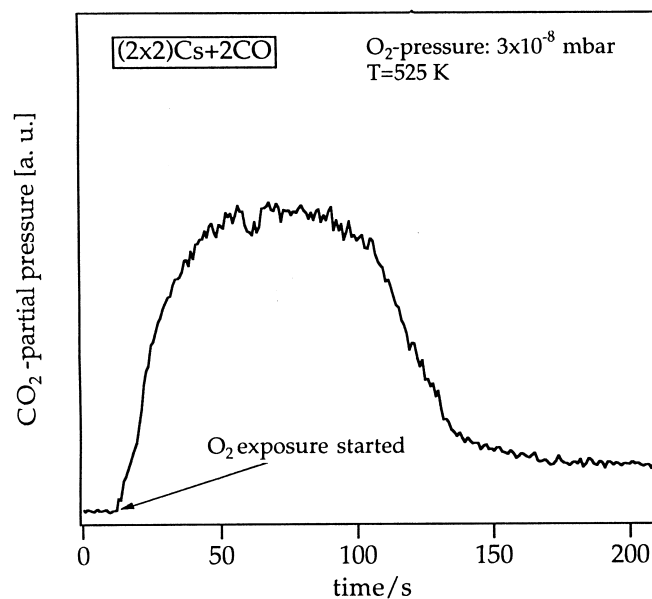


Fig. 1. The flux of CO₂ molecules from the Ru(0001)–(2 × 2)–Cs+CO surface which is produced by back filling the UHV chamber with molecular oxygen of 3×10^{-8} mbar at a sample temperature of 525 K [3].

ordered (2×2) overlayer on Ru(0001), thus being accessible to quantitative LEED investigations. Since all other binary systems also form (2×2) overlayers, we restrict the following discussions to systems with (2×2) periodicity. In Table 1, the corresponding overlayers on the Ru(0001) surface are compiled and their structural characteristics are summarized. Let us first discuss the (2×2) -O+Cs overlayer which is presumably a metastable phase [22,32,33] as it is only observed if the oxygen is exposed first. From Table 1, we see that neither the Ru–Cs nor the Ru–O bond lengths are appreciably affected by the presence of the other coadsorbed species (compare the values with those of the pure phases). Quite in contrast, exposing the surface first to Cs and then to oxygen leads to a wealth of ordered structures whose phase diagram is dominated by a surface oxide species of CsO₂ [13]. For the case of $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Cs + O [14] and $(\sqrt{3} \times \sqrt{3})R30^\circ$ -3Cs + 2O [15] structural results have demonstrated that the Cs radius decreases (by 0.05–0.10 Å), while the O radius increases (by 0.15–0.18 Å). This has been taken as evidence for a charge transfer taking place from the Cs atom to the O atom. As shown in Fig. 2, the He*–MD spectrum of (2×2) -O+Cs is very similar to that of the pure (2×2) -Cs. The emission of electrons with highest kinetic energy originates from the Cs-6 s level excited by singlet (20.3 eV) and triplet (19.1 eV) He* atoms. The majority ($\geq 90\%$) of impinging metastable He* atoms is originally in the singlet state (He*(2¹S)), and still the MD spectra show a strong Cs-6 s emission at a kinetic energy related to the He* triplet state. Therefore, an

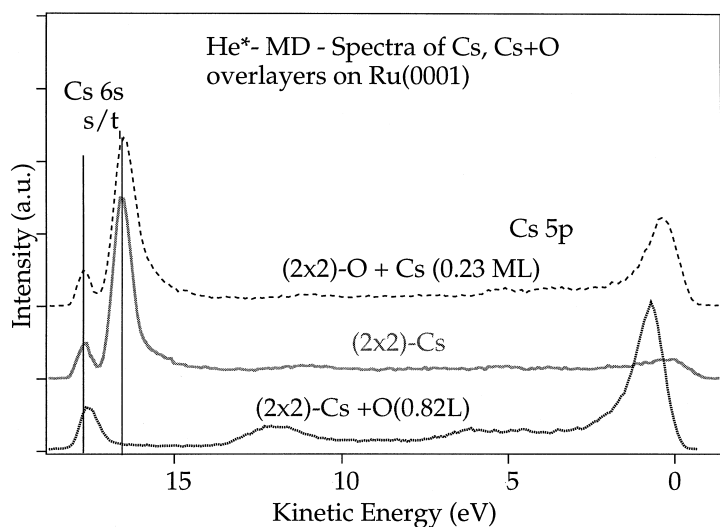


Fig. 2. He*–MD spectra from a Ru(0001)- (2×2) -Cs surface in comparison with those taken from surfaces where oxygen is postadsorbed to the Ru(0001)- (2×2) -Cs surface and where Cs is postadsorbed on a (2×2) -O-precovered Ru(0001) surface. The MD spectra of a (2×2) -Cs overlayer on the clean and the (2×2) -O-precovered Ru(0001) surface are virtually identical, indicating that the delocalized character of Cs-6 s state is preserved.

Table 1
Structural results of ordered overlayers of O, CO, Cs on Ru(0001) and their binary and ternary coadsorption systems. The coadsorption systems are prepared by starting from the Ru(0001)-(2 × 2)-O surface. Except for the ($\sqrt{3} \times \sqrt{3}$)R30°-CO overlayer, all overlayers are (2 × 2). Note that in particular the ternary system is able to form metastable phases (MS). The bond lengths of Ru-Cs, Ru-CO, Ru-O, C-O are given in Å. The structural parameters were determined by both LEED and DFT. The first number corresponds to LEED, the second (after the slash) to DFT results.

System on Ru(0001)	Site: Cs	Site: O	Site: CO	Ru-Cs	Ru-CO	Ru-O	C-O	Ref.
(2 × 2)-O	-	hcp	-	-	-	2.03 ± 0.06/2.07	-	[10]/[5]
($\sqrt{3} \times \sqrt{3}$)R30°-CO	-	-	On-top	-	1.93 ± 0.04/1.93	-	1.15 ± 0.05/1.16	[31]/[9]
(2 × 2)-Cs	On-top	-	-	3.25 ± 0.08/3.16	-	-	-	[14]/[9]
(2 × 2)O+Cs (MS)	On-top	hcp	-	3.16 ± 0.15/3.10	-	2.04 ± 0.07/2.13	-	[33]
(2 × 2)-O+CO	-	hcp	On-top	-	1.98 ± 0.08/1.95	2.06 ± 0.08/2.07	1.15 ± 0.06/1.15	[17]/[9]
(2 × 2)-Cs+1CO	On-top	-	hcp	3.30 ± 0.10/3.25	2.14 ± 0.06/2.14	-	1.15 ± 0.13/1.26	[19]/[20]
(2 × 2)-Cs+2CO	On-top	-	hcp + fcc	3.35 ± 0.10/3.37	2.18 ± 0.06/2.17	-	1.15 ± 0.13/1.23	[19]/[20]
(2 × 2)-O+CO+Cs	On-top	hcp	fcc	3.28 ± 0.12/3.21	2.13 ± 0.06/2.16	2.16 ± 0.08/2.14	1.20 ± 0.06/1.24	[16]/[21]
(2 × 2)-O+CO+Cs (MS)	fcc	hcp	On-top	3.70 ± 0.12/3.63	1.93 ± 0.04/2.00	2.07 ± 0.08/2.11	1.16 ± 0.06/1.21	[26]

efficient singlet-triplet conversion has been operative prior to the actual deexcitation process, reflecting the presence of a rather metallic Cs overlayer with delocalized Cs-6 s states [23].

By contrast, the Cs+O overlayer, which is prepared by first dosing Cs (0.25 μl) and then 0.8 l oxygen (which corresponds to an O coverage of about 0.25 μl), shows a much weaker and single Cs-6 s state (excited by the He singlet state) which is indicative of a demetallized Cs overlayer, owing to a charge transfer from Cs to O.

Fig. 3 depicts the asymptotic density above the Cs atoms (DFT results) in different structures on the Ru(0001) surface. Here we should focus on the region 5–8 Å above the Cs layer, since this is the region where the quenching process of metastable He* atoms occurs. It can be clearly seen that the asymptotic density of the (2 × 2)–Cs and the (2 × 2)–O+Cs are indeed very similar, while the asymptotic density is markedly reduced for the case of (2 × 2)–Cs+CO. Both results are fully compatible with the MDS data shown in Fig. 2.

We will continue our discussion with the (2 × 2)–Cs+CO coadsorption system. The chemisorption of a CO molecule on a transition metal surface is described by

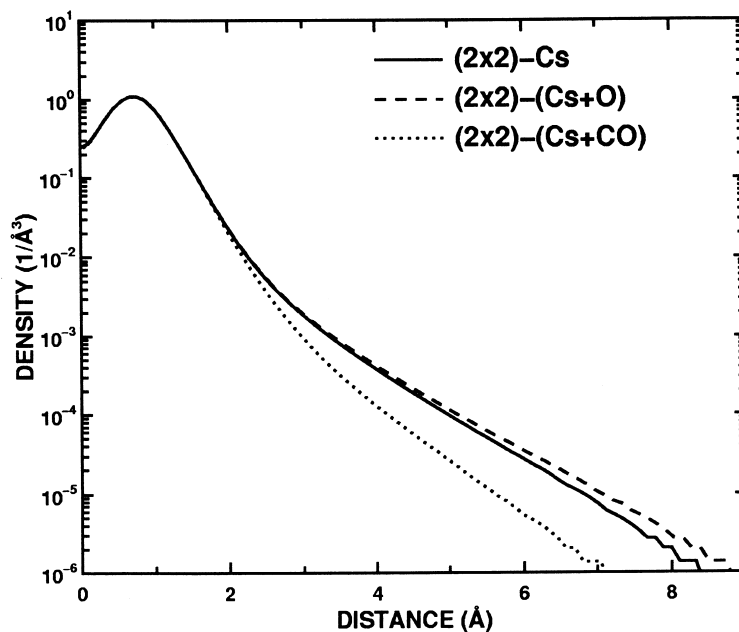


Fig. 3. The asymptotic density above the Cs atom is shown for various structures, (2 × 2)–Cs, (2 × 2)–O+Cs, (2 × 2)–Cs+CO on the Ru(0001) surface as obtained by DFT calculations. The asymptotic density of coadsorbed CO is shown with short-dashed and the structure with coadsorbed O with dot-dashed lines.

a concerted donor-acceptor mechanism called the Blyholder model [24]. The 5σ -CO *molecular orbital* (MO) donates part of its electronic charge to band states of the metal substrate, exhibiting σ symmetry (σ donation, σ bonding). Note that the filled 5σ state (HOMO) acts as a donor state, while the $2\pi^*$ MO (LUMO) serves as an acceptor state. The process of σ donation is counterbalanced by back donation of charge density with π symmetry from the metal to the $2\pi^*$ MO of the CO. The back donation strengthens the metal–CO bond (back bonding) and concomitantly weakens the internal C–O bond.

The relative importance of σ donation and TT back donation for the CO-metal bonding determines the CO adsorption site and therefore the minimum in the potential energy surface of this adsorption system. From simple symmetry arguments, the overlap of CO $2\pi^*$ orbitals with metal d_π orbitals works best in high-coordinated adsorption sites, while the overlap between CO- 5σ and metal d_σ orbitals is maximized for on-top adsorption.

The direct interaction between Cs and CO is very weak, as demonstrated by the inhibition of CO chemisorption on multilayers of Cs on Ru(0001) for temperatures as low as 100 K. However, when Cs and CO are coadsorbed onto a Ru(0001) surface, they interact strongly with each other, as evidenced by the effect of thermal stabilization of each adsorbate by several 100 K [25]. A recent LEED analysis of this coadsorbate system revealed that the Cs atoms remain in on-top position, while the CO molecules switch from on-top (clean Ru(0001) surface) to a threefold coordinated hcp site (Cs precovered surface). The presence of coadsorbed alkali-metal atoms enhances the electron charge density at the surface, and in order to improve the ability of back bonding, the CO molecules change their adsorption sites from on-top to high-coordination positions. A substrate mediated charge transfer from Cs to CO is also verified by the asymptotic electron density above the Cs atoms (cf Fig. 3). Our DFT studies indicate that the coadsorbate phase with Cs on-top and CO in hcp position is by 0.44 eV energetically more favorable than a phase with CO in on-top and Cs in fcc position. In addition, the DFT calculations show that the internal C–O bonding is by almost 0.1 Å longer than in the pure CO phase (cf Table 1) which is consistent with stronger back bonding of CO. In the Cs+CO phase both CO and Cs are substantially stabilized upon coadsorption, as reflected by a mixing energy of 0.85 eV. It is interesting to note that a similar stabilization in the (2×2) -O+Cs phase is much smaller as quantified by a mixing energy of only 0.37 eV. The mixing energy is defined as the total energy of the coadsorbate system minus the total energies of the corresponding single-adsorbate subsystems. A positive value of the mixing energy indicates that island formation of the coadsorbates is energetically favorable.

If, on the other hand, CO is coadsorbed with O, the on-top position is more favorable than the threefold hollow site, although, in principle, both the on-top and the threefold hollow sites are sterically accessible on a (2×2) -O-precovered Ru(0001). Again, the electronic situation at the surface is responsible for the actual CO adsorption site. Coadsorbed O weakens the back bonding of CO to the Ru(0001) surface since both O and CO are competing for the same electron

density, and consequently, on-top adsorption (where Π back donation is less pronounced) is preferred. Consistent with this picture, the C–O bond length with 1.15 Å (Table 1: DFT) is even shorter than in the pure CO phase. It should be noted that the mixing energy for this binary system is 0.18 eV, i.e., smaller than for the Cs+CO system but still attractive. Note, however, that CO molecules aggregate into $(\sqrt{3} \times \sqrt{3})R30^\circ$ –CO islands at low coverages. Since the $(\sqrt{3} \times \sqrt{3})R30^\circ$ –CO is by 80 meV [9] more favorable than the (2×2) –CO, the actual mixing energy in the (2×2) –O+CO phase is reduced to only 0.10 eV.

In conclusion, a general feature of CO adsorption has been captured [1]: oxygen coadsorption pushes the delicate energy balance of σ bonding and π back-bonding between the CO molecule and the transition metal surface towards on-top adsorption, while Cs coadsorption drives the CO adsorption into threefold hollow position.

Let us now move on with the ternary system (2×2) –O+Cs+CO on Ru(0001). Besides the stable phase, this ternary system is able to stabilize two metastable configurations (cf Table 1) [26], which can only be prepared at low temperatures (about 100 K). Their formation depends critically on the adsorption sequence of Cs and CO on the (2×2) –O-precovered Ru(0001) surface. The species (Cs or CO) which is adsorbed first will sit in on-top position, while the other species will reside in threefold hollow sites. The stable phase is always formed at room temperature irrespective of the adsorption sequence of Cs and CO. The stable phase can also be prepared by annealing any of the two metastable phases to room temperature.

The energetically stable configuration is characterized by Cs sitting in on-top and CO in fcc hollow position, although according to DFT calculations the metastable phase with CO sitting in on-top and Cs in fcc sites is only 0.11 eV less favorable. The metastable phase is synthesized by exposing 0.25 μl Cs to the (2×2) –O+CO overlayer at 100 K. This energy difference is much smaller than for the Cs+CO system without oxygen (0.44 eV). Apparently, the strongly donating character of the surface due to the presence of Cs is partly compensated by the coadsorbed (electron accepting) oxygen atoms. This simple view is also corroborated by the DFT-calculated C–O bond length of 1.24 Å (cf Table 1) for the stable (2×2) –O+Cs+CO phase which is smaller than in the (2×2) –Cs+CO phase (1.26 Å) but larger than that in the pure CO phase (1.16 Å). The O–Ru bond length in the stable (2×2) –O+Cs+CO phase is increased by 0.01 Å (DFT) as compared to the value found in the (2×2) –O+Cs overlayer. Generally, the trends in the variation of bond lengths are better estimated by DFT calculations than by LEED analyses due to the large error bars in LEED. However, the absolute values for the structural parameters found by DFT may be less reliable, since several (crude) approximations enter these calculations. As these approximations in the DFT calculations are the same for the various systems, the relative changes in the bond lengths are expected to be reliable. Once the metastable phase has been created, gentle annealing to 300 K transforms it into the stable configuration as followed by LEED.

The (2×2) LEED pattern disappeared completely at about 220 K and it

reappeared at 300 K. Corresponding LEED IV curves of these two overlayers are significantly different as judged from a Pendry r -factor of 0.35 between the two experimental data sets. The structural characteristics of both overlayers are compared in Fig. 4. The geometries were determined independently by employing the technique of LEED and DFT calculations. The agreement of the structural parameters obtained by LEED and DFT is striking. To study the electronic structure of these surfaces, MD spectra of the metastable phase and its transformation towards the stable phase were measured (cf Fig. 5). In particular, the emission from the Cs-6s state changes with increasing annealing temperature; note that after each annealing cycle the sample was cooled again to 120 K, at which temperature all MD spectra were taken. The metastable phase is characterized by a strong singlet peak and a weak triplet shoulder. Upon annealing the sample, this triplet shoulder disappeared gradually and disappeared completely at 297 K.

This electronic change is accompanied by the temperature-induced structural changes of the surface arrangement as mentioned before. Obviously, the metastable $(2 \times 2)\text{-O} + \text{CO} + \text{Cs}$ overlayer exposes partially delocalized Cs-6s density to the impinging beam of He^* atoms. Upon annealing the surface, the delocalized character of the Cs-6s state diminishes, while the metastable surface structure is driven into its stable configuration. We can rationalize this behavior as follows. In the metastable phase, where the Cs atoms occupy the threefold hollow fcc sites and the CO molecules the on-top positions, the back donation from the Cs modified surface to the CO molecule is less efficient than in the stable configuration. Accordingly, the Cs-6s state remains partially delocalized, as seen

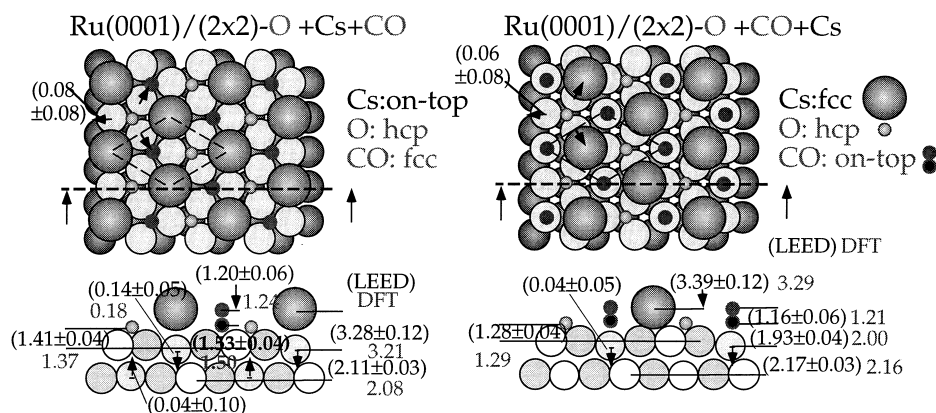


Fig. 4. The geometries for the ternary $(2 \times 2)\text{-O} + \text{Cs} + \text{CO}$ systems on Ru(0001) as obtained from LEED and DFT calculations. The LEED values are in parentheses. All parameters are given in Å. The left panel corresponds to the structure of the stable Ru(0001)- $(2 \times 2)\text{-O} + \text{Cs} + \text{CO}$ phase with Cs atoms occupying on-top positions and CO molecules the fcc hollow positions (Pendry r -factor $R_p = 0.30$). In the metastable phase (right) the adsorption sites of Cs and CO are interchanged ($R_p = 0.30$).

by the (albeit less pronounced) singlet to triplet conversion of the incident He* atoms.

A second metastable $(2 \times 2)\text{-O} + \text{Cs} + \text{CO}$ phase can be prepared by exposing the $(2 \times 2)\text{-O}$ -precovered Ru(0001) first to Cs (about $0.21 \mu\text{l}$) and then to CO at a sample temperature of 100 K. The surface symmetry of this structure is still (2×2) but the surface structure has not been determined so far. However, the LEED IV curves of this metastable phase are substantially different from those of the other binary and ternary phases listed in Table 1, as quantified by Pendry r -factors larger than 0.30.

MD spectra of this second metastable phase and its transformation towards the stable phase are presented in Fig. 6. At low sample temperatures when the metastable phase is fully developed, the emission from the Cs-6s state indicates a strong singlet-triplet conversion which in turn is indicative of a strongly delocalized character of the Cs-6s state. Upon annealing the surface, the ratio between singlet and triplet emission decreases until at about room temperature

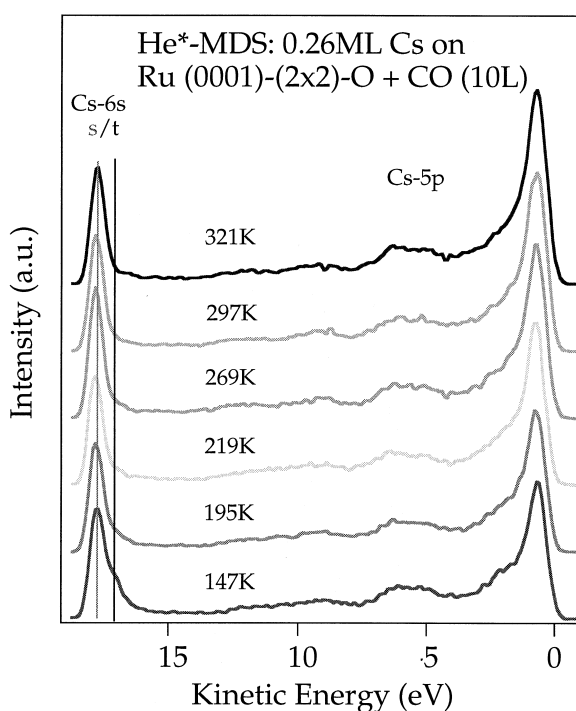


Fig. 5. The He*-MD spectrum (taken at 120 K) of the metastable Ru(0001)- $(2 \times 2)\text{-O} + \text{CO} + \text{Cs}$ surface with Cs sitting in fcc and CO in on-top position and how this MD spectrum changes upon annealing the surface to a particular temperature (as indicated); the MD spectra were always measured after cooling the surface to 120 K. Gradually the He* triplet excited emission from the Cs-6s state diminishes which indicates a transformation from a partially delocalized state towards a localized Cs-6s state.

only the singlet peak is left. Parallel to this observation, an additional peak associated with the adsorbed oxygen atom emerges in the spectra with annealing temperature. Both findings are consistent with a demetallization of the surface.

3. Summary

In conclusion, we have studied structural, electronic and energetic aspects of coadsorbate systems which were prepared by exposing a (2×2) -O-precovered Ru(0001) surface to Cs and CO. The ternary system may serve as a promising model system to study the Cs promoted CO oxidation reaction over Ru(0001). Structural and electronic properties of the Cs subsystem are only weakly influenced by the (2×2) -O overlayer, while the CO coadsorption removes the delocalization of the Cs-6s state, consistent with a demetallization of the Cs overlayer, as also seen in the asymptotic electron density above the Cs atoms (DFT). The ternary system reveals the presence of two metastable configurations. In the first one, Cs and CO have changed their adsorption sites as compared to the stable phase i.e., Cs and CO occupy the hcp and on-top site, respectively. Exploring the surface structure and the electronic properties of this metastable

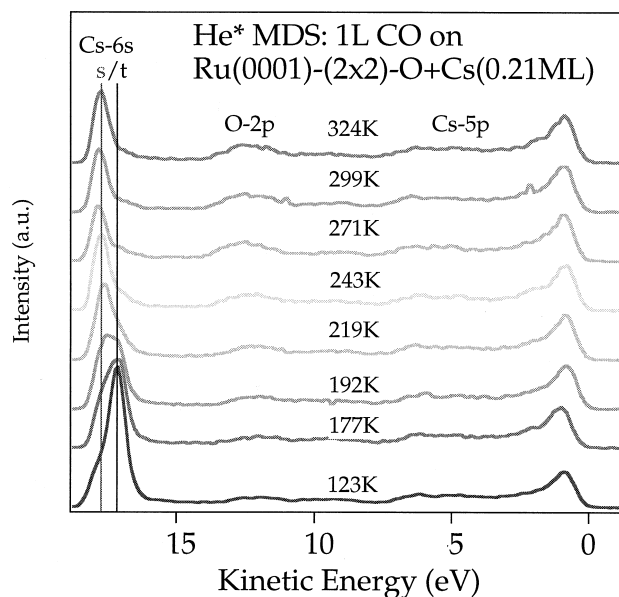


Fig. 6. The He*-MD spectrum (taken at 120 K) of the second metastable Ru(0001)- (2×2) -O+Cs+CO phase and how this spectrum changes when the surface is annealed to a predetermined temperature (as indicated); subsequently the MD spectrum was measured after cooling the surface to 120 K. Gradually the emission from the Cs-6s state changes from a partially delocalized state to a localized Cs-6s state.

phase underlines the importance of the threefold hollow site of CO for improving the back bonding and therefore strengthening the CO bonding to the surface. The surface structure of the second metastable (ternary) arrangement has not been determined by LEED. As shown by MDS, the electronic structure of the Cs subsystem changes, however, markedly with annealing temperature in that the metallic Cs overlayer turns from metallic into a non-metallic surface.

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References

- [1] H. Over, *Prog. Surf. Sci.* 58 (1998) 249.
- [2] G. Pirug, H.P. Bonzel, in: D.A. King, D.P. Woodruff (Eds.), *The Chemical Physics of Solid Surfaces, Coadsorption, Promoters, and Poisons*, vol. 6, Elsevier, Amsterdam, 1993, p. 51.
- [3] H. Bludau, H. Over, unpublished measurements.
- [4] C.H.F. Peden, D.W. Goodman, *J. Phys. Chem.* 90 (1986) 1360.
- [5] C. Stampfl, S. Schwegmann, H. Over, M. Scheffler, G. Ertl, *Phys. Rev. Lett.* 77 (1996) 3371.
- [6] S. Fichtner-Endruschat, V. De Renzi, A. Morgante, S. Schwegmann, H. Bludau, R. Schuster, A. Böttcher, H. Over, *J. Chem. Phys.* 108 (1998) 774.
- [7] H. Conrad, G. Ertl, J. Küppers, W. Sesselmann, H. Haberland, *Surf. Sci.* 121 (1982) 161.
- [8] H. Over, H. Bludau, M. Skottke-Klein, W. Moritz, G. Ertl, C.T. Campbell, *Phys. Rev. B* 45 (1992) 8638.
- [9] A.P. Seitsonen, PhD Thesis, Technical University, Berlin, 1999.
- [10] H. Pfnür, G. Held, M. Lindroos, D. Menzel, *Surf. Sci.* 220 (1989) 43.
- [11] Y.D. Kim, S. Wendt, S. Schwegmann, H. Over, G. Ertl, *Surf. Sci.* 418 (1998) 267.
- [12] G. Michalk, W. Moritz, H. Pfnür, D. Menzel, *Surf. Sci.* 129 (1983) 92.
- [13] H. Bludau, H. Over, T. Hertel, M. Gierer, G. Ertl, *Surf. Sci.* 342 (1995) 134.
- [14] H. Over, H. Bludau, M. Skottke-Klein, W. Moritz, G. Ertl, *Phys. Rev. B* 46 (1992) 4360.
- [15] M. Gierer, H. Bludau, H. Over, G. Ertl, *Z. Naturforsch.* 50a (1995) 453.
- [16] M. Gierer, H. Over, *Z. Kristallogr.* 214 (1999) 14.
- [17] B. Narloch, G. Held, D. Menzel, *Surf. Sci.* 340 (1995) 159.
- [18] B. Narloch, G. Held, D. Menzel, *Surf. Sci.* 317 (1994) 131.
- [19] H. Over, H. Bludau, R. Kose, G. Ertl, *Phys. Rev. B* 51 (1995) 4661.
- [20] A.P. Seitsonen, H. Over, to be published.
- [21] A.P. Seitsonen, H. Over, to be published.
- [22] Y.W. Yang, J. Hrbek, *J. Phys. Chem.* 99 (1995) 3229.
- [23] A. Böttcher, A. Morgante, R. Grobecker, T. Greber, G. Ertl, *Phys. Rev. B* 49 (1994) 10607.
- [24] G. Blyholder, *J. Phys. Chem.* 68 (1964) 2772.
- [25] H. Over, H. Bludau, R. Kose, G. Ertl, *Surf. Sci.* 331 (333) (1995) 62.
- [26] Y.J. Zhu, A. Morgante, S. Wendt, A.P. Seitsonen, H. Over, to be published.
- [27] S. Schwegmann, A. Böttcher, H. Over, unpublished measurements.
- [28] A. Böttcher, H. Niehus, S. Schwegmann, H. Over, G. Ertl, *J. Phys. Chem.* 101 (1997) 11185.

- [29] S. Schwegmann, A.P. Seitsonen, V. De Renzi, H. Dietrich, H. Bludau, M. Gierer, H. Over, K. Jacobi, M. Scheffler, G. Ertl, *Phys. Rev. B* 57 (1998) 15487.
- [30] M. Lindroos, H. Pfnür, G. Held, D. Menzel, *Surf. Sci.* 222 (1989) 451.
- [31] H. Over, W. Moritz, G. Ertl, *Phys. Rev. Lett.* 70 (1993) 315.
- [32] H. Bludau, H. Over, unpublished LEED experiments.
- [33] Y.D. Kim, Y.J. Zhu, S. Wendt, S. Schwegmann, A. Morgante, H. Bludau, A.P. Seitsonen, H. Over, submitted to *Phys. Rev. B*.