The orbital symmetry of carbon monoxide on a Cs-precovered Ru(1010) surface

The orbital symmetry of carbon monoxide on a Cs-precovered Ru(10$\bar{1}$0) surface*

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Abstract. The molecular orbitals of CO are rearranged under the strong influence of coadsorbed Cs atoms. The peak for CO on the clean Ru(10$\bar{1}$0) surface, at 7.5 eV BE attributed to the 5σ and 1π orbits, is split into two peaks; one is at 6.3 eV BE and the other 7.8 eV BE. The peak at 6.3 eV BE shows an anti-symmetry character about the plane parallel to the $\langle 0001 \rangle$ crystallographic direction in the surface.

1. Introduction

Coadsorption of CO and alkali metal atoms on ruthenium surfaces is considered to model the promoter action of related systems in heterogeneous catalysis and has hence been thoroughly studied in the last few years [1–5]. Our previous HREELS study shows that there are two molecular adsorption states of CO on a Cs-precovered Ru(10$\bar{1}$0) surface. One is with higher C–O stretch frequency, around 250 meV, and the other is with lower C–O stretch frequency, below 200 meV. The former is similar to that on the clean Ru(10$\bar{1}$0) surface, but the latter is not. In the latter case there is a strong and short-range interaction between the CO molecule and Cs atom; under ther influence of Cs the C–O stretch frequency is much lower than that on a clean Ru(10$\bar{1}$0) surface [6]. The CO adsorption state, with C–O stretch frequency below 200 meV, is observed not only in a Cs-precovered Ru(10$\bar{1}$0) surface, but also in other coadsorption systems [7–9]. The polarized ARUPS results of coadsorbed CO and K on the Ru(0001) surface showed some differences in the valence bands from CO on a clean surface, because the CO molecular orbits were rearranged [10, 11]. Due to the fact that there are three equivalent azimuths on Ru(0001) surface, only few information about the orbit of CO molecules can be obtained. The Ru(10$\bar{1}$0) surface, with lower symmetry, is an interesting surface, so more information should be obtained. In the following, we report our investigation of the system (CO + Cs)/Ru(10$\bar{1}$0) by using polarized angle resolved ultra-violet photoemission spectroscopy (ARUPS).

2. Experiment

The sample consisted of a circular Ru crystal of 2 mm thickness and 8 mm in diameter. The crystal was heated by electron bombardment from the backside of the sample. Cleaning

was achieved by repeated argon ion sputtering and annealing to 1500 K. The clean and well ordered surface was checked by AES and LEED.

Caesium was deposited from a thoroughly degassed SAES dispenser. The Cs coverage was defined with the ratio of Cs/Ru atoms in the top Ru(10$\bar{1}$0) layer. The measurements of Cs (563 eV) and Ru (276 eV) Auger signals combining with a simple calculation were used for the determination of Cs coverage. The CO for exposures was released from research grade gas and adsorbed at 150 K.

The ARUPS work was performed on an angle-resolved electronic energy spectrometer, in Beijing Synchrotron Radiation Facility (BSRF), with a spherical deflection analyser (SDA) which could be rotated inside the chamber. The light is 80% polarized. The photoelectrons were collected within an angle of $\pm 1.5°$ and overall energy resolution was 100 meV. The ultra-high vacuum was obtained by an ion pump and a turbopump; the base pressure was lower than 2.0×10^{-8} Pa.
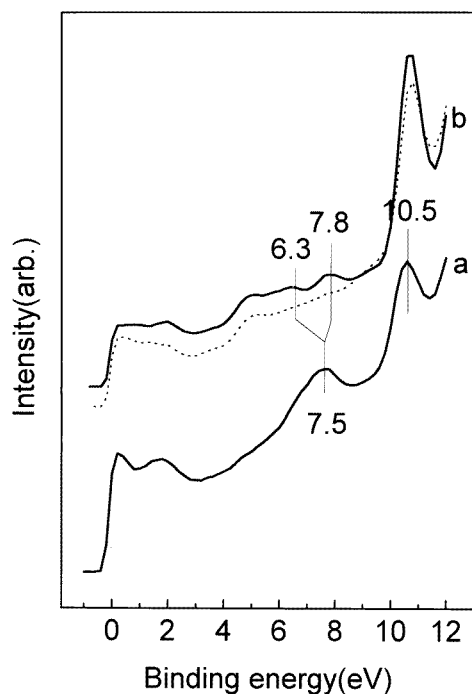

Figure 1. The p-polarized ARUP spectrum taken at normal emission and at photon energy of 23 eV with an incidence angle of 60° from the surface normal in the ⟨1$\bar{2}$10⟩ azimuth: spectrum a taken after 5 L CO dose at 150 K on a clean Ru(10$\bar{1}$0) surface; spectrum b taken after 5 L CO dose at 150 K on a Cs precovered, $\theta_{Cs} = 0.25$, surface; the spectrum in dots, takne on a Cs precovered surface before CO dose.

3. Results and discussion

The spectra a and b in figure 1 show the ARUPS results of CO molecules on clean and Cs precovered, $\theta_{Cs} = 0.25$, Ru(10$\bar{1}$0) surfaces respectively. The spectra were taken at normal emission and at photon energy of 23 eV with an incidence angle of 60° from the surface normal in the ⟨1$\bar{2}$10⟩ azimuth.

After 5 L CO dose at 150 K on the clean surface the peaks at 7.5 and 10.5 eV below the Fermi level, see spectrum a, are the CO valence levels of $5\sigma + 1\pi$ and 4σ respectively. Our previous HREELS results show that the surface with higher precoverage of Cs offers more adsorption sites for the CO with the C–O stretch frequency below 200 meV and fewer adsorption sites for the CO with higher C–O frequency similar to that on a clean surface [6]. Since the latter CO cannot be found when the coverage of Cs is beyond 0.20, there is only one adsorption state of CO with lower C–O stretch frequency in the case of spectrum b. It has been proved that the CO with the C–O stretch frequency below 200 meV interacts with Cs strongly and in a short range, and its valence levels, shown in spectrum b, are changed. The change up to 5.0 eV below the Fermi level comes from the precovered Cs layer, seen in the dotted curve in figure 1 taken from the Cs/Ru surface before CO dose. The shift of the 4σ peak is not clear because of the overlapping with the Cs $5p_{3/2}$ level. Similar to that on a K-precovered Ru(0001) surface [10, 11] the main change of CO valence levels under the influence of Cs is shown around the CO $5\sigma + 1\pi$ level: there are two peaks, at 6.3 eV and at 7.8 eV below the Fermi level, instead of the peak at 7.5 eV of CO on a clean surface. Since no dissociation of CO is seen with XPS, and since the peaks disappear after desorption of CO, they are unambiguously due to molecular CO [10, 11].

The change in the region of 6–8 eV in spectrum b shows the rearrangement of the molecular orbits of the CO which interacts with Cs strongly and in a short range. There are two concrete models proposed to describe the short-range alkali metal–CO interaction, namely, the CO sp^2 rehybridization model of Weimer and Umbach [11], and the direct CO 1π–alkali metal interaction model of Eberhardt *et al* [12]. In the direct interaction model, the 6.3 eV peak is ascribed to a CO 1π-derived state interacted with the alkali metal; the other 1π-derived state and 5σ state remain nearly unchanged and are still contained in the 7.8 eV peak. In the rehybridization model the Me–CO bond rehybridizes to sp^2, forming new σ and π bonds (a_1 and b_1, b_2 orbitals in the C_{2v} point group); the peaks at 6.3 eV and 7.8 eV are attributed to the rehybridized CO orbits.

Since the peak at 6.3 eV, in the direct interaction model, is ascribed to a CO 1π-derived state interacted with the alkali metal, it must be dependent on the alkali metal atom and on the distance between the CO molecule and alkali metal atom. Due to the fact that the 6.3 eV peak appears and does not shift on different substrate, even if CO is coadsorbed with different alkali metals [10, 11, 13], the direct interaction model is not reasonable; the rehybridization model therefore describes the ARUPS results better.

The rehybridization model cannot be confirmed by application of selection rules for emission from the CO orbital on the Ru(0001) surface due to the three possible orientations of the mirror plane of the sp^2 rehybridized CO molecule, but it is possible on the Ru($10\bar{1}0$) surface.

The p-polarized ARUP spectra of CO molecules on the Cs/Ru($10\bar{1}0$) surface are shown in figure 2. The curves a and b are spectra with an incidence plane parallel to the $\langle 1\bar{2}10 \rangle$ azimuth, a was taken with normal incidence and at 60° emission in the incidence plane, but b at normal emission and with an incidence angle of 60° from the surface normal. The peaks at 6.3 eV and at 7.8 eV could be both found in the spectra a and b. In the rehybridization model the 6.3 eV peak is attributed to a 'π' type rehybridized $1b_2$ orbit which is partly responsible for the Me–CO bond; another 'π' type rehybridized $1b_1$ orbit then remains at 7.8 eV [10, 11]. The 5σ orbit becomes the $5a_1$ orbit of the rehybridized CO molecule, but its position is not clear. The change in intensity of the peak at 7.8 eV with the increasing incidence angle in the case of b shows that the peak reflects emission from a 'σ' type a_1 orbit. The $5a_1$ orbit must be at 7.8 eV overlapping with the $1b_1$ orbit.

There is a c(2×2) LEED pattern on the Cs precovered, $\theta_{Cs} = 0.25$, Ru($10\bar{1}0$) surface.
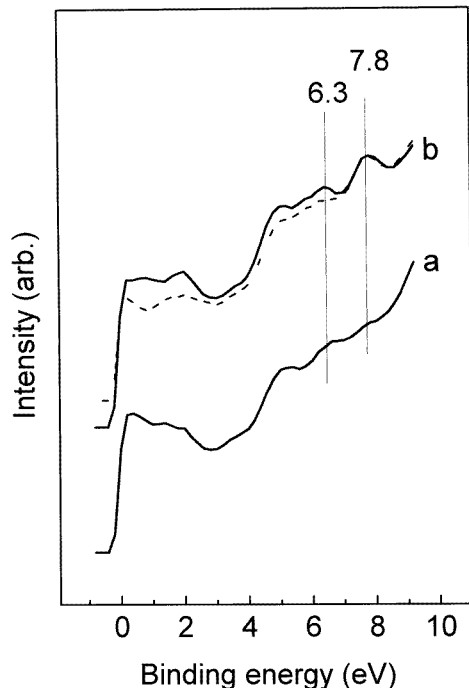
Figure 2. The p-polarized ARUP spectrum taken after 5 L CO dose at 150 K on a Cs precovered, $\theta_{Cs} = 0.25$, surface: spectrum a: normal incidence and at 60° emission in the incidence plane, incidence plane parallel to the $\langle 1\bar{2}10 \rangle$ azimuth; spectrum b: incidence angle of 60° from the surface normal and at normal emission, incidence plane parallel to the $\langle 1\bar{2}10 \rangle$ azimuth; the spectrum in dashed line taken at same conditions as spectrum b, but with an incidence plane parallel to the $\langle 0001 \rangle$ azimuth.

Although the pattern was blurred after the CO dose, the mirror plane of the rehybridized CO molecule with respect to the substrate can be found. The dashed curve in figure 2 is a spectrum taken at the same conditions as spectrum b, but with an incidence plane parallel to the $\langle 0001 \rangle$ azimuth: the main difference from that in spectrum b is that the peak at 6.3 eV almost vanishes. The symmetry information means that the $1b_2$ orbit shows an anti-symmetry character about the plane parallel to the $\langle 0001 \rangle$ crystallographic direction in the surface. The $1b_1$ orbit should show an anti-symmetry character about the plane parallel to the $\langle 1\bar{2}10 \rangle$ azimuth. Since the peak at 7.8 eV reflects emission from two overlapping orbits, the effect of the forbidden $1b_1$ orbit is not seen clearly in the case of spectrum b.

In the direct interaction model the 6.3 eV peak is ascribed to a CO 1π-derived state interacted with by the alkali metal, thus the symmetry of the CO molecule with respect to the substrate must be lost. The rehybridized model is an indirect interaction model: the alkali metal atoms do not interact with CO molecules directly but modify the electronic property of the substrate; the strong electron back-donation results in rearrangement of the CO molecule [10, 11]. The rehybridization of CO means that the normal CO with a double π bond between C and O is broken up into a single π bond between C and O [10]; the weaker C–O bond or the lower C–O stretch frequency of CO under the strong influence of coadsorbed Cs is due to the loss of one π bond. The rehybridized CO molecule can be viewed as similar to organic carbonyl and there is a bridging bond between C and two

Ru atoms [10]. The symmetry information suggests that the plane of the sp^2 rehybridized CO molecule is in the $\langle 1\bar{2}10\rangle$ azimuth, namely two neighbour Ru atoms bonding with the CO molecule arrange in the $\langle 1\bar{2}10\rangle$ azimuth. The schematic diagram of an sp^2 rehybridized CO molecule on the Cs precovered Ru(10$\bar{1}$0) surface, without Cs atoms, is shown in figure 3.
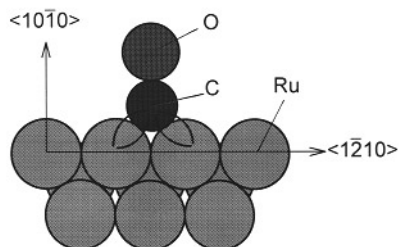

Figure 3. The schematic diagram of an sp^2 rehybridized CO molecule on the Cs precovered Ru(10$\bar{1}$0) surface.

In figure 3 the CO molecule on Cs/Ru(10$\bar{1}$0), under the C_{2v} point group, is upright. However the data are presented are also consistent with a tilted geometry and a Cs point group geometry. If the tilting were in the $\langle 1\bar{2}10\rangle$ direction and the Cs in the fourfold hollow site, then the ordering of the 1π-derived orbitals would be similar to that under the C_{2v} point group assumption. To show that the molecule retains C_{2v} symmetry it is necessary to show that the 4σ band disappears with normal emission and s-polarized light for incidence in both the $\langle 1\bar{2}10\rangle$ and $\langle 0001\rangle$ directions. Due to the overlapping of the 4σ band with the Cs $5p_{3/2}$ level, seen in figure 1, the ordering of the 4σ band is not clear. A similar experiment should be taken on other coadsorption systems, such as on the CO/K/Ru(10$\bar{1}$0) system.

Acknowledgment

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