High-resolution electron energy loss spectroscopy and angle-resolved ultra-violet

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High-resolution electron energy loss spectroscopy and angle-resolved ultra-violet photoemission spectroscopy studies of carbon monoxide on a Cs-precovered Ru(10$\bar{1}$0) surface

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Abstract. There are two molecular adsorption states of CO in the CO + Cs/Ru(10$\bar{1}$0) system. One is α_1-CO, with lower C–O frequency, and the other is α_2CO, with higher C–O frequency. The latter is similar to that on a clean Ru(10$\bar{1}$0) surface. The two states of CO are occupied sequentially during the exposure to CO. The C–O stretch frequency of both states shifts to a higher value with the exposure to CO and to a lower value with higher Cs precoverage. The electronic structure of the α_1-CO molecule is different from that of the α_2-CO molecule and is of the same character as CO in a tilted mode.

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]. Up to now most investigations have been made on the Ru(0001) surface [6, 7]. It is well known that the alkali metal atoms reduce the C–O bonding or lower the C–O stretch frequency: C–O stretch frequencies below 200 meV are observed on a Cs-precovered Ru(0001) surface [8, 9]. The Ru(10$\bar{1}$0) surface is an interesting one. More information about the orientation of CO molecules could be obtained on the Ru(10$\bar{1}$0) surface with C_{2v} symmetry than that on the Ru(0001) surface with three equivalent azimuths. On the Ru(10$\bar{1}$0) clean surface there is on CO adsorption state with higher C–O stretch frequency, about 250 meV, similar to that on the Ru(0001) clean surface [10]. Are there any CO adsorption states with lower C–O stretch frequency and what are they like on an alkali metal atom precovered surface? In the following, we report our investigation of the system (CO + Cs)/Ru(10$\bar{1}$0) using high-resolution electron energy loss spectroscopy (HREELS) and angle-resolved ultra-violet photoemission spectroscopy (ARUPS).

2. Experimental details

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 back-side 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 by 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 combined 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 HREELS experiment was carried out in a two-stage cylindrical HREELS system (ELS-22 spectrometer from Leybold–Heraeus) and the ARUPS work was performed on an angle-resolved electron spectrometer (ADES-400 from VG). The ultra-high vacuums were obtained by an ion pump and a diffusion pump respectively; the base pressure in both chambers is 1.5×10^{-8} Pa.

The HREEL spectra were taken at $60°$ angle of incidence with respect to the surface normal and emission in a specular direction. The primary edge was 5 eV and the energy resolution was 12 meV. Although the energy resolution was poor, it is good enough to show the two loss peaks assigned to the C–O stretching vibration distinctly and their shift.

3. Results and discussion

Figure 1 shows the HREEL spectra of CO molecules on clean Cs-precovered Ru($10\bar{1}0$) surfaces: the coverage of Cs varies from 0.025 to 0.10 in (b)–(e). A loss peak assigned to a C–O stretching vibration, labelled α_1, appears around 200 meV in the Cs-precovered case. The large downward shifts in C–O stretch frequency with the addition of Cs are similar to the shifts reported on the Cs-precovered Ru(0001) surface. Another loss peak, labelled α_2, is around 250 meV, close to the value of CO molecules adsorbed on a clean surface. During the exposure to CO, the α_2 peak appears after the α_1 peak grows. Since a CO molecule can most probably reach and adsorb in a state with the lowest energy, according to the sequential appearance of the adsorption states, α_1-CO must have a larger heat of adsorption than α_2-CO has.

It is well known that the back-donation from the metal surface to the CO $2\pi^*$ orbital should weaken the C–O bonding [11, 12]. On a Cs-precovered surface the C–O stretch frequency of α_1-CO is much lower than that of α_2-CO; this suggests that the Cs atoms enhance electron back-donation into the $2\pi^*$ orbital of α_1-CO strongly. The HREELS results in figure 1 show that the relative peak intensity of α_1 and α_2 changes with varying Cs precoverage: higher precoverage of Cs offers more adsorption sites for the α_1-CO state. The dependence of the CO-α_1 adsorption sites on the Cs precoverage suggests that there is a direct interaction between α_1-CO molecules and Cs atoms: this must be strong and short range.

The fact that the energy loss of two peaks depends on Cs precoverage shows another interaction between CO molecules and Cs atoms. The C–O stretch frequency is lower on a higher-Cs-precoverage surface after saturation exposure to CO. The change in stretch frequency is small, but for all CO molecules, both α_1-CO and α_2-CO, on the substrate, it suggests that the alkali atom offers not only an adsorption site for α_1-CO but also the back-donating electrons for other CO molecules on the substrate. Unlike the direct interaction between Cs and α_1-CO the other weak interaction must be long-range and indirect [1, 13, 14].

The HREEL spectra in figure 1 show that the α_2 peak on the clean surface and both peaks on the Cs-precovered surface shift to higher values with further exposure to CO, also reported for other coadsorption systems [2, 4]. The shifts of both peaks can be considered as simple dipole–dipole interactions [15]; the shifts also can be attributed to a long-range electronic mechanism affecting the back-bonding. The dependence of the C–O stretch frequency on the coverage of both Cs and CO, shown in figure 2, suggests such an indirect
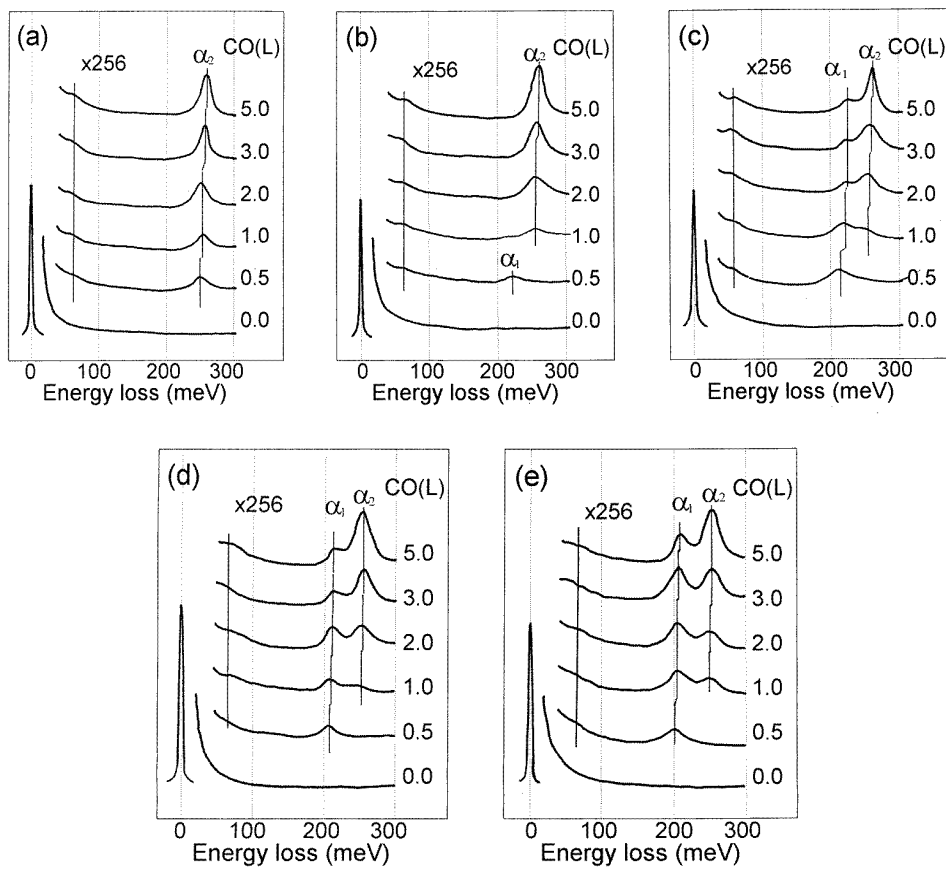
Figure 1. (a) The HREEL spectra of CO adsorbed on a clean Ru(10̄10) surface at 150 K; (b)–(e) the spectra of CO adsorbed on a Cs-precovered Ru(10̄10) surface: the Cs coverage is 0.025, 0.05, 0.075 and 0.10 respectively.

interaction mode between CO and Cs: the alkali metal atoms increase the back-donating electrons on the substrate and CO consume them. The continuous shift of the C–O stretch frequency with exposure to CO shows the reducing back-donation for each molecule with more CO molecules adsorbed on the substrate.

The interaction between α_1-CO and Cs is direct and short-range; the lower precoverage of Cs offers fewer adsorption sites of CO-α_1 state. For very low Cs precoverage ($\theta_{Cs} = 0.025$) a small loss peak assigned to a C–O stretching vibration of α_1-CO could be observed around 200 meV; its intensity reduces with further exposure to CO (see figure 1(b)). The near disappearance of the peak with increasing exposure raises a question: is there any adsorption site of α_1-CO after too many CO molecules consume the back-donating electrons? The answer must be yes. The reduction of the loss peak in HREELS may be due to the effect of electric screening of too many α_2-CO molecules and the fact that the lying-down orientation of α_1-CO leads a very small loss feature. We believe that each Cs atom, even if in the case of very low Cs precoverage with large CO exposure, can offer an adsorption site for α_1-CO. Further exposure to CO changes the indirect, or through-metal, interaction only.
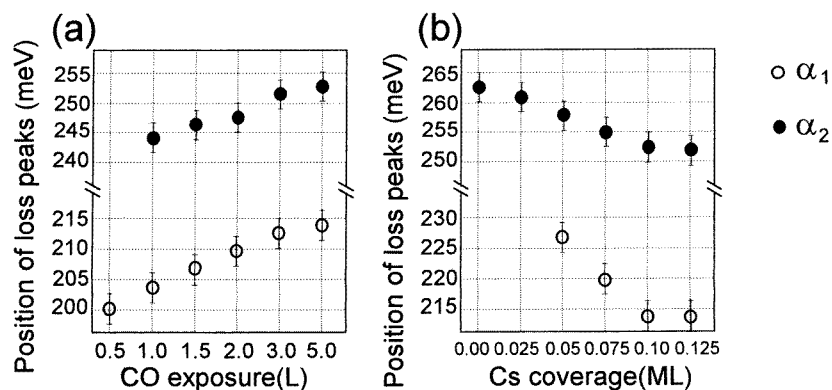
Figure 2. The position of loss peaks, the open and solid dots assigned to C–O stretching vibration of α_1-CO and α_2-CO molecules respectively: (a) exposure of CO varies from 0.5 to 5.0 L on a Cs-precovered Ru(10$\bar{1}$0) surface ($\theta_{Cs} = 0.010$); (b) saturated exposure to CO with the coverage of Cs varying from 0.0 to 0.125.

Some loss peaks appearing around 50–60 meV may be associated with the metal–carbon stretching. The losses from different adsorption modes cannot be distinguished due to the poor resolution and the influence from the elastic peak. The reduction in intensity with increasing Cs coverage shows an effect of screening similar to that on Ru(0001) [1].

The direct interaction between α_1-CO and Cs is a strong interaction. The large difference of the stretch frequency between α_1-CO and α_2-CO cannot be accounted for by different back-donation only. The α_1-CO may have rearranged molecular orbitals, or a different molecular orientation, or a different adsorption site from those of α_2-CO. The electronic structure of the α_1-CO molecule must be very different from that of the α_2-CO molecule.

Figure 3 shows a series of the HeII ARUP spectra (photon energy $h\nu = 40.8$ eV) taken at normal emission with an incidence angle of 30° from the surface normal in the $\langle 1\bar{2}10 \rangle$ azimuth. The spectrum (c) is taken after 5.0 L CO on the clean surface and (d) after 0.5 L dose on a Cs-precovered ($\theta_{Cs} = 0.1$) surface. According to the HREELS results it is known that only α_2-CO molecules adsorbed in the case of (c) and α_1-CO molecules in the case of (d) respectively. Three differences between spectra (c) and (d) could be found: the first is a shift in $5\sigma + 1\pi$ binding energy of 0.3 eV; the second is a change in peak intensity ratio of $4\sigma/(5\sigma + 1\pi)$ and the third is the appearance of the increase in the 6 eV peak.

On the Ru(0001) surface precovered with alkali metal a splitting of the CO ($5\sigma + 1\pi$) peak arises from a shift toward higher and lower binding energy of the 5σ and 1π orbitals respectively [1,4]. Here the change in binding energy of CO ($5\sigma + 1\pi$) shows the shift of 5σ level; the 1π peak with lower binding energy cannot be observed clearly due to the low cross-section using HeII light. The change in CO ($5\sigma + 1\pi$) level may result from a π-bonded configuration. The Cs atom plays an important role in creating this adsorption site.

Because of the low Cs coverage and the low cross-section, the peak from Cs $5p_{3/2}$ is very weak (see spectrum (b) taken from a Cs-precovered ($\theta_{Cs} = 0.1$) surface). The effect of the overlapping of the CO 4σ peak by the Cs $5p_{3/2}$ can be neglected. The change in peak intensity ratio shows another difference in electronic structure between α_1-CO and α_2-CO molecules. A low intensity ratio of $4\sigma/(5\sigma + 1\pi)$ suggests that the α_1-CO molecule, in the UP spectra, is of the same character as that of CO bound in a fourfold hollow site on
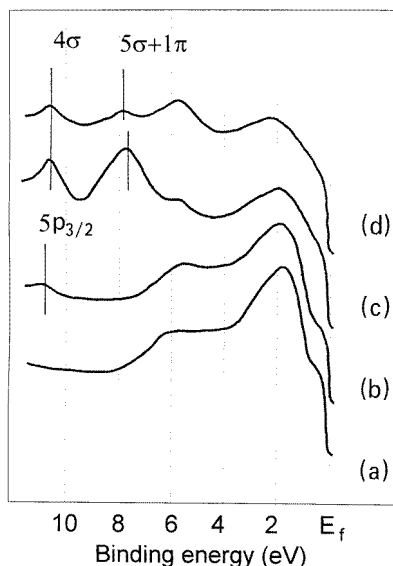
Figure 3. The HeII ($h\nu = 40.8$ eV) ARUP spectra taken at the surface normal with an incidence angle of 30° in $\langle 1\bar{2}10 \rangle$, of (a) the clean Ru(10$\bar{1}$0) surface; (b) the Cs-precovered ($\theta_{Cs} = 0.1$) surface; (c) 5.0 L CO exposure on the clean surface; (d) 0.5 L CO exposure on the Cs-precovered ($\theta_{Cs} = 0.1$) surface.

Fe(100); the latter, with lower C–O stretch, adsorbs in a side-on-bonding mode [16–18]. The α_1-CO molecules could be in a side-on-bonding mode too. It would be interesting to determine the orientation of the α_1-CO molecule in the tilted mode.

The features in the region below 6 eV originate from the d-band of ruthenium. The increase in the 6 eV peak shows that the possibility of CO dissociation cannot be eliminated. Kondoh and Nozoye clearly showed that CO dissociates on the Cs-precovered Ru(0001) surface [1]; the more open structure of this surface may result in greater reactivity.

Acknowledgments

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