Chemisorption and Dissociation of Carbon Monoxide on the Sm-Modified Ru(001) Surface

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The adsorption of CO on the Sm-precovered Ru(001) surface has been studied by means of high-resolution electron energy loss spectroscopy (HREELS). A highly inclined CO species with an extremely low C–O stretching [ν(C–O)] frequency of ~1060 cm^{-1} was identified in the Sm and CO coadsorbed layer. This unusual bonding geometry with a severely weakened C–O bond indicates a strong chemical interaction with neighboring Sm atoms. The Sm-induced dissociation of CO was found to result from this highly inclined precursor state when the surface was covered with more than ~0.4 monolayer (ML) of Sm or annealed above ~300 K. Several intermediate states with ν(C–O) modes in the range of ~1120–1560 cm^{-1}, whose C–O bonds were weakened but probably not tilted, also appeared along with a Sm-free CO species, depending on the coverages of both Sm and CO, as well as the thermal annealing temperature. Upon thermal annealing, a part of these intermediate states were converted into the highly inclined precursor state to dissociate, while the others desorbed without dissociation. In addition, a second-layer CO species with a high ν(C–O) frequency of ~2160 cm^{-1} was observed and adsorbed very weakly onto a cationic Sm atom in the coadsorbed layer.

1. Introduction

The interaction of molecular CO with transition metal surfaces has been the subject of a number of investigations,[1–10] due to its practical and fundamental importance. The presence of precursor states to CO dissociation has been reported on several transition metal single-crystal surfaces, such as Fe(100),[2,3] Mo-(100),[4] Mo(110),[5,6] and Cr(110).[7] These CO species have been identified by the observations of unusually low C–O stretching [ν(C–O)] modes in the range of 1065–1345 cm^{-1}, which are far below the ν(C–O) frequencies of conventionally bonded CO molecules on most transition metal surfaces, such as Ni(111),[8] Pt(111),[9] and Ru(001),[10] as well as that of a free CO molecule in gas phase.[11] Such extremely low frequencies of ν(C–O) modes indicate the significant weakening of C–O bonds and consequently lead to the facile dissociation of molecular CO. For these precursor states to CO dissociation, the tilted or lying-down bonding geometries with the C–O axes far from the surface normal are proposed to result in more serious overlap between the antibonding CO(2π*) molecular orbitals and the surface d-electron density.

Similar C–O bond weakening has been observed on several transition metal surfaces promoted by chemical additives as well. On alkali-precovered surfaces such as K/Pt(111),[12–14] K/Ru(001),[15,16] and Cs/Ru(001),[17–20] remarkable C–O bond weakening, with the ν(C–O) modes in the range of 1245–1810 cm^{-1}, has been found, simultaneously with an increase in the heat of CO adsorption. These findings are explained in terms of significant enhancement of the charge transfer to the CO-(2π*) orbital due to the electropositive nature of alkali metals and the mutual stabilization of both CO molecules and alkali metals due to an attractive interaction among them. However, no vibrational evidence for the CO dissociation has been generally reported for these alkali-promoted surfaces, except for the K-saturated Pt(111) surface.[12]

In the case of the CO adsorption on the Al(111) surface covered with Ni[21] or Cu,[22] on the other hand, the low ν(C–O) frequencies of 1260–1430 cm^{-1} have been associated with the dissociation of CO. Because Al is not a transition metal, the Al(111) surface has little ability to bind the CO molecules by itself. The substrate Al atom, however, must play an important role to promote the CO dissociation with its large affinity to oxygen, since the CO dissociation resulted in the oxidation of Al atoms to form Al_2O_3 upon these bimetallic surfaces. The Al atom probably interacts with the oxygen-end of the CO molecule and the Ni or Cu atom binds to the carbon-end. The di-σ bound CO species thus formed with a largely weakened C–O bond is proposed as a precursor to the CO dissociation. The corresponding results have been reported in the case with CO on the Al-covered Ni and Cu surfaces.[23]

In the present paper, we report the vibrational characterization of adsorption and dissociation of CO on the Ru(001) single-crystal surface covered with Sm atoms as a model system to understand the promoter effect of rare earth elements on transition metal catalysts. We have already investigated the CO adsorption on the Sm-modified Ru(001) surface by means of X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) and temperature-programmed desorption (TPD).[24] The XPS and UPS results have shown that the dissociation of molecularly adsorbed CO takes place upon thermal annealing, while no dissociation of CO is observed on the clean Ru(001) surface. The XPS and UPS data, however, have not been sufficient to describe the intermediate states leading to the Sm-promoted dissociation of CO in detail. The vibrational investigation in the present study using high-resolution electron energy loss spectroscopy (HREELS) revealed that the internal C–O bond is considerably weakened by neighboring Sm atoms. On the Sm-precovered surface, multiple low ν(C–O) modes were observed in the range between 1060 and 1560 cm^{-1} in addition to the ν(C–O) mode for CO on the Sm-free Ru site, depending on experimental conditions: the

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preadsorbed Sm coverage, the CO coverage, and the subsequent annealing temperature. The angular dependence of the ν(C−O) peak intensities observed in the HREELS measurements suggested that an extremely weakened C−O bond with the ν(C−O) frequency of 1060 cm^{-1} is highly tilted to the surface normal, that is the lying-down configuration. This lying-down CO species was proposed to be a precursor state to the CO dissociation observed on the Sm-modified Ru(001) surface.

2. Experimental Section

The experiments were performed in a multilevel ultrahigh-vacuum (UHV) chamber with a typical background pressure below 1×10^{-8} Pa. The lower level contains an HREELS instrument, where a rotatable monochromator allows both specular and off-specular data to be obtained. The upper level was equipped with an Ar$^+$ ion gun for sample cleaning, a quadrupole mass spectrometer (QMS), a shielded Sm evaporating source, a collimated gas doser with a glass capillary array, and facilities for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements. A Ru(001) single-crystal sample, ca. 10 mm in diameter and 1 mm in thickness, was held on a liquid N$_2$-cooled manipulator using two heating tantalum wires of 0.3 mm diameter. The sample temperature was monitored by a chromel/alumel thermocouple placed at the back of the crystal.

The Ru(001) surface was cleaned by repeating cycles of Ar$^+$ ion sputtering and annealing to 1200 K prior to each Sm deposition. The cleanliness of the surface was verified by AES, LEED, and HREELS measurements. Sm was vapor-deposited onto the atomically cleaned surface at 500 K, using the Sm evaporation source in which a small Sm piece was resistively heated by a tantalum filament. The increase in the base pressure, mainly due to outgassing of H$_2$ from the Sm piece, was kept below 8×10^{-8} Pa during the Sm deposition. In the present paper, Sm coverages are given in monolayers (ML). A distinct break in Sm Auger intensity as a function of the deposition time indicated the completion of the first Sm monolayer. At the completion of 1 ML, the ratio of Sm atoms to substrate Ru atoms has been previously found to be approximately 0.5.[25] On the basis of the assumption of a constant deposition rate of Sm, the Sm coverage below 1 ML was determined by means of an AES intensity ratio of [Sm(101 eV)]/[Ru(234 eV)] plotted as a function of the Sm deposition time. The estimated values for the Sm coverages were verified by measuring TPD spectra of CO after saturating the Sm-precovered surface with CO. The Sm coverage dependence of the TPD spectrum of CO has been previously investigated in detail.[24,25]

CO was introduced onto the freshly prepared Sm/Ru(001) surface at approximately 100 K through the gas doser. The amount of CO exposure was controlled by means of the CO dosing time with a constant backing pressure of 6.7×10^{-3} Pa. The calibration of the CO exposure was carried out by TPD spectra of CO as a function of the CO dosing time. The amount of CO exposure is given in langmuir unit (1 langmuir = 1.33 $\times 10^{-3}$ Pa s).

All HREELS data presented in this paper were recorded at 100 K with an incident electron beam energy of 4.0 eV and the fixed reflect beam direction (θ_r) of 70° with respect to the surface normal. The incident beam direction (θ_i) was varied depending on specular ($\theta_i = \theta_r = 70°$) or off-specular measurement. Each spectrum was scaled to the elastic peak shown in figures. A typical resolution (fwhm) of the elastic peak was 10 meV (80 cm^{-1}) for a clean or CO-saturated Ru(001) surface. For the Sm-precovered Ru(001) surface, however, the
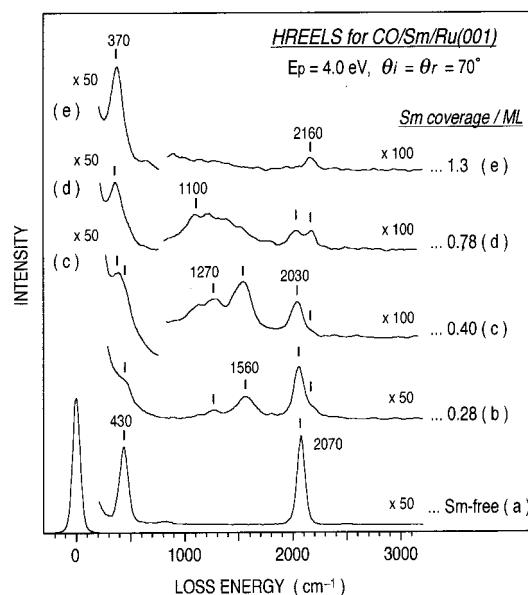

Figure 1. HREEL spectra recorded after CO adsorption (5.0 langmuir) on the Sm-precovered Ru(001) surface at 100 K for various Sm coverages as indicated.

adsorption of CO degraded the resolution to 11−14 meV (90−110 cm^{-1}) and decreased the elastic peak intensity by 1−2 orders of magnitude.

3. Results

3-1. Adsorption of a Saturated Amount of CO on Sm-Precovered Ru(001). Figure 1 shows a series of HREEL spectra taken for the Sm-precovered Ru(001) surface after adsorbing a saturated amount of CO at 100 K as a function of Sm coverage. A saturation coverage of CO was achieved by exposing 5 langmuir of CO on the surface as reported previously.[24] The HREEL spectrum for a saturated CO layer on the clean Ru-(001) surface (Figure 1a) has two energy loss features at 430 and 2070 cm^{-1}, corresponding to ν(Ru−CO) and ν(C−O) modes, respectively.[10,26] The ν(C−O) feature at 2070 cm^{-1} was shifted to slightly lower frequency by 30−50 cm^{-1} with Sm coverage less than 1 ML (Figure 1b−d). The intensity of this loss peak, which is due to CO on bare Ru, successively decreases with Sm coverage. The peak was no longer observed on the 1.3 ML Sm-covered surface (Figure 1e), indicating that no Sm-free Ru site remained on the surface after the completion of the Sm monolayer. The results agreed well with our previous study by TPD.[24] The lower shift of the ν(C−O) frequency suggests that this CO species was perturbed in some degree by a weak long-range interaction with Sm atoms although it did not interact directly with Sm atoms. On the other hand, a new ν(C−O) feature at 2160 cm^{-1} appeared on the surface above the Sm coverage of 0.28 ML and increased in intensity with the Sm coverage. The observed ν(C−O) frequency is even higher than that of the gas-phase CO molecule (2143 cm^{-1}).[11]

As shown in Figure 1b, the intensity of the ν(Ru−CO) mode at 430 cm^{-1}, which was observed on the Sm-free surface (Figure 1a), was remarkably reduced by a small amount of Sm, 0.28 ML, while the ν(C−O) mode was kept relatively intense. On increasing the Sm coverage to 0.40 ML, a new loss feature at 370 cm^{-1} appeared in addition to the ν(Ru−CO) mode, and it became progressively more intense with Sm coverage while the ν(Ru−CO) feature was hardly observed above 0.78 ML Sm coverage, as shown in Figure 1c−e. In the previous study, it has been suggested that a small part of CO molecules begin to
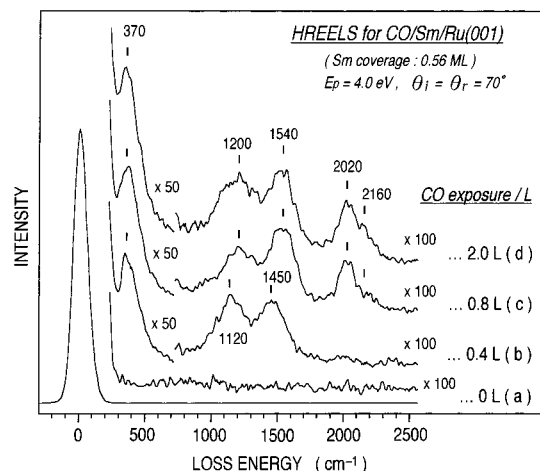
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Figure 2. HREEL spectra recorded after CO adsorption on the Sm-precovered Ru(001) surface (0.56 ML) at 100 K with increasing CO coverage.

dissociate on the surface with Sm coverage of nearly 0.4 ML at low substrate temperature and the amount of dissociatively chemisorbed CO increased with Sm coverage although it remained minor compared to that of molecular CO below 1 ML. The loss peak at 370 cm^{-1}, therefore, was associated to the decomposition products of CO molecules induced by precovered Sm.

Figure 1b−d reveals several loss peaks between 1120 and 1560 cm^{-1}. These frequencies are much lower than that of CO on clean Ru(001). The dominant part of adsorbed CO molecules was remained intact on the surface at 100 K without further reaction.[24] Consequently, the loss features between 1120 and 1560 cm^{-1} were attributed to the CO species with their C−O bonds weakened largely by the influence of Sm. The Sm adatoms produced at least three types of CO species with different strengths of C−O bonds at low temperature, since the ν(C−O) modes at 1560, 1270, and around 1120 cm^{-1} were distinguished. There are a number of different CO species on the 0.78 ML Sm-covered surface, since we observed no discrete loss peaks but some overlapped ν(C−O) features over an extensive range as shown in Figure 1d. The intensities of these peaks depended on the preadsorbed Sm coverage: the intensity of the ν(C−O) loss peak at 1560 cm^{-1} increased with Sm coverage up to 0.40 ML and subsequently decreased above this Sm coverage, the peak at 1270 cm^{-1} monotonically increased in intensity with Sm coverage, and the broad peak at around 1120 cm^{-1} was not observed at low Sm coverage as 0.28 ML but it became predominant at high Sm coverage as 0.78 ML. The observation of such multiple states also demonstrates a finite range of this strong interaction between Sm and CO. These results imply that the ratio of the number of the individual CO species to that of the Sm atoms affecting it increased with Sm coverage. The degree of weakening of the C−O bond also increased with Sm coverage.

3-2. Adsorption of Increasing Amounts of CO on 0.56 ML Sm-Precovered Ru(001). Figure 2 shows a series of HREEL spectra taken for the 0.56 ML Sm-precovered Ru(001) surface as a function CO exposure at 100 K. In the spectrum for the Sm-covered surface without CO exposure no vibrational feature was detectable, as shown in Figure 2a. After the CO exposure of 0.4 langmuir, three energy loss features were observed at 370, 1140, and 1450 cm^{-1} (Figure 2b). The loss peak at 370 cm^{-1} was assigned to dissociated CO as described above. The intensity of this peak remained almost constant with additional CO exposures, as shown in Figure 2c,d, suggesting that the
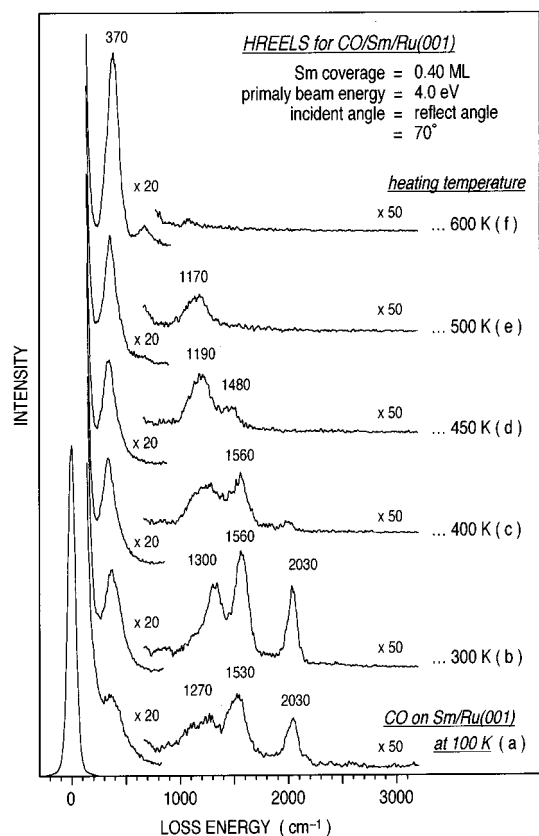

Figure 3. HREEL spectra for sequential annealing of the saturated CO layer on Sm/Ru(001). The 0.40 ML Sm-precovered surface was exposed to 5.0 langmuir of CO at 100 K (a), and annealed at various temperatures as indicated (b)−(f). Each spectrum was taken after cooling the sample to 100 K.

dissociative chemisorption of CO was almost completed in the initial stage of CO adsorption on the surface. On the other hand, the loss peaks at 1120 and 1450 cm^{-1} were assigned to the Sm-affected CO species with the weakened C−O bonds of different strength. After additional CO exposure, the loss peaks shifted to 1200 and 1540 cm^{-1} and the intensity of the peak at 1450 cm^{-1} increased slightly although the intensity of the peak at 1120 cm^{-1} did not, indicating that the adsorption of CO at the Sm-affected site was almost completed below 0.4 langmuir. These results support that the magnitude of the C−O bond weakening depends on the number of neighboring Sm atoms interacting with the individual CO molecule, in other word, the local stoichiometry of Sm atoms and CO molecules. The lower frequency state of CO, which was more strongly influenced by the coadsorbed Sm atoms, was populated predominantly on the surface at low CO coverage.

The loss peak at 2020 cm^{-1}, which was assigned to the ν(C−O) mode of the Sm-free CO species, appeared abruptly above 0.8 langmuir and the loss peak at 2160 cm^{-1} became obvious at 2.0 langmuir, as shown in Figure 2c,d. On increasing the CO exposure, the loss peak at 2160 cm^{-1} appeared after completion of the loss peaks at 2020 cm^{-1} and 1200−1540 cm^{-1}. Therefore, the loss peak at 2160 cm^{-1} was associated to the presence of the Sm-affected CO species.

3-3. Thermal Behavior of Adsorbed CO Species. In Figure 3, we show thermal behavior of the coadsorbed layer of Sm and CO. The 0.40 ML Sm-covered surface was saturated with CO at 100 K and annealed sequentially up to the temperatures indicated in Figure 3b−f. In the spectrum for the CO-saturated surface (Figure 3a), three loss peaks were observed at 1270, 1530, and 2030 cm^{-1}. On annealing the sample up to 300 K,

these peaks became sharp and intense, and the loss peaks at 1270 and 1530 cm^{-1} shifted to higher frequencies by ~30 cm^{-1}, respectively (Figure 3b). These observations probably resulted from reordering of adsorbates on the surface, although no clear LEED pattern was observed below 300 K. On the other hand, some CO species dissociated when the sample was heated to 300 K, since the loss peak at 370 cm^{-1}, which was due to the dissociated CO, increased in intensity. A LEED pattern of rotated $\sqrt{3}$ was observed after annealing at nearly 400 K. Since the decomposed amount of CO at this temperature is low,[24] this pattern comes from the CO/Sm coadsorption layer.

The loss peak at 2030 cm^{-1}, which was due to the Sm-free CO species, almost disappeared after annealing up to 400 K and completely disappeared after annealing to 450 K. The loss peak at 1560 cm^{-1}, which was due to a Sm-affected CO species, remained relatively intense after annealing to 400 K and was still observed after annealing to 450 K, although it was slightly shifted to 1480 cm^{-1} and decreased in intensity. The loss peak at 1480 cm^{-1} disappeared completely when the surface was annealed up to 500 K. Above 450 K, a relatively broad loss feature at around 1190 cm^{-1} was dominant. The CO species, which gave the ν(C−O) mode at around 1190 cm^{-1}, were thermally converted from any other CO species with higher ν-(C−O) modes of 1300−1560 cm^{-1}. This extremely low frequency peak was still observed although it slightly shifted to 1170 cm^{-1} after annealing to 500 K and disappeared after annealing to 600 K. Accordingly, an appreciable amount of the Sm-affected states still existed even at 500 K, while the Sm-effect free state of CO disappeared completely below 450 K. The Sm-effect-free CO and a part of the Sm-affected CO are considered to desorb during the thermal annealing, since the desorption of CO was observed around 450 K in TPD spectra.[24]

Above 500 K, on the other hand, a large amount of CO adsorbates were dissociated, since the loss peak at 370 cm^{-1} increased remarkably in intensity. At 600 K the loss peak at 740 cm^{-1} appeared. The dissociated CO was considered to react with neighboring Sm atoms and form a surface compound consisting of oxygen, carbon, and Sm atoms with the Sm-to-O ratio of 1:1.[24] This surface compound like samarium oxide, which is ionic in nature, retains a two-dimensional structure without thermal aggregation, since the obvious LEED pattern of a compressed hexagonal structure was observed after annealing to 600 K. Therefore, the loss peak is probably due to the surface optical phonon of the two-dimensional ionic structure and the loss peak at 740 cm^{-1} is the overtone of the vibration at 370 cm^{-1}.

The thermal behavior of the CO species with the ν(C−O) frequency of 2160 cm^{-1} was shown in Figure 4. The spectrum in Figure 4b, which is identical with Figure 1d, was obtained for the 0.78 ML Sm-covered surface saturated with CO at 100 K. As shown in Figure 4c, the loss peak at 2160 cm^{-1} disappeared completely after heating the sample up to 200 K, while the loss peak at 2020 cm^{-1}, which was due to the Sm-free CO species, was still observed. The desorption of the weakly adsorbed CO has been detected around 125 K in our previous TPD study.[24] The loss feature at 2160 cm^{-1}, therefore, was ascribed to a very weakly adsorbed CO species.

3-4. Angular-Dependent HREELS. In Figure 5, we show two HREEL spectra with different scattering geometries, i.e., specular and off-specular reflections, for a saturated CO layer on the 0.48 ML Sm-covered surface in order to discuss the bonding geometries of the adsorbates. The loss features at 370, 1240, 1520, 2030, and 2160 cm^{-1} appeared in the spectrum obtained with the specular reflection (Figure 5a). In the spectrum
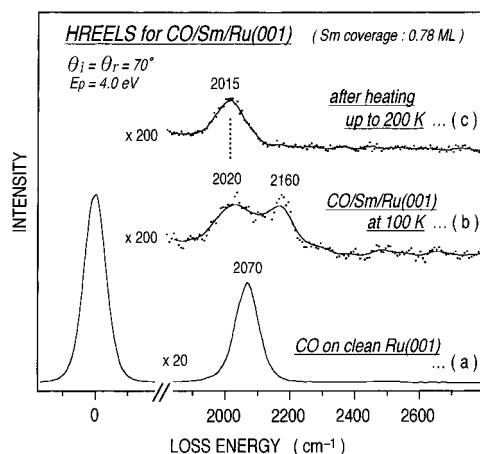

Figure 4. HREEL spectra of the C−O stretching region. Spectrum (a) was recorded for a saturated CO layer on clean Ru(001) at 100 K. Spectrum (b) was recorded on the Sm-precovered Ru(001) surface (0.78 ML) saturated with CO (5.0 langmuir) at 100 K, and spectrum (c) was recorded after heating the sample up to 200 K.
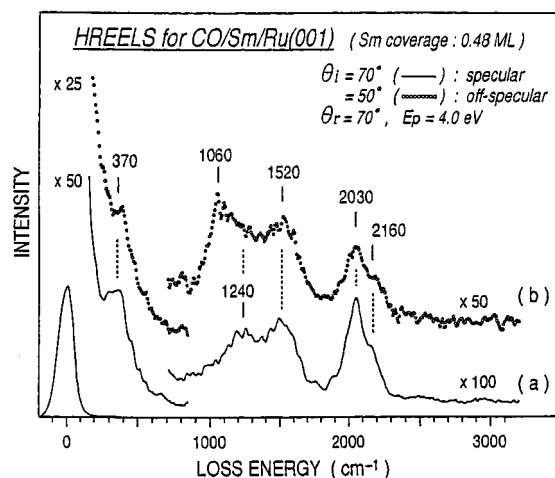

Figure 5. The angular dependence of HREEL spectrum for CO on Sm/Ru(001). The 0.48 ML Sm-precovered surface was saturated with CO (5.0 langmuir) at 100 K. The spectra were recorded with specular (a) and off-specular reflections (b), respectively.

with the off-specular reflection (Figure 5b), on the other hand, an intense loss peak was observed at 1070 cm^{-1}, which was not apparent with the specular reflection. In the specular reflection the dipole scattering is dominant and vibrational modes perpendicular to the surface are mainly observed; in contrast, the impact scattering is obvious in the off-specular reflection and all the modes are observed. Accordingly, the remarkable angular dependence of the intensity of the loss peak at 1070 cm^{-1} suggests that the species with the ν(C−O) mode of 1070 cm^{-1} has the adsorption geometry with its molecular C−O direction parallel or highly inclined to the surface, that is the lying-down configuration. In contrast, the Sm-affected species with the ν(C−O) of 1240 and 1520 cm^{-1}, as well as the weakly adsorbed species with the ν(C−O) of 2160 cm^{-1}, adsorb with their molecular axes perpendicular to the surface.

Figure 6 shows HREEL spectra for the 0.30 ML Sm-precovered surface with a saturation coverage of CO at 100 K. Figure 6a and 6b were obtained from the specular and off-specular reflections, respectively. Both spectra are almost identical, exhibiting three loss peaks at 370, 1540, and 2030 cm^{-1} along with a small broad feature around 1260 cm^{-1}. This result indicates that the molecular axis of each adsorbate is

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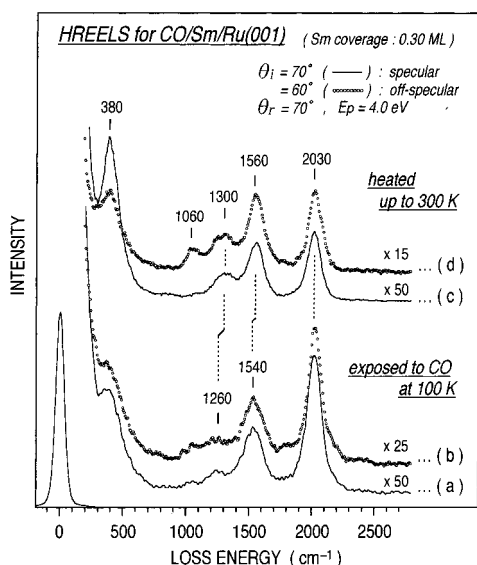*J. Phys. Chem. B, Vol. 106, No. 28, 2002* **7073**

Figure 6. The angular dependence of HREEL spectra for CO on Sm/Ru(001). The 0.30 ML Sm-precovered surface was saturated with CO (5.0 langmuir) at 100 K (a),(b), and subsequently annealed up to 300 K (c),(d). The spectra were recorded with specular (a),(c) and off-specular reflections (b),(d), respectively.

perpendicular to the surface, in agreement with the result from Figure 5.

As shown in Figure 6c, a remarkable increase in intensity of the loss peak at 370 cm^{-1} was observed with both specular and off-specular reflections when the surface was heated to 300 K. This result shows that a part of CO dissociated as a result of the thermal annealing while, at 100 K, most of the CO molecules adsorbed associatively on the surface covered with a small amount of Sm. The intensity of the loss peak at 370 cm^{-1} is appreciably small in the spectrum with the off-specular reflection (Figure 6d). Strong reduction of the intensity is compromised with the fact that the loss peak at 370 cm^{-1} is due to the optical phone of the two-dimensional islands such as samarium oxide.

As shown in Figure 6d, on the other hand, the spectrum with the off-specular reflection has a loss peak at 1060 cm^{-1} which was not observed with the specular reflection. The CO adsorbate with this extremely low frequency ν(C−O) was considered again to have the lying-down configuration and identical to the species observed in Figure 5b.

4. Discussion

4-1. Strong Interaction between Coadsorbed Sm and CO.
As shown in Figures 1 and 2, CO adsorbed on the Sm-precovered surface shows significantly low ν(C−O) frequency between 1100 and 1560 cm^{-1}, depending on Sm and CO coverage. Similar drastic changes of the ν(C−O) frequency with coadsorbed metals have been reported for CO adsorption on alkali-modified transition metal surfaces such as K/Pt(111),[12−14] K/Ru(001),[15,16] and Cs/Ru(001).[17−20] On the alkali-modified surface an attractive interaction between the alkali metals and the CO molecules leads to a formation of coadsorption islands where the alkali atoms and the CO molecules are mutually stabilized. The formation of such coadsorption islands has been identified in terms of the appearance of some characteristic LEED images.[13−20] An attractive interaction between Sm and CO was manifested by the fact that the Sm-effect-free CO species appeared subsequently to the population of the Sm-affected CO species as shown in Figure 2c,d. Considering the vibrational observations similar to the case of the alkali-covered

surfaces, the formation of Sm + CO coadsorption islands is supposed in the present system, at least, at 400 K since a LEED pattern was observed at 400 K.

As shown in Figure 1, the loss peaks except those at 370 and 2160 cm^{-1}, which are due to the decomposition products of CO and the weakly bound CO, respectively, decrease in intensity with Sm coverage and, at last, only the loss features at 370 and 2160 cm^{-1} remained on the 1.3 ML Sm-covered surface as shown in Figure 1e. Similar reduction of the intensity of the ν(Ru−CO) mode, which was due to the screening effect, has been reported in the case of CO adsorption on alkali-modified Ru(001) surfaces.[15−19] It seems that all of the CO molecules adsorbed onto the surface dissociated and the associative adsorbates no longer present except for the weakly bound species. The XPS results, however, have shown that in addition to the weakly bound state a considerable amount of CO were still kept intact without dissociating at 100 K even above 1 ML Sm coverage.[24] From the HREELS measurements with off-specular reflection the unusually low ν(C−O) mode at 1060 cm^{-1} was observed, although the corresponding loss peak was not observed with specular reflection. The intensity of the ν(C−O) mode is hardly detected with the specular geometry if the CO species adsorbed with its molecular axis parallel to the surface. It means that the CO species on the 1.3 ML Sm-covered surface associatively adsorbs on the surface with the lying-down configuration. Therefore, the ν(C−O) mode of the Sm-affected species was not observed at all because of the screening effects of the coadsorbed Sm atoms and the adsorption geometry of the CO species.

The lying-down configuration of the Sm-affected CO species_which has the lowest ν(C−O) mode in the coadsorbed layer of Sm and CO, has an extremely weakened C−O bond. The interaction to weaken the C−O bond is generally related with the enhancement of the charge transfer to the CO(2π*) orbital from the Ru substrate due to the electropositive nature of coadsorbed atoms as alkali atoms. In fact, we have previously observed a lower binding energy shift of the O1s photoemission peak of the Sm-affected CO species by ∼0.6 eV relative to that of the Sm-free CO species.[24] However, the extremely low frequencies of the ν(C−O) modes observed below 1270 cm^{-1} cannot be explained only by this indirect interaction through the substrate, since these frequencies are even lower than those of the CO species coadsorbed with alkali metals[15−20] such as K and Cs, which are far more electropositive than Sm. In agreement with their strong electropositive nature, the lower energy shift of the O1s level by 1.2 and 1.4 eV has been reported for CO on the K- and Cs-promoted Ru(001) surfaces, respectively, in XPS measurements.[16,17] These data suggest that the ability of Sm to enhance the charge-transfer toward the CO species is less than that of alkali metal. Hence, a presence of some kind of direct interaction between CO molecules and Sm atoms must be taken into account to explain the further C−O bond weakening. It is proposed that the Sm atom interacts directly with the oxygen-end of the CO molecule as in the case with the Ni- or Cu-covered Al(111) surface.[21,22] The previous UPS results have shown that the 4σ level of the Sm-affected CO species shifted to higher binding energy by ∼0.8 eV than that of the Sm-free CO species while either the 1π or 5σ level did not seem to be influenced.[24] The difference in the valence electronic structure of the CO molecule supports a presence of the direct interaction between Sm and CO leading to redistribution of the electronic charge among them.

It is reasonable that the thermal dissociation of CO occurred through the CO species with the ν(C−O) mode of 1060 cm^{-1}

as a precursor. In the previous study with TPD measurements, however, a substantial amount of CO was desorbed around 600 K at 0.4 ML although only the ν(C−O) mode of 1170 cm^{-1} was detected above 500 K.[24] Hence, the CO species, which can desorb at around 600 K without reacting with the Sm atoms, exists on the surface even at 500 K. One possible candidate of the species observed at 500 K is carbonates, which could be formed by the disproportionation reaction of CO. However, this possibility is denied because carbonate species such as CO_3^{2-} or CO_2^{2-} give vibrations at around 1300−1600 cm^{-1} and 600−800 cm^{-1} in the case of CO_2 and K coadsobed layer on Ru(001).[27] Therefore the species observed after annealing at 500 K, which gave a vibrational peak at 1170 cm^{-1}, is not carbonate species, CO_2^- or CO_2^{2-}. The CO species with the ν(C−O) mode at 1170 cm^{-1}, which is observed in Figure 4e, is an intermediate species of the desorption around 600 K as well as the decomposition. As clearly shown in Figure 6, the transformation to the species with lowest frequency at 1060−1070 cm^{-1} is a thermally activated process. The process depends on the condition of the surface, that is the Sm coverage and CO coverage.

4-2. Weakly Bound CO Species. The weakly bound CO species has been already detected for the CO adsorption onto the Sm-modified surface using photoemission spectroscopy and thermal desorption measurements.[24] It has been found that this species was desorbed around 125 K and was accompanied by photoemission features with extremely high binding energies. The high binding energies of both core and valence levels were explained by a lack of screening effect of the substrate in the photoemission process; in other words, a very weak surface−adsorbate interaction without the back-donation to the CO(2π*) orbital from the surface.[28,29]

The π*-back-donation from the substrate metal d-orbitals plays an important role in the chemisorption mechanism of CO on most of the transition metal surfaces, but in contrast the interaction between CO and ionic surfaces such as a metal oxide surface, is considered to have little contribution of the π*-back-donation. In fact, upon an oxidized Sm film on Ru(001), which has been prepared by exposing a deposited Sm film to O_2 in UHV, we have also reported the appearance of the weakly bound CO species with the nature identical to that observed here.[30] In several vibrational analyses for CO on metal oxide surfaces, the CO molecule interacting with the metal cation site has exhibited a ν(C−O) shift toward higher frequencies compared with that of gaseous CO.[31−34] The origin of such a blue shift of ν(C−O) mode may be a charge transfer from the CO(5σ) orbital to the substrate, namely the σ-donation, because of the fact that the $CO^+(5\sigma^1)$ species has a higher ν(C−O) frequency than the neutral $CO(5\sigma^2)$ species.[11] According to the results from theoretical calculations, however, in the case of the CO adsorption on a metal oxide surface any chemical interactions including the σ-donation are negligible and alternatively electrostatic effects exclusively give rise to the bond between the adsorbate and a metal cation site.[35,36] Instead of taking into account the σ-bond, Bagus et al. have explained the blue shift of ν(C−O) mode by two electrostatic effects:[37,38] the "wall effect" due to the repulsive interaction between the C-end charge density and the surface during the C−O stretching motion, and the electrostatic interaction between the C−O dipole and the nonuniform electric field of an ionic surface.

In the Sm + CO coadsorption layer, the Sm to CO ratio is 1:1.[24] The cationic character of Sm atom in the coadsorption layer was demonstrated by the Sm 3d photoemission peak observed at ~1083 eV, which was nearly equal to that of Sm^{3+}

cation in Sm_2O_3 and higher by ~2 eV than that of metallic Sm. Such a cationic Sm atom, which resulted by the charge transfer from the Sm atom to the Ru substrate and coadsorbed CO species, probably produces a new adsorption site similar to the metal cation sites on ionic surfaces.

Upon the present vibrational results, hence, it is concluded that the CO species giving the high ν(C−O) mode at 2160 cm^{-1} interacts weakly with the cationic Sm atom on the Sm + CO coadsorbed layer with its axis perpendicular or almost perpendicular to the surface normal.

Summary

To understand the unique character of the promoter effect of rare earth elements, comparing with alkali elements, the adsorption and dissociation of CO on the Sm-modified Ru(001) surface were investigated by HREELS. The atomically clean Ru(001) single-crystal surface was precovered with Sm atoms at 500 K and subsequently exposed to CO at 100 K. The dissociation of CO induced by Sm atoms, which is accompanied with an appearance of a loss peak at 370 cm^{-1}, was found to take place at high Sm coverage above ~0.4 ML or after thermal annealing above ~300 K, in agreement with the previous report.[24]

An extremely low ν(C−O) loss peak of ~1060 cm^{-1}, which indicated a significant C−O bond weakening due to a chemical effect of neighboring Sm adatoms, appeared in the experimental conditions where the Sm-induced CO dissociation was observed. A highly inclined bonding geometry was proposed for this CO species, because the loss peak at 1060 cm^{-1} was observed with a much larger intensity in the HREEL spectrum with the off-specular reflection. This unique species with an extremely weakened C−O bond was considered to be a precursor state to the Sm-induced CO dissociation.

In addition to the highly inclined precursor state to CO dissociation, intermediate states with weakened but probably not tilted C−O bonds were observed at the preadsorbed Sm coverage below 1 ML. Several different species of the intermediate states were identified with multiple ν(C−O) modes in the range of 1120−1560 cm^{-1}, their intensities and frequencies varied as a function of the coverages of Sm and CO, and the subsequent annealing temperature. The magnitude of the C−O bond weakening probably depends on the number of the adjacent Sm atoms affecting the individual CO molecule. The CO species with a low ν(C−O) mode below 1200 cm^{-1} populated predominantly on the surface with high Sm coverage and remained stable after thermal annealing even to 500 K while the other CO species with higher ν(C−O) modes, as well as the Sm-free CO species, disappeared completely. A part of these species with ν(C−O) modes of 1120−1560 cm^{-1} probably converted into the highly inclined precursor state to dissociate while the others desorbed upon annealing.

Furthermore, a weakly bound CO species with ν(C−O) of 2160 cm^{-1} has been identified and considered to interact with Sm atoms in the Sm and CO coadsorbed layer.

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