In-situ FT-IRAS study of the CO oxidation reaction over Ru(001): III. Observation of a 2140 cm^{-1} C-O stretching vibration

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Utilizing Fourier Transform Reflection Absorption-Infrared Spectroscopy (FT-IRAS), we have investigated the CO oxidation reaction in-situ on a Ru(001) surface at high ($\approx$ 10 Torr) pressures. Under certain temperature and reactant (CO and O_2) partial pressure conditions, we observe for the first time on unsupported Ru a weakly adsorbed CO species which is characterized by an unusually high C-O stretching frequency of 2140 cm^{-1}. A similar feature has been identified previously on small Ru particles in supported catalysts and attributed by some to a multicarbonyl species ($-Ru(CO)_n$, $n > 1$). By following the intensity of this feature on Ru(001) relative to other peaks in the spectra, we believe that the 2140 cm^{-1} peak observed here is most likely due to a highly perturbed linearly adsorbed monocarbonyl on partially oxidized Ru sites generated by locally high concentrations of coadsorbed oxygen.

Keywords: Ruthenium tricarbonyl; CO oxidation on Ru(001); CO and oxygen coadsorption on Ru

1. Introduction

The adsorption of CO on Ru has been extensively studied by vibrational spectroscopies on both small particle- (supported catalysts) [1–9] and unsupported single crystal-surfaces [9–12]. CO has been found to adsorb linearly on top of a single Ru atom (linear, atop) in both systems when the bulk metal surfaces were free of coadsorbed species. In infrared (IR) spectroscopic studies, this species was found to give rise to a peak at $\approx$ 2060 cm^{-1} at saturation coverages. When oxygen or sulfur are present as coadsorbates, the CO bond to

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the RU surface is weakened as evidenced by the shift of the CO IR peak to ≈ 2080 cm^{-1} [9–12], but the *predominant* adsorption mode [13] is still linear, atop. However, an additional CO species has been observed on supported-Ru catalysts with IR spectroscopy when oxygen or sulfur are present. The second adsorbed CO species is characterized by an unusually high C-O stretching frequency of 2130–2140 cm^{-1}. Some authors [1,3–8] have identified this latter feature, with a corresponding peak near 2080 cm^{-1}, as rising from the coupled vibrations of a multicarbonyl species, $-Ru(CO)_n$, $n > 1$, most likely directly attached to the oxide support surface. However, this assignment remains controversial. For example, Tatarchuk and coworkers [9] observe that there is significant variation in the relative intensities of the two highest frequency peaks in both their and other published spectra. From this, they conclude that the two peaks arise from separate species and propose a model in which CO adsorption on low coordination corner or stepped Ru sites, where several S (or O) atoms are coadsorbed nearby, accounts for the highest frequency peak. Even among those who conclude there is a multicarbonyl, there is disagreement as to whether the species contains two CO molecules, a gem-dicarbonyl [1,3–6], or three, $-Ru(CO)_3$ [7,8], although the recent work [7,8] using adsorption of isotopic $^{12}CO/^{13}CO$ mixtures presents strong evidence for the latter. In fact, Bell and coworkers [8] suggest that *two* distinct tricarbonyl species are present; one directly attached to the oxide surface (an isolated, monoatomic Ru tricarbonyl), and one formed on partially oxidized sites on the surface of Ru particles in a SiO_2-supported catalyst. While not wishing to cloud the issue further, we present here the first IR spectroscopic observation of a CO peak above 2100 cm^{-1} on unsupported Ru where isolated Ru atoms attached to the oxide support surface will *not* be present. We show that an assignment of a multicarbonyl species as responsible for the high frequency C-O stretch on *bulk* Ru surfaces is inconsistent with the data. Instead, we believe that a linearly adsorbed monocarbonyl on partially oxidized Ru sites is much more likely.

2. Experimental

The experiments reported here were performed in a multilevel UHV chamber (10^{-11} Torr range) equipped for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and thermal desorption mass spectroscopy (TDMS) in UHV, and for infrared spectroscopy in a high-pressure reactor [15]. The reactor could be isolated from the UHV chamber with a gate valve thus allowing control of gas pressures from 10^{-10} Torr to 1 atm. Sample mounting and cleaning of the Ru(001) crystal have been described earlier in detail [11]. Infrared spectra were recorded with a rapid scanning Perkin-Elmer 1800 FTIR in single reflection with 80° angle of incidence. The vibrational spectra to be shown in this paper were obtained with the spectrometer operating at 4 cm^{-1}

resolution in the 2500–1000 cm^{-1} range typically by adding 200 scans in a total measurement time of 60 seconds. The spectra were then ratioed against a stored background spectrum of the clean surface and sometimes subtracted from another ratioed spectrum; no other data manipulations except baseline corrections were performed.

A typical experiment proceeded in the following manner. The Ru crystal was cleaned and translated to the high-pressure reactor which was then isolated from the main UHV chamber. After a background scan of the clean crystal at room temperature was obtained, CO and O_2 were introduced into the reactor to the desired partial pressures, and FT-IRAS spectra were recorded with the crystal heated to various temperatures. Both reactant gases were of high purity; however, the CO was further purified by flowing the gas through a liquid nitrogen trap to remove residual carbonyls (particularly $Ni(CO)_4$). When this was not done, Auger spectra revealed the presence of Ni on the Ru surface. Following some of these IR experiments, the gas mixture was pumped out, the crystal reintroduced to the UHV chamber, and LEED and Auger measurements performed subsequent to a thermal flash at 600 K during which CO TDMS data were obtained.

3. Results

Fig. 1 shows the vibrational spectrum obtained during the CO oxidation reaction on a Ru(001) single crystal surface at 500 K in CO/O_2 pressures of 2.5/1.0 Torr. Contributions from the gas-phase spectrum of CO, whose unresolved R- and P-branches are labelled in the figure, are centered at 2143 cm^{-1}. A spectral feature from CO adsorbed on the Ru surface is observed at 2080 cm^{-1}. In addition, a peak of very weak intensity is identified at 2140 cm^{-1}, where it appears in the form of an asymmetry in the P-branch of the gas-phase spectrum of CO (indicated by an arrow).

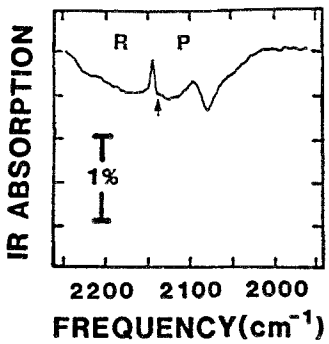

Fig. 1. Vibrational spectrum in the C-O stretch region during steady-state reaction at 500 K on Ru(001) for $P(CO) = 2.5$ Torr and $P(O_2) = 1.0$ Torr.

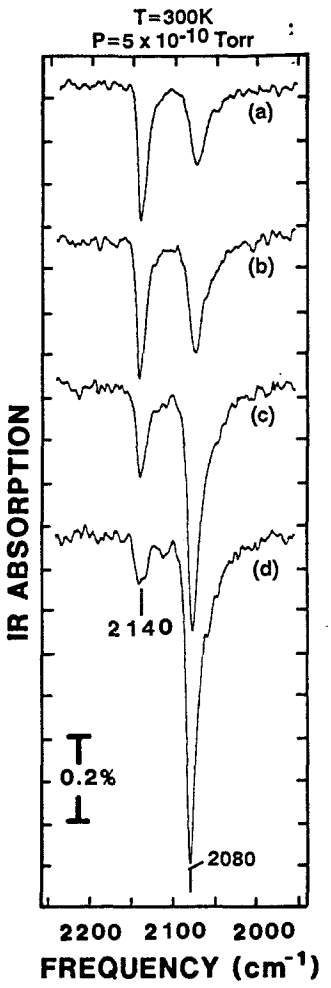

Fig. 2. FTIR spectra obtained after evacuation of the reactant gas mixtures at 300 K and subsequent to reaction on Ru(001) at 500 K. $P(CO) = 2.5$ Torr and $P(O_2) =$ (a) 5.0 Torr, (b) 2.5 Torr, (c) 1.0 Torr, (d) 0.5 Torr.

The intensity of 2140 cm^{-1} feature increases as the size of the 2080 cm^{-1} band decreases. This can be seen most clearly from post-reaction spectra obtained after cooling to 300 K and evacuation of the reaction chamber as illustrated in fig. 2, since there is no interference from gas-phase CO. In the figure, post-evacuation spectra are compared after reaction at 500 K in gas mixtures with CO/O_2 partial pressure ratios ranging from 0.5 (2a) to 5 (2d). The intensity of the 2140 cm^{-1} band is greatest under the most oxidizing (lowest CO/O_2 ratios) conditions (fig. 2a,b). However, the size of the peak still indicates the presence of only small, submonolayer (< 0.05 ML) quantities of CO. While these spectra were taken at room temperature after evacuation, further cooling of the ruthenium crystal to ≈ 100 K in UHV followed by

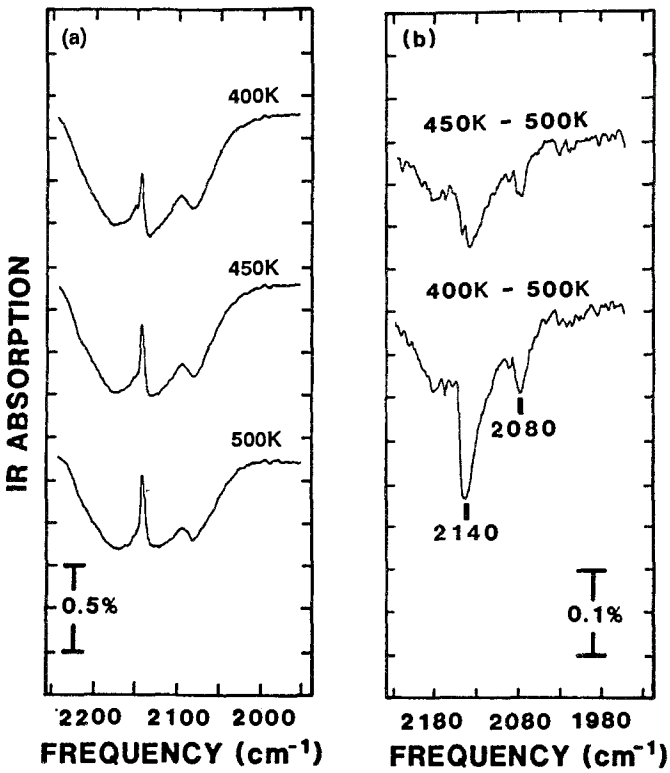

Fig. 3. (a) Vibrational spectra obtained in a 2.5 Torr CO/2.5 Torr O_2 reaction mixture at 400, 450 and 500 K. (b) Spectra obtained by subtracting the 500 K spectrum from the 450 and 400 K spectra.

exposure to CO did not produce any change in the size of either feature. The 2140 cm^{-1} band could be reproduced for a variety of oxidizing pressure combinations with CO/O_2 ratios < 2, but was consistently absent under the most reducing conditions examined in our studies (CO/O_2 ratios > 5), even when the 2080 cm^{-1} peak was present [16]. Thus, it appears that the two peaks can be assigned to two separate and distinct adsorbed CO species.

The intensity of the 2140 cm^{-1} feature under reaction conditions also exhibited a strong dependence on reaction temperature as demonstrated in fig. 3. Fig. 3a contains spectra obtained during reaction in an oxidizing gas mixture (2.5 Torr CO + 2.5 Torr O_2) at temperatures of 400 K, 450 K, and 500 K as indicated in the figure. The significant drop in intensity of the 2140 cm^{-1} feature with temperature is evident by the much more symmetrical appearance of the P-branch absorption feature due to gas-phase CO for the 500 K spectrum. This is more clearly seen in fig. 3b which illustrates the result of subtracting the spectrum obtained at 500 K from those obtained at 450 and 400 K. The fact that the intensity of the 2140 cm^{-1} band is much larger in the lower spectrum of fig. 3b (400 K minus 500 K) than in the upper spectrum (450 K minus 500 K)

demonstrates that the population of the CO species responsible for this peak *decreases with increasing reaction temperature*. Also evident from the difference spectra is that the intensity of the 2080 cm^{-1} band is much less sensitive to changes in reaction temperature under these conditions.

As additional probes of the surface composition during reaction, we performed TDMS, LEED and AES measurements subsequent to cooling of the crystal and pumpout of the reactant gases. The LEED and AES data are described in detail in another publication [16] but are briefly summarized here. Following a 600 K flash to remove adsorbed CO during which TDMS spectra were obtained (see below), LEED and AES data were recorded. Under the reaction conditions (temperature and reactant partial pressures) in which the 2140 cm^{-1} is observed, large quantities (≈ 1 ML) of adsorbed oxygen are observed by AES. The (1×1) LEED pattern for this surface is consistent with a 1 ML oxygen overlayer commensurate with the ruthenium surface. As discussed below, small amounts of dissolved oxygen are also likely present on this surface. The present FT-IRAS data clearly establish that the CO species assigned to the 2140 cm^{-1} feature is only present on surfaces with such high oxygen coverages, i.e., after reaction under oxidizing conditions. Post reaction thermal desorption of CO from this surface indicates that only very small amounts of CO ($\theta_{CO} < 0.05$) desorb molecularly from the surface in agreement with the very weak intensity of the IR band. Time-resolved FTIR spectra, obtained during slow heating of the sample in vacuum, show that the 2140 cm^{-1} band was present at temperatures up to 400 K while the 2080 cm^{-1} band was not completely removed until 440 K, again suggesting that the two bands arise from two distinct adsorbed CO species.

4. Discussion

There have been numerous vibrational spectroscopic studies of CO on Ru. These include measurements on small Ru particle surfaces in supported catalysts [1–9] and on macroscopic polycrystalline and single crystal surfaces [9–12]. On clean Ru(001), a single CO species adsorbs whose C-O stretching frequency (ν_{CO}) ranges from about 1950 to 2060 cm^{-1} as CO coverage increases to saturation ($\theta_{CO}(sat) \approx 0.65$ ML [11]). From these and other studies [17], it is apparent that CO bonds through the C atom to a single Ru atom in an upright, linear fashion (in a so-called atop position). In the presence of coadsorbed oxygen [10,12,17] or sulfur [9], the value of ν_{CO} at saturation coverages increases indicating a weakening of the metal-CO interaction with, however, in most cases [13] no change in the geometry of the bond. Exactly analogous results have been obtained on supported catalysts and the interpretation is the same [5–9]. In these latter systems, an additional feature is observed in the infrared spectra with a ν_{CO} of quite high frequency, 2130–2140 cm^{-1}. In the present study, we

report the first observation of a similar band in the FTIR spectrum of CO on a single crystal Ru surface in the presence of coadsorbed oxygen.

From the AES and LEED data obtained high-pressure reaction, it is clear that the CO species giving rise to the 2140 cm^{-1} peak on Ru(001) is only present when the surface is covered with very large quantities of oxygen (≈ 1 ML). Adsorption of CO on such a surface is drastically modified compared to the clean surface. The desorption temperature of CO is considerably lower compared to the clean surface and, again, the C-O stretch (ν_{CO}) is shifted to an unusually an unusually high frequency of 2140 cm^{-1}. Both observations indicate a weakly adsorbed species with greatly reduced back-donation. As discussed above, even in the case of more moderate oxygen coverages ($\theta_O = 0.5$), coadsorption of CO and oxygen results in a shift to higher C-O stretching frequency (2080 cm^{-1}) from a weakening of the M-CO bond. As the oxygen coverage is increased above the 1/2 ML level, saturation CO coverages at 80 K decrease dramatically [12]. In fact, the results indicate that CO does *not* adsorb on a surface that is *completely* covered with 1 ML of oxygen. The small amount of CO present at $0.5 < \theta_O < 1.0$ ML is believed to reside at the boundaries between O-(1 × 1) ($\theta_O = 1$) and O-(2 × 1) ($\theta_O = 1/2$) islands with C-O stretching frequencies as high as 2090 cm^{-1}. In these UHV experiments, an IR band above 2100 cm^{-1} was never observed [12]. We believe that the difference in the two studies results from the substrate temperature at which oxygen is adsorbed. For the UHV experiments, O_2 is adsorbed at 300 K. This can be contrasted with the high pressure experiments described here which yield high oxygen coverages (≈ 1 ML) during high temperature (500 K) reaction in oxidizing gas mixtures (CO/O_2 ratios < 2). In this case, small quantities of dissolved oxygen are likely present [16]. As such, it appears that subsurface oxygen is a necessary ingredient for the formation of the adsorbed CO species giving rise to the 2140 cm^{-1} band.

High frequency ν_{CO}'s are commonly observed on transition metal oxides when CO is adsorbed at high pressures, e.g., on polycrystalline nickel-oxide (2136 cm^{-1}) [18] and high surface area TiO_2 (2180 cm^{-1}) [7]. Similarly, they have been observed on oxygen-covered single crystal surfaces of Ni, Cu and Pd for adsorption of CO at low (< 300 K) temperatures in UHV; e.g., on oxidized Cu(111) (2100 and 2117 cm^{-1}) and Cu(110) (2140 cm^{-1}) [19], $c(2 \times 2)$O-Ni(100) (2137 cm^{-1}) [20] and on $p(2 \times 2)$O-Pd(100) (2125 cm^{-1}) [21]. Although we can firmly assign the 2140 cm^{-1} species to adsorption on a highly oxygen-covered Ru surface, the detailed nature of the adsorption site on this surface is less clear.

A possible model for the site is suggested by the recent results of Tatarchuk and coworkers [9] who studied CO adsorption on clean and sulfur modified supported- and single crystal-Ru surfaces. These authors assign a band near 2110 cm^{-1}, obtained on sulfided Ru/Al_2O_3, to linearly adsorbed CO on edge or corner sites. Such sites would provide less steric constraints relative to low-index surface planes allowing for more numerous S neighbours for CO. As discussed

above, we observe the 2140 cm^{-1} peak when oxygen coverages on the Ru(001) surface are ≈ 1 ML. Thus, a site at the boundary between a 1 ML oxygen island {O-(1 × 1)-Ru(001)} and a 1/2 ML island {O-(2 × 1)-Ru(001)} might be very similar to that proposed by Tatarchuk. However as discussed above, the presence of subsurface oxygen (oxide?) appears to be necessary ingredient for the observation of the 2140 cm^{-1} band on Ru. Such a species might provide the necessary ionic character for the exposed Ru atoms. That this might be important is demonstrated in the work by Zecchina and coworkers [18] who suggest that adsorption of CO onto ionic metal sites gives rise to C-O vibrational stretching frequencies similar to the 2140 cm^{-1} band upon exposure of NiO to CO ($\nu_{CO} = 2136$ cm^{-1}). For NiO, this model is particularly appealing because there exist homogeneous analogues (ccordination complexes) containing Ni^{2+}. Furthermore, these authors show that for CO on NiO, both the dynamical and the static frequency shift upon change in CO coverage indicate a metallic adsorption site where the σ- and π*-orbitals of the CO molecule overlap with the d-orbitals of the Ni^{2+} ions [18].

Another possible assignment for the 2140 cm^{-1} feature deserves to be discussed; namely that of a multicarbonyl species, $-Ru(CO)_n$, $n > 1$. A gem-dicarbonyl species on isolated, supported-Rh atoms is well established in highly dispersed Rh catalysts [22]. It should be emphasized here that such isolated atoms will not be present on the single crystal surfaces of Ru (and Ni, Cu or Pd). However, Bell and coworkers [8] suggest that multicarbonyl- (tricarbonyl-) Ru species can form on both isolated atoms *and* oxidized particles on SiO_2-supported Ru. As such, we consider in the following the possibility that the 2140 cm^{-1} and a portion of the 2080 cm^{-1} peaks could arise from a di- or tricarbonyl species on the oxygen-covered Ru(001) surface. In order to do so, we briefly summarize previous assignments of multicarbonyl species on supported Ru.

In analogy with the results on supported Rh [22], the presence $-Ru(CO)_2$ has been suggested by various authors based on IR studies of supported-Ru catalysts [1,3–6]. In the Ru case, the two bands observed at ≈ 2080 and ≈ 2140 cm^{-1} are assigned to the coupled out-of-phase (asymmetric) and in-phase (symmetric) C-O stretching vibrations, respectively, of the dicarbonyl species adsorbed on an oxidized ruthenium site. However, more recent studies in which the IR spectra of coadsorbed $^{12}CO/^{13}CO$ isotopic mixtures were measured have concluded that the species is a tricarbonyl, i.e., $-Ru(CO)_3$ [7,8]. This is most convincingly shown for the case of reduced Ru where it appears that adsorption of CO corrosively removes Ru atoms from the reduced particles leading to the formation of isolated $-Ru(CO)_3$ attached to the oxide support surface (e.g., $(-TiO)_2Ru(CO)_3$ [7]). Bell and coworkers [8] find that there is a slight shift in the two high frequency peaks when CO is adsorbed on "partially oxidized" Ru/SiO_2 (subsequent to O_2 exposures (160 Torr) at room temperature). These authors suggest that a separate tricarbonyl species can form on the surface of the Ru particles that now contain significant quantities of adsorbed

oxygen. Thus, we consider the present FT-IRAS results in view of the multicarbonyl model.

As shown in figs. 2 and 3 and in time-resolved FTIR experiments performed during thermal desorption (not shown), the bands we observe at 2140 and 2080 cm^{-1} display considerable variation in relative intensities suggesting that they arise from two distinct adsorbed CO species. However, the fact that we have not been able to observe the 2140 cm^{-1} species without a band in the 2080 cm^{-1} region does not allow us to completely rule out a multicarbonyl species. Thus as suggested in recent supported-Ru work [5,8], the 2080 cm^{-1} feature could be associated with overlapping bands due to a multicarbonyl species (with the 2140 cm^{-1} peak), and another oxygen-modified chemisorbed CO species. To pursue this suggestion further, note that the spectrum in fig. 2a represents the largest ratio of peak intensities for the 2140/2080 cm^{-1} peaks observed in this study. If we assume that this ratio represents the presence of a *di*carbonyl alone, we can estimate a bond angle between the two carbonyls ($=2\theta$) on the basis of the relative intensities of the two peaks according to eq. (1) [23]:

$$\frac{I(\text{symmetric})}{I(\text{asymmetric})} = \cot^2\theta. \tag{1}$$

The experimental intensity ratio from fig. 2a is about 1.7 which gives a bond angle (2θ) of 75°. This is unreasonably small for metal dicarbonyls [22] or dinitrosyl [24] species where 2θ values of $\geqslant 90°$ are observed. Additionally, the trend in the data shown in fig. 2 is for this ratio to get larger with a corresponding decrease in the bond angle (2θ). Therefore, it seems unlikely that the two spectral features observed in this study can be due to dicarbonyls. The case for tricarbonyls on *unsupported* Ru seems even less likely due to severe steric constraints on the formation of such a species. Furthermore, Bell and coworkers [8] calculate that the intensity ratio of the 2140/2080 cm^{-1} bands for a tricarbonyl should be much less than 1. Finally, there is overwhelming evidence from the above cited studies and, in particular from the elegant work of Zecchina and coworkers [18], where only a single band at 2135 cm^{-1} is observed which can be unambiguously assigned to linearly adsorbed CO on oxidized metal surfaces.

Based on the above discussion, we conclude that the 2140 cm^{-1} band observed in the work reported here can be assigned to a linearly-adsorbed (atop) CO species on an oxidized Ru site. Even for quite variable experimental conditions, the population of these species is never large (always < 0.05 MLs). As such, they are likely associated with "defects" in the O-(1 × 1)-Ru(001) layer in order to generate sufficiently unencumbered Ru atoms whose oxidation state is also modified by subsurface oxygen atoms. To reconcile this conclusion with the recent literature concerning CO adsorption on supported-Ru catalysts [7-9], it is important to reemphasize that the two systems differ with respect to their

ability to form isolated, atomic Ru species. Thus, it is possible that the confusion results from the similarity of the C-O stretching frequencies of quite different adsorbed CO species. For example, the peak assignments of the three distinct CO adsorption modes described above could be made in the following way: coadsorbed O + CO (2080 cm^{-1}), CO on an oxidized Ru site (2140 cm^{-1}), and a multicarbonyl species (2080 *and* 2140 cm^{-1}). The former two species would be present on both supported and unsupported Ru, while the latter species should only be observed on highly dispersed, oxide-supported Ru. There still remains the issue of the assignment of a separate tricarbonyl species on "partially oxidized" Ru *particles* supported on SiO_2 [8]. The surface of these particles should be somewhat similar to oxygen-covered Ru(001). If so, we believe based on the above discussion that the presence of linearly-adsorbed CO on both partially oxidized ($\approx$ 2140 cm^{-1}) and oxygen-modified (2080 cm^{-1}) bulk Ru surfaces should be accounted for when interpreting the spectra.

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