

Interaction of Hydrogen with RuO₂(110) Surfaces: Activity Differences between Various Oxygen Species

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The interaction of hydrogen with RuO₂(110) surfaces was studied by means of thermal desorption and vibration spectroscopies. The stoichiometric surface exposes two types of coordinatively unsaturated atoms: double-bonded O-bridge and five-fold-bonded Ru-cus, while at the O-rich surface the Ru-cus atoms are covered with single-bonded O-cus. On the stoichiometric RuO₂(110) surface at 90 K, H₂ either adsorbs molecularly on Ru-cus sites or dissociates and forms with O-bridge an H₂O-like surface group. If, in addition, also O-cus is present at the surface, hydrogen interacts exclusively with this species forming H₂O-cus. This demonstrates that hydrogen reacts much more readily with O-cus than with O-bridge as expected from the reduced bond order and smaller binding energy of O-cus. It is furthermore shown that at surface temperatures below 90 K free coordinatively unsaturated Ru-cus sites are needed to activate the incoming H₂ molecules prior to any reaction with O-cus or O-bridge. Generally, Ru-cus sites play a key role for reactions of a number of molecules at the RuO₂(110) surface. These findings are supported by recent DFT-based calculations but are at variance with other reports.

1. Introduction

Oxides play an important role in heterogeneous catalysis as support materials and as chemically active surfaces. Although a large amount of mostly experimental knowledge has been collected,^{1,2} not so much atomic-scale insight in the structure and functionality of oxides has been established. Recently, however, it has been shown that well characterized RuO₂(110) surfaces can provide insight of this kind. This surface has been demonstrated to serve, for example, as a very effective catalyst for CO oxidation^{3–5} and NH₃ oxidation.⁶ The successful experiments stimulated important theoretical work comprising the structure and stability of RuO₂ itself,⁷ the transition state for CO oxidation,⁸ and a complete surface phase diagram in its dependence on gas phase (CO and O₂) pressure and temperature.⁹ Even the steady state rate of CO oxidation has been simulated, and surprisingly good agreement has been achieved¹⁰ with our experiments performed at pressures up to 3×10^{-6} mbar.⁵ For real catalysts, i.e., highly dispersed Ru particles (2 nm in diameter) on both MgO and SiO₂ supports, RuO₂ was again identified as the catalytically active phase independent of the support for the oxidized catalyst.¹¹ In comparison with the above data,^{3–5} it has been shown that the surface science approach is applicable to supported Ru catalysts, and that a pressure gap does not exist.¹¹ The turnover frequencies (number of CO₂ molecules per metal surface site per second) were found¹¹ in good agreement with the values derived from RuO₂ single-crystal surfaces.⁵

The stoichiometric RuO₂(110) surface (see Figure 1) is characterized by two types of coordinatively unsaturated (cus) surface atoms organized in rows along [001]: (i) five-fold coordinated Ru atoms (Ru-cus) and (ii) two-fold coordinated

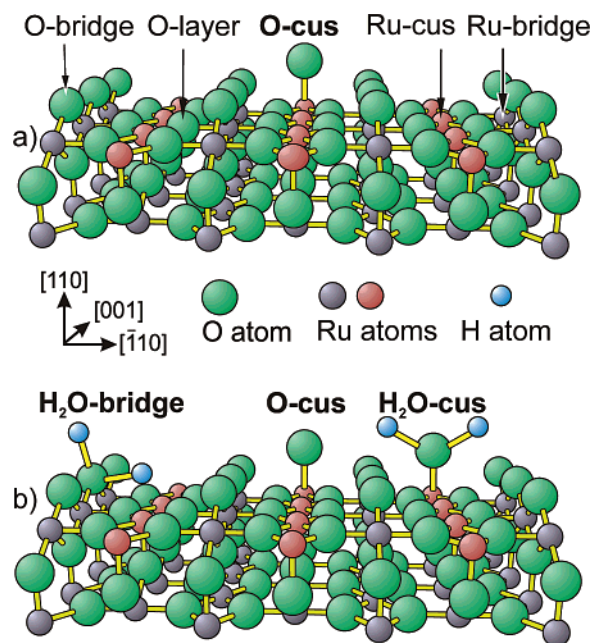


Figure 1. (a) Ball-and-stick model of the stoichiometric RuO₂(110) surface in perspective view together with adsorbed O atoms (O-cus). (b) Same as for (a) with reaction products H₂O-bridge and H₂O-cus.

oxygen atoms (O-bridge).¹² By exposure to O₂ at 300 K, additional oxygen atoms (called O-cus) can be adsorbed on top of Ru-cus. A maximum coverage of about 80% of the O-cus atoms can thus be achieved,^{13,14} as will be discussed in more detail below. This surface is called O-rich RuO₂(110). Like in previous publications we use the notation X-bridge/Y-cus to denote a configuration with a particle X occupying two bridge Ru-atoms and a particle Y occupying the cus Ru-atom. So, the stoichiometric surface will be denoted O-bridge/–, the O-saturated surface, where the Ru-cus atoms are also occupied

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by O, O-bridge/O-cus. The O-cus species is relatively weakly bonded to the surface (see below) and desorbs associatively at temperatures as low as 400–500 K.^{13,14}

Hydrogen is expected to form strong bonds, particularly with the oxygen anions at an oxide surface.² In a short note, we have shown recently that hydrogen interacts in a complicated manner with the stoichiometric RuO₂ surface.¹⁵ At 90 K, H₂ either molecularly adsorbs as dihydrogen on top of the Ru-cus atom or, at the same time, interacts dissociatively with the O-bridge atom to form a metastable dihydride (water-like, H₂O bridge) complex, which is transformed into monohydride (OH bridge) by release of hydrogen when slightly heated. These far reaching conclusions became possible through the comparison between experimental thermal desorption and vibration data and density functional theory (DFT) calculations. The calculations were published also in more detail in the meantime.¹⁶ Recently, Knapp et al.¹⁷ proposed that at 300 K hydrogen adsorbs directly on an O-bridge rather than via activation at Ru-cus sites and that O-cus is inactive for hydrogen adsorption. These conclusions are quite unexpected and are in contradiction to the DFT-based predictions.¹⁶

In this paper, we focus on the mechanistic study of hydrogen adsorption on both the stoichiometric (O-bridge/–) and oxygen-rich (O-bridge/O-cus) RuO₂(110) surfaces using high-resolution electron energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). We provide spectroscopic evidence that at a surface temperature of 85 or 90 K free Ru-cus sites are needed to activate the incoming molecular hydrogen prior to any reaction with O-cus or O-bridge. Furthermore, our detailed experiments demonstrate a large difference in chemical reactivity of the differently coordinated surface oxygen species: The O-cus species is much more active in the interaction with hydrogen than the O-bridge species. Finally we point out that the key role of Ru-cus and the difference in reactivity between O-cus and O-bridge holds also for a number of molecules whose reactions at RuO₂(110) have been studied recently.

2. Experimental Section

High-resolution electron energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS) were performed in an ultrahigh-vacuum (UHV) apparatus, consisting of two chambers separated by a valve. The upper chamber (base pressure 3×10^{-11} mbar) was used for sample preparation. It was equipped with an argon ion sputtering gun, gas exposing valves, a LEED optics, and a quadrupole mass spectrometer for TDS experiments. The heating rate for TDS was approximately 3 K s^{-1} . The lower chamber (base pressure 2×10^{-11} mbar) housed a HREEL spectrometer of commercial Ibach design (Delta 0.5, SPECS, Germany). HREEL spectra were recorded at an angle of incidence of 55° with respect to the surface normal in specular geometry. The energy of the primary electrons was set to 3 eV and the spectral resolution to better than 3 meV. The substrate, a Ru(0001) single crystal, was clamped between two Ta wires. A NiCr/Ni thermocouple was spot-welded to the back of the Ru crystal. The sample temperature could be varied between 85 and ~ 1300 K by combining cooling with liquid nitrogen and heating by radiation or by combined radiation and electron bombardment from the backside of the sample.

The RuO₂(110) surface was prepared in-situ following a procedure described in preceding publications.^{3,12} In short, the Ru crystal was cleaned by applying repeated sputtering and annealing cycles. A thin single-crystalline oxide film was then

grown epitaxially by exposing the clean Ru(0001) surface to about 10^7 L O₂ ($1 \text{ L} = 1.3 \times 10^{-6} \text{ mbar} \times \text{s}$) at 700 K, resulting in 2 nm thick platelets of RuO₂(110) orientation. The O-rich surfaces were prepared by exposing the stoichiometric RuO₂-(110) surface to O₂ at room temperature. For the low exposures used under UHV conditions, the maximum coverage of O-cus is reached for an exposure of 1 L, which corresponds to about 80% of Ru-cus sites being occupied by O-cus atoms. This limitation is a consequence of the linear chain of Ru-cus adsorption sites, since an incoming O₂ molecule needs a pair of empty Ru-cus sites in order to be dissociatively adsorbed. Furthermore, the diffusion barrier of O-cus is rather high so that the O-cus atoms are immobile at 300 K. From statistical considerations, this leads to a maximum coverage for O-cus of only about 83%.

Prior to each experiment, impurities such as hydrogen or CO were desorbed and the surface ordering was improved by heating the sample to 700 K for one minute. The surface cleanliness and order were controlled by standard techniques, i.e., HREELS, TDS, and LEED in our case. Gases exposed to the sample surface were ¹⁶O₂ (purity 99.998%, Messer Griesheim), ¹⁸O₂ (min. 99 atom % ¹⁸O, Isotec), CO (purity 99.997%, Messer Griesheim), H₂ (purity 99.95%, Messer Griesheim), and D₂ (min. 99 atom % D, Isotec).

3. Results

3.1. Thermal Desorption Spectra for Stoichiometric and O-Rich RuO₂(110). Figure 2a presents H₂ TDS spectra after exposing surfaces of varying oxygen content to 2.5 L H₂ at 90 K. The upper curve is for the stoichiometric surface and exhibits the known α and β desorption states of hydrogen.¹⁵ The α state at about 100 K is due to weakly adsorbed molecular hydrogen oriented parallel to the surface on-top of the Ru-cus sites. This state is only weakly occupied here because of the slightly higher sample temperature of 90 K as compared to 85 K in ref 15. The much more intense β state is due to associatively desorbing hydrogen during reduction of H₂O-bridge into OH-bridge as discussed below. The population of the β state decreases strongly with O-cus coverage: For O₂ exposure larger than or equal to 0.5 L, the β state is practically absent.

Figure 2b exhibits the H₂O TD spectra for the same sequence of surface preparation. The stoichiometric surface, at zero O₂ exposition, exhibits a broad peak centered at about 560 K which is understood as being due to disproportionation of 2 OH-bridge into H₂O, O-bridge, and -bridge, the latter being an oxygen vacancy at Ru-bridge. Obviously, the amount of H₂O from Ru-bridge decreases with increasing O-cus coverage and the desorption peak shifts to higher temperature, showing the expected second-order kinetics due to the disproportionation of OH-bridge. At O-cus coverage of ~ 0.65 ML the OH-bridge derived peak vanishes completely.

With increasing O-cus concentration in Figure 2b, a sharp peak develops at about 400 K with its shape being typical for first-order desorption. It is assigned to H₂O-cus since the TD spectra are identical to those found for H₂O adsorption at the stoichiometric RuO₂(110) surface.¹⁸ Obviously, hydrogen interacts in this case with O-cus to form H₂O-cus. This is further confirmed by the respective TD spectra of O₂ shown in Figure 2c. No O₂ desorption is detected for exposures below 0.5 L, revealing that all O-cus species have been reacted off. The weak shift in H₂O-cus peak temperature by only a couple of K in Figure 2b correlates with the occupancy of neighboring Ru-bridge sites by OH-bridge: Obviously, a neighboring OH-bridge slightly decreases the binding energy of H₂O-cus.

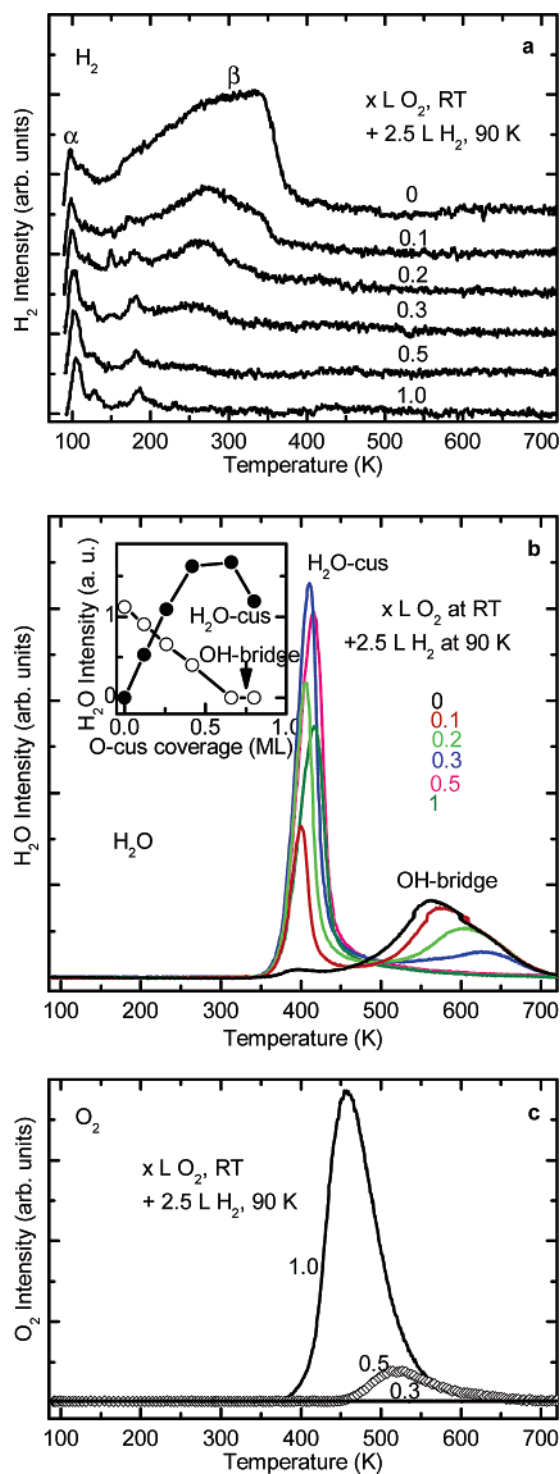


Figure 2. Thermal desorption spectra following exposure of 2.5 L of H₂ to the RuO₂(110) surface at 90 K for different preexposures to O₂ (x) as indicated. The exposure is given in units of Langmuir (L) (1 L = 1.33 × 10⁻⁶ mbar × s). (a) H₂ (mass 2); (b) H₂O (mass 18); (c) O₂ (mass 32). Similar spectra as those in (a) have been published already in reference 15.

The relative amounts of H₂O released from Ru-cus and Ru-bridge sites (see Figure 1) are determined by integrating the TD signals. The results are shown in the inset of Figure 2b. The amount of H₂O from Ru-bridge decreases with increasing O-cus coverage, and at the O-cus coverage of ~0.65 ML the OH-bridge derived peak vanishes completely, whereas the maximum H₂O-cus formation is achieved. This finding, together with the absence of β-H₂ state for O₂ exposure larger than 0.3

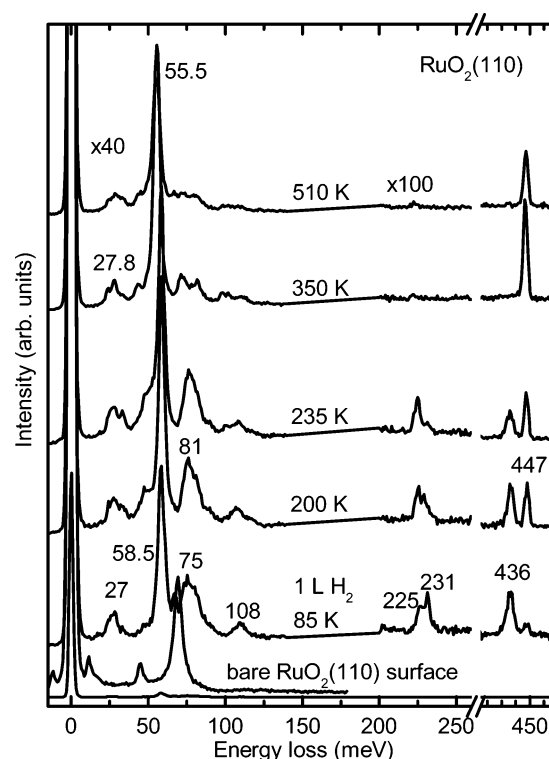


Figure 3. HREEL spectra for the bare stoichiometric RuO₂(110) surface (lowest curve) and after exposure of 1 L H₂ at 85 K and warming to the indicated temperatures. The peak of the elastically scattered electrons is depicted at 0 meV energy loss. The sensitivity factors of the energy-loss parts (× 40 and × 100) are given. All spectra were recorded at 90 K in specular geometry with an incidence angle of 55° with respect to the surface normal and with a primary energy of 3 eV. The first, second, and fifth spectra have been published already in reference 15.

L (see Figure 2a), reveal that hydrogen reacts preferentially with O-cus species instead of with O-bridge species.

Importantly, from the TDS results we can gain further insight into the reaction pathway of hydrogen on O-rich RuO₂(110). If there would be direct (through gas phase) interaction of H₂ with O-cus, then we would expect to see an increase of H₂O-cus production with increasing O-cus coverage. However, as shown in Figure 2b, the H₂O-cus formation rate is highest at an intermediate O-cus coverage, i.e., it is proportional to both the concentrations of O-cus and empty Ru-cus sites. Therefore, we conclude that before hydrogen interacts with O-cus it becomes activated at a Ru-cus site, as further demonstrated by the following HREELS data. As a consequence, at saturation of O-cus the H₂O-cus production is weakened; however, it does not go to zero since in this case ~20% Ru-cus sites are still unoccupied and therefore available for H₂ activation. At saturation of O-cus, the number of O-cus atoms obviously supersedes the number of empty Ru-cus sites, so that, when hydrogen is reacted off, some O-cus is left over which desorbs then between 520 and 450 K, as seen from Figure 2c.

In the following we like to substantiate the above results by means of vibrational spectroscopy. We do not present the vibrational data for all intermediate oxygen exposures, instead we present and discuss only the two extreme cases: The stoichiometric and the oxygen-saturated (O-rich) RuO₂(110) surface.

3.2. Vibrational Spectra for Hydrogen Adsorption on the Stoichiometric RuO₂(110) Surface. A stoichiometric surface was prepared as described above. Figure 3 exhibits a sequence of HREEL spectra following hydrogen interaction with the

stoichiometric surface at 90 K. The lowest lying curve is for the bare, stoichiometric surface with phonon contributions at 12 and 45 meV and an intense fingerprint peak at 69 meV arising from the Ru–O stretch vibration of the O-bridge atoms perpendicular to the surface.¹³

After exposure to 1 L H₂ at 85 K, which is near to saturation, the second spectrum from below reveals new intense peaks at 27, 58.5, 75, 108, 231, and 436 meV.¹⁵ These peaks remain unaffected by heating to 150 K and hence have to be attributed to the hydrogen β -state, since now the α -state has been completely desorbed. The strong suppression of the Ru–O-bridge mode at 69 meV suggests that in the β -state hydrogen bonding takes place with the under-coordinated O-bridge atoms.¹⁵ Since the β -state was already identified as dissociative adsorption, we conclude that hydrogen dissociatively adsorbs at O-bridge.

The data of the second spectrum from below in Figure 3 strongly suggest an interpretation of this dissociative hydrogen channel in terms of formation of a dihydride (water-like) group at the surface, in which the measured frequencies would correspond to translational (28 meV, 58 meV), librational (75, 108), scissor (231), and OH stretching (436) modes. In the DFT calculations,^{15,16} several alternative configurations were tested and finally the following result was achieved: The water-like group is not symmetrical to the surface as



Instead a more complex configuration is derived, in which the



plane is oriented toward the cus sites and one OH bond becomes nearly parallel (8°) to the surface. This dihydride species formed from H₂, and an O-bridge surface atom exhibits some similarities to the water molecule and therefore is called H₂O-bridge. The calculated adsorption energy of H₂ is 0.32 eV/H₂. Further details have been presented elsewhere.¹⁶

Due to the tilted geometry of H₂O bridge, we expect only one O–H stretch frequency, from the OH bond being directed more normally to the surface, which actually is observed at 436 meV. Therefore, we interpret the weak peak at 447 meV in the 85 K spectrum of Figure 3 as being due to some OH-bridge being also formed already from the very beginning. With slight warming to 200 and 235 K, the transformation from H₂O-bridge into OH-bridge proceeds until at 350 K no H₂O-bridge is left over. This wide transformation regime is in good agreement with the TD spectra of Figure 2a, which indicate a wide temperature window for the H₂ release.

In the second spectrum from below in Figure 3, some intensity from the bare O-bridge is observed, which vanishes during warming to 200 K. This may be due to the activated, highly mobile H atoms from the H₂O-bridge and may easily induce the transformation of the residual O-bridge into OH-bridge.

By warming to 350 K, the dihydride complex is completely transformed into monohydride by release of H₂ showing up in the β -peak of the TD spectra in Figure 2a. All dihydride features disappear (the peaks at 108 meV and 231 [225] meV) or change slightly their vibration energy (58.5→55.5 meV and 436→447 meV), in full accordance with the formation of monohydride with the O–H bond normal to the surface. The DFT calculations¹⁶ have shown that, under the experimentally present constraint of negligible O₂ partial pressure in the gas phase, this species indeed represents the thermodynamic ground state.

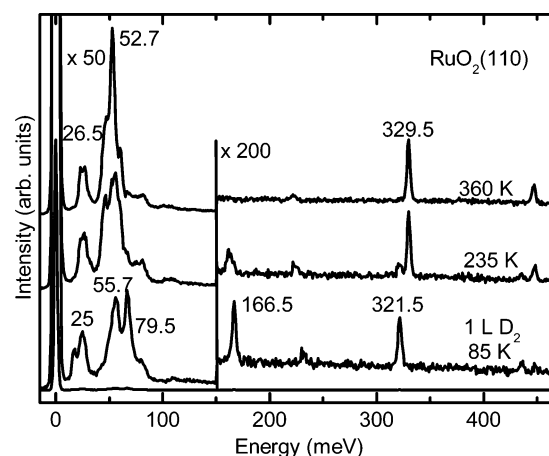


Figure 4. Same as Figure 3 for an exposure of 1 L D₂.

There is another fine detail in the spectra of Figure 3 which we have not touched upon until now: The scissor mode is split into two components at 225 and 231 meV from the very beginning and the intensity moves from the 231 meV peak to the 225 one, parallel to the growth of OH-bridge. From these observations we conclude that the two vibration energies are induced by different neighbor configurations: The scissor mode becomes slightly softer when H₂O-bridge at the neighboring adsorption site is changed into OH-bridge. This explanation is in line with a bond-order propagation effect described recently:¹⁶ A change in the O-bridge group changes the charge density of the next-neighbor Ru-cus atoms, which weakens the interaction with the O–H group of the H₂O-bridge, obviously softening the scissor mode. On the same line we can explain why the T_⊥ mode of OH-bridge shifts to 55.5 meV only when all H₂O-bridge have been transformed into OH-bridge.

All above conclusions are confirmed by the experiment of Figure 4 in which we expose 1 L D₂, instead of H₂, at 85 K. The sticking coefficient for D₂ is smaller than that of H₂, so that for the same exposure the overall intensity of the D-derived modes in the HREEL spectra is smaller (intensity factor 200 versus 100). Also, some amount of O-bridge is left over after exposure to 1 L D₂, as indicated by the mode at 69 meV. The missing saturation with D₂ is also confirmed by TD spectra (not shown). Furthermore, the activation barrier for D transfer to form OD-bridge seems to be higher. At 85 K, we observe therefore exclusively D₂O-bridge and, in line with this, only one D₂O-bridge scissor mode at 166.5 meV. Spurious amounts of H₂ are inevitable under the experimental conditions giving rise to the respective spurious H₂O HREELS signals. All mode energies and assignments are listed in Table 1.

3.3. Vibrational Spectra for Hydrogen Adsorption on the O-Rich RuO₂(110) Surface. A better understanding of the interaction of hydrogen with O-rich RuO₂(110) (O-bridge/O-cus) is provided by the HREELS data. (Following an exposure of 1 L O₂ at RT, the surface turns out to be saturated by oxygen.) Figure 5 (curve a) shows HREEL spectra of the O-saturated RuO₂(110) surface prior to exposure to H₂. Besides phonon modes at 12 and 45 meV and the intense loss at 69 meV due to the T_⊥ mode of O-bridge, the second surface oxygen species O-cus produces the very intense loss at 103 meV.¹³ Exposure to 2.5 L H₂ at 90 K changes the spectrum markedly (Figure 5, curve b): O–H stretching modes at 434 and 446 meV together with the scissor mode at 196 meV occur, which are typical fingerprints for chemisorbed H₂O. These features compare very well with the data of Lobo and Conrad¹⁸ reported after exposing the stoichiometric RuO₂(110) surface directly to H₂O. They

TABLE 1: Mode Assignments, Vibrational Energies (in meV), and Isotope Shifts for Different Products Formed through Reactions of Hydrogen on the Stoichiometric and Oxygen-Rich RuO₂(110) Surfaces

mode ^a	H ₂ O-bridge meV	D ₂ O-bridge meV	OH-bridge meV	OD-bridge meV	H ₂ O-cus ref 18, meV	H ₂ O-cus this work, meV
T	27	25(1.08)	27.8	26.5(1.05)		15
T _⊥	58.5	55.7(1.05)	55.5	52.7(1.05)	62	61
R	75	79.5(1.35)			100	97
	81				108	109
	108				129	128
Δ	225	166.5(1.35)			199	196
	231	161(1.43)				
ν(OH)/ν(OD)	436	321.5(1.36)	447	329.5(1.35)	446	446

^a T translational mode, || and ⊥ to the surface plane; R librational mode; δ scissor mode; ν(OH) stretching mode.

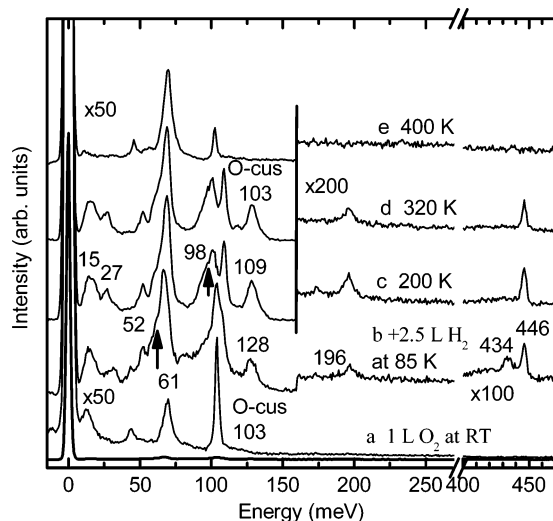


Figure 5. HREEL spectra for the bare oxygen-rich RuO₂(110) surface (lowest curve) prepared by an exposure of 1 L O₂ at 300 K and after an additional exposure of 2.5 L H₂ at 90 K and warming to the indicated temperatures. Parameters as for Figure 3.

concluded that this H₂O bonds to Ru-cus and is therefore called H₂O-cus here. Furthermore, the intensity of the O-cus mode at 103 meV apparently decreased during hydrogen exposure, whereas the intensity of the O-bridge related mode is hardly affected, showing that it is not involved here in any chemisorption bond, which is in line with the absence of a scissor mode at ~230 meV, typical for H₂O-bridge as seen in Figure 3 for the stoichiometric surface. All these findings demonstrate that H₂O-cus instead of H₂O-bridge is formed by exposing the O-saturated RuO₂(110) surface (O-bridge/O-cus) to H₂. The broadening of the O–H stretch mode at 434 meV and the slight red shift of the O-bridge mode from 69 to 67 meV with respect to the bare surface may be due to weak interaction of H₂O-cus with O-bridge through hydrogen bonding. The peak energies and assignments are summarized in Table 1.

After warming to 200 K (Figure 5, curve c) the H₂O-derived features are better resolved in the low energy region, in which the measured losses are attributed to the frustrated translational (15; 27; 61 meV) and librational (97; 109; 128 meV) modes. In the O–H stretching region the hydrogen bond related broadening is significantly reduced. Accordingly, the O-bridge mode is detected again at 69 meV. Only one loss remains at 446 being typical for a single symmetric stretch mode of an O-bonded upright H₂O.

All H₂O-cus modes disappear after warming to 400 K (Figure 5, curve e), in very good agreement with the TDS results which exhibit a sharp first-order peak at 400 K. The spectrum now exhibits the typical features of the bare RuO₂(110) surface with

the most prominent O-bridge peak at 69 meV. In addition, a less intense O-cus loss at 103 meV is still observed, indicating that some O-cus species are left over, in good agreement with the observation of O₂ desorption in TDS for a starting surface saturated by oxygen (Figure 2c).

Comparing the curves for highest annealing in Figures 3 and 5, one gains further insight in the different activities of the surface oxygen species. The corresponding spectrum of Figure 3 is characteristic for OH-bridge species, and the two intense losses at 55.5 and 447 meV have been attributed to the translational mode perpendicular to the surface and the O–H stretch vibration, respectively. Obviously, the OH-bridge species is still stable at a temperature as high as 510 K in full accordance with the TDS results (Figure 2b). In contrast, in Figure 5 all hydrogen-related modes disappear already by warming at 400 K. Thus, the high-temperature curves of Figures 3 and 5 provide a definite proof that hydrogen reacts preferentially with O-cus – if it is available at the surface – in forming H₂O-cus and that O-cus is more reactive than O-bridge.

Interestingly, in Figure 5 a weak feature at 52 meV is also resolved in addition to the H₂O-cus derived losses after exposing the O-rich RuO₂(110) surface to 2.5 L hydrogen at 90 K. In our recent study of NH₃ oxidation on RuO₂(110) surfaces,⁶ the same loss was observed and attributed to the hydroxyl group at Ru-cus as a reaction intermediate confirmed by the isotope shift of 1.04 with respect to OD. Thus, the peak at 52 meV is indicative of the formation of some OH-cus species. For the stoichiometric RuO₂(110) surface, only OH-bridge species are detected at higher temperatures, as they present the thermodynamic ground state of the reduced RuO₂(110) surface.¹⁶ The OH-cus related loss at 52 meV remains unchanged in intensity when warming the sample to higher temperature. The related O–H stretch mode overlaps with the respective mode of H₂O-cus. The low OH-cus concentration may be associated with the high barrier for the transition from O-bridge/H₂O-cus to O-bridge/OH-cus, although from DFT calculations it was derived that O-bridge/OH-cus is at least as stable as O-bridge/H₂O-cus.¹⁶

3.4. Activation of Molecular Hydrogen at Ru-cus. In the following we focus on the reaction mechanism of H₂ with the stoichiometric RuO₂(110) surface first. The respective HREEL spectra have been shown in Figure 3. To determine the entrance channel of hydrogen we performed the following experiments: First, the Ru-cus atoms were completely covered by CO through exposing the stoichiometric RuO₂(110) surface to 1 L CO at 90 K. The HREEL spectrum is reproduced in Figure 6 (curve a). The dominant peaks are at 262 and 38 meV being characteristic for CO adsorbed on Ru-cus.^{3,4} Then, the surface was exposed to 2.5 L H₂ at 90 K, and, interestingly, the spectrum (curve b) is not changed at all. If O-bridge would be able to

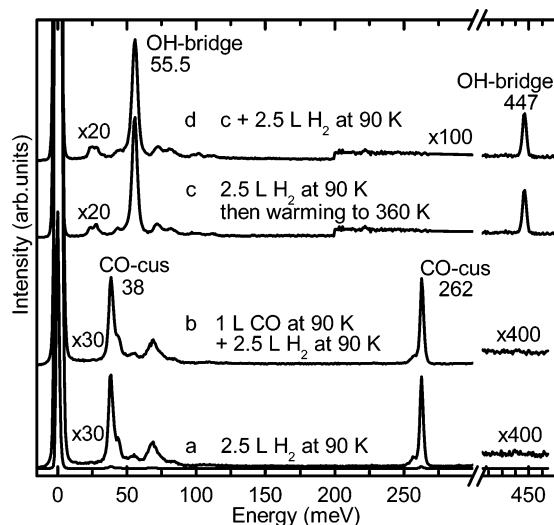


Figure 6. HREEL spectra for the stoichiometric $\text{RuO}_2(110)$ surface (a) after an exposure of 1 L CO at 90 K; (b) plus an additional exposure to 2.5 L H_2 at 90 K; (c) after an exposure to 2.5 L H_2 at 90 K and warming to 360 K; (d) same as (c) plus an exposure to 2.5 L H_2 at 90 K. Parameters as for Figure 3.

adsorb hydrogen directly from the gas phase, the blocking of the Ru-cus sites by CO should not suppress the H_2O -bridge formation. However, no H_2O -bridge derived losses are observed in curve b. We conclude therefore that, at a surface temperature of 85 or 90 K, hydrogen adsorption requires the molecular H_2 state at Ru-cus as precursor for any reaction with O-bridge and that a direct interaction of gas-phase H_2 with O-bridge does not occur. Our conclusion is fully in line with the recent DFT calculations.¹⁶

Also an OH-bridge/- surface is inert against any interaction with molecular hydrogen as shown in Figure 6 (curves c and d): An OH-bridge/- surface is prepared by exposing a stoichiometric $\text{RuO}_2(110)$ surface to 2.5 L H_2 at 90 K and then annealing to 360 K. The resulting spectrum is shown as curve c. This surface is again inert with respect to molecular hydrogen (see curve d) in very good agreement with the DFT calculations which have shown that OH-bridge/- is the ground state of the reduced $\text{RuO}_2(110)$ surface.¹⁶

Our experiments at 90 K support the following picture on the interaction of H_2 with the stoichiometric $\text{RuO}_2(110)$ surface: H_2 adsorbs first molecularly on Ru-cus as a necessary precursor to the interaction with O-bridge. Remarkably, although the H-H bond is weakened, the adsorption on Ru-cus site cannot induce its dissociation.^{15,16} The latter process occurs via the interaction of the molecular H_2 -cus with the neighboring O-bridge atom in forming a metastable H_2O -like complex, which transforms into the stable hydroxyl groups by releasing hydrogen when heated further. The reaction channel for H_2O -bridge formation through the interaction of hydroxyl species with a dissociated H atom can be excluded.

Now we turn to the O-rich surface. The TDS data in section 3.1 have demonstrated that the Ru-cus sites play the key role for the interaction of hydrogen also with O-cus. This conclusion is further supported by the following HREELS experiments. First, we saturated the stoichiometric $\text{RuO}_2(110)$ surface with oxygen at 300 K. Then we exposed the O-saturated surface to CO at 90 K. We know that at 90 K CO is not reacting with O-cus or O-bridge; instead it is going to chemisorb at Ru-cus if these sites are available. The corresponding HREEL spectrum is shown in Figure 7 (curve a). We observe CO-cus bands at 266 and 35 meV besides the strong spectral features from

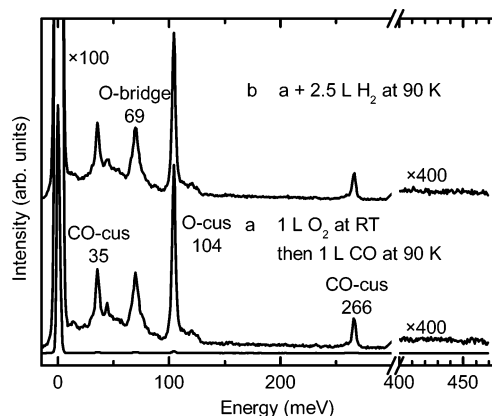


Figure 7. HREEL spectra for (a) the oxygen-rich $\text{RuO}_2(110)$ surface prepared by exposure to 1 L O_2 at RT and an additional exposure to 1 L CO at 90 K in order to fill the remaining empty Ru-cus sites and (b) after an additional exposure to 2.5 L H_2 at 90 K. Parameters as for Figure 3.

O-bridge and O-cus. This demonstrates that at O-cus saturation still free Ru-cus sites are available, allowing the coadsorption of CO. If we now expose this surface to 2.5 L H_2 at 90 K, no reaction is observed, neither with O-cus nor with O-bridge. Therefore we conclude that, at least at 90 K, empty Ru-cus sites are definitively needed to activate the incoming molecular hydrogen prior to any reaction with O-cus or O-bridge. In comparison with the full CO-cus layer discussed above, we can estimate the occupancy of 85% for O-cus at saturation. This is in agreement with the theoretical amount of 83% in view of the fact that the HREELS intensity is not a strictly linear measure over the full coverage range.

Finally, our conclusion is also confirmed by the observation that for the O-rich surface some O-cus is left after exposure to a high amount of H_2 and annealing to desorb all reaction products (see the 400 K curve of Figure 5). There were not enough empty Ru-cus sites available to activate enough hydrogen to remove all O-cus atoms.

4. Discussion

4.1. Reaction of O-cus and O-bridge with Hydrogen.

Generally, the surfaces were exposed to hydrogen at a surface temperature of 85 or 90 K. From the experiments presented in the foregoing section, the following picture for the hydrogen reaction emerges:

(1) If there is O-cus on the surface together with some empty Ru-cus sites, the incoming hydrogen interacts preferentially with O-cus in forming H_2O -cus, which desorbs at ~ 400 K. In addition, some OH-cus species are also observed pointing to incomplete reduction of O-cus.

(2) If O-cus is not available at the surface, two interaction channels are observed at 85 K: (a) hydrogen adsorbs weakly in molecular form at Ru-cus; (b) hydrogen interacts with the more strongly bound O-bridge and a H_2O -like group, called H_2O -bridge, is formed with one of the OH bonds oriented nearly parallel to the surface. Already at 200 to 350 K, hydrogen is released and OH-bridge is formed at the surface. At much higher temperatures, i.e., 600 to 550 K, OH-bridge disproportionates into O-bridge and H_2O , whereby the latter is released into the gas phase.

(3) Very important for the understanding of the chemical reactions at the $\text{RuO}_2(110)$ surface is the next point. If all Ru-cus sites are blocked, hydrogen can neither interact with O-bridge nor with O-cus, although both species are fully

accessible from the gas phase. Quite obviously, hydrogen needs some activation at Ru-cus prior to reaction with O-bridge or O-cus. So, we conclude that, e.g., a RuO₂(110) surface, completely saturated with O-cus, does not react with hydrogen.

(4) All observations demonstrate that O-cus is much more reactive than O-bridge.

In the following we like to briefly compare our results to conclusions obtained by Knapp et al. from TDS measurements for the same system.¹⁷ These authors reported the formation of D₂O after exposing the O-saturated RuO₂(110) surface to 50 L D₂ at 300 K. Although the authors did not differentiate between H₂O-bridge and H₂O-cus, it follows from their TD spectra that they observed H₂O-cus. They concluded that hydrogen preferentially reacts with O-bridge rather than via Ru-cus atoms, with the underlying assumption that all Ru-cus were blocked by O-cus and that the hydrogen atoms, after dissociation at O-bridge, jump to O-cus to form H₂O-cus. However, we know that, as pointed out above, Ru-cus cannot be completely saturated by O-cus under the given UHV (low pressure) conditions since the saturation reaches only about 80%. If one really saturates all Ru-cus sites, as we did, e.g., by filling the remaining empty sites between the O-cus atoms by CO (Figure 7), formation of H₂O-cus is not observed. Therefore, we propose that this part of the experiment by Knapp et al.¹⁷ may be interpreted as follows: There are empty sites of Ru-cus, where D₂ can be activated for further interaction with O-cus in forming D₂O-cus so that the very profound DFT calculations¹⁶ are no longer “challenged”.

We further add that at 300 K it is even more likely that the Ru-cus atoms cannot be completely saturated by O-cus. Therefore, at 300 K one cannot decide from experiment whether H₂ reacts immediately with O-bridge or has to be activated at Ru-cus first. Such a differentiation can be made only at lower temperature, e.g., at 90 K in our case. In principle it is possible that at higher surface temperature new reaction channels may open up. However, we consider it very unlikely that this would be a direct (Eley-Rideal) reaction between gas-phase H₂ and O-bridge. First, Eley-Rideal reactions are quite generally very scarce. Second, an increase in surface temperature from 85 to 300 K opens up only energetically very low-lying excitations. For example, we have seen that the vibration energy for the perpendicular movement of O-bridge is 69 meV and of O-cus is 103 meV. Thus we conclude that from our experiment starting at 90 K we can exclude an Eley-Rideal reaction at 85 K, but not at 300 K. On the other hand, such a reaction also cannot be demonstrated at 300 K due to the existence of about 20% free Ru-cus sites at O-cus saturation.

Knapp et al.¹⁷ also studied the activity differences between the surface oxygen species and concluded that O-cus is hardly able to adsorb hydrogen. This conclusion was based on the following experiment. First, all the O-bridge atoms were replaced by CO-bridge through exposing the stoichiometric RuO₂(110) surface to CO at RT. Subsequently, the Ru-cus atoms were saturated by O-cus (exposure of 5 L O₂ at 200 K). If this surface was exposed to 500 L D₂ at 200 K, no D₂O-cus was detected with TDS. However, we know that, if one is not waiting long enough to pump down the residual gas after exposing RuO₂(110) to CO at RT, one collects CO from the residual gas at Ru-cus, which is stable at 200 K.¹⁹ In this case the free Ru-cus sites are blocked by CO from residual gas, so that D₂ adsorption is suppressed and finally no D₂O-cus can be observed. This also shows how important it is to control the surface species by a spectroscopic method such as HREELS before and after exposing the surface to gases and prior to the

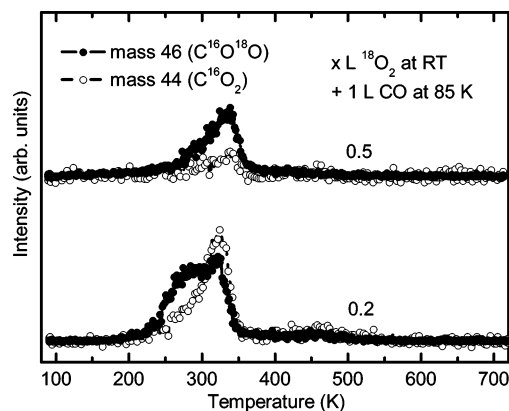


Figure 8. Thermal desorption spectra for masses 44 and 46 for the oxygen-rich RuO₂(110) surface, (a) prepared by exposure to 0.5 L ¹⁸O₂ at RT so that the surface layer is given by ¹⁶O-bridge from the starting stoichiometric surface and about 80% of ¹⁸O-cus, followed by an exposure to 1 L CO at 85 K; (b) the same for an exposure to 0.2 L ¹⁸O₂.

TDS experiments. Our HREELS and TDS data, presented in section 3, clearly demonstrate that O-cus is more reactive than O-bridge for hydrogen adsorption. This is in complete agreement with the DFT-based calculations: O-cus is less strongly (by 1.4 eV) bonded than O-bridge according to Kim et al.,¹³ in agreement with the value of 1.3 eV found by Reuter et al.⁷

4.2 The Reactivity of O-cus and O-bridge in CO Oxidation. As Knapp et al.¹⁷ concluded that O-cus is less active both toward hydrogen and CO, we briefly comment on the latter case, too. In a recent study, Wendt et al.²⁰ repeated our isotope labeling HREELS experiment⁴ by TDS. First they occupied Ru-cus with ¹⁸O-cus, whereas O-bridge was the normal ¹⁶O-bridge. Then they exposed C¹⁶O at 300 K. If this CO would interact preferentially with ¹⁸O-cus, one would expect in TDS to observe C¹⁶O¹⁸O (mass 46) for the CO₂ product from the reaction CO + O-cus → CO₂. They did, however, observe much more mass 44 than mass 46 and concluded that the incoming CO, despite the presence of O-cus, reacts preferentially with O-bridge. This result was and is in contradiction to our isotope labeling HREELS experiment.⁴

To resolve this controversy, we have repeated the TDS experiment as shown in Figure 8 for the same set of parameters. Clearly we observe much more mass 46 than mass 44, as expected from our HREELS results.⁴ For an exposure of 0.5 L (upper curve) the mass 46 signal is stronger by a factor of 4. The small amount of mass 44 is very likely due to some C¹⁶O₂ collected from the residual gas during cooling of the sample from RT to 85 K. For an exposure of 0.2 L ¹⁸O₂, only 30 to 40% of the Ru-cus sites are occupied by ¹⁸O-cus so that there are enough empty Ru-cus sites so that the incoming C¹⁶O can also react with ¹⁶O-bridge, resulting in the mass-44 signal. From these experiments one has to conclude that the incoming CO reacts preferentially with O-cus. There is thus again agreement with the trend expected on the basis of the calculated oxygen bond strengths,^{13,16} and no “violation of the Brønsted–Evans–Polanyi relationship” as claimed by Wendt et al.²⁰ We suspect the following reason for their erroneous conclusion: during UHV experiments of this kind, if one does not wait long enough to pump down the residual gas after preparation of the thin RuO₂(110) layer, one collects C¹⁶O₂ from the residual gas at the surface which is known to weakly adsorb at 200 K.^{14,21} We could reproduce this effect by working at a residual pressure of 1 × 10^{−9} mbar instead of 1 × 10^{−10} mbar.

4.3 The Reactivity of O-cus and O-bridge in Interacting with Various other Molecules. The enhanced activity of O-cus as compared to O-bridge is also observed in experiments with a variety of other molecules. Apart from hydrogen, as discussed in the present contribution, this also holds for CO oxidation as being derived not only from experiments^{3–5} but also from ab initio DFT-based calculations.^{9,10} Reuter et al.¹⁰ were even able to calculate the rate of CO₂ formation in a Monte Carlo simulation under the use of purely DFT-based calculated binding energies and activation barriers in surprisingly good agreement with our experiments.⁵ As pointed out,¹⁰ the movies of the simulations for a number of parameter sets, can be found at the respective home page.²² All our conclusions from our HREELS^{3,4} and steady-state TDS⁵ experiments are reflected there in one of the movies.²² At stoichiometric gas composition, the whole CO oxidation reaction runs on Ru-cus, whereas the O-bridge stays only as a spectator all the time to take over only if the O₂ partial pressure is reduced.

The interaction of ethylene (C₂H₄) with RuO₂(110) can be summarized as follows.²³ On the stoichiometric RuO₂(110) surface, ethylene adsorbs molecularly at 85 K and desorbs molecularly at 310 K; i.e., no reaction takes place. In contrast, on the O-rich surface ethylene adsorbs molecularly at 85 K and is completely oxidized through interaction with O-cus and O-bridge upon annealing to 500 K. Here again no reaction takes place without Ru-cus.

The interaction of CO₂ results in the following.^{14,21} Only the O-rich surface is reactive in forming carbonate. The mechanism of carbonate formation involves two adsorbed species as reactants, an O-cus and an activated, bent CO₂^{δ-} molecule, both chemisorbed at neighboring Ru-cus sites. Again, a reaction of CO₂ takes place only for a local situation in which O-cus and a nearby empty Ru-cus are available.

Finally, we have also investigated the reactions of NH₃ with the stoichiometric and the O-rich RuO₂(110) surfaces.⁶ The coordinatively unsaturated Ru-cus atoms in the RuO₂(110) surface were identified as catalytically active sites onto which either ammonia or oxygen are adsorbed from the gas phase. The concentration of O-cus determines both the reactivity and selectivity. Without the presence of O-cus, adsorbed NH₃ simply desorbs. However, a neighboring O-cus abstracts readily one of the H-atoms from NH₃ initiating complete dissociation. The resulting adsorbed N-atoms either recombine with each other to N₂ or with O-cus to NO. The selectivity under steady-state conditions is thus determined by the local surface configurations of the adsorbates and thereby by the relative partial pressures of the reactants. This case clearly demonstrates that O-cus is again much more reactive than O-bridge.

5. Conclusion

It has been shown recently that the RuO₂(110) surface is highly active in a number of catalytic surface reactions and nicely serves as a model system to study some basic questions in catalysis on oxides. Reactions can be followed including structural details on an atomic level. Most importantly, at the oxygen-rich RuO₂(110) surface there are three different, coordinatively unsaturated surface atoms, O-bridge, O-cus, and Ru-cus, which can be identified with structural and vibrational experimental methods elucidating structure, as well as vibrational and electronic surface properties.

The different chemical activity in hydrogen oxidation is demonstrated for the two differently coordinated surface oxygen

species, O-cus and O-bridge. For the O-rich RuO₂(110) surface, i.e., in the presence of O-cus, in addition to empty Ru-cus sites, H₂O-cus (adsorbed at Ru-cus) is formed which desorbs in a first-order reaction at about 400 K, but no interaction at all takes place with O-bridge. This is in very good agreement with recent DFT-based calculations.¹⁶

For the stoichiometric surface, i.e., if there is no O-cus present, at 90 K H₂ weakly chemisorbs at Ru-cus or dissociatively adsorbs at O-bridge in forming a water-like H₂O-bridge surface group. During warming, first the weakly adsorbed H₂ desorbs and then additional H₂ is released under the formation of OH-bridge, which later disproportionates into H₂O and O-bridge, the former being released immediately into the gas phase.

Furthermore, it is obvious that the reactions of hydrogen with O-cus as well as with O-bridge are all between adsorbed species, i.e., the reactions proceed according to the Langmuir–Hinselwood mechanism. If all Ru-cus sites are covered (even by oxygen), the surface is inactive with respect to chemical reactions with H₂, CO, CO₂, NH₃, and C₂H₄. In all cases, the coordinatively unsaturated Ru-cus surface atom is a prerequisite for any reaction because of its ability to chemisorb and thus activate the incoming molecules. Taking into account the experiments with H₂, CO, CO₂, NH₃, and C₂H₄, there is overwhelming evidence for the higher activity of O-cus compared to O-bridge.

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