

Ruthenium Oxide Surface Chemistry

Surface Coordination Chemistry: Dihydrogen versus Hydride Complexes on RuO₂(110)**

Jinhai Wang, Chao Yang Fan, Qiang Sun,
Karsten Reuter, Karl Jacobi,* Matthias Scheffler, and
Gerhard Ertl

Similarities between bond formation in transition metal complexes and chemisorption on solid surfaces form the basis of the relationship between homogeneous and heterogeneous catalysis. We find that hydrogen interacts in a complicated manner with the two sites that have an incomplete coordination environment—Ru^{cus} and O^{bridge}—on the RuO₂(110) surface (Figure 1). Upon exposure at 85 K of the RuO₂ catalyst to hydrogen gas, a H₂ molecule, instead of dissociating at Ru^{cus}, weakly adsorbs as dihydrogen on top of the Ru^{cus} atom and interacts dissociatively with the O^{bridge} atom to form a metastable dihydride (waterlike) complex, which transforms into the stable monohydride when heated further. The combination of low-temperature ultrahigh vacuum experiments in conjunction with density-functional theory (DFT) calculations provides a detailed insight into the coordination chemistry of a solid surface, which exhibits a remarkable correlation with the chemistry of single-atom transition-metal complexes.

The binding of hydrogen, both with transition-metal complexes (i.e. hydride formation)^[1] and with surfaces,^[2] generally occurs concurrently with dissociation of the ligand. The discovery of η^2 -H₂ (dihydrogen) complexes, in which the H–H bond remains intact, was surprising,^[3] since

[*] Prof. Dr. K. Jacobi, Dr. J. Wang, Dr. C. Y. Fan, Dr. Q. Sun, Dr. K. Reuter, Prof. Dr. M. Scheffler, Prof. Dr. G. Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6, 14195 Berlin (Germany)
Fax: (+49) 30-8413-5106
E-mail: jacobi@fhi-berlin.mpg.de

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then the list of such compounds has been growing continuously.^[4] Likewise the observation of nondissociative chemisorption of H₂ on transition-metal surfaces has so far been restricted to a few situations.^[5,6] Herein we report that, remarkably, the particular atomic configuration of the RuO₂(110) surface enables the coexistence of both non-dissociated (dihydrogen) and dissociated (mono- and dihydride) species bound to different sites.

High-resolution electron energy-loss spectroscopy (HREELS)^[7] with a resolution of 20 cm⁻¹ was used to record vibrational spectra. The RuO₂(110) surface was formed as a thin, stoichiometrically terminated epitaxial layer by exposing the Ru(0001) surface of a single crystal to O₂ (1 × 10⁷ L; 1 L = 1.3 × 10⁻⁶ mbars) at 700 K.^[7,8] For DFT calculations the full-potential linear augmented plane wave scheme^[9] was employed by using the following basis-set parameters: $R_{\text{MT}}^{\text{Ru}} = 0.95 \text{ \AA}$, $R_{\text{MT}}^{\text{O}} = 0.53 \text{ \AA}$, $R_{\text{MT}}^{\text{H}} = 0.32 \text{ \AA}$, $E_{\text{wavefunction}} = 27.54 \text{ eV}$, $E_{\text{max}}^{\text{potential}} = 5440 \text{ eV}$, 18 **k**-points in the irreducible wedge of the (1 × 1) Brillouin-zone. The DFT calculations used the PBE^[10] generalized gradient approximation for the exchange-correlation functional to solve the Kohn–Sham equations. The surface was modeled in a supercell geometry with three O–Ru–O trilayers where all atomic positions except those in the central Ru layer were fully relaxed.

The surface geometry of RuO₂(110) (Figure 1) illustrates the two kinds of coordinatively unsaturated sites exhibited by the rutile(110) faces, (Ru^{cus} and O^{bridge}). The TD spectra of H₂

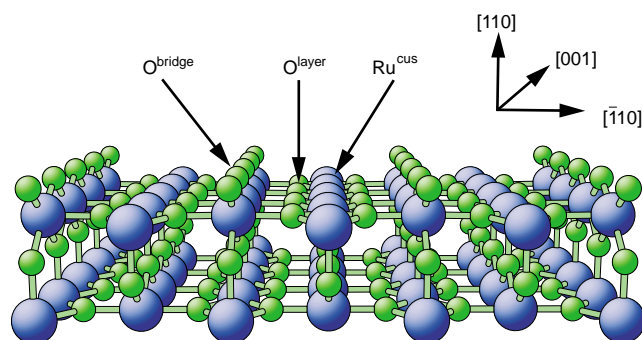


Figure 1. Ball-and-stick model of the bare stoichiometric RuO₂(110) surface in perspective view (O: green, Ru: violet).

from the RuO₂(110) surface exhibit two maxima centered at 95 K (α) and around 260 K (β) (Figure 2). The inset of Figure 2 shows the data for HD evolution after exposure of the RuO₂(110) surface to D₂ (0.5 L) and then to H₂ (0.5 L); the intensity of the α peak is largely suppressed. This result indicates that there is almost no isotope exchange within the α state, which suggests that the peak originates from molecules that had not been dissociatively adsorbed. In contrast, the pronounced isotope scrambling of the β state is indicative of the recombination of chemisorbed atoms. In addition to H₂ molecules, above 400 K an appreciable quantity of H₂O molecules come off the surface, which indicates that apart from the recombinative desorption of H₂ in a different reaction, the whole surface entity H–O–H may be released.

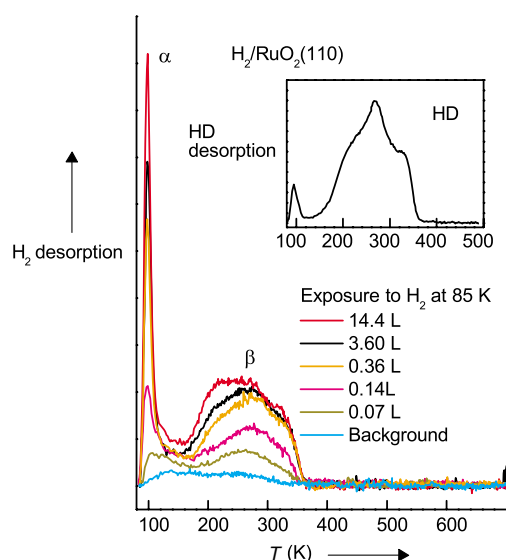


Figure 2. Thermal desorption (TD) spectra of H₂ (HD in the inset) after exposure to varying quantities of H₂ to the RuO₂(110) surface at 85 K. The exposure is given in Langmuir units L (1 L = 1.3 × 10⁻⁶ mbars).

A greater understanding of the nature of these surface hydrogen species is provided by the HREELS data (Figure 3). Spectrum A, obtained from the bare RuO₂(110) surface, shows an intense fingerprint peak at $\tilde{\nu} = 557 \text{ cm}^{-1}$ arising from the Ru–O stretch vibration of the O^{bridge} atoms.^[11] After the RuO₂(110) surface was saturated with hydrogen, the corresponding spectrum, B, reveals new intense peaks at $\tilde{\nu} = 226$,

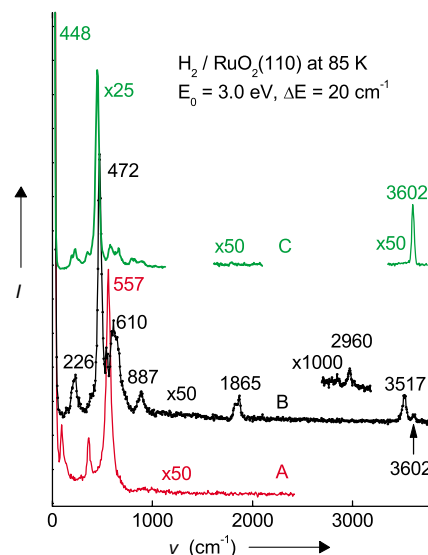


Figure 3. HREEL spectra for a primary electron energy E_0 , at an energy resolution ΔE , in specular geometry at an angle of incidence of 60°. The factors $\times 50$, etc. give the intensity enlargement with respect to the elastically scattered electrons (I = intensity, arbitrary units). A) Bare stoichiometric RuO₂(110) surface. b) After exposure of 1 L H₂ at 85 K. From the TD spectra it is concluded that about 75% of O^{bridge} sites are occupied by the dihydride complex and about 12% of Ru^{cus} by the dihydrogen species. C) After warming to 350 K complete transformation of the dihydride at O^{bridge} into monohydride occurred.

472, 610, 887, 1865, and 3517 cm^{-1} . These peaks remain in the spectrum after the sample has been heated to 150 K and hence have to be attributed to the β state, as at this moment the α state has been completely desorbed. The strong suppression of the Ru-O^{bridge} mode at $\tilde{\nu}=557\text{ cm}^{-1}$ suggests that in the β state hydrogen bonding takes place with the coordinatively unsaturated O^{bridge} atoms.

The data of spectrum B in Figure 3 strongly suggest an interpretation of this dissociative hydrogen channel in terms of the formation of a waterlike group at the surface, in which the measured frequencies would correspond to translational ($\tilde{\nu}=226, 472\text{ cm}^{-1}$), librational ($\tilde{\nu}=610, 887\text{ cm}^{-1}$), scissor ($\tilde{\nu}=1865\text{ cm}^{-1}$), and OH stretching ($\tilde{\nu}=3517\text{ cm}^{-1}$) modes. In our DFT calculations we tested several alternative configurations. Interestingly, the waterlike group is not symmetrical to the surface as H-O-H, because a scissor mode frequency above the gas phase value cannot be achieved for this configuration. It turned out that a more complex configuration is likely, where the H-O-H plane oriented towards the cus sites (compare Figure 4a and 4b). The OH bond lengths and bonding angle are indicated in Figure 4b. The calculated scissor frequency is $\tilde{\nu}=1702\text{ cm}^{-1}$, which is well above the gas phase value of $\tilde{\nu}=1524\text{ cm}^{-1}$.

This dihydride species formed from H₂ and an O^{bridge} surface atom exhibits some similarities with a water molecule: The back bonds of O^{bridge} are elongated from 1.91 to 2.27 Å with respect to the bare surface. Compared to a free water molecule some charge is transferred to the RuO₂ matrix, which makes the H-O-H angle larger and hypothetically reduces the scissor mode frequency. The latter effect is overcompensated by the hydrogen-bondlike interaction of one H atom with two O^{layer} and Ru^{cus}. This effect tilts the whole group so that one OH bond becomes nearly parallel

(8°) to the surface (see Figure 4b), the OH bond length becomes further elongated, and the scissor mode increases even beyond the gas-phase value. The calculated adsorption energy of H₂ is 0.32 eV per H₂ molecule. Further details will be discussed elsewhere.

By warming the sample to 350 K, the dihydride complex is transformed into monohydride by releasing hydrogen, evidence for which is shown in the β peak of the TD spectra in Figure 2. All features arising from the dihydride species disappear (i.e. the peaks at $\tilde{\nu}=887$ and 1865 (1815) cm^{-1}) or change slightly their frequency (472→448 cm^{-1} and 3517→3602 cm^{-1}) in full accordance with the formation of monohydride or hydroxyl groups with the O-H bond perpendicular to the surface (see Figure 4c). The DFT calculations show that under the experimental constraint of negligible O₂ partial pressure in the gas phase, this species indeed represent the thermodynamic ground state.

The only feature in the HREELS spectrum that disappears upon heating the corresponding sample to 150 K is a very weak peak at $\tilde{\nu}=2960\text{ cm}^{-1}$, which is hence attributed to the H-H stretch vibration of molecular hydrogen adsorbed on the α state. For D₂, the analogous peak is found at $\tilde{\nu}=2073\text{ cm}^{-1}$ and yields an isotope ratio of 1.42, which is in perfect agreement with the expectations for a (weakly held) molecular species. The value of the H-H frequency for adsorbed H₂ on the α state ($\tilde{\nu}=2960\text{ cm}^{-1}$) is considerably smaller than that for free H₂ ($\tilde{\nu}=4407\text{ cm}^{-1}$) or for physisorbed molecules (e.g. $\tilde{\nu}=4121\text{ cm}^{-1}$ for H₂/Ag(111)^[12]), thus indicating that in the present case the rather strong binding to the surface appreciably weakens the H-H bond. The DFT calculations give an adsorption energy of 0.3 eV per H₂ molecule and show that such a molecular species can only be stabilized at the RuO₂(110) surface on top of the coordinatively unsaturated Ru^{cus} atoms in the side-on configuration (Figure 5), with a H-H stretch frequency of $\tilde{\nu}=3331\text{ cm}^{-1}$, which is in reasonable agreement with the experimental value. The H₂ molecule is separated by 1.8 Å from the Ru^{cus} atoms, while the H-H bond length is increased from 0.74 Å to 0.89 Å, again is very similar to results for $\eta^2\text{-H}_2$

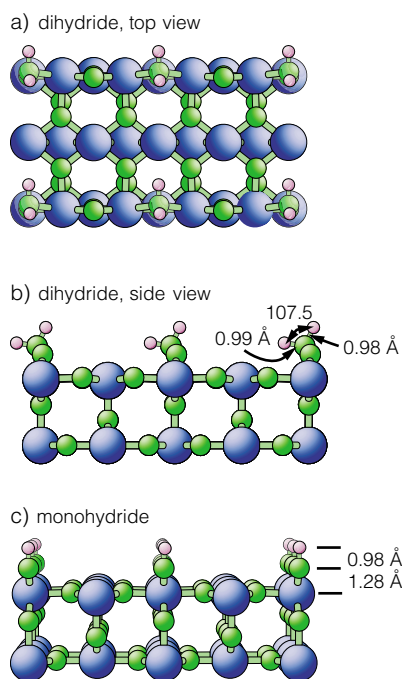


Figure 4. a) Top view and b) side view of the waterlike dihydride. c) Side view of the monohydride (O: green, Ru: violet, H: pink).

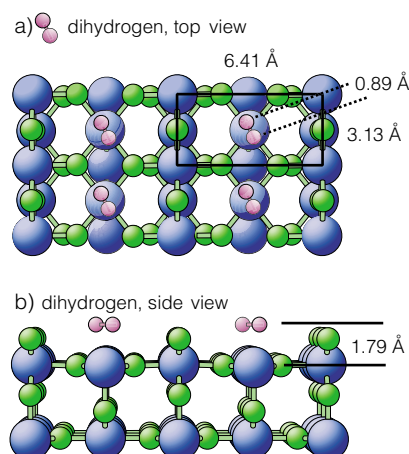


Figure 5. a) Top view and b) side view of dihydrogen bonded to Ru^{cus}. Note that the azimuthal orientation of dihydrogen is arbitrary as it is freely rotating. The (1 × 1) unit cell is indicated (O: green, Ru: violet, H: pink).

complexes for which values in the range 0.8–0.9 Å have been reported.^[13,14]

Analyzing the computed local density of states, we find the bonding is governed by the interaction between Ru- d_{z^2} and H_2 - σ orbitals, as well as between Ru- d_{xz}/d_{yz} and H_2 - σ^* orbitals, respectively. As a consequence, the Ru- d_{z^2} hybridizes with the occupied H_2 - σ leading to a small $H \rightarrow Ru$ charge transfer. On the other hand, there is some back-donation of electronic charge from the metal to the H_2 - σ^* orbital, whereby coupling to the surface is strengthened while the H–H bond is weakened and elongated. Correspondingly, the H–H stretch frequency gets significantly red-shifted, close to the values around $\tilde{\nu} = 2400\text{--}2800\text{ cm}^{-1}$ known from dihydrogen complex chemistry.^[15,16]

In summary, we have conclusively identified both dissociative hydride and non-dissociative dihydrogen species at the $RuO_2(110)$ surface. Although we find strong similarities for both types of species with data from transition-metal complex chemistry, the major difference is that with the surface both atomic and molecular hydrogen types are related to different sites: the dissociated β state to O^{bridge} and the molecular α state to Ru^{cus} atoms.

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