Ruthenium Oxide Surface Chemistry

Surface Coordination Chemistry: Dihydrogen versus Hydride Complexes on RuO$_2$(110)**

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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 RuO$_2$(110) surface (Figure 1). Upon exposure at 85 K of the RuO$_2$ catalyst to hydrogen gas, a H$_2$ 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-H$_2$ (dihydrogen) complexes, in which the H–H bond remains intact, was surprising,[3] since

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then the list of such compounds has been growing continuously.[4] Likewise the observation of nondissociative chemisorption of H_2 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 $RuO_2(110)$ surface enables the coexistence of both nondissociated (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 $RuO_2(110)$ surface was formed as a thin, stoichiometrically terminated epitaxial layer by exposing the Ru(0001) surface of a single crystal to O_2 (1×10^7 L; 1 L $= 1.3 \times 10^{-6}$ 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: $R_{MT}^{Ru} = 0.95$ Å, $R_{MT}^0 = 0.53$ Å, $R_{MT}^H = 0.32$ Å, $E_{max}^{wavefunction} = 27.54$ eV, $E_{max}^{potential} = 5440$ 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 $RuO_2(110)$ (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 H_2
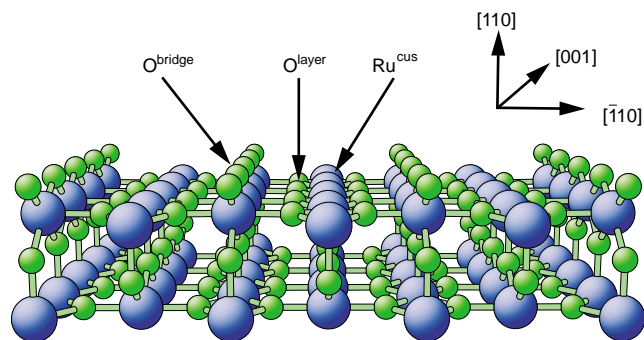

Figure 2. Thermal desorption (TD) spectra of H_2 (HD in the inset) after exposure to varying quantities of H_2 to the $RuO_2(110)$ surface at 85 K. The exposure is given in Langmuir units L (1 L $= 1.3 \times 10^{-6}$ mbars).

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 $RuO_2(110)$ surface, shows an intense fingerprint peak at $\tilde{\nu} = 557$ cm^{-1} arising from the Ru−O stretch vibration of the O^{bridge} atoms.[11] After the $RuO_2(110)$ surface was saturated with hydrogen, the corresponding spectrum, B, reveals new intense peaks at $\tilde{\nu} = 226$,

Figure 1. Ball-and-stick model of the bare stoichiometric $RuO_2(110)$ surface in perspective view (O: green, Ru: violet).

from the $RuO_2(110)$ 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 $RuO_2(110)$ surface to D_2 (0.5 L) and then to H_2 (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 H_2 molecules, above 400 K an appreciable quantity of H_2O molecules come off the surface, which indicates that apart from the recombinative desorption of H_2 in a different reaction, the whole surface entity H−O−H may be released.
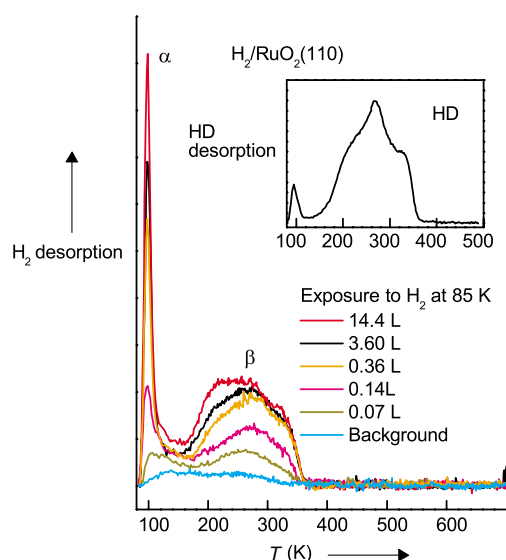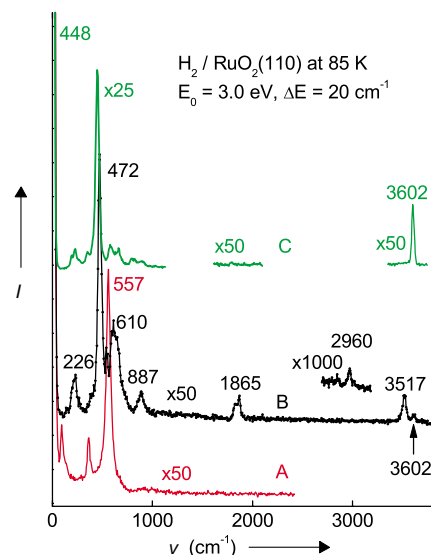

Figure 3. HREEL spectra for a primary electron energy E_0, at an energy resolution ΔE, in specular geometry at an angle of incidence of 60°. The factors ×50, etc. give the intensity enlargement with respect to the elastically scattered electrons ($I =$ intensity, arbitrary units). A) Bare stoichiometric $RuO_2(110)$ surface. b) After exposure of 1 L H_2 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 occured.

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 $\tilde{v} = 557$ 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 ($\tilde{v} = 226$, 472 cm^{-1}), librational ($\tilde{v} = 610$, 887 cm^{-1}), scissor ($\tilde{v} = 1865$ cm^{-1}), and OH stretching ($\tilde{v} = 3517$ 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 $\tilde{v} = 1702$ cm^{-1}, which is well above the gas phase value of $\tilde{v} = 1524$ cm^{-1}.

This dihydride species formed from H$_2$ 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 RuO$_2$ 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
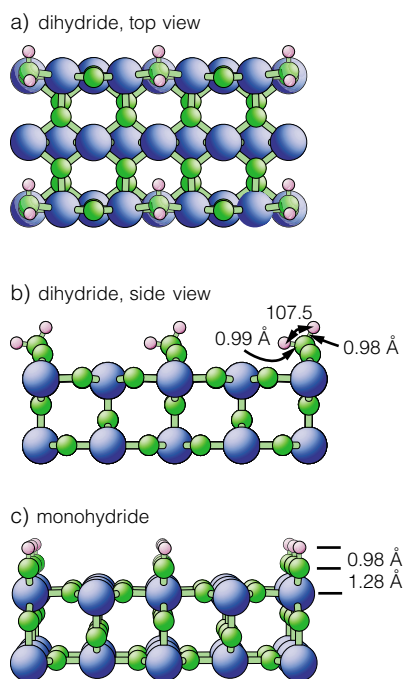
(8°) to the surface (see Figure 4b), the OH bond length becomes further elongated, and the scissor mode increases even beyond the gas-phase value. The calculated adsorption energy of H$_2$ is 0.32 eV per H$_2$ molecule. Further details will be discussed elsewhere.

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 $\tilde{v} = 887$ 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 O$_2$ 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 $\tilde{v} = 2960$ cm^{-1}, which is hence attributed to the H−H stretch vibration of molecular hydrogen adsorbed on the α state. For D$_2$, the analogous peak is found at $\tilde{v} = 2073$ 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 H$_2$ on the α state ($\tilde{v} = 2960$ cm^{-1}) is considerably smaller than that for free H$_2$ ($\tilde{v} = 4407$ cm^{-1}) or for physisorbed molecules (e.g. $\tilde{v} = 4121$ cm^{-1} for H$_2$/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 H$_2$ molecule and show that such a molecular species can only be stabilized at the RuO$_2$(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 $\tilde{v} = 3331$ cm^{-1}, which is in reasonable agreement with the experimental value. The H$_2$ 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 η^2-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).
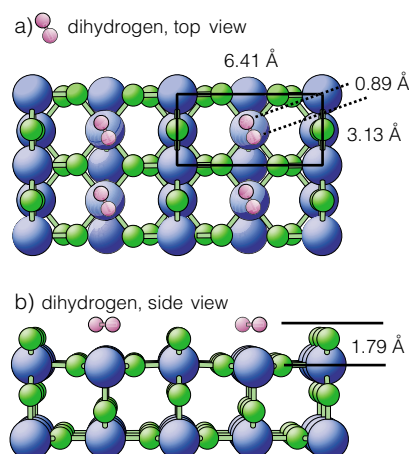

Figure 5. a) Top view and b) side view of dihydrogen bonded to Ru^{cus}. Note that the azimuthal orientation of dihydrogen is arbitrary as it is freely rotating. The (1×1) unit cell is indicated (O: green, Ru: violet, H: pink).

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→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 $\tilde{v} = 2400$–2800 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.

[1] H. Brunner, *Applied homogeneous catalysis with organometallic compounds*, VCH, Weinheim, **1996**, p. 201.

[2] K. Christmann, *Surf. Sci. Rep.* **1988**, *9*, 1–163.

[3] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, H. J. Wasserman, *J. Am. Chem. Soc.* **1984**, *106*, 451–452.

[4] G. J. Kubas, *Acc. Chem. Res.* **1988**, *21*, 120; R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828–845; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789–805.

[5] A. S. Mårtensson, C. Nyberg, S. Andersson, *Phys. Rev. Lett.* **1986**, *57*, 2045–2048.

[6] D. K. Schmidt, K. Christmann, G. Kresse, J. Hafner, M. Lischka, A. Groß, *Phys. Rev. Lett.* **2001**, *87*, 096103.

[7] J. Wang, C. Y. Fan, K. Jacobi, G. Ertl, *Surf. Sci.* **2000**, *481*, 113–118; C. Y. Fan, J. Wang, K. Jacobi, G. Ertl, *J. Chem. Phys.* **2001**, *114*, 10058–10062.

[8] H. Over, Y. D. Kim, A. P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, G. Ertl, *Science* **2000**, *287*, 1474–1476.

[9] P. Blaha, K. Schwarz, J. Luitz, WIEN97, Technische Universität, Wien, Austria, **1999**, ISBN 3-9501031-0-4.

[10] J. P. Perdew, S. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[11] Y. D. Kim, A. P. Seitsonen, S. Wendt, J. Wang, C. Fan, K. Jacobi, H. Over, G. Ertl, *J. Phys. Chem. B* **2001**, *105*, 3752–3758.

[12] M. Gruyters, K. Jacobi, *Chem. Phys. Lett.* **1994**, *225*, 309–314.

[13] K. W. Zilm, R. A. Merrill, M. W. Kummer, G. J. Kubas, *J. Am. Chem. Soc.* **1986**, *108*, 7837–7839.

[14] L. S. Van der Sluys, J. Eckert, O. Eisenstein, J. H. Hall, J. C. Huffman, S. A. Jackson, T. F. Koetzle, G. J. Kubas, P. J. Vergamini, K. G. Caulon, *J. Am. Chem. Soc.* **1990**, *112*, 4831–4841.

[15] R. H. Crabtree, D. G. Hamilton, *J. Am. Chem. Soc.* **1986**, *108*, 3124–3125.

[16] G. J. Kubas, *J. Less-Common Met.* **1991**, *172*, 475–484.