Supporting Information

Dimerization Induced Deprotonation of Water on $RuO_2(110)$

Rentao Mu,[‡, a, c] David C. Cantu,[‡, a, c] Xiao Lin,[†, a, c] Vassiliki-Alexandra Glezakou,[a,c] Zhitao Wang,[b, c] Igor Lyubinetsky,[b, c] Roger Rousseau,*[, a, c] and Zdenek Dohnálek*[, a, c]

[a] *Fundamental and Computational Sciences Directorate,* [b] *Environmental Molecular Sciences Laboratory,* [c] *Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, United States*

1. STM Images of Clean Stoichiometric $RuO_2(110)$

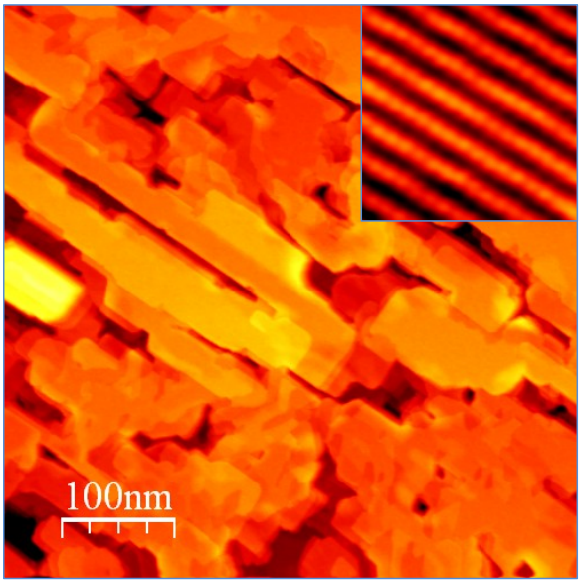

Figure S1: A large scale STM image of stoichiometric $RuO_2(110)$ thin film grown on Ru(0001) substrate. Inset: A high-magnification image (5×5 nm^2) illustrating surface structure composed of the rows of bright bridge-bonded oxygen (O_b) and dark five-fold-coordinated Ru (Ru_{cus}) atoms.

2. Computed Properties of $RuO_2(110)$

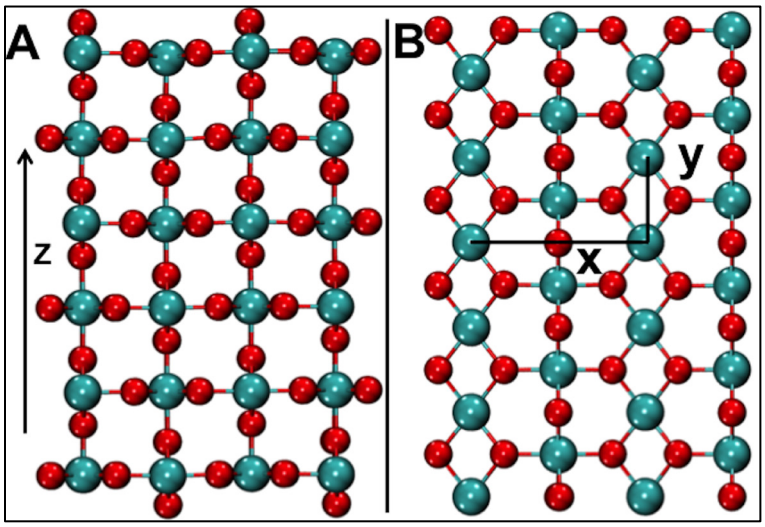

Figure S2: A: Side view of the six-layer thick RuO_2 slab. B: $RuO_2(110)$ surface viewed from above. Red: oxygen; blue: ruthenium.

RuO_2 Surface	This work	Ref. 1	Ref. 2
Surface Dimension x (Å)	6.41	6.38	
Surface Dimension y (Å)	3.13	3.11	
Work Function (eV)	5.6	5.9	5.8

Table S1: Computed Properties of $RuO_2(110)$

References

(1) Kim, Y. D.; Seitsonen, A. P.; Wendt, S.; Wang, J.; Fan, C.; Jacobi, K.; Over, H.; Ertl, G., Characterization of Various Oxygen Species on an Oxide Surface: $RuO_2(110)$. *J. Phys. Chem. B* **2001**, *105*, 3752-3758.
(2) Bottcher, A.; Niehus, H., Oxygen Adsorbed on Oxidized Ru(0001). *Phys. Rev. B* **1999**, *60*, 14396-14404.

3. STM Images Illustrating Dimerization of Water Molecules

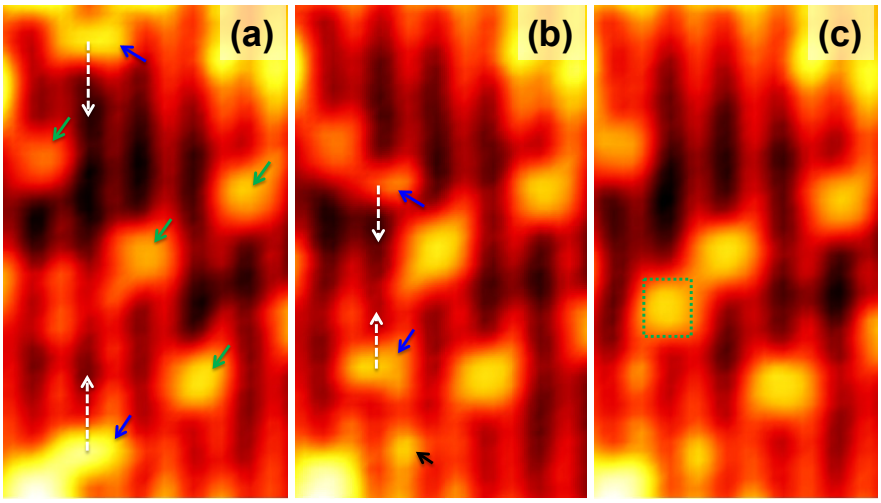

Figure S3: A time-lapse sequence of high-magnification STM images (4×7 nm^2) obtained after H_2O dose on RuO_2(110) at 238 K. (b) = (a) + 577 sec, (c) = (b) + 193 s. White dashed arrows illustrate the direction of water monomer diffusion and water dimer formation (green rectangle) in (c). Blue, green and black solid arrows mark water monomers, dimers, and bridging hydroxyl species, respectively.

4. Water Dimer Deprotonation

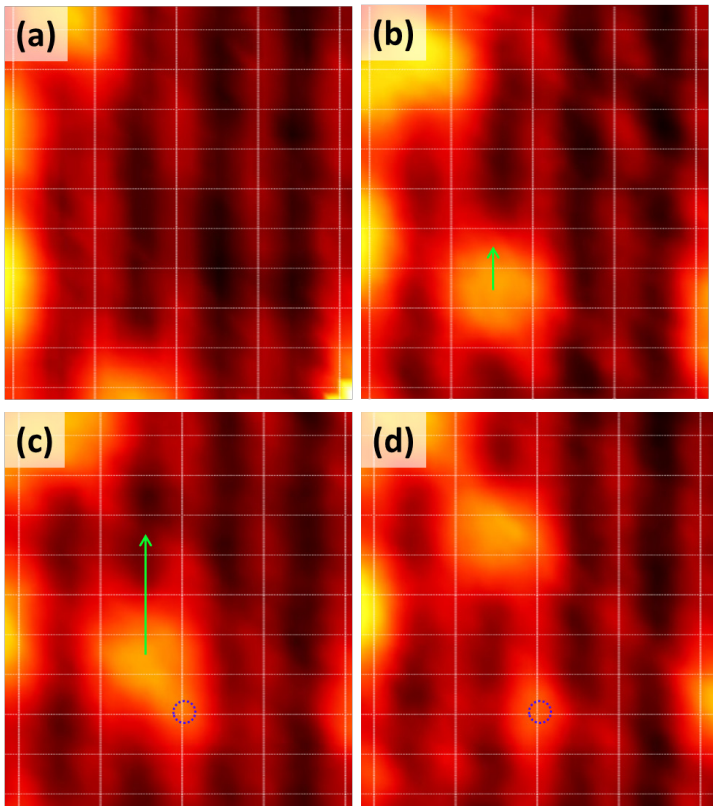

Figure S4: Sequence of STM images (3.2 × 3.6 nm^2) illustrating the deprotonation of water dimer at 295 K. (b) = (a) + 427 s, (c) = (b) + 256 s, (d) = (c) + 128 s. Green arrows in (b) and (c) illustrate the diffusion of H_3O_2 feature formed by $(H_2O)_2$ dissociation. Blue circles in (c) and (d) indicate the HO_b species formed as a result of $(H_2O)_2$ dissociation The positions of O_b atoms in (a-d) are marked with white lines.

5. Dumbbell Structure of HO_t…H_2O Pair

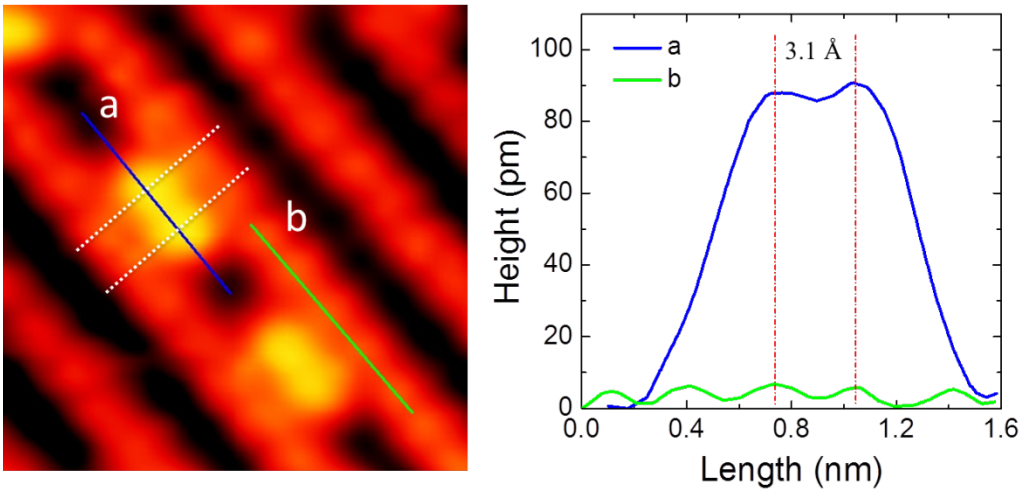

Figure S5: Left: High resolution STM image (3 × 3 nm^2, -0.9 V, 1 nA) of H_3O_2 species on *s*-RuO_2(110), illustrating fast proton transfer between two sides of the HO_t…H_2O pair. Right: Line profiles along the Ru_{cus} row (green: bare surface, blue: H_3O_2).

6. Comparison of Water Energetics on RuO_2(110) at Different Levels of Theory

RuO_2(110)	**Adsorption**	**Deprotonation**	
	ΔE (eV/water)	$E_{BARRIER}$ (eV)	ΔE (eV)
Water Monomer			
DFT	-1.15	0.22	-0.02
DFT + D3	-1.36	0.22	0.00
DFT + D3 + ZPE	-1.43	0.03	-0.02
Water Dimer			
DFT	-1.10	0.06	-0.30
DFT + D3	-1.24	0.06	-0.44
DFT + D3 + ZPE	-1.25	No barrier	-0.27

Table S2: Water monomer and dimer on RuO_2(110) adsorption and dissociation (deprotonation) energies with and without D3 and ZPE corrections

RuO_2(110)	**Diffusion Barrier, $E_{BARRIER}$ (eV)**			
	Water Monomer	Water Dimer	H_3O_2 with neighboring HO_b	H_3O_2 with separated HO_b
DFT	0.65	0.50	0.65	0.75
DFT + D3	0.65	0.50	0.65	0.75
DFT + D3 + ZPE	0.58	0.45	0.61	0.67

Table S3: Water monomer and dimer on RuO_2(110) diffusion energies with and without D3 and ZPE corrections

7. Comparing the Acid/Base Properties of RuO_2 and TiO_2

Water behavior on both RuO_2(110) and TiO_2(110) can be further understood in terms of their acid-base properties. The ratio of our calculated binding energies of water dimers on RuO_2 (110) over water dimers on TiO_2 (110) is 1.28, close to the experimental ratio of 1.3 (See Tables S2 and S4). The stronger water binding on RuO_2 implies a stronger water-metal contact (Lewis acidity), which should, by inductive effects, lead to weaker O-H bonds and therefore a higher Brønsted acidity for the bound waters. To quantify this we consider a hypothetical water adsorption configuration where hydrogen-bonding contacts with the O_b sites are minimized (see Figure S6). The adsorption energy increases by 0.2 and 0.1 eV for RuO_2 and TiO_2 respectively; hence the overall trend in Lewis acidity (as reflected by the binding energy of the global minimum) is preserved. The impact this has upon the water monomer O-H bond strength (via electrostatic induction) can be measured by the computed red shift in OH frequency, which is found to be 140 and 90 cm^{-1} for water on RuO_2(110) and TiO_2(110) respectively, indicating that water bound to the Ru site is more acidic than when bound to the Ti site. As a result on the, TiO_2(110) surface (Table S4) the deprotonated water state is practically isoenergetic (0.03 eV lower) with the molecular water state for the monomer and dimer (0.10 eV lower), but such is not the case on RuO_2(110). However the deprotonation barriers of water on the TiO_2(110) surface are considerably higher than on the RuO_2(110) surface being 0.23 eV for the water monomer and 0.16 eV for the dimer. Consistent with lower adsorption energies due to weaker metal-water interactions, our calculated individual diffusion event barriers for water are lower on the TiO_2 (110) surface than on the RuO_2 (110) surface being 0.35 eV for the monomer and 0.22 eV for the dimer, supporting the role of ruthenium as a stronger Lewis acid.

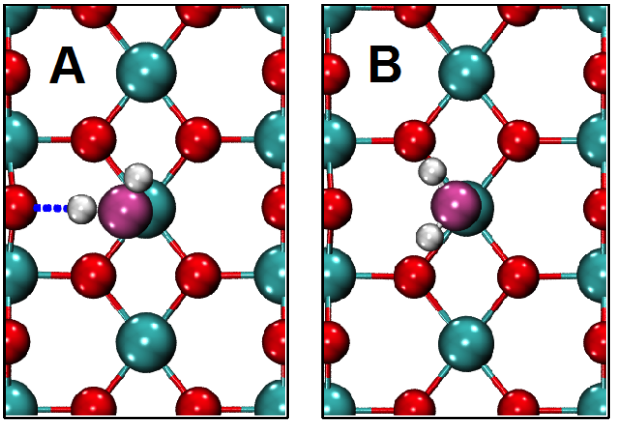

Figure S6: Water monomer bound to RuO_2(110) in (A) the preferred conformation with a hydrogen bond with neighboring O_b, and (B) without the hydrogen bond. Red: oxygen; pink: oxygen in H_2O; blue: ruthenium; white: hydrogen.

TiO_2	Adsorption	Deprotonation	
	ΔE (eV/water)	$E_{BARRIER}$ (eV)	ΔE (eV)
Water Monomer			
DFT	-0.96	0.40	0.02
DFT + D3	-0.91	0.40	0.03
DFT + D3 + ZPE	-0.92	0.23	-0.03
Water Dimer			
DFT	-0.87	0.32	-0.07
DFT + D3	-0.97	0.32	-0.05
DFT + D3 + ZPE	-0.97	0.16	-0.10

Table S4: Water monomer and dimer on TiO_2(110) adsorption, dissociation (deprotonation), and diffusion energies with and without D3 and ZPE corrections.

TiO_2(110)	Diffusion Barrier, $E_{BARRIER}$ (eV)			
	Water Monomer	Water Dimer	H_3O_2 with neighboring HO_b	H_3O_2 with separated HO_b
DFT	0.38	0.32	0.20	0.18
DFT + D3	0.39	0.31	0.19	0.19
DFT + D3 + ZPE	0.35	0.22	0.14	0.12

Table S5: Water monomer and dimer on TiO_2(110) diffusion energies with and without D3 and ZPE corrections

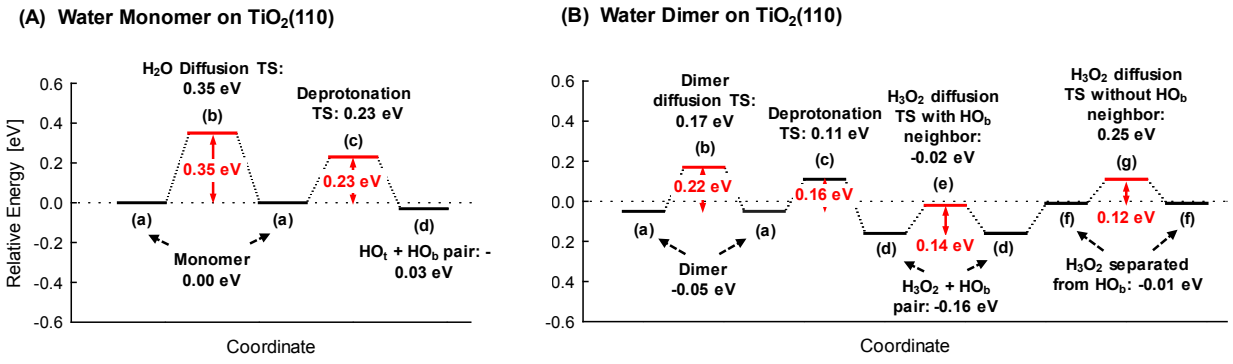

Figure S7: Computed potential energy landscape for deprotonation and diffusion of water monomer (A) and dimer (B) on Ti_{5c} sites of TiO_2(110). All energies are calculated using DFT+D3 and corrected for ZPE, using water monomer adsorption as a reference state. Lower values correspond to higher thermodynamic stability.