

COMMENTS

Comment on “Interaction of Hydrogen with RuO₂(110) Surfaces: Activity Differences between Various Oxygen Species”D. Crihan,[†] M. Knapp,[†] A. P. Seitsonen,[‡] and H. Over^{*,†}

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In a recent *JACS* communication to the Editor,¹ we identified an efficient *hydrogen transfer* channel from the bridging O to the O-cus species on RuO₂(110) which can well explain many of the new high-resolution energy electron loss spectroscopy (HREELS) data in ref 2.³ In addition, we drew two conclusions for the O-saturated RuO₂(110) surface on which were “challenged” in ref 2. First, hydrogen does not need the presence of free Ru-cus (cus stands for coordinatively unsaturated sites) atoms to be adsorbed on the RuO₂(110) surface.⁴ Second, an O-bridge is more prone to adsorb hydrogen than an O-cus when the Ru-cus sites are blocked.

With a well-defined stoichiometric RuO₂(110) surface,⁵ we performed a clear-cut experiment, demonstrating that Ru-cus atoms are *not* required for the accommodation of hydrogen on the RuO₂(110) surface.⁶ First, we saturate all Ru-cus atoms by O-cus atoms, cooling the RuO₂(110) film in an oxygen atmosphere of 1×10^{-7} mbar from 500 down to 300 K. The corresponding thermal desorption (TD) spectrum of oxygen (cf. Figure 1) indeed shows 20% more oxygen than from a RuO₂(110) surface which has been saturated by oxygen at 300 K. The scanning tunneling microscopy (STM) image of the fully O-saturated surface indicates only one O-cus vacancy (dark cross in Figure 1, left inset). From many STM images, we estimate an O-cus vacancy density of 1–2% for this O-saturated RuO₂(110) surface. The O-saturated RuO₂(110) surface is subsequently exposed to 50 L of H₂. After hydrogen exposure, we took a water TD spectrum which is compared to the water TDS from the stoichiometric RuO₂(110) surface (right inset). The integral water TD signal is a direct measure of the total amount of hydrogen adsorbed on the RuO₂(110) surface. Clearly, hydrogen adsorption does take place on the O-saturated RuO₂(110) surface, *not* requiring free Ru-cus atoms.

To clarify whether hydrogen enters the O-saturated RuO₂(110) surface either via the bridging O or via the O-cus atoms, all bridging O atoms have been replaced by bridging CO and coadsorbed with O-cus at low temperature.¹ When this surface is subsequently exposed to molecular hydrogen, we do not find any evidence for hydrogen adsorption consistent with ref 2. Hence, O-cus is less prone to adsorb hydrogen than the O-bridge.^{8,9}

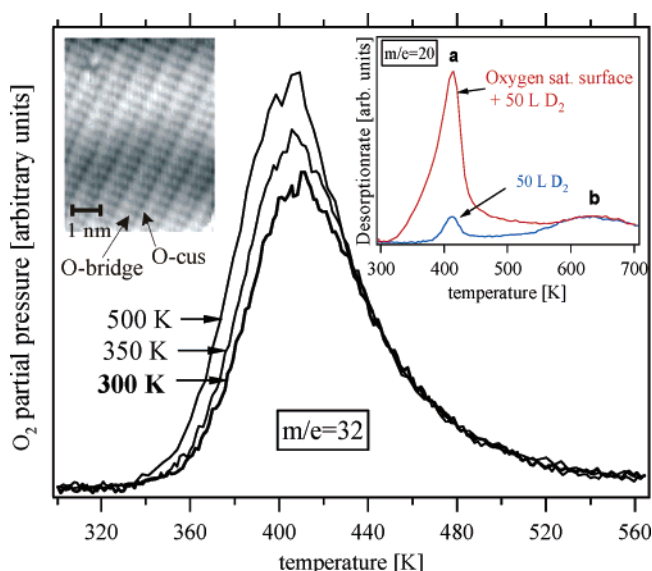


Figure 1. Oxygen TD spectra of RuO₂(110) which was exposed to 5 L of O₂ at 300 and 350 K. For the “500 K” spectrum, we kept the RuO₂(110) in 1×10^{-7} mbar of oxygen while cooling the sample from 500 to 300 K by 1 K/s. (left inset) STM image from a “500 K” O-saturated RuO₂(110) surface. The bright rows are O-cus rows. In the left upper corner of the STM image, we discern a single O-cus vacancy as a dark cross.⁷ (right inset) Water TD spectrum from the O-saturated RuO₂(110) surface which is exposed to 50 L of H₂ compared with that from the stoichiometric surface.

References and Notes

- (1) Knapp, M.; Crihan, D.; Seitsonen, A. P.; Over, H. *J. Am. Chem. Soc.* **2005**, *127*, 3236.
- (2) Jacobi, K.; Wang, Y.; Ertl, G. *J. Phys. Chem. B* **2006**, *110*, 6115.
- (3) The concept of hydrogen transfer is unfortunately not discussed at all in ref 2.
- (4) At no place in ref 1 did “we proposed that at 300 K hydrogen adsorbs directly on the O-bridge atoms rather than via activation at Ru-cus atoms” (ref 2). What we *did* propose is that hydrogen forms bridging hydroxyl groups even if the Ru-cus atoms are blocked.
- (5) For keeping the RuO₂(110) film stoichiometric when working with reducing agencies, repeated oxygen exposure/annealing cycles are required after each experiment. (*Surf. Sci.* **2002**, *505*, 137). Otherwise, the RuO₂(110) will progressively be reduced. Therefore, the particular preparation/restoration method in ref 2 will unavoidably lead to a clean but heterogeneous surface, consisting of RuO₂(110) with metallic Ru islands decorating holes in RuO₂(110) (the STM image in the Supporting Information of *J. Phys. Chem. B* **2006**, *110*, 14007). This has dramatic consequences on the hydrogen adsorption properties of RuO₂(110).
- (6) Reference 2 addresses most of its discussion part to the question of whether Ru-cus are required for hydrogen accommodation on RuO₂(110), comparing their experiments at 90 K with ours in ref 1 at room temperature. Note that hydrogen adsorption may be activated and therefore temperature dependent.
- (7) This STM image is part of a forthcoming paper by M. Knapp et al. It was taken at the TU in Vienna in P. Varga and M. Schmid’s group.
- (8) We emphasize that we discuss here a situation where Ru-cus atoms are capped by O-cus atoms; therefore, Ru-cus is not available for the hydrogen adsorption. If, however, part of the Ru-cus atoms are free, then both adsorption via the undercoordinated O atoms and via the Ru-cus atoms are possible.
- (9) The authors in ref 2 conclude that in the presence of O-cus atoms on the RuO₂(110) surface, hydrogen (sitting molecularly on the Ru-cus atoms) will “preferentially react with O-cus instead of with O-bridge species”. Since there is an efficient hydrogen transfer reaction between the O-bridge and the O-cus species (see ref 1), such a conclusion cannot be drawn from the HREELS data in ref 2, that only monitor the final state.

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