

## Reply to “Comment on ‘Interaction of Hydrogen with RuO<sub>2</sub>(110) Surfaces: Activity Differences between Various Oxygen Species’”

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In two recent contributions, we have presented experimental results on the interaction of hydrogen with RuO<sub>2</sub>(110) surfaces<sup>1,2</sup> which can be prepared in (a) the stoichiometric state<sup>3,4</sup> by annealing at 700 K within O<sub>2</sub> at a pressure of  $1 \times 10^{-7}$  mbar and in (b) a more oxygen-rich state<sup>5</sup> by further exposing the surface to O<sub>2</sub> at 300 K. In the stoichiometric state, the RuO<sub>2</sub>-(110) surface consists of rows of doubly bonded O-atoms (called O-bridges) alternating with rows of 5-fold coordinated Ru-atoms (Ru-cus); cus stands for coordinatively unsaturated sites. In the oxygen-rich state, about 80% of the Ru-cus atoms are covered by oxygen atoms (O-cus). From these studies, the following conclusions have been derived:<sup>1,2</sup>

(1) If O-cus species exist on the surface together with some empty Ru-cus sites, the incoming H<sub>2</sub> interacts preferentially with O-cus in forming H<sub>2</sub>O-cus which desorbs at  $\sim 400$  K.

(2) If O-cus is not available, two interaction channels are observed at 85 K: (a) H<sub>2</sub> may adsorb weakly in molecular form at Ru-cus or (b) it may interact with the more strongly bound O-bridge in forming a H<sub>2</sub>O-like group, called an H<sub>2</sub>O-bridge. At 200–350 K, H<sub>2</sub> is released and an OH-bridge is left at the surface. At 600–550 K, the OH-bridge species disproportionates into an O-bridge and H<sub>2</sub>O, whereby the latter is released into the gas phase.

(3) If all Ru-cus sites are blocked, e.g., by CO adsorption at 85 K, H<sub>2</sub> interacts with neither an O-bridge nor O-cus although both species are fully accessible from the gas phase. Quite obviously, H<sub>2</sub> needs some activation at Ru-cus prior to reaction with an O-bridge or O-cus.

These findings are in fact at variance with the conclusions by Knapp et al.<sup>6</sup> who summarized with the following: “The bridging O atoms (our O-bridge) harvest the hydrogen from the gas phase, while the on-top O atoms (our O-cus) pick-up those adsorbed hydrogen atoms from the bridging O atoms to form water.”

In a comment on our contribution, Crihan et al.<sup>7</sup> underline previous conclusions of Knapp et al.<sup>6</sup> and present a further experiment: They kept “the RuO<sub>2</sub>(110) surface in  $1 \times 10^{-7}$  mbar of oxygen while cooling the sample from 500 to 300 K by 1 K/s”. This surface is more rich in oxygen than after preparing O-cus at 300 K as demonstrated by temperature desorption spectroscopy (TDS) and scanning tunneling microscopy (STM). After exposing this surface then to 50 langmuir D<sub>2</sub> (1 langmuir =  $1.3 \times 10^{-6}$  mbar s), they observed desorption of D<sub>2</sub>O-cus (D<sub>2</sub>O bonded to Ru-cus). From this observation, they concluded that D<sub>2</sub> does not need a vacant Ru-cus site for activation, in contrast to our conclusion.

Knapp et al.<sup>6</sup> and Crihan et al.<sup>7</sup> do not mention our conclusive experiment concerning the entrance channel of hydrogen: In one of our experiments, the Ru-cus atoms were completely

covered by CO through exposing the stoichiometric RuO<sub>2</sub>(110) surface to 1 langmuir CO at 90 K. Then, the surface was exposed to 2.5 langmuir H<sub>2</sub> at 90 K, but the vibration spectrum did not change at all. We concluded therefore that hydrogen adsorption requires the molecular H<sub>2</sub> state at Ru-cus as a precursor for any reaction with O-bridges or O-cus and that a direct interaction of gas-phase H<sub>2</sub> with O-bridge species does not occur. Our conclusion is fully in line with the recent DFT calculations.<sup>8</sup> In their ref 6, Crihan et al.<sup>7</sup> note that their experiments were performed at 300 K and that the interaction of H<sub>2</sub> with O-bridges may be activated and therefore may become effective at 300 K. Since at this temperature H<sub>2</sub> is not (molecularly) adsorbed at all, this would require an Eley–Rideal type of reaction which is rather unlikely.

Given our experimental evidence that H<sub>2</sub> must be activated first before any interaction with O-bridge species is effective, one may ask what happened in the experiment of Crihan et al.<sup>7</sup> First of all, from our experience, we know that at 300 K a defect-free O-rich surface can be neither prepared under ultrahigh vacuum conditions nor kept defect-free under those conditions. Specifically for the experiment reported in the comment, the authors themselves admit the existence of 1–2% O-cus vacancies. Furthermore, as can be seen in the inset of their Figure 1, the D<sub>2</sub>O-cus desorption curve tails down to 300 K so that, during D<sub>2</sub> exposure, D<sub>2</sub>O can be formed and desorbed leaving back an additional vacancy for D<sub>2</sub> activation. This effect can be even more important keeping in mind that achieving 300 K after annealing is a rather slow process, so that many experiments reported to be done at 300 K might actually have been performed at still higher temperatures. Also the rather high dose of 50 langmuir—as compared to 2.5 langmuir in our experiment—enforces the same process of creating empty Ru-cus sites. Finally, CO from the residual gas is also creating O-cus vacancies by CO<sub>2</sub> formation even at 300 K.<sup>4</sup> Concerning the entrance channel of H<sub>2</sub>, the situation is different in our experiment at about 100 K: the rows of Ru-cus sites were completely blocked by CO.

Finally, there is some controversy in the references<sup>7</sup> which should be answered briefly. Regarding ref 3,<sup>7</sup> there is nothing special to be discussed with the “concept of hydrogen transfer”. The basis for this concept is the assumption of a higher activity of an O-bridge compared to O-cus which we do not agree upon. With respect to ref 5,<sup>7</sup> there is no basis to question our preparation. After each experiment, we have freshly prepared our sample and—opposite to Knapp et al.<sup>6</sup> and Crihan et al.<sup>7</sup>—we have examined the correct state of the surface by vibration spectroscopy. We also have controlled our preparation by STM in a separate chamber in collaboration with J. Wintterlin’s group.<sup>9</sup> Furthermore, our reducing exposure was smaller by a factor of 20 than that of Knapp et al.,<sup>6</sup> and the base pressure of our chamber was at the X-ray limit of  $3 \times 10^{-11}$  mbar.

In summary, we see no evidence to revise our conclusions. The conclusion of Knapp et al.<sup>6</sup> that the more strongly (by 1 eV, with two backbonds) bonded O-bridge is more reactive against hydrogen than the less strongly bonded (with one backbond) O-cus, is contradicting our experimental results, chemical intuition, and theoretical ab-initio calculations.

## References and Notes

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