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LETTERS TO THE EDITORS

The Implications of One-Dimensional Ordering of Rh on the (110) Surface of Rutile[1]

In a recent EXAFS study of Rh supported on TiO_2 prepared by ion exchange, we presented evidence for direct Rh–Ti bonding following high-temperature reduction at 773 K (*1*). Based on high-resolution electron micrographs of ion-exchanged Rh/TiO_2 catalysts presented by Galicia *et al.* (*2*), we described a possible model for the precursor to the structure which forms upon high-temperature reduction (*1*). This model involved Rh atoms forming rows, as seen in the Galicia *et al.* micrographs, in the valleys on the ideal TiO_2 (110) surface as shown in Fig. 1. Recently in this journal these same micrographs were published after treatment with image-processing techniques to filter the noise and to enhance the contrast (*3*). The micrographs show two-dimensional structures of Rh with about 1-nm cross-section and one-dimensional rows of Rh along the [001] direction of the (110) surface of rutile. In the naive model shown in Fig. 1, which does not take into account preparation chemistry, the Rh atoms are in valleys between bridging oxygen ridges and the Rh atom rows would be separated by 0.65 nm. However, in the computer-enhanced micrographs (see Fig. 3 of Ref. (*3*)), the Rh atom rows are only separated by 0.325 nm (*4*), implying that the Rh atom rows not only occupy the valley positions, but also the positions of the *bridging oxygen ridges*. This was suggested in Fig. 5 of Ref. (*3*), although the atom positions shown in that figure are not accurate. (See Fig. 3 of Ref. (*5*) for the geometry of the TiO_2 (110) surface.) Fuentes *et al.* make no comments concerning the implications of their model.

If the model presented by Fuentes *et al.* (*3*) in their Fig. 5 is the correct interpretation of the electron micrographs, can it be rationalized in terms of the genesis of the catalyst? In our opinion, it can with some modifications and corrections. We begin with the perfect (110) surface of rutile (Fig. 1 in which the Rh atoms have been removed). Exposed to water, we can expect this surface to be fully hydroxylated. This would occur by dissociating H_2O heterolytically and placing the hydroxyl ions in the valleys over each of the exposed, fivefold oxide coordinated Ti^{4+} cations and the protons on each of the oxide ions of the bridging ridges. Recall that in the ion-exchange procedure (*1*) the TiO_2 is first treated with NH_4OH solution to ion exchange some of the protons with NH_4^+ ions which are, in turn, exchanged with rhodium cations. The nitrate salt was used in our preparation and that of Fuentes *et al.*, who used a sample provided by Katzer *et al.* (*6*). In solution, a stable yellow aquo ion, $[Rh(H_2O)_6]^{3+}$, is first formed, but this ion is acidic (pK_a about 3.3) and quickly hydrolyzes to $[Rh(H_2O)_5(OH)]^{2+}$ in acid solution (*7*) and presumably to $[Rh(H_2O)_4(OH)_2]^+$ in the more basic solutions used for ion-exchange procedure. Which of the two kinds of surface hydroxyls are more likely to participate in exchange with NH_4^+ and then with $[Rh(H_2O)_4(OH)_2]^+$? Inspecting a model of the surface one finds that the hydroxyls in the valleys are bound to one Ti^{4+} cation while those hydroxyls which form the

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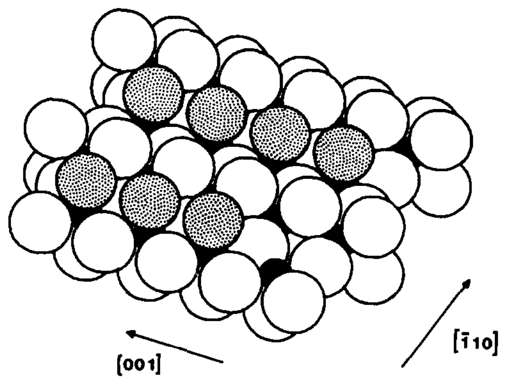

FIG. 1. The perfect (110) TiO_2 surface with rows of Rh atoms placed over fivefold exposed Ti^{4+} cations. ●, Ti cation; ○, oxygen anion; ◎, Rh atom.

bridging ridge are bonded to two. This suggests that the bridging hydroxyls will be the more acidic so that these will preferentially hold the NH_4^+ and therefore the $[Rh(H_2O)_4(OH)_2]^+$ ions. The chemistry by which the precursor to the metal loses water, adsorbs H_2, and reduces to the metal is difficult to imagine in detail, but formally we can write:

$$\tfrac{3}{2}H_2 + [Rh(H_2O)_3(OH)_2(OTi)]^{3+} \rightarrow 5H_2O + [Rh(HOTi)].^{3+} \quad (1)$$

As written, only the Rh has been reduced and all of the titanium cations remain Ti^{4+}. Moreover, Eq. (1) does not treat surface hydroxyls explicitly and we assume that *all* surface hydroxyl ions are retained by the surface in both the valley and bridging positions. This is approximately the case for low-temperature reduction (as used for the micrographs shown in Ref. (*3*)) and Rh atoms would not take up positions over the fivefold Ti^{4+} as shown in Fig. 1 because they probably do not exist after low-temperature reduction. Practically, however, some dehydroxylation must occur and presumably the bridging hydroxyls are preferentially retained because they are coordinated to two Ti^{4+} cations while the other hydroxyls are coordinated to only one. A possible structure with approximately 0.325 nm spaced rows is shown in Fig. 2. It is clear that in the structure shown in Fig. 2 and in the Fuentes *et al.* micrographs there must be some migration of Rh species because the spacing in both Fig. 2 and the micrographs is closer than physically possible for the bulky $[Rh(H_2O)_4(OH)_2]^+$ complex. The autocatalytic reduction of a Rh complex, by a previously reduced Rh atom, and metal–metal bonding between Rh atoms would provide the driving forces for this migration. In this structure each Rh is fourfold coordinated to four hydroxyl ions. Note that this structure has the same row direction and spacing as that shown in Fig. 5 of Ref. (*3*) and it retains the Rh in its normal state. This is what would be expected in the Fuentes *et al.* experiment because their sample had only been reduced at 473 K. Moreover, their catalyst exhibited hydrogenation activity and hydrogenolysis selectivity, respectively, which were about the same as for Rh/SiO_2, confirming that the Rh was not in the SMSI state. In our sample, which had been reduced at 773 K and which exhibited direct Rh–Ti bonding, the reduction can be formally written as

$$2H_2 + [Rh(H_2O)_3(OH)_2(OTi)]^{3+} \rightarrow 6H_2O + [Rh{-}Ti]^{3+} \quad (2)$$

or

$$[Rh(HOTi)]^{3+} + \tfrac{1}{2}H_2 \rightarrow [Rh{-}Ti]^{3+} + H_2O \quad (3)$$

if we start with the 473 K reduced surface. As written, one Ti^{3+} has been produced for every Rh reduced. For simplicity, we also

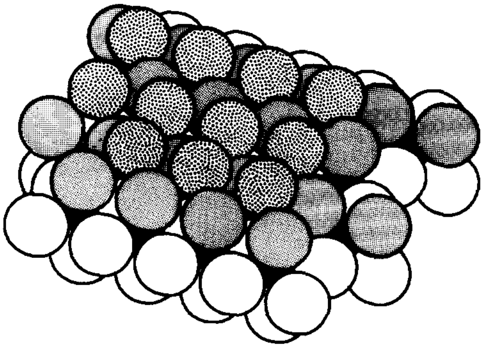

FIG. 2. The completely hydroxylated perfect (110) TiO_2 surface with rows of Rh placed between rows of hydroxyls. ◎, OH^- ion.

assume complete dehydroxylation of the surface although this is not explicit in Eq. (2) and in practice there will be a modest number of hydroxyls retained. There are two possible positions for anion vacancy defects: the bridged oxide positions of Fig. 1 (or hydroxyls in Fig. 2) and the in-plane oxide positions of Fig. 1. Removal of the bridging oxide ions (or hydroxyls) produces fivefold Ti^{3+}, and removal of the in-plane oxide ions produces fourfold cations (see Fig. 3 of Ref. (*3*)). Experimentally the spacing of the rows after high- and low-temperature reduction is found to be the same (*8*), i.e., 0.325 nm. A possible structure that retains the 0.325 nm row spacing after high-temperature reduction and which incorporates direct Rh–Ti bonding is shown in Fig. 3. Here, all of the bridging hydroxyls (or oxides) have been removed, effectively reducing the surface to Ti_2O_3 in the vicinity of high Rh density (*9*). As shown, half of the Rh atoms have taken up the bridging hydroxyl positions and the other half have moved to the valley positions over cations. In fact, some of the Ti^{3+} may migrate into the surface to leave some which are formally Ti^{4+} while others are Ti^{3+}. However, a similar charge situation occurs in Ti_4O_7 where alternating Ti^{4+} and Ti^{3+} layers exist formally. Because the average Ti–O distances for individual octahedra range from 0.2004 to 0.2022 nm, it appears that the titanium charge is very nearly equally distributed among the different sites (*10*). Presumably a similar charge sharing could occur between positions on the surface, such that the Rh–Ti bonding is similar in both positions even if all sites are not formally Ti^{3+}. In any case, we cannot see any other way to retain the 0.325 nm row spacing and produce Rh–Ti bonding after high-temperature reduction. Note that we do not invoke migration of TiO_x species, as seen in other studies (*11, 12*), because it would not be required for atomically dispersed Rh where direct bonding to titanium is possible without migration.

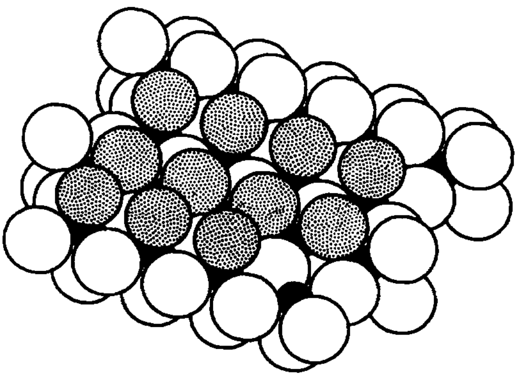

FIG. 3. The (110) TiO_2 surface after complete dehydroxylation and reduction of the surface with rows of Rh atoms placed over fivefold Ti cations and in place of the bridging oxide ions of Fig. 1.

One might ask if there is any way that some of these speculations might be tested. It is possible to perform the ion exchange at different pH so that cation exchange occurs primarily with protons of the more acidic bridging hydroxyls and at low pH where anion exchange occurs primarily with the more basic hydroxyls in the valley positions. Of course, appropriate Rh complexes, e.g., $[Rh(H_2O)_2(Cl)_4]^-$ for anion exchange, would also have to be chosen for these different exchange processes. In the extreme case, the bridging hydroxyls are the dominant positions for the Rh metal precursors at very high pH and the valley hydroxyls are the dominant positions for the Rh metal precursors at very low pH. These might lead to different structures after low-temperature reduction, conceivably to 0.325 nm spaced Rh rows when high pH is used and 0.65 nm spaced Rh rows when low pH is used. Such experiments are now being contemplated.

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4. Using the marker shown in Fig. 3 of Ref. (*3*), the rows of Rh appear to be 0.295 nm apart. However, this is a blow-up of Fig. 1 of Ref. (*3*) where the

lattice spacing of the (110) surface is shown with the known 0.325 nm spacing and we will assume this is correct for Fig. 3 also.

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9. Because of the one-to-one stoichiometry of oxide ions to Ti cations under the bridging oxides, complete reduction to Ti^{3+} in these sites would remove only every other oxide from the perfect (110) surface. Complete removal of the bridging oxides constitutes reduction of all surface cations to Ti^{3+}, a structure which would be stabilized by Rh bonding as shown in Fig. 3.

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