

Lattice Oxygen Deficiency as the Origin of Strong Metal–Support Interaction in the Rhodium/Titanium Dioxide System

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Reduction of Ti^{4+} to Ti^{3+} , a primary step in the origin of strong metal–support interaction, can be brought about by hydrogen spillover or by lattice oxygen deficiency in the oxide surface, or by both.

Reducibility of a support is one of the characteristics that determines the kind and the extent of interaction between metal and support and hence the dispersability of the metal. When TiO_2 , a reducible oxide, is used as support for a transition metal there is a possibility of strong metal–support interaction (SMSI).¹ The ability to chemisorb hydrogen or CO either was strongly suppressed or vanished entirely when metals supported on titania were activated in hydrogen at temperatures greater than 723 K. SMSI refers only to the bond that exists at the interface between the metal and the support rather than to the catalytic properties derived from it.² Although migration of reduced titanium dioxide species (TiO_x) to the metal surface has been accepted as an explanation of SMSI behaviour, the mechanism is not yet understood.² One must consider also the contribution from hydrogen spillover.^{3,4} Thus understanding of the origin of SMSI and the consequent catalytic activity deserves a new look. In this communication, we report the origin of SMSI in Rh/TiO_2 under two different activation conditions, viz. in the presence and in the absence of hydrogen.

Rh/TiO_2 (1 wt %) was prepared from $RhCl_3 \cdot 3H_2O$ and TiO_2 by wet impregnation and dried overnight at 393 K. The product was calcined at 573 K for 3 h and subjected to low temperature reduction in hydrogen at 473 for 8 h. Hydrogen uptake measurements on the sample at room temperature were carried out using a conventional volumetric apparatus. The sample was subjected to two different high temperature activation procedures. In one case, it was reduced in hydrogen at 573, 673, or 773 K for 3 h (high temperature reduction) and evacuated for 1 h before hydrogen adsorption measurement at room temperature. In the other case, the sample was not reduced but was only evacuated at the same temperatures for 3 h (high temperature evacuation) before hydrogen adsorption measurement at room temperature. Figure 1 shows the

decrease in hydrogen uptake by the two types of samples. Under the influence of hydrogen spillover the SMSI effect (in terms of decrease in hydrogen uptake) is more pronounced than after high temperature evacuation. In both cases, the hydrogen uptake could be brought closer to the original value after reoxidation and low temperature reduction. If the suppression of hydrogen uptake after high temperature activation (with or without hydrogen) is any indication of SMSI, then this experiment proves that SMSI in Rh/TiO_2 can

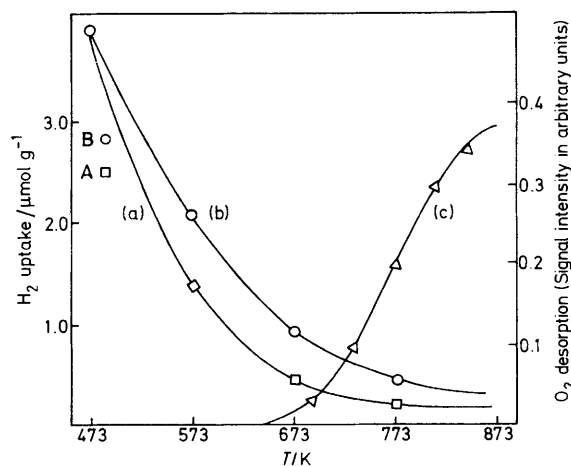
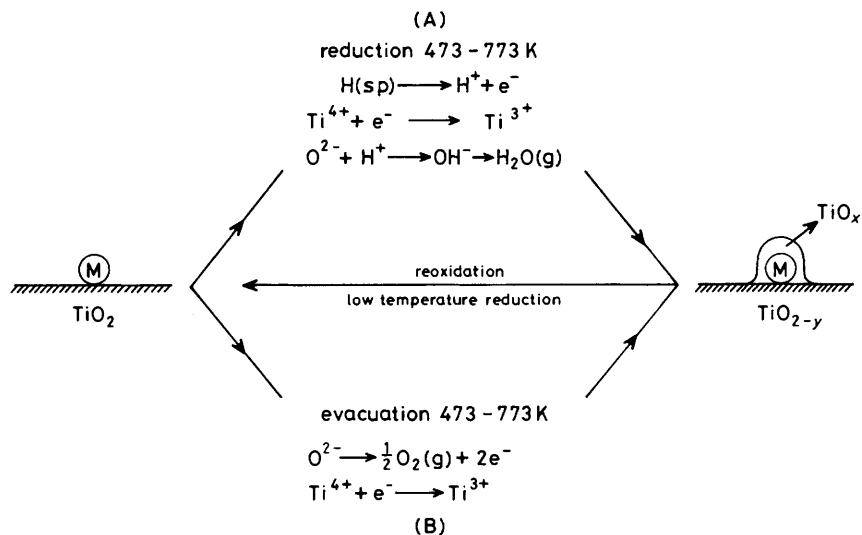


Figure 1. Hydrogen uptake on Rh/TiO_2 under the influence of (a) high temperature reduction and (b) high temperature evacuation. Curve (c) represents the temperature-programmed desorption of oxygen from Rh/TiO_2 . The open symbols (A, B) represent hydrogen uptake after reoxidation and reduction at 473 K.



Scheme 1. Schematic representation of the origin of strong metal-support interaction, (A) *via* hydrogen spillover; (B) *via* lattice oxygen deficiency.

be brought about under high temperature evacuation as well as high temperature reduction conditions.

During reduction at high temperature the reduction of Ti^{4+} to Ti^{3+} can be induced by hydrogen spillover, which could take place as shown in Scheme 1(A). In the absence of activation by hydrogen there is no possibility of hydrogen spillover. During high temperature evacuation there could be a loss of lattice oxygen from the oxide surface, creating anion vacancies which could reduce Ti^{4+} to Ti^{3+} as shown in Scheme 1(B). The occurrence of oxygen desorption from the oxide surface is supported by temperature-programmed desorption experiments on the low temperature reduction samples. To prove the evolution of oxygen under high temperature evacuation conditions, the low-temperature-reduced sample, previously evacuated at room temperature, was heated (temperature program) at 10 K min^{-1} from ambient temperature to 873 K. Desorption of oxygen was significant only beyond 623 K, as analysed by an on-line mass spectrometer (VG-micromass 2A), and thereafter increased with temperature [Figure 1(c)].

The formation of Ti^{3+} can thus be explained by either of the two mechanisms (or both), and the migration of TiO_x species

to the metal surface will follow, resulting in SMSI behaviour. This study thus supports a mechanism where lattice oxygen deficiency is a cause of the formation of Ti^{3+} species. This, we believe, would explain the absence of SMSI behaviour where a transition metal is supported on an oxide that is difficult to reduce, and also where the spillover phenomenon could not be evoked. In reducible oxides, of course, one might expect the hydrogen spillover mechanism to be involved, possibly together with lattice oxygen deficiency in the formation of Ti^{3+} from Ti^{4+} .

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