

Strong-metal-support-interaction in titania-supported rhodium, ruthenium, and rhodium–ruthenium bimetallic catalysts

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Abstract. Titania-supported rhodium, ruthenium and rhodium–ruthenium catalysts were prepared by impregnation followed by reduction at 573 K (low temperature reduced – LTR) and 773 K (high temperature reduced – HTR). Temperature programmed desorption of hydrogen showed the existence of strong-metal-support-interaction (SMSI) in rhodium and ruthenium catalysts, but not in the bimetallic catalyst. In either case, metal–hydrogen bond strength had undergone change in going from an LTR to HTR sample. X-ray photoelectron spectroscopy (XPS) results did not show any electron transfer between metal and support in any of the catalysts but electron transfer from rhodium to ruthenium was indicated in the bimetallic catalyst under HTR.

Keywords. Titania-supported catalysts; strong-metal-support-interaction; X-ray photoelectron spectroscopy.

1. Introduction

Studies on titania-supported group VIII metals have been reported by several laboratories since the first report by Tauster *et al* (1978) of a dramatic suppression in hydrogen and CO chemisorption capacities when these were reduced at a higher temperature (≥ 773 K). This was termed as strong-metal-support-interaction (SMSI). The occurrence of SMSI was soon widely confirmed on these and other systems and several explanations were put forward (Tauster 1987). Confirmation of the most widely accepted rationalisation came from investigations of model thin film systems of metal/titania that showed a migration of species labelled TiO_x ($1 < x < 2$) over the metal particles (Belton *et al* 1984). It has been a subject of intensive debate whether SMSI involves mere site-blocking by TiO_x (Ko and Gorte 1984) or there is, in addition, electron transfer from support to metal (Takatani and Chung 1984).

Almost all studies reporting SMSI have been based on determining the amounts of hydrogen and CO uptake using volumetric adsorption method. Temperature programmed desorption (TPD) is a simple yet powerful tool which, in addition to the amount of gas adsorbed, can reveal certain features of the adsorbate–adsorbent bond strength. This paper describes the preparation, and study of the titania–supported rhodium–ruthenium systems by X-ray diffraction (XRD), XPS, TPD of hydrogen, and electron spin resonance (ESR) spectroscopy with a view to understand SMSI in them.

2. Experimental

2.1 Materials

The compounds used for catalyst preparation were $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Alfa Products), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Johnson Mathey), and TiO_2 (anatase, May and Baker). Hydrogen and nitrogen (UHP grade) obtained from Indian Oxygen Ltd. were further purified using standard procedure.

2.2 Catalyst preparation

The support was soaked in a solution of the metal chloride(s) and stirred vigorously for about twelve hours. The slurry was then dried in vacuum. Each such composition was separately reduced in hydrogen for six hours – one at 573 K and the other at 773 K, and designated LTR (for low temperature reduction) and HTR (for high temperature reduction) respectively. Following this method, supported rhodium, ruthenium, and rhodium-ruthenium (metal ratio 1:1) were prepared and designated TiRh-LTR, TiRu-LTR, TiRhRu-LTR, TiRh-HTR, TiRu-HTR, TiRhRu-HTR. The total metal loading was maintained at one mole percent.

2.3 Catalyst characterisation

XRD studies were carried out on a Philips PW1140 diffractometer using CuK_α radiation filtered through a nickel foil at a scanning speed of 0.5 deg/min. Metal particle sizes were determined using the Scherrer equation (Bond 1987).

TPD of hydrogen was studied in a flow system with a quartz reactor and thermal conductivity detectors. The sample was freshly reduced in hydrogen flow at the specified reduction temperature, cooled to room temperature and hydrogen was adsorbed for about ten hours. The flow was switched to nitrogen (40 ml/min). Once a smooth baseline was obtained in the recorder, the sample was heated at a rate of 20°C/min and the TPD profile was recorded. Two hundred milligrams of sample were used in each run.

XPS spectra were recorded on a VG ESCAIII Mark II spectrometer. A pellet of each sample was loaded on a copper sample holder. Charging correction was done by referring to the $\text{Ti}(2p_{3/2})$ binding energy (459 eV) as an internal standard. The ratio (n_A/n_B) of elements A and B was calculated using the relation:

$$(n_A/n_B) = (I_A/I_B) \times (\sigma_A/\sigma_B)$$

where I and σ refer to the peak area and photo-ionisation cross-section respectively.

ESR spectra were recorded on a Varian E112 X-band instrument at room temperature as well as at 77 K.

3. Results and discussion

3.1 Occurrence of SMSI

The TPD spectra of hydrogen for the various catalysts are presented in figures 1–3. Two features are to be noted in going from an LTR to a corresponding HTR catalyst:

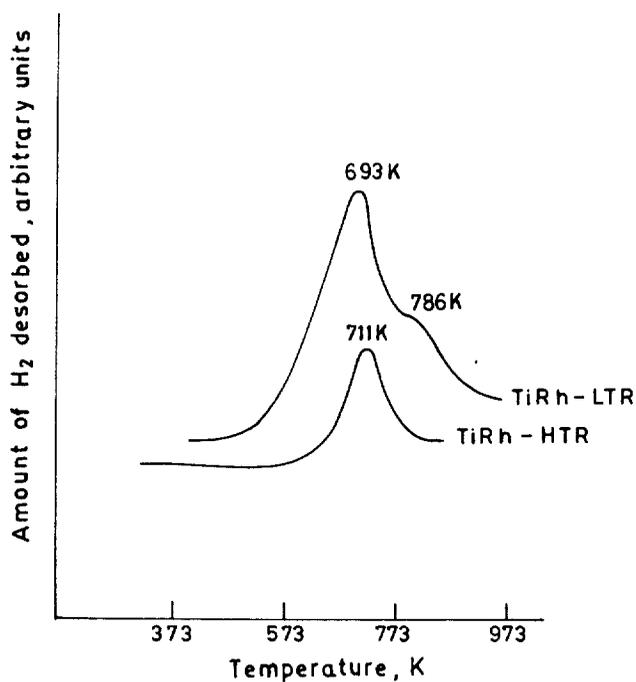


Figure 1. Hydrogen TPD profiles of titania-supported rhodium reduced at 573 K (TiRh-LTR) and 773 K (TiRh-HTR).

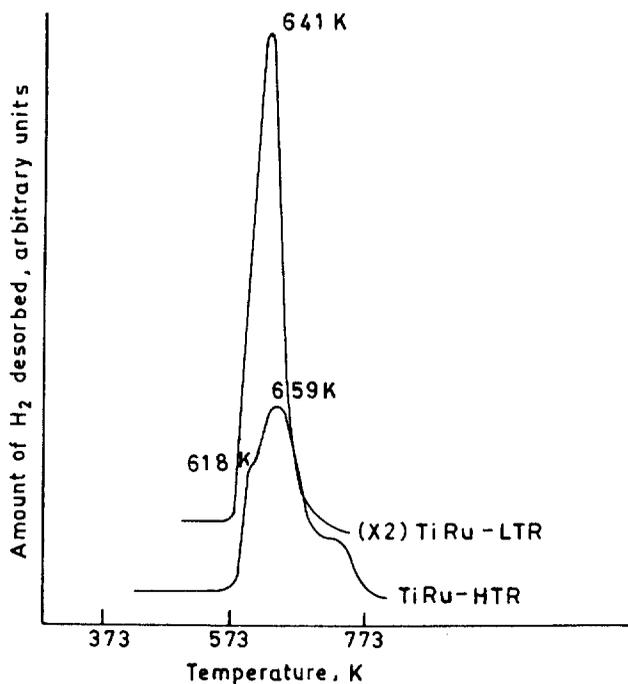


Figure 2. Hydrogen TPD profiles of titania-supported ruthenium reduced at 573 K (TiRu-LTR) and 773 K (TiRu-HTR).

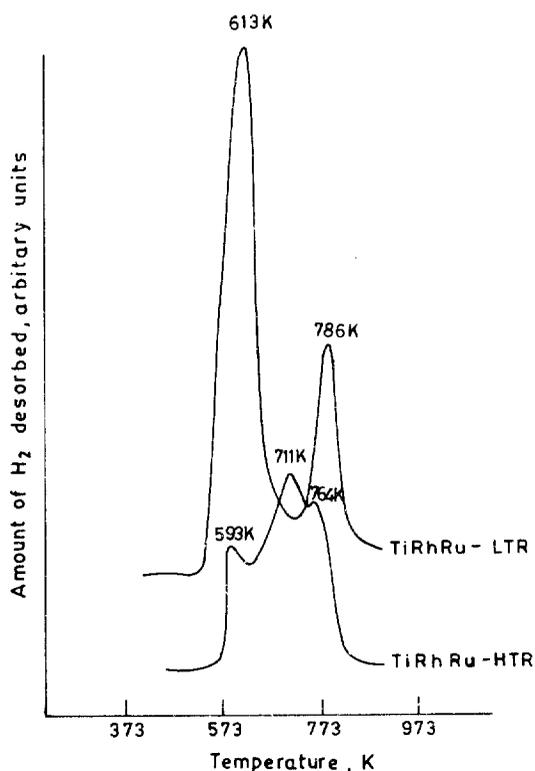


Figure 3. Hydrogen TPD profiles of titania-supported bimetallic rhodium-ruthenium reduced at 573 K (TiRhRu-LTR) and 773 K (TiRhRu-HTR).

the decrease in the quantity of hydrogen desorbed as indicated by the peak area, and the change in the metal-hydrogen bond strength as indicated by the peak temperature.

In the case of the rhodium catalysts, there is a five-fold suppression of hydrogen chemisorption in going from the LTR to the HTR sample. In the case of the ruthenium catalysts, hydrogen chemisorption drops to nearly one-third. For the bimetallic catalyst, the decrease in the quantity of hydrogen desorbed in going from LTR to HTR samples is much less pronounced. Thus TPD results suggest that SMSI is prevalent in titania-supported rhodium and ruthenium, but not in the bimetallic catalyst. The results are summarised in table 1.

In order to find out whether the fall in hydrogen chemisorption is due to sintering of the metal particles, metal-to-titanium ratio (M/Ti) was calculated in all the catalysts using $Ti(2p_{3/2})$, and $Rh(3d_{5/2})$, and $Ru(3d_{5/2})$ XPS core level peaks. The results are presented in table 2. It can be seen that the Rh/Ti ratio is higher for TiRh-LTR as compared to that for TiRh-HTR by a factor of 1.4. The Ru/Ti ratio is 1.6 times higher for TiRu-LTR than that for TiRu-HTR. The lower M/Ti ratio in the catalyst reduced at high temperature can be attributed to sintering. But this small change obviously cannot account for the large suppression in hydrogen chemisorption. This observation supports the occurrence of SMSI in titania-supported rhodium and ruthenium. However, TiRhRu-LTR adsorbs only 1.7 times more hydrogen than

Table 1. Comparison of hydrogen chemisorption capacity (obtained from TPD) and surface metal-to-support concentration (from XPS) in going from LTR to HTR catalysts.

Catalyst composition	Ratio of desorbed hydrogen (LTR catalyst/HTR catalyst)	Ratio of surface metal-to-support $\frac{\{(M/Ti)_{LTR}\}}{\{(M/Ti)_{HTR}\}}$
Rh	4.9	1.4
Ru	2.9	1.6
RhRu	1.7	1.3

Table 2. Concentration ratios determined from XPS peak intensities.

Catalyst	(n_{Rh}/n_{Ti})	(n_{Ru}/n_{Ti})	(n_{TM}/n_{Ti})	(n_O/n_{Ti})	(n_{Rh}/n_{Ru})
TiRh-LTR	0.037			4.2	
TiRh-HTR	0.027			6.1	
TiRu-LTR		0.142		4.6	
TiRu-HTR		0.091		7.3	
TiRhRu-LTR	0.077	0.167	0.244	5.8	0.5
TiRhRu-HTR	0.089	0.099	0.188	4.9	0.9

TiRhRu-HTR and the M/Ti ratio in the former is only 1.3 times greater than in the latter. Considering the widely differing nature of the two methods, the agreement is good and we may conclude that the small suppression of hydrogen chemisorption in the bimetallic rhodium-ruthenium catalyst is due to sintering and there is no SMSI in this system.

It is further seen from the XPS results that although TiRhRu-LTR has its surface enriched in ruthenium as compared to rhodium, the surface Rh/Ru ratio is close to the bulk composition for TiRhRu-HTR.

XRD results showed that all the supported catalysts except rhodium had metal particles smaller than the detection limit of this method. Titania-supported rhodium showed distinct reflection due to Rh(111) and the mean particle size changed from 104 to 140 Å in going from TiRh-LTR to TiRh-HTR. This points to sintering, the extent of which is in agreement with the XPS intensity results. The titania support was anatase and no change was seen in the support structure after reduction.

XPS intensities of HTR catalysts do not indicate any encapsulation of the metal particles by the support in which case a large decrease in the metal peak intensity is expected. If there is any migration of TiO_x species on the metal particles as suggested by many workers (Tauster 1987), such a TiO_x layer should be extremely thin. The same conclusion has recently been arrived at by Shpiro *et al* (1988). A recent study of SMSI in the Pt/ TiO_2 system by Sheng *et al* (1988) showed very little particle growth upto 550°C reduction temperature which is essentially in agreement with our conclusions from XPS on the Rh/ TiO_2 and Ru/ TiO_2 systems. Based on AES results, they postulated the formation of surface compound Pt_nTiO_x as the cause of SMSI.

3.2 Effects of SMSI on metal-hydrogen bond strength

Studies on CO and NO chemisorption on model thin films of Rh/TiO₂ before and after inducing SMSI have shown that formation of a TiO_x layer on the surface produces new adsorption sites in addition to blocking of adsorption sites already present (Belton *et al* 1986). Initial heats of adsorption of hydrogen and CO on Pt/TiO₂ were found to decrease after high temperature reduction pointing to a decrease in adsorption strength (Hermann *et al* 1987). In this connection, the hydrogen peak desorption temperatures of the LTR and HTR catalysts are of interest.

Let us first consider the effect of SMSI on the hydrogen desorption profiles. We shall exclude the bimetallic catalyst here as it did not show SMSI. In going from TiRh-LTR to TiRh-HTR, the strongly bound hydrogen disappeared. This means a considerable modification of the rhodium-hydrogen bond strength before and after SMSI. The rhodium sites responsible for the formation of strong rhodium-hydrogen bonds are either blocked or modified. The effect is just opposite in the ruthenium catalysts. The hydrogen desorption profile shows in this case stronger adsorption sites after SMSI. Thus the effect of SMSI on the metal-hydrogen bond strength is not the same for different group VIII metals.

Comparison of the TPD profiles of TiRh-HTR and TiRu-HTR with that of TiRhRu-HTR is interesting. The high temperature reduced bimetallic catalyst more or less retains the peaks of the high temperature reduced monometallic catalysts, although a quantitative comparison is not possible because of varying metal particle size in these samples. It should be remembered that TiRh-HTR and TiRu-HTR are SMSI states whereas TiRhRu-HTR is not. Hence, SMSI cannot be held solely responsible for the change in metal-hydrogen bond strength in going from LTR to HTR catalysts.

3.3 Electronic effects in SMSI

XPS binding energies are given in table 3. However, it was felt that it would be more circumspect to talk of the differences in binding energies of peaks of two elements rather than the absolute values.

It can be seen from table 2 that $\Delta[\text{Ti}(2p_{3/2})-\text{Rh}(3d_{5/2})]$ remains unchanged in going from TiRh-LTR to TiRh-HTR. The difference $\Delta[\text{Ti}(2p_{3/2})-\text{Ru}(3d_{5/2})]$ changes by 0.2 eV from TiRu-LTR to TiRu-HTR. Thus XPS does not give any direct evidence of electron transfer between metal and support due to SMSI (figure 4). The 0.5 eV shift

Table 3. XPS binding energies in the low temperature and high temperature reduced catalysts.

Sample	Binding energy (eV) ^a					
	Rh(3d _{5/2})	Ru(3d _{5/2})	Ti(2p _{3/2})	Δ(Ti-Rh)	Δ(Ti-Ru)	Δ(Rh-Ru)
TiRh-LTR	307.6		459.0	151.4		
TiRh-HTR	307.6		459.0	151.4		
TiRu-LTR		280.7	459.0		178.3	
TiRu-HTR		280.5	459.0		178.5	
TiRhRu-LTR	307.0	280.8	459.0	152.0	178.2	26.2
TiRhRu-HTR	307.9	280.0	459.0	151.1	179.0	27.9

^a Reference energy: Ti(2p_{3/2}) = 459.0

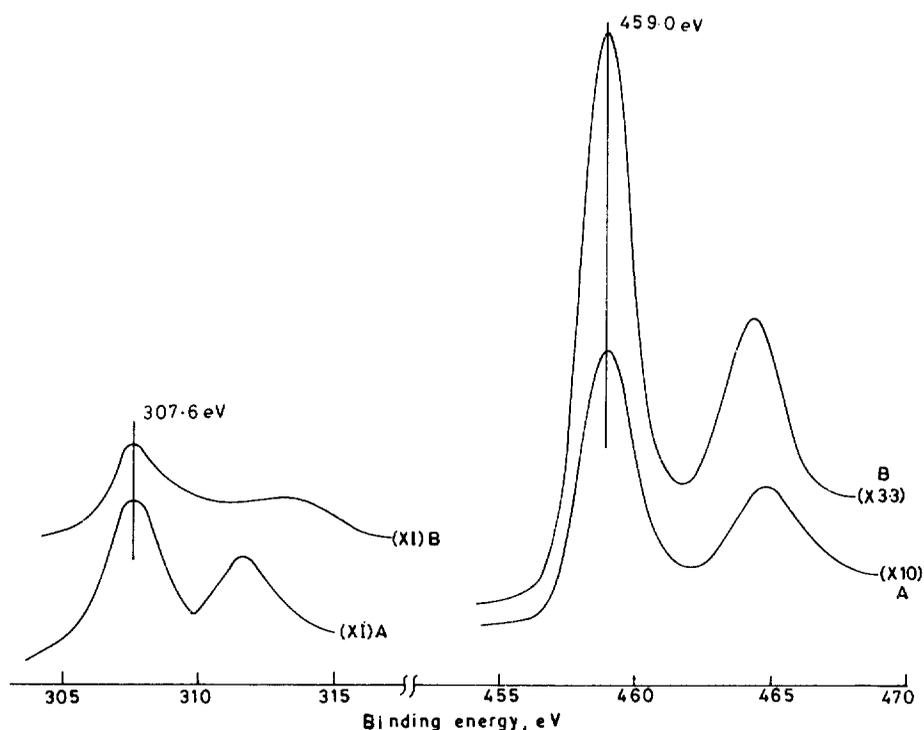


Figure 4. X-ray photoelectron spectra of the Rh(3d) and Ti(2p) region for titania-supported rhodium reduced at 573 K (A) and 773 K (B).

for Rh/TiO₂ reported by Blasco *et al* (1988) has not been noticed by us. In none of the samples could we detect any XPS peak due to Ti³⁺ as has been reported by Fung (1982). This would suggest that there are no Ti³⁺ species present on the surface. Shpiro *et al* (1988) have shown that Ti³⁺ can be detected only after etching the surface with Ar⁺ ions indicating that Ti³⁺ is actually present in the bulk. However, the possibility of Ti⁴⁺ being reduced to Ti³⁺ due to Ar⁺ ion etching cannot be ruled out. We could also detect Ti³⁺ in the bulk by ESR that showed a nearly symmetric ESR peak ($g = 1.99$), and thus unambiguously established the presence of Ti³⁺ in the bulk (Bonnevot and Haller 1988). In the bimetallic RhRu catalyst also, we could see a single symmetric XPS Ti(2p_{3/2}) peak that is due to Ti⁴⁺. With reference to this, the binding energy of Rh(3d_{5/2}) showed a negative shift and that of Ru(3d_{5/2}) showed a positive shift in going from TiRhRu-LTR to TiRhRu-HTR. Since there was no Ti³⁺ species nearby, these shifts may be interpreted as due to electron transfer from rhodium to ruthenium in forming bimetallic clusters. Most probably, isolated rhodium and ruthenium clusters formed on the support during low temperature reduction get transformed into bimetallic clusters on reduction at 773 K.

Huizinga and Prins (1981) have suggested that -OH groups are formed on titania due to spillover of hydrogen from metal to support. Jiang *et al* (1983) explained the slow hydrogen uptake by Pt/TiO₂ reduced at 770 K by similar reasoning. If -OH is formed near the surface, the O(1s) XPS peak should show splitting due to O²⁻ and -OH. The O(1s) peak was broad and could be resolved into two component peaks with binding energies near 530.0 eV and 531.9 eV (figure 5). It is tempting to assign the

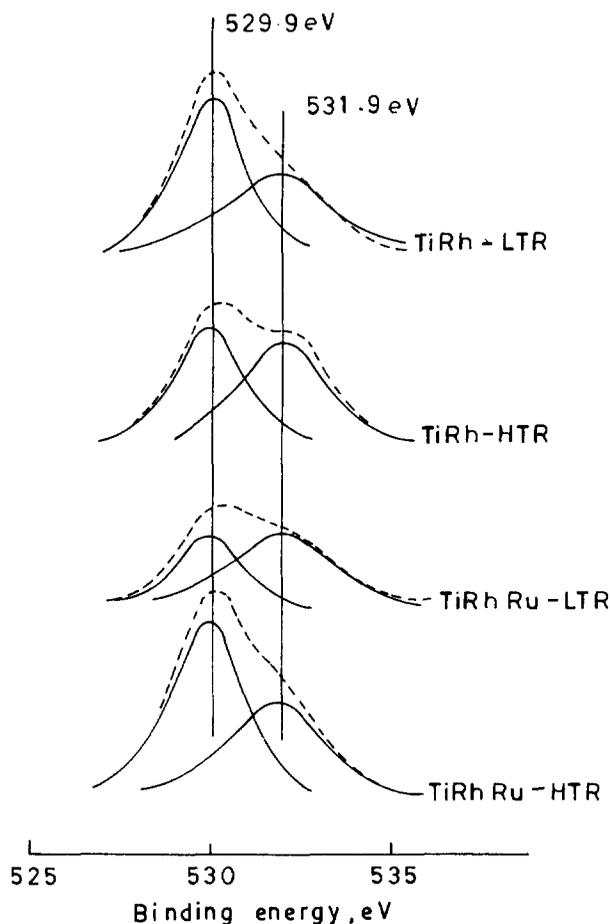


Figure 5. X-ray photoelectron spectra of the O(1s) region for titania-supported rhodium and bimetallic rhodium-ruthenium catalysts.

532 eV O(1s) peak to $-\text{OH}$. However, this will not explain the high O/Ti ratio as calculated from XPS peak intensity (table 2). It can be seen that the O/Ti ratio increases after inducing SMSI in the sample. Similar results on the intensity of the O(1s) have been recently reported by Shpiro *et al* (1988) but no explanation was put forth. The formation of carbonate species on the surface that would give an oxygen peak similar in binding energy to that of chemisorbed oxygen can be ruled out as no C(1s) peak at 289.3 eV characteristic of carbonate (Fleisch *et al* 1984) was observed. We are inclined to assign the 532 eV O(1s) peak to chemisorbed oxygen and $-\text{OH}$. The SMSI samples have more chemisorbed oxygen. Thus, SMSI not only drastically reduces the hydrogen chemisorption, but also increases chemisorption of oxygen which is an electron acceptor. This lends support to the electronic effect. It could be that some Ti^{3+} has actually been formed in SMSI that charges to Ti^{4+} by interaction with oxygen as a result of which no Ti^{3+} is detected near the surface. In fact, surface Ti^{3+} was detected by Bonneviot and Haller (1988) only in a hydrogen atmosphere.

In the bimetallic TiRhRu-HTR catalyst that does not show any SMSI, the intensity of the 532 eV O(1s) peak actually decreases with respect to TiRhRu-LTR.

The question arises – Why does the RhRu catalyst not exhibit SMSI? If SMSI involves chemical (electronic) interaction between the metal and the support, this may not occur in the supported bimetallic catalyst if the two metals interact with each other and thereby lower their chemical potential. XPS results show that such an interaction has actually occurred.

4. Conclusions

- (i) SMSI is prevalent in titania-supported rhodium and ruthenium catalysts but the rhodium–ruthenium bimetallic catalyst does not exhibit SMSI.
- (ii) The suppression of hydrogen chemisorption is not due to sintering of the metal particles.
- (iii) High temperature reduction of the catalysts appreciably modifies the metal-hydrogen bond strength irrespective of whether the catalyst is in an SMSI state or not.
- (iv) No encapsulation of the metal particle by the support occurs and the layer of TiO_x if formed must be extremely thin.
- (v) There is indirect evidence suggesting that SMSI is an electronic effect and not a mere physical blockage of the surface.

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