Electronic Interactions in the Rhodium/TiO$_2$ System

HASSAN R. SADEGHI[1] AND VICTOR E. HENRICH

Applied Physics, Yale University, P.O. Box 2157, New Haven, Connecticut 06520

A variety of electron spectroscopic techniques has been used with model catalysts fabricated on single-crystal substrates to study charge transfer in the Rh/TiO$_2$ system. In order to avoid the morphological changes and encapsulation that occur when catalysts are reduced at high temperatures to induce SMSI, TiO$_2$ substrates have been reduced by inert gas ion bombardment prior to Rh deposition. Comparison of model catalysts prepared on reduced supports with those prepared on fully oxidized supports indicates that electronic charge is transferred from reduced Ti cations to Rh particles, resulting in a partially ionic Rh–Ti bond. The Rh–Ti bonding may provide a driving force for encapsulation of the Rh but does not lead to a large-scale suppression of the capacity of the Rh to chemisorb CO. We also present the first direct evidence for modification of the valence levels of the Rh due to the presence of the encapsulating Ti suboxide moieties during SMSI. © 1988 Academic Press, Inc.

INTRODUCTION

Eight years have passed since the discovery of the strong metal–support interaction (SMSI) state that occurs after high-temperature reduction (HTR) treatments of metals of groups 8–10 dispersed and supported on reducible transition-metal oxides (1). During that time there have been a great many experimental studies of SMSI systems; that work has been summarized in recent reviews of the field (2, 3). Theoretical efforts at understanding SMSI, however, have been few and far between (4–6).

Although the processes occurring in SMSI are complex, it is useful to consider them first in broad terms. Following Bond and Burch (7), the two types of phenomena that could be at the heart of SMSI are of either an electronic or a geometric nature. In other words, it is because of a modification of the electronic properties of the metal due to its interaction with the support and/or because of some structural modification of the metal–support system that the

chemisorptive and catalytic properties of the metal are modified. Both types of interaction in the catalyst can, of course, ultimately be explained in terms of electronic effects since any changes in catalyst morphology would be accompanied, if not driven, by changes in electronic structure. The very earliest experimental results showed clearly the correlation of SMSI with the reduction of the support (1), which led to a widespread belief that the effects were due to a delocalized charge transfer between the components of the system (8). Many contradictory results based upon this interpretation were published (9) until some of the inconsistencies inherent in the model were pointed out (10).

Just as the charge transfer hypothesis began losing ground, Meriaudeau et al. (11) speculated that the drastic loss of H$_2$ and CO chemisorption in the SMSI state might be due to the migration of some suboxide moiety from the support onto the metal particles. This idea became the root of a new impetus in SMSI research. Many different types of experiments were performed on a number of catalyst–support systems, and it is now well established that

[1] Present address: Sachs/Freeman Assoc., Inc., Landover, MD 20785.

1

such suboxide migration plays a major role in SMSI (12, 13).

Most of the experimental studies of SMSI have been carried out on "real" metal catalysts dispersed on powder supports of high surface area, which are extremely complex systems. In order to reduce the complexity, we have studied model catalysts consisting of controlled amounts of metal supported on well characterized single-crystal oxide supports; our approach has been described previously (14, 15). The specific system on which we have concentrated is Rh/TiO_2. After some indirect evidence in support of the migration hypothesis was gathered on powdered catalysts (16, 17), we obtained direct evidence from model catalyst studies that SMSI is indeed intimately linked to the appearance of Ti suboxide moieties on top of the Rh and that those moieties are directly responsible for the altered chemisorption properties of the metal (14, 15). We subsequently addressed the migration's need for oxygen vacancies on the support surface and evaluated the role of hydrogen during HTR (18). Other groups then showed that the migration (or encapsulation or decoration) phenomenon was occurring in other SMSI systems as well (19, 20). Recently several groups have investigated the subtle catalytic aspects of SMSI by studying suboxide-on-metal systems (21–24).

Despite the present understanding of the geometric nature of SMSI, several points remain to be clarified. In an effort to isolate possible electronic contributions to SMSI, we have studied Rh/TiO_2 model catalysts prepared by room temperature deposition of Rh onto both fully oxidized and reduced TiO_2 (110) surfaces that were *not* subjected to HTR or any other treatment. In this way the morphological changes and encapsulation that occur when catalysts are reduced at high temperatures to induce SMSI can be avoided. The results of measurements on these model catalysts employing a variety of surface-sensitive electron spectroscopic techniques have allowed us to address the following questions:

1. What types of bonding interactions occur in the metal–support system?

2. Could these bonding interactions lead to any changes in the electronic structure of the catalyst that would play a significant role in SMSI?

EXPERIMENTAL METHODS

Our experimental surface analysis system and the techniques used to prepare model catalysts have been described previously (14, 15). Briefly, model catalysts are prepared by depositing various amounts of Rh onto well-characterized single-crystal TiO_2 supports *in situ* in our ultrahigh-vacuum (UHV) surface analysis system; the methods by which we prepare and characterize the rutile TiO_2 (110) support surface have been discussed in Ref. (15). We then use a variety of electron spectroscopic techniques, including ultraviolet and x-ray photoemission (UPS and XPS), Auger and electron energy loss (ELS) spectroscopies, low-energy electron diffraction (LEED), and work function measurements, to characterize their surface properties.

In the experiments reported here, we used a small electron-beam-heated Rh source that permits more uniform and reproducible deposition rates than we were previously able to obtain. The Rh source consists of a Rh foil 0.127 mm thick (Alfa Products, 99.9% pure) attached to the front end of the grounded outer case of a Physical Electronics Model 04-121 electron gun. The Rh foil intercepts all of the emitted electrons, thus preventing them from reaching the support onto which the Rh is being deposited. When the electron gun is operated at 2.5 keV and 24 mA, at a power of 60 W, the Rh foil is white hot. Rh deposition is not accompanied by any measurable contamination of the sample, the temperature of the TiO_2 support does not rise more than 20 K above room tempera-

ture, and typical deposition rates are about 0.2 monolayers per minute. In our studies, Rh thicknesses from less than one up to five monolayers equivalent (ML) were used, as determined by Auger and XPS.

RESULTS AND DISCUSSION

Properties of the TiO₂ Supports

The preparation and properties of both nearly perfect TiO$_2$ (110) single-crystal surfaces and of surfaces containing reduced cations adjacent to O-vacancy defects have been thoroughly studied by both our group and others (25). Slightly bulk-reduced rutile is an n-type semiconductor that has enough Ti $3d$ electrons to pin the Fermi level, E_F, just below the Ti $3d$ conduction band. The nearly perfect, stoichiometric (110) surface has all of its cations in a Ti^{4+} ($3d^0$) electronic state; Fig. 1a shows the UPS spectrum for such a surface. It exhibits emission only from the filled O $2p$ valence band, which is roughly 6 eV wide. The O $2p$–Ti $3d$ band gap is 3.1 eV, and the work function for the surface is 5.2 eV. We will refer to this surface as TiO$_2$ (110).

TiO$_2$ (110) can be reduced by inert gas ion bombardment (sputtering), which preferentially removes O anions from the surface.

The requirement of local charge neutrality leads to partial population of the $3d$ orbitals of Ti ions adjacent to the O vacancies. As the O-vacancy defect density increases, surface cations having valences of 3+ and lower will exist on the surface. The sputtered surfaces that we have used in this work have an average surface stoichiometry close to Ti$_2$O$_3$, so the average surface cation valence is 3+ (26). Figure 1b shows the UPS spectrum for such a reduced surface. It exhibits emission from the partially occupied Ti $3d$ orbitals just below E_F and from the 6-eV-wide O $2p$ valence band. Note that the population of surface Ti $3d$ orbitals bends the bands at the surface so that the O $2p$ valence band moves away from E_F by about 0.8 eV. The work function for the reduced surface is roughly 4.1 eV. We will refer to such a reduced surface as r-TiO$_2$. Oxidation of the r-TiO$_2$ surface by either thermal annealing or O$_2$ exposure restores the surface cations to their Ti^{4+} ($3d^0$) configuration, with attendant depopulation of the Ti $3d$ defect states and restoration of the O $2p$ valence band to its initial position (15).

In the work reported here we have used TiO$_2$ (110) as the model support for fully oxidized TiO$_2$. The r-TiO$_2$ surface is used to
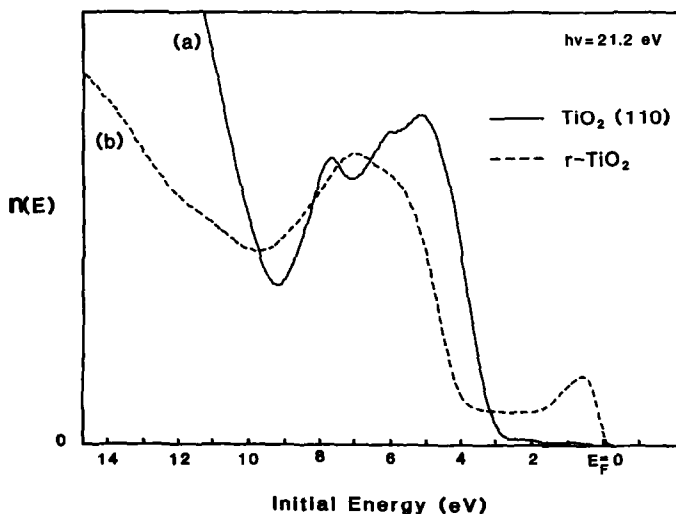

FIG. 1. UPS spectra of valence region for (a) TiO$_2$ (110) and (b) r-TiO$_2$.

model both reduced TiO_2 supports, where some of the surface cations have their $3d$ orbitals partially populated, and the reduced titania species that migrate onto catalyst particles in SMSI. We are thus able to simulate supported catalysts both before and after high-temperature reduction without the problems of encapsulation and morphology changes that accompany thermal reduction.

The remainder of this section describes the experimental results obtained when the two types of surfaces described above were used as supports in model Rh/TiO_2 catalysts.

ELS Results

The electron energy loss spectra for TiO_2 (110) and r-TiO_2 have been measured by several groups (26–29). The solid curve in Fig. 2 shows the low-energy region of the loss spectrum for r-TiO_2 with its characteristic loss at about 2 eV, which arises from Ti d–d transitions on the reduced surface cations; this loss feature is absent for TiO_2 (110). The dashed curve in Fig. 2 is obtained after deposition of approximately 1.5 ML of Rh. The main effect of Rh deposition is that the peak due to the Ti d–d

transitions is attenuated much more than the others, which do not involve Ti $3d$ electrons. A similar reduction in amplitude of the Ti d–d excitation is seen when r-TiO_2 is oxidized by exposure to O_2. The ELS spectra are thus indicative of a decrease in the number of Ti $3d$ electrons on the r-TiO_2 surface (i.e., a net oxidation of the surface) through an interaction with the Rh adsorbate.

Auger Results

Auger spectra for TiO_2 taken in the first derivative mode show fine structure in the 416-eV Ti peak, which arises from the overlap of two Ti LMV Auger transitions. One is an interatomic LMV_O transition involving O $2p$ valence electrons, while the second is an intraatomic LMV_{Ti} transition involving Ti $3d$ electrons. Following Ref. (30), the degree of oxidation of the surface Ti ions can be correlated with the experimental ratio A/B graphically defined in the insert in Fig. 3 (from Ref. (30)), where A is a measure of the intensity of LMV_{Ti} and B measures LMV_O; the A/B ratio increases with increasing reduction of the surface. Figure 3 shows the A/B ratio as a function of Rh deposition on r-TiO_2. The ratio drops
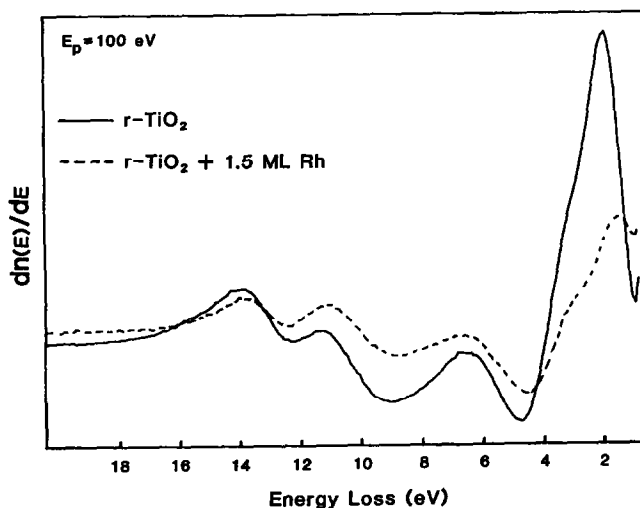

FIG. 2. Electron energy loss spectra of r-TiO_2 (solid curve) and r-TiO_2 + 1.5 ML Rh (dashed curve). Primary electron energy, 100 eV.
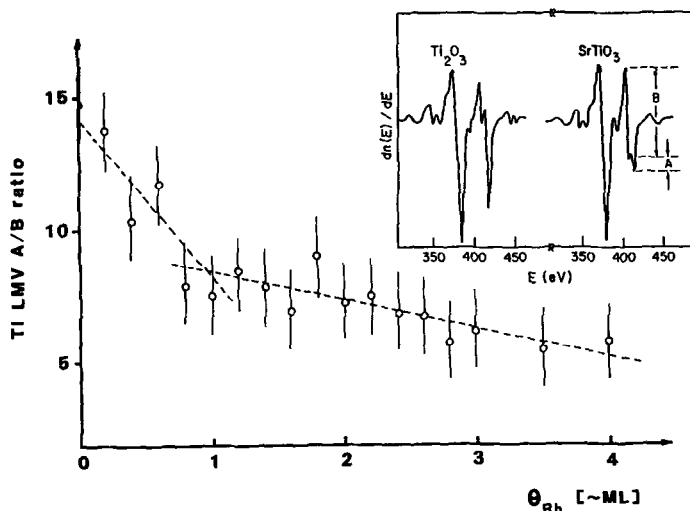
FIG. 3. Amplitude ratio of LMV$_{Ti}$ (A) to LMV$_O$ (B) versus Rh coverage on r-TiO$_2$. A and B defined on Auger spectra in insert (from Ref. (30)).

by a factor of two by 1 ML of Rh and continues to decrease slowly as more metal is deposited. This is thus also indicative of oxidation of the surface Ti ions upon Rh adsorption, suggesting that electrons are being transferred from the reduced Ti ions to the Rh.

XPS Results

XPS has been one of the most widely used techniques in attempts to measure charge transfer between the substrate and the metal. Generally one looks for chemical shifts of the catalyst metal core levels upon reduction or oxidation. As the literature shows, this is an especially tricky task. A number of experiments yielded conflicting results before Huizinga *et al.* (*31*) questioned the possibility of isolating the contribution of any charge transfer to the binding energy of the core levels of the metal in this way. Generally, the behavior of the core-level binding energies of supported metallic clusters is still a matter of debate (*32–35*).

However, it is possible to obtain some useful information about metal–substrate interactions from XPS. We have taken XPS spectra of the Rh, Ti, and O core levels before, during, and after Rh deposition for all of our model catalysts; the Ti 2*p* core level spectra for two of them are shown in Figs. 4 and 5. The spectra have been referenced to E_F. (Our TiO$_2$ supports have sufficient conductivity that no surface charging occurs.) It is possible to interpret the data qualitatively as follows:

TiO$_2$ (110). Adsorption of Rh on TiO$_2$ (110) leads merely to an attenuation of the O 1*s* and Ti 2*p* features and to an increase in the amplitude of the Rh 3*d* spin-orbit split doublet. The Rh 3*d* peaks, as reported previously (*15*), shift to slightly lower binding energies (i.e., toward the metallic value) as the Rh coverage increases. This can be attributed to an increase in the extra-atomic relaxation shift as the size of metallic particles increases (*15, 31*).

Slightly reduced TiO$_2$ (110). As shown in Fig. 4, the primary effect that occurs when Rh is adsorbed on a slightly reduced TiO$_2$ surface (i.e., one containing less than a monolayer of Ti^{3+}–O vacancy defects and less reduced than r-TiO$_2$) is suppression of the low-binding-energy shoulder on the Ti 2*p* levels, which arises from the presence of Ti^{3+} ions. This observation supports the suggestion under ELS Results and Auger Results that Rh oxidizes surface Ti ions.
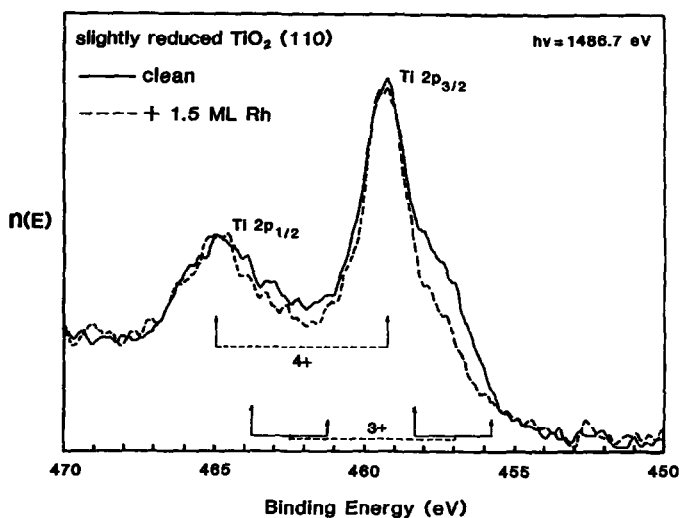
FIG. 4. XPS spectra of Ti $2p$ core levels for slightly reduced TiO_2 (110) before (solid curve) and after (dashed curve) deposition of 1.5 ML Rh.

r-TiO₂. The XPS spectra for Rh deposited on r-TiO₂ show several things. First, the Rh levels occur at slightly lower binding energies than they do for Rh on TiO₂ (110) for similar coverages. This could be accounted for either because the r-TiO₂ surface has a higher density of available electrons to screen the core hole on the Rh (i.e., a relaxation shift, final state effect) or because there is some charge transferred to the Rh atoms (a chemical shift, initial state effect). Second, the Ti $2p$ emission from such a surface is notoriously difficult to interpret. Even for nearly perfect Ti_2O_3 surfaces where all of the Ti ions are in a 3+ valence state, the XPS spectrum consists of
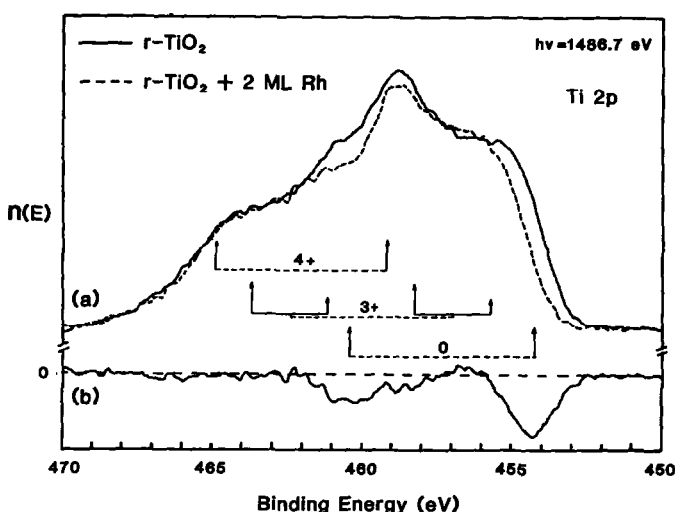

FIG. 5. (a) XPS spectra of Ti $2p$ core levels for r-TiO₂ before (solid curve) and after (dashed curve) deposition of 2 ML Rh (spectra normalized at Ti^{4+} peaks); (b) difference between spectra in (a) showing changes induced by Rh deposition.

a pair of overlapping Ti $2p$ doublets because of the competition of various final state screening effects (*36*). For r-TiO₂, not only Ti^{3+} but also further reduced Ti species are present on the surface. The spectra therefore consist of a rather broad and structureless band of emission. Nevertheless, as Fig. 5 shows, there is a considerable suppression of the emission due to the lower-valence Ti ions after Rh adsorption. This is consistent with oxidation of the surface by the adsorbed Rh atoms. Finally, upon Rh deposition, the O $1s$ line, without changing shape, shifts to lower binding energy by an amount that correlates with the shift of the O $2p$-derived valence band, which is discussed under UPS Results. It is important to note that the O $1s$ line does not broaden and that the Rh binding energy is that of metallic Rh, showing that there is little Rh–O interaction (*37*).

UPS Results

The experimental results described in the three preceding sections all suggest the existence of an adsorbate–substrate interaction involving a transfer of electrons from reduced Ti cations to the Rh. In this section, we present UPS results that not only

support this conclusively, but yield valuable additional information about the nature of the Rh–Ti interaction and its effect on CO chemisorption.

As shown in Fig. 6, Rh deposited in amounts less than 1 ML onto TiO₂ (110) leads to emission from Rh $4d$, $5s$-derived levels, which lie between the support O $2p$ valence band and E_F. The emission from the O $2p$ valence band is attenuated slightly, but the band does not move at all in energy upon deposition of Rh. The emission from those Rh levels (0–3.5 eV initial energy) is rather featureless. These results are in agreement with the XPS results presented above and with the suggestion made by Koningsberger *et al.* (*37*) that on fully oxidized supports the metal is essentially physisorbed.

As shown in Fig. 7, the deposition of Rh onto r-TiO₂ also leads to an increased emission in the region of the TiO₂ band gap. But this time it is accompanied by a shift of the O $2p$-derived valence band toward E_F. The amount by which the band shifts can be best determined from the location of the bottom of the valence band, where there is no interfering contribution from Rh emission; this band motion is plotted versus Rh
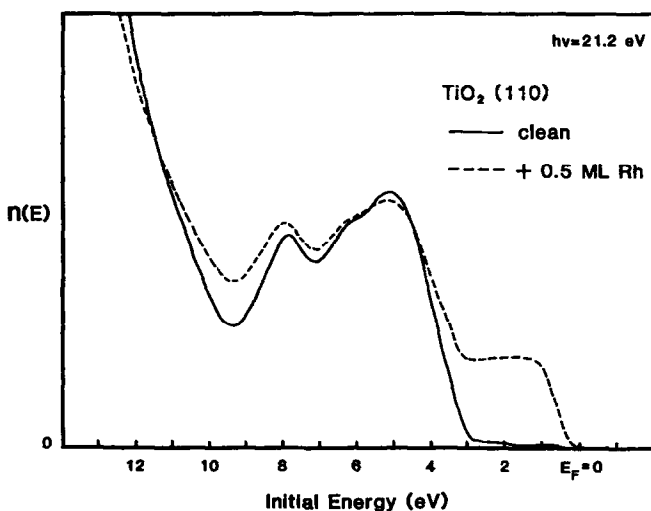

FIG. 6. UPS spectra of valence region for TiO₂ (110) before (solid curve) and after (dashed curve) deposition of about 0.5 ML Rh.
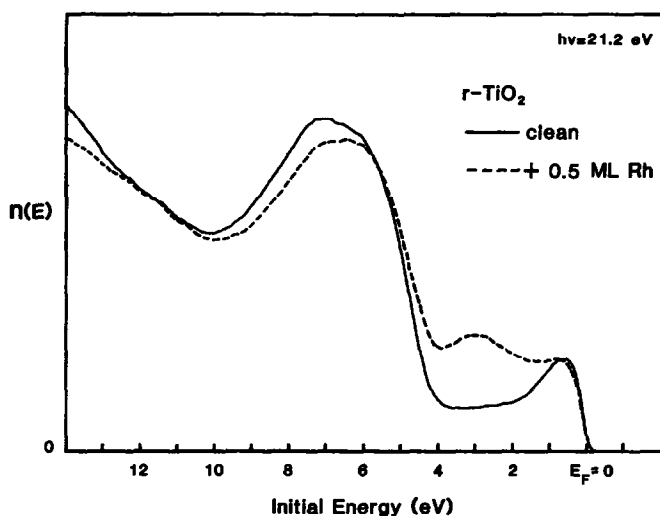
FIG. 7. UPS spectra for r-TiO$_2$ before (solid curve) and after (dashed curve) deposition of about 0.5 ML Rh.

coverage in Fig. 8. Upon Rh adsorption the valence band, which was initially bent down on the r-TiO$_2$ surface relative to TiO$_2$ (110), moves back up toward E_F in the same manner, and by the same amount, as it does for the oxidation of r-TiO$_2$ by O$_2$. As in the case of Fig. 3, most of the change occurs by roughly 1 ML of Rh. This indicates that there is a rapid removal of essentially all of the electronic charge from the reduced Ti cations; we estimate that roughly 10^{15} electrons/cm^2 are transferred to the Rh particles, which corresponds to a charge transfer of the order of one-half an electron

per Rh atom. The magnitude of the transfer leads us to conclude that, as has been suggested theoretically (4, 5), the Rh–Ti cation bond is partially ionic, with the Rh being negatively charged.

The photoemission density in the region 0–3.5 eV below E_F in Fig. 7 exhibits a local maximum at an initial energy of approximately 2.7 eV. This maximum was not present for Rh on TiO$_2$ (110) (see Fig. 6) and thus is probably a consequence of the Rh–Ti bonding rehybridization. A similar increase in the photoemission intensity of the lower part of the valence bands of Ni
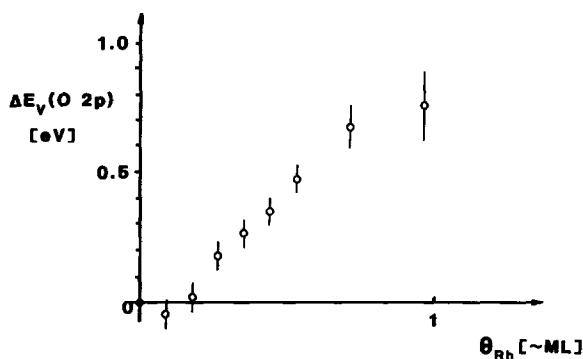

FIG. 8. O 2p valence band shift versus Rh coverage on r-TiO$_2$.

and Pt has been seen for Ni₃Ti (38) and Pt₃Ti (39); it is associated with a relative decrease in emission at E_F, with a shift of the valence band centroid to higher initial energy, and it cannot be obtained by a simple superposition of the elemental valence bands. In both alloys the intermetallic bond was found to have a partially ionic character.

The differences in the UPS spectra for Rh weakly adsorbed on fully oxidized TiO₂ (110) and for Rh (ionically) bonded to reduced Ti ions on r-TiO₂ suggest an interpretation for some previously unexplained features in the UPS spectra of reduced Rh/TiO₂ model catalysts (15). Figure 9 shows UPS spectra for a Rh on TiO₂ (110) catalyst before (solid line) and after (dashed line) reduction in 10^{-3} Torr H₂ (1 Torr = 133.32 Pa) at 673 K; in the latter case the catalyst is in the SMSI state. The integrated intensity of the Rh emission is reduced after HTR because of the migration of Ti suboxide moieties onto the metal particles (14, 15). What is of interest is the change in shape of the Rh emission band. After HTR it exhibits a local maximum in the density of states near 2.7 eV and a relative reduction in emission at E_F. In light of the results

obtained above, these changes suggest that similar bonding occurs after HTR between the Rh and the migrated suboxide moieties.

In view of all the results that have been presented above, we propose the following answer to the first question posed in the Introduction:

Reduced titania species bond to Rh through a somewhat ionic Ti–Rh bond, with electronic charge transferred to the Rh from reduced surface Ti cations. This type of bonding occurs between the components of the SMSI system, specifically between the Ti suboxide that migrates and the metal that it covers after HTR.

CO Adsorption Measurements

In order to clarify the implications of the Rh–Ti cation interaction on the chemisorption of CO, we have exposed various model catalysts to CO and have monitored its chemisorption by UPS difference spectra (see Ref. (15)). In our previous work on encapsulation in Rh/TiO₂ (110) model catalysts, we found that CO would again chemisorb on catalysts reduced to the SMSI state after the encapsulating moieties had been removed by ion bombardment
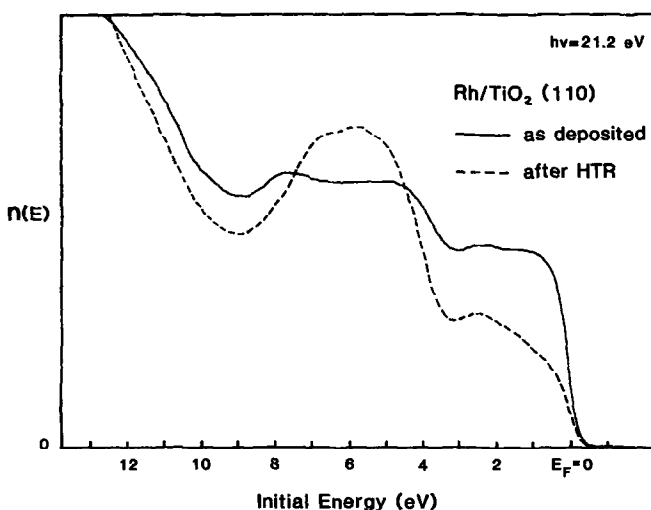

FIG. 9. UPS spectra of valence band region for 3.5 ML Rh on TiO₂ (110) before (solid curve) and after (dashed curve) reduction at 673 K.

(14, 15). In the present series of exper-
iments, we have studied CO chemisorption
on Rh/TiO$_2$ (110) and Rh/r-TiO$_2$ samples
containing as little as $\frac{1}{2}$ ML Rh. Both cata-
lysts adsorbed comparable amounts of CO,
in marked contrast to the SMSI case. In
other words, in spite of the Rh–Ti elec-
tronic interaction, CO chemisorbs on the
Rh/r-TiO$_2$ samples, while model catalysts
containing equal amounts of Rh do not
chemisorb CO following HTR and its atten-
dant suboxide migration.

In view of these results, we propose the
following answer to the second question
posed in the Introduction:

In the Rh/TiO$_2$ system, bonding interac-
tions between Rh and Ti do not lead to the
large scale-suppression of CO chemisorp-
tion per se, as occurs in SMSI. However,
we cannot exclude the possibility that in the
SMSI state the modification of the elec-
tronic density of states of the metal at E_F
may lead to a weakening of the CO–Rh
bond in the immediate vicinity of the encap-
sulating moieties (24).

CONCLUSIONS

We have used model Rh/TiO$_2$ catalysts
fabricated both on fully oxidized and on
partially reduced single-crystal supports
and a variety of surface-sensitive electron
spectroscopies to study charge transfer
processes between the metal and the sup-
port. In this way it has been possible to
observe support-to-metal charge transfer in
the absence of the encapsulation that
accompanies high-temperature reduction.
The experimental results show that

1. Reduced titania species and Rh inter-
act with each other through a partially ionic
bond, with electronic charge transferred
from reduced Ti cations to the Rh.

2. This bonding interaction is pre-
sumably a part of the thermodynamic driv-
ing force that leads to encapsulation of the
Rh during SMSI, and its effect on the
electronic structure of the Rh can be

observed directly in UPS data obtained
from Rh/TiO$_2$ (110) model catalysts before
and after HTR.

3. This Ti–Rh charge transfer interaction
does not lead to a large-scale suppression of
CO chemisorption, but it may give rise to
local bonding effects.

REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., J.
Amer. Chem. Soc. 100, 170 (1978); Tauster, S. J.,
and Fung, S. C., J. Catal. 55, 29 (1978).
2. Stevenson, S. A., Raupp, G. B., Dumesic, J. A.,
Tauster, S. J., and Baker, R. T. K., in "Cataly-
sis" (B. Davis, Ed.). Van Nostrand–Reinhold,
Princeton, N.J., in press.
3. Haller, G. L., and Resasco, D. E., in "Advances
in Catalysis." Academic Press, Orlando, FL, in
press.
4. Horsley, J. A., J. Amer. Chem. Soc. 101, 2870
(1979).
5. Haberlandt, H., and Ritschl, F., J. Phys. Chem.
90, 4322 (1986).
6. Spencer, M. S., J. Catal. 93, 216 (1985).
7. Bond, G. C., and Burch, R., in "Catalysis"
(Specialist Periodical Report) (G. C. Bond and G.
Webb, Eds.), Vol. 6, p. 27. R. Soc. Chem.,
London, 1983.
8. Meriaudeau, P., Ellestad, O. H., Dufaux, M., and
Naccache, C., J. Catal. 75, 243 (1982).
9. See, for example, "Metal–Support and Metal–
Additive Effects in Catalysis" (B. Imelik et al.,
Eds.). Elsevier, Amsterdam, 1982.
10. Ponec, V., in "Metal–Support and Metal–
Additive Effects in Catalysis" (B. Imelik et al.,
Eds.), p. 63. Elsevier, Amsterdam, 1982.
11. Meriaudeau, P., Dutel, J. F., Dufaux, M., and
Naccache, C., in "Metal–Support and Metal–
Additive Effects in Catalysis" (B. Imelik et al.,
Eds.), p. 95. Elsevier, Amsterdam, 1982.
12. See, for example, "Proceedings of the Eighth
International Congress on Catalysis,"
DECHEMA, Verlag Chemie, Weinheim, 1984.
13. 189th ACS National Meeting, Symposium on
Metal–Support Interactions, Miami Beach, FL
(April 1985).
14. Sadeghi, H. R., and Henrich, V. E., J. Catal. 87,
279 (1984).
15. Sadeghi, H. R., and Henrich, V. E., Appl. Surf.
Sci. 19, 330 (1984).

16. Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81,** 147 (1983).

17. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).

18. Henrich, V. E., and Sadeghi, H. R., 189th ACS National Meeting, Symposium on Metal–Support Interactions, Miami Beach, Fl. (April, 1985); Sadeghi, H. R., Ph.D. Thesis, Yale University, 1987.

19. Takatani, S., and Chung, Y.-W., *J. Catal.* **90,** 75 (1984).

20. Sun, Y.-M., Belton, D. N., and White, J. M., *ACS Symp. Ser.* **288,** 80 (1985).

21. Raupp, G. B., and Dumesic, J. A., *J. Phys. Chem.* **88,** 660 (1984).

22. Demmin, R. A., Ko, C. S., and Gorte, R. J., *J. Phys. Chem.* **89,** 1151 (1985).

23. Dwyer, D. J., Cameron, S. D., and Gland, J., *Surf. Sci.* **159,** 430 (1985).

24. Levin, M., Salmeron, M., Bell, A. T., and Somorjai, G. A., *Surf. Sci.* **169,** 123 (1986).

25. Henrich, V. E., *Rep. Prog. Phys.* **48,** 1481 (1985), and references therein.

26. Henrich, V. E., Dresselhaus, G., and Zeiger, H. J., *Phys. Rev. Lett.* **36,** 1335 (1976).

27. Lo, W. J., Chung, Y.-W., and Somorjai, G. A., *Surf. Sci.* **71,** 199 (1978).

28. Henrich, V. E., and Kurtz, R. L., *Phys. Rev. B* **23,** 6280 (1981).

29. Rocker, G., Schaefer, J. A., and Gopel, W., *Phys. Rev. B* **30,** 3704 (1984).

30. Henrich, V. E., Dresselhaus, G., and Zeiger, H. J., *Phys. Rev. B* **17,** 4908 (1978).

31. Huizinga, T., Van't Blik, H. F. J., Vis, J. C., and Prins, R., *Surf. Sci.* **135,** 580 (1983).

32. Citrin, P. H., and Wertheim, G. K., *Phys. Rev. B* **27,** 3176 (1983).

33. Cheung, T. T. P., *Surf. Sci.* **140,** 151 (1984).

34. Dicenzo, S. B., and Wertheim, G. K., *Comments Solid State Phys.* **11,** 203 (1985).

35. Parmigiani, F., Kay, E., Bagus, P. S., and Nelin, C. J., *J. Electron Spectrosc. Relat. Phenom.* **36,** 257 (1985).

36. Kurtz, R. L., Ph.D. Thesis, Yale University, 1983.

37. Koningsberger, D. C., Martens, J. H. A., Prins, R., Short, D. R., and Sayers, D. E., *J. Phys. Chem.* **30,** 3047 (1986).

38. Fischer, T. E., Kelemen, S. R., Wang, K. P., and Johnson, K. H., *Phys. Rev. B* **20,** 3124 (1979).

39. Derry, G. N., and Ross, P. N., *Solid State Commun.* **52,** 151 (1984).