Properties of Pt Supported on Oxides of Titanium

by

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Prepared for publication

in

Journal of Physical Chemistry

Department of Chemistry

University of Texas at Austin

Austin, Texas 78712

June 9, 1982

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Platinum, supported on TiO₂, TiO and Ti₂O₃ in various forms, has been investigated using a variety of physical and chemical techniques. On H₂ pretreated TiO₂, on TiO and on Ti₂O₃ samples (all platinized), SMSI behavior, i.e. limited H₂ uptake, was noted. Very fast H-for-D exchange rates were observed for H₂D₂ mixtures on all these materials indicating that dissociative adsorption still occurs readily. Using XPS, SAES, TEM and STEM data we conclude that surface contamination, diffusion of Pt into the bulk oxide, formation of...
Surface mixed metal oxides and metal agglomeration are not significant contributors to the observed loss of \( \text{H}_2 \) uptake capacity. On the basis of qualitative bulk electrical conductivity data and XPS data, we suggest that the SMSI effect is best understood in terms of a bulk oxide reduction model. In this model, bulk conduction band electrons tunnel readily through a thin \( \text{TiO}_2 \) layer at the surface to reach Pt particles where they are trapped and furnish a negatively charged Pt particle with good capacity for dissociating \( \text{H}_2 \) but weak binding of atoms.
ABSTRACT

Platinum, supported on TiO₂, TiO and Ti₂O₃ in various forms, has been investigated using a variety of physical and chemical techniques. On H₂ pretreated TiO₂, on TiO and on Ti₂O₃ samples (all platinized), SMSI behaviour, i.e. limited H₂ uptake, was noted. Very fast H-for-D exchange rates were observed for H₂-D₂ mixtures on all these materials indicating that dissociative adsorption still occurs readily. Using XPS, SAE, TEM and STEM data, we conclude that surface contamination, diffusion of Pt into the bulk oxide, formation of surface mixed metal oxides and metal agglomeration are not significant contributors to the observed loss of H₂ uptake capacity. On the basis of qualitative bulk electrical conductivity data and XPS data, we suggest that the SMSI effect is best understood in terms of a bulk oxide reduction model. In this model, bulk conduction band electrons tunnel readily through a thin TiO₂ layer at the surface to reach Pt particles where they are trapped and furnish a negatively charged Pt particle with good capacity for dissociating H₂ but weak binding of H atoms.

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1. INTRODUCTION

The use of transition metal/titania systems has recently received considerable attention in two areas—photoassisted reactions at the gas-solid or liquid-solid interface and strong metal-support interaction phenomena. As part of our continuing research on photoassisted reactions, we have undertaken work to characterize the substrates we have been using in an effort to understand the role of SMSI effects. This paper reports part of that work.

The SMSI effect, which is characterized by a strongly reduced uptake of hydrogen and carbon monoxide on supported transition metals, has recently drawn intense attention because of promising potential in controlling the activity and selectivity of catalysts. The alteration of catalytic properties through interactions with the substrate is a very interesting approach to the development of promising catalytic materials for both conventional and photoassisted heterogeneous reactions.

In this paper we report studies of platinized oxides of titanium, including various forms of TiO₂, TiO and Ti₂O₃. A variety of bulk and surface measurements are reported which provide some clarification of the nature of the interactions between platinum and the oxide supports.

2. EXPERIMENTAL

The TiO₂ (reagent grade anatase, < 125 μm diameter particles) was obtained from H.C. White. Ti₂O₃ and TiO powders (99%, optical grade) were obtained from Alfa Products. Chloroplatinic acid, H₂PtCl₆, was prepared by dissolving Pt foil (99.99%) in aqua regia. Research grade H₂ and D₂ (99.5%) were obtained from Linde. Both were purified by passage through a 5A molecular sieve trap immersed in liquid nitrogen.

Two types of anatase were used as support materials: (1) as received from the manufacturer and (2) an H₂ pretreated sample prepared by reducing the above anatase in flowing H₂ (30 ml/min) at 875°C for 6 hr and denoted as TiO₂(H₂ pre).

One set of 2 wt.% Pt catalysts was prepared by impregnating all the support powders with 0.1 N H₂PtCl₆ solution. A second set was prepared by a photodecomposition method. An oxidized form of the TiO₂(H₂ pre) catalyst was prepared exposing the reduced material to 550 Torr of O₂ at 500°C for 17 hr.

Surface areas (H₂ adsorption at 77 K) and H₂ chemisorption measurements were carried out in a standard static volumetric apparatus. For the H₂ uptake measurements, each sample was: (1) degassed for one hr at 200°C under dynamic vacuum of 10⁻⁶ Torr, (2) reduced for 2 hr with 550 Torr of H₂ at 200°C, (3) degassed again at 200°C for one hr, (4) cooled to room temperature under dynamic vacuum and (5) exposed to H₂ for the uptake measurement. For one sample, the temperature in steps (1), (2) and (3) was raised to 400°C with no detectable effect on the H₂ uptake isotherm. Therefore, 200°C was used routinely.

The H₂-D₂ isotope exchange studies were carried out in an evacuable, circulation-pumped system (230 ml volume) which was connected to a mass
spectrometer for reaction product analysis. The catalyst was spread uniformly on one face of a quartz reaction vessel (used in related photoassisted reactions) which was part of the circulation loop. In each exchange experiment, 1 L of an equimolar H₂-H₂O mixture was dosed into the reaction loop from a pressurized storage vessel.

Qualitative electrical conductivity measurements were made by pressing the powdered catalyst into a pellet die under 10,000 psi for 5 min. The electrical resistance of the pellet was determined by measuring the current through the pellet-die assembly when a fixed voltage was applied. The thickness and the cross-section of the pellet were measured so that the specific electrical conductivity could be calculated. These measurements have been used only for qualitative guidance.

X-ray powder diffraction patterns were obtained using a conventional diffractometer (Phillips). The TEM studies utilized a model DSM-100, JEM model 200 system. The TEM and SEM measurements were done on a Jeol 100CX system. For the SEM study, samples were dispersed on carbon-coated grids using a microtome mixture of catalyst and ultrasonic.

X-ray photoelectron spectra (XPS) and scanning Auger spectra (SAXS) were done with the Physical Electronics Industries (PEI) instruments. In the XPS studies, the samples pellets were pre-treated in a reaction chamber attached to the X-ray source. Mercury vapor conditions could be chosen to simulate the reaction process. For these experiments, a H₂ or H₂O flow was used to hold the sample against a radiation heater. In cases where no sample heating was necessary, the powders were pressed into thin films. The relative atomic compositions of the surface layers studied by SAXS were calculated from the relative peak areas adjusted for atomic sensitivities taken from the PHI handbook. The SANS measurements were made in a background pressure of 1 x 10⁻⁷ torr using a 3 keV electron beam.

Atomic composition ratios were calculated from peak-to-peak height ratios and tabulated atomic sensitivity factors.
In this study, we observed the effect of hydrogen on the catalyst. We found that the amount of hydrogen adsorbed on the catalyst surface increased with increasing pressure. This is consistent with previous studies showing that hydrogen adsorption is a characteristic feature of Pt catalysts.

However, it is important to note that the amount of hydrogen adsorbed is not related to the presence of oxygen. This indicates that the surface of the Pt catalyst is oxidized. Since the reaction is performed in the absence of oxygen, the adsorption of hydrogen is likely due to the presence of Pt oxide. This is further supported by the observation that the adsorption of hydrogen increases with increasing pressure.

It is important to note that strong hydrogen chemisorption is also found on Pt/TiO₂ using titania that is neither preduced nor oxidized before the H₂ chemisorption experiment. This demonstrates that the strong chemisorption noted in the previous paper is not the result of cleaning off impurities during oxidation.

Curves (a) and (b) of Fig. 1 are for platinum (by impregnation) on TiO₂ and TiO₃ respectively. They show the chemisorption step and follow the same uptake curve with increasing H₂ pressure as the other samples.

The absence of a chemisorption step in the hydrogen uptake is a characteristic feature of Pt catalysts. However, it is important to note here that this indicates that the surfaces of all the Pt catalysts are oxidized to TiO₂. Since the reaction is performed in the absence of oxygen, it is not surprising that the surfaces were oxidized. The implication is that the Pt catalysts are present as catalysts and in their oxidized form. This will be discussed further below.

Figure 2 shows an indication that the H₂ uptake is increased in the absence of Pt. As expected, there is a decrease in the rate of chemisorption due to the absence of Pt. The uptake is shown to decrease and then increase at higher pressures. This is due to the presence of Pt oxide which is not present in the absence of Pt. This is further supported by the observation that the uptake is consistent with the presence of Pt oxide.
that the uptake of hydrogen at 48 °C with peaks roughly 10 Å apart is
a multilayer over the oxide support based on x-ray diffraction data of the Pt/Al,
and a single monolayer concentration at 34 °C. The low energy patterns shown in Figs. 1 and 2 are reversible. After removing the system overnight at both temperatures and 12 °C, heating with a flow
of the same likely giving uptake above. The strongly adsorbed hydrogen
problems in Figs. 3 can also be completely recovered by reducing the
sample to 400 °C for one hour. A significant fraction, but certainly not
all, of the peak observed by heating in H2 at 400 °C for one hour and the adsorption
was noted during one hour heating at either 100 or 200 °C.

The inset of Fig. 2 shows the results of a 3.5 ml experiment with a
commercial Pt/Al2O3 catalyst (the elastor), according to the
manufacturer, a dispersed 5% Pt. The result extrapolated to zero
temperature, gives 8 kw which we regard as acceptable agreement.

3.2 Catalyst characterization by x-ray absorption methods.

X-ray diffraction data are shown in Table 1. Prior to the H2 treatment
the x-ray powder diffraction pattern was identified by matching peaks at 2θ
values of 20.7°, 42.4°, 54.8°, 80.4°, and 84.1° and no rutile peaks
were found. After reduction, rutile peaks appeared at 27.4°, 47.5°, 54.2°, 61.8°, 71.6° and 75.1°. Even though those samples were dominated by rutile, we note that samples dominated either by rutile or anatase show strong hydrogenation.
Crystallite size provided the substrate is oxidized. For example, Pt/Al2O3,
treated under H2 at 1000 °C is dominated by anatase and shows the same hydrogen uptake as a heavily reduced Pt/Al2O3 that is oxidized (dominated by rutile). Additional peaks, which we attribute to TiO2, appear in the spectra for samples 2 and 4, i.e. at 26.9°, 28.1°, 35.1° and 55.4° (not resolved). Upon oxidation, these TiO2 peaks disappear.

Small peaks due to Pt crystallites were observable for all of the
platinized samples. Judging from the intensity and apparent widths of these
peaks, we are in agreement as noted that the lattice in Pt catalysts may also cause the Pt/Al2O3. The Pt peaks for Pt/Al2O3 and TiO2 are broadest, as expected from the sample. The Pt peaks

It is important to note that the ignition line at 121 °C and the catalyst at
200 °C with 10% O2 is very similar to room temperature and is open to oxidation by either a reduction in temperature. Oxide line (500 °C H2/Al2O3)/Pt is not only believed to be the TiO2 x-ray peaks but also reduces the shift only in the presence of Pt and is more stable to
heat. The spectrum of Pt indicates that the catalyst has characteristics of catalyst.
spectrometer detection threshold. Ake was used to examine the PT/TiO$_2$ and Pt/Ti$_2$O$_3$ samples.

The results, summarised in Table 2, indicate that a relatively large amount of surface carbon is present in every case although the XPS data are consistent with the TiO$_2$ and Pt/TiO$_2$ samples. This surface carbon, which we were unable to reduce significantly by pretreatment in the reactor chamber, did not interfere with high-spin saturation of the PT/TiO$_2$ and modified Pt/Ti$_2$O$_3$ pre-catalysts. Moreover, samples using TiO$_2$ and Ti$_2$O$_3$, which have smaller relative amounts of surface carbon (based on XPS results and probably due to overnight purging before taking spectra), show very little desorption of hydrogen at low pre-zeo. This evidence is consistent with that the presence of surface carbon is not correlated with H$_2$ desorption, we take this to mean that most of the carbon is on the oxide support.

Other possible poisons, including sulfur, phosphorus and chlorine, may also be ruled out as controlling the nature of the H$_2$ adsorption in these experiments. This is supported by the XPS data for both the oxidized and non-oxidized Pt/TiO$_2$ (pre) samples show none of these species but their H$_2$ pre-adsorption properties are very different.

The binding energies shown in Table 2 are all referenced to the Cl(1s) signal which was set at 284.6 eV after initial calibration using the Au(4f$_{7/2}$) peak at 83.9 eV. The carbon K peak energy was first determined as 284.6 eV using a pellet of graphite coated with carbon-containing material as a result of pressing it with paraffin paper on the die faces. In the absence of this carbon XPS gave a much lower Cl(1s) intensity at the same BE.

The Ti(2p$_{3/2}$) BE's listed in Table 2 all lie within a 1 eV region and the shifts do not correlate with SSI behavior. For example, the BE of the surface Ti(2p$_{3/2}$) is 458.9 eV for both Pt/TiO$_2$ (catalyst F) which shows the SOI property and for oxidized Pt/TiO$_2$, while catalyst K, which does not show the SOI property. The data of all the TiO$_2$ and Ti$_2$O$_3$ samples is definitely dominated by Ti$^{4+}$ and Ti$^{3+}$ respectively although, while the surface is oxidised to Ti$^{4+}$, Figure and Discussion (12) reported that the binding energy shifts. And finally Ti(2p$_{3/2}$) peaks in the oxidation state of Ti but is nearly independent of the physical form of the titanium oxides. They find for TiO$_2$ samples, Aem = 2.2 ± 0.4 eV, while for Ti$_2$O$_3$ and Ti$_3$O$_5$ samples, the values are 2.1 ± 0.4 eV and 2.0 ± 0.4 eV, respectively. Our results give Aem = 2.1 ± 0.2 eV for oxidized catalysts with and without SSI property (k to n; Table 2) indicating that there are detectable Ti$^{4+}$ or Ti$^{3+}$ species present in the samples at the Pt peaks heights showing the SSI property. We conclude that there is no relation between the BE shift and the oxidation state of the detectable surface Ti ion.

High resolution XPS spectra (0.5 eV peak width) with an analyser resolution of 0.4 eV of catalysts with (E, F and N) and without (B) SSI behavior are shown in Fig. 3. The peak positions and half-widths are given in Table 2. Reduction does not lead to a significant increase in BPS of the Ti(2p$_{3/2}$) peak, rather a decrease from 1.60 to 1.44 eV is noted as indicated in Table 2, samples 6 and 8. Thus, there is no evidence for mixed Ti states upon reduction. We attribute the linewidth variations to changes in surface heterogeneity.

Figure 4 shows XPS for the Pt(4f) region of materials with (E, F and N) and without (B) SSI behavior. The BE's range from 70.5 to 71.1 eV with no correlation with the SSI property. Catalyst F, with SSI, has a Pt(4f$_{7/2}$) BE of 70.9 eV while catalyst N, non-SSI, has a peak at 71.1 eV.

The surface atomic Pt/Ti ratios calculated from the XPS peak areas are also listed in Table 2. The results indicate that the SSI property is not due to diffusion of Pt into the subsurface during reduction. Materials with SSI behavior (C, E, F and N) show Pt/Ti between 0.04 and 0.34 clearly
indicating that a significant amount of Pt is present on the surface. The results from XPS also confirm this point although their values (Table 2), Catalysts I and J) are somewhat different from the XPS results. Comparing B and C in Table 2 shows that the Pt/Ti ratio decreases from 0.11 to 0.07 upon reduction at 500°C but this loss cannot account for the total depression of measurable H₂ chemisorption that is observed. In fact, the observed loss is almost within the limits of our ability to detect a significant change in the surface Pt concentration. With reduction, changes in surface morphology (roughness) and changes in surface contamination can account for the observed Pt/Ti variations.

3.3 H₂-D₂ Isotope Exchange.

The results of exposing the catalyst to an equilibrium mixture of hydrogen and deuterium are summarized in Table 3 using a concentration function in the form of the equilibrium constant. As thermodynamic equilibrium is approached, the value of this function will increase. The values were calculated from mass spectrometric peak heights assuming no difference in sensitivity among the isotopic forms of molecular hydrogen.

The results are very informative in the sense that none of the Pt-free substrates show much activity for the exchange. On the other hand, all of the platinized catalysts exhibit very rapid exchange and the rate of approach to equilibrium is at least as fast for the Pt/TiO₂/H₂ (pre, post) as it is for the unreduced Pt/TiO₂. Even though the former shows no chemisorption, while the latter does, both readily catalyze the H₂-D₂ exchange reaction. We take this as evidence for the ready dissociation of hydrogen by Pt on both samples with a much more rapid desorption on the former. The same kind of process is proposed to account for the relatively rapid isotope exchange on both Pt/TiO₂ and Pt/TiO₂-D₀, neither of which shows any measurable chemisorption of hydrogen at room temperature. The observation of rapid isotope exchange also supports the conclusion drawn in section 3.2 that the relatively large amounts of surface carbon detected by XPS are located primarily on the oxide support and do not interfere with hydrogen adsorption at Pt sites.

It is important to consider the possibility that the exchange reaction is catalyzed by a small number of Pt sites in contact with TiO₂, i.e. only a small fraction of the total amount of Pt is active for the dissociation of H₂. If this is the case, then the observed exchange rate per site is extremely fast and exceeds the rate of Pt which shows strong chemisorption of hydrogen. Although we do not favor this model, it is a possibility if
the interaction between Pt and the underlying TiO₂ activates certain of the
Pt atoms.

3.4 Electrical Conductivity Measurements.

The results for electrical conductivity and surface area are summarized
in Table 3. The starting material A has a specific electrical conductivity
of less than $2 \times 10^{-11} \text{S cm}^{-1}$. This increases by more than two orders of
magnitude after heating in hydrogen for 17 hr at 875°C, sample C. Sample B
is the same material as C except it was carried through the
photoplatinization procedure without using any PtCl₆ in the solution.
Platinization of C gives a sample D which has lower specific electrical
conductivity, $4.7 \times 10^{-10} \text{S cm}^{-1}$. Our reproducibility is about ±20%,
compare D and E, so this change is significant. Comparing the pairs F, G
and H, I, indicates that platinization reduces the specific electrical
conductivity of TiO and Ti₃O₅ samples by about one order of magnitude. We
attribute these decreases to electrons being tied up at surface Pt
particles, or species attached to the Pt, thereby decreasing the conduction
electron density. With these measurements alone, we cannot rule out the
possibility that conductivity changes are the result of variations in either
particle-particle contact resistance or charge localization at species
chemisorbed on Pt. However, taken with the other data presented here, an
internally consistent model involves localization of charge on Pt particles
when the underlying oxide is reduced.

4. DISCUSSION

As noted above, the H₂ uptake data, the XRD patterns, the isotope
exchange rates, the XPS and SANS data, the electron microscopy results and
the electrical conductivity data are all consistent with a model in which
the SMSI behavior is dependent upon the ability of the support to donate
electrons to the Pt particles. We discuss here in more detail our views
about the requirement of bulk reduction in order to observe SMSI and why
catalysts which do not accumulate significant coverages of dissociated
hydrogen nevertheless exchange hydrogen isotopes very rapidly.

The inability to detect measurable amounts of Ti²⁺ or Ti¹⁺ species by
XPS on TiO, Ti₃O₅ or TiO₂(H₂ pre) surfaces exposed to air at room
temperature (Section 3.2), all of which show SMSI behavior, suggests that
electron transfer occurs from reduced subsurface regions to Pt crystallites
through a thin barrier layer of TiO₂. Without significant bulk
conductivity, it is difficult to explain the observed effects in terms of
Pt-TiO₂ metal-metal bonds (n × 4) because the surface is oxidized before the
Pt is deposited. Consequently, differences in the subsurface (bulk) regions
of these materials may play a key role. This bulk conductivity model
correlates the SMSI and electrical conductivity data quite well,
particularly when we keep in mind the XRD and XPS results. The electrical
conductivity decreases in TiO₂(H₂ pre), Ti₃O₅ and TiO when platinized while
it increases in TiO₂. The SMSI effect follows the same pattern.

Using ESR to detect Ti¹⁺, Haizing and Prins (1) studied the surface
reduction of Pt/TiO₂ at 300°C and 500°C finding reversibility at the lower
but not the higher temperature. They attribute this to the formation of
microcrystals of Ti₄O₇ formed at the higher temperature as the result of
dehydration. Since SMSI behavior is observed after 500°C, but not 300°C,
reduction (2), we infer that local low temperature surface reduction of
titania by spillover of H to form Ti\(^{1+}\) and OH\(^-\) is not the source of the SMSI behavior. The irreversible formation of TiOH or TiOH\(_2\) microcrystals (i.e., bulk reduction) at the higher temperatures is consistent with the ESR data and the observed SMSI character. Huizinga and Prins\(^{11}\) suggest that the appearance of these crystallites near the surface leads to morphological and electronic structure changes in the Pt particles as proposed by others\(^{2,14}\). In related work, Apple et al.\(^{15}\) report that strong H\(_2\) chemisorption is found by NMR for Ni/\(\text{TiO}_2\) catalysts with both large and small ESR signals due to Ti\(^{3+}\). Since, for their conditions, surface reduction would dominate, we infer that the presence of significant surface Ti\(^{3+}\) concentrations does not guarantee SMSI behavior. Our results are also consistent with a model requiring more than surface Ti\(^{3+}\). Indeed, recent ESR work in our laboratory\(^{16}\) shows that the SMSI property is correlated with the presence of bulk Ti\(^{3+}\) signals that are not subject to reversible formation/removal upon exposure/evacuation of H\(_2\) at around room temperature.

The isotope exchange and H\(_2\) uptake data suggest that the dissociative reaction probabilities are about the same on SMSI and non-SMSI catalysts. The heats of adsorption are, however, significantly different, the SMSI catalysts having lower values. A more quantitative description could be developed using a Langmuir isotherm formulation but our data does not permit a quantitative evaluation. Figure 5a shows schematically how H\(_2\) interacts with a Pt catalyst which does not exhibit SMSI. There is a small activation energy, \(E_{a1}\), for dissociative adsorption and a rather large activation energy, \(E_{a2}\), for desorption. The high value of the latter favors a high surface coverage at equilibrium and temperatures near 200°C. Rapid isotope exchange in the H\(_2\)-D\(_2\) equilibration is the result of high surface coverages compensating partially for the relatively high activation energy of desorption. In the SMSI case, Fig. 5b, the activation energy for dissociative adsorption, \(E_{a2}\), is assumed to be equal to \(E_{a1}\) but the heat of adsorption, \(E_{d2}\), is taken to be much smaller than \(E_{d1}\). Here, low hydrogen coverages at equilibrium are expected, as observed. The unfavorable effect of low hydrogen coverage on the isotope exchange rate is compensated by the low energy required for desorption. In fact, we should not be surprised to find exchange rates proceeding more rapidly on the SMSI materials; the lifetime of a hydrogen atom on the surface is shorter but the dissociative adsorption probability at zero coverage is about the same with the model of Fig. 5. Consequently, the steady state rate of adsorption, and the rate of exchange, will be more rapid for the SMSI case.

Shorter residence times for H atoms on SMSI surfaces have been proposed by Tauster et al.\(^{17}\) to account for the higher activity and selectivity of Ni/\(\text{TiO}_2\) as compared with Ni/\(\text{SiO}_2\) or Ni/\(\text{Al}_2\text{O}_3\) for Fischer-Tropsch synthesis. The model of Fig. 5 can account for these differences. The shorter lifetime is beneficial to higher activity so long as it is long enough to allow the reaction of interest to compete effectively with other reactions.

In agreement with Baker et al.\(^{14}\), who used TEM, our results using XRD and TEM indicate that SMSI is not the result of agglomeration of Pt during various treatments. Neither surface impurity poisons nor diffusion of Pt into subsurface regions are significant contributors to the SMSI effect according to our XPS, H\(_2\) uptake and H-D\(_2\) exchange results.

Tauster et al.\(^{17}\) have suggested that the degree of SMSI effect reached depends upon the ease with which the metal oxide is reduced to provide electron rich cations at the surface which form metal-metal bonds with deposited Group VIII metals like Pt. Our results are consistent, in part, with this model. However, we favor a model in which attention is focussed on the reduction of the bulk which supplies electrons to the adsorbed Pt and lowers their ability to bind atomic hydrogen. A slight change in the language, will bring the two models into agreement. In
selecting materials for an SMSI effect, we propose choosing a support with relatively high electrical conductivity and a work function lower than the deposited metal. To achieve n-type electrical conductivity in typical metal oxides, reduction to remove lattice oxygen must be carried out. The more readily this occurs, the stronger the SMSI effect. By reduction, not only is the conductivity changed, the work function also decreases as the Fermi level moves toward the bottom of the conduction band. For charge transfer from support to Pt upon platinization, the work function of the support must be smaller than that of the metal, i.e., the highest occupied levels of the support lie above the highest occupied levels of the Pt before contacting the two. Materials with low conductivity will not show SMSI unless dopants supplying charge carriers to the conduction band are introduced.

Although p-type semiconductors can be included in this description, electron transfer to Pt from the support will require a "hopping" scheme from one acceptor site to another. Consequently, relatively high doping, to bring these sites close enough for orbital overlap, is required. For n-type material, the conduction band is utilized, so all one needs is thermal excitation into the conduction band and tunneling through the contact barrier at the support/metal interface, i.e., at the TiO₂/Pt junction.

Supporting evidence based on electrical conductivity and type of charge carrier is given in Table 4. We agree completely with Tauster et al. in considering the oxides which show SMSI; however, our description is somewhat broader and includes materials which are not easily reduced. For example, SIC is not in the oxide category and is not readily reduced. In a separate study, we have found SMSI behavior for Pt/SIC and an increased \( \text{H}_2\text{O}_2 \) exchange rate upon platinization. This is consistent with our model and suggests that metal-metal bond formation is not a necessary condition for observing SMSI behavior.

Other \( \text{H}_2 \) uptake studies also support the importance of the bulk electrical conductivity and Fermi level position in SMSI. For example, no SMSI property is observed for the Pt/TiO₂ system if the titania is pretreated in flowing \( \text{H}_2 \) for 6 hr at 700°C and then platinized. As in the work reported here, we expect the surface to reoxidize during platinization and/or exposure to air. The absence of SMSI then suggests that the reduction process did not increase the bulk conductivity sufficiently and/or did not raise the Fermi level of the titania to a value high enough to permit charge transfer. Note that the work functions of undoped TiO₂ and Pt are 6.2 eV\(^{(21)}\) and 5.7 eV\(^{(22)}\), respectively.

We have also observed electron transfer from Pt to rutile by measuring the electrical properties\( (1, 5, 4, 8, 10, 11, 12) \) of a thin film of Pt deposited on single crystal rutile, pretreated in flowing \( \text{H}_2 \) for 1 hr at 500°C.\(^{(19)}\)

The bulk effect charge transfer model suggested here is not new. Baddour and Dibert\(^{(23)}\) proposed a similar model in 1966 to explain the promotion of Ni supported on Ge in the catalysis of formic acid decomposition. In another important contribution, Solymosi\(^{(24)}\) has reviewed the catalytic importance of the electrical properties of supports. The implication of the bulk conductivity model for electron transfer is that as the metal crystallite or cluster size becomes smaller, the surface charge density will increase. This may account for the different catalytic behavior and the observed resistance to sintering for smaller particles.\(^{(25)}\) Our model emphasizes the importance of electron transfer from the bulk of the support to the metal as the key for SMSI behavior. Electron transfer through interfacial metal-metal bonds or through tunneling, as described above, can result in SMSI effects. The negatively charged metal particles will tend to increase their surface areas to reduce their surface charge densities. The expected morphological changes have been observed by Baker, et al.\(^{(14)}\) who found a tendency towards flatter pill-box Pt structures when Pt/TiO₂ was reduced at elevated temperatures.
Prior to reduction or after oxidation, the Pt particles had hemispherical shapes. We have found similar morphology differences. PL/TiO<sub>2</sub> shows hemispherical Pt particles, PT/TiO<sub>2</sub> shows polyhedral particles, and PT/TiO shows raft-like particles.

One SMSI support which appears to fall completely outside the proposed selection rule is MnO; the reason is not clear, but it is worth noting that nonstoichiometric MnO is a semiconductor while, in stoichiometric form, it is an insulator. Further study is required to clear up this question.

Speculation about the formation of mixed metal oxides in SMSI systems is not warranted here but it does deserve additional study. However, we note that the formation of mixed metal oxides typically requires an oxidizing environment in excess of 500°C. In order to avoid their formation, and the possibility of significant impurity and/or diffusion of metal catalyst into the bulk of the support, our catalysts never encounter a temperature higher than 500°C, during or after platinization, so such mixed metal oxide effects are not likely to contribute significantly.

ACKNOWLEDGMENTS

The authors would like to express their hearty thanks to Dr. Marvin Deviney and Dr. Paul Buccemi for their kindness in taking most of the TEM and STEM micrographs for us. Thanks are also extended to Miss L. J. Fu for her assistance in running the SANS and Mr. Shiu-Hin Pang for his assistance in making electrical conductivity measurements.

REFERENCES

11. Technical Service Department, Matheson Coleman & Bell Company, Cincinnati, Ohio.

Table I. Summary of the Properties of Representative Compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T服饰 (ppm)</th>
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<th>T服饰 (ppm)</th>
<th>Average Pt Particle Size (nm)</th>
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<td>6. T服饰 (ppm)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100 A</td>
</tr>
<tr>
<td>7. T服饰 (ppm)</td>
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<tr>
<td>8. T服饰 (ppm)</td>
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<tr>
<td>9. T服饰 (ppm)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100 A</td>
</tr>
</tbody>
</table>

Notes: (--) in the dispersion column indicates that this property can not be determined.

a. -- Not detectable, b. -- Radioactive, c. -- Preparation, d. -- Deposition, e. -- Preparation, f. -- Deposition, g. -- Preparation.
Table 3. Surface Area, Electrical Conductivity and Isotope Exchange Data

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Surface Area (m²)</th>
<th>Specific Electrical Conductivity (ohm⁻¹cm⁻¹)</th>
<th>(HD)²/(H₂)(D₂)</th>
<th>25 sec</th>
<th>60 sec</th>
<th>300 sec</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TIO₂(a)</td>
<td>4.65</td>
<td>4 x 10⁻¹¹</td>
<td>0.39 gm</td>
<td>10⁻³</td>
<td>0.006</td>
<td>0.017</td>
<td>200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>100°C</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>TIO₂(b)</td>
<td>3.7 x 10⁻⁹</td>
<td>2.8 x 10⁻¹⁰</td>
<td>0.39</td>
<td>0.12</td>
<td>0.21</td>
<td>200°C</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>25°C</td>
</tr>
<tr>
<td>C</td>
<td>TIO₂(c)</td>
<td>2.4 x 10⁻⁹</td>
<td>3.3 x 10⁻¹⁰</td>
<td>0.35  gm</td>
<td>1.20</td>
<td>2.8 ± 0.2</td>
<td>3.31 ± 0.01</td>
<td>200°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.05</td>
<td>2.51 ± 0.03</td>
<td>3.20 ± 0.07</td>
<td>100°C</td>
</tr>
<tr>
<td>D</td>
<td>Pt/TIO₂(a)</td>
<td>4.7 x 10⁻¹⁰</td>
<td>1.01 ± 0.01</td>
<td>0.35  gm</td>
<td>1.01</td>
<td>2.30 ± 0.10</td>
<td>3.07 ± 0.15</td>
<td>25°C</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1.18 ± 0.02</td>
<td>2.4 ± 0.2</td>
<td>3.1 ± 0.1</td>
<td>200°C</td>
</tr>
<tr>
<td>E</td>
<td>Pt/TIO₂(b)</td>
<td>5.0 x 10⁻¹⁰</td>
<td>0.92 ± 0.02</td>
<td>0.35  gm</td>
<td>0.92 ± 0.01</td>
<td>2.0 ± 0.1</td>
<td>2.97 ± 0.01</td>
<td>100°C</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.71 ± 0.02</td>
<td>1.92 ± 0.01</td>
<td>2.77 ± 0.02</td>
<td>25°C</td>
</tr>
<tr>
<td>F</td>
<td>TIO₂</td>
<td>1.2 x 10⁻¹⁰</td>
<td>10⁻⁴</td>
<td>0.11  gm</td>
<td>10⁻⁴</td>
<td>5.4 x 10⁻⁶</td>
<td>1.1 x 10⁻²</td>
<td>200°C</td>
</tr>
<tr>
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<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>100°C</td>
</tr>
<tr>
<td>G</td>
<td>Pt/TIO₂</td>
<td>3.4 x 10⁻¹⁰</td>
<td>1.3</td>
<td>0.11  gm</td>
<td>1.3</td>
<td>2.82 ± 0.04</td>
<td>3.6 ± 0.1</td>
<td>200°C</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>1.1 ± 0.01</td>
<td>2.61 ± 0.03</td>
<td>3.49 ± 0.02</td>
<td>100°C</td>
</tr>
<tr>
<td>H</td>
<td>TIO₂(a)</td>
<td>6.1 x 10⁻¹⁰</td>
<td>Not Done</td>
<td>0.25  gm</td>
<td>Not Done</td>
<td>Not Done</td>
<td>Not Done</td>
<td>25°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Pt/TIO₂(b)</td>
<td>6.2 x 10⁻¹⁰</td>
<td>Not Done</td>
<td>0.25  gm</td>
<td>Not Done</td>
<td>Not Done</td>
<td>Not Done</td>
<td>25°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.71 ± 0.09</td>
<td>2.33 ± 0.02</td>
<td>3.3 ± 0.1</td>
<td>25°C</td>
</tr>
</tbody>
</table>

(a) is TIO₂(H₂ pre)

(a') is TIO₂(H₂ pre) treated using photoreduction conditions but without adding H₂PtCl₆.
Table 4. The correlation of SBSI behavior with electronic properties of supports.

<table>
<thead>
<tr>
<th>Support Material</th>
<th>Carrier Type</th>
<th>Electrical Conductivity $\text{cm}^{-1}$</th>
<th>SBSI</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO</td>
<td>Metal</td>
<td>$10^{-1}$</td>
<td>Y</td>
<td>a</td>
</tr>
<tr>
<td>Ti$_2$O$_3$</td>
<td>n</td>
<td>$10^{-3}$</td>
<td>Y</td>
<td>a</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>n</td>
<td>$10^{-11}$</td>
<td>N</td>
<td>a</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>n</td>
<td>$10^{-7}$ (200°C)</td>
<td>Y</td>
<td>17</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>Metal</td>
<td>$10^{-3}$</td>
<td>Y</td>
<td>17, 31</td>
</tr>
<tr>
<td>HSO$_4$</td>
<td>p</td>
<td>$10^{-5}$ (400°C)</td>
<td>N</td>
<td>17, 31</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>p</td>
<td>$10^{-5}$ (400°C)</td>
<td>N</td>
<td>17</td>
</tr>
<tr>
<td>Ge$_2$O$_3$</td>
<td>p</td>
<td>$10^{-7}$ (650°C)</td>
<td>N</td>
<td>17, 31</td>
</tr>
<tr>
<td>MgS</td>
<td>n</td>
<td>$10^{-12}$</td>
<td>N</td>
<td>17, 31</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Insul$^D$</td>
<td>$10^{-12}$</td>
<td>N</td>
<td>17, 31</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Insul</td>
<td>$10^{-12}$</td>
<td>N</td>
<td>17, 31</td>
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<td>SiC</td>
<td>Metal</td>
<td>$10^{-3}$</td>
<td>Y</td>
<td>19</td>
</tr>
</tbody>
</table>

(a) This paper.
(b) Insulator.

**Figure Captions**

Figure 1. $H_2$ uptake curves for platinized titanium oxides. (a) oxidized Pt/TiO$_2$($H_2$ pre), (b) Pt/TiO$_2$($H_2$ pre), (c) Pt/Ti$_2$O$_3$, (d) Pt/TiO.

Figure 2. $H_2$ uptake curves for titanium oxides. TiO$_2$, Ti$_2$O$_3$, TiO$_2$($H_2$ pre); insert in $H_2$ uptake curve for Pt/Al$_2$O$_3$ and the axes plot the same variables as the larger figure.

Figure 3. Ti(2p) XPS spectra for some of the systems listed in Table 2. (a) Oxidized Pt/TiO$_2$($H_2$ pre), (b) Pt/Ti$_2$O$_3$, $H_2$ reduction at 200°C, (c) oxidized Pt/TiO$_2$($H_2$ pre), reduced in-situ at 500°C, (d) Pt/TiO, $H_2$ reduction at 200°C, (e) Pt/Ti$_2$O$_3$, $H_2$ reduction at 500°C.

Figure 4. Pt(4f) XPS spectra for some of the systems of Table 2. (a) Oxidized Pt/TiO$_2$($H_2$ pre), 50 eV pass energy, (b) Pt/TiO$_2$($H_2$ pre), $H_2$ reduction at 200°C, 50 eV pass energy, (c) Pt/Ti$_2$O$_3$, $H_2$ reduction at 200°C, 25 eV pass energy, (d) Pt/TiO, $H_2$ reduction at 200°C, 25 eV pass energy.

Figure 5. Schematic reaction profiles for $H_2$ interacting with Pt/TiO$_2$ systems without, (a), and with, (b), the SBSI property.
H₂ UPTAKE (μ mole·g⁻¹)

PRESURE H₂ (torr)

(a) (b) (c) (d)

100 200 300 400

H₂ UPTAKE (μ mole·g⁻¹)

PRESURE H₂ (torr)

TiO₂ (H₂ pre)

Ti₂O₃

TiO₂

Clay, white: Fig. 1

Clay, white: Fig. 2