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Metal–Support Interactions: An *in Situ* Electrical Conductivity Study of Pt/TiO_2 Catalysts

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An *in situ* investigation of the electrical conductivity of Pt/TiO_2 catalysts (0.5 and 5 wt% Pt) has been carried out under various conditions corresponding to two pretreatments (473 and 773 K in H_2), to H_2 or O_2 adsorptions and to H_2–O_2 titrations at 295 K. To explain the results the following hypotheses have been proposed: (i) in H_2, H atoms migrated from Pt onto the O^{2-} sites of TiO_2 and released one electron per OH^- group formed, and (ii) under vacuum at 295 K an "electron pumping effect" of the metal decreased the conductivity of the reduced oxide. When the cataust was under strong metal–support interaction (SMSI) conditions (viz. after reduction in H_2 at 773 K), the metal was markedly enriched in electrons. Accordingly, the particular chemisorption and catalytic properties of Pt under these conditions have been interpreted by the filling of its *d* orbitals which tend to the d^{10} configuration. The disappearance of the SMSI state after exposure to O_2 has been attributed to the back donation of electrons to the titania by the platinum which thus recovered its normal electronic configuration.

INTRODUCTION

It has been observed that when titanium dioxide was used as a support for group VIII metals, these metals lost their chemisorptive properties toward H_2 and CO and exhibited markedly modified catalytic behaviors in various reactions (hydrogenation, hydrogenolysis, Fischer–Tropsch synthesis), provided the catalysts were reduced at a temperature ≥ 773 K (*1–20*). This was attributed to a strong metal–support interaction (SMSI). It also occurs for other reducible, transition metal oxide supports after treatment in H_2 at comparable temperatures (*2, 4–6*). More recently, analogous effects were found in the case of the supports Al_2O_3 and SiO_2 (*6, 21*).

Various hypotheses have been presented to explain the suppression of the chemisorptive properties of the catalysts in the SMSI state. Agglomeration and encapsulation of the metal particles as well as the effect of impurities were rejected on the basis of various arguments (*1*). In the particular case of Pt/TiO_2, electron microscopy studies have shown that in the SMSI state, the platinum aggregates into "pillbox" structures on a lower oxide of titanium Ti_4O_7 (*16*). From these data and from molecular orbital calculations (*3*), as well as from spectroscopic investigations dealing with other systems (Pt/$SrTiO_3$, Ni/TiO_2) (*22–25*), it was inferred that electrons can be transferred to the metal from the reduced oxide. For the calculations, a localized bonding model was used rather than a model taking into account the collective electronic properties of TiO_2 in order to extend the results to other types of supports. For Ni deposited on TiO_2, Al_2O_3, and SiO_2, it was speculated that, on the contrary, electrons are withdrawn from the metal crystallites by the oxide leading to a metallic behavior more characteristic of cobalt (*17*).

The present study was undertaken to corroborate, for the most typical catalyst, Pt/TiO_2, this transfer of electrons between the metal and its support and to establish the

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direction of this transfer by measuring *in situ* the electrical conductivity of the semiconductor support, not only under the SMSI conditions but also during various reducing and oxidizing treatments, in parallel with chemisorption determinations. Whereas the previous works on SMSI were mainly concerned with the metal modifications, this method gives information on the variations of the electronic state of the support. This investigation is also connected with other studies of our group dealing with the photocatalytic (*26, 27*) and photoconductive (*28*) properties of these solids, where exchanges of electrons and hydrogen atoms between the platinum and the anatase have been proposed.

EXPERIMENTAL

1. Catalytic Preparation

The two Pt/TiO_2 catalysts were prepared by the impregnation of the nonporous Degussa P-25 anatse (50 m^2 g^{-1}) with the required quantity of chloroplatinic acid according to the method desribed in Refs. (*26*) and (*27*). For nominal contents in Pt of 0.5 and 5 wt%, the chemical analyses indicated 0.48 and 5.0 wt%. These samples will be simply denoted 0.5-Pt and 5-Pt throughout the text.

2. Catalyst Characterization

Electron microscopy. The transmission electron microscopy (TEM) showed for the two specimens a good homodispersion of the Pt crystallites centered around a mean diameter of 2.0 nm in both cases, so that the average numbers of Pt particles deposited per titania particle were in the ratio of the Pt contents: ~10 Pt particles/TiO_2 particle in the 5-Pt sample and ~1 Pt particle/TiO_2 particle in the 0.5-Pt sample. A representative micrograph of the 5-Pt sample was included in Ref. (*26*). More details on the particle size distribution of this type of catalysts is reported in another article (*28*).

Dispersion measurements by chemisorption. The percentage of platinum exposed was determined by hydrogen and oxygen adsorptions and oxygen–hydrogen titrations assuming Pt_s–H and Pt_s–O stoichiometries. The amounts of gases which have reacted during the sequence (hydrogen adsorption, oxygen titration, hydrogen titration, evacuation at 673 K, oxygen adsorption, hydrogen titration, and, finally, oxygen titration) are listed in Table 1 for the samples previously reduced under 250 Torr H_2 at 473 or 773 K and then evacuated in a vacuum of 10^{-6} Torr (1 Torr = 133.3 Pa) at 673 K, a temperature high enough to remove all the chemisorbed hydrogen according to Ref. (*29*).

The quantities corresponding to the samples reduced at the lower temperature (LTR samples) were in close agreement with equal stoichiometries for H_2 and O_2. The dispersions calculated from these values were equal to 34 and 54% for the 5-Pt and 0.5-Pt samples, respectively, and were consistent with the TEM data. For the samples reduced at the higher temperature (HTR samples), the initial amounts of chemisorbed hydrogen were drastically decreased (no chemisorption was even detected for 0.5-Pt). However, after exposure of the samples to oxygen, the subsequent titrations and chemisorptions were affected only to a small extent. In the case of the 5-Pt sample, the apparent dispersion based on the initial hydrogen chemisorption was decreased by a factor of ~7. These behaviors are in accord with the previous studies dealing with the SMSI.

3. Electrical Conductivity Measurements

Apparatus. The electrical conductivity measurements were performed in a static cell built to study *in situ* the electronic interactions between a powder catalyst and various gaseous reactants (*30, 31*). About 500 mg catalyst was placed between two platinum electrodes (1.00 cm diameter) and compressed under a constant pressure

TABLE 1

Amounts of Gases Which Have Reacted (in μmol/g · catalyst) during the H_2 or O_2 Adsorptions and H_2–O_2 Reciprocal Titrations[a]

Catalyst	T_R(K)	H_2 ads.	O_2 tit.	H_2 tit.	O_2 ads.	H_2 tit.	O_2 tit.
5-Pt	473	41	65	126	45	134	66
	773	6	56	105	37	114	53
0.5-Pt	473	6.5	9	18	6.4	16	7.8
	773	0			6.0		

[a] T_R, temperature of reduction in H_2.

($\sim 10^5$ Pa) for good electrical contacts between the catalyst particles without modifying the texture. Thermocouples soldered on each electrode were used either to monitor the temperature or to measure the electrical resistance using an R-meter (Schlumberger model V.M.1613) for $R \leq 1$ MΩ or a digital teraohmmeter (Guildline Instruments, model 9520) for higher values. The electrical conductivity σ (in Ω^{-1} cm^{-1}) was calculated from the conductance $1/R$ by taking into account the geometric factor t/S of the sample (t is the thickness of the compressed powder ($\simeq 0.6$ cm) and S is the section area of the electrodes): $\sigma = 1/R \cdot t/S$.

Procedure. The electrical conductivity was measured at the steady state corresponding to each stage of the following sequences which were similar to those employed for the dispersion measurements: after an evacuation at room temperature for 1 h, the sample was reduced overnight at 473 K under 250 Torr H_2, outgassed at 673 K for 2 h to be sure that all the hydrogen was evolved, and finally cooled to room temperature. Increasing pressures of H_2 (50–250 Torr) were then admitted onto the catalyst which was afterward briefly outgassed before exposure to oxygen (50–100 Torr). These H_2–O_2 successions were repeated twice. Then the solid was reduced at 773 K under 250 Torr H_2 for 2 h, a long enough period to obtain a stable conductivity value, and evacuated at the same temperature for 2 h. After that, the same sequence of H_2–O_2 exposures was performed.

RESULTS

1. Samples Reduced at 473 K (LTR Samples)

Figure 1 shows the variations of the logarithm of the conductivity σ (5-Pt catalyst) and σ_0 (pure TiO_2) for the various steps of the sequence specified in the preceding paragraph. For clarity, the values referring to the 0.5-Pt catalyst have been omitted in this figure but they will be indicated in the text when necessary. Figure 2 presents Arrhenius plots of the conductivity corresponding to the stepwise decrease in temperature from 673 to 295 K under vacuum (Fig. 1, phase 4). Linear transforms were obtained only for the Pt-loaded catalysts; activation energies of conduction E_c equal to 3.3 (0.5-Pt) and 6.8 kcal mol^{-1} (5-Pt) were deduced (1 kcal mol^{-1} = 4.185 kJ mol^{-1}). In the case of pure titania, E_c was very low and not constant: it increased with decreasing temperature.

2. Samples Reduced at 773 K (HTR Samples)

Figure 3 indicates the changes in σ and σ_0 under the various conditions of the sequence described in the experimental section. In Fig. 4 are shown Arrhenius plots of the conductivity for the stepwise decrease in temperature from 773 to 295 K under

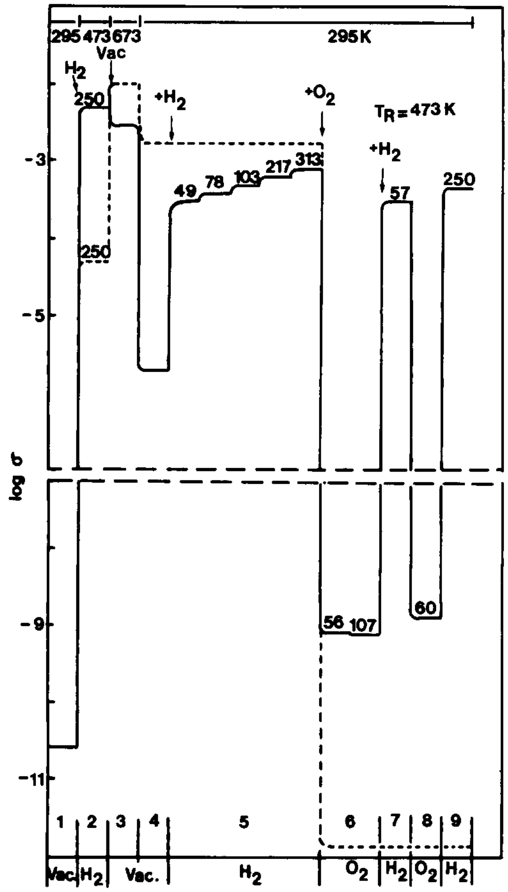

FIG. 1. Logarithm of the electrical conductivity (in Ω^{-1} cm^{-1}) of TiO_2 (dotted line) and of the 5-Pt sample (solid line) reduced at 473 K in H_2 as a function of the different phases described in the text. The numbers of the curves indicate the pressures (in Torr) of the corresponding gas.

vacuum (Fig. 4, phase 4). Straight lines were not obtained. At high temperatures, the solids exhibited a metal-like conduction ($E_c \leq 0$). At lower temperatures, E_c increased, which showed that the support recovered—at least partially—a semiconductor character, this recovery increasing with the Pt content.

INTERPRETATION AND DISCUSSION

Absolute values cannot be obtained from conductivity measurements performed with powders. However previous studies on TiO_2 (*30, 31*) have shown that energetic quantities (such as the enthalpies of formation of anionic vacancies or the energy of electron ionization) can be drawn on powders in excellent agreement with data arising from conductivity mesurements carried out with single crystals (*32*) or from measurements made on polycrystalline solids with other techniques such as thermogravimetry (*33*). This means that these quantities are not controlled by grain boundary effects.

On the other hand, in the present case, the presence of a maximum of 5 wt% of platinum did not modify the conduction mode between the anatase particles since the probability of finding Pt crystallites just at the contact points between the grains is nil as may be seen on the micrograph of Ref. (*26*): only ~1 (0.5-Pt) or ~10 (5-Pt) platinum particles (2 nm diameter) were deposited on the surface of each nonporous anatase grain (20–30 nm diameter). Therefore, the conductivity measured ex-

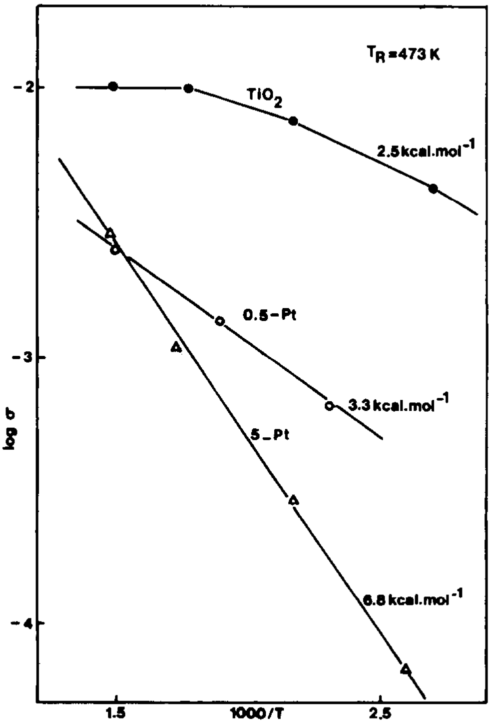

FIG. 2. Arrhenius plots of the electrical conductivity (in Ω^{-1} cm^{-1}) of the LTR samples under vacuum.

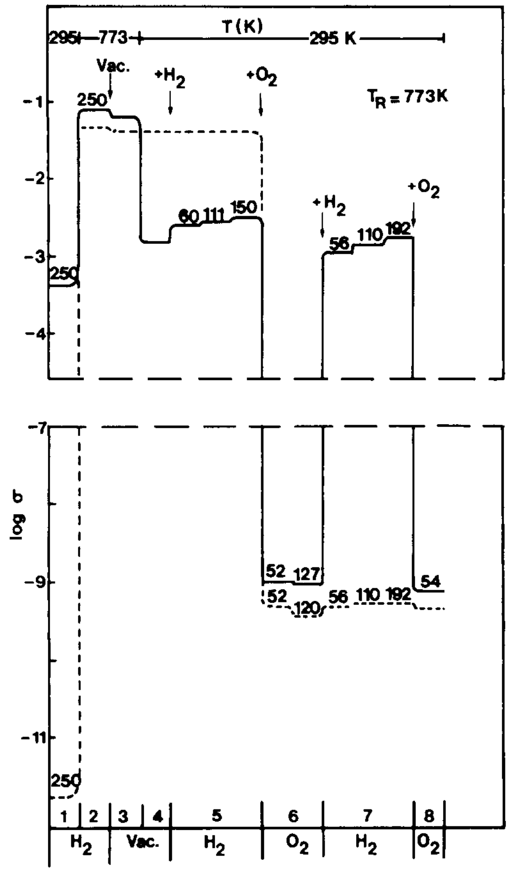

FIG. 3. Logarithm of the electrical conductivity (in Ω^{-1} cm^{-1}) of TiO_2 (dotted line) and of the 5-Pt sample (solid line) reduced at 773 K in H_2 as a function of the different phases described in the text; the numbers on the curves indicate the pressures (in Torr) of the corresponding gas.

clusively referred to TiO_2, and the differences between σ and σ_0 give information on metal–support interactions. These differences will be discussed stage by stage, separately for the solids reduced at low temperature (473 K; LTR samples) and at high temperature (773 K; HTR samples).

1. LTR Samples

Hydrogen at 473 K (Fig. 1, phase 2). Previous studies on the electrical conductivity of TiO_2 (*30a*) have shown that hydrogen reduces this oxide and creates anionic vacancies $V_{O^{2-}}$. These vacancies are produced via the formation of hydroxyl groups and the subsequent dehydration of the surface:

$$H_2 + 2O^{2-} \rightleftarrows H_2O + O^{2-} + V_{O^{2-}} \qquad (1)$$

An increase in conductivity results from the ionization of the first electron of these vacancies.

$$V_{O^{2-}} \rightleftarrows V^{+}_{O^{2-}} + e^{-} \qquad (2)$$

where $V_{O^{2-}}$ represents an anionic vacancy with two trapped electrons (neutral entity in the surface lattice) and $V^{+}_{O^{2-}}$ an ionized vacancy with only one electron trapped (positive entity). The difference observed here between σ and σ_0 (Fig. 1) can be attributed to an increase in the reduction of TiO_2 by H_2 which is catalyzed by Pt (*6, 7, 16, 18*). The dissociative adsorption of this gas on the metal and its subsequent migration on the support has been reported (*34, 35*). The conductivity of 0.5-Pt is situated between that of 5-Pt and σ_0, which shows that at 473 K the reduction degree of TiO_2 increased with the platinum loading.

Evacuation at 673 K (Fig. 1, phase 3). This evacuation inversed the values of σ

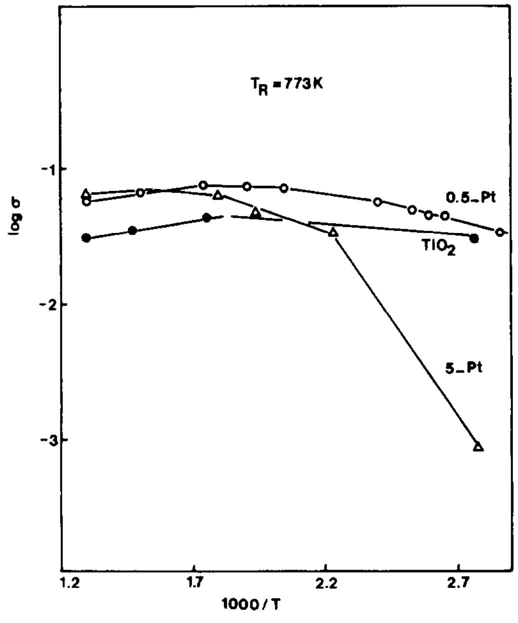

FIG. 4. Arrhenius plots of the electrical conductivity (in Ω^{-1} cm^{-1}) of the HTR samples under vacuum.

and σ_0 with respect to the previous step. We attribute the increase in σ_0 to an increase in the concentration of anionic vacancies because (i) of a more pronounced dehydroxylation of titania and (ii) of a partial removal of surface lattice oxygen (*30, 31*)

$$O^{2-} \rightleftarrows \tfrac{1}{2}O_2(g) + V^{+}_{O^{2-}} + e^- \qquad (3)$$

The same phenomenon should also take place on the surface of the oxide in the case of the Pt/TiO$_2$ specimens and, accordingly, σ should have increased and it should be higher than or at least equal to σ_0. It is suggested to attribute the difference between the behaviors of TiO$_2$ and Pt/TiO$_2$ ($\sigma < \sigma_0$) to a migration of electrons from the support to the metal in agreement with the theoretical calculations of Ref. (*3*) where an electron transfer occurs from Ti^{3+} to Pt, and with surface spectroscopic studies dealing with Pt/SrTiO$_3$ (*22, 23*) and Ni/rutile (*24, 25*). This is symbolized by

$$e^- + \mathrm{Pt} \rightleftarrows e_{\mathrm{Pt}}^- \qquad (4)$$

where e_{Pt}^- represents an electron trapped by the platinum. Such an effect probably occurred during phase 2 but could not be distinguished because of the reduction of TiO$_2$ by Pt and of the influence of the H$_2$ adsorption (see below).

Cooling from 673 K to 295 K (Fig. 1, phase 4). Pure titania appears as a quasimetallic conductor ($E_c \simeq 0$) at high temperatures. The difference between the Arrhenius plots of the three samples in Fig. 2 can also be explained by an "electron pumping effect" of the platinum which in fact appears more substantial at low temperatures because of the exothermicity of Eq. (4) ($\Delta H_4 < 0$) corresponding to the electron affinity of the deposited platinum. For 0.5 Pt, free electrons are available from shallow donor levels located at 3.3 kcal mol^{-1} (0.14 eV) below the conduction band, while for 5-Pt free conduction electrons are ionized from deeper levels (6.8 kcal mol^{-1} (0.30 eV)) as a result of a more important pumping by a greater number of metal crystallites.

Conductivity isotherm $\sigma = f(P_{H_2})$ at 295 K (Fig. 1, phase 5). Hydrogen did not affect σ_0, whereas it increased σ according to the experimental law:

$$\sigma = a + bP_{\mathrm{H}_2}^{1/2} \qquad (5)$$

which is illustrated in Fig. 5,I. The exponent +1/2 shows (i) the electron-donor character of hydrogen ($\partial\sigma/\partial P_{\mathrm{H}_2} > 0$) and (ii) the dissociative nature of its adsorption on TiO$_2$. Note that this adsorption necessarily involved platinum since bare titania is insensitive to P_{H_2} under the same conditions. The relationship (5) can be accounted for by the two following equations

$$\tfrac{1}{2}H_2(g) + \mathrm{Pt_s} \rightleftarrows \mathrm{Pt_s\text{–}H} \qquad (6)$$

$$\mathrm{Pt_s\text{–}H} + O^{2-} \rightleftarrows \mathrm{Pt_s} + OH^- + e^- \qquad (7)$$

Equation (6) represents the strong dissociative adsorption on surface platinum atoms Pt$_s$, and Eq. (7) the migration of hydrogen atoms on the support where they ionosorb as protons (*18, 36*) on anionic sites and yield hydroxide ions, thus releasing free electrons to the support. By taking into account Eqs. (4) and (7) the steady-state principle applied to the concentration $[e^-]$ of free electrons in the support yields:

$$\begin{aligned}\frac{d[e^-]}{dt} &= k_7[\mathrm{Pt_s\text{–}H}][O^{2-}] \\ &\quad + k_{-4}[e_{\mathrm{Pt}}^-] - k_4[e^-][\mathrm{Pt}] \\ &\quad - k_{-7}[\mathrm{Pt_s}][OH^-][e^-] = 0 \qquad (8)\end{aligned}$$

while the mass action law of Eq. (6) gives:

$$K_6 = \frac{[\mathrm{Pt_s\text{–}H}]}{P_{\mathrm{H}_2}^{1/2}[\mathrm{Pt_s}]}. \qquad (9)$$

The combination of Eqs. (8) and (9) leads to the relation:

$$[e^-] = \frac{k_{-4}[e_{\mathrm{Pt}}^-]}{k_4[\mathrm{Pt}] + k_{-7}[\mathrm{Pt_s}][OH^-]} + K_6\frac{k_7[\mathrm{Pt_s}][O^{2-}]P_{\mathrm{H}_2}^{1/2}}{k_4[\mathrm{Pt}] + k_{-7}[\mathrm{Pt_s}][OH^-]} \qquad (10)$$

which is formally identical to Eq. (5) and

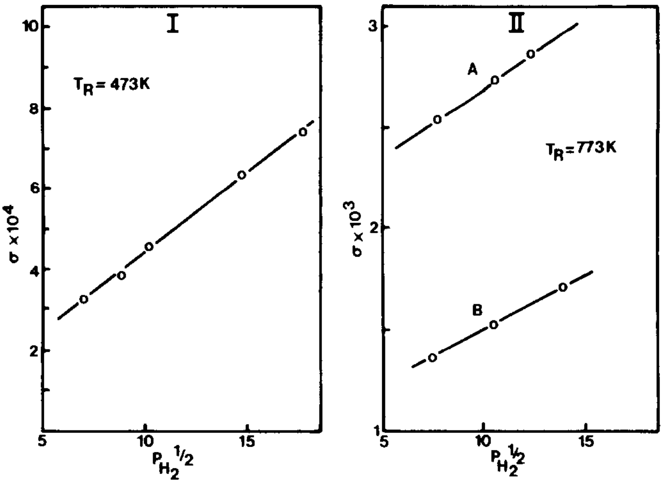

FIG. 5. Linear transforms of the isotherms $\sigma = f(P_{H_2})$ for the 5-Pt sample pretreated at 473 K (I) or 773 K (II): Curve A, first H_2 adsorption; Curve B, second H_2 (after O_2 adsorption); σ in Ω^1 cm^{-1}; P_{H_2} in Torr.

which will be discussed in a following paragraph.

Oxygen adsorption (Fig. 1, phase 6). Besides the titration of Pt_s–H species which formed water plus Pt_s–O species, oxygen reoxidized the oxide surface by filling the anionic vacancies according to the reverse reaction of Eq. (3), thus considerably decreasing the conductivity. However, σ was higher than σ_0 by more than three orders of magnitude in the same pressure range (a pressure of ~50 Torr was sufficient to reach the equilibrium state), whereas the conductivity of 0.5-Pt was not distinguishable of σ_0. This difference can be tentatively interpreted as indicating that titania supporting a sufficient loading of platinum has undergone a deeper reducing treatment by H_2 at 473 K. Consequently, there would remain more anionic vacancies in the sublayers of titania in the 5-Pt sample which cannot be reoccupied by oxygen at room temperature according to reaction (−3) because of a low diffusion coefficient of oxygen.

Hydrogen–oxygen titrations (Fig. 1, phases 7–9). For the two Pt/TiO_2 specimens the σ values obtained during the subsequent H_2–O_2 cycles were close to those found for the first H_2 or O_2 adsorptions, whereas σ_0 remained at the low level reached as a result of the first O_2 adsorption. This means that electrons could be repeatedly released on the support in the presence of Pt and H_2 according to Eqs. (6) and (7).

2. *HTR Samples*

The temperature of 773 K was chosen in agreement with the literature data because it is high enough to induce SMSI and low enough to avoid (i) a sintering of both metal and oxide particles and (ii) the conversion of anatase into rutile.

Hydrogen reduction at 773 K (Fig. 3, phase 2). The increase in temperature from 473 to 773 K increased the reduction of TiO_2, but greatly diminished the difference between σ and σ_0; the same σ level was reached for 0.5-Pt and 5-Pt. This shows that at 773 K the importance of the catalytic reduction of the support by Pt in the presence of H_2 has substantially decreased as compared with the noncatalytic chemical reduction of TiO_2 by this gas. The evacuation at 773 K only slightly decreased σ and σ_0 because of the small coverage in H_2 at this temperature (Fig. 3, phase 3).

Cooling to 295 K (Fig. 3, phase 4). The quasimetallic behavior of pure titania in the 573–773 K temperature range where $E_c \leq 0$ (Fig. 4) was a consequence of its high reduction degree corresponding to a high concentration of singly ionized anionic vacancies whose first electrons have been excited to the conduction band (Eq. (2)).

The Pt/TiO_2 samples also behaved as quasimetallic conductors at high temperatures, but an increase in their activation energies of conduction was observed for temperatures <473 K and was neatly more important for 5-Pt, so that at 295 K

$$\sigma_0 \simeq \sigma_{0.5\text{-Pt}} \gg \sigma_{5\text{-Pt}}.$$

As in the case of the LTR samples, this effect is consistent with an electron migration from the support to the metal (Eq. 4)) which increases (i) with increasing amounts of Pt and (ii) with decreasing temperature.

Conductivity isotherm $\sigma = f(P_{H_2})$ *at 295 K (Fig. 3, phase 5).* The introduction of 60 Torr H_2 had no effect upon the electrical conductivity of pure TiO_2 and of 0.5-Pt. This result is in agreement with the adsorption measurements in Table 1 showing the absence of H_2 adsorption for this latter sample which is in SMSI conditions. The relative increase of σ of 5-Pt caused by the admission of 60 Torr H_2 was about 100 times lower than that corresponding to the LTR sample because of the higher conductivity level. But the linear isotherm $\sigma = f(P_{H_2}{}^{1/2})$ (Fig. 5,II, curve A) indicates a dissociative adsorption of hydrogen in conformity with Eqs. (5)–(7) with a slope b comparable to that obtained for the LTR sample (Table 2).

TABLE 2

Coefficient a and b of Eq. (5) for the 5-Pt Sample[a]

T_R	Corresponding figure	$b = \partial\sigma/\partial P_{H_2}{}^{1/2}$ (Ω^{-1} cm^{-1} Torr$^{-1/2}$)	a/Ω^{-1} cm^{-1}
473 K	5,I	4.0×10^{-5}	4.5×10^{-5}
773 K	5,II curve A	6.9×10^{-5}	2.0×10^{-3}
	5,II curve B	5.4×10^{-5}	0.96×10^{-3}

[a] T_R, temperature of reduction in H_2.

This supports these equations and shows that the smaller amount of H_2 chemisorbed on the platinum of the HTR sample (Table 1) was sufficient to influence the TiO_2 conductivity according to the same law as in the case of the LTR sample.

Oxygen adsorption (Fig. 3, phase 6). Qualitatively, oxygen had the same effect as in the case of the LTR samples, i.e. (i) the generation of Pt–O species on the metal and (ii) the filling of the superficial anionic vacancies of the oxide (Eq. (3)) which seemed independent of the presence of the deposited metal, since $\sigma \simeq \sigma_0$. The difference of several orders of magnitude between the semiconductivity values of pure titania in oxygen for the LTR and HTR samples could be accounted for by the creation, at high temperature, in the sublayers of the oxide, of deeper donor defects (vacancies) which cannot be oxidized by gaseous oxygen at room temperature, possibly because of the high activation energy for the diffusion coefficient of oxygen within the lattice (*37*).

Second H_2 *Adsorption (Fig. 3, phase 7).* As expected, exposure to H_2 did not affect σ_0. In the case of 5-Pt the linear relationship between σ and $P_{H_2}{}^{1/2}$ was again observed as shown in Fig. 5,II, curve B, with a slope b (Eq. (5)) almost unchanged (Table 2). This was due to the reproducibility of Eqs. (6) and (7) after an exposure to oxygen as evidenced, in parallel, by the results of Table 1. The validity of Eq. (10), which makes explicit the empirical relation (5), is supported by the fact that the slopes $b = \partial\sigma/\partial P_{H_2}{}^{1/2}$ of the lines in Fig. 5,I and 5,II are very close to each other, irrespective of the reduction temperature T_R, in agreement with the constant factors which compose b under the same conditions. The relative enrichment in extra electrons of the platinum particles can tentatively be evaluated from the coefficient a of Eq. (5) which is proportional to

$$a = \frac{k_{-4}[e_{Pt}^-]}{k_4[Pt] + k_{-7}[Pt_s][OH^-]} \quad (11)$$

according to Eq. (10). Considering that in the denominator of Eq. (11) the second term can be neglected because it corresponds to the hydrogen spillover, whereas the first term refers to an exchange of electrons, the coefficient a, whose values are listed in Table 2 for 5-Pt, is proportional to $[e_{\mathrm{Pt}}^-]/[\mathrm{Pt}]$. Therefore, semiquantitatively, the ratio

$$R = \frac{a_{773}}{a_{473}} = \frac{([e_{\mathrm{Pt}}^-]/[\mathrm{Pt}])_{773}}{([e_{\mathrm{Pt}}^-]/[\mathrm{Pt}])_{473}} = \frac{2.0 \times 10^{-3}}{4.5 \times 10^{-5}} \simeq 44$$

is indicative of the *relative* content in extra electrons of the Pt particles reduced at 773 and 473 K. The consequence of this relative excess of supplementary electrons upon the chemisorptive and catalytic properties will be discussed in the concluding remarks.

Second oxygen adsorption (*Fig. 3, phase 8*). The next adsorption of oxygen brought σ down to its level at $\sim 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Therefore, as in the case of the LTR samples, oxygen, besides the titration of $\mathrm{Pt_s}$–H species and the creation of $\mathrm{Pt_s}$–O entities, captured the free electrons of the support which have been generated during the preceding period under hydrogen.

CONCLUDING REMARKS

In the preceding paragraphs, the conductivity variations observed have been interpreted partly on the basis of processes previously proposed for TiO_2, such as (i) the formation of singly ionized oxygen vacancies in H_2 or under vacuum at high temperatures, (ii) the partial filling of these vacancies by oxygen at room temperature, and (iii) the ionosorption of O_2.

However, to explain the differences found in the presence of supported platinum particles, two other processes have been invoked. First, in agreement with the authors of Refs. (*18*, *36*), it has been suggested that hydrogen atoms chemisorbed on platinum migrate onto the support ("spillover") where they generate OH^- ions at O^{2-} sites and release electrons to the support (Eq. (7)). Second, we think that the present measurements reflect an electron donation of the reduced anatase support to the metal. When a semiconductor and a metal are in contact, their Fermi levels should be aligned. For monocrystals placed in vacuum, the work function of platinum (~5.36 eV) (*38*) exceeds that of reduced TiO_2 (~4.6 eV) (*39*). Consequently, the alignment of the Fermi levels of monocrystals of these materials will correspond to a transfer of electrons from the semiconductor to the metal. The present conclusions are in agreement with the direction of this electron transfer, which tends to show that the positions of the Fermi levels of TiO_2 and Pt are not inverted with respect to the monocrystals for the divided powders studied here. However, the various treatments and atmospheres should affect the work functions of both materials (*40*) (particularly if TiO_2 is partly reduced to a lower oxide such as Ti_4O_7 (*16*)) and in consequence modify the importance of the electron transfer. For instance, in H_2 the density in electrons of the Pt/TiO_2 samples was greater under the SMSI conditions.

This excess of electrons in the metal crystallites, which would preferentially affect the outer atom layers for electrostatic reasons, would modify the electronic structure of platinum by progressively filling its *d* orbitals and therefore would change its chemisorptive properties. Gold which follows platinum in the periodic table, does not chemisorb H_2 and does not catalyze the reactions involving dissociatively chemisorbed hydrogen (*41*). Accordingly, it is suggested that the decrease in chemisorptive and catalytic properties of Pt/TiO_2 under SMSI conditions observed in various investigations may arise from the filling of the metal *d* orbitals with electrons donated by the support. The restoration of the chemisorptive properties of the metal after an intermediate admission of oxygen may be explained by the reoxidation of the oxide which becomes electron-demanding because of oxygen ionosorption, so that the metal gives back its excess electrons to the support and thus recovers its normal electronic configuration. In terms of semiconductor band diagram, this back transfer is justified by the increased exhaustion in electrons of the anatase surface layer because of negatively adsorbed oxygen, which requires a new charge equilibrium.

In short, the conductivity method indicates that the collective properties of TiO_2 are influenced by the deposited platinum. This conclusion cannot be extended to other supports on the basis of the present data, which, however, show the importance of conductivity measurements in the study of electronic metal–support interactions for semiconducting supports.

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