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Thermodynamic Considerations of Strong Metal–Support Interaction in a Real Pt/TiO$_2$ Catalyst

JEAN-MARIE HERRMANN

Equipe CNRS, Photocatalyse, Ecole Centrale de Lyon, BP 163-69131 Ecully Cedex, France

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The nature of lattice defects induced by strong metal–support interaction (SMSI) treatment in titania supporting platinum has been studied by *in situ* electrical conductivity measurements as a function of oxygen pressure. The variations between 425 and 500°C of the electrical conductivity σ vs P_{O_2} ($\sigma = k \cdot P_{O_2}^{-1/4}$) are indicative of the presence of singly ionized vacancies. Their heats of formation are equal to twice the activation energy of conduction ($\Delta H = +81$ kcal mol^{-1}). The heat of Pt/TiO$_2$ regeneration determined by microcalorimetry corresponds, in absolute value, to the heat of filling two anionic vacancies by one molecule of O$_2$. It is substantially lower than the heats of titanium suboxide reoxidation, which rules out the presence of such species on Pt/TiO$_2$ real catalysts in the SMSI state. Titania has a stoichiometry of TiO$_{1.996}$, i.e., still close to that of anatase. These anionic vacancies can be filled by the oxygen of water molecules arising from the methanation reaction ($\Delta H = -23$ kcal mol^{-1}), thus explaining the suppression of the SMSI state under working conditions. To each singly ionized anionic vacancy corresponds one free electron of conduction, which increases the Fermi level of titania and makes possible an electron transfer to the metal. The electron transfer can inhibit H$_2$ or CO chemisorption, if these molecules chemisorb as dipoles with a donor character to the metal as evidenced by conductivity.

INTRODUCTION

In recent years titania has become a widely used material in catalysis (*1*). It often appears as a nonconventional support for metal catalysts, since it is able to induce some effects on the activity and the selectivity of the supported metal. The most striking effect is the so-called strong metal–support interaction (SMSI) in which a *M*/TiO$_2$ catalyst is reduced at high temperature (500°C) and the metal loses, at least partially, its chemisorptive properties with respect to H$_2$ and CO. This effect was first discovered by Tauster *et al.* on titania (*2*) and then extended to other reducible supports (*3*). It was universally accepted since, up to now, no counterexample was reported in the literature. Two symposia have been devoted to this effect (*4, 5*).

Since 1978, many articles have been written on this subject and it would be impossible to cite all of them. However, several reviews that indicate most of the papers on the subject have appeared (*6–10*).

Several explanations have been given to account for the loss of chemisorptive and catalytic properties: the occurrence of an electronic effect with an electron transfer from the support to the metal (*11–18*), the formation of intermetallic compounds (*19–24*), the existence of hydrogen spillover (*25–28*), and more recently the decoration of the metal by TiO$_x$ mobile species (*29–34*). In the last case, most of the studies were concerned with model catalysts, whereas for real catalysts, with well-dispersed metal particles on high-surface-area titania, no firm evidence of overlayer formation was available, as noted by Tauster (*7*).

In the present study, an attempt has been made to identify the nature of the defects generated on titania by SMSI as well as their heats of formation by measuring *in situ* the electrical conductivity of real Pt/

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TiO_2 catalysts. The results are tentatively correlated to previous calorimetric data (*35*), and some thermodynamic considerations are presented to account for the reactivity of Pt/TiO_2 in the SMSI state.

EXPERIMENTAL

Catalyst Preparation

Pt/TiO_2 was prepared by the impregnation of nonporous Degussa P-25 anatase (50 m^2/g) with the required quantity of hexachloroplatinic acid. The suspension was then dried in a rotating flask by evacuation at 80°C and then in an oven at 110°C for 2 h. The resulting batch was then reduced in a hydrogen flow (35 $cm^3\ m^{-1}$) at 480°C for 15 h. The reduction was preceded and followed by a nitrogen flush during the increase and decrease in temperature. The batch was kept in a closed vial until further use.

Catalyst Characterization

The platinum dispersion—or percentage exposed—corresponding to the ratio of surface Pt atoms to the total number of Pt atoms measured by chemical analysis (5 wt%) was determined by hydrogen chemisorption and H_2–O_2 titration. After reduction at 20°C, the catalyst chemisorbed 1 cm^3 H_2 per gram (44.6 μmol $H_2\ g^{-1}$), which corresponds to a dispersion of 35%. This value is in good agreement with the mean particle size determined by transmission electron microscopy (TEM), which showed homodispersed platinum particles of ~1.5 nm, regularly distributed on all the particles of the support (Fig. 1).

When the temperature of reduction was raised to 500°C, the amount of chemisorbed hydrogen decreased, as expected from the SMSI effect, from 44.6 to 6 μmol g^{-1}, i.e., by a factor of 7.8.

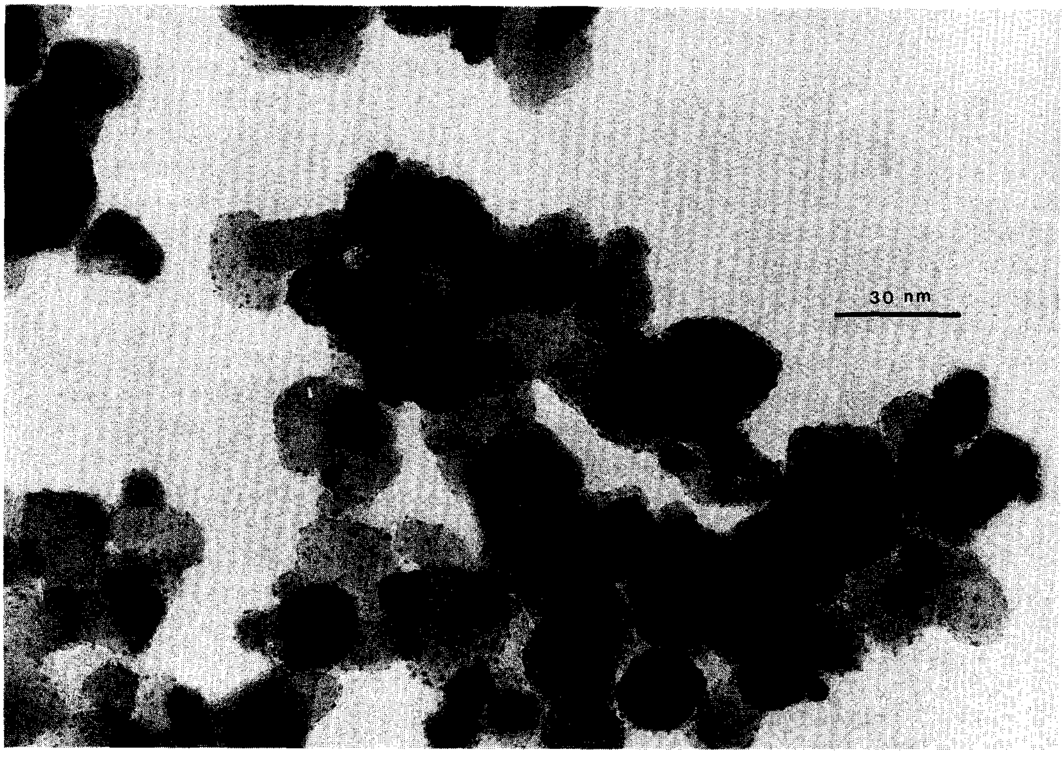

FIG. 1. TEM micrograph of 5 wt% Pt/TiO_2.

Electrical Conductivity Measurements

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 (described in Ref. (*36*)). About 500 mg of catalyst was placed between two platinum electrodes (1.00 cm in diameter) and compressed under a constant pressure of ~10^5 Pa for good electrical contacts between particles without modification of the texture. 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 compressed powder (0.6 cm) and S the section area of the electrodes): $\sigma = 1/R \cdot t/S$.

RESULTS AND DISCUSSION

Preliminary Remarks

Absolute values cannot be obtained from conductivity measurements performed with powders. However, previous studies on TiO_2 (*37, 38*) have shown that the energetic quantities (such as the enthalpies of formation of anionic vacancies or the energy of electron ionization) that can be drawn from measurements on powders are in excellent agreement with those arising from conductivity measurements carried out on single crystals (*39*) or from measurements made on polycrystalline solids with other techniques such as thermogravimetry (*40*). This means that the determination of these quantities is not controlled by grain-boundary effects.

On the other hand, in the present case, the presence of 5 wt% platinum did not modify the conduction mode between the anatase particles since the probability of finding Pt crystallites at all the contact points between the TiO_2 grains is nil, as may be directly observed from TEM micrographs (Fig. 1). An average of only ~10 platinum particles (1.5 nm) was deposited on the surface of each nonporous anatase grain (20–30 nm in diameter). Therefore, the conductivity measured referred exclusively to TiO_2. This is in agreement with the percolation theory for conductivities of composite mixtures comprising metallic and semiconducting components (*41* and references therein).

Evidence for Anionic Vacancies

For pure semiconductor oxides, anionic vacancies can be evidenced by electrical conductivity measurements at the thermodynamic equilibrium with various oxygen pressures at different temperatures (*36–40*).

The solid was first put in the SMSI state by the following treatment: evacuation (10^{-6} Torr; 1 Torr = 133.3 Pa) for 1 h at room temperature, introduction of 250 Torr H_2, heating to 500°C, and reduction at this temperature for 2 h. The catalyst was then outgassed under 10^{-6} Torr for 30 min. Once the SMSI state was obtained, oxygen was introduced at 500°C under a pressure of 160 Torr. Instantaneously, the electrical conductivity decreased by more than six orders of magnitude and was followed by steady state. P_{O_2} was subsequently decreased to various values. The corresponding electrical conductivity data are presented in Fig. 2. Similar isotherms were obtained at different temperatures. It must be noted that all the variations of σ vs T or P_{O_2} were reversible.

Under constant oxygen pressure (160 Torr) the electrical conductivity varied exponentially with temperature as evidenced by the Arrhenius plot of Fig. 3. An activation energy of conduction of 40.5 kcal mol^{-1} (169.5 kJ mol^{-1}) was found.

Since the slopes of the isotherms in Fig. 2 are close to $-\frac{1}{4}$, the anionic vacancy model can be applied.

Anionic vacancies have been produced by hydrogen reduction at 500°C,

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

$V_{O^{2-}}$ represents an anionic vacancy with two trapped electrons. This entity is neutral with respect to the lattice as are the oxygen

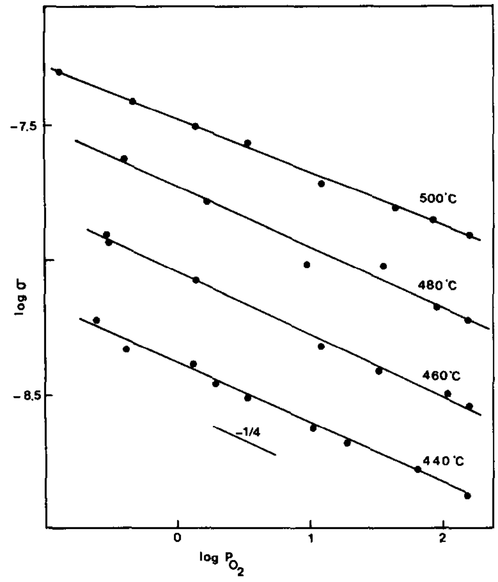

FIG. 2. Variations of the electrical conductivity σ (in Ω^{-1} cm^{-1}) of Pt/TiO$_2$ as a function of P_{O_2} (in Torr).

anions O^{2-} of TiO$_2$. The charge balance of Eq. (1) is obtained by taking into account the charges of the exponent of O^{2-} and of the subscript of $V_{O^{2-}}$.

When oxygen is introduced, two reactions occur simultaneously:

(i) the coverage of the surface platinum atoms,

$$\mathrm{Pt_S} + \tfrac{1}{2}\mathrm{O_2} \rightleftarrows \mathrm{Pt_S} - \mathrm{O}, \qquad (2)$$

(ii) the partial filling of anionic vacancies whose concentration is governed by the thermodynamic equilibrium

$$O^{2-} \rightleftarrows V_{O^{2-}} + \tfrac{1}{2}O_2(g). \qquad (3)$$

At 500°C, anionic vacancies do not remain neutral. The thermal energy is sufficient to ionize their first electron into the conduction band,

$$V_{O^{2-}} \rightleftarrows V^{+}_{O^{2+}} + e^{-}. \qquad (4)$$

The singly ionized anionic vacancies are positively charged with respect to the lattice.

The mass action law, applied to Eqs. (3) and (4), yields

$$K_3 = [V_{O^{2-}}]P_{O_2}^{1/2} \qquad (5)$$

$$K_4 = \frac{[V^{+}_{O^{2-}}][e^{-}]}{[V_{O^{2-}}]}. \qquad (6)$$

Equations (5) and (6) combined with the electrical neutrality condition ($[e^{-}] = [V^{+}_{O^{2-}}]$) give the relationship

$$\begin{aligned}\sigma \propto [e^{-}] &= (K_3K_4)^{1/2}P_{O_2}^{-1/4}\\ &= [(K_3)_0(K_4)_0]^{1/2}\exp[-(\Delta H_3\\ &\qquad + \Delta H_4)/2RT]P_{O_2}^{-1/4}. \qquad (7)\end{aligned}$$

The exponent $-\frac{1}{4}$ found from the slopes of the log–log plot of Fig. 2 is therefore indicative of anionic vacancies formed by hydrogen reduction.

Experimentally, σ was found to vary as

$$\sigma = k \cdot P_{O_2}^{-1/4}\exp(-E_c/RT). \qquad (8)$$

By comparison of Eqs. (7) and (8),

$$\Delta H_3 + \Delta H_4 = 2E_c. \qquad (9)$$

Since the ionization energy of the first electron ΔH_4 is generally small compared to the heat of formation of anionic vacancies, ΔH_3, one obtains $\Delta H_3 \sim 2E_c = +81$ kcal mol^{-1} (339 kJ mol^{-1}). This value is the same as that obtained for pure bare titania (*37*), and for Ga^{3+} or Nb^{5+} doped TiO$_2$ (*38*). It is also identical to that obtained for single crystals of TiO$_2$ (*39*) as well as to that ob-

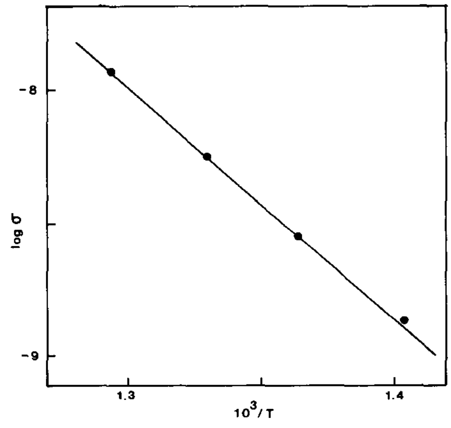

FIG. 3. Arrhenius plot log $\sigma = f(1/T)$ of the electrical conductivity of Pt/TiO$_2$ under a pressure of 160 Torr O$_2$.

tained by other techniques such as thermogravimetry (*40*). It should be emphasized that it corresponds to a thermodynamic parameter which is not affected by the presence of deposited platinum. This means that Eqs. (2)–(4) are independent. It should be noted that these anionic vacancies can be produced also during high-temperature evacuation (*38*).

Comparison with Microcalorimetry

The destruction of the SMSI state, corresponding to the almost complete regeneration of Pt/TiO_2 properties relative to H_2 chemisorption, was previously studied at room temperature by microcalorimetry (*35*). It required 0.5 cm^3 O_2 per gram of catalyst. The corresponding heat of regeneration ΔH_r was found equal to -156 kcal mol^{-1} O_2 (653 kJ mol^{-1}). In the electrical conductivity study, the reoxidation of the support corresponds to Eq. (-3) whose enthalpy ΔH_{-3} is equal to -81 kcal mol^{-1} of anionic vacancies, i.e., -162 kcal mol^{-1} O_2. The nearly equal values found for ΔH_r and ΔH_{-3} mean that the destruction of the SMSI state of Pt/TiO_2 by exposure to oxygen proceeds only via the filling of the anionic vacancies created by hydrogen reduction. The presence of Pt, which catalyzes the reduction of TiO_2 (*15, 16*), has, however, no effect on ΔH_r, since an identical heat of reoxidation of bare titania has been found (-150 to -160 kcal mol^{-1}) (*42*).

The heat of regeneration ΔH_r is much smaller than the heat of oxidation of titanium suboxides collected in Table 1, which does not support the existence of such oxides at the surface of reduced titania. Similarly, ΔH_r is much smaller than the heat of oxidation of titanium into TiO_2, which rules out the presence of Ti metal under SMSI conditions.

TABLE 1

Enthalpies of Oxidation of Titanium Suboxides

	ΔH (kcal mol^{-1})	
	Oxide	O_2
TiO (α) + $\frac{1}{2}O_2 \rightarrow TiO_2$ (rutile)	103	206
Ti_2O_3 (α) + $\frac{1}{2}O_2 \rightarrow TiO_2$ (rutile)	96	192
Ti_3O_5 (α) + $\frac{1}{2}O_2 \rightarrow TiO_2$	97	193.5
Ti_4O_7 + $\frac{1}{2}O_2 \rightarrow TiO_2$	112	224

The results of both electrical conductivity and microcalorimetry concerning the regeneration treatment indicate that on *real catalyst* the presence of suboxides TiO_x could not be thermodynamically evidenced. This is in line with the degree of reduction of titania, deduced from the quantity of oxygen necessary to regenerate the support (0.5 cm^3 g^{-1}). It corresponds to the formula $TiO_{1.996}$, which is in good agreement with previous results (*43*) and is very close to the anatase stoichiometry.

Adsorption of H_2

After low-temperature reduction (LTR) treatment, the catalyst chemisorbed ca. 1 cm^3 g^{-1} H_2 under a maximum pressure of 1.5 Torr. The corresponding initial heat of adsorption was found equal to 22 kcal mol^{-1} (*35*), in excellent agreement with previous results obtained on platinum (*44, 45*). After high-temperature reduction (HTR) treatment, it chemisorbed only 0.13 cm^3 g^{-1} H_2 while the initial heat of adsorption decreased to 18.5 kcal mol^{-1}. Moreover, hydrogen chemisorption was almost completely reversible. This is in agreement with previous results which evidenced a weakly bound hydrogen species (*14, 47–49*).

The substantial change in the energetics of H_2 chemisorption can be interpreted in terms of an electronic factor. Electrochemists consider that chemisorption of hydrogen occurs with the formation of dipoles at the surface of the metal (*50–52*). Consequently, if the metal is enriched with excess electrons coming from the reduced support, the formation of $Pt_s^{\delta-}$–$H^{\delta+}$ dipoles will be counteracted. This can explain why both the heat of chemisorption and the amount of chemisorbed H atoms decrease under SMSI conditions. These effects are progressive between LTR (200°C) and HTR

TABLE 2

Pt/TiO$_2$: Inhibition Factor R for Various Platinum Loadings at Constant Metal Particle Size (~2 nm)

Metal content (wt%)	n_{H_2} (ads) T_R = 200°C	n_{H_2} (ads) T_R = 500°C	$R = n_{H_2}$ (200°C)/n_{H_2} (500°C)
0.5	6.5	0	∞
5	44.6	6	7.8
5[a]	42	6	7
10	90.5	26	3.5

[a] From Ref. (*16*).

(500°C) treatments. The decrease in the amount of H$_2$ adsorbed is already detectable for T_R = 300°C (n_{H_2} ads(300°C) = 0.86 cm^3 g^{-1}), whereas the decrease in the heat of adsorption occurs only for $T_R \geq$ 400°C. Increasing reduction temperatures yield a higher degree of reduction which progressively increases titania's Fermi level, making stronger the electron transfer from the support to the metal (*53*). The electron transfer remains limited since the contact concerns a metal with a high electron density (10^{23} cm^{-3}) and a reduced semiconductor whose electron density is 10^3 times lower and estimated from the present electrical conductivity measurements to be ca 10^{20} cm^{-3}. However, the small size of the Pt crystallites (1.5 nm) makes the electronic interaction with the adsorbed phase particularly intense.

From a quantitative point of view, the inhibition of H$_2$ chemisorption decreases with the metal loading (Table 2). When the weight percentage of platinum increases from 0.5 to 10% at a constant mean particle size ($d \sim$ 1.5 nm), the inhibition factor defined as the ratio of H$_2$ adsorbed in the normal state to that adsorbed in the SMSI state decreases from ∞ to 3.5. It seems that the relative electron enrichment per particle of Pt decreases when the number of these particles increases, as if the electron reservoir constituted by the support had the same initial concentration of free electrons to be shared between the metal crystallites. A similar trend for the inhibition factor was observed for the catalytic cyclopentane–deuterium isotopic exchange on the same samples under uv illumination (*54*).

Adsorption of CO

Under SMSI conditions the initial heat of adsorption remains constant (32 kcal mol^{-1}), but strongly decreases with the coverage (*35*). As for hydrogen, CO adsorption is almost totally reversible under SMSI conditions. This can be accounted for also by the existence of an electronic factor which counteracts the chemisorption of CO molecules as dipoles at the surface of the metal.

CO + H$_2$ Interactions on Pt/TiO$_2$ in the SMSI State

CO + H$_2$ interactions have been studied both at room temperature and at reaction temperature (290°C).

Room temperature. At room temperature, when CO is first introduced, the electrical conductivity σ increases instantaneously and then remains constant and independent of P_{CO} (Fig. 4). The initial increase in σ means that CO chemisorbs on Pt with a donor character and that some excess electrons in the metal are then restituted to titania whose conductivity in-

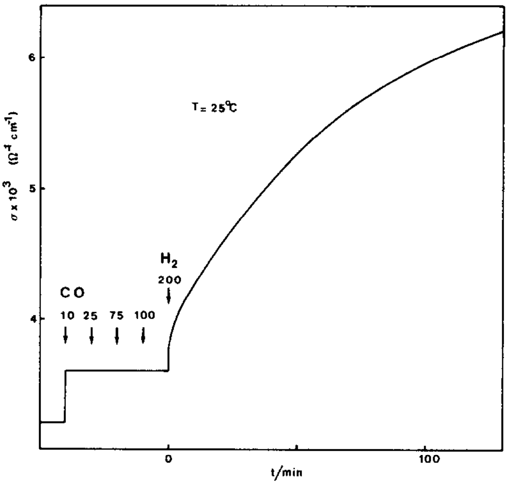

FIG. 4. (CO + H$_2$) interactions on Pt/TiO$_2$ (5%) in the SMSI state at room temperature (pressures in Torr).

creases. No σ variation is observed as a function of P_{CO} on bare titania, which demonstrates that the variation of $\sigma(Pt/TiO_2)$ is due to the chemisorption of CO on Pt. Such a donor character is in favor of the formation of dipoles at the surface of the metal. The absence of a decrease in σ at the introduction of CO implies that CO does not decompose either on TiO_2 or at the metal–oxide interface since, otherwise, the atomic oxygen produced would have filled anionic vacancies with the consumption of free electrons (Eq. (−3)). The lack of influence upon σ of subsequent increasing CO pressures means that the platinum surface is already saturated.

When hydrogen is introduced, the electrical conductivity increases slowly similarly to hydrogen spillover (*55*),

$$H_2 + 2Pt_S \rightleftarrows 2Pt_S - H \qquad (10)$$

$$Pt_S - H + O^{2-} \rightleftarrows Pt_S + OH^- + e^-. \qquad (11)$$

This means that hydrogen is able to displace CO from certain of its sites (*56*). This is thermodynamically possible since the strong adsorption sites for hydrogen under SMSI conditions have a higher heat of adsorption (18 kcal mol^{-1}) than the weakest adsorption sites for CO (12 kcal mol^{-1}) (*35*). These sites must be located close to the metal–support interface since they enable hydrogen to spill over the surface of titania (Fig. 4).

Reaction temperature. The same experiments were repeated at 290°C at which the temperature methanation occurs. The electrical conductivity variations are presented in Fig. 5. Similarly to what happens at room temperature, the adsorption of CO on platinum still has a donor character and some excess electrons are retrodonated to the support, thus increasing the conductivity of the sample.

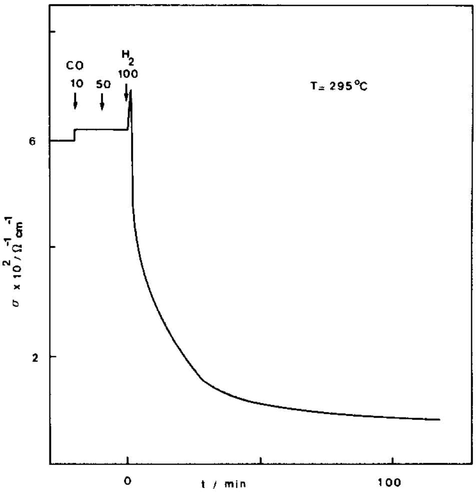

FIG. 5. (CO + H_2) interactions on Pt/TiO_2 in the SMSI state at reaction temperature (290°C) (pressures in Torr).

When hydrogen is introduced (H_2/CO = 2) there is a sharp initial increase in σ followed by a slow decrease for 2 h. The change in σ at the introduction of H_2 is still indicative that H_2 has been able to chemisorb by displacing CO from certain of its weakest adsorption sites. The slow decrease in σ means that titania is progressively partly reoxidized. The reoxidation cannot originate from CO decomposition, since, otherwise, it would have occurred during the previous CO adsorption. Oxygen must intervene from a reaction product, namely water. This was confirmed by introducing water in contact with Pt/TiO_2 under identical conditions, which gave the same decay.

Because reoxidation of titania by water is a spontaneous process, ΔG is negative, and, from the formula $\Delta G = \Delta H - T\Delta S$, $(\Delta H - T\Delta S)$ must also be negative, or equally $T\Delta S$ must be larger than ΔH. Now ΔS will also be negative because titania's reoxidation produces a more ordered system (reduced substoichiometry, destruction of lattice defects, disappearance of free electrons of conduction); hence ΔH must also be negative, and the process must therefore be exothermic. This is confirmed by the calculation of the enthalpy of the reaction,

$$V^{+}_{O^{2-}} + H_2O + e^- \rightleftarrows O^{2-} + H_2 \qquad (12)$$

$$\begin{aligned}\Delta H_{12} &= \Sigma\Delta H_{\text{prod.}} - \Sigma\Delta H_{\text{react}}\\ &= -(\Delta H_{H_2O} + \Delta H_3)\\ &= +58 - 81 = -23 \text{ kcal mol}^{-1} < 0,\end{aligned}$$

where ΔH_{H_2O} is the heat of formation of water and ΔH_3, the heat of formation of anionic vacancies determined here above from $\sigma(T, P_{O_2})$ measurements. The exothermicity of Eq. (12) is responsible for the sharp initial increase in σ in Fig. 5. The hydrogen production in Eq. (12) has been evidenced by pulse chromatography (*57*). The decrease in conductivity connected with the partial reoxidation of titania by water (Fig. 5) is much more limited than that due to pure oxygen. This is not unexpected since (i) pure O_2 is a stronger oxidizing agent, i.e., strongly electrophilic, and (ii) the presence of the (H_2 + CO) reacting mixture maintains titania in a partially reduced state.

Concerning the (CO + H_2) reaction, it is known that SMSI conditions do not inhibit the activity of the metal. The first explanation is that active CO and H_2 species are only those whose chemisorption sites are not affected by SMSI (*58*) and are close to the interface perimeter (*59*). The second explanation is that, as soon as the catalyst works, the water formed by the reaction reoxidizes the support (Eq. 12) and destroys, at least partially, the SMSI state (*60, 61*). The initial reaction rate can even be accelerated by the initial increase in temperature due to the exothermicity of reaction (12).

CONCLUSIONS

Under SMSI conditions, real Pt/TiO_2 catalysts contain ionic vacancies in the singly ionized state. The heat of formation of these defects is equal to +81 kcal mol^{-1} and corresponds to the absolute value of the heat of reoxidation of titania by oxygen. These anionic vacancies can be partially filled with oxygen arising from water produced by the methanation reaction, which destroys the SMSI state.

The electrons originating from the first ionization of anionic vacancies are partially trapped by the metal. This electron enrichment of Pt can counteract H_2 or CO chemisorption if the adsorbed species behave as dipoles with a donor character evidenced by electrical conductivity measurements. This could, in particular, explain the decrease in the initial heat of adsorption of hydrogen from 22 to 18.5 kcal mol^{-1} determined by microcalorimetry (*35*).

The occurrence of an electronic factor, in line with previous pioneer works (*46, 62, 63,* and references therein) for metals deposited on semiconductors, is supported by recent papers based on spectroscopic methods, which have evidenced an electron transfer from the support to the metal (*64–66*). It is also substantiated by the existence of SMSI effects induced by replacing the high-temperature reduction of Pt/TiO_2 either by introducing an alkaline additive (*67*) or by doping titania with penta- or hexavalent heterocations (*68, 69*).

In addition, the same concept of electron transfer is commonly used in heterogeneous photocatalysis to account for the reactivity of the same Pt/TiO_2 catalysts when they are illuminated at room temperature with photons capable of exciting electrons from the valence band to the conduction band (*54, 70, 71*).

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