JOURNAL OF CATALYSIS **104**, 136–146 (1987)

A Microcalorimetric Study of Metal–Support Interaction in the Pt/TiO_2 System

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Received March 27, 1986; revised July 31, 1986

Adsorption of hydrogen and carbon monoxide at the surface of anatase-supported platinum was studied by heat-flow calorimetry. When strong metal–support interaction (SMSI) is created by high-temperature (773 K) reduction of the sample in hydrogen, the metal area available for adsorption decreases to 10% of the total area initially present in the sample. However, the reactivity of the remaining metal surface, with respect to either carbon monoxide or hydrogen at 296 K, is similar to the reactivity of normal platinum. These results may be considered as indirect evidence for encapsulation (or decoration) of the metal by the reduced support. The small but significant decrease of the initial heat of adsorption of hydrogen following the development of SMSI indicates that the reduced support modifies the chemical properties of the surface metal atoms. Oxygen interacts at 296 K with the high-temperature pretreated Pt/TiO_2 sample and almost completely suppresses SMSI. The heat of regeneration is identical to the heat of reoxidation of titanium oxide (anatase), pretreated in the same conditions as the Pt/TiO_2 sample. It is close, in absolute value, to the heat of formation of anionic vacancies in the TiO_2 lattice, calculated from equilibrium measurements of electrical conductivity.

INTRODUCTION

When Group VIII metals deposited on transition metal oxide supports are heated in hydrogen at sufficiently high temperatures, their ability to chemisorb hydrogen and carbon monoxide is greatly decreased. This anomalous behavior has been attributed to the existence of strong metal–support interaction (SMSI) (*1*). It is remarkable that SMSI and its consequences can be suppressed simply by oxidation and rereduction at low temperature.

Such an intriguing phenomenon naturally has attracted the attention of many researchers and various hypotheses have been proposed to account for the inhibition of chemisorption at the surface of metals. The SMSI exhibited by titania-supported platinum, for instance, has been attributed variously to (i) the formation of a Pt–Ti alloy (*1*), (ii) the formation of thin raft, pillboxlike structures of Pt atoms (*2*), (iii) the formation of a bond between Pt atoms and Ti^{3+} cations (*1, 3*), and (iv) an electron transfer from the $3d^1$ unpaired electrons of Ti^{3+} to the $5d$ orbitals of Pt atoms (equilibrium between the Fermi levels of electrons in the metal and the semiconducting support) (*4*).

Recently, studies with model catalysts have provided evidence that the unusual adsorptive (and catalytic) properties associated with SMSI are related to the migration of titania onto the metal surface (*5*, and Ref. (*4–11*) therein). However, the stoichiometry of the oxide phase decorating the metal surface is not known. Moreover, some authors claim that suppressed adsorption in the case of SMSI is due to physical blocking of the surface (*5*), whereas others (*6*) believe that, in addition, a chemical interaction between the metal and the segregated oxide film is taking place which modifies the reactivity of the uncovered metal surface.

The present calorimetric study was undertaken with the hope to bring an answer

0021-9517/87 $3.00

TABLE 1

Successive Adsorption Steps on Sample of Pt/TiO$_2$[a]

Step no.[b]	Pretreatment temperature (K)		Adsorption
	In hydrogen	*In vacuo*	
1[c]	473	473	Hydrogen
3	473	673	Hydrogen
5	—	296	Oxygen
6	—	296	Hydrogen
8	573	673	Hydrogen
10	673	773	Hydrogen
12	773	773	Hydrogen
14	—	296	Oxygen
15	—	296	Hydrogen
17	773	773	Oxygen
18	—	296	Hydrogen
19	473	673	Oxygen
20	—	296	Hydrogen
23	473	673	Carbon monoxide
25	773	773	Carbon monoxide

[a] Sample pretreatment sequence: 10^{-3} Pa, 296 K; hydrogen 3.3×10^4 Pa, 296 K; reduction in hydrogen, 2 h, see column 2; treatment under reduced pressure 10^{-3} Pa, 3 h, see column 3; 10^{-3} Pa, 296 K.

[b] Missing numbers correspond to experiments during which the reversibility of adsorption was investigated.

[c] The pretreatment procedure before the first adsorption step is given in the text.

to some of these questions. Previous work has indeed demonstrated that adsorption calorimetry is a sensitive tool for probing the changes of surface reactivity caused, e.g., by alloying (*7*) or induced by preadsorbed species (*8*). Moreover, thermochemical data may also be used to identify the titanium oxide species associated with SMSI.

EXPERIMENTAL

A batch of Pt/TiO$_2$ catalyst was prepared by the impregnation of nonporous Degussa P-25 anatase (50 m^2 g^{-1}) with chloroplatinic acid. The suspension was dried in a rotating flask by evacuation at 353 K and then in an oven at 383 K for 2 h. The reduction in a hydrogen flow at 753 K for 15 h was preceded and followed by a nitrogen flush during the increase and decrease in temperature. The batch was kept in a vial until further use.

Chemical analysis indicated that the metal loading was 5.0 wt%. Transmission electron microscopy showed that the sizes of the platinum particles in the sample ranged from 1 to 3 nm, with an average at ca. 2.0 nm (*4*). Hydrogen adsorption (42 μmol g^{-1}) indicated a 34% dispersion of the metal (*4*).

A single sample (264 mg) was taken from the batch and used for all experiments described in this paper. After being introduced into the calorimeter cell, the sample was first placed under reduced pressure (10^{-3} Pa) at 296 K, and then reduced overnight in hydrogen at 473 K. Hydrogen was evacuated at 473 K and the sample, kept under reduced pressure at 473 K for 3 h and then cooled to 296 K, was used in the first adsorption experiment (hydrogen). All the successive adsorption steps carried out with this sample are reported in Table 1, which moreover indicates the temperatures selected, in each case, for the sample pretreatment in hydrogen and then *in vacuo*. In the text and particularly in the Figures, the code, e.g., (R200V400)(3), designates adsorption step 3, in Table 1, which followed the pretreatment of the sample in hydrogen at 473 K (200°C) and then *in vacuo* at 673 K (400°C).

In all cases, adsorption was carried out by introducing successive doses of adsorptive onto the sample located in the calorimeter cell. The heat evolved, the quantity of gas adsorbed, and the equilibrium pressure were measured at the end of the interaction of each dose, i.e., when the calorimeter had returned to thermal equilibrium. Introduction of doses was repeated until the equilibrium pressure reached ca. 200 Pa. Evacuation of the gas phase produced the desorption of the adsorbate fraction reversibly held at 296 K. In some cases (Table 1, note b), a second adsorption of the same gas allowed determination of the volume

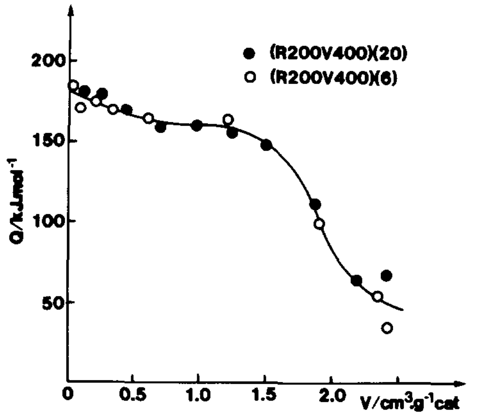

FIG. 1. Differential heats for the adsorption of hydrogen at 296 K on a Pt/TiO_2 sample precovered with oxygen.

and the differential heats of adsorption of the reversible fraction. Comparison of the two successive adsorption experiments gave the volume of the irreversible fraction.

The heat-flow microcalorimeter, the ancillary volumetric line, and the calibration procedures have already been described (*9*). Throughout this work, the calorimeter was maintained at 296 K.

RESULTS

Reproducibility of the results and a possible aging of the sample were tested by repeating some steps in the adsorption sequence. Figure 1, for instance, reports the calorimetric data for steps 6 and 20 in Table 1 (adsorption of hydrogen on the oxygen-precovered sample). The results of both experiments are identical within experimental error. The same observation was also made in the case of steps 1 and 8 in Table 1 (see Fig. 3). Thus, it appears that, even though the sample was studied for more than a year and was pretreated several times at 773 K in order to develop SMSI, no permanent aging was detected and SMSI was found to be reversible.

As expected, reduction in hydrogen at 773 K develops SMSI and drastically decreases the subsequent affinity of the sample for hydrogen at 296 K (Fig. 2, curve 3). Moreover, the small adsorption of hydrogen which remains is reversible: a desorption at 296 K, following the hydrogen adsorption (step 12, Table 1), apparently removes all the adsorbed hydrogen from the surface since a second adsorption of hydrogen (step 13) yields volumetric (Fig. 2, curve 3) and calorimetric results which are nearly identical to those recorded during the first adsorption.

After a pretreatment in hydrogen and then *in vacuum* at 473 K, the behavior of the sample is normal (Fig. 2, curve 1). The hydrogen coverage attained at 200 Pa is close to the monolayer capacity (0.98 cm^3 g^{-1}) (*4*). Reduction in hydrogen at 673 K, followed by a treatment under reduced pressure at 773K, already generates some SMSI since adsorption of hydrogen is then smaller than expected for a normal oxide-supported platinum sample (Fig. 2, curve 2).

In all cases, the differential heats of adsorption of hydrogen at 296 K decrease regularly with increasing surface coverage (Fig. 3), the Q vs θ curves being nearly straight lines. This is in agreement with previous calorimetric results for the adsorption of hydrogen on platinum (*10*) and on nickel (*7*). The platinum surface reactivity with respect to hydrogen remains unchanged when the pretreatment temperature increases from 473 to 673 K (Fig. 3, curve 1). As already shown in Fig. 2 (curve 2), the

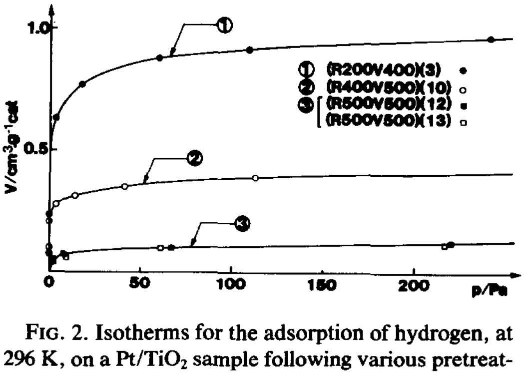

FIG. 2. Isotherms for the adsorption of hydrogen, at 296 K, on a Pt/TiO_2 sample following various pretreatments.

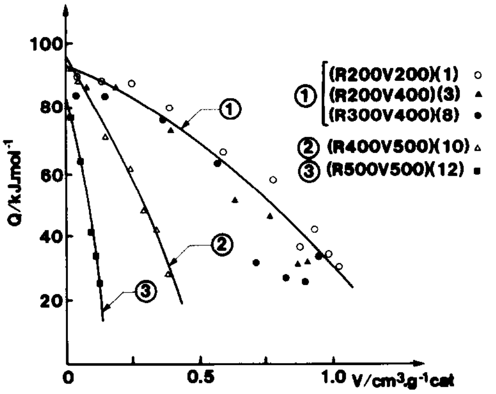

FIG. 3. Differential heats for the adsorption of hydrogen at 296 K on a Pt/TiO$_2$ sample following various pretreatments.

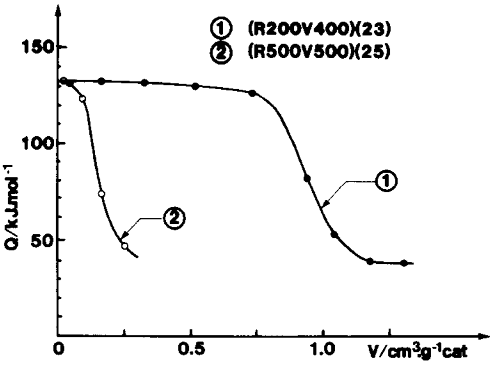

FIG. 4. Differential heats for the adsorption of carbon monoxide at 296 K on a Pt/TiO$_2$ sample following various pretreatments.

(R400V500) pretreatment decreases the amount of hydrogen adsorbed at a maximum pressure of 200 Pa but the initial heat of adsorption (Fig. 3, curve 2) is still identical to that recorded on a normal platinum surface (Fig. 3, curve 1). Finally, when SMSI are present, the initial heat of adsorption of hydrogen decreases (Fig. 3, curve 3). However, the decrease is moderate (from 93 kJ mol^{-1}, curves 1 and 2 to 80 kJ mol^{-1}, curve 3) so that one could almost exactly reconstruct the curves in Fig. 3 by simply multiplying all the abscissae of a given curve by constant factors.

The Q vs θ curve for the adsorption of carbon monoxide at 296 K on a normal platinum surface (Fig. 4, curve 1) is qualitatively very similar to the curve recorded in the case of nickel (*11*). In both cases, differential heats are constant for low surface coverages and then decrease rapidly, probably when direct or indirect lateral interactions between adspecies appear. When SMSI is present (Fig. 4, curve 2), the initial heat of adsorption of carbon monoxide is not modified, but a further adsorption produces lower heats: thus the Q vs θ curve does not exhibit any plateau but immediately resembles the final part of the Q vs θ curve recorded for a normal platinum sample.

Since it has been shown that SMSI is related to the reduction of the support (*12*), the adsorption of oxygen was studied on the Pt/TiO$_2$ sample in the presence or the absence of SMSI (Fig. 5).

However, before attempting an interpretation of these data, it is useful to consider the results obtained during the successive adsorption of hydrogen, oxygen, and hydrogen carried out on the Pt/TiO$_2$ sample when SMSI was present (steps 12, 14, and 15, Table 1) or not (steps, 3, 5, and 6, Table 1). Between each adsorption in the sequences, the sample was simply outgassed at 296 K (Table 1).

The volumetric and calorimetric data for

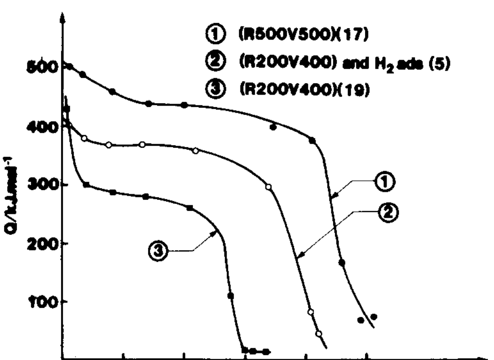

FIG. 5. Differential heats for the interaction of oxygen at 296 K with a Pt/TiO$_2$ sample after various pretreatments.

TABLE 2

Volumetric and Calorimetric Data for the Adsorption of Oxygen (Step 19) and for the Successive Adsorptions of Hydrogen (Step 3), Oxygen (Step 5), and Hydrogen (Step 6) on a Pt/TiO_2 Sample after the (R200V400) Pretreatment

Step	Adsorptive	V_{ads} (total) ($cm^3\ g^{-1}$)	V_{ads} (irrev) ($cm^3\ g^{-1}$)	ΔH ($kJ\ mol^{-1}$)
19	Oxygen	0.85	0.75	−301
3	Hydrogen	1	0.5	−76
5	Oxygen	1	1	−360
6	Hydrogen	2.5	2	−167

the adsorption of oxygen and for the H_2–O_2–H_2 adsorption sequence, in the case of the normal platinum surface, are collected in Table 2. Column 3 lists the (total) amounts adsorbed at approx 200 Pa; the amounts remaining adsorbed after outgassing are collected in column 4, and the average heats of adsorption for the fractions irreversibly adsorbed on the metal surface are given in column 5. The stoichiometry of the successive surface interactions can be easily deduced from the volumetric data in Table 2 (hereafter, the volume of gas consumed in each surface interaction will be given in parentheses).

As already mentioned, the total amount of hydrogen adsorbed at ca. 200 Pa approximately corresponds to the formation of a complete monolayer, when it is assumed, as usual, that each surface platinum atom adsorbs one hydrogen atom:

$$2H_2 + 4Pt_s \rightarrow 4Pt_s\text{–}H\ (1\ cm^3\ g^{-1}).$$

However, after evacuation of the gas phase, the irreversibly adsorbed hydrogen species only correspond to half a monolayer:

$$\text{Step 3: } 4Pt_s + H_2 \rightarrow 2Pt_s\text{–}H + 2Pt_s \quad (0.5\ cm^3\ g^{-1}).$$

When oxygen contacts the sample containing preadsorbed hydrogen (step 5 in Tables 1 and 2), it reacts with preadsorbed hydrogen:

$$2Pt_s\text{–}H + \tfrac{1}{2}O_2 \rightarrow 2Pt_s + H_2O_x \quad (0.25\ cm^3\ g^{-1})$$

("x" means that generated water may either desorb or remain in the adsorbed state). Then, oxygen reacts at the metal surface: this interaction has been investigated separately (step 19 in Tables 1 and 2):

$$\text{Step 19: } 4Pt_s + \tfrac{3}{2}O_2 \rightarrow (Pt_4O_3)_s \quad (0.75\ cm^3\ g^{-1}).$$

The formula $(Pt_4O_3)_s$ is a convenient representation of the average composition of the platinum surface containing irreversibly adsorbed oxygen; it does not imply the existence of a specified oxide phase. The present data on Pt_s–O and Pt_s–H stoichiometries are in agreement with previous results concerning Pt/SiO_2 samples (*13*).

Step 5 (Tables 1 and 2) may therefore be summarized by

$$\text{Step 5: } 2Pt_s\text{–}H + 2Pt_s + 2O_2 \rightarrow (Pt_4O_3)_s + H_2O_x\ (1\ cm^3\ g^{-1}).$$

Finally, when hydrogen (step 6 in Tables 1 and 2) reacts with the sample containing preadsorbed oxygen, two interactions take place:

$$(Pt_4O_3)_s + 3H_2 \rightarrow 4Pt_s + 3H_2O_x \quad (1.5\ cm^3\ g^{-1})$$

$$\text{Step 3: } 4Pt_s + H_2 \rightarrow 2Pt_s\text{–}H + 2Pt_s \quad (0.5\ cm^3\ g^{-1})$$

so that

$$\text{Step 6: } (Pt_4O_3)_s + 4H_2 \rightarrow 2Pt_s\text{–}H + 2Pt_s + H_2O_x\ (2\ cm^3\ g^{-1}).$$

The calorimetric data in Table 2 may be used in thermochemical cycles to check the validity of this analysis of the adsorption sequence. Cycle 1 in Table 3 indicates that water produced during the sequence (steps 5 and 6, Table 2) remains adsorbed with the production of an average enthalpy of adsorption equal to −104 kJ mol^{-1}. Cycle 2 is

TABLE 3

Thermochemical Cycles Based on the Calorimetric Data for the Successive Adsorptions of Hydrogen, Oxygen, and Hydrogen on a normal Pt/TiO$_2$ Sample

		(kJ mol^{-1})	$\Delta H_{\text{reaction}}$ (kJ)
Cycle 1			
Step 5	$2Pt_s–H + 2O_2 \rightarrow (Pt_4O_3)_s + H_2O_x$	−360	−720
Step 6	$(Pt_4O_3)_s + 4H_2 \rightarrow 2Pt_s–H + 2Pt_s + 3H_2O_x$	−167	−668
	$4H_2O \rightarrow 4H_2 + 2O_2$	+243	+972
	$4H_2O \rightarrow 4H_2O_x$	−104	−416
Cycle 2			
Step 5	$2Pt_s–H + 2Pt_s + 2O_2 \rightarrow (Pt_4O_3)_s + H_2O_x$	−360	−720
	$H_2O_x \rightarrow H_2O$	+104	+104
Step 19	$(Pt_4O_3)_s \rightarrow 4Pt_s + \frac{3}{2}O_2$	+301	+452
	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	+243	+243
Step 3	$2Pt_s–H + 2Pt_s \rightarrow 4Pt_s + H_2$	+76	+79

a test of the internal coherence of volumetric and thermochemical data: the heat of adsorption of hydrogen deduced from the cycle is, indeed, identical to the heat experimentally measured during step 3 (Table 2). Cycle 2 may therefore be considered an indication that the hypotheses which were introduced in the calculations are valid. Two of them are particularly important:

(i) The water molecules produced during the adsorption sequence remain adsorbed on the TiO$_2$ support and not at the metal surface (this hypothesis is included in the derivation of the equations for steps 6 and 5).

(ii) Adsorptions of oxygen on a freshly reduced Pt/TiO$_2$ sample (step 19, Tables 1 and 2) or on a Pt/TiO$_2$ sample containing preadsorbed hydrogen (step 5, Tables 1 and 2) yield identical oxygen adspecies at the metal surface, which therefore have the same reactivity with respect to hydrogen (the $(Pt_4O_3)_s$ species are supposed to be identical in steps 5 and 19, Table 3, cycle 2).

A similar titration sequence was performed when SMSI was present in the sample (successive adsorptions of hydrogen, oxygen, and hydrogen, steps 12, 14, and 15 in Table 1). It must be first observed that, since adsorption of hydrogen on Pt/TiO$_2$ is reversible when SMSI is present (Fig. 2), the volumetric and calorimetric data for the adsorption of oxygen following the (R500V500) pretreatment of the sample (step 17, Table 1) are similar to the data recorded during the second step (oxygen interaction) of the titration sequence (step 14, Table 1). In this case, the titration sequence is reduced to two steps (O$_2$–H$_2$). They are presented in Figs. 5 and 6 (adsorption of oxygen) and Fig. 7 (adsorption of hydrogen).

When SMSI is present, the sample reacts with more oxygen than in its absence (Fig. 6) and the differential heats produced by the interaction are higher (Fig. 5). These large differences are in sharp contrast with the nearly identical results recorded for the last step of the two titration sequences (hydrogen interaction, Fig. 7). From the similarity of curves 1 and 2 in Fig. 7, one may conclude that, after the oxygen step in both titration sequences, the sample has the same reactivity with respect to hydrogen.

This is not completely true, since there

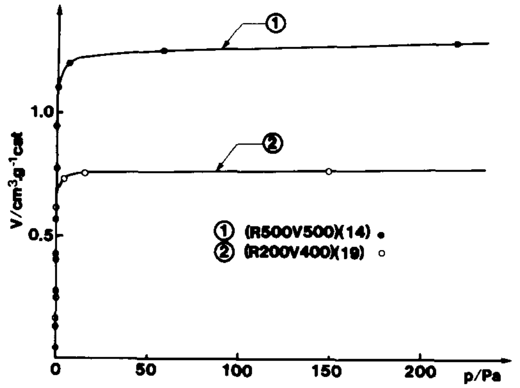

FIG. 6. Isotherms for the interaction of oxygen at 296 K with a Pt/TiO$_2$ sample following various pretreatments.

are indeed some differences between curves 1 and 2 (Fig. 7): the initial values of curve 2 are higher than those corresponding to curve 1 and the descending branches of the curves are not superimposed. Since steps 6 and 15 (Table 1), corresponding to curves 1 and 2 in Fig. 7, include several interactions (see the discussion for step 6 presented hereabove), it is not possible to propose a detailed interpretation for these differences and, in the following discussion, we shall simply consider that oxygen at 296 K almost completely regenerates the normal behavior in Pt/TiO$_2$ and, therefore, almost completely removes the strong metal–support interactions.

Without introducing any additional hypothesis, it is possible to consider that all interactions taking place during steps 14 or 17 (Table 1, Fig. 5) belong to two groups: the interactions which regenerate the normal Pt/TiO$_2$ sample and the interactions between oxygen and the regenerated sample. As a first approximation (see the preceding paragraph), the volumetric and calorimetric data relative to the interactions of the second group are identical for the regenerated sample and for the normal sample: therefore, they are given in Fig. 6 (curve 2) and Fig. 5 (curve 3). Consequently the volumetric and calorimetric data corresponding to the interactions of the first group (sample regeneration) may be deduced from the difference between curves 1 and 2 in Fig. 6 and between curves 1 and 3 in Fig. 5. Thus, the amount of oxygen which is consumed for the sample regeneration (supposed to be complete) equals 0.5 cm^3 g^{-1} (difference between curves 1 and 2 in Fig. 6). The average heat produced by the regeneration can be calculated from the difference between the integral heats recorded during steps 17 and 19 (Table 1) for a given oxygen equilibrium pressure (e.g., 100 Pa). The calculated heat of regeneration is 653 kJ mol^{-1} O$_2$.

DISCUSSION

Titanium oxide is reduced when it is heated in hydrogen (or carbon monoxide) at 773 K. Gravimetric experiments have shown, for instance, that a sample of anatase (41 m^2 g^{-1}), similar to the support used in the present study, loses 0.26 mg O$_2$ g^{-1} TiO$_2$ (0.15 cm^3 O$_2$ g^{-1} TiO$_2$) when it is reduced by hydrogen (1.3 × 10^4 Pa) at 773 K (*14*). However, the weight loss is very slow and the value was recorded after a 24-h treatment. Platinum in the Pt/TiO$_2$ system clearly acts as a catalyst for the activation of hydrogen since the support in Pt/TiO$_2$ loses more oxygen (0.5 cm^3 g^{-1}) compared to 0.15 cm^3 g^{-1}) in a shorter time (2 h com-

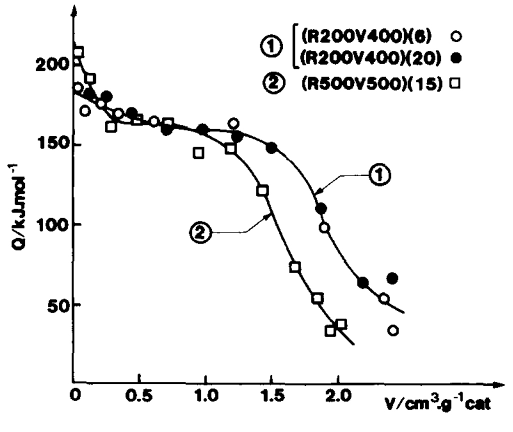

FIG. 7. Differential heats for the interaction of hydrogen at 296 K with a Pt/TiO$_2$ sample following an oxygen adsorption.

pared to 24 h) than pure titania. Therefore, it is likely that the support reduction in the Pt/TiO_2 sample begins in the vicinity of the metal particles and involves hydrogen species, activated by the metal then migrating to the support. Similar conclusions were already deduced from electrical conductivity measurements (*4*).

The high-temperature (773 K) hydrogen treatment of pure anatase produces extensive modifications in the oxide surface composition and structure, as demonstrated, for instance, by the appearance of a titanium metal mirror on the cold trap walls, corresponding to the vaporization of 8.8×10^{17} atom Ti g^{-1} TiO_2 out of the titania sample in 24 h (14). However, there is no evidence indicating that, with the procedure used in the present study, the support in the Pt/TiO_2 system is reduced to metal.

If oxygen (0.5 cm^3 g^{-1}) consumed during the sample regeneration reacted with defects regularly distributed in the bulk or at the surface of the reduced oxide, the oxide stoichiometry would be respectively equal to $TiO_{1.996}$ (in agreement with previous results) (*15*) or $TiO_{1.95}$, i.e., in either case, very close to that of anatase. However, there is not evidence indicating that the distribution of defects is uniform either in the bulk or at the surface of the reduced support.

During the regeneration of the Pt/TiO_2 sample in oxygen at 296 K, the support recovers its initial surface properties. As discussed earlier, the nearly identical results recorded during the interaction of hydrogen with oxygen-pretreated samples, in which SMSI had been initially developed or not (Fig. 7), indeed show not only that the same $(Pt_4O_3)_s$ species are present at the metal surface but also that the support, in both cases, retains water with the production of the same heat of adsorption (step 5 in cycle 2, Table 3).

The calculated heat of regeneration (653 kJ mol^{-1} O_2) is much lower than all the values collected in Table 4. Therefore neither titanium metal nor one of the oxides, listed in Table 4 exist in, or on, the reduced support.

TABLE 4

Enthalpies of Formation of Titanium Oxides

	$\Delta H_{298.16\,K}$		Ref.
	kJ mol^{-1} oxide	kJ mol^{-1} O_2	
$Ti(\alpha) + \frac{1}{2}O_2 \rightarrow TiO(\alpha)$	−523	−1046	(*16*)
$2Ti(\alpha) + \frac{3}{2}O_2 \rightarrow Ti_2O_3(\alpha)$	−1509	−1006	(*16*)
$3Ti(\alpha) + \frac{5}{2}O_2 \rightarrow Ti_3O_5(\alpha)$	−2460	−984	(*16*)
$4Ti(\alpha) + \frac{7}{2}O_2 \rightarrow Ti_4O_7$	−3351[a]	−957.5	(*17*)
$Ti(\alpha) + O_2 \rightarrow TiO_2(rutile)$	−955	−955	(*16*)
$2TiO(\alpha) + \frac{1}{2}O_2 \rightarrow Ti_2O_3(\alpha)$	−463	−926	
$3TiO(\alpha) + O_2 \rightarrow Ti_3O_5(\alpha)$	−891	−891	
$TiO(\alpha) + \frac{1}{2}O_2 \rightarrow TiO_2(rutile)$	−432	−864	
$Ti_2O_3(\alpha) + \frac{1}{2}O_2 \rightarrow 2TiO_2(rutile)$	−401	−802	
$Ti_3O_5(\alpha) + \frac{1}{2}O_2 \rightarrow 3TiO_2(rutile)$	−405	−810	
$Ti_4O_7 + \frac{1}{2}O_2 \rightarrow 4TiO_2(rutile)$	−469	−938	

[a] Calculated for $T = 1673$ K.

The substoichiometric oxide generated in Pt/TiO_2 by the high-temperature reduction treatment is the same one that a similar treatment creates in pure titania: the average heat of regeneration, deduced from the present calorimetric data (653 kJ mol^{-1} O_2), is indeed in excellent agreement with the differential heats of reoxidation of reduced anatase, calorimetrically measured at 773 K (628 to 670 kJ mol^{-1} O_2) (*14*). This agreement indicates, moreover, that any modification of the metal phase in Pt/TiO_2 which may occur during the regeneration treatment does not influence the calorimetric results in an appreciable manner.

The average heat of regeneration, calculated from the present calorimetric data, is also similar to the enthalpy change (−686 kJ mol^{-1} O_2) produced by the filling of singly ionized, anionic vacancies by oxygen, which was calculated from electrical conductivity measurements for pure anatase in equilibrium with reduced oxygen pressures (*18*).

Finally, it appears that the high-temperature reduction, which generates SMSI in Pt/TiO_2, creates lattice defects in or on the support which are not different from those created by a similar treatment in pure anatase, i.e., in both cases, singly ionized anionic vacancies. The calorimetric data recorded during the regeneration treatment provide no direct evidence on the nature of SMSI. They simply indicate that the results formerly obtained for the high-temperature reduction of anatase are still valid for Pt/TiO_2 samples.

The calorimetric data for the adsorption of both hydrogen and carbon monoxide (Figs. 3 and 4) yield more useful evidence on SMSI than the regeneration data.

As discussed earlier (*7*) and confirmed in the present study by the constant heats recorded up to a coverage of 0.75 $cm^3\ g^{-1}$, in the case of carbon monoxide adsorption (Fig. 4), the almost linear decrease of the differential heats of adsorption of hydrogen with increasing coverage (Fig. 3) is the result not of a preexisting heterogeneity at the metal surface but of an energetic heterogeneity induced by previously adsorbed hydrogen species. Therefore, the steeper decline of the hydrogen adsorption heats, observed when the sample has been subjected to progressively more rigorous reduction treatments (Fig. 3), could be explained either by a more intense induction effect of preadsorbed hydrogen, related to some progressive modification of the metal electronic properties or by the same induction effect applied to a progressively smaller metal area. Calorimetric studies of the adsorption of hydrogen on pure and alloyed nickel catalysts (*7*) have indicated that the Q vs θ curves have the same slope for both pure nickel metal and its copper alloys. Therefore, in the case of nickel, induced heterogeneity is not very sensitive to a modification of the metal electronic properties. Some results obtained with Pt/SiO_2, Pt/NaY zeolite, and Pt–Mo/SiO_2 catalysts indicate that this is also the case for platinum (*19*). Therefore, the curves in Fig. 3 suggest that the metal area available for hydrogen adsorption is drastically decreased when SMSI is present: from the slopes of the curves, one can estimate that 10% only of the total metal sites in the normal Pt/TiO_2 sample remain available after the high-temperature treatment.

The value of the initial heat of adsorption of hydrogen, extrapolated to zero coverage, is related to the metal electronic properties: when nickel is, for example, alloyed with 20 at% Cu, the initial heat of adsorption of hydrogen decreases from 112 to 85 kJ mol^{-1} and the decrease has been correlated with the decrease, upon alloying, of the electron density of states, at the Fermi level, for surface nickel atoms (*7*). There is a small, yet significant, decrease of the initial heat of adsorption of hydrogen when SMSI is generated in the Pt/TiO_2 system (from 93 to 80 kJ mol^{-1}, Fig. 3). This decrease could be taken as an indication that SMSI decreases the electron density of states, at the Fermi level, for surface platinum atoms, as a result of either a progressive filling of the 5*d* empty levels with $3d^1$ unpaired electrons of Ti^{3+} ions, as suggested earlier (*4*), or a displacement of the relative position of the 5*d* and 6*s* bands in surface platinum atoms.

As long as the density of carbon monoxide adspecies remains low at a nickel surface (less than 20%), the differential heat of adsorption of carbon monoxide remains constant (*11*). Induced heterogeneity develops when this coverage is exceeded and, consequently, the heat of adsorption of further quantities of carbon monoxide decreases. Similar results were obtained in the present study when carbon monoxide was adsorbed on the normal Pt/TiO_2 sample (Fig. 4), although the limiting coverage value appears to be close to 37.5% in the case of platinum. After a high-temperature reduction which develops the SMSI, the affinity of the sample for carbon monoxide decreases regularly with increasing coverage and the maximum coverage attained at, e.g., 100 Pa is only 20% of that for normal Pt/TiO_2. Since the initial heat of adsorption of carbon monoxide is not modified by the presence of the SMSI, the low maximum coverage and the regular decrease of the Q vs θ curves indicate that the free metal surface is small in the presence of SMSI.

From the data reported in Figs. 3 and 4, average heats of adsorption (for a constant, equilibrium pressure of ca. 150 Pa) can be easily calculated. For both hydrogen and carbon monoxide, the average heat of adsorption decreases when the Pt/TiO$_2$ sample is subjected to a more rigorous pretreatment, developing SMSI. It decreases from 62.2 to 53.9 kJ mol^{-1} in the case of hydrogen, and from 105.5 to 86.4 kJ mol^{-1} in the case of carbon monoxide. The present results are in qualitative agreement with the integral heats, recently reported for similar systems by Vannice *et al.* (*20*). According to these authors, the calorimetric results clearly indicate "a change in the chemical nature of surface Pt atoms because of its contact with a TiO$_x$ surface." We agree with this conclusion in the case of hydrogen since the decrease of the average heat of adsorption then reflects the decrease of the initial heat of adsorption (Fig. 3) and, therefore, as discussed earlier, a modification of the electronic nature of surface Pt atoms. However, in the case of carbon monoxide, SMSI does not modify the initial heat of adsorption (Fig. 4); it drastically decreases the number of available adsorption sites and thus strongly enhances induced heterogeneity. The decrease of the average heat of adsorption is then due to coverage effects and not to a modification of the properties of the metal. Since both so-called "electronic" and "geometric" effects can similarly modify the average energy of adsorbate–adsorbent bonds, the interpretation of observed changes in integral heats of adsorption is not straightforward. Plots of differential heats of adsorption vs coverage yield more information and therefore are more easily and reliably interpreted. Whenever possible, the determination of differential heats of adsorption should be preferred to that of average or integral heats of adsorption.

CONCLUSIONS

In the course of the present calorimetric study of SMSI in the Pt/TiO$_2$ system, the following observations have been made:

After a prolonged series of oxidizing or reducing treatments, including several severe ones at a high temperature (773 K), no aging has been detected and the Pt/TiO$_2$ sample still demonstrates the same surface properties, with respect to hydrogen, carbon monoxide, or oxygen.

The phenomenon responsible for SMSI is totally reversible. SMSI was almost completely suppressed in our sample by an oxygen treatment at 296 K.

After a high-temperature reduction generating SMSI, the Pt/TiO$_2$ system is more reduced than pure anatase would be after the same treatment; the metal acts as a catalyst for the reduction of the support.

The heat produced during the oxygen regeneration treatment at 296 K is (i) larger than the heat corresponding to the interaction of oxygen with preadsorbed hydrogen, and (ii) smaller than the heats produced by the oxidation of titanium or known suboxides to TiO$_2$. The experimental heat of regeneration of the Pt/TiO$_2$ sample is identical to the calorimetrically determined heat of reoxidation of reduced anatase and, in absolute value, it is close to the heat of formation of singly ionized, anionic vacancies in anatase.

After a high-temperature reduction generating SMSI in the sample, 90% of the metal adsorption sites present in a normal Pt/TiO$_2$ sample are inactive with respect to either hydrogen or carbon monoxide.

In the SMSI state, the initial heat of hydrogen chemisorption is decreased and adsorption is almost totally reversible. On the contrary, the major part of carbon monoxide is irreversibly adsorbed and the initial heat of its adsorption is equal to that measured with a normal sample.

In recent publications (*6, 21*), SMSI is explained by the combined effects of (i) encapsulation or decoration of the metal by the reduced support and (ii) electronic interaction of the reduced support with the metal. The small, yet significant, decrease of the initial heat of adsorption of hydrogen, following a high-temperature reduction of the Pt/TiO_2 sample, may be considered as direct evidence that the reduced support induces a change in the electronic properties of surface platinum atoms, e.g., their electron density of states at the Fermi level (*7*). Carbon monoxide is a less sensitive probe of this modification.

The present calorimetric study has not provided any direct evidence on encapsulation. The fact that the adsorptive properties of the small metal area which is still reactive after a high-temperature reduction remain similar to that of platinum at the surface of a normal sample of Pt/TiO_2 may be construed as indirect evidence for encapsulation or decoration. However, no new oxide phase, which would for instance migrate and encapsulate the metal particles, has been identified. The support in Pt/TiO_2 after a high-temperature reduction is, within experimental incertitude, not different from pure, reduced anatase. In both cases, the lattice defects created by reduction at 773 K probably are isolated, singly ionized, anionic vancancies.

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