JOURNAL OF CATALYSIS **113**, 96–105 (1988)

EPR Characterization of Ti^{3+} Ions at the Metal–Support Interface in Pt/TiO_2 Catalysts

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Received December 22, 1987; revised March 7, 1988

Titania-supported Pt catalysts prepared by cation exchange 0.44 and 1.0 wt% loading and reduced at low, medium, and high temperatures (513, 573, and 773 K, respectively) were studied by EPR. The spectra of four different Ti^{3+} ions have been resolved at 17 K; only two of these species are surface Ti^{3+} which are sensitive to CO or H_2 adsorption. One of these surface species, characterized by an axial g tensor at $g_\perp = 1.969$ and $g_\parallel = 1.936$, is specific of the presence of platinum since it does not exist in reduced TiO_2. Its signal undergoes a temperature-dependent broadening effect which is mostly removed at 17 K; this is related to its proximity to a platinum particle allowing an efficient relaxation mechanism through the conduction electrons of the metal. This ion can be titrated reversibly by hydrogen and irreversibly by carbon monoxide. Its intensity relative to other Ti^{3+} ions increases when the reduction temperature increases from 373 to 573 K. This trend is probably maintained for the reduction at 773 K, but no accurate conclusions can be drawn since the EPR signal undergoes a strong decrease in intensity and line broadening due to spin pairing and spin–spin relaxation mechanisms. These two effects are related to the increase of Ti^{3+} concentration in the vicinity of platinum, the metal promoting the reduction of the support. This species, located at the metal–support interface, may either account for the TiO_x fragments of the support which migrate on the metal particles in the SMSI state or be a precursor of these fragments.

INTRODUCTION

The strong metal–support interaction (SMSI) is produced by reduction in hydrogen at high temperatures (>700 K) of a Group VIII metal supported on a reducible oxide such as TiO_2; it has been operationally characterized by a strong depression of the hydrogen uptake without sintering (*1*) of the metal particles. In the case of the Pt/TiO_2 system, it has been associated with a change of morphology of the Pt particle which adopts a pillbox shape, while the support around the particle develops a Ti_4O_7 crystalline phase (*2*). A loss of catalytic activity is also observed and was previously attributed to an electronic effect (*1b, 3*). In this model, an electron transfer from the support to the metal was required to explain the effect of SMSI on chemisorption and activity; it was proposed that the transfer occurs when the Fermi level of the M/TiO_2 system is raised by the concentration of Ti^{3+} in the support which increases during the reduction process (*4a–c*). In fact XPS studies evidence a shift of the binding energy consistent with an electron transfer to the metal (*5a–c*), but it is a very small effect (binding energy shift of ~0.2 eV). A purely geometric origin for SMSI, due to TiO_x suboxide covering the metal particles, was suggested in 1982 by Mériaudeau *et al.* (*6a*) as a possible alternative to the electronic model. This hypothesis was previously used by von Engels in 1981 to explain the selectivity of a Ni/TiO_2 catalyst (*6b*). The geometric model was quickly adopted in 1983 with more direct evidence such as the Mössbauer spectroscopic study of the Fe/TiO_2 system (*7*), and the deac-

0021-9517/88 $3.00

tivation kinetics of Rh/TiO_2. In the latter, SMSI was found to be a local effect kinetically controlled by diffusion of the support onto the particle from their periphery deactivating the active sites by covering them (*8*). Several studies very recently (*9*) reviewed have confirmed the geometric model. In particular, model catalyst surface studies such as the early work on the Pt/TiO_2 system (*10*) confirm the migration model. The nature of the titanium species which migrates and the state of the metal at the interface is still a matter of discussion. Since reduction of the support is involved at least locally near the particles, the migrating species are supposed to be a suboxide form of titanium, TiO_x, where x is smaller than 2. It has been recently pointed out that H_2 is not only necessary for reduction but also necessary to induce mobility of the support fragments which can be viewed as $HTiO_x$ species (*11*).

This species could involve any oxidation state of titanium lower than 4+. Only the Ti^{3+} ion which is a d^1 system can be detected by electron paramagnetic resonance (EPR) but the characterization of such a $HTiO_x$ species has never been made. The reason for this may be attributed to an oxidation state other than 3+ for titanium in the fragment or to the conditions of observation of such species. In fact, on contact with a metal, a paramagnetic species is expected to have a very short relaxation time due to the interaction of the paramagnetic electron with the conduction electrons of the metal particles. Such a characteristic has been pointed out for Pt^+ ions in the Pt/TiO_2 system (*12*) and recently for Ni^+ ions (*13*) in the Ni/SiO_2 system, whose ions act as an anchoring site for the metal particles.

This study reports an EPR investigation at low temperatures (17 K) of Pt/TiO_2 catalysts reduced at low (513 K), medium (573 K), and high temperatures (773 K) referred to as LTR, MTR, and HTR in the text. Only at such low temperatures for the EPR experiments, were we able to differentiate four different Ti^{3+} species. Two of them are known to be bulk and the third a surface TiO_2 species. The last one, of most interest here, has never been characterized before and is related to the presence of platinum and is located at the metal–support interface; it is either a precursor of the fragment of the support which migrates onto the particle or a part of it.

In a forthcoming paper (*14a*), the reactivity of these catalysts for hydrogenolysis, isomerization, and dehydrogenation of *n*-butane is reported. The results show that the depression of activity is two orders of magnitude between LTR and HTR for platinum relative to four orders of magnitude for rhodium (*14b*) because platinum is already in an intermediate state of interaction between normal and SMSI state at 573 K (minimum temperature necessary to get sufficient hydrogenolysis activity on platinum to measure practically).

EXPERIMENTAL SECTION

Catalysts were prepared by cation exchange from 600 cm^3 of a 10^{-2} *M* solution of $Pt(NH_3)_4(NO_3)_2$ (provided by Alfa/Ventron), and 10 g of a Degussa P-25 TiO_2. Prior to the exchange, TiO_2 was treated at pH 11 in a solution of $NH_4(OH)$ and washed with distilled water until the pH reached the value chosen for the exchange. The pH of the exchange solution was adjusted with NH_3 to 7.5 or 9.1 and the resulting catalyst loading was 0.44 and 1.0 wt%, respectively. The metal content was determined by atomic adsorption of solution obtained from an acid extraction of the platinum. The preparation process is similar to the process used for Rh/TiO_2 and Ir/TiO_2 catalysts (*14b*). Subsequently, the standard reduction treatment was carried out: initial reduction at 773 K in a pure H_2 flow at a rate of 50 cm^3/min, heating rate 3 K/min; storage in a desiccator at 298 K. For each new experiment, the catalyst was oxidized followed by reduction (same heating and flow rate) from 298 K to a temperature indicated as follows: (O 673, R 773) for an oxidation at 673 K, and a reduction at 773 K, respectively, with a final temperature maintained in both cases for 2 h.

The treatments (oxidation, reduction, gas adsorptions) were performed on a vacuum line directly connected to the flow system. The Pyrex reactor was equipped with side arm EPR tubes where the catalyst was transferred and sealed off under reduced pressure of H_2 (~15 Torr). The sealed EPR tubes were mounted with grease-free valves via a break seal allowing subsequent gas adsorption experiments without air exposure. The EPR active O_2^- species (*15*), which are readily produced by a trace of oxygen adsorption or air contamination, were taken as an ultimate probe of leak problems in our experimental process; they were not observed in experiments reported here. For EPR and hydrogen uptakes, H_2, purified in a palladium diffuser, was used for adsorption gas and pressures were measured with a Baratron pressure gauge. Carbon monoxide was purified over reduced Cr/SiO_2 catalysts prior to adsorption on catalysts and pressures monitored as for hydrogen uptakes.

The *X*-band EPR spectra were recorded by an E-9 Varian spectrometer equipped with an E101 Varian microwave bridge and an E-231-T-E102 single cavity. The temperature was controlled by an Air Products LTD-3 Helitran-Cryostat unit working with liquid He and monitored by a thermocouple located near the sample allowing good regulation down to 15 K.

RESULTS

Hydrogen Uptakes

Platinum is not a very active metal for hydrogenolysis and a temperature of at least 573 K was necessary to get a substantial activity for a LTR catalyst (*14a*). We discovered that the hydrogen uptake at that temperature was low for a catalyst prepared by ion exchange. In fact, at a lower temperature of reduction, 513 K, the uptake was greater and this is also reported here.

The hydrogen uptakes of the 0.44 wt% Pt/TiO_2 catalysts after reduction at 513, 573, and 773 K gave the following H/Pt ratios, 0.89, 0.60, 0.07, and, for the higher loading of 1.0 wt%, the H/Pt ratios were 0.59, 0.40, 0.03, respectively. The ratio for low-temperature reduction (LTR = 513 K) indicates good metal dispersion while for the high-temperature reduction (HTR = 773 K) the very low value indicates that the metal particles experience a pronounced SMSI effect. At the medium-temperature reduction (MTR = 573 K) fairly close to LTR conditions, there is an appreciable depression of the hydrogen uptake by about one-third which can be considered an intermediate state of the metal between the normal and the SMSI states. After oxidation at 673 K and reduction under MTR conditions, the original hydrogen uptakes were recovered and were 0.64 and 0.52 expressed as a H/Pt ratio for 0.44 and 1.0 wt% Pt/TiO_2 catalysts, respectively (to be compared with 0.60 and 0.40).

Effect of the Temperature of Reduction on the EPR Signals

All the EPR active species reported in this study are characterized by *g* values ranging from 1.99 to 1.93. These signals are typical of less than half-full *d* orbital metal ions and are attributed to the Ti^{3+} (d^1) ions in different environments. This is consistent with the literature concerning M/TiO_2 systems (*4a*, *16–21*). No signal was detected at lower field in the region corresponding to *g* values greater than 2 where the signal of Pt^+ (d^9) or Pt^{3+} (d^7) ions (*12*) should lie in either the oxidized or the reduced state. Other conditions of treatment such as oxidation in static oxygen can lead to such species (*22*).

The first experiments, depicted in Fig. 1, concern the effect of the temperature of reduction on the EPR signals of 1 wt% Pt/TiO_2 catalyst pretreated in oxygen at 673 K and reduced at 295, 373, 573, and 773 K. At 295 K (spectrum 1a), the reduction leads mainly to two EPR active species charac-

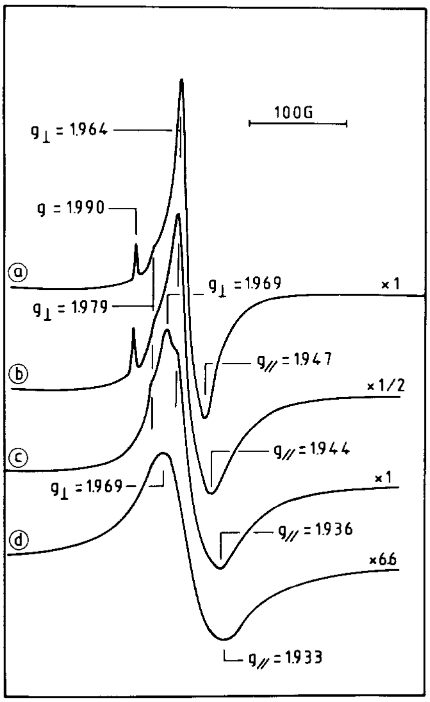

FIG. 1. EPR spectra (*X* band at 17 K) of the 1 wt% Pt/TiO_2 catalyst (O 773, E 773) reduced in a flow of hydrogen at (a) 298, (b) 373, (c) 573, and (d) 773 K. In each case the pressure of H_2 was lowered to 15 Torr at 298 K.

terized by their *g* tensor components at $g_\perp = 1.990$ for the first one and at $g_\perp = 1.964$ and $g_\parallel = 1.947$ for the second referred to as species C. If the reduction was performed at 373 K (spectrum 1b), a third signal at $g_\perp = 1.979$, referred to as species A, arose while the $g_\parallel$ component was shifted from 1.947 to 1.944. In fact, a careful observation of spectrum 1a reveals that species A is already present as a trace after a reduction at 295 K. Increasing the temperature of reduction to 573 K (spectrum 1c) caused the signal at 1.990 to disappear, enhanced the concentration of species A, and shifted further the $g_\parallel$ component toward 1.936. But the striking point is the appearance of a new species B at $g_\perp = 1.969$. Finally, after a reduction of the catalysts at 773 K (spectrum 1d), a broad EPR signal at $g_\perp = 1.969$ and $g_\parallel = 1.933$ was observed with a one order of magnitude less intense signal than the other cases. The spectrum 1d, characterized by a $g_\perp$ component which lies over species B (spectrum 1c), can be viewed as a spectrum dominated by species B with a signal undergoing a broadening effect. Nevertheless, there are little features at the positions where species A, B, and C would lie and spectrum 1d can also be interpreted as the superimposition of the signals of species A, B, and C contributing about equally. The signal at 1.990 is absent after HTR treatment.

Figure 2 shows the EPR spectrum for a reduction at 513 K (spectrum with the full line); the species at 1.990 has almost completely disappeared while species C is observed at $g_\perp = 1.966$ and $g_\parallel = 1.945$. The signal at $g = 1.973$ can be attributed to the superimposition of the signals of species A and B unresolved and located at an intermediate position between the $g_\perp$ components of these two species. The contribution of each species in the spectra has been

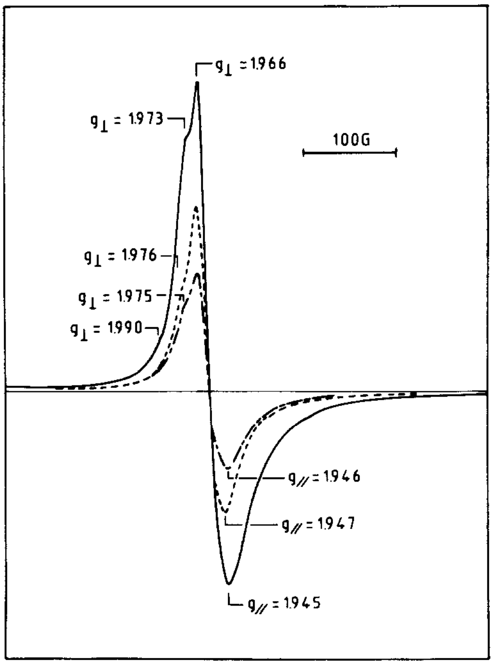

FIG. 2. EPR spectra (*X* band at 17 K) of 1 wt% Pt/TiO_2 (O 673, E 673, R 413), (—) under a pressure of 15 Torr of H_2, (—) evacuated 1 min, and (---) evacuated 5 min under 10^{-4} Torr.

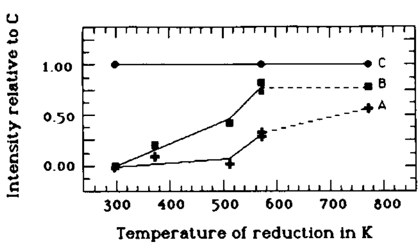

FIG. 3. Relative variation of intensity of Ti^{3+} EPR signals versus the temperature of reduction of the 1 wt% Pt/TiO_2 catalyst with signal C at $g_\perp = 1.964$ taken as reference: species A (+), B (■) and C (●).

obtained by deconvolving the EPR signal taken as a sum of the signal of each species A, B, and C. The result is reported in Fig. 3 versus the temperature of reduction with species C taken as a reference in order to put more emphasis on the relative variation of species A and B. The variation of intensity of species C is plotted separately in Fig. 4.

The spectra of 1 wt% Pt/TiO_2 catalyst after reduction at 573 and 773 K shown in Fig. 5 were taken at 123 K. The comparison of these spectra with spectra c and d of Fig. 1 taken at 17 K makes two points: (i) at 123 K, the spectra look almost isotropic, and (ii) the $g_\parallel$ are shifted upfield (toward low g values) from 1.936 and 1.933 to 1.933 and 1.921 for MTR and HTR conditions, respectively. This is typically due to a line broadening effect which can be attributed to a very efficient relaxation mechanism. This could be due to short distances between Ti^{3+} ions which favor the spin–spin relaxation mechanism which is a temperature-independent action. This mechanism accounts for a part of the broadening of the signals of HTR catalysts. In fact, at 17 or 123 K, the quasi-isotropic line in both cases is due to a broad intrinsic linewidth washing out the powder pattern shape of the anisotropic g tensor expected for surface species. A temperature-dependent relaxation mechanism removed only at very low tempertures is characteristic of the interaction of unpaired electrons with conduction electrons of a metal which can be encountered here in platinum particles. This is particularly true for the spectra of MTR sample (Figs. 1c and 5, full line). The broadening for MTR sample is due to the proximity of Ti^{3+} ions and the metal particles and not to an effect of concentration near the particles as is the case for HTR samples. The spectrum of TiO_2 without platinum reduced at 573 K exhibits a signal due to the superimposition of the signal of species A and C; no species B was detected in this case.

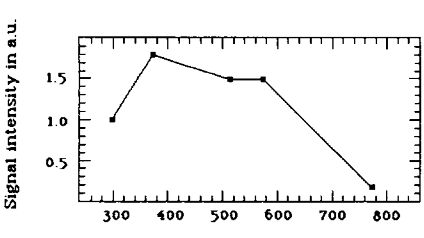

FIG. 4. Variation of EPR signal intensity of species C versus the temperature of reduction of the 1 wt% Pt/TiO_2 catalyst.

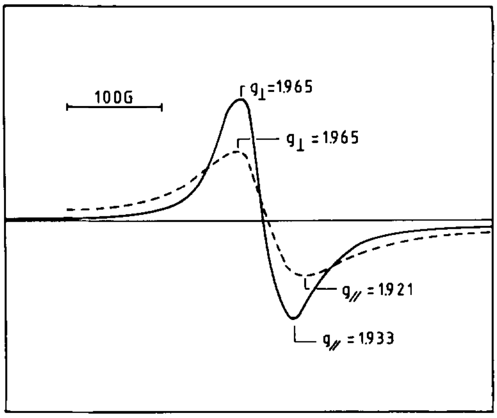

FIG. 5. EPR spectra (X band at 123 K) of 1 wt% Pt/TiO_2 (O 673), reduced in a flow of hydrogen (—) at 573 K and (---) at 773 K, and kept in each case under a pressure of 15 Torr of H_2.

Effect of H_2 or CO Adsorption and Evacuation on the EPR Signals

If the samples were evacuated at the temperature of reduction species B was never observed while the others were still there. Since species B was closely related to the presence of hydrogen, a second type of experiment was performed to study the variation of the EPR spectrum versus the evacuation of hydrogen on the 1 wt% Pt/TiO_2 catalysts reduced at 513 K. It was observed that the intensity of the EPR signals of species B and C decreases with the evacuation time with a full recovery of the signal after readsorption of 17 Torr of H_2. After evacuation, a slow recovery of the intensity of signal C was observed. No evolution occurred during the EPR experiments which were performed at a temperature sufficiently low (17 K). Therefore, prior to an EPR experiment, the sample was kept in liquid nitrogen after evacuation to minimize this evolution. Unfortunately, the cooling rate for a powder held under vacuum in a 4-mm-o.d. EPR tube at 77 K is approximately 30 min, and this is not fast enough to quench the mechanism which leads to the recovery of the EPR signal; one can observe an unexpected reverse situation where the signal is more intense after a longer evacuation time. In Fig. 2, this latter point is illustrated for a sample evacuated for 1 min at 295 K and transferred in the EPR probe with a 3-min transit time in liquid nitrogen (spectrum with the broken line in Fig. 2) which has smaller EPR signals than the same sample evacuated later for 5 min at 295 K with a transit time of 1 h at 77 K before the EPR experiment (spectrum with the dashed line in Fig. 2). This problem made systematic studies of the recovery of the EPR signal quite difficult and they were not performed on our samples. Only qualitative information on the relative variation of the signal intensity was obtained.

Carbon monoxide adsorption was performed under low pressures, typically 7.5 Torr, on a catalyst reduced at 513 K and evacuated at room temperature. The main observations are (i) the disappearance of species B, (ii) a drastic increase in signal C by a factor of 3, and (iii) an irreversible effect since the evacuation at room temperature does not alter the changes brought on by CO adsorption. A subsequent adsorption of H_2 does affect the EPR spectrum; there is no recovery of species B but the intensity of signal C decreases by one-third. A further evacuation of hydrogen leads only to a slight decrease in signal C with no reappearance of signal B. The latter results are reported in Fig. 6 for species B, and in Fig. 7 for species C.

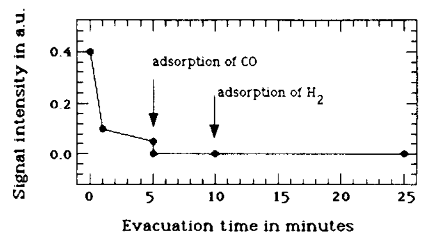

FIG. 6. Effect of the H_2 and CO adsorption and evacuation time on the EPR signal intensity of species B on the 1 wt% Pt/TiO_2 sample (O 673, E 673, R 413).

Results obtained for the 0.44 wt% Pt/TiO_2 sample were similar to the results described here for the 1.0 wt% Pt/TiO_2 sample. The only noticeable difference was the overall concentration of Ti^{3+} ions which was found to be approximately two-thirds of the concentration of Ti^{3+} ions of the 1.0 wt% Pt/TiO_2 for an identical treatment. This indicates that the majority of the Ti^{3+} is formed in proximity of Pt particles by hydrogen spillover.

DISCUSSION

Since at 573 K the rate of diffusion of the support on the particle is expected to be

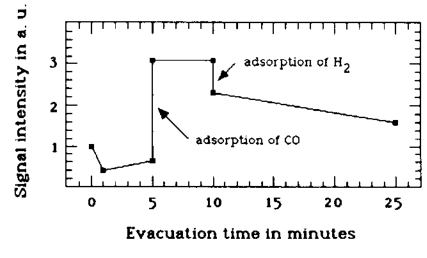

FIG. 7. Effect of the H_2 and CO adsorption and evacuation time on the EPR signal intensity of species C on the 1 wt% Pt/TiO_2 sample (O 673, E 673, R 413).

TABLE 1

EPR Parameters and Characteristics of Ti^{3+} Species in TiO_2 and Pt/TiO_2 Systems

Species referred as	EPR parameters		Localization phase and nature	References[a]
	$g_\perp$	$g_\parallel$		
1[b]	1.990	1.960	Anatase-bulk	(*26*)
2	1.978	1.958	Anatase-bulk	(*26*)
3	1.966	1.946	Anatase-surface	(*26*)
4	1.965	1.947	Rutile-surface	(*26*)
5	1.973	1.946	Rutile-bulk	(*26*)
A	1.979	—	Similar to species 2-bulk	(*20*) and this work
B	1.969	1.936	At the contact of Pt-surface	This work
C	1.964 1.966	1.947 1.945	Similar to species 3 or 4-surface	(*20*) and this work

[a] Reference (*26*) concerns TiO_2, Ref. (*20*) the Rh/TiO_2 system, and this work Pt/TiO_2.

[b] This species is also observed in this work and characterized by its $g_\perp$ component only.

very slow compared to 773 K, the 30% decrease in H_2 uptake can be accounted for by covering of the periphery of the particle. This is a consistent interpretation given the size of the particles involved in these catalysts (~1.0 nm). This surprising result is also consistent with the low reactivity of these catalysts in *n*-butane hydrogenolysis compared to Pt/Al_2O_3 catalysts (*14a*). In fact, independent results show consistently that platinum enters the SMSI state faster than Rh (*23*). Differences between these two metals in the SMSI state have been pointed out already. Platinum particles spread out to form pillbox particles (*24*) while no change occurs for Rh particles (*4a*). This change of morphology for platinum only has been correlated to the difference observed in TPD of benzene and benzene hydrogenation reaction and can account for a stronger metal–support interaction for Pt than for Rh (*25*). Here we want to stress that the MTR conditions lead to metal particles having partially entered the SMSI state at their periphery with the metal–support interface. The EPR results for MTR catalysts can account for the precursor step of SMSI.

The EPR signals generated in these catalysts are all attributed to Ti^{3+} ions in different environments. From the literature (*26*), one finds that reduction of TiO_2 leads to the formation of several Ti^{3+} species characterized by EPR and located in the anatase or rutile phase in the bulk or at the surface as reported in Table 1. Our results are also included in this table for comparison. From the similarity of the *g* tensor one can assign signals A and C and the signal at 1.990 to species located at the surface or in the bulk of TiO_2.

The signal at 1.990 corresponds to the perpendicular component of a species located in the bulk anatase phase of TiO_2. Its parallel component, expected at 1.960 (*26*), is hidden by the presence of the other signal in this region of the spectrum. This species disappears for temperatures of reduction higher than 513 K. This could be due to the transformation of anatase to rutile. This transformation is usually expected to occur at 1300 K but it can be accelerated by the removal of oxygen by the reduction process (*27*) catalyzed by Pt. X-ray diffraction pattern indeed shows that this occurs at 773 K for Rh/TiO_2 catalysts (*20*).

Species A is not sensitive to the presence of hydrogen and is attributed to a bulk species assigned to an impurity in the Degussa P-25 (*26*); this species is irrelevant to the problem treated here. Species B and C, sensitive to hydrogen pressure or carbon monoxide adsorption, are located at the surface of the catalysts and are of special interest.

Species C which exists in the support reduced at 573 K has its concentration enhanced by the presence of Pt. The intensity of its EPR signal decreases when hydrogen is evacuated but when evacuation is stopped a recovery of intensity occurs slowly even at 77 K. This can be explained by the spillover of hydrogen, located on the metal particles, toward the support. The particle acts as a hydrogen reservoir from which hydrogen can be either withdrawn from the sample during evacuation or spillover to the support when the system reaches an equilibrium in a closed cell. This process involves weakly adsorbed hydrogen in equilibrium with the gas phase and the support during evacuation. During the recovery, the strongly adsorbed hydrogen phase slowly rearranges to release weakly adsorbed hydrogen molecules which equilibrate with the support and increase the concentration of Ti^{3+} ions on the support. This process implies a region of the support in close proximity to the metal and is consistent with the results found by Conesa *et al.* (*20*) for the Rh/TiO_2 system. The increase in signal C intensity under the adsorption of CO molecules is not likely due to reduction of the support as in the case of H_2 adsorption but rather due to direct adsorption of CO on the support, the CO binding to Ti^{3+} ions and breaking the spin pairing between these ions.

Species B, as C, is a Ti^{3+} ion located at the surface of the catalysts but its *g* tensor is different from those of species at the surface of pure TiO_2. This species does not undergo the back-spillover process involving the recovery of the signal intensity of species C. The species B signal is significant only under hydrogen pressure. The concentration of this species increases when the temperature of reduction of the sample is increased. This is particularly sensitive from 573 to 773 K corresponding to a depression of H_2 uptake of 30 to 90% respectively, i.e., to increasing extent of SMSI. The irreversible disappearance of species B when CO is adsorbed at room temperature may be correlated to the reoxidation of Ti^{3+} into Ti^{4+} ions by O atoms produced at the metal interface during CO dissociation. This dissociation which usually does not take place on platinum may be promoted by the presence of Ti^{3+} ions.

In fact, TiO_2, as a support, is known to promote CO hydrogenation (*28*) and it has been speculated that this is probably due to the ability of the catalysts to adsorb CO at metal interface sites involving Ti^{3+} (*29*). Rieck and Bell have shown that the addition of TiO_2 to Pd catalysts facilitates the disproportionation of CO (*30*). They proposed a mechanism involving adsorbed CO molecules interacting via their oxygen atom with oxygen deficient TiO_x moieties residing at the Pd surface; the dissociation of carbon monoxide is assisted, in this mechanism, by the reoxidation of the TiO_x moieties. Studies of model systems clearly evidence the presence of TiO_x moieties on Rh (*31a,b*) or Pt (*32, 33*) although there is no agreement on the mechanism of site blocking which could be either simple or accompanied by inhibition of CO and H_2 chemisorption on uncovered adjacent sites.

Carbon monoxide hydrogenation, which produces O atoms, can reverse SMSI and has been used to titrate the amount of oxygen necessary to recover a normal state of the particle (*10, 28*). Recently, Baker *et al.* proposed, on the basis of their *in situ* electron microscopy, XPS, and EELS experiments on graphite hydrogenation (no oxygen in this system as in the case of CO hydrogenation), that the high activity of Pt/TiO_2 compared to Pt, working under the SMSI condition, is attributed to a $PtTiO_x$ mixed oxide (*34*). Species B may account for a Ti^{3+} ion in a support fragment whatever its nature, TiO_x, $HTiO_x$, or $PtTiO_x$. In fact, this species appears progressively with an increasing temperature of reduction, its concentration is affected by the removal of hydrogen pressure, and it can be irreversibly titrated by CO. Finally, the temperature dependence of its EPR signal is consistent with the close vicinity of species B with the metal particles.

Nevertheless, one cannot exclude the possibility that the suboxide fragments contain a lower oxidation state of titanium. In fact, the species B has been clearly characterized only in an intermediary state of SMSI and its EPR signal intensity decreases drastically in the full SMSI state. This decrease in intensity could be attributed to a further reduction of Ti^{3+} ions. However, XPS measurements of TiO_2 deposited on Pt foil (*33, 35*) or added to the Pt/graphite system (*34*) do not evidence an oxidation state lower than three. This does not necessarily imply that Ti^{3+} is the only case in the real catalysts since the conditions of reduction are different, but it is a point against it. Another satisfactory explanation is the spin pairing due to a local high concentration of Ti^{3+} ions. This concentration effect is usually observed at a much higher temperature in pure TiO_2. Here the Pt particles catalyze the reduction of the support adjacent to them which can occur at temperatures as low as 295 K (Fig. 1a). In the HTR case, one clearly may expect a concentration effect.

CONCLUSION

On the Pt/TiO_2 system prepared by ion exchange highly dispersed platinum particles are obtained. They enter partially the SMSI state at a medium temperature of reduction, 573 K. *In situ* EPR measurements at a low temperature (17 K) of Pt/TiO_2 catalysts reduced in highly purified hydrogen at low, medium, and high temperatures show four signals of Ti^{3+} ions. Only two of these species, B and C, belong to the surface. Species C, characterized by an axial tensor at $g_\perp = 1.964$ and $g_\parallel = 1.947$, is located at the surface of TiO_2 and is involved in the hydrogen spillover or backspillover process. Species B, characterized by its axial tensor at $g_\perp = 1.969$ and $g_\parallel = 1.936$, is believed to be correlated to SMSI: (i) its concentration increases, in comparison with the other surface species C, particularly when the temperature of reduction is high enough to initiate SMSI, (ii) this surface species survives only in the presence of a pressure of hydrogen, and (iii) CO irreversibly titrates this species in the presence of H_2. It is now recognized that SMSI is due to migration of fragments of the support on top of metal particles blocking sites for hydrogen uptake or catalytic reactions. Species B can account for these TiO_x or $HTiO_x$ species which migrate on the support in the SMSI state or to a precursor state of the migrating species which may involve an oxidation state lower than three.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract DE-AC02-81ER10829. We also thank NSF/CNRS for support from the U.S.–France Cooperative Science Program which makes possible the cooperation between our two laboratories.

REFERENCES

1. (*a*) Tauster, C. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978); (*b*)Tauster, C. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211,** 1121 (1981).

2. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **59,** 293 (1979).

3. Resasco, D. E., and Haller, G. L., *Stud. Surf. Sci. Catal.* **11,** 105 (1982).

4. (*a*) Mériaudeau, P., Ellestad, O. H., Dufaux, M., and Naccache, C., *J. Catal.* **75,** 243 (1982); (*b*) Hermann, J. M., and Pichat, P., *J. Catal.* **78,** 425 (1982); (*c*) Chen, B.-H., and White, J. M., *J. Phys. Chem.* **86,** 3534 (1982).

5. (*a*) Fung, S. C., *J. Catal.* **76,** 225 (1982); (*b*) Sexton, B. A., Hughes, A. E., and Foger, K., *J. Catal.* **77,** 85 (1982); (*c*) Chien, S.-H., Shelimov, B. N., Resasco, D. E., Lee, E. H., and Haller, G. L., *J. Catal.* **77,** 301 (1982).

6. (*a*) Mériaudeau, P., Dutel, J. F., Dufaux, M., and Naccache, C., *Stud. Surf. Sci. Catal.* **11,** 95 (1982); (*b*) von Engels, S., Freitag, B., Morke, W., Roschke, W., and Wilde, M., *Z. Anorg. Allg. Chem.* **474,** 209 (1981).

7. Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81,** 273 (1983).

8. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).
9. Haller, G. L., and Resasco, D. E., "Advances in Catalysis," Vol. 35. Academic Press, San Diego, 1988.
10. Cairns, J. A., Baglin, J. E. E., Clark, G. J., and Ziegler, J. F., *J. Catal.* **83,** 301 (1983).
11. Munuera, G., Gonzalez-Elipe, A. R., Espinos, J. P., Conesa, J. C., Soria, J., and Sanz, J., *J. Phys. Chem.*, in press.
12. Huizinga, T., and Prins, R., *J. Phys. Chem.* **87,** 173 (1983).
13. Bonneviot, L., Che, M., Olivier, D., Martin, G. A., and Freund, E., *J. Phys. Chem.* **90,** 2112 (1986).
14. (*a*) Bonneviot, L., and Haller, G. L., in press; (*b*) Resasco, D. E., and Haller, G. L., *J. Phys. Chem.* **88,** 4552 (1984).
15. Che, M., and Tench, A., "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 32, p. 1. Academic Press, San Diego, 1983.
16. Huizinga, T., and Prins, R., *J. Phys. Chem.* **85,** 2156 (1981).
17. DeCanio, S. J., Miller, J. B., Michel, J. B., and Dybowski, C., *J. Phys. Chem.* **87,** 4619 (1983).
18. DeCanio, J. B., Apple, T. M., and Dybowski, C., *J. Phys. Chem.* **87,** 4619 (1983).
19. Chen, B.-H., and White, J. M., *J. Phys. Chem.* **87,** 1327 (1983).
20. Conesa, J. C., Malet, P., Munuera, G., Sanz, J., and Soria, J., *J. Phys. Chem.* **88,** 2986 (1984).
21. Conesa, J. C., and Soria, J., *J. Phys. Chem.* **86,** 1392 (1982).
22. Bonneviot, L., and Haller, G. L., in press.
23. Huang, H., Ph.D. thesis, Yale University, 1986.
24. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **56,** 390 (1979).
25. Resasco, D. E., Fenoglio, R. J., Suarez, M. P., and Cechini, J. O., *J. Phys. Chem.* **90,** 4330 (1986).
26. Mériaudeau, P., Che, M., Gravelle, P. C., and Teichner, S. J., *Bull. Soc. France,* 13 (1971).
27. Shanon, R. D., and Pask, J. A., *J. Amer. Cer. Soc.* **48,** 391 (1965).
28. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1979); **63,** 255 (1980).
29. Burch, R., and Flambard, A. R., *J. Catal.* **78,** 389 (1982).
30. Rieck, J. S., and Bell, A. T., *J. Catal.* **99,** 262 (1986).
31. (*a*) Sadeghi, H. R., and Henrich, V. E., *J. Catal.* **87,** 279 (1984); *Appl. Surf. Sci.* **19,** 330 (1984); (*b*) Levin, M., Salmeron, M., Bell, A. T., and Somorjai, G. A., *Surf. Sci.* **160,** 123 (1986).
32. Dwyer, D. J., Robbins, J. L., Cameron, S. D., Dudash, N., and Hardenberg, J., *ACS Symp. Ser.* **298,** 21 (1986).
33. Dwyer, D. J., Cameron, S. D., and Gland, J., *Surf. Sci.* **159,** 430 (1985).
34. Baker, R. T. K., Kim, K. S., Emerson, A. B., and Dumesic, J. A., *J. Phys. Chem.* **90,** 860 (1986).
35. Ocal, C., and Ferrer, S., *Surf. Sci.* **178,** 850 (1986).