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Articles

Electron Paramagnetic Resonance Studies of Reduced Platinum Supported on Titanium Oxide: Effect of Hydrogen Adsorption–Desorption on Paramagnetic Platinum(I) and Titanium(III) Species

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The paramagnetic species Pt^+, Ti^{3+}, and O^-, which are formed on Pt/TiO_2 catalyst by interaction with hydrogen, are studied by EPR spectroscopy. The signals (Pt^+ and Ti^{3+}) appeared on reduction of the catalyst with hydrogen at 623 and 773 K followed by evacuation. On increase of the evacuation temperature from 295 to 673 K, the Pt^+ signal intensity slightly increased while the Ti^{3+} signal intensity decreased. This phenomenon is explained by electron transfer from Pt crystallites to the proximate oxidized Ti^{4+} ions due to the hydrogen evolution during evacuation. The chemisorption of hydrogen at 295 K into the prereduced sample at 773 K resulted in the generation of a new Ti^{3+} species characterized by their **g** tensor components at $g_1 = 1.991$ and $g_{11} = 1.960$ while the Pt^+ signal at $g = 2.005$ became narrow and weak. The new Ti^{3+} species is formed by hydrogen spillover from the surface of Pt to the titania surface. The signals of this species decreased in intensity by the evacuation for 2 min at 295 K, whereas the Pt^+ signal became symmetric and strong. By increasing the evacuation time to 10 min, the new Ti^{3+} species vanished with the simultaneous appearance of a narrow doublet at $g_1 = 2.026$ and $g_{11} = 2.016$, along with the Pt^+ signal. The adsorption of D_2 at the hydrogen adsorption conditions led to the same Ti^{3+} species which is reversible by the evacuation for 2 and 10 min at 295 K but to a lesser extent. The Pt^+ signal did not recover by the D_2 evacuation. On the other hand, the same doublet at $g_1 = 2.026$ and $g_{11} = 2.016$ arose after 10-min evacuation. This doublet is due to O^- radicals associated with a hydrogen bond on the surface support and near by regions of the Pt metal.

Introduction

It has been shown that treatment of catalysts containing group 8 metals supported on TiO_2 under H_2 at high temperatures (>750 K) gives rise to strong metal–support interaction (SMSI). This state is characterized by a strong decrease in the metal ability to adsorb H_2, together with morphological changes in the metallic particles, which have been related to the reduced state of the support.[1,2] It follows that the specific activity of the exposed surface of supported metal catalysts is dependent on the chemical nature of the support.[3,4]

Although a rather large volume of literature has been produced on the characteristics of the SMSI state, only few studies assess the understanding of SMSI in the viewpoint of the Pt states. To our knowledge, there is no study combining information on the nature of the paramagnetic Pt^+ (d^9) and Ti^{3+} (d^1) ions in the reduced Pt/TiO_2 catalyst, although Huizinga and Prins[5,6] have identified separately in two papers the signal of Pt^+ lying in the reduced state and the Ti^{3+} signal.

The objectives of the present work are to determine the paramagnetic Pt ions which are present in the various stages in the genesis of a supported Pt catalyst and to determine how the support is involved in the formation of such ions.

Experimental Section

The catalyst precursor (2 wt % Pt) was prepared by incipient wetness impregnation of TiO_2 (obtained from the Catalysis Society of Japan, type TIO-4, surface area = 50 $m^2\ g^{-1}$) with an aqueous solution of H_2PtCl_6 and subsequent air-drying at 383 K, according to the method described elsewhere.[7] The treatments (reduction and gas adsorptions) were performed on a vacuum line directly connected to the flow system. The Pyrex reactor with grease-free valves was equipped with sidearm EPR tubes where the catalyst was transferred to be inserted directly to the EPR cavity. The catalyst was oxidized in static oxygen overnight

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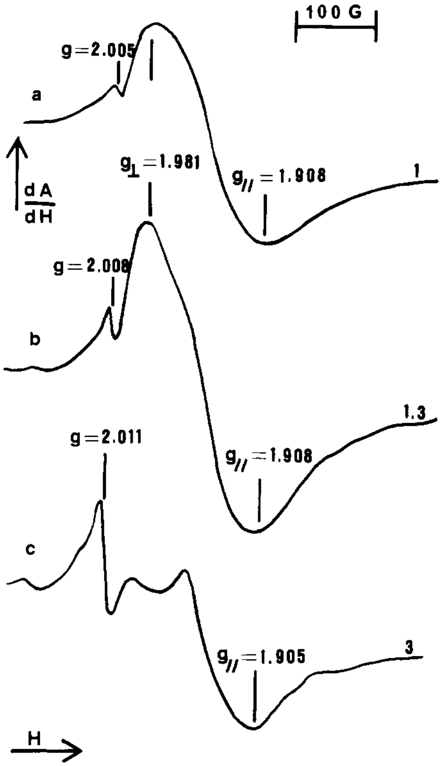

Figure 1. EPR spectra of Pt/TiO_2 reduced at 623 K in a hydrogen flow and followed by evacuation at (a) 295, (b) 473, and (c) 573 K. EPR spectra were recorded at 77 K.

at 573 K before reduction. For reduction, H_2 was purified in a hydrogen diffusion purifier, and for adsorption it was further purified by passing over 13X molecular sieves kept at 77 K. Deuterium was purchased from Takachiho Kagaku Kogyo Co. and was used without further purification. The H_2 (or D_2) adsorption was carried out with 20 Torr of either gas at 295 K for 10 h.

EPR spectra (X-band) were recorded with a varian E-3 spectrometer equipped with a cold, dry N_2 flow cryostat at a frequency of about 9.3 GHz. The line position was calibrated with DPPH (1,1-diphenyl-2-picrylhydrazyl) (g = 2.0036).Ti^{3+} radical ion concentrations were estimated by comparison of the areas obtained by double integration of the first-derivative curves for the samples and a standard benzene solution of DPPH. The two lines of Pt^+ signal superimposed on a Much broader Ti^{3+} siganl were not separable in the derivative mode. As the former is small compared to the latter, application of a baseline correction techniqe and integration of the Pt^+ curve did not give the desired area. This integration error enables us to calculate of the spin number of Pt^+ ions at low evacuation temperatures. The EPR spectra were recorded at 77 K (liquid N_2) to avoid the rapid relaxation due to the spin–orbit coupling.

Results and Discussion

Effect of the Evacuation Temperature on Pt^+ and Ti^{3+} Paramagnetic Species for the Reduced Pt/TiO_2 Sample. Figure 1 shows the EPR spectra of a Pt/TiO_2 sample after reduction in a flow of hydrogen at 623 K and evacuation at increasing temperatures. The signal about g = 2 in the spectra for the different evacuation temperature is due to Pt^+ (d^9, $S = {}^1/_2$) ions. The signal undergoes a slight shift to down field (toward high g values) by increasing the evacuation temperature, i.e., from 2.005 to 2.01. However, Huizinga and Prins[5,6] reported this signal for reduced Pt/TiO_2 and attributed it to the presence of Pt^+ ions at the metal–titania interface. Although, Bonneviot and Haller[8] did not rule out this signal in a similar study, it appears that the exact chemical environment of Pt on the surface varies considerably depending on the method of catalyst preparation and treatment. However, they concluded the same meaning for not detecting a signal in the region corresponding to g values greater than 2.

The signal cannot be ascribed to either Pt^{3+} (d^7, $S = {}^1/_2$) ions nor to carbonaceous impurities. The Pt^{3+} signal has three different g values and was observed only for oxidized Pt/TiO_2.[6,9–11] The signal may also be assigned to carbonaceous impurities because of using a grease-free reduction system on one hand and the reduction of TiO_2 at the same conditions showed no signal being observed on the other hand. Increasing evidence for the fact that this signal is not due to carboneous deposits comes from oxidizing the sample in static oxygen at 573 K before reduction.

The presence of Pt^+ ions may be explained by either incomplete reduction of Pt particles or to electron transfer from Pt crystallites to the support. Our temperature-programmed reduction (TPR) results have shown that the reduction of Pt precursor in a Pt/TiO_2 catalyst was complete at 573 K.[7] Thus, the presence of Pt^+ ions in the Pt/TiO_2 sample treated with H_2 at 623 K should not be ascribed to incomplete reduction of Pt cations. Therefore, we infer an electron-transfer model to explain the generation of Pt^+ sites by evacuation of reduced Pt/TiO_2.

Our recent EXAFS/XANES study[12] of Pt supported on titania dispersed on silica explored an increase in the number of unfilled d states of Pt atoms. A fraction of the Pt atoms (those on the interface) will approach the atomic configuration $[Xe]4f^{14}5d^96s^1$, which has more empty d states than the bulk. As the 6s electron is formed, its energy is lowered and the chance is opened to transfer to a neighboring Ti^{4+} cation. The small Pt^+ signal shift to higher values by increasing the evacuation temperature from 295 to 573 K (Figure 1) indicates an increasing in the unfilled d states of Pt. Further explanation for this shift in connection with entities of Ti^{3+} species is given below.

The electron transfer from Pt crystallites to the surrounding support have been reported in the following papers. With Pt/TiO_2, Chen and White[13] have observed electron transfer from Pt to rutile for a thin film of Pt deposited on single-crystal rutile, pretreated in flowing H_2 for 1 h at 773 K. Katzer et al.[10] studied EXAFS of supported Pt and shown that electron transfer occurred from small Pt crystallites to Al_2O_3, which are increased with decreasing Pt crystallite size. EXAFS results of Lytle also showed electron transfer from supported Pt to silica.[14] Short et al.[15] reported form the X-ray absorption edge studies that there is always a greater number of unfilled d states for Pt/TiO_2 than for bulk Pt, indicating a charge transfer into TiO_2 support. Moreover, by means of XPS measurements, Kawai et al.[16] advocate an electron transfer

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Table 1. Intensity of the Ti^{3+} Signal with Pt/TiO_2 Catalyst

treatment[a]	no. of Ti^{3+} ions/ no. of Ti^{4+} ions
R = 623 K, E = 295 K	4.09×10^{-5}
R = 623 K, E = 573 K	6.70×10^{-6}
R = 773 K, E = 295 K	1.07×10^{-5}
R = 773 K, E = 695 K	3.83×10^{-6}
R = 773 K, E = 695 K, H = 295 K	1.17×10^{-4}
R = 773 K, E = 695 K, H = 295 K, E = 295 K[b]	2.99×10^{-6}

[a] R donated reduction, E, evacuation, and H, hydrogen adsorption. [b] Evacuation for 10 min. EPR spectra were recorded at 77 K.

from Rh to Ti or Zr through oxygen in $Rh/TiO_2,ZrO_2$, which resulted in forming a cationic Rh state. It has been suggested that surface hydroxyl on the support are effective in converting Rh^0 to Rh^+.[17]

In addition to the signal attributable to Pt^+, there is an average signal in the EPR spectra of reduced Pt/TiO_2 (Figure 1). This resonance mainly occurs at $g_1 = 1.981$ and $g_{11} = 1.908$ ($H_{pp} = 135$ G). The $g < 2$ values can be assigned to Ti^{3+} ($3d^1$) species in different coordination environments. The g values ($g_1 = 1.981$, $g_{11} = 1.908$) in the spectra of Pt/TiO_2 correspond to defects in the bulk of the TiO_2 support according to a work by Conesa et al.[18] The g_{11} is shifted toward lower g value, i.e., from 1.908 to 1.905 upon increasing the evacuation temperature up to 573 K, indicating an increase of Ti^{3+} bulk species at the expense of Ti^{3+} surface species.[18]

As clearly seen in Figure 1, the intensity of the Pt^+ signal increased as the evacuation temperatures increased from 295 to 573 K. The weak Pt^+ signal intensity at low evacuation temperatures as well as the Pt^+ signal superimposed on the signal of Ti^{3+} makes estimation of the former difficult. The Pt^+ ions at 573 K evacuation is 0.25% of the total Pt content. The estimation of Ti^{3+} centers is not highly accurate due to the signals broadening. Table 1 summarizes the number of Ti^{3+} ions/number of Ti^{4+} ions at different treatments. The Ti^{3+} spin followed by evacuation at 295 K for 30 min is about 1 order of magnitude larger after increasing the evacuation temperature to 573 K. Some of this decrease in the number of Ti^{3+} centers upon increasing the evacuation temperatures corresponds to the increase in the intensity of the Pt^+ signal in the same spectrum. The signal of Pt^+ ions undergoes broadening after evacuation at 573 K which is characteristic for highly efficient spin–spin relaxation mechanism due to the increase in the number of Pt^+ ions in short distance. Table 1 also shows that when the reduction temperature of the sample was increased from 623 to 773 K, followed by the evacuation at 295 K, the concentration of Ti^{3+} sites was decreased to one-fourth.

The foregoing observations can be explained as follows: the evacuation of the sample after reduction brings about the removal of H^+ in the form of molecular hydrogen, as evidenced by H_2-TPD study,[7] therefore leading to reoxidation of Ti^{3+} ions to Ti^{4+} ions:

$$Ti^{3+} + OH^- \rightarrow Ti^{4+} + O^{2-} + {}^1/_2H_2 \qquad (1)$$

Since this process is accelerated in the vicinity of Pt particles, the migration of one electron from the Pt metal to a proximate coordinately unsaturated Ti^{4+} site is facilitated, causing a partial reduction of the surface:

$$Ti^{4+} + Pt^0 \rightarrow Ti^{3+} + Pt^+ \qquad (2)$$

Katzer et al.[10] have given a similar interpretation for Pt^{3+} EPR signals arising after evacuation of Pt/Al_2O_3 at 623 K. They proposed that evacuation caused a partial reduction of the surface by removing oxygen anions and that the oxidation state of Pt^{4+} becomes Pt^{2+}. Once the latter is in contact with a Lewis acid site represented by an Al^{3+} ion, and electron transferred to it and the resulting Pt^{3+} gave a characteristic EPR signal.

Ti^{3+} in eq 2 is expected to be migrated to the bulk of the TiO_2 crystal lattice from the shift of the g_{11} value toward higher field after evacuation at 573 K. Since vacuum or hydrogen reduction of TiO_2 does not result in the formation of cation vacancies, the diffusion of Ti^{3+} surface species should primarily involve an exchange between this species and Ti^{4+} in the interior.[19] The increased unfilled d states of Pt atoms by increasing the evacuation temperature is associated with the increase of Ti^{3+} bulk species, therefore, is accounted for migration of an electron from Pt crystallite to TiO_2.

Metal ions have been proven to be present in macroscopic interfaces between metals and oxidic materials.[20,21] If Pt^+ ions in reduced Pt particles are concentrated at the metal–support interface, then an ionic interaction with the oxygen anions of the oxidic support exists as evidenced by Huizinga and prins.[6] The presence of Pt^+ is accounted for the lower rate value for butane hydrogenolysis for a Pt/TiO_2 sample reduced at 773 K than after reduction at 632 K.[22]

H_2 Chemisorption onto the Prereduced Pt/TiO_2 Sample. When hydrogen was allowed to chemisorb at 295 K into the prereduced sample at 773 K and the EPR spectrum was monitored under hydrogen pressure (20 Torr), the Pt^+ signal is observed as shown in Figure 2b. The Pt^+ signal is seen as a weak signal compared with that before the hydrogen adsorption. By the hydrogen adsorption, the Pt^+ ions at the platinum–titania interface captured additional electrons to give undetectable diamagnetic species. The small spectral feature of Pt^+ ions in the presence of hydrogen may provide evidence that some of these ions were located in energetic sites which cannot be reduced to the metallic state at room temperature.

It is interesting to note that the hydrogen chemisorption at 295 K leads to a new Ti^{3+} species characterized by their **g** tensor components at $g_1 = 1.991$ and $g_{11} = 1.960$ (Figure 2). The original signal of Ti^{3+} with parameters $g_1 = 1.981$ and $g_{11} = 1.905$ were also increased in intensity by the hydrogen chemisorption. Such increase in the number of Ti^{3+} ions/number of total Ti^{4+} ions (Table 1) by H_2 adsorption is attributed to the diffusion of hydrogen atoms from the platinum particles to the surrounding support surface and is related to the so-called spillover phenomenon. For low reduction temperatures, the formation of

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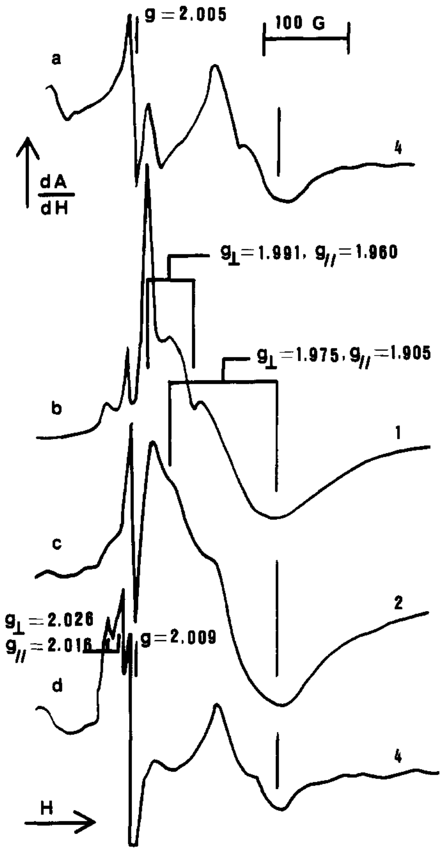

Figure 2. EPR spectra of Pt/TiO_2 reduced at 773 K in a hydrogen flow: (a) evacuated at 673 K, (b) after H_2 adsorption (20 Torr) and 395 K, (c) evacuation of H_2 at 295 K for 2 and (d) evacuation of H_2 at 295 K for 10 min.

Ti^{3}+ and OH^- is not the source of SMSI, since the electrons are not transferred into the conductivity band of the metal.[18]

Similar signals of the new species (g_1 = 1.991 and g_{11} = 1.960) but with lower intensity have been observed in the spectrum of a Pt/TiO_2 catalyst reduced in hydrogen at 298 K.[8] These signals were attributed to Ti^{3+} species located in bulk anatase according to a work by a Meriaudeau et al.[23] The signals, however, disappeared by increasing the reduction and evacuation temperatures from 289 to 573 K, and such disappearance was explained according to the phase transformation of anatase to rutile by the removal of oxygen atoms during the reduction of rutile by the removal of oxygen atoms during the reduction process. Although the same species was observed in the spectrum of Pt/TiO_x/SiO_2 at the same treatments,[24] it is reported that SiO_2 retarded the anatase phase transition to rutile.[25,26] The sharpness of the signal at g_1 = 1.991 suggests that this species is isolated, and since it is catalyzed by Pt, the species is considered to be located in the vicinity of Pt.

When the sample is evacuated at 295 K for 2 min, the Ti^{3+} signals at g_1 = 1.981 and g_{11} = 1.905 decreased in intensity with a pronounced declining of the new species Figure 2c. Simultaneously, the Pt^+ signal became symmetric and strong. This observation indicates that the reversible generation of the new species is associated with hydrogen species weakly adsorbed on the Pt^+ ions. By the desorption of this weakly adsorbed hydrogen, the Pt^+ ions regenerate. The weak adsorption may be ascribed to the generation of a highly polarizable H-bonded protonic species, where the H^+ lies in a nearly symmetric potential well.[27] Meanwhile, electrons are transferred to the support to give Ti^{3+} paramagnetic centers. This result also shows that hydrogen spillover and back-spillover occur at room temperature.

Increasing the evacuation time from 2 to 10 min led to a complicated paramagnetic structure in the region >2. Besides the signal characteristic of Pt^+, there is a new doublet delivered in the spectrum at g_1 = 2.026 and g_{11} = 2.016. The change of the spectrum shape by increasing the evacuation time at room temperature is crucial in showing the role of hyrogen back-spillover in developing a new species. The line shape and g values of this doublet coincide those characteristic of O^- anions radicals adsorbed on TiO_2 supported on silica.[28] This species is not stable at high temperatures.[28] The O^- doublet arising after 10 min of evacuation is related to the hydrogen diffusion and recovery time. The rate at which hydrogen can enter TiO_2 through Pt atoms and move within it is proved to be 10 s.[29] The recovery time is considerably larger and is governed by the rate at which H atoms can be removed from the surface. The absence of O^- anion radicals after 2 min of evacuation indicates that the system is still in equilibrium with weakly adsorbed hydrogen. This result is confirmed from the presence of Ti^{3+} ions underneath and around the metal after 2 min of evacuation. The prolonged evacuation time (10 min) allowing almost complete release of weakly adsorbed hydrogen from electron or hydrogen rich support to be held near the Pt side of TiO_2. Table 1 shows the number of Ti^{3+} ions is almost recovered to its initial value (before H_2 adsorption) by the evacuation for 10 min.

The appearance of the O^- doublet is probably due to surface changes produced by reaction with H_2. From the IR results of Conesa et al.,[30] it has been shown that OH groups and H_2O molecules were almost absent after the high-temperature reduction–evacuation treatment of Rh/TiO_2 at 773 K. The OH and H_2O were generated easily on hydrogen adsorption at 295 K and remain to a large extent irreversibly adsorbed after pumping, while polarizable protons appear more slowly. In the present study, the generation of O^- species is steamed from neither the OH groups nor H_2O molecules on the surface. Since O^- is not stable at high temperatures as well as had appeared after the disappearance of Ti^{3+} surface species, one may think its dependence on the weakly adsorbed hydrogen (hydrogen bonds). The following mechanism seems reasonable and, in particular, close homogeneous analogies to it have developed:

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$$2Ti^{4+}O^{2-} + H_2 \xrightarrow{Pt} 2Ti^{3+}OH^- \qquad (3)$$

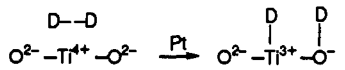
$$2Ti^{3+}OH^- \xrightarrow[295\ K]{eva.} Ti^{4+}\text{-}(O\text{-}H\cdots O)^-\text{-}Ti^{4+} + {}^1/_2H_2 \qquad (4)$$

The hydrogen bond in eq 4 is not strictly linear.

The O$^-$ species is to be associated with Ti^{4+} and nearby regions of Pt. O$_2^-$ or O$^-$ formation is not expected on reduced Pt surfaces and was not found. On the other hand, complete exchange between O$^-$ and O^{2-} is reported for semiconductor oxide.[31] By means of EXAFS measurements, van Zon et al.[32] and Martens et al.[33] ruled out that the metal–support interaction for Rh/TiO$_2$ is possibly through an ion–induced dipole (O^{2-}- -Rh^0) interaction of the metal with the support. Although the hydrogen back-spillover of Pt/TiO^2 reduced at low temperatures is not the source of SMSI, we invoke that this hydrogen led to significant changes in the electronic states of the oxide.

It is worth mentioning that the observation of a doublet due to O$^-$ is accompanied by a slight Pt$^+$ line shift to higher *g* value i.e., from $g = 2.005$ to $g = 2.009$. This is due to a slight change in the environment around the Pt$^+$ ion. Some of the Pt$^+$ ions were embedded in O$^-$ enviroment rather than O^{2-}, leading to a slight increase in the density of the unfilled d states of Pt.

D$_2$ Chemisorption onto the Prereduced Pt/TiO$_2$ Sample. The D$_2$ adsorption at 295 K onto the sample prereduced at 773 K gave figures different from those in the case of H$_2$ adsorption (Figure 2). When the sample was saturated with D$_2$ (Figure 3b), the same Ti^{3+} spectral feature was observed which associated with a complete disappearance of the Pt$^+$ signal. D$_2$ is dissociated on the Pt top layer into D atoms. The electron driven from D where captured by Pt$^+$ where the d orbitals between more occupied to give undetectable diamagnetic species. On the other hand, the reduction of surface TiO$_2$ mechanistically can be represented as follows:



$$\overset{D\text{—}D}{O^{2-}\text{–}Ti^{4+}\text{–}O^{2-}} \xrightarrow{Pt} O^{2-}\text{–}Ti^{3+}\text{–}\overset{D}{\underset{|}{}}\!\!O^- \quad \overset{D}{|}$$

As shown by NMR analysis, significant amounts of hydrogen remain in the reduced catalyst even after pumping at 773 K.[30] A similar fact (strong retention of hydrogen in highly reduced Pt/TiO$_2$ catalysts) has been reported by Ebitani and Hattori[7] and Hongli et al.[34] When D$_2$ is adsorbed instead of H^2 at room temperature, isotopic exchange of the hydroxyls on the TiO$_2$ surface by spillover deuterium has occurred.[35] The IR results of Conesa et al.[30] revealed this exchange for Rh/TiO$_2$ at the same conditions.

The 2-min evacuation at room temperature resulted in the Ti^{3+} signals slightly decreased in intensity while maintaining the same shape. At the same time, a very small Pt$^+$ signal appeared. In the case of H$_2$ desorption, the Pt$^+$ signal enhanced by 2-min evacuation. Therefore, it is suggested that the rate of desorption is slower for D$_2$ than for H$_2$ from the catalyst surface. In addition, the dependence of the Pt$^+$ signal on the decrease of Ti^{3+} surface species.

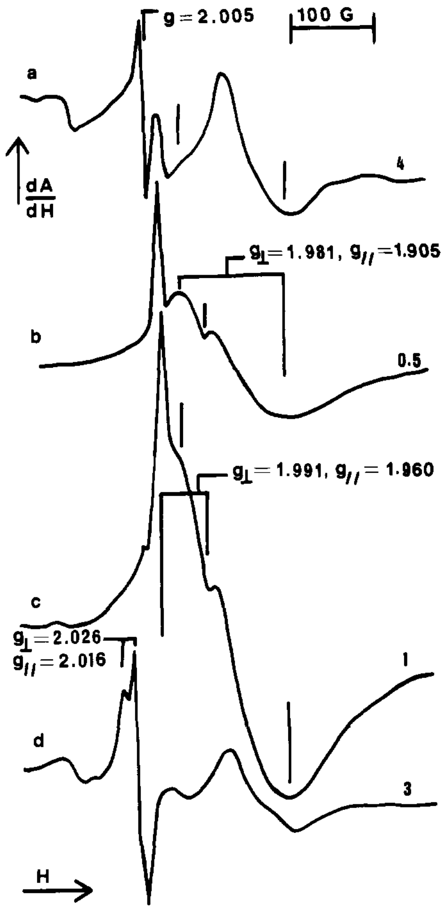


Figure 3. EPR spectra of Pt/TiO$_2$ reduced at 773 K in a hydrogen flow: (a) evacuated at 673 K, (b) after D$_2$ adsorption (20 Torr) at 295 K, (c) evacuation of D$_2$ at 295 K for 2 min, and (d) evacuation of D$_2$ at 295 K for 10 min.

Increasing the evacuation time to 10 min led to significant changes in the EPR spectrum of sample chemisorbing D$_2$ (Figure 3d). The Ti^{3+} species characterized by $g_\perp = 1.991$ and $g_\parallel = 1.960$ disappeared with simultaneous development of an anisotropic sharp doublet at $g_\perp = 2.026$ and $g_\parallel = 2.016$, which is almost the same as that observed in Figure 2d. Yet the Pt$^+$ signal did not recover any more after evacuation.

It is clear now that the arising of the O$^-$ doublet corresponds to the decrease in Ti^{3+} surface species (reoxidation of surface TiO$_2$) in the vicinity of Pt which in turn depends on the D$_2$ desorption. The D$_2$ desorption at 295 K can be achieved only by the aid of Pt. Since the line shape and *g* values of this doublet are analogies to the corresponding doublet developed by hydrogen desorption, one mechanism is operative for both cases. The nondevelopment of a Pt$^+$ signal by D back-spillover leads us to think that this signal is associated with polarizable H$^+$. Further study is needed to establish the location of this proton in the metal–titania interface.

In view of these observations, one should consider the possibility that the electron transferred from the support to the metal could take place directly and not through the action of the back-diffusing hydrogen species. In other words, hydrogen back-spillover occurs as back-diffusion

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of H^+ rather than atomic hydrogen. The generation of O^- anion radicals is related to the presence of hydrogen bonds formed by hydrogen adsorption at 295 K. This process does not involve Pt^+.

Conclusions

From this and many other studies in this field, it is clear that SMSI is a comlplex phenomenon and may vary from system to system. It may well prove impossible to condense this complexity into one model. The present study indicates that by increasing the evacuation temperature for a Pt/TiO_2 sample reduced at 623 K, a signal ascribed to Pt^+ was developed. The generation of Pt^+ ions in the metal–support interface cannot be ignored as a cause for generation of the SMSI state by the interaction with the oxide surface. Adsorption of H_2 at 295 K onto the sample prereduced at 773 K proved that hydrogen is adsorbed reversibly on Pt^0 and Pt^+. The back-spillover hydrogen affects the surface electronic states of the support after evacuation at 295 K for 10 min. The hydrogen adsorbed on Pt^+ is not involved in this process as evidenced from D_2 adsorption. Properly speaking, the back-spillover hydrogen for sample-adsorbed hydrogen at room temperature plays a very important role in changing the electronic states of the oxide.

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