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Citation for published version (APA):

Huizinga, T., & Prins, R. (1981). Behavior of Ti^{3+} centers in the low- and high-temperature reduction of Pt/TiO_2 , studied by ESR. *Journal of Physical Chemistry*, 85(15), 2156-2158. <https://doi.org/10.1021/j150615a003>

DOI:

[10.1021/j150615a003](https://doi.org/10.1021/j150615a003)

Document status and date:

Published: 01/01/1981

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Behavior of Ti^{3+} Centers in the Low- and High-Temperature Reduction of Pt/TiO_2 , Studied by ESR

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(Received: March 27, 1981; In Final Form: June 5, 1981)

Reduction of Pt/TiO_2 at 573 K leads to the formation of a Ti^{3+} ESR signal, which disappears after a subsequent evacuation at 573 K. Readmission of hydrogen at room temperature makes the signal reappear. Such a reversibility is not observed when reduction takes place at 773 K. These observations are explained by a spillover of hydrogen atoms under the formation of Ti^{3+} and OH^- ions. During the high-temperature reduction the hydrogenated TiO_2 surface around the platinum is dehydrated and a Ti_4O_7 layer is formed, thereby inhibiting the reversibility.

Introduction

Recently interest in titanium dioxide as a support in heterogeneous catalysis has grown appreciably. Especially the findings of Tauster et al.,¹ that the chemisorption capabilities of platinum for hydrogen disappeared when Pt/TiO_2 systems were reduced at relatively high temperatures (773 K), created great interest. Transmission electron microscopy showed that the reduced chemisorption capabilities were not due to trivial effects such as sintering of the metal. The reason for the change in behavior of the metal on titanium dioxide after a high temperature reduction has been ascribed to a special metal-support interaction. Baker, who showed with electron diffraction that in Pt/TiO_2 catalysts after a high-temperature reduction layers of Ti_4O_7 are formed,² has suggested that reducibility plays an important role in this so-called strong metal-support interaction (SMSI).³ That the SMSI properties are indeed related to the reducibility of the support is proved by the fact that noble metals on V_2O_5 , Nb_2O_5 , and (weakly) Ta_2O_5 also exhibit SMSI properties.⁴ Until now the nature of this strong metal-support interaction has not been explained, although proposals have been put forward.⁴

Not only the chemisorption properties but also activities and selectivities of metals on titanium dioxide may be different from metals on conventional supports. Thus it was found that Ni/TiO_2 is a much better catalyst for the hydrogenation of carbon monoxide.⁵ Both activity and selectivity toward higher hydrocarbons are increased compared to conventional $\text{Ni}/\text{Al}_2\text{O}_3$ systems.⁶

In this Letter we present the results of an ESR study of platinum on TiO_2 . Our results demonstrate that, at temperatures as low as 573 K, Ti^{3+} ions are formed presumably in the neighborhood of the platinum particles. The Ti^{3+} ions, when formed by a low-temperature reduction, can easily be retransformed into Ti^{4+} ions, but this is not the case for Ti^{3+} ions formed at 773 K. It will be shown that this can be explained by the formation of Ti_4O_7 by dehydration of the TiO_2 support in the neighborhood of the metal particles.

Experimental Section

The titanium dioxide used (anatase, Tioxide Ltd., CLDD 1367) had a surface area of $50 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.9 \text{ cm}^3 \text{ g}^{-1}$. Platinum was put on the support in the form of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ (Johnson Matthey Chemicals Ltd.) by using a combined ion-exchange and wet impregnation method; a known amount of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ was added to a well-stirred aqueous slurry of titanium dioxide at pH 9 and stirring was continued for 6 h. Subsequently, the water was evaporated by slowly heating to 363 K at reduced pressure. The platinum content was 2 wt %.

To determine the metal particle size of the reduced samples X-ray diffraction, transmission electron microscopy, and hydrogen chemisorption were applied. The electron micrographs were taken on a Philips 400 electron microscope and hydrogen chemisorption measurements were carried out in a conventional volumetric glass system. ESR spectra (X-band) were recorded with a Varian E-15 spectrometer equipped with a TE-104 dual sample cavity and a liquid helium flow cryostat. An in-situ cell was used⁷ and the temperature of the sample was kept constant between 20 and 293 K with a Cryoson CE 5348 temperature controller. Signal intensity and position were calibrated with the aid of the Varian strong pitch ($g = 2.0028$, $3.01 \times 10^{15} \text{ spins cm}^{-1}$). Quantitative measurements of signal intensities were performed at 20 K.

Results and Discussion

The combined ion-exchange and impregnation technique leads to a rather well-dispersed platinum phase on the titanium dioxide support, as is indicated by the absence of any metallic platinum X-ray diffraction line after reduction at 573 K and passivation of the Pt/TiO_2 sample. Electron micrographs showed the presence of raftlike metallic structures on the support, the mean particle diameter of which was found to be 3.1 nm. This particle diameter is in reasonable agreement with the H/Pt ratio of 0.7 found in hydrogen chemisorption, determined after subtraction of reversibly adsorbed hydrogen.

The influence of oxidation and reduction treatments on the Pt/TiO_2 sample was followed with electron spin resonance measurements, which yielded information on the state of the platinum, as will be discussed elsewhere.⁸ Here we will be mainly concerned with the titanium ESR signal found after reduction of the Pt/TiO_2 sample.

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Figure 1. X-band ESR spectrum for a Ti^{3+} species, recorded at 20 K after reduction at 573 K and evacuation at 293 K.

TABLE I: Intensity of the Ti^{3+} Signal

sample	pretreatment ^a	no. of Ti^{3+} / no. of Ti^{4+} ions
TiO_2	R 375, E 293	1×10^{-4}
Pt/ TiO_2	R 573	2.8×10^{-3}
	R 573, E 293	3.0×10^{-3}
	R 573, E 293, E 573	3.4×10^{-5}
	R 573, E 573	3.3×10^{-5}
	R 573, E 573, H 293, E 293	2.2×10^{-3}
	R 773, E 293	3.5×10^{-3}
	R 773, E 573	1.8×10^{-3}
	R 773, E 573, H 293, E 293	1.9×10^{-3}

^a R denoted reduction, E, evacuation, and H, hydrogen admission. Numbers indicate temperatures (K). The heating rate was 4 K/min. Time of the pretreatments at elevated temperatures 1 h, at 293 K 5 min. ESR spectra were recorded at 20 K.

This signal at $g = 1.92$ with $\Delta H = 100$ G (cf. Figure 1) is assigned to a Ti^{3+} species in an octahedral environment. The g value is in accordance with expectations from second-order perturbation theory for a $\text{Ti}^{3+} 3d^1$ system. This signal has been observed before in pure TiO_2 systems.⁹ The Ti^{3+} ESR signal observed after reduction of a Pt/ TiO_2 sample at 573 K for 1 h is about 30 times larger than that observed after reduction of pure TiO_2 under the same conditions (cf. Table I). This demonstrates that the reduction of the TiO_2 by hydrogen is catalyzed by the platinum. Apparently hydrogen chemisorbs dissociatively on platinum, after which the hydrogen atoms diffuse to the support and reduce Ti^{4+} ions to Ti^{3+} :

A similar reduction mechanism has been proposed for the uncatalyzed reduction of pure TiO_2 .¹⁰ In that case defect structures at the surface function as centers for the dissociative adsorption of the hydrogen.

Evacuation of the reduced Pt/ TiO_2 sample at room temperature did not change the intensity of the ESR signal. However, evacuation at 573 K after reduction at the same temperature decreased the intensity by approximately two orders of magnitude. On the other hand, evacuation at 573 K of a Pt/ TiO_2 sample reduced at 773 K made the ESR intensity decrease by only a factor of two.

At first glance these results seem inconsistent but one can find a natural explanation if closer attention is paid to the properties of the hydrogen atoms on the TiO_2 surface. After reduction of the Ti^{4+} cation by a hydrogen atom the resulting proton combines with an oxygen anion to form a hydroxyl anion. To compensate the decreased charge of the reduced titanium cation this hydroxyl anion will be in the immediate surroundings of this cation. As long as this hydroxyl anion does not diffuse too far away from its place of birth reactions 1 and 2 may be reversed upon evacuation:

The removal of H^+ in the form of H_2 brings about the oxidation of the Ti^{3+} ion to a Ti^{4+} ion and the decrease of the ESR signal. Also in this reverse process the platinum metal functions as a catalyst by aiding the formation of molecular hydrogen gas.

That no decrease in the ESR intensity is observed after reduction at 773 K followed by evacuation at 573 K must be due to the fact that in this case the reverse reaction cannot take place because the hydroxyl anions have disappeared at high reduction temperatures by dehydration of the TiO_2 surface:

From the work of Iwaki et al.¹¹ on pure TiO_2 it is indeed known that an appreciable loss in weight takes place when TiO_2 is reduced at temperatures above 673 K. An alternative explanation for the fact that after reduction at 773 K the ESR signal intensity is but weakly influenced by evacuation could be that the platinum is no longer capable of catalyzing the association reaction of hydrogen atoms, or is incapable of transferring protons into hydrogen atoms. This would be in line with observations reported in the literature that Rh/ TiO_2 and Pt/ TiO_2 were incapable of adsorbing hydrogen and of catalyzing the reduction of benzene after a high-temperature reduction.¹² This alternative explanation cannot be excluded completely, but the fact that the protons have left the surface in the form of water molecules¹¹ means that the reoxidation of the Ti^{3+} ions cannot take place, even if the platinum metal was still active.

The above explanation of our ESR observation means that in the Pt/ TiO_2 system not only reduction of the support plays an important role but also the intermediary presence of hydroxyl ions. The diffusion of hydrogen atoms from the platinum particles to the surrounding support surface during the formation of protons and reduced titanium ions is related to the so-called spillover phenomenon. In view of the observed catalytic effect of platinum (and of metals such as rhodium and iridium as well, to be published elsewhere⁸) on the formation of Ti^{3+} ions it is logical to assume that these Ti^{3+} ions are formed around (and beneath) platinum particles in the first place. This is confirmed by an experiment in which hydrogen is admitted at room temperature to a Pt/ TiO_2 sample which had been reduced and evacuated at 573 K. This sample therefore showed a small ESR intensity. After contacting the sample again with hydrogen at room temperature almost 70% of the ESR signal intensity that had been observed after reduction at 573 K was regained. This proves also the reversibility of reactions 1 and 2. The fact that not all the intensity was regained must be due to the

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Figure 2. Formation of Ti^{3+} ions at low reduction temperatures.

smaller diffusivity at room temperature.

The picture that emerges from the ESR experiments is that when small particles of platinum on TiO_2 are contacted with hydrogen at 573 K a surface layer on Ti^{3+} and OH^- ions is formed around the metal particles (cf. Figure 2). In a recent publication Gajardo et al. described ^1H -NMR measurements on the Rh/TiO_2 system.¹³ After reduction in hydrogen at 573 K and cooling the sample to room temperature under hydrogen they observed a signal ascribed to hydrogen atoms adsorbed on the metal and another signal shifted 140 ppm to higher fields. Because of this large shift they assigned this signal to protons on the support in the proximity of paramagnetic Ti^{3+} ions. These findings seem to support our ESR results.

From the figures presented in Table I a semiquantitative estimate can be made of the size of the particle area surrounding the metal particles. After reduction at 573 K 0.3% of the total number of titanium ions is reduced to Ti^{3+} . Given a load of 2 wt % Pt on TiO_2 and assuming the average platinum particle on the support to consist of 100 platinum atoms (dispersion = 0.7, $\bar{d}$ = 3.1 nm, rafts) this means that on the average 37 Ti^{3+} ions are present in the neighborhood of each platinum particle. In view of the dimensions of the TiO_2 lattice cell one may conclude that the hydrogen atoms that are spilled over to the TiO_2 support occupy an area that has about the size of a cross section through the average platinum particle. Depending on the shape of the metal particle the Ti^{3+} and OH^- ions may be under the particle if it is spherical- or droplet-like, or around the metal particle if its shape is half-spherical. The ESR results indicate that dehydration of the support

Figure 3. Dehydration of the TiO_2 surface at high reduction temperatures.

takes place at 773 K in the neighborhood of the metal particles; as a result a reduced form of titanium dioxide is formed. In accordance herewith Baker² has inferred from electron diffraction measurements that reduction of Pt/TiO_2 at 773 K leads to the formation of Ti_4O_7 layers at the surface of TiO_2 and that the noble metal particles spread as rafts over these Ti_4O_7 layers. The combination of ESR and electron microscopy techniques suggests that the formation of the so-called SMSI state might be a consequence of the formation of the Ti_4O_7 layer. In that case after reduction and dehydration of the support surface in the neighborhood of the metal particles Ti_4O_7 layers are formed and the metal particles start spreading over these layers. We suggest that in this special configuration the properties of the metal undergo a change (Figure 3). The reason for this special interaction between noble metal atoms and the Ti_4O_7 layer and thus for the special metal-support interaction has not become clear from the present investigation. If the above explanation for the formation of the SMSI state is correct it is especially the formation of the Ti_4O_7 layer which is crucial. Several studies have shown that the SMSI state can be returned to a normal metal-on- TiO_2 state when oxygen or water vapor is admitted to the sample.¹⁴ This is in accordance with the above explanation, since water destroys it by formation of OH^- groups, after which the Ti^{3+} ion can return to the Ti^{4+} state via reaction 3.

Acknowledgment. The present investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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