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Electron Exchange in TiO_2-Supported Silver Catalysts

I. Effect of the Reducing Pretreatments

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A study has been made of the effect of different reducing pretreatments on a highly dispersed TiO_2-supported silver sample, showing an EPR signal due to Ag^{2+} ions formed during impregnation. The reduction treatment using hydrogen produces silver aggregates and their formation is proposed to proceed through an electron transfer from a certain type of F-center in the TiO_2 surface to Ag^+. If the reduced sample is put into contact with oxygen, the silver aggregates are destroyed and the signal due to Ag^{2+} is partially regenerated, while adsorbed oxygen diffuses to the TiO_2 support where it is stabilized as O_2^-. Ultraviolet irradiation produces the same results as the hydrogen treatment, though in a smaller degree, provided that the surface of the TiO_2 support is in a fully hydrated state. In the case of reduction *in vacuo* or CO at 623 K the reduced silver is stabilized on the TiO_2, probably by strong metal–support interaction, and treatments at $T > 573$ K, in oxygen, are necessary to return the sample to its original state.

INTRODUCTION

During the last few years interest in the properties of TiO_2 has revived in a surprising way largely due to its new applications as a support for catalysts in different chemical processes, such as partial oxidation (*1*) and the control of nitrogen oxide pollutants (*2*), as an electrode in photoassisted water dissociation using electrochemical cells (*3*) and finally in modifying the properties of supported noble metals by a strong Brewer-type metal–support interaction (*4*). The use of TiO_2 as a support instead of more inert materials such as silica or alumina is due to the improvement of the catalyst properties because of the interaction between the support and the active phase. To study this type of interaction we have chosen the Ag^+/TiO_2 system, trying to determine the way in which the support modifies the properties of the silver and how these modifications affect the silver-catalyzed oxidation of ethylene to form ethylene oxide. In this part of the work we have studied the effects of the reduction method on oxygen adsorption on the catalyst, treating the Ag^+/TiO_2 sample under vacuum, carbon monoxide, hydrogen, or uv irradiation.

EXPERIMENTAL

Materials. The TiO_2 used was an anatase P 25 from Degussa having a BET surface of 49 ± 1 m^2 g^{-1}. A detailed study of its surface has been carried out previously using several techniques (*5*). The TiO_2-supported Ag^+ specimen (Ag^+/TiO_2) was prepared in the dark by impregnation of the oxidized TiO_2 support, previously treated in air at 623 K to remove most organic contaminants. A 0.1 *M* $AgNO_3$ solution was used in an oxygen-free atmosphere, followed by drying at 323 K to obtain a white sample loaded with ca. 1% Ag after reduction. Once prepared, the Ag^+/TiO_2 specimen was stored under N_2 atmosphere in the dark.

Reduction of the specimen in H_2 at 473 K leads to a uniform dark brown sample with a small pink tinge, whereas outgassing at 623 K for 3 h or reduction with CO at 623 K only produces grey-bluish colored samples with an intensity that increases with successive treatments, or higher temperatures.

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Methods. A Jeol JES-PE spectrometer working in the X-band was used for the EPR study, while ir spectra were recorded with a Perkin–Elmer 577 spectrometer, using self-supported pellets of the sample in a vacuum cell that could be outgassed to 10^{-4} N m^{-2}.

Adsorption and photoadsorption experiments were carried out in the same cells as previously used in the study of oxygen photoadsorption on TiO_2 (*6*).

RESULTS

Study of the Ag^+/TiO_2 Original Sample

The infrared spectrum of the original Ag^+/TiO_2 sample outgassed at 300 K was rather similar to the spectrum of the TiO_2 support. A broad band centered at 3480 cm^{-1} and a shoulder at 3720 cm^{-1} appear in the OH region, while a band at 1610 cm^{-1} indicates the presence of molecular water adsorbed on the surface. Bands at 2920 and 2860 cm^{-1} due to organic contamination are also resolved in the spectra with much higher intensities than in the original TiO_2 support.

Adsorption of C_2H_4 on the sample at 300 K after outgassing at the same temperature leads to the isotherm shown in Fig. 1, giving a V_m value which corresponds to ca. 0.7 C_2H_4/Ag^+, once the small adsorption on the TiO_2 support is subtracted. This value indicates a highly dispersed state of the Ag^+ ions at the TiO_2 surface.

In contrast with the oxidized TiO_2 support, which shows no EPR signal even at 77 K, the original Ag^+/TiO_2 specimen shows the spectrum of Fig. 2a, which could be detected even at room temperature. The spectrum is formed by a signal with axial symmetry, with $g_\perp$ = 2.066 and the parallel component not too well resolved, $g_\parallel \simeq 2.30$. It does not present a clear hyperfine structure, but in both zones of the spectrum, $g_\perp$ and $g_\parallel$, there are some shoulders which are better resolved after a treatment in vacuum at 623 K followed by reoxidation in oxygen at the same temperature. At 77 K, a small signal with axial symmetry, and $g_\perp$ = 1.981 and $g_\parallel$ = 1.972, is also observed in the original Ag^+/TiO_2 sample. This signal can be assigned to Ti^{3+} in substitutional position (*7*). The fact that the *g* values of the first of the two signals are higher then g_e, the free electron *g* value, indicates that it is due to a paramagnetic species with the unpaired electron in a more than half-full band. The *g* values of this signal are close to those given by McMillan and Smaller (*8*) for Ag^{2+}, a $4d^9$ ion, placed in an octahedral crystalline field with a tetragonal distortion. The lack of resolution of the Ag^{2+} hyperfine structure ($I = \frac{1}{2}$) can be attributed, in principle, to broadening by magnetic interactions of dipolar and/or exchange type.

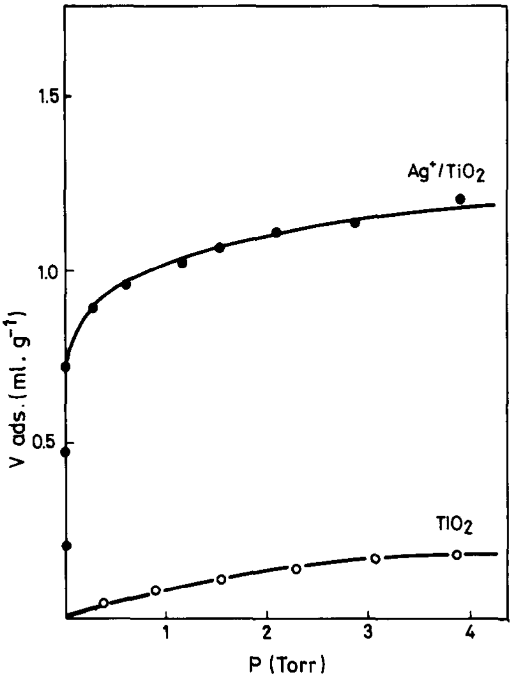


FIG. 1. Adsorption isotherms of C_2H_4 on Ag^+/TiO_2 and TiO_2 at 300 K.

Effect of Treatment in Vacuum of CO

Infrared spectra due to hydroxyl groups in the Ag^+/TiO_2 sample after successive outgassing treatments at increasing temperature are shown in Fig. 3. After outgassing at 623 K for 3 h the sample still shows a

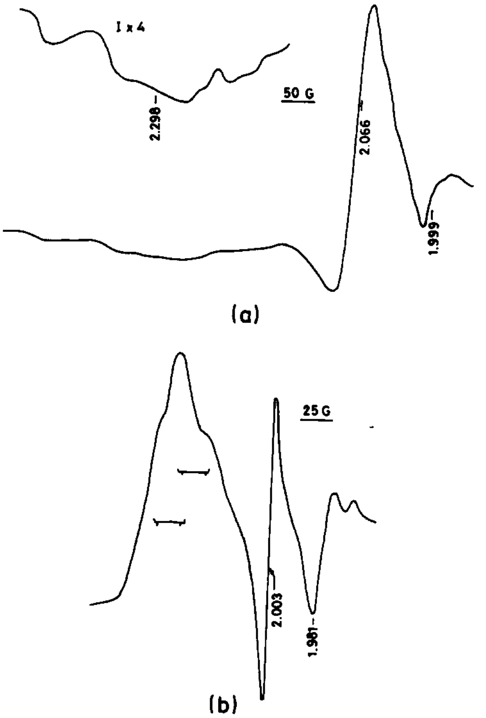


FIG. 2. EPR spectra, at 77 K. (a) Untreated Ag^+/TiO_2. (b) Ag^+/TiO_2 heated at 623 K, under vacuum.

strong band at 3720 cm^{-1}, which contrasts with the small band at this value observed in the spectrum of the TiO_2 support treated in the same conditions. The broad band at 3480 cm^{-1} and the band at 1610 cm^{-1} indicate the presence of molecular water in the original Ag^+/TiO_2 surface, but they are removed by heating at ca. 473 K as previously observed for the TiO_2 support (*6*). The presence of a considerable amount of hydrocarbon impurities may be detected in all the spectra by strong bands at 2960 and 2860 cm^{-1}, which almost vanish after outgassing at 623 K. As previously mentioned, this poisoning was much higher than for the TiO_2 support, indicating that the presence of the silver has enhanced in some way the adsorption of organic species.

When the sample was heated at 623 K for 3 h under vacuum, it showed a greyish-blue color which became darker after several of these treatments. The EPR spectrum at 77 K is also changed. The signal of Ag^{2+} now has about half the original intensity, but shows a better resolved shoulders (Fig. 2b) while a new symmetric signal with g = 2.002 and ΔH = 6 G is present. This signal saturates easily and does not disappear at 300 K or in presence of a high oxygen pressure. Signals with the characteristics of this line are generally attributed to carbonaceous residues (*9*). In the same spectra, a signal due to Ti^{3+} is also present, but with an intensity lower than in the TiO_2 support after a similar treatment. After being heated at 773 K under vacuum, the signal due to carbonaceous material became narrower and higher. This confirms that the Ag^+/TiO_2 sample strongly adsorbs hydrocarbons as previously revealed by its ir spectra, their elimination being difficult under vacuum.

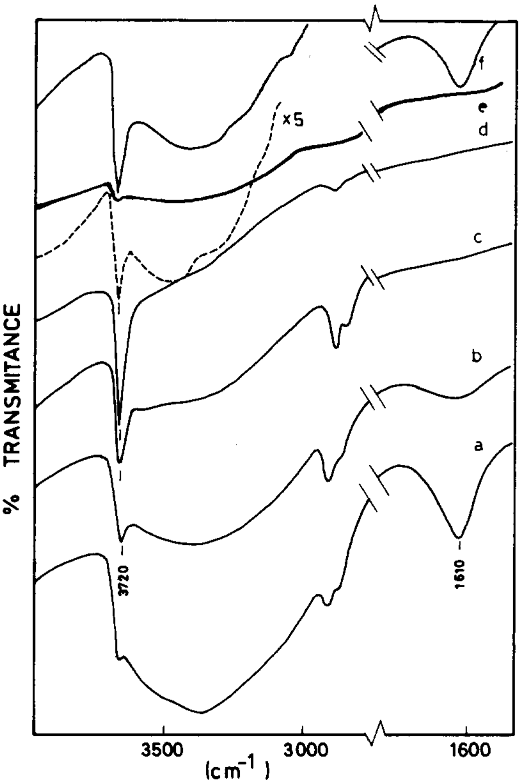


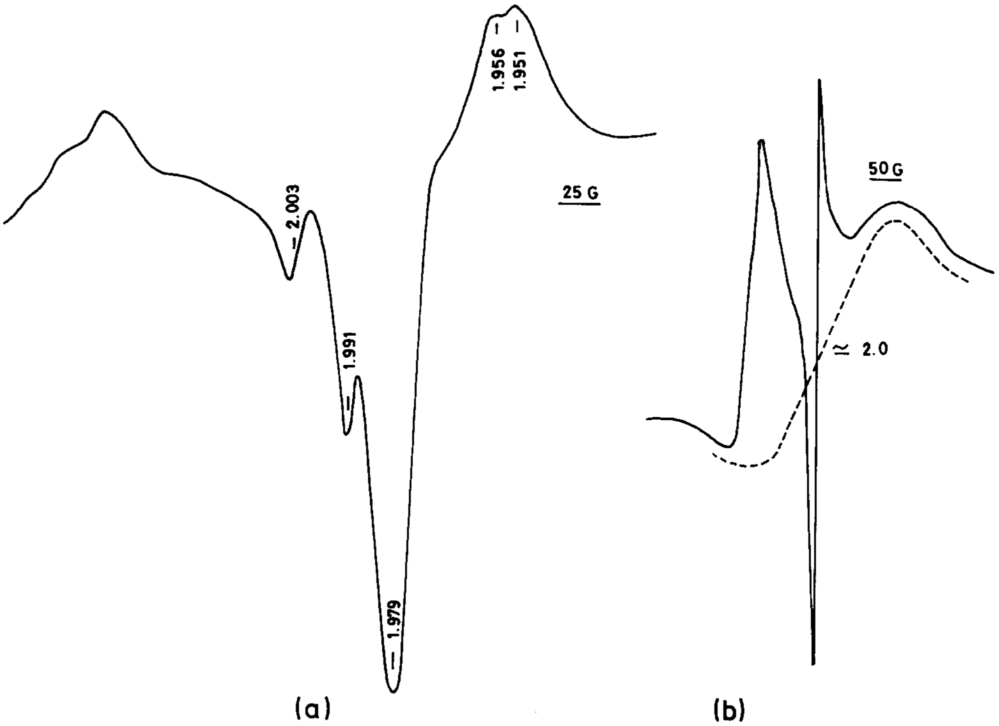
FIG. 3. Infrared spectra of Ag^+/TiO_2 heated under vacuum at different temperatures: (a) 300 K; (b) 373 K; (c) 473 K; (d) 623 K; (e) TiO_2 support outgassed at 623 K (dashed line ×5); (f) ir spectra of Ag^+/TiO_2 reduced in H_2 at 473 K.

Similar results were obtained when the sample was reduced in CO at 623 K, though in this case a more intense Ti^{3+} signal was observed, approximately double that in the vacuum-reduced sample, while the signal due to Ag^{2+} ions was further reduced and the sample had a somewhat darker greyish-blue color.

Effect of Hydrogen Treatments

If a Ag^+/TiO_2 sample treated for 3 h at 623 K under vacuum, and then reoxidized at the same temperature, is treated in hydrogen under mild conditions (383 K for 10 min.) there is a change from the original white to a brownish color with a pink tinge. The EPR spectrum, at 77 K, is given in Fig. 4a. The features observed in the zone $g \simeq 2$ can be described as consisting of two signals, with $g_\perp = 1.979$, $g_\parallel = 1.956$, and $g_\perp = 1.991$, $g_\parallel = 1.951$, which have been previously assigned (*7*) to substitutional and interstitial Ti^{3+} ions, respectively. The signal due to Ag^{2+} was still present, though with a much lower intensity, as well as the small narrow signal ($g \simeq g_e$) previously assigned to carbonaceous material. At 300 K (Fig. 4b) besides these two signals due to Ag^{2+} and carbon impurities, a new symmetric and broad line is observed, with $g \simeq 2$ and $\Delta H \simeq 100G$. This signal is not detected at 77 K, probably because of its overlapping with the other lines, particularly those of Ti^{3+} which are not observed at 300 K.

With stronger reduction conditions (hydrogen at 473 K during 1 h) the Ag^{2+} signal completely vanishes from the spectrum at 77 K. The interstitial Ti^{3+} signal is no longer observed, probably due to overlapping with the substitutional Ti^{3+} signal, which is now broadened and shows an increased intensity, about 30 times larger than in the vacuum or CO-reduced samples. The brown color of the sample becomes darker than in the former case and the broad signal at $g \simeq g_e$ disappears.



(a) (b)

FIG. 4. EPR spectra of Ag^+/TiO_2 treated in hydrogen at 383 K: (a) spectrum at 77 K; (b) spectrum at 300 K.

The ir spectrum of this sample, included in Fig. 3, indicates that reduction under H_2 at 473 K, followed by 300 K outgassing, leaves a rehydrated surface, as shown by the band at 1610 cm^{-1} due to molecular water. Outgassing at $T \geq 473$ K removes this band, leading to a spectrum with a single band at 3720 cm^{-1}, which was almost similar to that observed after outgassing at 673 K the original Ag^+/TiO_2 sample.

Oxygen Adsorption in the Dark on Reduced Samples

If oxygen (1–10 N m^{-2}) is contacted at 300 K with the vacuum or CO-reduced greyish-blue samples no noticeable change in the EPR spectrum occurs. Heating at 623 K in oxygen is required to produce an increase in the Ag^{2+} signal, but the value observed in the original sample is not reached. The carbon signal and the signal due to Ti^{3+} ions almost disappear, while the sample recovers its initial white color.

In contrast with the above results, the samples reduced with hydrogen under strong conditions readily adsorb oxygen (1–10 N m^{-2}), at 300 K, in the dark and recover their original white color in a few minutes. The variation of the oxygen pressure could be described by a kinetic law of the form $P_{\text{ads } O_2} = kt^{1/2}$, which indicates that O_2 uptake is a diffusion-controlled process in these conditions. In fact, similar results were obtained using vacuum or CO-reduced greyish-blue samples when water vapor was allowed to contact these samples before oxygen. Water immediately produces in this case a change from the characteristic greyish-blue tinge to a homogeneous dark brown color which readily bleaches in the presence of oxygen.

The changes in the surface species during the oxygen adsorption on one of these dark brown colored samples was followed by EPR, at 77 K, as a function of time. With the sample at 77 K *in vacuo*, oxygen was introduced into the EPR cell at a pressure of 0.1 N m^{-2} and the change of the EPR spectrum was followed in a cyclic way. First was observed an immediate growth of the Ag^{2+} signal, parallel to a slow fall of the Ti^{3+} signal. Only when these two signals were very strong and very weak, respectively, was a new signal detected. The g values of this new signal, of orthorhombic symmetry, shown in Fig. 5, were $g_1 = 2.0225$, $g_2 = 2.009$, and $g_3 = 2.002$, which are similar to those of O_2^- species adsorbed on the reduced TiO_2 support (*10*). After some time at 77 K, under a large O_2 pressure, the sample recovers its original white color. Similar results were obtained at 300 K recording the Ti^{3+} EPR signal at intervals at 77 K, though in this case the rate of the process was much larger. It is worthy of note that the Ag^{2+} signal restored by reoxidation is not affected by oxygen pressure through dipolar interactions, probably indicating that those ions are screened from the gas phase.

Effect of uv Irradiation on the Samples

To complete our study of the interactions in the TiO_2-supported silver samples, the photoactivity of both the original Ag^+/TiO_2 sample (outgassed at 300 K) and a sample outgassed at 623 K for 3 h and then reoxidized in oxygen at the same temperature, was examined.

Ultraviolet irradiation *in vacuo* of the Ag^+/TiO_2 sample outgassed at 300 K leads to a homogeneously pink-brown colored surface, but it completely bleaches in a few minutes in contact with oxygen in the dark. On the contrary, changes were not observed with the sample outgassed and reoxidized at 613 K, which remains white when it is irradiated under vacuum.

Oxygen adsorption was not observed in the dark for either of the two specimens. However, irradiation with uv light ($\lambda \sim 360$ nm) leads to O_2 photoadsorption, as shown in Fig. 6, followed by a slow photodesorption of O_2 after a few minutes of irradiation in the sample outgassed at 300 K. By comparing these results with photoadsorption of oxygen on the TiO_2 support, pretreated under similar conditions, shown in the same figure, it may be concluded that the pres-

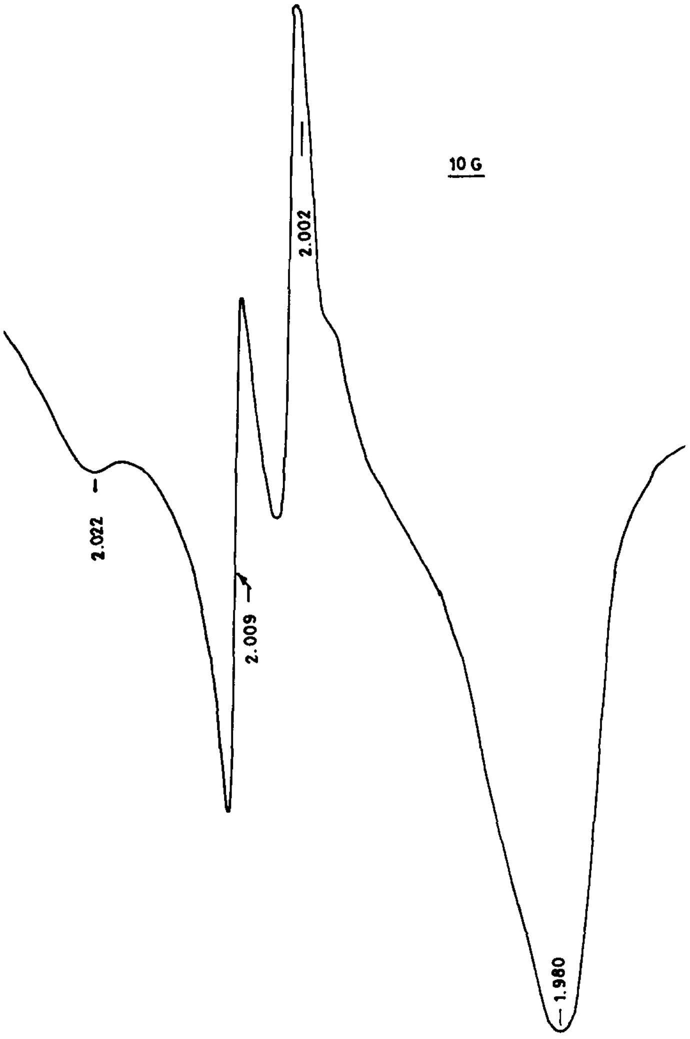


FIG. 5. EPR spectrum of oxygen adsorbed on reduced Ag^+/TiO_2 at 77 K.

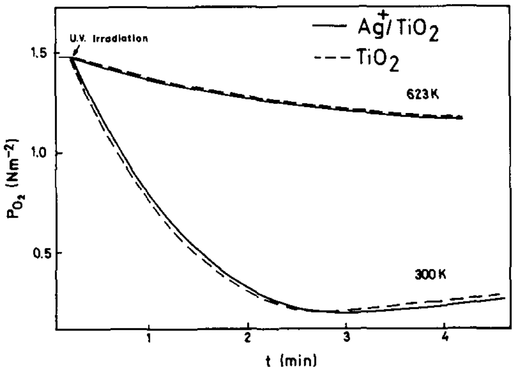


FIG. 6. Oxygen photoadsorption at 300 K on hydrated and dehydroxylated Ag^+/TiO_2 (full lines) and TiO_2 samples (broken lines). Outgassing temperatures in the figure.

ence of Ag^+ does not modify the photoactivity for oxygen uptake of the TiO_2 support in our conditions. Moreover, irradiation in the presence of oxygen does not change the white color of either of the two samples, indicating that oxygen prevents the uv-induced darkening of the original surfaces characteristic of Ag^+ reduction.

The assessment of the samples irradiated at 77 K in oxygen by the EPR technique shows the presence of signals due to O_2^-, O_3^-, and O_3^{3-} species previously reported on uv-irradiated TiO_2 surfaces (*11*). In particular, the sample outgassed at 623 K shows signals due to the three species on the surface at 77 K, but only the one corresponding to O_2^- remains at 300 K. The g values of this O_2^- species at 77 K are similar to those previously measured on TiO_2, but they are slightly displaced ($g_1 = 2.023$, $g_2 = 2.009$, and $g_3 = 2.003$) at 300 K, suggesting a possible influence of the presence of the Ag^+ ions on the crystal field affecting these species on the Ag^+/TiO_2 surfaces.

DISCUSSION

The impregnation of TiO_2 with a 0.1 *M* $AgNO_3$ solution leads to Ag^+ ions on the support in a highly dispersed state, as deduced from the C_2H_4 adsorption isotherms at 300 K on the original sample. In addition, the presence of Ag^{2+} ions is observed by EPR even at 300 K, which indicates the existence of a small number of sites with a high electron affinity at the oxidized TiO_2 surface where the reaction $Ag^+ \rightarrow Ag^{2+} + e^-_{\text{trapped}}$ occurs, with transference of electrons to the oxide and stabilization of the Ag^{2+} ions in a site producing a tetragonally distorted octahedral field. The broadening of the EPR signal due to these ions can be ascribed to different origins, but it is likely that heterogeneity of the sites, where the Ag^{2+} are adsorbed, might account for this fact owing to the large radius of this ion (0.89 Å), when compared with Ti^{4+} (0.68 Å), which would induce distortions in the surroundings, showing slightly different crystal fields. Actually, part of the Ag^{2+} ions are irreversibly removed by heating *in vacuo* at 623 K and they are not reformed by reoxidation at the same temperature, indicating their poor stability on the TiO_2 support.

In principle, the electrons resulting from the oxidation of Ag^+ should be responsible for the small Ti^{3+} signal observed in the EPR spectrum of the original sample at 77 K. However, considering the low intensity of this signal in relation to that of Ag^{2+}, we must assume that part of the Ti^{3+} ions are coupled together or have further reacted giving up their unpaired electron, thus becoming undetectable by EPR. Although the existence of Ti^{3+} bands has been recently reported in slightly reduced TiO_2 single crystals (*12*) from UPS and ELS studies, it seems unlikely in our fully oxidized support. We must therefore assume that generated Ti^{3+} donors in contact with the aqueous silver solution might react by reducing Ag^+ to Ag^0.

Figure 7a shows pinning of the Fermi level of TiO_2 at the Ag^+/Ag^0 potential (0.79 V vs NHE) in the wet Ag^+/TiO_2 sample. It is worthy of note, from this scheme, that reduction would displace the Ag^+/Ag^0 standard potential upward, with the Fermi level of the TiO_2 support moving in the same direction upon reduction of the samples. A reduction to metallic silver (after total H_2 reduction) will produce a change in the position of E_F, to become pinned at the work function of the silver (4.49 eV), leading to the near flat band situation shown in Fig. 7b.

Since the thermal treatment of the original hydrated Ag^+/TiO_2 sample, under vacuum or CO, produces a change of color from white to greyish-blue, with simultaneous formation of a signal due to Ti^{3+}, which is always comparatively much smaller than in the TiO_2 support treated under similar conditions, we may conclude that electrons are being transferred from Ti^{3+} to Ag^+ ions to produce metallic silver. The observed change in color must then be attributed to partial reduction of Ag^+ into Ag^0 and formation of small and well-dispersed crystallites, all over the reduced TiO_2 surface, with some kind of metal–support interaction.

In fact, the lower effect of the outgassing treatment in reducing the ir band at 3720 cm^{-1} from the Ag^+/TiO_2 samples, compared with the TiO_2 support (see Fig. 3), suggests that silver is affecting the thermal stability of these groups at the TiO_2 surface, either by direct interaction or merely by blocking the diffusion process required for their removal (*6*). Since no shift in the wavenumber was observed, the situation is not incompatible with a position of Ag^0 atoms or clusters on the top of exposed Ti^{4+} ions at

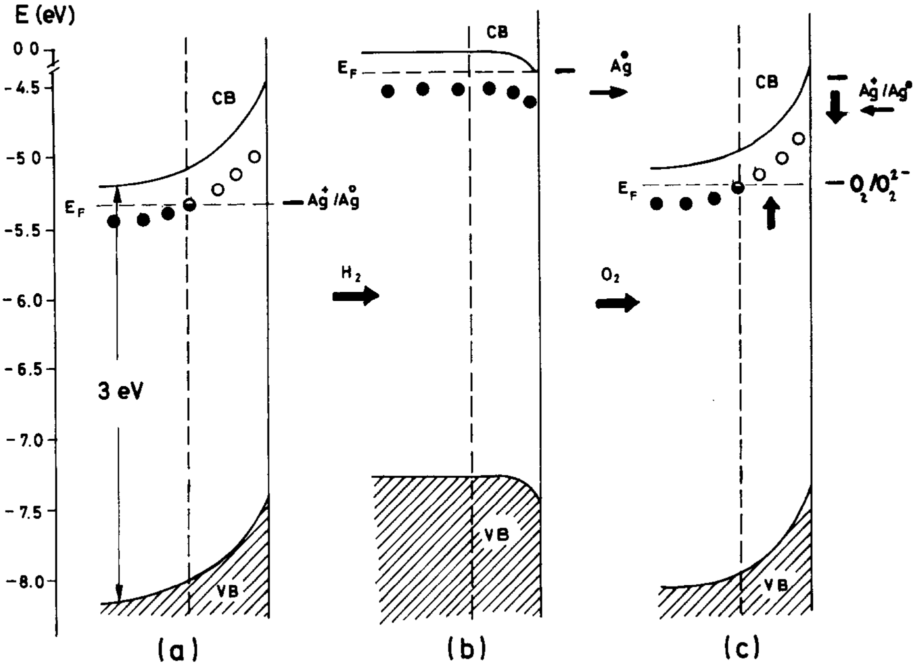
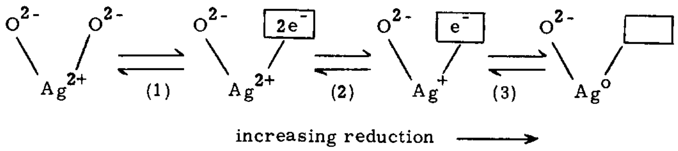


FIG. 7. Scheme of bands in the Ag^+/TiO_2 system. (a) Original sample showing Fermi level pinning at the Ag^+/Ag^0 potential. (b) After reduction in hydrogen. (c) During adsorption of oxygen showing pinning at the O_2/O_2^{2-} potential and reoxidation of silver.

the progressively dehydroxylated surface, blocking the diffusional pathway for residual hydroxyl elimination. This situation must give rise to an incipient strong metal–support interaction (through Brewer-type bonding), as previously observed for other TiO_2-supported metals (*4, 13*), which seems confirmed by the higher stability of the reduced samples to oxidation at 300 K. It is worthy of note that water preadsorption seems to be able to remove this interaction leading to a color change from grey to brown, making possible now the fast reoxidation of the silver with oxygen.

According to Reymond *et al.* (*14*), CO or vacuum reduction would produce oxygen vacancies on the TiO_2 support, and this probably allows closer contact between the small silver crystallites and the Ti^{4+} or Ti^{3+} ions of the reduced support, as previously observed for Pt and Rh on TiO_2 (*15–17*). In fact, vacuum or CO reduction would increase the number of Ti^{3+} ions in the surface of the support, so, immediate reduction of Ag^+ will occur while the Fermi level, originally pinned at the Ag^+/Ag^0 potential, will slowly move upward to become closer to the work function of metallic silver. However, isolated silver atoms, whose EPR spectrum is well known (*18*), have not been detected in our samples, which might be due either to fast clustering at the reduction temperatures or to interactions of the metal atoms with the support. In principle, our EPR evidence can be accounted for by assuming the formation of very small silver particles.

In comparison with vacuum or CO, the two main effects of the hydrogen treatment of the samples are, first, to increase the Ti^{3+} signal, indicating that total reduction of the silver might be achieved in these conditions and a great excess of Ti^{3+} ions does exist now at the support (Fig. 4a), and, second, to produce a highly hydrated surface. Isolated silver atoms could not be observed also in this case, but a broad signal ($g = g_e$, $\Delta H = 100$ G) was present in the sample reduced in H_2 under milder conditions, which disappears for a stronger treatment together with the Ag^{2+} signal. A similar broad signal has been observed by Abou-Kaïs *et al.* (*19*) in γ-irradiated AgY zeolites and tentatively assigned to F-centers. Signals of this type have also been detected in other systems when a supported metal forms small metallic particles, as in the case of platinum on TiO_2 (*20*) or palladium on Y-type zeolite (*21*). The signal is too broad to be assigned, on the base of its parameters, to conduction electrons in small silver particles (*22*). Although this interpretation cannot be totally rejected, we think that the most probable origin of this signal is a species of the type "Ag^+-F-center," previously assumed by Clark and Vondjidis (*23*) to explain the wide increase in absorbance observed in the infrared spectra of samples of TiO_2-supported silver upon hydrogen reduction. An explanation for the "Ag^+-F-center" sites can be given in terms of partial reduction of the "Ag^{2+}-sites" assuming that in the oxidized state the Ag^{2+} ions are buried in subsurface layers, though reduction removes oxygen from their coordination sphere, thus becoming exposed and simultaneously reduced according to Scheme 1.



(1)

If one F-center becomes associated with a Ag^+ ion, as in Step 2 of Scheme 1, this cation will look very much like a silver atom and it may be considered as a precursor of the total transfer to produce an exposed silver atom (Step 3). Further silver clustering, which according to Clark and Vondjidis (*23*) is much faster on wet TiO_2 surfaces, would lead now to growth of silver crystallites producing the dark brown colored samples.

In agreement with Clark and Vondjidis (*23*), we also found that homogeneous brown colored surfaces appear either after uv irradiation *in vacuo* of hydrated Ag^+/TiO_2 samples or when water vapor is added to a vacuum-reduced sample. According to our previous results on TiO_2 (*6*), hydroxyl groups will act as trapping centers for photogenerated holes, leaving the electrons that may now be given to Ag^+ ions to promote Ag^0 according to:

$$OH_b^- + h \sim e \to OH^\cdot + e_{CB} \qquad (2)$$

$$OH^\cdot \to \tfrac{1}{2}H_2O_2 \to \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \qquad (3)$$

$$e_{CB} + Ag^+ \to Ag^0 \qquad (4)$$

This mechanism is similar to that assumed by Reiche *et al.* (*24*) for reduction of Cu^{2+} to Cu^0 in uv-irradiated TiO_2 aqueous suspensions, and recently by Kawai and Sakata (*25*) for reduction of Ag^+ to Ag^0 in uv-irradiated Ag^+/TiO_2 aqueous suspensions. This mechanism is supported by the observed photodesorption of oxygen from the hydroxylated Ag^+/TiO_2 sample, as previously found for highly hydroxylated TiO_2 surfaces (*6*). Photogenerated silver atoms would readily diffuse on the wet TiO_2 surface to form bigger dark-brown conglomerates, as previously observed by Clark and Vondjidis (*23*). According to our results, oxygen can favorably compete with silver for the photoelectrons, since as shown in Fig. 6 Ag^+ loading does not appreciably modify the photoadsorption of oxygen by the TiO_2 support and, in the dark, bleaching immediately occurs when oxygen is adsorbed on a vacuum irradiated sample indicating the oxidation of the silver, particularly under wet conditions.

It is likely that water would inhibit the metal–support interaction in the samples reduced under water-free conditions (i.e., *in vacuo* or CO reduction) as our wetting experiments with these surfaces suggest. Our results are similar to those recently reported by Baker *et al.* (*15, 16*) for TiO_2-supported platinum, where these authors have found that water at 525 K or oxygen at 875 K are required to remove strong metal–support interaction. In our vacuum or CO-reduced samples a similar though weaker effect is observed at 300 and 428 K for H_2O and O_2, respectively. However, here oxygen leads to simultaneous reoxidation of the less noble silver metal, producing the total bleaching of the sample. When the dark oxygen adsorption leading to bleaching of the brown samples is followed by EPR, the observed fast increase of the Ag^{2+} signal at the earliest stages of this process suggests that oxygen adsorption drastically changes the position of the Fermi level, so that reduced "Ag^{2+} sites," buried in subsurface layers, act just as a paramagnetic probe, according to the equilibria above (Scheme 1) involving an F-center.

In fact, our results for oxygen adsorption can be interpreted in terms of the molecular orbital analysis made by Beran *et al.* (*26*) for oxygen adsorption on silver, using the band model for Ag^+/TiO_2, if we consider the possibility of electron transfer between silver and the TiO_2 support. Let us assume that only O_2^*, O_2^-, and O_2^{2-} are formed upon oxygen adsorption on our sample. In a first stage, when the electron density at the silver is at its highest level (H_2 reduced sample), formation of O_2^{2-} would occur on the reduced silver while the Fermi level of the TiO_2 support readily falls as shown in Fig. 7c to become close to the O_2/O_2^{2-} potential (+0.76 V vs NHE), so silver would readily oxidize to Ag^+ according to:

$$Ag^0 + O_2 \rightarrow Ag^+ + O_2^- \qquad (5)$$

$$Ag^0 + O_2^- \rightarrow Ag^+ + O_2^{2-} \qquad (6)$$

The newly formed Ag^+ ions would be immediately reduced by the Ti^{3+} ions, so that the EPR signal of these latter decreases until it completely vanishes. Thus electron transfer from the TiO_2 support to the silver crystallite through the generated Schottky barrier probably accounts for the diffusion controlled kinetics for oxygen adsorption. During this stage the TiO_2 Fermi level must become close to the O_2/O_2^{2-} potential while the silver remains in its metallic form. In a second stage, once all the Ti^{3+} have been consumed, the silver crystallites become progressively oxidized, and probably redispersed, while the less reduced O_2^- species are not readily reduced to O_2^{2-} and they spill over onto the TiO_2 support, where they become stabilized on Ti^{4+} sites. In fact, the observed O_2^- species have $g_z = 2.0225$, corresponding to a species bonded to a cation with charge +4, though it is slightly higher than the value observed in hydrogen-reduced TiO_2 ($g_z = 2.020$), but rather similar to the values previously obtained by us in the system H_2O_2/TiO_2 (*27*), where differences in g_z have been found depending on the hydroxylation state of the TiO_2 surface. In this second stage, the Fermi level would be again pinned close to the standard potential of Ag^+/Ag^0, most of the silver being now in the form of Ag^+, as in the original Ag^+/TiO_2 sample.

Finally, it is interesting to compare the behavior of our reduced Ag^+/TiO_2 sample with silver supported on SiO_2 and Vycor glass, where O_2^- species bonded to silver have been detected by EPR (*28, 29*). In our hydrogen-reduced sample the high electron density on the silver, induced by the support, seems to produce a deeper oxidation up to O_2^{2-}, which, according to the MO calculations of Beran *et al.* (*26*) would produce total oxidation of C_2H_4. While silver supported on silica or alumina is a well-known catalyst for partial oxidation of C_2H_4 into C_2H_4O, our reduced sample only produces total oxidation into CO_2 and H_2O (*30*). In fact, the formation of strongly reduced O_2^{2-} species would readily produce very reactive O^- radicals under rather mild thermal conditions, which are effective species in total oxidation processes (*31*). In a similar way, it has recently been shown (*17*) that TiO_2-supported Rh catalysts enhance CO reduction of NO by increasing dissociative (strongly reductive) adsorption of NO on the supported rhodium as a consequence of the enhanced donor properties of the TiO_2-supported Rh.

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