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Electron Spin Resonance Studies on Titanium Dioxide and Magnesium Oxide—Electron Donor Properties[1]

M. CHE, C. NACCACHE, AND B. IMELIK

Institut de Recherches sur la Catalyse, C.N.R.S., 39, Bd du 11 Novembre 1918, 69-Villeurbanne, France

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The electron donor properties of TiO_2 and MgO have been investigated by tetracyanoethylene and trinitrobenzene adsorption. The electron donor centers are associated with OH^- groups present on the surfaces of the solids activated at low temperature (<300°). During the dehydration of TiO_2 and MgO at higher temperature, weakly coordinated O^{2-} ions are formed on their surfaces, and these are responsible for the reducing properties of these solids.

INTRODUCTION

The adsorption of tetracyanoethylene (T.C.N.E.) on transition aluminas leads to the formation of radical–anions $(T.C.N.E.)^-$ (*1*). The electron donor centers have been identified with OH^- ions and AlO^- ions (*2*) and more recently (*3*) these sites were associated with unsolvated hydroxyl ions and defect centers involving oxide ions. Tench and Nelson have shown that magnesium oxide possesses similar properties (*4*). Nevertheless, without contradicting the previous hypothesis on the nature of the electron-donor sites in aluminas, these authors conclude that negative ion formation involves electron transfer from a surface O^{2-} ion to the acceptor molecule. This transfer depends on the electron affinity of the adsorbate. For example, with oxygen, such a transfer is not possible without a source of energy (γ or uv rays) (*5*), whereas sym–trinitrobenzene (T.N.B.), because of its strong electron affinity, readily yields the corresponding anion (*6*).

In the work of Tench and Nelson (*4*), no quantitative study of the phenomenon was carried out and the experiments were confined to a "high temperature" magnesium oxide. We have therefore carried out a systematic study of the adsorption of electron acceptor compounds on the surface of TiO_2 and of MgO.

EXPERIMENTAL METHODS

Materials

Titanium dioxide was prepared by hydrolysis at 0°C of the tetrachloride. The solution was neutralized by 6N caustic soda and the precipitate was washed until free from Cl^- ions. It was then dried at 120°C. The solid heated at 300°C for 20 hr had the anatase structure and gave a measured specific surface area about 300 m^2/g.

Magnesium oxide was prepared by decomposition of the hydroxide following the method described elsewhere (*7*). Benzene was stored over active silica–alumina catalyst and filtered before use. TCNE, and T.N.B. (Eastman organic chemical products) were used without further purification.

Sample preparation. Samples were activated by two methods: (i) heating *in vacuo,* (ii) heating in flowing oxygen. The pretreatment temperature varied between 100°C and 800°C. Samples for ESR measurements were contained in 5 mm

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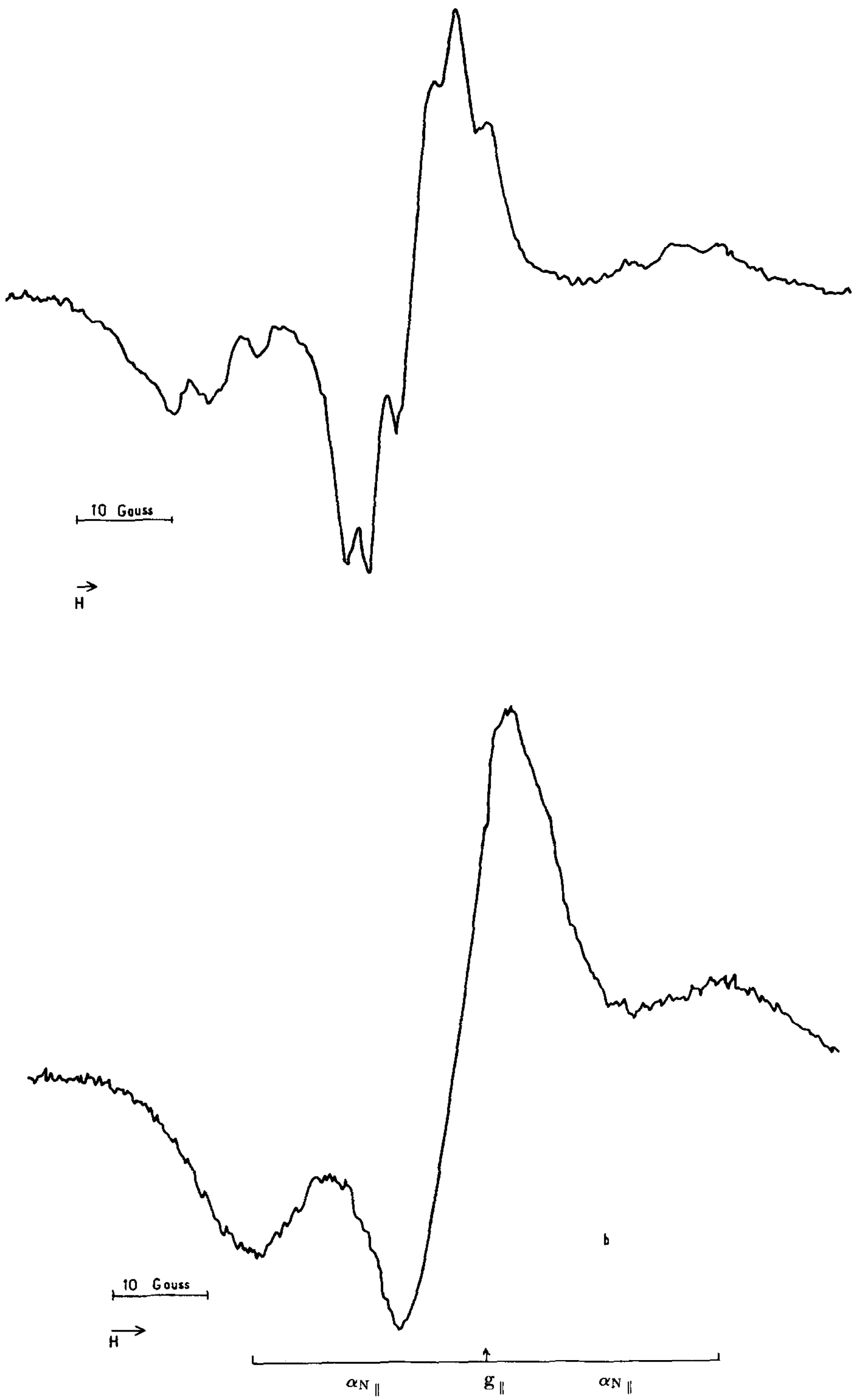


FIG. 1. Electron spin resonance spectra (first derivative) of T.N.B. on TiO_2: (a) adsorbed from benzene at 20°C on sample dehydrated at temperature lower than 300°C; (b) adsorbed from benzene at 20°C on sample dehydrated at temperature higher than 300°C.

OD quartz tubes. These were joined to wider glass tubing which could be attached directly to a high vacuum system (10^{-6} Torr). The adsorption of T.C.N.E., T.N.B. and D.N.B. in benzene solution was carried out in the absence of oxygen following a method described elsewhere (*2*).

Electron spin resonance. ESR spectra were obtained on a Varian Spectrometer (model V.4502) with 100 kcps field modulation at 9.3 Gc/s. All spectra were recorded at room temperature. Radical–ion concentrations were estimated by comparison of the areas obtained by double integration of the first derivative curves for the sample and standard solutions of 1-1-diphenyl-2-picrylhydrazyl in benzene.

RESULTS

ESR Spectra. When a titanium oxide sample, heated *in vacuo* or in an oxygen stream at temperatures lower than 300°C, was saturated by adsorption of T.C.N.E. from benzene solution, the catalyst immediately developed a reddish-brown color and gave the nine line spectrum attributable to the radical–ion of T.C.N.E. The radical–ion spectrum obtained after adsorption of T.N.B. was much better resolved. It consisted of three principal lines, each of them possessing in addition a hyperfine structure with five components (Fig. 1a).

When TiO_2 samples were heated at temperatures higher than 300°C a single ESR line was observed for the radical–ion of T.C.N.E., whereas the spectrum of the T.N.B. anion showed three lines without additional hyperfine structure (Fig. 1b).

With magnesium oxide the spectrum similar to Fig. 1a was obtained for treatment temperatures lower than 200°C and that of Fig. 1b for higher temperatures.

Influence of Activation Temperature on the Formation of Negative Ions

TiO_2. Figures 2a and 2b show the effect of activation temperature on the formation of T.C.N.E. anions on TiO_2. The radical–anion concentration increased with pretreatment temperature. A first maximum was reached at about 250°C, and a second at about 500–600°C.

$Mg(OH)_2$. Figure 3 shows the curves giving the T.C.N.E.$^-$ radical–ion concentration versus the pretreatment temperature.

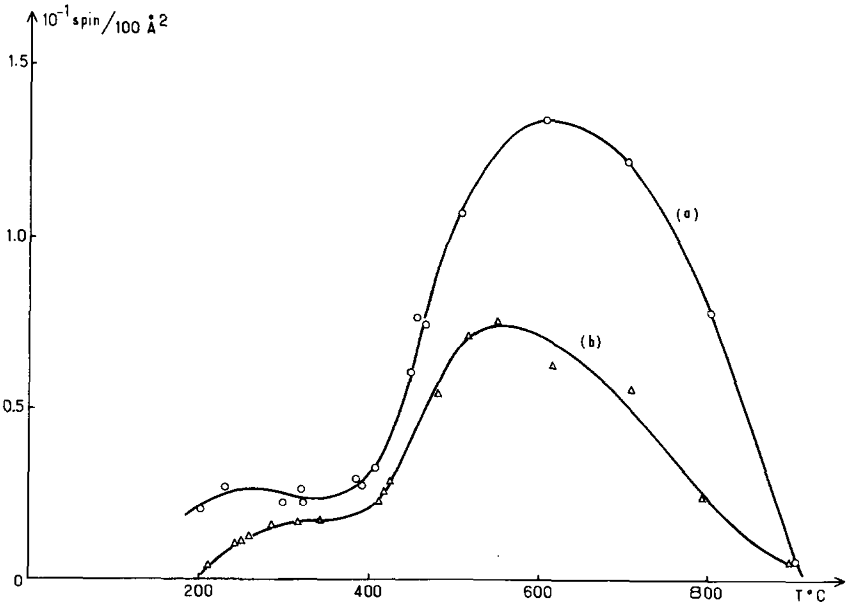


FIG. 2. Radical-forming activity of TiO_2 as a function of activation temperature with tetracyanoethylene as adsorbate: (a) Treatment *in vacuo;* (b) Treatment in oxygen.

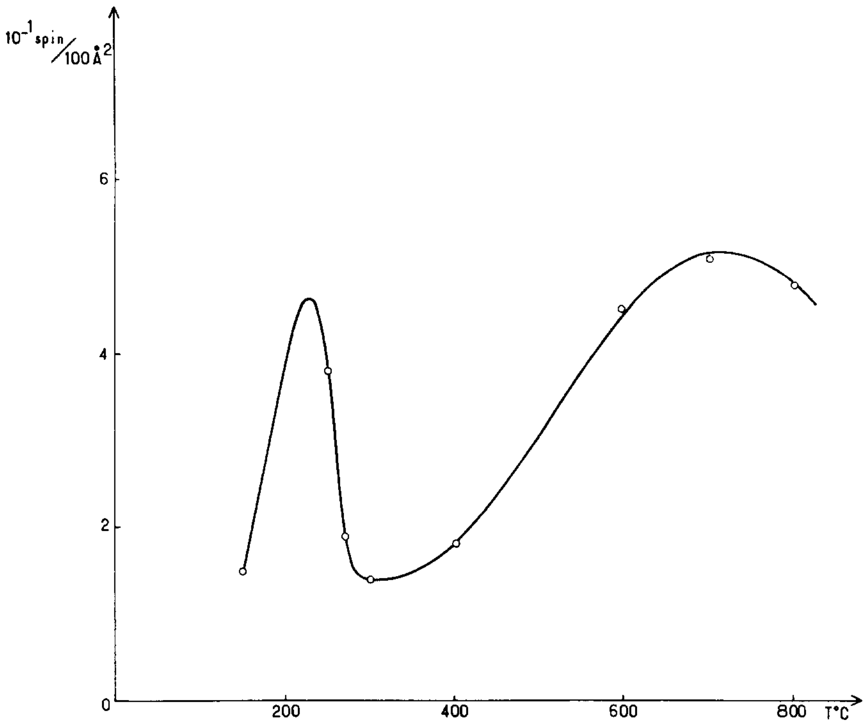


FIG. 3. Radical-forming activity of MgO as a function of activation temperature with T.C.N.E. as adsorbate.

Thermogravimetric Study

$Mg(OH)_2$. The thermal decomposition of $Mg(OH)_2$ to MgO is influenced by the water vapour pressure in the reactor (*7, 8*). Therefore, it was important to perform the thermogravimetric analysis of $Mg(OH)_2$ in the same experimental conditions as those used for the negative radical formation study. The results are shown in Fig. 4. In agreement with a previous study (*7*), $Mg(OH)_2$ at room temperature retained physically adsorbed water, which was completely removed at about 180°C. Between 180°C and 220°C, the weight loss was $\sim 30\%$, which corresponds approximately to the theoretical loss in the equation: $Mg(OH)_2 \rightarrow MgO + H_2O$. It seems therefore that in our experimental conditions the thermal decomposition of the hydroxide started at 180°C and was more or less complete at 220°C. However, the weight loss observed between 220°C and 800°C suggested the presence of some water of constitution in the MgO.

It should be pointed out that the sharp increase in anion concentration on MgO occurred in the temperature range in which the magnesium hydroxide was converted into the oxide.

TiO_2. The weight loss of TiO_2 versus the treatment is plotted in Fig. 5. The behavior was simpler than for $Mg(OH)_2$. First, the physically adsorbed water was removed. Then as the dehydration temperature was raised the weight loss corresponded to the elimination of bound water by condensation between two OH groups.

DISCUSSION

The spectrum of Fig. 1b, which is also observed after adsorption of trinitrobenzene on alumina (*6*), magnesium oxide (*4*) and stannic oxide (*9*) is essentially due to the anisotropic interaction of the electron with one nitrogen nucleus, with a nuclear spin of one. The hyperfine structure of the T.N.B.$^-$ radical produced on TiO_2 and

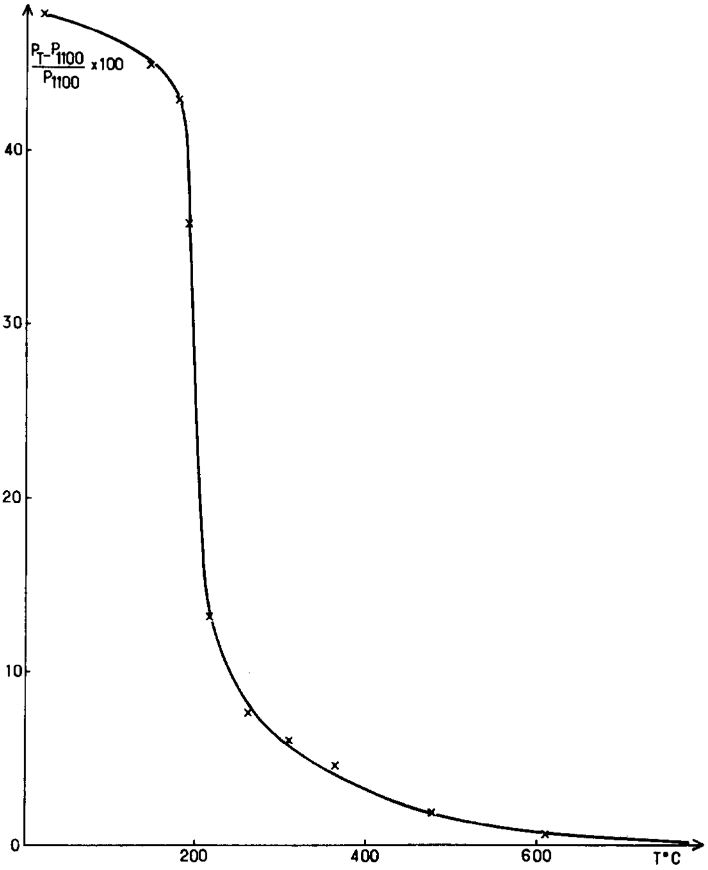


FIG. 4. Thermogravimetric curve of MgO sample heated *in vacuo*. P_T weight of the sample at T°C. P_{1100} weight of the sample at 1100°C.

MgO samples dehydrated at high temperatures indicates that the electron is highly localized on only one nitrogen nucleus.

The presence of an additional hyperfine structure of five components in each major line shows that in the case of T.N.B.$^-$ formed on "low temperature" samples the electron is delocalized over all the molecule, the two others nitrogen nucleus interacting more weakly with the uncoupled spin.

Nitrogen, with a nuclear spin of one, is normally expected to give three lines of equal intensity; however, when any hyperfine anisotropy is present, the lines corresponding to $m_I = \pm 1$ will be broadened in powders as compared to the line with $m_I = 0$.

In addition, the radical possesses an axial symmetry (the g tensor has two principal components $g_\parallel$ and $g_\perp$). In the present case, in which $g_\perp > g_\parallel$, since the low-field portion of the spectrum moves towards the center line and the high-field side to higher fields, this effect will tend to sharpen the low field lines and broaden the high field lines. Such an overall effect is evident in Fig. 1 (a and b).

It has been shown (*10*, *11*) that the low field observed spectrum is simply a set of absorption lines, each of the form S, so that a study of the spectrum can immediately yield the line shape S, its width and its position. By using a recent method (*12*) based on the linear transformation of Lorentzian or Gaussian curves, we find a Lorentzian line shape for the low field

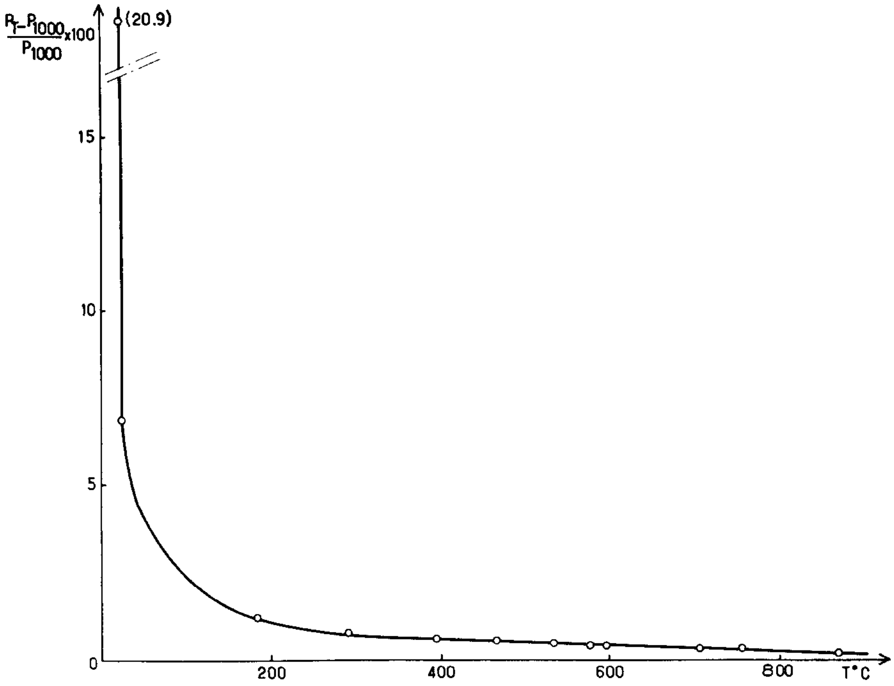


FIG. 5. Thermogravimetric curve of TiO_2 sample heated *in vacuo*. P_T weight of the sample at T°C. P_{1000} weight of the sample at 1000°C.

wing of the spectrum. The relation (*11*) $2\tau = 1/\pi T_2$ yields the spin-spin relaxation time $T_2 (3.7 \times 10^{-8}$ sec).

The Hamiltonian for this type of radical can be written in the general form:

$$\mathcal{H} = \beta[g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)] + \mathcal{H}_a + \mathcal{H}_i$$

with $S = \frac{1}{2}$, $g_{\parallel} < 2.006$ and $g_{\perp} \simeq 2.006$. In this formula β is the Bohr magneton, and $\mathcal{H}_a$ and $\mathcal{H}_i$ are, respectively, the isotropic and the anisotropic interaction.

The components of the anisotropic hyperfine tensor have been calculated for the spectrum of Fig. 1b. For an electron in a nitrogen $2p$ orbital and for axial symmetry, the observed hyperfine term α is given (*13*) by the relation:

$$\alpha^2 = [A^2 + 2AB\,(3\cos^2\theta - 1) + B^2(3\cos^2\theta + 1)],$$

where A and B are the isotropic and the traceless anisotropic terms respectively, and θ the angle between the magnetic field and the principal axis of the $2p$ nitrogen orbital. For a powder spectrum, the turning points are observed for $\theta = 0$ at H_0 and $H_0 \pm |A + 2B|$ and for $\theta = \pi/2$ at H_0 and $H_0 - |A - B|$. The value $2|A + 2B|$ is given by the distance between the outer wings. By assuming the center line width equals $2|A - B|$, we obtain $A = 11.5$ gauss and $B = 6$ gauss.

The formation of negative radicals on the hydrated alumina surface has been attributed to the presence of hydroxyl ions (*2*). Infrared spectroscopy has shown that the surfaces of $Mg(OH)_2$ and MgO (*7, 14*), and TiO_2 (*15*) contain hydroxyl groups when the solids are heated at low temperatures. In addition, in the case of MgO and also for TiO_2 heated in oxygen, thermal treatment produces no defects. We have identified the electron donor centers with surface OH^- ions. It is no longer possible to detect OH groups by thermogravimetry and I.R. spectroscopy for the same solids when heated at high temperatures. The sites responsible for the electron donor properties must then be identified with structural species like O^{2-} ions in weak coordination, in agreement with the hypothesis of Tench and Nelson (*4*).

It seems likely, for TiO_2 as well for MgO, that two electron–donor centers are to be taken into account in the formation of the negative radicals: OH^- ions and O^{2-} ions at the surface.

The experimental results show that the numbers of $T.N.B.^-$ negative radicals formed by unit surface are, respectively, 0.2×10^{16}, 0.3×10^{17} and 7.8×10^{17} spins/m^2 for Al_2O_3, TiO_2 and MgO activated at 220°C.

Another phenomenon seems to be occurring in the reducing specific activity of the OH^- ions. Faure, Fraissard and one of us (*7*) have shown that the hydroxyl groups present on MgO are less firmly bound. The stretching vibration of the OH in the hydroxide appears at 3690 cm^{-1} while the corresponding vibration in the oxide is at 3740 cm^{-1}.

Since the magnesium oxide reducing activity is about 20 times that of the hydroxide, it may be concluded that the more the OH^- ions are bound the smaller is their reducing activity. This hypothesis may explain the curve of Fig. 3.

The thermogravimétric study of the magnesium hydroxide thermal decomposition shows that the latter is complete at about 220°C. The transformation of $Mg(OH)_2$ to MgO leads then to an increase in the number of negative radicals formed per unit area. At about 220°C the magnesium oxide surface is entirely covered by OH^- ions, which gives a maximum in the reducing activity. The surface of magnesium oxide can be schematically represented for a (100) face as follows:

Mg	O^{2-}	Mg	O^{2-}	Mg	O^{2-}
O^{2-}	Mg	O^{2-}	Mg	O^{2-}	Mg

The ideal hydrated surface is depicted by:

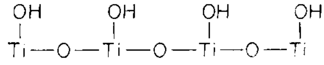
OH^-		OH^-		OH^-	
Mg	OH^-	Mg	OH^-	Mg	OH^-
O^{2-}	Mg	O^{2-}	Mg	O^{2-}	Mg

Two distinct surface OH groups can then exist; free OH^- ions (type *A* hydroxyls) and type *B* OH^- ions (*14*). Only OH^- ions of type *A* are electron donors. During magnesium oxide calcination dehydration of the solid takes place by condensation of the OH^- ions. Elimination of a water molecule by condensation of two OH^- ions in different configurations proceeds primarily via a tunneling mechanism of the protons (*16*) and leads to a decrease of the free OH^- ions and the number of electron donor sites therefore decreases. During the dehydroxylation, some O^{2-} structural ions in normal coordination are formed. However, for high dehydration temperatures, because of the low density of OH groups at the surface water desorption can occur by interaction of two OH ions adsorbed on Mg^{2+} ions leading in this way to the formation of weakly coordinated oxide ions, which are the same as the centers involving oxide ions proposed by Pink *et al.* (*3*).

In agreement with Tench and Nelson (*4*), these O^{2-} ions can act as electron donor sites and form negative radicals in the presence of T.N.B. The number of these O^{2-} ions then increases with the activation temperature paralleled by an increase in the magnesium oxide reducing activity, which is in agreement with our experimental results.

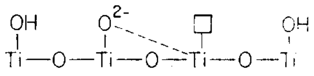
Similar phenomena are observed in the case of TiO_2 and may be interpreted in an analogous way. Infrared spectroscopy has shown that hydroxyl groups in strong interaction are present on the surface of the solid activated to temperatures lower than 100°C (*15*), these interactions diminishing with increasing activation temperature. At about 250°C only free OH groups are present. The increase in the number of negative radicals formed can then be attributed to the decrease of the interaction between OH groups. Above 250°C dehydroxylation involves a decrease in the number of the OH^- donor sites.

The hydrated TiO_2 surface can be represented schematically as follows (*15*):

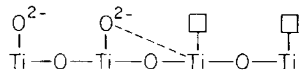


$$\overset{\displaystyle OH}{\overset{|}{Ti}}-O-\overset{\displaystyle OH}{\overset{|}{Ti}}-O-\overset{\displaystyle OH}{\overset{|}{Ti}}-O-\overset{\displaystyle OH}{\overset{|}{Ti}}$$

The dehydration between two neighboring OH leads to O^{2-} ions:



Then, when the surface density of OH groups becomes small, the elimination of a water molecule will lead to a surface O^{2-} ion weakly coordinated and therefore a potential electron donor site.



If the thermal treatment is effected *in vacuo*, we have shown (*17*) that Ti^{3+} electron donor ions are formed, which explains why the reducing power of TiO_2 treated *in vacuo* is always greater than that of TiO_2 dehydrated in oxygen.

CONCLUSION

We have shown that, for TiO_2 as well for MgO, the formation of negative radicals is due to the presence of OH^- ions and weakly coordinated O^{2-} ions, the number of the latter increasing at high activation temperatures. Consideration of the ESR spectra leads to the conclusion that the charge transfer complexes are weakly adsorbed on OH^- ions at the surface. The unpaired spin is then delocalized over the whole adsorbate molecule. In contrast to this, when the sites concerned are the weakly coordinated O^{2-} ions the negative radical is more strongly adsorbed; the electron is then localized at one site on the molecule (one nitrogen nucleus).

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