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Dehydration of Formic Acid on Titanium Dioxides. Nature of Active Centers

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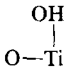
Titanium dioxide catalyses the dehydration of formic acid. A comparative study of the variation of surface properties and the catalytic activity of TiO_2 samples with their *in vacuo* pretreatment temperature has shown that the active sites in this reaction are electron-donor centers, the number of which has been determined by the adsorption of tetracyanoethylene or trinitrobenzene and ESR analysis of the paramagnetic anions formed. These centers are Ti^{3+} ions and



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

groups for high and low pretreatment temperatures, respectively. The reduction of the catalytic activity of a surface prepoisoned by an electron acceptor and the demonstration by ESR of a Ti^{3+}–HCO_2H interaction have confirmed the above conclusions.

INTRODUCTION

The decomposition of formic acid has often been used as a test reaction of dehydration or dehydrogenation (*1*, *2*) because of the ease of product analysis and the simplicity of the molecule. This complex is simple enough to be studied quantum mechanically by ab initio methods without simplifying hypotheses (*3*). Moreover, the fact that there is only one C atom and two H atoms facilitates spectral analysis of the chemisorbed complex by NMR (*4*). We present here results on the decomposition kinetics of HCO_2H on TiO_2 and on the nature of the active centers in this reaction.

EXPERIMENTAL

Materials and Procedures

We used three specimens of TiO_2 denoted by the symbols A, D, and AM followed by the pretreatment temperature T_t in degrees Celsius at which they were held for 12 h at 10^{-5} Torr before use. Solids A and D, prepared from $TiCl_4$ in a flame reactor, consist of nonporous particles about 60 and 100–250 Å in size, respectively (*5*). They are anatase type, but about 15% by weight of the second is in the rutile form. Their specific areas are 318 and 62 $m^2\ g^{-1}$, respectively, when $T_t \leq 400°C$. Solid AM, prepared by hydrolysis of $TiCl_4$ and neutralised by NaOH (*6*), is amorphous according to X-ray analysis. Its specific area decreases from 432 to 162 $m^2\ g^{-1}$ when T_t increases from 150 to 400°C.

The kinetic study was carried out in the gas phase. Formic acid contained in a saturator at constant temperature is carried by a stream of pure nitrogen. In order to define the HCO_2H flow rate, this mixture then passes into a condenser at the same temperature as the saturator. The CO and CO_2 produced by the decomposition of HCO_2H are determined by ONERA type 80 ir analysers.

With the experimental conditions of an acid flow rate of 2×10^{-6} moles s^{-1} and a catalyst weight in the reactor of 15 mg, the reaction is zero order in acid, at least as long as the reaction temperature T_r is not too high ($< 250°C$).

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We determined the number of electron-acceptor or -donor sites at the surface of TiO_2 by the adsorption of an electron donor (perylene, 10^{-2} *M* in benzene) (*7*) or an electron acceptor (tetracyanoethylene (TCNE) or trinitrobenzene (TNB), 10^{-2} *M* in benzene) (*8*) and EPR analysis of the paramagnetic ions formed. The EPR spectra were recorded at −196°C.

Finally, the decomposition of HCO_2H was in some cases carried out on TiO_2 surfaces previously exposed for 12 h at 200°C to benzene vapour or to a benzene solution of TCNE or TNB. Before the HCO_2H reaction, the benzene, TCNE, or TNB which had not reacted with the solid is eliminated by passing nitrogen and pumping under vacuum.

RESULTS AND DISCUSSION

Kinetics

The titanium oxides are essentially dehydration catalysts. Dehydrogenation activity appears from about 200°C onwards, but it is always negligible compared to dehydration. For example, for T_r = 210°C, the rates of formation of CO and CO_2 are 17.90×10^{-9} and 18.60×10^{-11} moles m^{-2} s^{-1} in the presence of AM-300.

Whatever the sample and the pretreatment temperature, the logarithm of the acid dehydration rate *V*(CO) (expressed in moles of CO per square meter of surface and per second) varies linearly with T_r^{-1} at least as long as the temperature is less than about 210°C. Within the limits of experimental error (1.1 kcal $mole^{-1}$), the value of the resulting activation energy is practically constant (17 kcal $mole^{-1}$) for all three samples, whatever T_t.

Figure 1 represents the dependence of *V*(CO) on T_t for the three samples, at T_r = 190 or 200°C. The curve for solid A shows two maxima c (T_t ~ 250°C) and g (T_t ~ 400°C) and three zones a, e, and j of low activity at T_t ~ 180, 300, and 500°C, respectively. Much the same behaviour is observed for catalysts AM and D, in particular the falling (c → e) and rising (e → g) sections. However, the curves are more spread out along the T_t axis. For example, for sample D, there is a slight shift in the maximum g towards high values of T_t (430°C) and the minimum e towards lower values (235°C). The activity of the three samples decreases in the order D > A > AM. For example, at T_r = 210°C, the maximum activities at g are 815×10^{-9}, 510×10^{-9}, and 37×10^{-9} moles CO m^{-2} s^{-1}, respectively.

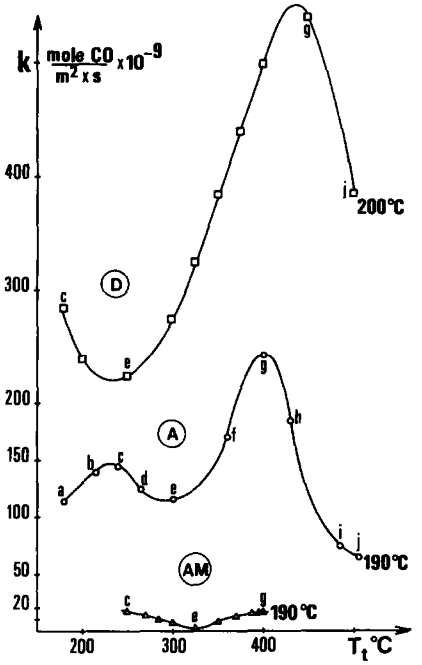


FIG. 1. Dependence of the catalytic activity on pretreatment temperature T_t of samples (AM and A: T_r = 190°C; D: T_r = 200°C).

We have also checked that the reaction products have no effect on the dehydration kinetics of HCO_2H. In fact, the activity and the activation energy *E*(CO) are unchanged when the carrier gas contains small amounts of CO, CO_2, or H_2. It is the same when the reactant contains a small quantity of water. Consequently *V*(CO) is equal to the rate constant *k* and the dependence of the frequency factor k_0(CO) on T_t is similar to that of *V*(CO).

Acidic and Basic Sites

Several authors (*9–11*) have studied acid and basic properties of titanium dioxide samples similar (and sometimes identical) to ours. They have demonstrated that these solid surfaces bear basic sites (terminal OH groups attached to a single Ti^{4+}) and Brønsted acid sites (bidentate OH groups on two Ti^{4+}) or Lewis sites (Ti^{4+} after dehydroxylation). However, the dependence of these chemical properties on T_t does not follow that of the catalytic activity for dehydration by these solids. The acidic and basic sites do not seem to be the active centers in the dehydration of HCO_2H, in disagreement with the conclusions of Munuera (*12*).

Electron-Acceptor Sites (EAS)

The number of electron-acceptor sites (EAS) in sample A increases with T_t from 1.20×10^{15} m^{-2} for $T_t = 150°C$ up to its maximum value of 1.75×10^{15} m^{-2} for $T_t = 200°C$, then decreases to zero at about $T_t = 400°C$. For solid D, the variation of the EAS number is similar, but shifted towards higher T_t values; its maximum is at about 350°C. Finally, we have been unable to detect this type of site at the surface of AM, for any value of T_t. It does not appear therefore that there is a relationship between the number of EAS and the dehydrogenation activity of these solids.

Electron-Donor Sites (EDS)

The total number (N) of electron-donor sites (EDS) for solid A, determined by TCNE analysis, increases first of all with T_t (Fig. 2, section a′ → c′), goes through a maximum around $T_t = 240°C$, then decreases (c′ → e′); after a minimum near $T_t = 325°C$, the number increases again with T_t (e′ → g′), goes through a very definite maximum for $T_t \sim 400°C$, then decreases progressively (g′ → j′). The form of the curve is the same for solid AM but the total number of EDS per square meter is two or three times greater than that for solid A, depending on T_t. The variation of the total number of EDS with T_t (Fig. 2) is slightly different for solid D; there is only the section e′ → g′ → j′ and this is much more spread out in terms of the temperature T_t; the minimum e′ and the maximum g′ are at about 200 and 500°C, respectively.

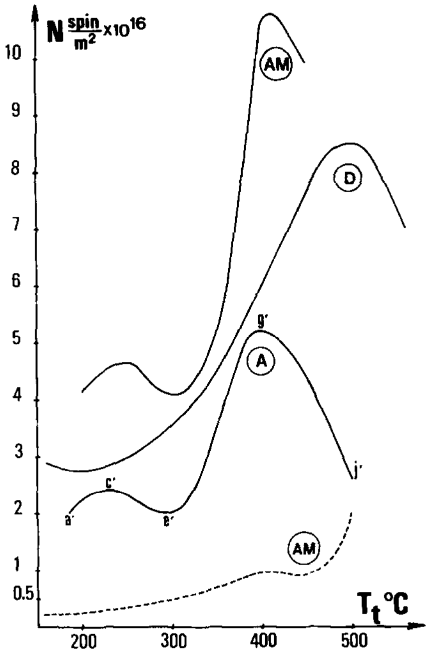


FIG. 2. Number N of electron-donor sites as a function of activation temperature T_t with TCNE (solid lines) or TNB (broken line) as adsorbate.

The number of strong electron-donor sites for sample AM, analysed by TNB (Fig. 2), increases continuously with the pretreatment temperature for $200 \leq T_t \leq 400°C$. After a slight decrease between 400 and 475°C, this number again increases with T_t. For each T_t, the number of sites determined by TNB is about 10–20% of the total number determined by TCNE. For example, for $T_t = 400°C$, the numbers of sites found by TNB and TCNE are 0.95×10^{16} and 10.75×10^{16}, respectively.

Comparison of the curves in Figs. 1 and 2 reveals that the dehydration activity V(CO) and the total number of EDS show the same dependence of T_t, for all three solids considered. This strongly suggests that these sites must be important in the mechanism of the dehydration of formic acid on these catalysts.

Catalytic Activity of Poisoned Surfaces

In order to confirm the role of EDS, we carried out HCO_2H decomposition on surfaces which had previously adsorbed C_6H_6, TCNE, or TNB. The results show that these electron-acceptor compounds decrease the reaction rate by poisoning the EDS. The latter are therefore clearly the active sites in the reaction, as we have already suggested (*13*). Poisoning depends on:

(i) the number of preadsorbed molecules; for example, with A-400 at T_r = 150°C, the degree of poisoning increases from 50 to 90% when the TCNE concentration goes from 0.5×10^{-3} to 7.5×10^{-3};

(ii) the nature of the electron acceptor. The same concentration of TNB causes less poisoning than TCNE, in agreement with the number of sites determined by means of these two compounds. Although its electron affinity is low, even benzene causes a certain amount of poisoning. Consequently, poisoning by C_6H_6 cannot be negligible when the EDS are analysed by TNB and TCNE in benzene solution.

Finally, the activation energy, determined from the Arrhenius plots, increases from 17 to 22 kcal $mole^{-1}$ when the degree of poisoning increases from 0 to 90%. This confirms that the EDS are not all of the same strength. The strongest are poisoned first and the dehydration of HCO_2H is increasingly difficult on the weaker sites.

Nature of Electron-Donor Sites

The above results indicate that the active centers in the dehydration of HCO_2H on titanium oxides are the EDS. More exactly, Figs. 1 and 2 represent for each solid the evolution of two types of EDS in two T_t ranges, and for each one of them a corresponding variation in the catalytic activity. Figure 3 (where the letters, a, b, . . . , j correspond to the experimental points a, b, . . . and a′, b′, . . . of Figs. 1 and 2) shows that the variation $k = f(N)$ for sample A presents, for each reaction temperature T_r, two distinct linear sections related to the number of EDS analysed in the ranges $T_t \leq$ 300°C and $350 \leq T_t \leq$ 500°C, respectively, with a discontinuity at $T_t \sim$ 325°C.

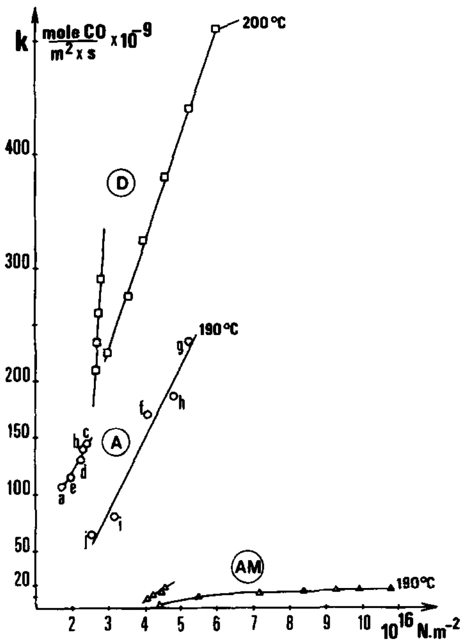


FIG. 3. Dehydration rate constant k versus number N of electron-donor sites (AM and A: T_r = 190°C; D: T_r = 200°C).

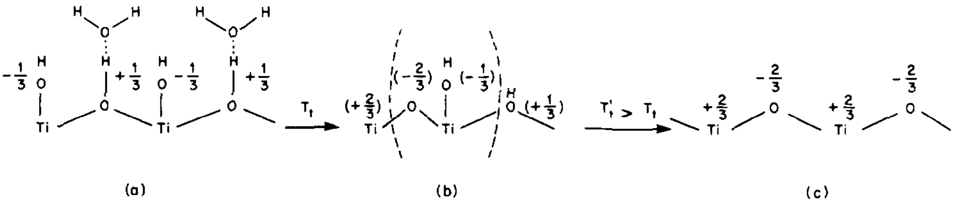
Analogous variations are found in the case of sample D (discontinuity at about T_t = 250°C). The catalytic activity of solid AM is also linearly dependent on N for $T_t <$ 325°C. However, in the second range the slope of this curve decreases constantly with N (that is with T_t). We discuss below the nature of the sites, but whatever type they are, their activity must depend on their environment which varies considerably with the sintering. The activity of the thermally stable solids A and D must therefore be linearly dependent on N regardless of T_t. In the case of AM, however, the sintering temperature is relatively low, and this can lead to a continuous variation in the quality of the sites with T_t and therefore to a nonlinear dependence of V(CO) on N.

The nature of the EDS is rather easy to determine in the range where $T_t > 300°C$. When there is extensive dehydration, paramagnetic Ti^{3+} ions are detected on the solid surface and characterised by their ESR spectrum *a* at −196°C (anisotropic line $g_\perp = 1.966$, $g_\| = 1.946$) in agreement with the results of other authors (*16, 17*). After TCNE adsorption, the replacement of this signal by that of TCNE shows clearly that these ions are EDS. Moreover, the parallel decrease in catalyst activity and the strength of signal *a* with the quantity of preadsorbed TCNE shows that the centers active in the reaction studied are essentially these Ti^{3+} ions. It has not, however, been possible to prove that they are the only EDS in this temperature range ($T_t > 300°C$).

After HCO_2H adsorption the initial Ti^{3+} spectrum is replaced by a signal *b* with $g_\perp = 1.973$ and $g_\| = 1.948$. This trend is associated with the existence of a strong interaction between the Ti^{3+} centers and the adsorbed HCO_2H molecules. Moreover, the initial signal *a* of Ti^{3+} does not disappear completely in favour of signal *b* until the number of adsorbed HCO_2H molecules is twice that of the Ti^{3+} ions. This indicates either that the molecules of acid are not all preferentially adsorbed on Ti^{3+} or that the acid is chemisorbed as the dimer, or at least that one HCO_2H molecule is interacting strongly with the (Ti^{3+}–HCO_2H) complex. This second hypothesis is akin to the scheme proposed by certain authors for the adsorption of HCO_2H on oxides (*18*) or on metals (*19*).

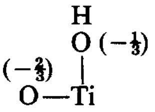
In the low-treatment-temperature range (<300°C approximately) the nature of the EDS and the variation of their number with T_t is more difficult to understand. We can only suggest a solution by using the results obtained by wide-line NMR on the state of surface constitutive water in these solids and the mechanism of their dehydration (*14*). We shall take sample A as an example. However, the conclusions will be valid for all the samples, with simply a shift in the treatment temperature scale. After treatment at 22°C under vacuum, the total amount of constitutive water (OH and H_2O) expressed in equivalents of water molecules is 8.9 molecules/nm^2. About 50% of the H atoms belong to the OH groups, either bidentate, bonding two adjacent Ti (25%), or monodentate. Assuming charge localisation resulting from the discontinuity of the crystal, the surface can be represented by Scheme 1 where the monodentate and bidentate OH groups possess a theoretical charge of $-\frac{1}{3}$ and $+\frac{1}{3}$, respectively. We have, moreover, proved that the molecular water is totally desorbed at $T_t = 190°C$ and that between 22 and 250°C (point c′, Fig. 2) most of the OH groups are eliminated by condensation of an $(OH)^{-1/3}$ with the proton of an $(OH)^{+1/3}$ freed by the departure of the water molecule which it carried.

Contrary to certain ideas put forward by other authors (*15*) the EDS (for $T_t \leq 300°C$) cannot therefore be exclusively the $(OH)^{-1/3}$ borne by the Ti atoms since their number should decrease monotonically with increase of T_t. Nor can they be only the bidentate oxygens, arising from condensation of OH groups, the number of



SCHEME 1. Variation of electron-donor sites with temperature of pretreatment.

which rises steadily with the dehydration temperature. These results prove therefore that in the range $T_t \leq 300°C$ the nature of the EDS is complex. We suggest that they could be the groups



$$\begin{array}{ccc} & & \mathrm{H} \\ & & \mathrm{O}\,(-\frac{1}{3}) \\ (-\frac{2}{3}) & & | \\ \mathrm{O} & — & \mathrm{Ti} \end{array}$$

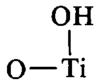
in which each $O^{-2/3}$ center (or $(OH)^{-1/3}$) can operate as an EDS because the aptitude for electron release is enhanced by the presence of the neighbouring negative charge $(OH)^{-1/3}$ (or $O^{-2/3}$), in spite of a positive charge $(+\frac{2}{3})$ on the adjacent dehydroxylated Ti atom. At low temperature T_t reaction $a \rightarrow b$ increases the concentration of these groups. However, their variation with T_t goes necessarily through a maximum since the number of $O^{-2/3}$ increases and that of $(OH)^{-1/3}$ decreases steadily with increasing T_t.

The numerical values of the above charges are theoretical and result from our working hypothesis. On the other hand, the existence of the two types of very different OH groups has been proved by NMR (*14*), by ir spectroscopy, and by their difference in chemical behaviour as basic (monodentate) or acidic (bidentate) sites (*9–11*).

CONCLUSION

Titanium dioxide catalyses the dehydration of formic acid; there is some dehydrogenation observed at high temperature but it is negligible.

A comparative study of the variation of surface properties and the catalytic activity of each of the solids investigated with their *in vacuo* pretreatment temperature T_t has shown that the active sites in this reaction are the electron-donor centers. These are Ti^{3+} ions, when T_t is sufficiently high (greater than about 300°C). For low values of T_t the nature of the EDS is more complex. We have suggested that they are



$$\begin{array}{ccc} & & \mathrm{OH} \\ & & | \\ \mathrm{O} & — & \mathrm{Ti} \end{array}$$

groups obtained by partial dehydration of the surface.

The reduction of the catalytic activity of surfaces prepoisoned by an electron acceptor and the demonstration by ESR of the existence of a strong Ti^{3+}–HCO_2H interaction have confirmed the above conclusions.

The electron transfer from the solid to HCO_2H, the form of the chemisorbed complex, and the mechanism of the reaction have been determined by an ab initio SCF study of HCO_2H, HCO_2H^+, and HCO_2H^- and by NMR of the adsorbed phase. The results appear in the succeeding two papers (*3, 4*).

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