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Influence of the Morphology and the Size of Titanium Dioxide (Anatase) Particles on the Catalytic Oxidation of Carbon Monoxide

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Two families of anatase nonporous particles of various diameters (or surface area), differing in their shape, namely, spherical or polyhedral, give two distinct compensation effect laws when, for the catalytic oxidation of carbon monoxide, the logarithm of the preexponential factor is plotted as a function of the activation energy. This behavior, which is found when anatase is activated in vacuum or in hydrogen, before the catalytic reaction, is no longer observed if the activation is carried out in carbon monoxide (noncompensation effect). The nature of active sites involved after each activation is discussed and the effect of catalytic "heredity" is examined in an attempt to correlate the catalytic activity in "demanding" and "facile" reactions with some other properties of oxide catalysts.

INTRODUCTION

In the search for correlations between catalytic activity and some properties of solid oxide catalysts, various parameters were taken into account, such as the position of the element in the periodic table, the stoichiometric formula of the oxide and its crystal structure and also the bond strength between oxygen and metal (*1*). Surprisingly enough, the catalytic activity of oxides was never considered as being dependent on the state of dispersion of the oxide, whereas this type of correlation was envisaged for metals (*2*).

A second problem arises when the catalyst has to follow an activation pretreatment in order to exhibit a catalytic activity. Indeed, different pretreatments may induce different activity patterns. Moreover, the mechanism of the catalytic reaction may depend on the nature of the activation pretreatment. This is precisely the case of titania (anatase) used as catalyst in the oxidation of CO (*3*) where activation at 500°C in vacuum, in carbon monoxide or in hydrogen leads to three different mechanisms of the reaction on the same sample of titania.

The method of preparation of titania as homodispersed nonporous particles in a hydrogen–oxygen flame reactor (*4*) offers the flexibility of production of titania (or other oxides) in various degrees of dispersion. Indeed, particles of anatase of a diameter of 60 Å up to 2000 Å, depending on the preparation, are commonly obtained (*5*). It was shown recently (*6*) that the morphology of titania particles may also be controlled. Particles of spherical shape or of polyhedral shape can be obtained for anatase prepared in the hydrogen–oxygen flame reactor. For these reasons, it seemed attractive to follow the catalytic activity in the oxidation of CO of various samples of anatase, differing by their particle size and shape, namely, spherical or polyhedral. Because the nature of the activation pretreatment determines the order and the mechanism of the reaction (*3*), the activity patterns of various samples of titania were registered after three different activation treatments, in vacuum (order ½), in carbon monoxide (order 1) and in hydrogen (apparent order 1).

EXPERIMENTAL METHODS

Anatase particles were prepared in a hydrogen–oxygen flame reactor by decomposition of titanium tetrachloride vapor (*4*,*5*). If the temperature of the flame is higher than the melting point of titania (2100 K), the particles have a spherical shape. If the previous conditions are reversed, the particles are polyhedral (*6*). The diameter for a given temperature of the flame depends on the flow rate of $TiCl_4$ into the burner and on the residence time of this reagent in the flame (*5*). Electron microscope pictures of polyhedral and spherical particles were published elsewhere (*5*). The mean diameter computed from the electron micrographs is in good agreement with the mean diameter calculated from the BET surface area. In this paper the samples are designated by their surface areas.

In Table 1 are given the characteristics of the anatase samples prepared.

For all particles of the two families, X-ray diffraction indicates the presence of anatase, with rutile not exceeding 2 to 7%. Infrared spectroscopy gives qualitatively the same proportion for the surface layer, and adsorption bands of CO, OH and H_2O adsorbed on various samples are consistent with the absence of an amorphous titania layer on the surface (*7*).

The oxidation of CO on anatase was followed in a static reactor, already described (*3*), by monitoring the total pressure. The initial pressure of the mixture ($CO + \frac{1}{2} O_2$) was 1.5 Torr. Liquid nitrogen traps were included in the circuit in order to condense CO_2. The mass of the catalyst was 0.500 g in each case and the temperature range used for the catalytic reaction was between 425 and 500°C. All samples were, previously to the test, evacuated at 10^{-6} Torr during 1 hr at room temperature and then: (i) heated to 500°C and maintained at this temperature in vacuum for 15 hr, (ii) or under 120 Torr of CO, (iii) or under 100 Torr of H_2. These treatments, which do not change the surface area, are required in order to observe the catalytic activity of anatase in the oxidation of CO, starting at 400°C (*3*). A fresh sample of the catalyst was used in each test.

EXPERIMENTAL RESULTS

A. Activation of Titania in Vacuum

For all catalysts used in this work, the overall order of reaction was ½, and corre-

TABLE 1

MORPHOLOGY, SURFACE AREA, MEAN DIAMETER[a] OF ANATASE PARTICLES AND THEIR ARRHENIUS PARAMETERS IN THE CO OXIDATION AFTER VACUUM PRETREATMENT

Polyhedral particles				Spherical particles			
Surface area (m^2/g)	Mean diameter (Å)	*E* (kcal/mole)	log *A* (*A* in $Torr^{1/2}$ min^{-1} m^{-2})	Surface area (m^2/g)	Mean diameter (Å)	*E* (kcal/mole)	log *A* (*A* in $Torr^{1/2}$ min^{-1} m^{-2})
13	1200	37	6.886	9	1730	22	2.748
68	230	30.7	4.554	23.5	660	18.8	2.233
93	170	26.9	3.5725	35	445	4.8	$\bar{1}.269$
140	110	21	1.703	41	380	24	3.176

[a] Calculated from BET surface area *S* by the equation $d = 6/\rho S$, where ρ is the density of anatase.

sponded to the partial order with respect to oxygen, the partial order with respect to carbon monoxide being zero. This behavior is that observed after activation of anatase in vacuum (*3*).

If P is the pressure of the stoichiometric mixture ($CO + {}^1\!/_2\, O_2$), the rate r of the reaction may be written:

$$r = -\frac{dP}{dt} = kP^{1/2} \qquad (1)$$

or in the integral form:

$$P_0^{1/2} - P^{1/2} = \frac{k}{2}\, t, \qquad (2)$$

where P_0 is the pressure at time zero and k the rate constant of the order ½. This rate law and the rate laws quoted below for carbon monixide and hydrogen activation were found to hold over 95% of total reaction. In order to compare the activity of all samples listed in Table 1 the rate constant refers to 1 m² of the solid:

$$k_s = \frac{k}{M \cdot S}, \qquad (3)$$

where M was the mass of the catalyst in the test and S its surface area. Figure 1 shows the Arrhenius plot for all samples where the best straight lines were drawn by the method of least squares. The corresponding activation energies of the reaction E and preexponential factors A are listed in Table 1.

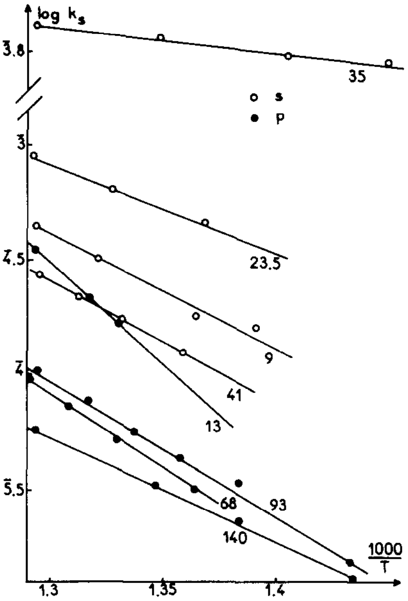

FIG. 1. Arrhenius plot for CO oxidation on anatase samples: (○) s, spherical particles; (●) p, polyhedral particles. The numbers by the lines refer to the surface area of the sample (m²/g).

If a reaction, performed under the same conditions, is followed for a series of catalysts three cases may be observed concerning the values of E and A (*8*): (i) E remains constant while A varies, (ii) E varies and A is constant, (iii) E varies simultaneously with A. Table 1 shows that the third case is observed here. Moreover, the compensation law, (*9,10*):

$$\log A = aE + b, \qquad (4)$$

is perfectly observed in Fig. 2 where polyhedral particles (line I) and spherical particles (line II) give separate plots. Therefore the initial classification of samples, based on their morphology, is found again here. Finally, for polyhedral but not for spherical particles a linear relationship is found between the activation energy and the surface area (Fig. 3). In summary, the

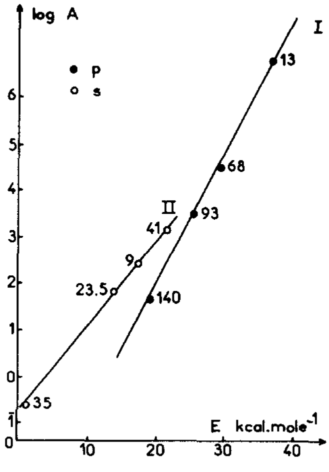

FIG. 2. Compensation effect for polyhedral particles (I) and spherical particles (II). The numbers close to the experimental points refer to the surface area of samples (m²/g).

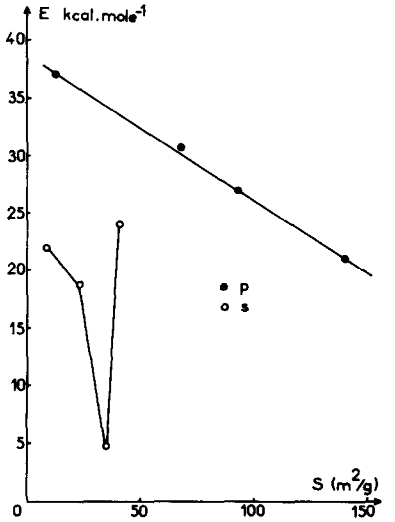

FIG. 3. Variation of the activation energy with the surface area of polyhedral (●) and spherical (○) particles.

catalytic activity of anatase activated in vacuum, depicted by the rate constant referred to 1 m^2 of surface, varies with the state of dispersion of the solid (surface area or particle diameter) and with its morphology (polyhedral or spherical particles).

B. *Activation of Titania in Hydrogen*

For all samples used (polyhedral and spherical particles) the overall order of reaction was unity. If P is the pressure of the stoichiometric mixture, the rate of the reaction may be written:

$$r = -\frac{dP}{dt} = kP$$

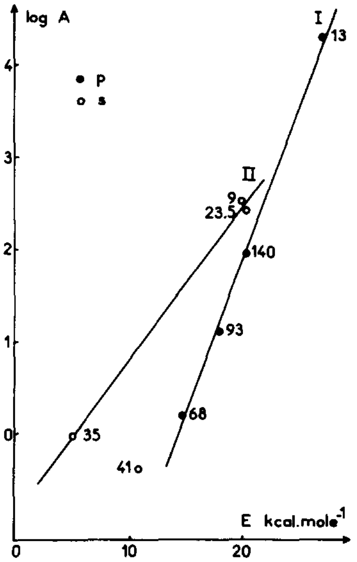

FIG. 4. Compensation effect for polyhedral particles (I) and spherical particles (II).

or, in the integral form:

$$\ln\frac{P_0}{P} = kt,$$

where P_0 is the pressure at time zero and k the rate constant of order unity. Again, for comparison of the activity of all samples, the rate constant k_s refers to 1 m^2 of the solid. The corresponding values of the activation energy of the reaction, E, and of the preexponential factor, A, are listed in Table 2. The compensation law is again perfectly observed in Fig. 4 where polyhedral particles (line I) and spherical particles (line II) give separate plots with the

TABLE 2

APPARENT ACTIVATION ENERGY IN THE OXIDATION OF CO AND PREEXPONENTIAL FACTOR FOR ANATASE POLYHEDRAL AND SPHERICAL PARTICLES ACTIVATED IN HYDROGEN

Polyhedral particles			Spherical particles		
Surface area (m^2/g)	E (kcal/mole)	log A (A in min^{-1} m^{-2})	Surface area (m^2/g)	E (kcal/mole)	log A (A in min^{-1} m^{-2})
13	27.1	4.280	9	20.0	2.516
68	14.8	0.215	23.5	20.4	2.430
93	18.0	1.155	35	5.1	−0.031
140	20.5	1.955	41	10.9	−0.380

exception of the sample of 41 m^2/g(380 Å) which is in an intermediate position. In fact, the electron microscope examination of this sample shows that although it is mainly composed of spherical particles, it also exhibits a small proportion of polyhedral particles. Indeed spherical particles of diameter smaller than 350 Å were never obtained in the flame reactor (*5,6*). The sample of 41 m^2/g is therefore at the limit for obtaining spherical particles. Figure 4 shows that the initial classification of samples into spheres and polyhedra is found again here. The slopes a_{I} and a_{II} of the straight lines I and II are, respectively, 0.33 and 0.17 mole/kcal. These values are very close to the values of corresponding slopes observed after activation in vacuum (0.325 and 0.18) (Fig. 2).

C. Activation of Titania in Carbon Monoxide

For all samples used (polyhedral and spherical particles) the overall order of unity was again observed (*3*). The corresponding values of the activation energy of the reaction, E, and of the preexponential factor, A, are listed in Table 3.

Table 3 shows that the activation energy of the reaction, E, remains practically constant, irrespective of the nature of the catalyst (morphology and surface area). The diagram $\log A = f(E)$ exhibits a mean straight line, perpendicular to the abscissa with $E = 11.5 \pm 1.5$ kcal/mole. Such a case was called by Bond (*17*) "noncompensation effect." It was previously mentioned by Boudart (*8*). Summing up, the behavior of anatase samples towards the catalytic oxidation of carbon monoxide, activated either in vacuum (order ½) and in hydrogen (apparent order 1) or in carbon monoxide (true order 1) is different with respect to the compensation effect. Vacuum and hydrogen activated anatase exhibits two distinct compensation laws, for spherical and for polyhedral particles, whereas carbon monoxide activated anatase gives a noncompensation effect.

DISCUSSION

Various experimental causes may induce the compensation effect between A and E (*10*), among the most common of which are diffusion controlled reaction, variation of the surface area of the catalyst during the reaction, simultaneous homogeneous phase reaction and finally, the variation of the order of the reaction from one catalyst to another in the series. None of these phenomena are involved here. The absence of the intergranular diffusion (intragranular diffusion is avoided for nonporous particles) was verified for the most finely divided sample ($S = 140$ m^2/g) through the proportionality of the rate constant with the mass of the catalyst (up to 0.750 g). All catalysts exhibit a stable surface area which is not modified by the pretreatment or by the reaction. The homoge-

TABLE 3

ACTIVATION ENERGY IN THE OXIDATION OF CO AND PREEXPONENTIAL FACTOR FOR ANATASE POLYHEDRAL AND SPHERICAL PARTICLES ACTIVATED IN CARBON MONOXIDE

Polyhedral particles			Spherical particles		
Surface area (m^2/g)	E (kcal/mole)	log A (A in min^{-1} m^{-2})	Surface area (m^2/g)	E (kcal/mole)	log A (A in min^{-1} m^{-2})
13	11.6	0.108	9	11.7	0.83
68	12.4	$\bar{1}.51$	23.5	11.3	0.155
93	10.6	$\bar{1}.20$	41	12.6	0.62
140	10.0	2.914			

neous phase reaction (in the absence of the catalyst) was found to be negligible. Finally the overall order ½ was observed for all catalysts activated in vacuum, and the order 1 for those activated in hydrogen or in carbon monoxide.

As far as we are aware, this is the first time that the compensation effect has been observed on a series of catalysts where only the particle size varies, the composition, the chemical nature and the structure of the surface remaining the same.

The compensation effect was explained (*10*) by the heterogeneity of the surface of the catalyst. The less active sites are in greater abundance and the higher their activation energy, the larger their number. Assuming an exponential distribution of sites:

$$dn = n_0 \exp\left(\frac{E_i}{E_0}\right) dE_i, \qquad (5)$$

where dn sites have an activation energy between E_i and $E_i + dE_i$ (n_0 and E_0 being constant). The total number of sites N whose activation energy varies from $E_{\min}$ to $E_{\max}$ is obtained by integration of Eq. (5):

$$\begin{aligned} N &= \int_{E_{\min}}^{E_{\max}} n_0 \exp\left(\frac{E_i}{E_0}\right) dE_i \\ &= n_0 E_0 \left[\exp\left(\frac{E_{\max}}{E_0}\right) - \exp\left(\frac{E_{\min}}{E_0}\right)\right]. \end{aligned} \qquad (6)$$

The resulting rate constant k_s includes all sites:

$$k_s = \int_{E_{\min}}^{E_{\max}} A' \exp\left(-\frac{E_i}{RT}\right) dn. \qquad (7)$$

In the experimental conditions previously described $(E_{\max} - E_{\min}) >> E_0 > RT$; therefore, by introducing Eq. (6) into Eq. (7), it is found:

$$k_s = \frac{A'N}{(E_0/\mathrm{RT}) - 1} \cdot \exp\left(-\frac{E_{\max} - E_{\min}}{E_0}\right) \cdot \exp\left(-\frac{E_{\min}}{RT}\right), \qquad (8)$$

instead of an ordinary Arrhenius law:

$$k_s = A \exp\left(-\frac{E}{RT}\right). \qquad (9)$$

But if the activation energy of the reaction determined from the Arrhenius plot is assigned to the activation energy of the most active sites, $E_{\min}$, the preexponential Arrhenius factor A is represented by the first factor of Eq. (8). The result therefore is that for a series of catalysts, A is proportional to the total number of active sites N and its logarithm varies linearly with the activation energy $E_{\min}$ (or E). Two distinct compensation laws, for polyhedral and spherical particles, may be then related to two energy distribution laws, for each family of catalysts, according to Eq. (8).

On the other hand, the catalysts of each family exhibit a temperature for which all the catalysts present the same activity. This isokinetic temperature is deduced from Arrhenius plot of Fig. 2 where the straight lines (for each family) converge into the same single point. This temperature is still better determined from the compensation law (*4*), considering:

$$\begin{aligned} \ln A &= 2.303\ a \cdot E + 2.303\ b \\ &= (E/RT_i) + \ln A_0, \end{aligned} \qquad (10)$$

if

$$T_i = \frac{1}{2.303\ a \cdot R}.$$

Introducing this quantity, analogous to a temperature, into the Arrhenius Eq. (9), through Eq. (10), it follows that:

$$k_s = A_0 \exp\left[-E\left(\frac{1}{RT} - \frac{1}{RT_i}\right)\right]. \qquad (11)$$

At temperature $T = T_i$, all catalysts present the same rate constant $k_s = A_0$. The calculated isokinetic temperatures T_i are 673 K for polyhedral particles and 1193 K for spherical particles activated in vacuum. This catalytic criterion constitutes a second element in the differentiation between the two families of particles.

It is noteworthy here that the main experimental parameter differentiating the origin of the two families of particles is the temperature T_f of the flame in the reactor. For polyhedral particles this temperature is about 1700 K and about 3000 K for spherical particles. Now the ratio T_i/T_f is equal to 0.40 for *both* families. It is difficult to assign a physical meaning to this result. Probably it represents some link between the catalytic properties of a series of solids and the thermal conditions of their preparation. The active sites would be distributed on the surface of the catalyst during its preparation at a given temperature and then quenched (*10,11*).

A third element in the differentiation between the two families of particles is the linear relationship found for polyhedral particles activated in vacuum between the activation energy E and the surface area of samples (Fig. 3), whereas for spherical particles no simple law was found.

This empirical law corresponds to the equation:

$$E = -0.12\,S + 39. \qquad (12)$$

Two interesting limits may be found by extrapolation of Eq. (12). For $S = 0$ or in the absence of the catalyst (homogeneous reaction with perhaps some reaction on the walls) the activation energy of 39 kcal/mole is in very good agreement with the experimental activation energy (40 kcal/mole) of homogeneous oxidation of CO (*12*). For $E = 0$ the maximum surface area of polyhedric particles of anatase would be of 317 m^2/g which corresponds to a mean particle diameter of 50 Å. This value may be considered as a minimum limit below which the probability of finding a well-defined crystalline plane becomes zero (*13,14*). It also coincides with the minimum diameter of particles which can be obtained in the flame reactor.

Now the apparent activation energy E, for a reaction with order 0 with respect to CO and order ½ with respect to O_2 (vacuum activation) depends on the heat Q_{O_2} of the adsorption of oxygen (*15*) according to:

$$E = E_v - \tfrac{1}{2}\,Q_{O_2},$$

where E_v is the true activation energy. This last value, determined with oxygen rich mixtures where the overall order is now zero, is very nearly the same as that obtained with the stoichiometric mixture ($CO + \tfrac{1}{2}\,O_2$) for a sample of 140 m^2/g. The heat of chemisorption of the oxygen active in catalysis, Q_{O_2}, must be therefore very low, as is also verified by a direct calorimetric determination (*16*). The experimental activation energy is therefore equal to the true activation energy. Similarly, for hydrogen activated samples, where the reaction takes place between reagents adsorbed at saturation, but where self-inhibition by CO_2 results in an apparent order 1 (*3*), the apparent activation energy:

$$E = E_v + Q_{CO_2}.$$

But the activation energy computed from initial rates (in the absence of self-inhibition by CO_2) is very nearly the same for all catalysts as that obtained previously. Therefore, $Q_{CO_2} \simeq 0$ and in both cases the compensation law is not correlated with the variation of the heat of adsorption of reagents or products. But the compensation law [Eq. (4)] shows that for polyhedral particles activated in vacuum the number of active sites per square meter (or A) decreases when the particles diameter decreases (or the surface area increases) but the activity of these sites increases (E decreases) [Eq. (12)].

Now, when the particle diameter decreases, the coordination number of surface ions decreases. These ions must then exhibit an increase in the bond strength with the activated complex. Instead of considering the variation in the number of active sites, one may also understand the compensation effect in terms of the absolute rate theory as a decrease of $\Delta S\dagger$ of formation of the activated complex ($CO_2\dagger$) when the activation energy (or $\Delta H\dagger$) and the particle size of the catalyst decrease. But the experimental activation energy, according to the reaction coordinate, is equal to the activation energy of the homogeneous reaction decreased by the heat of adsorption of the activated complex onto the catalyst:

$$E = E_{\mathrm{hom}} - Q_{\mathrm{ads}}\dagger. \qquad (13)$$

Equation (13) assumes the same composition of the activated complex in homogeneous and adsorbed phase. This hypothesis seems reasonable considering the simplicity of the molecules (CO and O_2) in this associative reaction. For the family of polyhedral particles activated in vacuum it is then possible to compare:

$$E = 39 - 0.12\ S \qquad (12)$$

and

$$E = E_{\mathrm{hom}} - Q_{\mathrm{ads}}\dagger. \qquad (13)$$

It was shown that $E_{\mathrm{hom}} \simeq 39$ kcal/mole, and therefore $Q_{\mathrm{ads}}\dagger = 0.12\ S$.

The energy of adsorption of the complex on polyhedral particles increases linearly with the surface area of the vacuum activated catalyst or with its state of dispersion. The stability of the adsorbed complex increases with the surface area of the catalyst. If the number of active sites per unit surface simultaneously decreases, it is probably because for smaller and smaller particles some less stable crystallographic planes containing the active site are less developed. For spherical particles, the statistical probability for the presence of all the crystallographic planes remains virtually unmodified. The compensation effect for these particles is not then directly related to the state of dispersion of the sample.

Finally, oxidation of carbon monoxide on anatase follows three different kinetics, depending on the nature of the activation pretreatment (*3*). Activation in H_2 or in vacuum brings about the formation of defects which are anionic vacancies for hydrogen pretreatment and anionic vacancies together with titanium ion interstitials for vacuum pretreatment (*18*). In both cases, anionic vacancies are thus developed, this kind of defect being therefore common to both activation procedures. In both cases also, two laws of compensation effect are observed, one for spherical particles and one for polyhedral particles; in the case of carbon monoxide activation pretreatment, however, no more anionic vacancies are formed, the defects present (*18*) are only titanium interstitials. Simultaneously, this absence of anionic vacancies seems to lead to the absence of the compensation effect with respect to the morphology and the surface area of particles.

If the compensation effect is correlated with the energetic heterogeneity of the surface of catalysts, the identity of slopes (Figs. 2 and 4) a_{I} and a_{II} for hydrogen activation and vacuum activation (a_{I} for polyhedra and a_{II} for spheres) tends to show that the same law of energy distribution for the active sites applies for both activation treatments, having in common the creation of anionic vacancies. The absence of the compensation effect in the case of activation in CO seems to indicate that the active sites may be of a different nature. Indeed, in this activation no anionic vacancies are formed.

It has already been suggested (*3*) that the partial order of zero with respect to CO, observed in all three types of activation, results from the saturation coverage of the corresponding sites (titanium ions, normal or interstitial). In the case of hydrogen activation the (true) partial order with respect to oxygen is also zero; therefore, oxygen is chemisorbed at saturation coverage, probably on anionic sites, particularly abundant in this case (*18*).

On vacuum activated anatase, the anionic sites being less abundant (the dissociation of O_2 requiring two neighboring sites), the dissociative adsorption of oxygen is not realized at saturation and the partial order with respect to this gas is $1/2$. The compensation effect for the anatase samples activated in hydrogen or in vacuum is therefore correlated with the need for oxygen to be adsorbed in order to react and results from the energetic heterogeneity of its adsorption sites, which are probably anionic vacancies.

For the catalyst samples activated in carbon monoxide, the noncompensation effect with a constant activation energy (11.5 kcal/mole) should be correlated with the Rideal mechanism which accounts for the partial order of unity with respect to oxygen (*3*). But if the carbon monoxide adsorbed at saturation on its sites is able to react directly with oxygen from the gas phase, it is probably because of the peculiar character of these sites. It has been pointed out (*18*) that carbon monoxide activation develops titanium interstitial ions and no anionic vacancies are formed. If these interstitials are the sites for the adsorption of carbon monoxide, the constant activation energy, irrespective of the size and morphology of particles, tends to show that these sites are isoenergetic. The preexponential factor *A* which varies here only within a limit of two orders (instead of 5 to 8 orders for vacuum and hydrogen activation) also indicates that surface concentration of these sites is more homogeneous from one catalyst to another. This hypothesis is backed by the ESR determination of the concentration of paramagnetic Ti^{3+} ions, in nodal and/or interstitial positions (*19*) formed after activation of different samples of anatase in CO. Figure 5 shows this concentration as a function of the surface area of polyhedric or spherical particles. The slope of the resulting straight lines, which is practically the same, represents the number of Ti^{3+} ions per unit surface area after the activation in carbon monoxide. Therefore the number of titanium ions per unit surface area, which are susceptible to be converted by CO activation into Ti^{3+} interstitial and/or nodal ions is constant. The effect of the structure (surface area and morphology of the particles) disappears in this plot similarly as does the compensation effect. In this way, the results of the carbon monoxide activation procedure strongly suggest that titanium ion interstitials, developed by this pretreatment (*18*), are the active sites for CO adsorption at saturation and its reaction with gaseous oxygen. There is no additional need therefore to form active sites (anionic vacancies) for oxygen adsorption which can only introduce the complications linked with the surface heterogeneity (compensation effect).

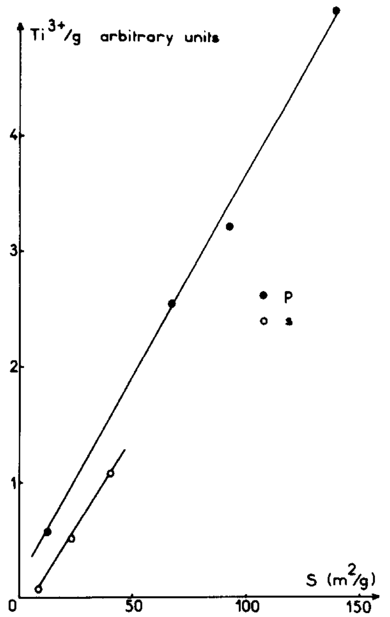

FIG. 5. ESR titration of Ti^{3+} ions for anatase samples activated in carbon monoxide as a function of the surface area. (○) s, spherical particles; (●) p, polyhedral particles.

If the compensation effect found for vacuum or hydrogen activation is then correlated with the presence of anionic vacancies, considered as active sites for oxygen adsorption, an additional parameter, common to these two activation procedures, is found.

It has been shown that the two distinct plots of the compensation effect, for spherical and polyhedral particles lead to two distinct isokinetic temperatures T_i, which were found for vacuum and hydrogen activation. The slopes a_I and a_{II} for spherical and polyhedral particles (Figs. 2 and 4) are found to be practically the same. Therefore the isokinetic temperatures T_i are also almost the same for spheres and polyhedra irrespective of the nature of the activation treatment, in vacuum or in hydrogen. Table 4 summarizes these results.

The isokinetic temperature appears therefore as a property characteristic only of the morphology of particles and independent of the activation pretreatment. The main experimental parameter differentiating the origin of the two families of particles is the temperature T_f of the flame in the reactor (*4–6*). The ratio T_i/T_f is equal to 0.40 for both families (spheres and polyhedra) and does not depend on the activation treatment. The thermal conditions of the preparation of the solid catalyst seem therefore to impose some potential properties [a peculiar distribution of potential surface active sites (*10,11*)] which are finally developed after the activation treatment (vacuum or hydrogen). These potential properties would be those concerning anionic vacancies, because anionic vacancies are the common property for both activation treatments. This "line of descent" is no longer detectable in the case of activation in carbon monoxide, where anionic vacancies do not seem to be formed any more and where titanium ion interstitials seem to exhibit an energetic homogeneity in the distribution.

TABLE 4

ISOKINETIC TEMPERATURES FOR ANATASE SPHERICAL AND POLYHEDRAL PARTICLES

	a (mole/kcal)		T_i (K)	
	Activation			
Particle morphology	in vacuum	in H_2	in vacuum	in H_2
Polyhedra	0.325	0.33	673	659
Spheres	0.18	0.17	1 193	1 279

In conclusion, it was shown that the catalytic activity of anatase particles in the oxidation of carbon monoxide after vacuum or hydrogen pretreatment is very strongly dependent on the texture (surface area and morphology) of the catalyst. The compensation effect allows a clear distinction between polyhedral and spherical particles and its origin may come from the history of the two classes of catalysts and, in particular, from the temperature of their formation. But in this case, the oxidation of carbon monoxide on vacuum or hydrogen activated anatase would be a "demanding reaction" (*14*). The same catalytic reaction would be "facile" on anatase samples activated in carbon monoxide.

A "line of descent" of a series of catalysts resulting from the preparation conditions and from the activation treatment, conferring catalytic "heredity" may be established. But in this case, a simple definition of the catalytic activity, which would be useful in the search for correlations between this activity and a series of various oxide catalysts (*1*), is difficult to establish and seems to bring into question the established correlations.

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REFERENCES

1. Teichner, S. J., *in* "Catalysis, Progress in Research" (F. Basolo and R. L. Burwell, Jr., Eds.), p. 91. Plenum, London, 1973.

2. Boudart M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6**, 92 (1966).

3. Vainchtock, M. T., Vergnon, P., Juillet, F., and Teichner, S. J., *Bull. Soc. Chim. Fr.* 2806 and 2812 (1972).

4. Long, J., and Teichner, S. J., *Rev. Hautes Temp. Refract.* **2,** 47 (1965).
5. Formenti, M., Juillet, F., Meriaudeau, P., Teichner, S. J., and Vergnon, P., *J. Colloid Interface Sci.* **39,** 79 (1972).
6. Juillet, F., Lecomte, F., Mozzanega, H., Teichner, S. J., Thevenet, A., and Vergnon, P., *Faraday Symp. Chem. Soc.* **7,** 57 (1973).
7. Primet, M., Pichat, P., and Mathieu, M. V., *J. Phys. Chem.* **75,** 1216 (1971).
8. Boudart, M., *Chem. Eng. Progr.* **57,** 33 (1961).
9. Constable, F. H., *Proc. Roy. Soc., Ser A* **108,** 355 (1925).
10. Cremer, E., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Eds.), Vol. 7, p. 75. Academic Press, New York, 1955.
11. Schwab, G. M., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Eds.), Vol 2, p. 251. Academic Press, New York, 1950.
12. Tsvetskova, V. I., Voevodski, V. V., and Chirkov, N. N., *Zh. Fiz. Khim.* **29,** 355 (1955).
13. van Hardeveld, R., and Hartog, F., *Surface Sci.* **15,** 189 (1969).
14. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, New York, 1969.
15. Teichner, S. J., *J. Catal.* **4,** 724 (1965).
16. Reymond, J. P., unpublished data.
17. Bond, G. C., "Catalysis by metals." Academic Press, London, 1962.
18. Herrmann, J. M., Vergnon, P., and Teichner, S. J., *Bull. Soc. Chim.* p. 3034 (1972).
19. Meriaudeau, P., Che, M., Gravelle, P. C., and Teichner, S. J., *Bull. Soc. Chim.* p. 13 (1970).