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Interfacial Reactions between V_2O_5 and TiO_2 (Anatase): Role of the Structural Properties

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Microgravimetric experiments under isothermal conditions between 565 and 615°C in flowing atmosphere of nitrogen suggest that both the reduction of V_2O_5 and the transformation of anatase into rutile are topotactic reactions activated by a remarkable fit of the crystallographic patterns in contact at the V_2O_5–TiO_2 (anatase) interface. These structural properties, allowing changes ordered in space and time, are thought to be responsible, during the reactions, for atomic movements, which cannot occur otherwise.

Introduction

It is well known that V_2O_5 supported on TiO_2 (anatase[1]) is an active and selective catalyst for the mild oxidation of *o*-xylene into phthalic anhydride (*1–6*).

Some authors have qualitatively correlated this property to the fact that V_2O_5 loses oxygen when in the presence of TiO_2 (anatase) (*4*, *7*). However, such a phenomenon, observed with nitrogen, air, or oxygen under atmospheric pressure and at temperatures of 600–700°C, apparently contradicts the established bulk thermodynamic properties of V_2O_5 (*8–12*). Moreover, in an attempt to reinforce the correlation, Cole *et al.* (*4*, *7*) submitted V_2O_5–TiO_2 (anatase) mixtures to increasing temperatures. Associated with the reduction reaction they observed a gradual transformation of anatase into rutile. This raises another question since the transformation normally occurs at much higher temperatures (*13–16*).

The mechanisms by which on the one hand, anatase-supported V_2O_5 is reduced, and on the other hand, anatase transforms into rutile are not yet understood, as it is often the case when interfacial relationships between two solids are involved. Further study of this question appeared justified by both its fundamental interest and its practical implications in heterogeneous catalysis, as it concerns the way supports affect selectivity.

The present paper reports additional investigation carried out with the working hypothesis that a kinetic study of the thermal behavior of the system could greatly help in the understanding of the phenomena indicated above. Microgravimetric experiments under isothermal conditions suggest that both the reduction of V_2O_5 and the transformation of anatase into rutile are activated by structural interactions at the V_2O_5–TiO_2 (anatase) interface. Should this interpretation be directly confirmed, it would underline the importance in such reactions of cooperative atomic movements initiated by interfacial relationships between solid phases, and their role in the selectivity of oxides responsible for heterogeneous catalytic processes of oxidation.

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[1] What is said of anatase applies to brookite as well. Anatase and brookite are two of the metastable forms of TiO_2, and both exhibit, as shown in Remark II, very similar structural features making possible the phenomena discussed in this paper.

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Experimental

1. *Materials*

Pure TiO_2 (anatase) was supplied by Rhone Poulenc Industries (specific area 7 m^2/g). Pure TiO_2 (rutile) was supplied by Merck–France S.A. V_2O_5 was prepared by decomposing at 500°C ($P_{O_2} = 1$ atm) a washed and oven-dried complex, previously obtained by precipitating a mixture of ammonium metavanadate and pure oxalic acid (Merck–France S.A.). V_2O_5 supported on TiO_2 (anatase or rutile) was prepared as pure V_2O_5, except for the precipitation carried out in the presence of TiO_2. V_2O_5–TiO_2 mixtures of four different compositions were considered (5, 10, 15, 25 mole% V_2O_5).

2. *Microgravimetric Analysis*

The thermal behavior under nitrogen (Air Liquide U grade; $P_{O_2} \simeq 5 \times 10^{-6}$ atm) of the materials listed above was studied using a Setaram microbalance MTB 10-8. Isotherms were recorded for temperatures ranging from 565 to 615°C. Nitrogen flow of 1 liter at STP per hour under atmospheric pressure was used. With 20-mg loads the balance allowed to detect weight losses as small as 2×10^{-5} g.

3. *X-Ray Diffraction*

X-Ray diffraction photographs from specimens as prepared and after heat treatment were obtained using a C.G.R. 2080 Generator fitted with a Seeman–Bohling Chamber ($CoK\alpha$ radiation).

4. *Electron Microscopy*

Particle size and structure of the TiO_2 supports were checked in a JEOL 100 C electron microscope.

Results

1. *Pure TiO_2 (anatase)*

Figure 1 shows the general morphology of the TiO_2 (anatase) powder used. The average diameter was estimated to be approximately 1000–2000 Å. Considering the established fact that pure or doped TiO_2-anatase transforms into rutile only at temperatures of 850–1100°C (*14*), samples of pure anatase were submitted for calibration purposes to the thermogravimetric treatment indicated above. As expected, and in accordance with other observations no modification occurred within the 565–615°C temperature range, in flowing nitrogen under atmospheric pressure (*7*, *15–20*).

2. *Pure V_2O_5*

Likewise, under the same conditions, no modification of V_2O_5 was observed. Given the low melting point of V_2O_5 and the decomposition phenomena occurring in the neighborhood of the phase transformation, the maximum temperature of 615°C was conservatively chosen in order to apply the thermogravimetric measurements to a practically pure solid-state process. This remark will be of even greater concern in the case of V_2O_5–TiO_2 mixtures, which are to be studied as solid phases, i.e., with no risk of any chemical interaction involving V^{5+} in vapor or pseudoliquid state.

3. *V_2O_5–TiO_2 Mixtures*

(*a*). *Anatase-supported V_2O_5*. The weight losses, corresponding to a series of thermogravimetric isotherms performed, for the reasons indicated in the previous section, within the temperature range 565 and 615°C, were found to vary with the V_2O_5 content in a way similar to that described by Cole and Hucknall (*4*, *7*). These workers verified by mass spectrometry that oxygen during heating evolved from V_2O_5.

In the selected 565–615°C temperature range, thermogravimetric isotherms showed an induction period, which grew longer the lower the temperature (1 hr at 615°C and 50 hr at 585°C). The induction period was followed by a continuous and sigmoïd weight loss, i.e., the weight loss was at first accelerated until approximately half of the loss was attained, whereby the transformation slowed down gradually.

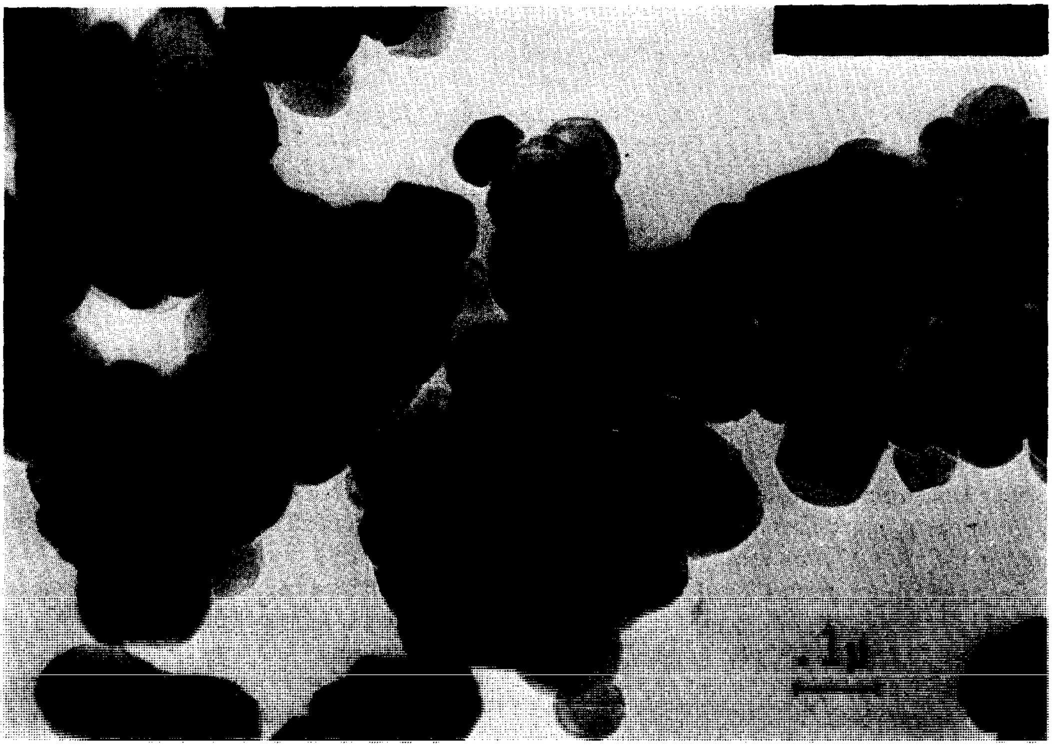

FIG. 1. Electron micrograph of the anatase used, yielding an average particle size of 1000–2000 Å, i.e., a calculated geometric area approximately equal to the specific area (7 m^2/g). Consequently the TiO_2–anatase support can be considered as pore free, and covered in average with a 50-Å thick V_2O_5 layer in a 15 wt% V_2O_5–TiO_2 mixture.

The X-ray diffraction data obtained can be summarized as in Table I. These results indicated that the reduction of V_2O_5 was incomplete except for the low V_2O_5-containing mixtures where V_2O_5 disappeared altogether (at least to the extent of the sensitivity of the X-ray film). On the other hand, anatase (within the same limit of sensitivity) com-

TABLE I

QUALITATIVE INTENSITIES OF X-RAY DIFFRACTION LINES BEFORE AND AFTER HEAT TREATMENT

V_2O_5–TiO_2 mixtures (mole% V_2O_5)	Before heat treatment	→	After heat treatment
15	V_2O_5 vw[a]	→	—
	TiO_2 s (anatase)	→	w (anatase) s (rutile)
15	V_2O_5 w	→	w
	TiO_2 s (anatase)	→	s (rutile)
25	V_2O_5 w	→	w
	TiO_2 s (anatase)	→	s (rutile)

[a] vw = very weak, w = weak, s = strong.

TABLE II
COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL WEIGHT LOSS

Possible suboxides	5 mole% V_2O_5 mixture		25 mole% V_2O_5 mixture	
	Weight loss[a]		Weight loss	
	Calculated	Observed	Calculated	Observed
$V_2O_5 \rightarrow V_3O_7$	6.3	·	17	·
$\rightarrow V_4O_9$	9.4	·	25.5	·
$\rightarrow V_6O_{13}$	12.6	·	34	·
$\rightarrow VO_2$	18.8	16	54	·

[a] Weight loss in mg x 10^{-2} corresponding to 20-mg samples.

pletely transformed into well-crystallized rutile in most cases, light traces of anatase remaining only in the 5% V_2O_5 mixtures.

In Table II are given the calculated weight losses corresponding to complete transformation of 20 mg of V_2O_5 into various possible suboxides. Comparing with the experimental data it appears that VO_2 is the sole stoichiometry accounting for the weight change obtained from 5% V_2O_5 samples. For mixtures containing more V_2O_5 the same calculations are inconclusive, but since we see no reason for the V_2O_5 content to affect the nature of the reduction process, we are led to assume VO_2 to be the final suboxide obtained in all cases. On this basis, about 90 wt% of V_2O_5 is transformed into VO_2 in the case of 5% mixtures, and 50 wt% in that of 15% mixtures.

Attempts at linearizing the sigmoïd reduction led us to choose the model $\log (x/1 - x) = k(t - \tau)$, frequently used for autocatalytic reactions, where x (ranging between 0 and 1)

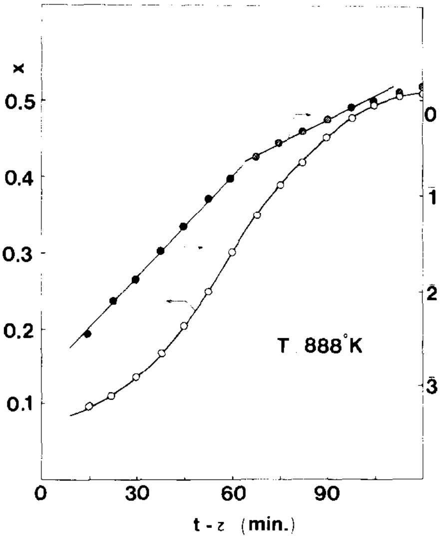

FIG. 2. (a) Typical micrograviraetric x, $(t - \tau)$ curve obtained at 615°C under nitrogen in the thermal reduction of V_2O_5 supported on TiO_2–anatase. (b) Transform: $\log (x/(1 - x)) = k(t - \tau)$ with x = fraction decomposed, t = time, τ = induction period.

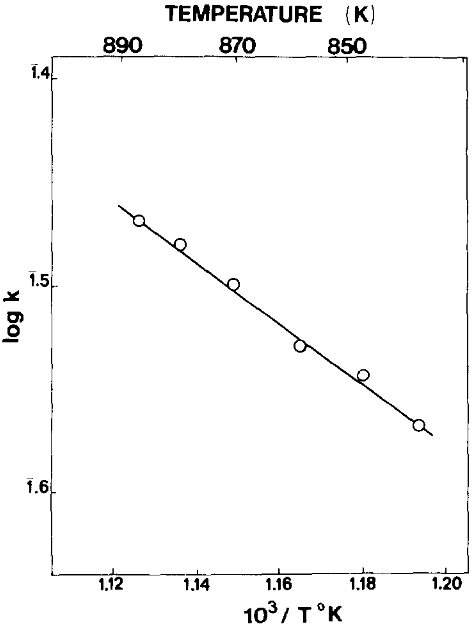

FIG. 3. Apparent activation energy $E = 10 \pm 2$ kcal. $\log k$ plotted versus $10^3/T$ (°K).

is the weight fraction of V_2O_5 transformed into VO_2, and τ the induction period. Within the 565–615°C temperature range, two straight lines were so determined, one corresponding to the accelerated phase of the transformation, the other to the decelerated part (Fig. 2). Apparent rate constants obtained from the former straight line yielded 10 ± 2 kcal, as an estimate for the apparent activation energy of the reduction of V_2O_5 (Fig. 3).

(*b*). *Rutile-supported* V_2O_5. V_2O_5–TiO_2 mixtures, made up of highly pure rutile, gave rise within the same temperature range to small and insignificant weight losses. However, rutile purity had to be carefully checked, since this material frequently contains a substantial amount of anatase. Of course, anatase-contaminated rutile caused weight loss to occur in agreement with the previous section.

Discussion

Our observations, in accordance with the literature (*8–12*), confirmed that bulk V_2O_5 cannot be reduced at 615°C under an oxygen partial pressure of 10^{-5} atm. This fact is due either to an effective thermodynamic impossibility or to an extremely slow reaction rate, a consequence of the imposed experimental conditions (T_f V_2O_5 = 690°C). The latter view implies the possibility of accelerating the reaction, and experimental evidence suggests that such is the case for the anatase-containing V_2O_5 mixtures; whilst V_2O_5 alone is not reduced, a weight loss is observed when V_2O_5 is supported on TiO_2–anatase (or brookite[1]). In other words, it appears that anatase exhibits in this context an activating property making the reduction of V_2O_5 fast enough to be observable. This property is specific, since neither rutile nor any other support or addition allows the reduction to occur. Moreover, the sigmoid shape of the thermogravimetric curves points out the character continuous and autocatalytic of the activated reduction of V_2O_5. Finally, the anomalous occurrence of the anatase–rutile transformation, classically observed at much higher temperature, indicates that this transformation is also activated in the process.

Satisfactory elucidation of these phenomena requires us to answer the two following questions:

How does the reduction of V_2O_5 get started and go on according to an auto-accelerated process?

How does anatase simultaneously transform into rutile?

(*a*). *Reduction of* TiO_2*-supported* V_2O_5. Reported models relative to the ReO_3-type matrices supply satisfactory interpretation of the phenomena attending the early stages of the reduction of V_2O_5 (*21–26*).

Anderson and Hyde (*24*) proposed that random oxygen vacancies in V_2O_5 by an appropriate clustering process produce disordered elements of the *CS* plane, the crystallographic shear vector being $[1\bar{3}0]$ V_2O_5 (*22, 25*).[2] Concerning the interfacial V_2O_5–TiO_2 area, Johnson suggested (*27*) that in such an environment V_2O_5 exhibits an aptitude to transform into V^{4+} ions (reduction thought (*28, 29*) to be enhanced by anionic vacancies acting as electron donors).

On this basis, the results of our experiments with pure V_2O_5 or TiO_2 (rutile)–V_2O_5 mixtures are explained as follows. Bulk V_2O_5 tends to reduce according to a *CS* process, but to an insignificant extent under our experimental conditions because of the very high activation energy required; near the V_2O_5–TiO_2 interface the reaction $V^{5+} \rightarrow V^{4+}$ adds a factor favorable to the reduction, whose contribution however is again negligible in our experimental conditions, though it may become effective at higher temperatures[3] as shown by Cole *et al.* (*7*).

Next, we have to elucidate why the reduction of V_2O_5 proceeds in a different fashion,

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[2] In Bachmann *et al.*'s notation (*32*).

[3] In this case the enhancement of the electronic interaction between the V^{5+} and TiO_2 (rutile) surface is due to the reactivity of V_2O_5, whose temperature is then about the melting temperature of pure V_2O_5. Such a condition was deliberately not considered in the present work in order to deal unambiguously with a solid-state reaction.

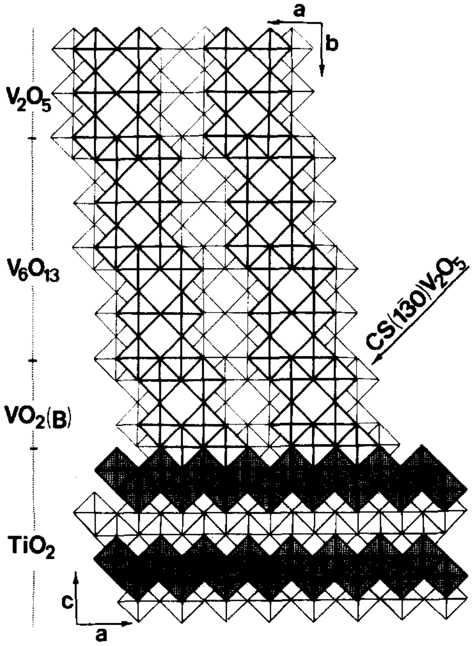

FIG. 4. Schematic representation of the gradual building of reduced phases from the (010)V_2O_5/(001)anatase interface during the topotactic reduction of V_2O_5. Direction of the $\frac{1}{6}CS$ [1$\bar{3}$0] V_2O_5 indicated with an arrow. For simplicity, only parts of unit cells are represented. Bachmann's notation for V_2O_5 (*32*).

when the support is anatase (or brookite), everything else being equal.

The difference between the two situations should primarily result from structural conditions, since it is the main factor at variance. First, it will be shown that anatase (or brookite) and V_2O_5 have several important structural features in common. Then, the combined effect of this system on the reduction of V_2O_5 will be discussed.

i. The crystalline structure of anatase (*30*, *31*) and that of V_2O_5 (*31*, *32*) and known suboxides such as V_4O_9 (*34*, *36*), V_6O_{13} (*31*, *33*), $VO_{2(B)}$ (*35*, *36*)[4] have in common the same type of tridimensional pattern as illustrated in Fig. 4; these structures are all of the Wadsley-matrix nature.

ii. A close crystallographic fit, shown in Fig. 4 and 5, exists between the V_2O_5 plane (010) and the anatase planes (001) and (010). The lattice constants of anatase and various vanadium oxides are gathered in Table III, along with some misfit calculations.[5]

iii. Due to its lamelar structure[6] V_2O_5 naturally occurs in the form of platelets, whose faces correspond to the (010) planes. The bidimensional pattern of this plane appears also on the faces of the other suboxides mentioned above, similarly shaped for the same reasons.

iv. The anatase cleavage plane (001) and also the plane (010) are the most commonly found at the surface (*39*, *40*). There is therefore a strong likelihood in a TiO_2–V_2O_5 mixture for these planes to be in contact with faces (010) of V_2O_5 lamellae.

Remark I. One is well aware of the fact that the anatase surface is not clean but covered with adsorbed species such as hydroxyl ions (*39*). It seems however that the preparative technique of the V_2O_5–TiO_2 system and the effect of temperature should displace the hydroxyl ions and leave the surface of the two oxides in good contact.

Regarding the reduction of V_2O_5, let us first consider again the situation where this substance is pure. The well recognized difficulty of reducing it under nitrogen atmosphere or vacuum (*38*), is thought by Hyde and Bursill (*25*) to be a consequence of the stress associated with the reduction and the subsequent formation of "hybrid" crystals following Ubbelohde's theory (*44*). According to this last author the molecules or atoms near the interface of two structurally very similar hybrid crystals I and II tend to remain in excited states and very mobile because of random tension and compression adding to the free energy of each of the two structures I and II, and cannot find positions of lower potential energy. Besides, these features are closely

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[4] V_4O_9 and VO_2(B) are actually stable only up to 450°C, as opposed to V_6O_{13} (*34–36*).

[5] The "linear lattice misfit" α_l along the *a* V_2O_5 direction increases with the degree of reduction, whereas the misfit γ_l decreases along the *c* V_2O_5 direction. It appears also that the product π_l is minimum for V_6O_{13}.

[6] The lamellar structure of V_2O_5 (*31*, *32*, *38*) results from the alternating in one direction (normal to the faces) of short (σ, π) and long bonds lying in the symmetry plane of the *V* site (point group of *V*: C_s).

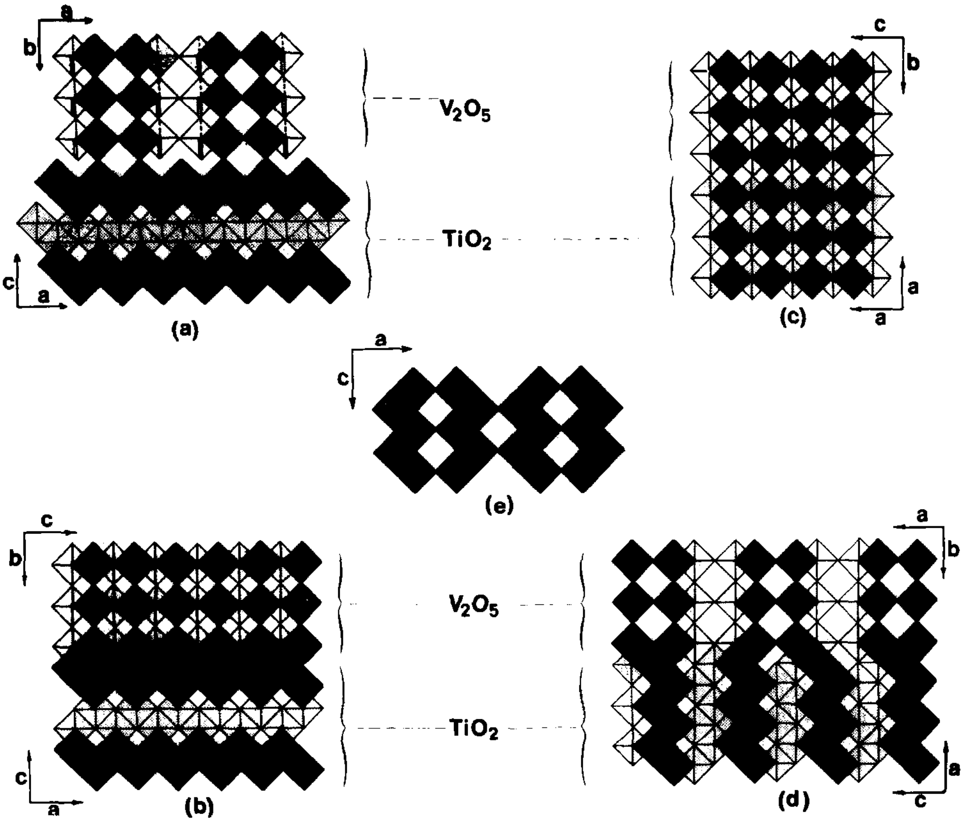

FIG. 5. Examples of crystallographic matching between (010)V_2O_5 and (001) or (010)anatase. A few possible idealized arrangements of the two phases are given: In (a) and (c) oxygen octahedra are sharing corners, in (b) and (d) they are sharing edges. In (a) the (σ, π) short bonds of the real structure are schematized by double lines, and the long bonds are represented by dotted lines. These four examples are not exhaustive. Scheme (e) indicates the idealized bidimensional pattern of the V_2O_5 plane (010), common to the other suboxides, and fitting with the TiO_2–anatase planes (001) and (010). The pattern appears in real dimensions in Fig. 6.

related to the hysteresis phenomena observed in other systems (*25*, *44*). In the case of V_2O_5 containing substitutional or interstitial impurities, an effect of "lubrication" is assumed to result from the presence of these irregularities (rutile-supported V_2O_5 belongs to this situation because of the lack of any crystallographic fit). This "lubrication,"

TABLE III
LATTICE MISFIT BETWEEN ANATASE AND VANADIUM OXIDES

	a_i (Å)	d_i (Å)[b]	$a_i \times d_i$	α_i (%)[a]	γ_i (%)[a]	π_i (%)[a]
Anatase	$a_0 = 3.78$	$d_0 = 11.34$	$a_0d_0 = 42.87$	—	—	—
V_2O_5	$a_1 = 3.56$	$d_1 = 11.51$	$a_1d_1 = 40.98$	5.8	1.5	4.4
V_6O_{13}	$a_2 = 3.67$	$d_2 = 11.90$	$a_2d_2 = 43.67$	2.9	4.9	1.9
VO_2(B)	$a_3 = 3.69$	$d_3 = 12.00$	$a_3d_3 = 44.28$	2.4	5.8	3.3

[a] "Relative" lattice misfit: $\alpha_i = ((a_i - a_0)/a_0) \times 100$, $\gamma_i = ((d_i - d_0)/d_0) \times 100$, $\pi_i = ((a_i d_i - a_0 d_0)/a_0 d_0) \times 100$.

[b] a_i and d_i were approximately calculated from effective lattice constants, with the following correspondence: $a_0 \simeq a_{\text{anatase}}$, $d_0 \simeq 3a_{\text{anatase}}$, $a_1 \simeq a_{V_2O_5}$, $d_1 \simeq c_{V_2O_5}$, $a_2 \simeq b_{V_6O_{13}}$, $d_2 \simeq a_{V_6O_{13}}$, $a_3 \simeq b_{VO_2(B)}$, $d_3 \simeq a_{VO_2(B)}$.

however, has only an assisting influence on the solid–solid reactions, and does not suffice to account for autocatalytic processes.

As for anatase-supported V_2O_5, our present concern, the crystallographic fit of the V_2O_5 plane (010) and the anatase planes (010) or (001) implies the possibility of interaction between the surface of these two compounds. The primary feature of the interaction is the stabilization at the interface of the bidimensional pattern (common to the surface of anatase and of V_2O_5 and its suboxides). The stabilized interface induces an ordering process in the nucleation of the developing *CS* planes, as opposed to the disordered reduction of pure V_2O_5. In other words the atomic movements along the direction of the *CS* vector $[1\bar{3}0]$ V_2O_5, cooperative only locally in the general case of the reduction of V_2O_5, occur here in larger domains, resulting in structural *coherence*. The origin of such a *coherence* may be seen in the small misfit between anatase and V_2O_5 (and between V_2O_5 and its suboxides as well), which can be accommodated without misfit dislocations, as commonly admitted in studies on epitaxial growth (*42*) and on "extended defects in oxides" (*43*). Since the lattice misfit gives rise to interfacial elastic stress and therefore to substantial surface energy, which corresponds to excited atoms in V_2O_5 crystals near the interface, and since no relaxation through the formation of vacancies occurs, the lifetime of the excited states increases considerably. As shown by Ubbelohde (*44*) "excited states that are difficult to destroy are indicative either of high metastability (case of pure or doped V_2O_5), or of chain reaction kinetics." The latter case implies of course an extra factor such as cooperative fluctuations (*45*, *46*) or a specific external cause, which in the anatase–V_2O_5 system derives from the exceptional interfacial relationship involved. Such an autocatalytic process is evidenced by the first part of the transformation (Fig. 2), whose apparent activation energy is about 10 kcal/mole (it is conceivable, moreover, that the evolution toward suboxides corresponding for the system to a seemingly even more favorable lattice fit,[5] i.e., toward lower potential energy, be an added factor to the chain reaction kinetics).

The second part of the curve describing the deceleration of the reaction is discussed in the next section relative to the anatase–rutile transformation.

(*b*). *Transformation of anatase into rutile.* Whereas in our V_2O_5–TiO_2 mixtures, anatase transformed into rutile under nitrogen at

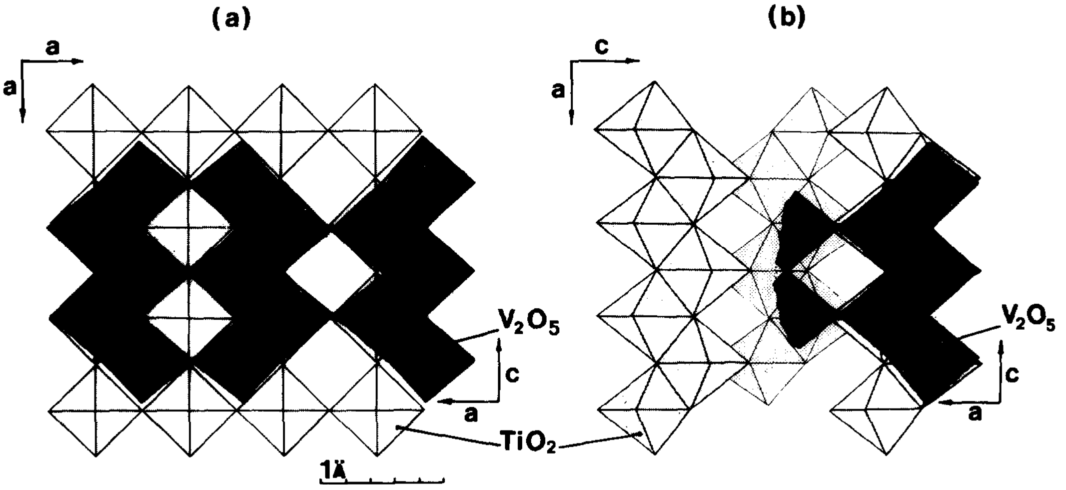

FIG. 6. Crystallographic fits: $(010)V_2O_5/(001)$anatase shown in (a), $(010)V_2O_5/(010)$anatase in (b). Real dimensions.

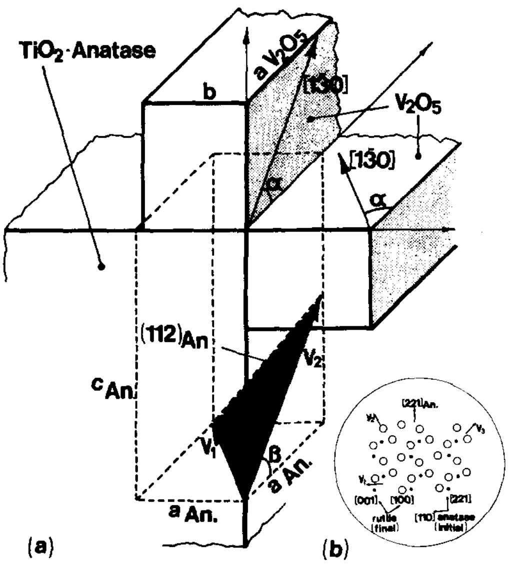

FIG. 7. (a) Two examples of possible crystallographic matching models between V_2O_5 and anatase: (010)V_2O_5/(001)anatase and (010)V_2O_5/(010)anatase. The *CS* vector [1$\bar{3}$0] is nearly colinear with $\bar{V}_1$ (or $\bar{V}_2$) in the (112) plane of anatase ($\alpha = 49.9° \simeq \beta = 51.5°$). (b) Pseudo-cubic-closest-packing plane (112) of anatase, showing three possible directions $\bar{V}_1$, $\bar{V}_2$, $\bar{V}_3$ for the rutile *c* axis after the transformation anatase → rutile (*13*, *16*).

615°C (and even at 565°C), it is well known that pure or simply doped anatase transforms into rutile only at high temperature (850–1100°C) because of the important activation energy needed (185 kcal/mole) (*14*).

In the latter case Shannon and Pask (*13*) demonstrated this structural change to be an incomplete topotactic transformation: The (112) pseudo-CCP oxygen planes are retained as the pseudo-HCP planes in rutile. In Fig. 7b, which is a projection perpendicular to the (112) plane of anatase, the directions $\bar{V}_1$, $\bar{V}_2$, and $\bar{V}_3$ indicate possible *c*-axis directions in rutile, which are also possible directions of realignment of the Ti atoms during the transformation. In $\bar{V}_1$ and $\bar{V}_2$ directions according to these authors "there is a diffusion-type of movement of half the cations in an anion structure that remains essentially fixed, in which the cations break four (Ti–O) bonds and retain only two original neighbors." The rearrangement in the third direction $\bar{V}_3$ which would require that two (Ti–O) bonds only should be broken during movement would be energetically more favorable. They concluded that pure anatase transforms into rutile according to the latter mechanism.

In the case of anatase supporting V_2O_5, the situation is similar to that of V_2O_5 discussed earlier, namely the existence of elastic stress due to particular structural relationship at the interface. Thus the TiO_2 molecules are in excited states within large domains and the character cooperative, coherent and bulky of the resulting situation makes possible this transformation normally inhibited by a high activation energy.

The transformation mechanism may differ here from the one invoked by Shannon (*14*) in the case of pure anatase. It is conceivable that the realignment of the titanium atoms giving the rutile structure occur along the vector $\bar{V}_1$ or $\bar{V}_2$ (Fig. 7), since these vectors are practically colinear with the crystallographic shear vector [1$\bar{3}$0] V_2O_5. Such a mutual induction could be also an added factor in the lowering of the activation energy of the transformation. This view is supported by the experimental evidence that anatase when associated with V_2O_5 transforms under nitrogen into rutile at much lower temperature and with a considerably lower activation energy: Since the anatase → rutile transformation occurs completely and simultaneously during the reduction of V_2O_5, one may assume that the activation energy of about 10 kcal/mole determined for the latter represents also an upper limit for that of the anatase → rutile transformation.

A consequence of this transformation is the gradual vanishing from the interface of the anatase bidimensional pattern favorable to the formation of suboxides till VO_2(B) (which is not stable at our temperatures), and its replacement by the rutile pattern enhancing the nucleation of rutile-type VO_2.

The vanishing from the interface of the anatase pattern implies that of the reduction mechanism described above, which accounts for the deceleration exhibited by the second part of the thermogravimetric curve (Fig. 2). A V_2O_5–TiO_2 solid solution may form at the interface, but its presence does not fundamentally modify the rationale above, i.e., development of the anatase–rutile transformation and slowing down of the V_2O_5 reduction.

Remark II. As already mentioned in footnote 1 most of the points concerning anatase and discussed in this paper would be relevant to brookite, because of the similar structures of the two materials (*31*, *37*, *41*). Anatase and brookite are two of the metastable forms of TiO_2:

the structure of anatase is built on a distorted pseudo-cubic close-packed (CCP) of oxygen with Ti atoms occupying one-half of the octahedral interstices. The (112) plane is the close-packed plane with Ti atoms forming zigzag chains along [221]. Each TiO_6 octahedron shares four edges;

the structure of brookite consists of oxygen layers arranged in a pseudo-doubly-hexagonal-close-packing scheme (DHCP), with Ti atoms occupying one-half of the octahedra. The (100) plane is the close-packed plane with Ti atoms forming also zigzag chains along [001]. Each TiO_6 octahedron shares in this case three edges.

In the direction parallel to the close-packed planes of oxygen ((112) in anatase and (001) in brookite), an elementary arrangement common to the two structures can be recognized, involving the linking of two zigzag strings of TiO_6 octahedron (forming a first layer of octahedra) by a third string (forming a second layer) behind the two others. The only difference lies in the stacking of this arrangement in the direction perpendicular to the close-packed planes. The anatase structure is obtained by simply stacking the two-dimensional pattern in the third direction. As for brookite the stacking is slightly more involved, i.e., each string of octahedra belonging to a layer is shifted alternately by half of an octahedron. Consequently brookite presents two symmetrical directions of planes exhibiting alternate sequence of patterns similar to those of either the (001) or the (010) plane of anatase.

Naturally, these structural similarities of anatase and brookite result in the analogous behavior under nitrogen of the V_2O_5–anatase and V_2O_5–brookite systems. In particular it is not surprising, as reported by Cole *et al.* (*7*), to observe a similar loss of oxygen with a simultaneous topotactic and direct brookite → rutile transformation, already interpreted (*16*) by a shift of oxygen and titanium atoms in the close-packed planes (001).

Conclusion

The kinetic study within 565 and 615°C of the reduction under nitrogen of V_2O_5 supported on anatase reveals an interfacial synergetic effect, namely a catalysis of the topotactic reduction of V_2O_5 and a considerable lowering of the activation barrier in the anatase–rutile transformation, which develops concurrently and cooperatively.

Without overlooking the importance of other studies based on electronic properties, acidity–basicity, etc., we have shown that simple structural and thermodynamic considerations, applied to ions no longer isolated but in their context in solid state, allow new insights into some exceptional kinetic mechanisms involved in solid–solid, solid–gas reactions and in heterogeneous catalysis as well.

In a later paper (*6*) it will be shown how these surface interactions can be correlated to the selectivity of TiO_2 (anatase)-supported V_2O_5 catalysts in the oxidation of *o*-xylene into phthalic anhydride. An electron microscope investigation of the surface interactions between anatase and V_2O_5 is in progress.

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