

Ethylene Oxidation to Acetic Acid with Pd-V₂O₅ Type Catalysts

I. Gas-Solid Reactions

JOSÉ LUIS SEOANE,¹ PIERRE BOUTRY, AND ROGER MONTARNAL²

Institut Français du Pétrole, Boîte Postale 311, 92506 Rueil-Malmaison, France.

Received May 22, 1978; revised September 10, 1979

Palladium added to V₂O₅ enhances the reducibility of this oxide. The reduction can then be performed at low temperature so as to produce selectively a reduced phase with the formula V₄O₉. The influence of ethylene partial pressure on the initial reduction rate of Pd-V₂O₅ and the influence of oxygen partial pressure on the initial oxidation rate of the reduced phase have been established. Kinetic equations are proposed for these two gas-solid reactions. The selective formation of acetaldehyde and acetic acid occurs during the reduction. In the presence of both ethylene and oxygen reactants, i.e., for the condition of catalytic reaction, we observe a change of the initial composition of the solid toward a final state which depends on the partial pressure of the reactants. Qualitatively, from an initially oxidized form, there is a partial reduction, while from an initially reduced form, V₄O₉, there is a partial oxidation.

I. INTRODUCTION

The mild oxidation of ethylene can be used to produce acetaldehyde very selectively by the use of homogeneous catalysts (1). The acetaldehyde can in turn be selectively oxidized to acetic acid over solid catalysts. This constitutes an industrial method for producing acetic acid, and each stage has generated a great deal of fundamental research. On the other hand, the direct oxidation of ethylene into acetic acid in only one stage has not promoted much research. Some patents (2-5) claim performances of interest, thanks to the use of vanadium pentoxide to which a compound of palladium or other metal has been added. Furthermore, the catalytic activity of certain metals or metal oxides has been studied in order to produce acetaldehyde and acetic acid from ethylene. However, the published results are essentially related to the production of acetaldehyde.

We have thought it interesting to study in a more complete way the performances

obtained with a catalyst of the Pd-V₂O₅ type, i.e., 0.02 wt% Pd deposited on vanadium pentoxide. Our first experiments (6, 7) had demonstrated that, by the addition of palladium, vanadium pentoxide can be active at a temperature as low as 230°C for the oxidation of ethylene into acetic acid, while V₂O₅ alone has an appreciable activity only at a higher temperature. Furthermore, these first experiments also demonstrated that the addition of 0.02% Pd to the V₂O₅ accelerated the reduction rate of this oxide. These phenomena suggested the presence of a redox mechanism for the catalytic reaction in which palladium would play a particular role. A redox mechanism has also been suggested by Evin *et al.* (8) for the oxidation of ethylene over Pd-V₂O₅, but at a lower temperature (110-175°C), which essentially limits the oxidation to the production of acetaldehyde. Moreover, these authors claim that, as in the Wacker process, the palladium compounds are the catalyst and that V₂O₅ is the co-catalyst promoting the reoxidation of the metallic palladium.

Thus, in order to obtain more complete information on the oxidation of ethylene

¹ Present address: Instituto de Calalísis y Petroleoquímica, Serrano 119, Madrid 6, Spain.

² Dr. R. Montarnal died on February 15, 1979.

into acetic acid over Pd-V₂O₅, at about 250°C, as well as on the reaction mechanism, we started a more systematic investigation of the gas-solid interactions and of the catalytic reaction itself.

This first paper essentially deals with the study of the gas-solid reactions with ethylene and acetaldehyde as reducing agents and oxygen as the oxidant. A second paper (Part II) deals with the kinetics of the catalytic reaction (9).

II. EXPERIMENTAL METHODS

1. APPARATUS AND PROCEDURE

The kinetic study of the reduction of V₂O₅ and reoxidation of the reduced phase was made by gravimetry, using a Mettler thermobalance with a sensitivity of 1.2 mg for a sample of 0.3 g. The partial pressures of ethylene, P_E , and oxygen, P_{O_2} , were changed between 0.05 and 0.4 atm and between 0.1 and 1.0 atm, respectively. The diluent was high-purity nitrogen.

Experiments concerning changes in the solid in the presence of the two reactants, ethylene and oxygen, and the catalytic transformations of these reactants were carried out in the same catalytic flow reactor as used in Part II (9) and with 20 g of catalyst. The output of the reactor passes through a series of water bubblers which are maintained at 0°C, so that the condensable and soluble products are separated. The remaining gas goes through samplers and, finally, its volume is measured by a gas meter. The transformations related to the gas phase will be defined by the conversion of ethylene and the yields of each product. These yields will be expressed as the corresponding fraction of the transformed ethylene. The same apparatus was used to study the transformations of the gas phase during the gas-solid reduction reactions of the solid by ethylene or acetaldehyde.

For all experiments, the contact time will be defined as the ratio W/F , W being the catalyst weight in grams and F the total flow in cubic centimeters (STP) per second.

It is a formal contact time which is given here in $g \cdot s/cm^{-3}$.

2. ANALYSIS

In the condensed phase, the following products were found: acetaldehyde (AcH), acetic acid (AcOH), H₂O, and very small quantities of acetone and acrolein, whereas the exit gas was a mixture of N₂, O₂, C₂H₄, CO, and CO₂. These products were analyzed by gas chromatography, using the following columns:

(a) Aldehydes and ketones: 15% of Carbowax 4000 over firebrick. Length $L = 3.5$ m, diameter $\phi = 3.18$ mm, $T = 105^\circ\text{C}$.

(b) Acetic acid: Porapak T. $L = 3$ m, $\phi = 3.18$ mm, $T = 150^\circ\text{C}$.

(c) CO, N₂, and O₂: molecular sieve 13X. $L = 1$ m, $\phi = 6.3$ mm, $T = 30^\circ\text{C}$.

(d) C₂H₄ and CO₂: Two columns in series, the first being hexadecane over firebrick (20 wt%), $L = 1.5$ m, $\phi = 6.3$ mm, and the second 30 wt% of a mixture of 30 wt % glutaronitrile and 70% propylene carbonate over firebrick, $L = 17$ m, $\phi = 6.3$ mm, $T = 50^\circ\text{C}$.

The acetic acid was also measured by titration with 0.1 *N* NaOH, using phenolphthalein as the indicator.

The solids were analyzed after a quench with a nitrogen flow. We used both X-ray diffraction and chemical analysis of V³⁺ and V⁴⁺ ions. The V³⁺ ions were analyzed by reduction with iron salts in the presence of phosphoric acid, using sulfonic diphenylamine as the indicator, while the V⁴⁺ ions were determined by potentiometry using 0.1 *N* KMnO₄ in an acid medium (pH = 1.5) at 40–50°C (10).

3. CATALYSTS

A. Preparation of Oxidized Phases

Vanadium pentoxide was produced by thermal decomposition of powdered ammonium metavanadate on a fluidized bed (particle size 0.20 to 0.25 mm) with air at 300°C. the V₂O₅ was extruded to cylinders of 1 × 3

mm and later activated under an air flow at 400°C for 2 h.

Palladium was then introduced by impregnation, without excess solution, of the appropriate amount of aqueous palladium nitrate. After the solution was completely absorbed, the solid was vacuum dried at room temperature. Palladium nitrate was decomposed by heating in air at 400°C for 2 h. The final catalyst contained 0.02 wt% Pd.

B. Preparation of Reduced Phases

The reduction of V_2O_5 at a temperature lower than 280°C enabled us to obtain a reduced phase different from those generally obtained by reduction at higher temperature, such as V_2O_4 or V_6O_{13} . This phase, called A, was characterized by the weight loss of V_2O_5 , by X-ray diffraction (11) (Fig. 6), by infrared spectrometry (12), and by its chemical composition (50 to 53% V^{4+}), approximating the overall formula V_4O_9 . This compound has also been described by other authors (13, 14), who however obtained it mixed with other oxides such as V_2O_4 or V_2O_5 , since its selective preparation is particularly delicate and requires very mild reduction conditions (11). The addition of 0.02 wt% Pd to V_2O_5 enabled us to carry out the reduction at a temperature as low as 250°C and thus to obtain the A phase quite selectively. The reduction was conducted with 20% volume of ethylene diluted in nitrogen with a contact time of $3 \text{ g} \cdot \text{s}/\text{cm}^{-3}$ for 6 h. When starting with V_2O_5 alone, without Pd addition, it was necessary to use pure ethylene at 280°C in order to obtain a product containing essentially phase A, with a small quantity of V_2O_5 and V_2O_4 . The two reduced phases thus obtained will be called $A(\text{Pd}-V_2O_5)$ and $A(V_2O_5)$ respectively.

During the catalytic reaction, carried out between 230 and 250°C, only phase A appeared in the catalyst together with the V_2O_5 phase. We can write, therefore, that for the catalyst bulk:

$$[V_2O_5] + [A] = 1$$

and, as a working hypothesis, that this balance can also be written for the surface of the catalyst. In order to simplify the writing of the equations, we shall designate the bulk and surface fractions of the V_2O_5 and A phases by $[V^{5+}]$ and $[V^{4+}]$ respectively. Let us recall that $[V^{4+}] = 1$ corresponds to about 50% of V^{4+} .

Figure 1 shows, for the four catalysts, the curves for mercury porosimetry and the values of the specific surface areas. The reduction increases the pore volume, without modifying the surface areas very much; the latter are slightly different, depending on whether palladium was or was not added to V_2O_5 .

The color of both V_2O_5 and $\text{Pd}-V_2O_5$ is light brown. The A phase is dark green and, in general, the more reduced the darker the catalyst becomes.

III. RESULTS

Experimentation concerned first the study of changes in the solid during the reduction of the oxidized phase, the reoxidation of the reduced phase, and in the presence of the two reactants ethylene and oxygen. Then, the analysis of the product of the gas phase was performed during the reduction of the oxidized solid by ethylene and acetaldehyde.

1. CHANGES IN THE SOLID.

The reduction and oxidation of the solid were performed in the thermobalance with

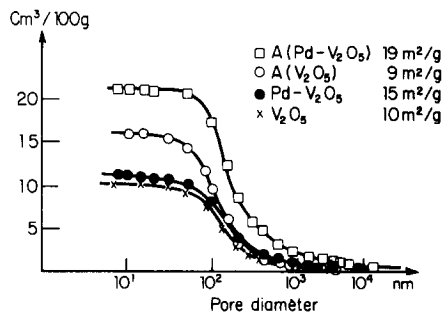


FIG. 1. Mercury porosimeter curves.

a short contact time of circulating gases so as to produce a quite low conversion of ethylene or oxygen.

(a) The reduction by ethylene was carried out on Pd-V₂O₅ and V₂O₅ (Fig. 2). It will be noticed that the complete reduction into V₄O₉ (A phase) corresponds to a weight loss of 44 mg/g of V₂O₅, while the reduction of PdO corresponds only to 0.32 mg/g of solid, for 0.02 wt% of Pd added. The curves of weight loss versus time for several ethylene partial pressures show a hyperbolic shape, without induction period (6), making it possible to define an initial reduction rate at time zero, r_{ir} . Figure 2 shows the change in this rate, at 250°C, when the partial pressure of ethylene varies from 0.05 to 0.4 atm.

(b) The reoxidation with oxygen was carried out starting with phases A(Pd-V₂O₅) and A(V₂O₅). The shape of the curves for weight increases versus time, at 300°C (6), is the same as that of the reduction. Figure 3 shows the change in the initial oxidation rate, r_{io} , when the oxygen partial pressure varies from 0.1 to 0.6 atm.

(c) The study of the changes in the solids in the presence of both reactants, carried out in the catalytic flow reactor used in Part II (9), was first made with a short contact time, $W/F = 0.25$, and then with a long one of $3 \text{ g} \cdot \text{s cm}^{-3}$.

With $W/F = 0.25$, at 230°C, $P_{O_2} = 0.6$ atm and $P_E = 0.1$ atm, the conversion was quite low and the reactor was differential. Figure 4 shows the course of events for

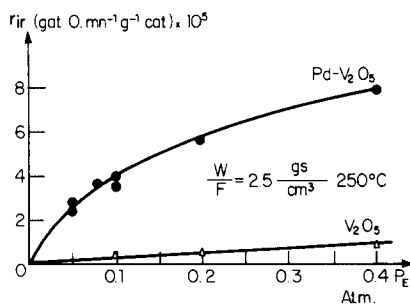


FIG. 2. Influence of ethylene partial pressure on the initial reduction rate of V₂O₅ and of Pd-V₂O₅; diluent N₂.

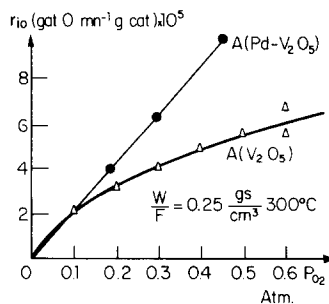


FIG. 3. Influence of oxygen partial pressure on the initial oxidation rate of A(V₂O₅) and of A(Pd-V₂O₅); diluent N₂.

V₂O₅, Pd-V₂O₅, A(V₂O₅) and A(Pd-V₂O₅) as a function of time. In both cases, the initially oxidized solid is reduced and the initially reduced solid is oxidized. However, even after 8 h, a common steady state is not attained from these extreme oxidized or reduced starting states. Moreover, the oxidation of A(Pd-V₂O₅) is much slower than that of A(V₂O₅) and does not seem to lead to the same steady state.

With $W/F = 3$, at 230°C, the conversion of each reactant may be high, and so the change in the solid is governed both by reactants and reaction products. Figure 5a shows the change as a function of time of Pd-V₂O₅ for $P_{O_2} = 0.23$ atm and $P_E = 0.47$ atm. After a transient period of reduction, a

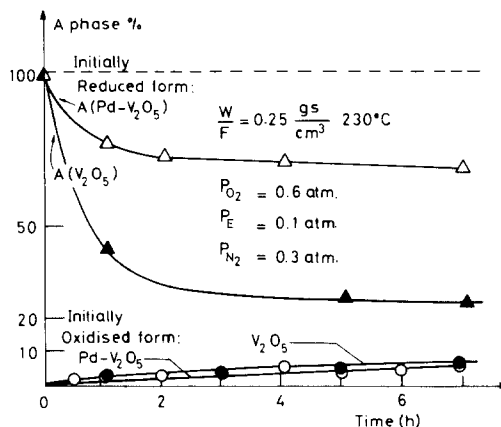


FIG. 4. Transformation of the solid as a function of working time in the presence of both ethylene and oxygen. (Δ) A(Pd-V₂O₅); (\blacktriangle) A(V₂O₅); (\circ) Pd-V₂O₅; (\bullet) V₂O₅ initially.

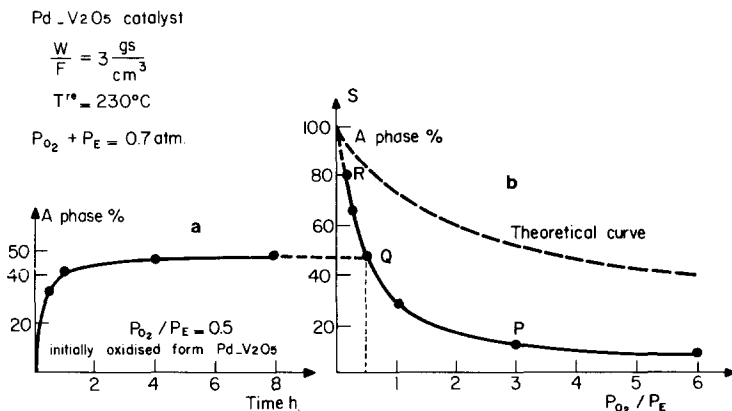


FIG. 5. Transformation of Pd-V₂O₅ in the presence of both ethylene and oxygen. (a) Transient states for $P_{\text{O}_2} = 0.23 \text{ atm}$ and $P_{\text{E}} = 0.47 \text{ atm}$. (b) Final state obtained for each value of the ratio $P_{\text{O}_2}/P_{\text{E}}$, the sum $P_{\text{O}_2} + P_{\text{E}}$ being constant = 0.7 atm.

stabilization occurs after 4 h, and the percentage of A phase is about 50%. This steady state of the solid changes, as shown by Fig. 5b, with the ratio $P_{\text{O}_2}/P_{\text{E}}$ of the initial partial pressure of reactants with $P_{\text{O}_2} + P_{\text{E}}$ being maintained constant at the value of 0.7 atm. The mean final state of the catalytic bed goes from a reduced to an oxidized level when $P_{\text{O}_2}/P_{\text{E}}$ increases.

This change deduced from chemical analysis of the solid is confirmed by X-ray diffraction, as shown by Fig. 6. We observe, as previously emphasized, that the A phase is the only reduced phase which appears alongside the residual V₂O₅.

2. ANALYSIS OF REACTION PRODUCTS

The reaction products obtained during the reduction of Pd-V₂O₅ with 10% of ethylene or 20% of acetaldehyde in nitrogen at 250°C were analyzed. The reduction was carried out in the catalytic flow reactor at very short contact time ($W/F = 0.25 \text{ g} \cdot \text{s cm}^{-3}$) in order to be in differential conditions.

With ethylene, there is a very selective formation of acetaldehyde (~85%) with small amounts of acetic acid. In the case of acetaldehyde as a reactant, the acetic acid is formed with high selectivity (~90%). In both cases the appearance of CO and CO₂ is

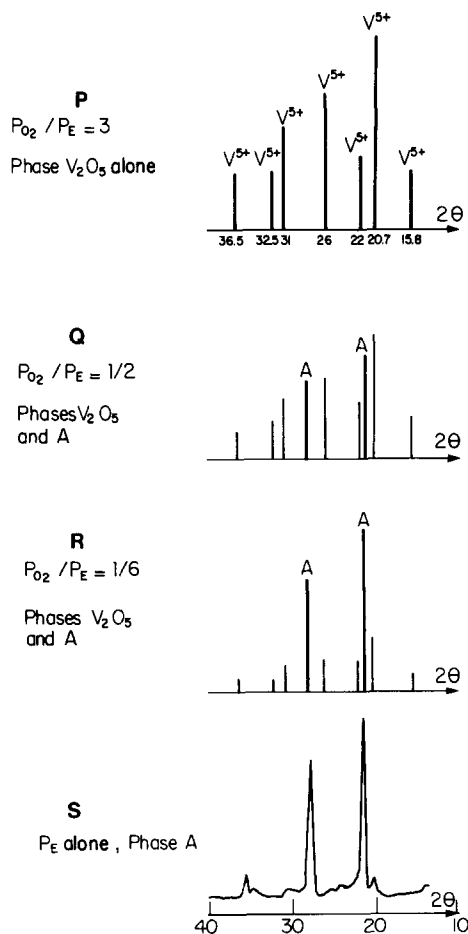


FIG. 6. X-Ray diffraction diagrams of the final catalyst for the final states P, Q, R, and S of Fig. 5 (anticathode Cu, $\lambda_{\text{Cu}} = 1.54 \text{ \AA}$).

very slight. On the other hand, the initial conversions of ethylene and acetaldehyde, 1.4 and 1.1% respectively, decrease very rapidly with time, i.e., with the actual percent reduction of the solid. After 45 min on stream, both conversions are about 0.4% and the percentage of A phase in the solids is about 40% with ethylene and 30% with acetaldehyde.

The solid analysis made at the end of the experiments agreed with the calculated results. It can be seen that the intervention of oxygen from PdO introduces only a negligible correction in the above calculations and consequently plays only a minor role in the formation of the oxygenated products.

IV. DISCUSSION

1. DETERMINING KINETIC CONSTANTS OF GAS-SOLID REACTIONS

A. Catalyst Reduction

The reduction process (Fig. 2) can be represented by a formal equation of Langmuir type:

$$r_{ir} = k_r \frac{a_r P_E}{1 + a_r P_E}, \quad (1)$$

k_r and a_r being formal kinetic constants. It is also interesting to consider the constant $\lambda_r = k_r a_r$, which we shall call the reactivity for the reduction.

Equation (1) can be transformed into the well-known linear form:

$$\frac{1}{r_{ir}} = \frac{1}{k_r} + \frac{1}{k_r a_r} \cdot \frac{1}{P_E}$$

In Fig. 7, $1/r_{ir}$ is plotted as a function of $1/P_E$. The fact that the points fall on a straight line confirms the validity of the equation and makes it possible to determine k_r , $\lambda_r = k_r a_r$ and a_r . For Pd-V₂O₅, the results at 250°C are

$$k_r = 9.6 \times 10^{-5} \text{ oxygen g} \cdot \text{atom min}^{-1} \text{ g}^{-1}$$

$$\lambda_r = k_r a_r = 75 \times 10^{-5} \text{ oxygen g} \cdot \text{atom min}^{-1} \text{ g}^{-1} \text{ atm}^{-1}$$

$$a_r = 7.8 \text{ atm}^{-1}.$$

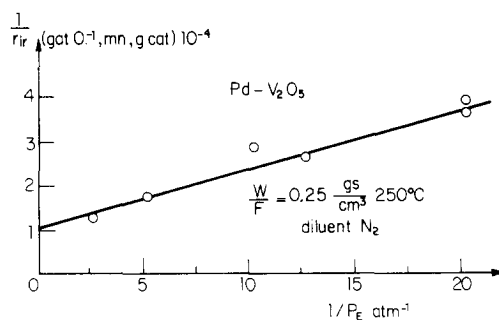


FIG. 7. Reciprocal of the initial reduction rate of Pd-V₂O₅ by ethylene vs $1/P_E$.

For V₂O₅, the quasi-linearity of r_{ir} as a function of P_E results from a weak adsorption of the ethylene and allows one to calculate the reactivity:

$$\lambda_r = k_r a_r = 2.75 \times 10^{-5} \text{ oxygen g} \cdot \text{atom min}^{-1} \text{ g}^{-1} \text{ atm}^{-1} \quad (\text{at } 250^\circ\text{C}).$$

The reduction of the two solids was later carried out at different temperatures and under partial pressures of ethylene low enough so that the term $a_r P_E$ is much smaller than 1 in the rate equation and, therefore, $r_{ir} = \lambda_r P_E$. The Arrhenius plot of λ_r (Fig. 8) gives an apparent activation energy of reduction, which is similar for both solids, i.e., $E_r = 16$ kcal/mole for Pd-V₂O₅ and $E_r = 18$ kcal/mole for V₂O₅. This figure shows that the increase in reducibility, as the result of Pd addition, remains within the entire range of temperatures studied.

B. Catalyst Reoxidation

The curves in Fig. 3 also obey a formal Langmuir equation:

$$r_{io} = k_o \frac{a_o P_{O_2}}{1 + a_o P_{O_2}}, \quad (2)$$

where k_o and a_o are formal kinetic constants and $\lambda_o = k_o a_o$, the oxidation reactivity. Figure 9 shows the linear transform of Eq. (2) for A(V₂O₅), from which at 300°C we obtain:

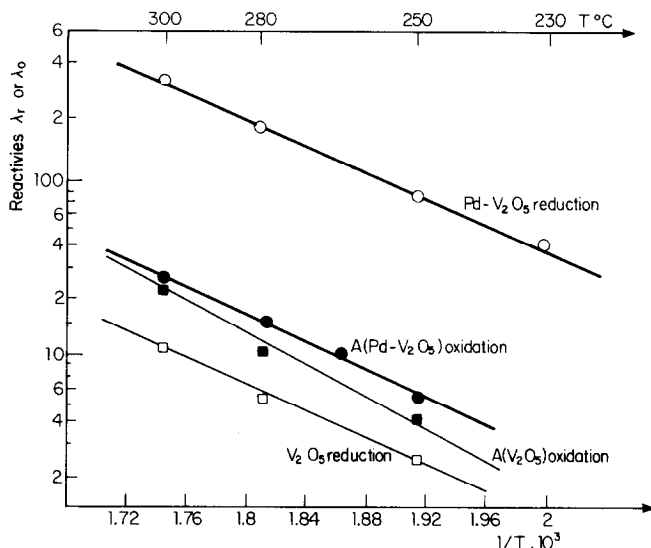


FIG. 8. Arrhenius plots for the reactivities of reduction and oxidation of the oxidized or reduced solids, respectively.

$$k_0 = 10.5 \times 10^{-5} \text{ oxygen g} \cdot \text{atom min}^{-1} \text{ g}^{-1}$$

$$\lambda_0 = k_0 a_0 = 23.4 \times 10^{-5} \text{ oxygen g} \cdot \text{atom min}^{-1} \text{ g}^{-1} \text{ atm}^{-1}$$

$$a_0 = 2.2 \text{ atm}^{-1}.$$

For the solid A(Pd-V₂O₅), in view of the linear influence of P_{O_2} due to the weak adsorption of oxygen, we only obtain the value:

$$\lambda_0 = 25 \times 10^{-5} \text{ oxygen g} \cdot \text{atom min}^{-1} \text{ g}^{-1} \text{ atm}^{-1} \quad (\text{at } 300^\circ\text{C})$$

The reoxidation of these two solids was carried out later at different temperatures

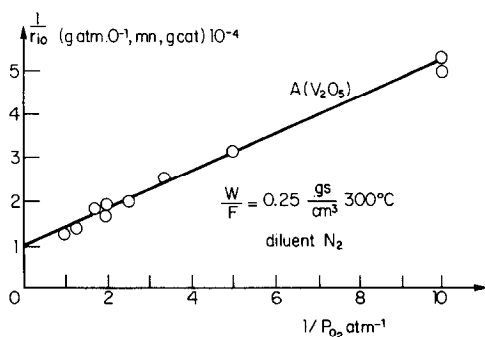


FIG. 9. Reciprocal of the initial oxidation rate of A(V₂O₅) by oxygen vs $1/P_{O_2}$.

and with an oxygen partial pressure such that $a_0 P_{O_2}$ can be neglected. From the Arrhenius plot of λ_0 (Fig. 8), we calculated the following apparent activation energies of oxidation: $E_0 = 18.5$ kcal/mole for A(Pd-V₂O₅) and $E_0 = 21$ kcal/mole for A(V₂O₅).

Table 1, which shows the values of the reactivities at 250°C, will enable us to reach some formal conclusions. In this table, the reactivities have not been referred to unit surface area since the surface change between the oxidized and the corresponding reduced phase is too small to be significant. It can be seen that the addition of Pd considerably increases the reactivity of Pd reduction but has little effect on the reoxidation of the reduced phases. Since the four apparent activation energies are very simi-

TABLE I
Reactivities of Reduction and Reoxidation (250°C)

	Starting from	S_{sp} (m ² /g ⁻¹)	Reactivities $\times 10^5$ (O g · atom min ⁻¹ g ⁻¹ atm ⁻¹)
Reduction	V ₂ O ₅	9.6	$\lambda_r = 2.75$
	Pd-V ₂ O ₅	15.0	$\lambda_r = 75$
Reoxidation	A(V ₂ O ₅)	8.5	$\lambda_o = 4.1$
	A(Pd-V ₂ O ₅)	19.0	$\lambda_o = 5.4$

lar, these conclusions are valid for the whole range of temperatures studied.

2. STATE OF THE SOLID IN THE PRESENCE OF BOTH REACTANTS

Parallel to the catalytic surface processes of oxidation–reduction, the solid bulk reaches a steady state, which is the result of two reverse oxidation and reduction reactions. It is interesting to analyze whether this steady state can be predicted from the value of the initial rates measured for the reduction and oxidation. From Eq. (1) and (2), which give the rates of reduction and oxidation for $[V^{5+}] = 1$ and $[V^{A+}] = 1$, and assuming that in the steady state the rates are proportional to the two-phase fractions, we can write for this steady state:

$$r_{ir}[V^{5+}] = r_{io}[V^{A+}]$$

with

$$[V^{5+}] + [V^{A+}] = 1.$$

By using the calculated values of the kinetic constants, the fraction of phase A in the steady state can then be obtained as a function of the partial pressures of the reactants:

$$[V^{A+}] = \frac{\lambda_r P_E}{\lambda_r P_E + \lambda_o P_{O_2} (1 + \lambda_r P_E)}$$

This calculation was made in the range of conditions used in Fig. 5b by taking for P_E and P_{O_2} the mean partial pressure of ethylene and oxygen in the catalytic bed. It gives the theoretical curve plotted as a dashed line in Fig. 5b. This curve corresponds to a higher state of reduction than the experimental one, but its direction of variation agrees with experimentation. Such a difference comes from the complexity of the phenomena which govern the attainment of the steady state of the solid bulk. Indeed, it is not surprising that the processes of reduction and reoxidation of the solid would be different, in the presence of the two reactants, from those observed with each one separately. The competition between reactants and the influence of the products

of the reaction should be taken into account, and the study should be carried out over each slice of catalyst instead of over the whole catalytic bed. Part II will show that a similar calculation carried out with kinetic constants deduced from catalysis produces a theoretical curve for the degree of reduction of the solid which is closer to the experimental values.

3. MECHANISM OF THE CATALYTIC REACTIONS

The first important point concerns the possibility of selectively oxidizing ethylene and acetaldehyde into acetic acid by means of the lattice oxygen of V₂O₅. This suggests a redox surface mechanism for the selective catalytic oxidation of both reactants. The decrease in conversions and yields with the degree of reduction of the initial solid can be explained by a diffusional limitation of the reacting oxygen through the lattice of the solid in order to reach its surface and perform the selective oxidation.

The second important point concerns the acceleration of the reducibility of V₂O₅ by the addition of palladium. Due to the fact that palladium oxide is easily reduced above 100°C, it can be suggested that metallic palladium is at the origin of the increase in reducibility. This increase in reducibility of metallic oxides by addition of metals such as Pt, Pd, Ni, and even Cu has been observed many times (15, 16). The effect of the metal may come from the chemisorption on this metal of the reducing agent, which then adopts an active form more able to carry out the oxide reduction. Another interpretation concerns the acceleration, caused by the reduced metal, of the process of nucleation necessary for the reduction of the oxide. Due to the fact that the rate of reoxidation is not greatly affected by the presence of palladium, only the reduction step would be accelerated during the catalytic process of oxidation–reduction. According to the results of Table 1, the slow step of catalysis for the case of V₂O₅ would

rather be the reduction, but for Pd-V₂O₅ it would become the oxidation.

V. CONCLUSIONS

During the reduction of vanadium pentoxide by ethylene or acetaldehyde, acetic acid is selectively produced. This result enables us to invoke a redox mechanism for the selective catalytic oxidation of ethylene or acetaldehyde into acetic acid. The addition of palladium to vanadium pentoxide enhances the rates of both the gas-solid reaction of reduction and the catalytic reaction, which is in accordance with the redox mechanism. If the reduction is performed at sufficiently low temperature, thanks to the influence of palladium, the only reduced phase which appears is the A phase, i.e., V₄O₉. During catalysis at low temperature, the A phase is also the only reduced phase existing at the steady state besides the remaining unreduced vanadium pentoxide. The kinetics laws established respectively for the reduction or the oxidation of the oxidized or reduced phases are not sufficient by themselves to calculate the steady state of the catalyst bulk in the

presence of both reactants, ethylene and oxygen, i.e., in the condition of catalysis.

REFERENCES

1. Smidt, J., Hapner, W., Jira, R., Sieber, R., Selmeiter, J., and Sabel, A., *Angew. Chem. Int. Ed. Engl.* **1**(2), 80 (1962).
2. U. S. Patent 3,240,805.
3. French Patent 1,536,185.
4. French Patent 1,527,716.
5. French Patent 1,568,742.
6. Seoane, J. L., Thèse, Paris, 1970.
7. Seoane, J. L., Boutry, P., and Montarnal, R., *C. R. Acad. Sci. Paris Ser. C*, **278**, 565 (1974).
8. Evin, A. B., Rabo, J. A., and Kasai, P. H., *J. Catal.* **30**, 109 (1973).
9. Seoane, J. L., Boutry, P., and Montarnal, R., *J. Catal.* **63**, 191 (1980).
10. Charlot, G., "Analyse Minérale Quantitative," p. 972. Masson, Paris, 1961.
11. C. Blejean, P. Boutry, and R. Montarnal, *C. R. Acad. Sci. Paris Ser. C*, **270**, 257 (1970).
12. Unpublished results.
13. Sata, T., Komada, E., and Ito, Y., *Kogyo Kagaku Zasshi* **71**, 643 (1968).
14. Theobald, F., Cabala, R., and Bernard, J., *C. R. Acad. Sci. Paris Ser. C*, **269**, 1209 (1969).
15. Naumann, A. W., and Behan, A. S., Jr., *J. Catal.* **39**, 432 (1975).
16. Charcosset, H., and Delmon, B., *Ind. Chim. Belg.* **38**, 481 (1973).