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Ethylene Oxidation to Acetic Acid with Pd–V_2O_5 Catalysts

II. Kinetics of the Catalytic Reaction

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The kinetics of the catalytic oxidation of ethylene into acetic acid over Pd–V_2O_5 was investigated. We studied, in a first stage, the enhancement of catalytic performance by the addition of palladium to V_2O_5. Then, the influence of reactant partial pressures on the initial catalytic reaction rates and on the final composition of the catalyst was established. The parallelism observed between enhancement of V_2O_5 reducibility and of catalytic performance, and the possibility of obtaining acetaldehyde and acetic acid from ethylene oxidation by lattice oxygen of V_2O_5, leads us to invoke a redox mechanism for the catalysis. Moreover, the simultaneous formation, at low conversions, of acetic acid and acetaldehyde is due to the occurrence of the consecutive oxidation process in the adsorbed phase, according to what has been called a rakelike scheme. A kinetic equation is proposed which fits the experimental results and permits the calculation of kinetic constants from these experimental results. An attempt has been made to determine, on the basis of the simplest redox mechanism, the theoretical steady state of bulk composition of the catalyst, as a function of reactant partial pressure. Comparison with experiment shows that there is a reasonable agreement if we consider the approximation which we have been obliged to make.

I. INTRODUCTION

In earlier studies concerning ethylene oxidation over V_2O_5 and Pd–V_2O_5 (*1, 2*), we observed that the addition of Pd to V_2O_5 brings about a parallel enhancement of the catalytic conversion of ethylene into acetic acid and of the reduction rate of V_2O_5 by ethylene in a gas–solid reaction. In Part I of this series (*3*) we studied the reduction of the oxidized form of the catalyst by ethylene and the oxidation of the reduced form (phase A) by molecular oxygen. In the first part, we showed that during reduction the lattice oxygen of the oxidized catalyst is able to form, in the absence of gaseous oxygen, the products of mild catalytic ethylene oxidation (acetaldehyde and acetic acid). The overall results obtained lead us to invoke a redox mechanism for catalytic ethylene oxidation.

This second part deals with the kinetics of this catalytic reaction. We have first studied the influence on the catalytic performances of adding palladium to the catalyst and of adding water to the reactants. Second, the oxidation of acetaldehyde and of acetic acid is studied. The third investigation concerns the influence of reactant partial pressures on the initial reaction rates. And last, an interpretation of the experimental results is proposed within the scope of the redox mechanism.

Although other work has been reported on the catalytic oxidation of ethylene, on V_2O_5 modified by the addition of palladium compounds (*4*) and of MoO_3 or GeO_3 (*5*), it has been carried out at lower temperatures, and the main product was acetaldehyde instead of acetic acid.

II. EXPERIMENTAL METHODS

Our experiments were performed at atmospheric pressure in conventional stainless-steel tubular reactor (length 100 cm,

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internal diameter 2 cm) with a fixed bed of unsupported catalyst. The reaction temperature was measured with an iron–constantan thermocouple and, since the reaction is highly exothermic (60 to 337 kcal/mole according to the selectivity level), the reactor was heated with a bath of molten salts and the catalyst was diluted with carborundum ($\frac{1}{4}$ vol/vol). The flows of gases (N_2, O_2, and C_2H_4) were adjusted with capillary tubes, and the water was fed by a minipump. In the case of acetaldehyde (AcH), the gaseous reactants were bubbled through a liquid container with acetaldehyde at −20°C, while for acetic acid (AcOH) the temperature was kept at 60°C. Product analysis and catalyst preparation have been described in detail in Part I (*3*). The catalysts used are the oxidized phases, V_2O_5 and Pd–V_2O_5, and the reduced phases, A(V_2O_5) and A(Pd–V_2O_5) (*3*). The amount of Pd on the catalysts was 0.02 wt%.

The catalytic performance will be characterized by the percentage total ethylene conversion and percentage partial molar conversion of ethylene into acetaldehyde, acetic acid, CO_2, and CO. These partial conversions will be called yields (Y) for the sake of simplicity. We shall also use the selectivities toward reaction products, defined as the ratio of the yield in the product considered to the ethylene conversion. For example, if for 100 moles of ethylene 40 are converted, of which 5 give AcH, 20 give AcOH, 13 give 26 moles of CO_2, and 2 give 4 moles of CO, we have $Y_{AcH} = 5\%$, $Y_{AcOH} = 20\%$, $Y_{CO_2} = 13\%$, $Y_{CO} = 2\%$, and $S_{AcH} = 0.125$, $S_{AcOH} = 0.5$. The contact time will be defined as the ratio $\theta = W/F$ between the catalyst weight in grams and the total STP flow rate in cubic centimeters per second. According to these units, θ is a formal contact time given in $s \cdot g\ cm^{-3}$. From conversion, yield, contact time, and ratio of ethylene to oxygen, it is possible to calculate the rate of ethylene disappearance or of product formation. These rates can be expressed in ethylene $g \cdot mole\ min^{-1}\ g^{-1}$. To compare with Part I, they can also be expressed in corresponding oxygen $g \cdot atom\ min^{-1}\ g^{-1}$ by using the stoichiometric coefficient γ of the transformation considered: thus for $C_2H_4 \rightarrow CH_3CHO$, $\gamma = 1$, and for $C_2H_4 \rightarrow CH_3COOH$, $\gamma = 2$.

III. EXPERIMENTAL RESULTS

1. Preliminary Experiments

Blank experiments were carried out in the reactor filled with carborundum without catalyst (Table 1). Ethylene and acetic acid do not undergo any homogeneous oxidation, but acetaldehyde, on the contrary, is significantly and fairly selectively oxidized to acetic acid. The pure thermal decomposition of acetaldehyde was found to be negligible.

Another important point relates to the

TABLE 1

Blank Experiments (Without Catalyst)[a]

Feed composition (%)					Total flow rate ($cm^3\ s^{-1}$)	Temp. (°C)	Conversion (%)			Selectivities (%)				
O_2	C_2H_4	N_2	AcH	AcOH			C_2H_4	AcH	AcOH	AcOH	CO	CO_2	Acetone	Acrolein
60	10	30			6	250	0							
60	10	30			2	230	0							
62		36		2	2	230			0					
53		35	12		6	250		28		55	8.2	24	7.5	5
		88	12		6	250		0						

[a] With 100 g of carborundum in the reactor.

attaining of a steady state or a "pseudo-state" for the catalyst composition during the course of the reaction. We have seen in Part I that it takes several hours to reach a stable level in catalyst composition. However, this level seems different depending on whether we start from the oxidized or the reduced form of the same catalyst formula (Fig. 4 in Part I). In addition, Fig. 1 in this present paper shows that after 7 h on stream, where the bulk catalyst composition seems stabilized, the catalytic performances are different depending on the starting phases. Ethylene conversion and selectivity to acetaldehyde, for example, are higher when starting from the oxidized form than from the reduced form. Furthermore, from the reduced catalyst, the conversion and yields are still changing after 7 h on stream. This is why the catalytic experiments have been done from the initially oxidized form, checking for each measurement that a steady state of performances was attained.

Moreover, we chose the appropriate reactant flow rate and particle size of the catalyst in order to avoid diffusional limitations.

2. Influence of Palladium and Steam in the Oxidation of Ethylene

The experiments were performed over Pd–V_2O_5 and V_2O_5 at 230°C and atmospheric pressure, with P_{O_2} = 0.6 atm, P_E = 0.1 atm, and the remainder N_2 or steam. The contact time was varied between 0.25 and 6 s · g cm^{-3}.

Figure 2 presents, by means of conventional curves giving the yield vs conversion (*6*), the influence of Pd (0.02 wt%) and H_2O on the product yields. On the *x* axis, the contact time required to perform the con-

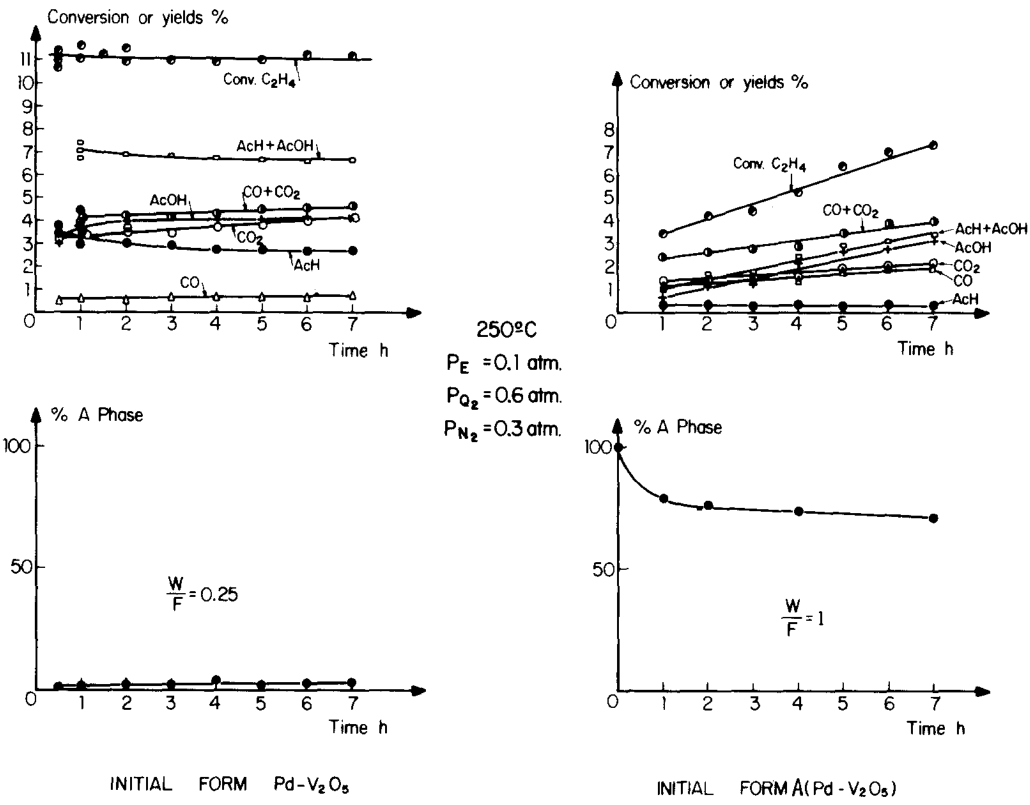

FIG. 1. Transformation of the catalyst and of catalytic performance for a Pd–V_2O_5 type catalyst from initially oxidized or reduced form.

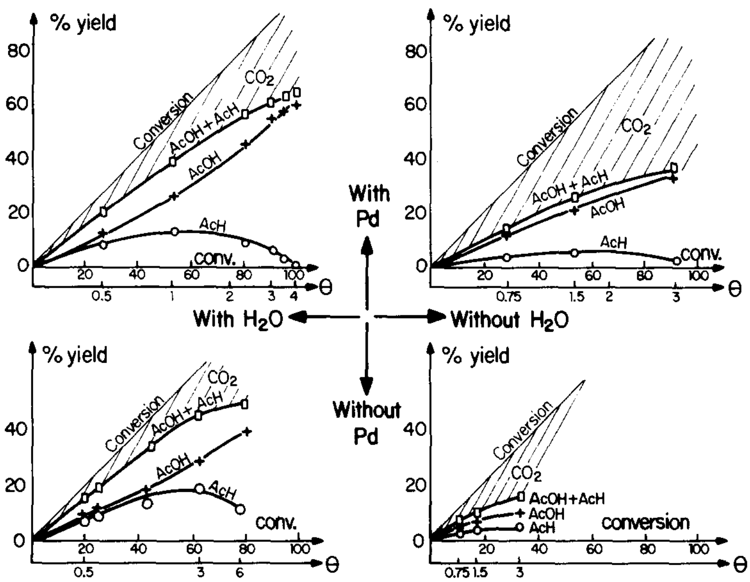

FIG. 2. Yields vs conversion for $Pd-V_2O_5$ and V_2O_5 in the presence or absence of water at 230°C. P_E = 0.1 atm, P_{O_2} = 0.6 atm, and P_{N_2} or P_{H_2O} = 0.3 atm.

version is also indicated. We observe that adding Pd to the catalyst increases the ethylene conversion. The effect of different Pd percentages has already been published (*2*). Otherwise, adding steam to the reactants also increases the overall activity, particularly for V_2O_5 without Pd, and decreases the formation of CO + CO_2, thus improving the selectivity into AcH and AcOH.

In all cases, the yield of acetaldehyde goes through a maximum, while acetic acid yield increases evenly. These results indicate that AcH is an intermediate in the formation of AcOH from ethylene. Moreover, at high conversion close to 100%, we see that, while the acetaldehyde yield is reduced to zero, the acetic acid yield attains its maximum value, showing that this molecule is quite stable under the reaction conditions. Another important point concerns the parallel production at low conversion (initial kinetic conditions) of acetic acid and acetaldehyde, despite the fact the aldehyde is the precursor of the acid. The ratio of the initial formation rate of AcOH to AcH can even be greater than one.

3. Oxidation of Reaction Products

A. *Oxidation of Acetaldehyde*

In order to check the role of acetaldehyde as an intermediate product in the formation of acetic acid, we performed the oxidation of acetaldehyde itself over $Pd-V_2O_5$, at 230°C, W/F = 3 s · g cm^{-3}, P_{O_2} = 0.6 atm, P_{AcH} = 0.1 atm, and P_{H_2O} = 0.3 atm. Under these conditions, the AcH is completely transformed into AcOH (46%) and CO_2 (54%). At the end of the experiment (2 h), the catalyst contained (6% V^{4+}. The catalytic oxidation of acetaldehyde is therefore much greater than the homogeneous oxidation (cf. Table 1).

B. *Oxidation of Acetic Acid*

The oxidation of AcOH (P_{O_2} = 0.9 atm, P_{AcH} = 0.1 atm) at 230°C and W/F = 3 s · g cm^{-3} shows that its degradation is very slight and that the catalyst, which was initially in the oxidized state, does not suffer any significant modification.

4. Initial Kinetics over $Pd-V_2O_5$

In order to work under initial rate conditions, we used a contact time of W/F = 0.25.

A. *Influence of Ethylene Partial Pressure (Fig. 3)*

The ethylene partial pressure was changed between 0.025 and 0.3 atm, with a constant P_{O_2} = 0.6 atm and N_2 as diluent gas. All the measurements were performed under steady-state conditions. For $P_E > 0.1$ atm, the steady state of the catalyst composition begins to be displaced toward the reduced form, so that it works as a mixture of V_2O_5 and phase A (Fig. 3b). The reaction rates as a function of P_E are shown in Fig. 3a. The ratio $\rho = r(AcOH)/r(AcH)$, between the initial rates of formation of acetic acid and acetaldehyde, decreases with P_E, whereas the overall selectivity of valuable products, S(AcH + AcOH), does not change significantly, as illustrated in Fig. 5a.

B. *Influence of Oxygen Partial Pressure (Fig. 4).*

The partial pressure of oxygen was changed between 0.1 and 0.9 atm, with constant P_E = 0.1 atm and N_2 as diluent gas. The steady state of the catalyst composition changes from a partially reduced form, in which phase A is the only reduced species found, toward a completely oxidized form when P_{O_2} increases (Fig. 4b). The initial rates also follow a hyperbolic law as a function of P_{O_2} (Fig. 4a). In this case, the ratio $\rho = r(AcOH)/r(AcH)$ increases with P_{O_2}, while the selectivity S(AcH + AcOH) becomes smaller, as illustrated in Fig. 5b.

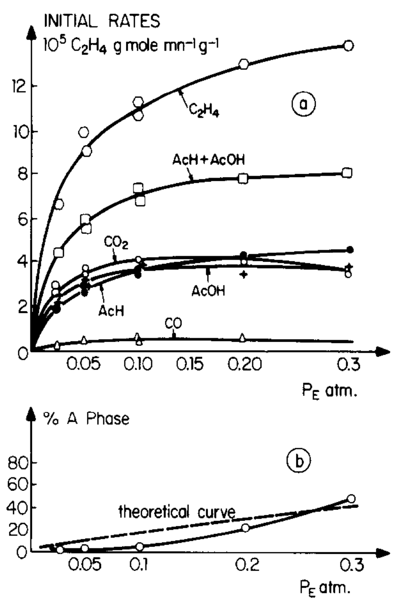

FIG. 3. Influence of ethylene partial pressure with $Pd-V_2O_5$ at 250°C P_{O_2} = const = 0.6 atm, N_2 as diluent, $W/F = 0.25$ g · s cm^{-3}. (a) On initial catalytic reaction rates; (b) on catalyst bulk composition.

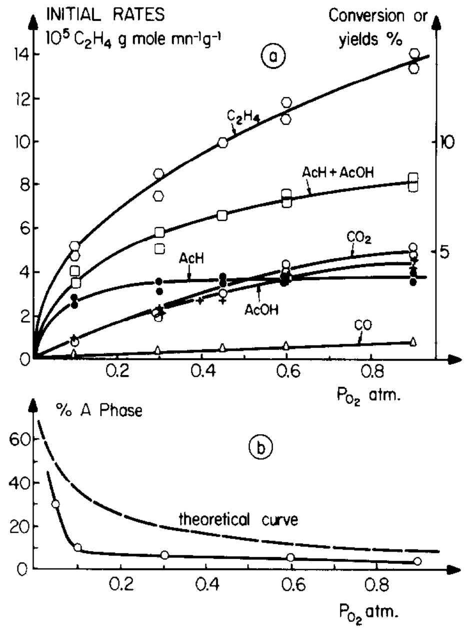

FIG. 4. Influence of oxygen partial pressure with $Pd-V_2O_5$ at 250°C. P_E = const = 0.1 atm, N_2 as diluent, $W/F = 0.25$ g · s cm^{-3}. (a) On initial catalytic reaction rates; (b) on catalyst bulk composition.

Figures 5c and d also show the variation of the total stoichiometry, γ, for selective oxidation as a function of P_E or P_{O_2}. This stoichiometric coefficient was calculated according to the equation:

$$C_2H_4 + \gamma\text{-}O \rightarrow AcH + AcOH.$$

IV. DISCUSSION

Any mechanism proposed for the catalytic reaction has to include two types of basic phenomena.

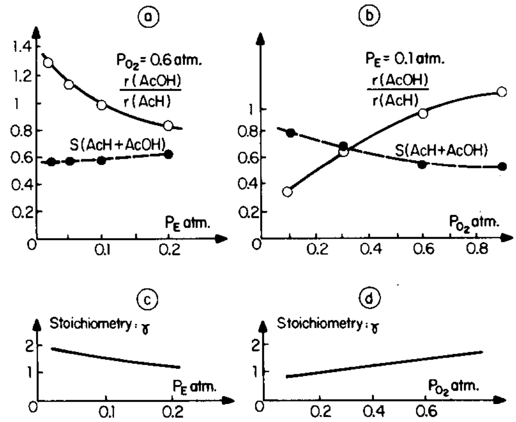

FIG. 5. Evolution of the ratio $\rho = r(AcOH)/r(AcH)$, of the selectivity S into (AcH + AcOH), and of the stoichiometry (γ), as a function of P_E (Figs. 5a and c) or of P_{O_2} (Figs. 5b and d). (Curves deduced from the results of Figs. 3 and 4.)

(1) The first type of phenomenon concerns both the possibility of carrying out selective oxidation by the lattice oxygen of V_2O_5, and the parallelism observed between the enhancement, by adding palladium, of the reducibility and of the catalytic activity of V_2O_5. These results have led us to invoke a redox mechanism (*1*). A redox mechanism has also been proposed for the ethylene oxidation into acetaldehyde over Pd–V_2O_5 (*4*), but, as in the Wacker process, the authors then considered that the Pd compound was the catalyst and V_2O_5 the co-catalyst. In our case, since V_2O_5 alone can oxidize ethylene into acetic acid at 230–250°C in both the catalytic and gas–solid reactions, we consider that V_2O_5 itself is the catalyst and the Pd compound is a promoter or a co-catalyst.

(2) The second type of phenomenon is the parallel formation, at very low conversions, of acetic acid and of acetaldehyde, with the amount of AcOH even being the greater for high values of the P_{O_2}/P_E ratio. We must therefore propose a direct formation route for each of these two products, although AcH can be the precursor of AcOH. In order to reconcile these results, we have already suggested, in similar cases, the "rake reaction scheme" (*7*), which merely emphasizes the occurrence of a consecutive process in the adsorbed phase.

An association of the above considerations will lead us:

(a) to propose a model of the reaction path,

(b) to propose a kinetic equation for the catalysis, and

(c) to discuss the transformation of the catalyst composition as a function of the experimental conditions. We must note that the catalytic degradation of ethylene into carbon monoxide and carbon dioxide is more difficult to interpret with our results and therefore will not be discussed here.

A. Proposed Reaction Path Model

The simplest representation of the consecutive process in the adsorbed phase for ethylene oxidation explains how from σ_{AcH}, which is the precursor of σ_{AcOH}, two parallel ways lead to AcH and AcOH (*2*). But, in order to introduce the redox mechanism, a more complex model will be considered in Fig. 6, still involving of course the consecutive steps in the adsorbed phase.

A1. The ethylene is chemisorbed (σ_E) on the oxidized sites V^{5+}.

A2. This chemisorbed ethylene is transformed into chemisorbed acetaldehyde (σ_{AcH}) by the underlying lattice oxygen, according to a rate constant k_T. After this step, the acetaldehyde is found chemisorbed on reduced sites V^{A+}.

A3. This chemisorbed acetaldehyde can desorb to the gas phase, according to a rate constant k_D thus liberating the reduced sites.

A4. The reoxidation of the reduced sites underlying the chemisorbed acetaldehyde can however take place at the same time, due to the diffusion of oxygen atoms belonging to neighboring oxidized sites (D_0 represents the diffusion coefficient for these oxygen atoms in the lattice). The acetaldehyde chemisorbed on the reduced sites (σ_{AcH}) is thus transformed into another form (σ_{AcH}) on the oxidized sites V^{5+}.

A5. This chemisorbed acetaldehyde can

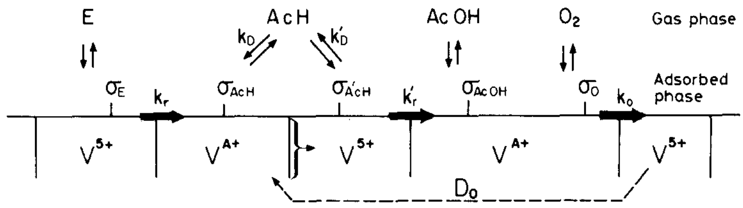

FIG. 6. Catalytic process involving a redox mechanism and a rakelike scheme. V^{5+} and V^{A+} correspond to the oxidized and reduced sites. σ characterizes both a chemisorbed molecule and the fraction of a given site covered by this molecule. For example, the fraction of reduced sites is $[V^{A+}]$, the fractions of this site covered by AcH, AcOH, and O_2 are σ_{AcH}, σ_{AcOH}, and σ_O and the fractions of the total catalyst surface covered by AcH, AcOH, and O_2 are $[V^{A+}]\sigma_{AcH}$, $[V^{A+}]\sigma_{AcOH}$, and $[V^{A+}]\sigma_O$. All rate constants are defined in the text.

desorb to the gas phase, according to a rate constant k'_D.

A6. But σ'_{AcH} can also, like σ_E, be oxidized by the underlying lattice oxygen according, in this case, to the rate constant k'_r. In this way, we obtain chemisorbed acetic acid on reduced sites (σ_{AcOH} on V^{A+}).

A7. This chemisorbed acetic acid can easily desorb because it is not as strongly chemisorbed as ethylene or acetaldehyde, for which the respective double bond permits the chemisorption into an active form capable of undergoing oxidation. Hence, degradation of acetic acid in the adsorbed phase is very slight. Free reduced sites reappear after desorption.

We should remember that the possibility of selective oxidation of acetaldehyde over an oxidized catalyst has been experimentally proven both for the gas–solid (cf. III.1 in Part I) and the catalytic reaction (see above). Therefore, it seems reasonable to consider that the acetaldehyde can be chemisorbed on both oxidized sites (like σ'_{AcH}) and reduced sites (like σ_{AcH}).

A8. The molecular oxygen is chemisorbed on the reduced sites V^{A+}, oxidizing them by incorporation into the crystalline lattice of vanadium oxide, according to a rate constant k_0. Later, oxygen can diffuse, according to D_0, toward the neighboring reduced sites.

We now consider what may be the role of the addition of palladium to V_2O_5 through such reaction paths. Palladium would favor the ethylene reaction with lattice oxygen of V_2O_5 by giving a particularly active form of chemisorbed ethylene σ^*_E. Ethylene chemisorbed on palladium compounds would be able to react with lattice oxygen on account of the proximity of the sites or to some "spillover" from palladium sites to V_2O_5 sites. The increase in this step of ethylene oxidation explains the parallel enhancement of V_2O_5 reducibility and of catalysis. We must note that, in the gas–solid reduction of V_2O_5, it was reasonable to suppose that Pd compounds were reduced and that the ethylene chemisorption occurred on Pd metal. The state of Pd is not so clear for the catalytic reaction in the presence of both reactants ethylene and oxygen.

On the other hand, the role of steam, which enhances the selectivity of mild oxidation, would be to favor the desorption of AcH and AcOH, by an effect of competition, thus preventing their later catalytic degradation. This role of steam has often been mentioned.

The proposed mechanism must moreover also explain the increase in the ratio $\rho = r(\text{AcOH})/r(\text{AcH})$ for initial rates, when the reactant ratio $\rho_r = P_{O_2}/P_E$ increases, as shown in Fig. 5b. For this, let us consider the parallel formation of AcOH and AcH from σ'_{AcH} and from σ_{AcH} chemisorbed either on V^{5+} or on V^{A+} sites (Fig. 6). From $V^{5+} + \sigma'_{AcH}$, the two ways of oxidation and desorption proceed according to the respective rate constants k'_r and k'_D; hence their rate ratio is equal to k'_r/k'_D and is independent of P_{O_2}/P_E.

From $V^{A+} \vdash \sigma_{AcH}$, on the other hand, when P_{O_2} increases the concentration of V^{5+} sites becoming higher and therefore the greater the probability of further oxidation of AcH rather than desorption. This explains the increase in ρ, in accordance with the experimental results. The contrary happens when P_E increases, as shown in Fig. 5a. In conclusion, although not excluding the obtaining of AcH by desorption from σ'_{AcH}, we must invoke an important contribution of desorption from σ_{AcH} to interpret the experimental results.

B. Kinetic Equations

For the sake of simplification, we shall apply the conventional redox mechanism of Mars and van Krevelen to the total formation of (AcH + AcOH), according to the following two steps of reduction and oxidation:

$$C_2H_4 + V^{5+} \xrightarrow[\text{or } \lambda_r]{k_r} (\text{AcH} + \text{AcOH}) + V^{A+}$$

$$O_2 + V^{A+} \xrightarrow[\text{or } \lambda_o]{k_o} V^{5+},$$

where λ_r and λ_0 are as defined in Part I (*3*).

For each elementary step, we shall use the model equation obtained in Part I for gas–solid reactions. Thus, for Pd–V_2O_5 we shall take:

Reduction step

$$r_r = k_r \frac{a_r P_E}{1 + a_r P_E} [V^{5+}] = \frac{\lambda_r P_E}{1 + a_r P_E} [V^{5+}] \quad (1)$$

Oxidation step

$$r_o = \lambda_o P_{O_2} [V^{A+}] \quad (2)$$

with

$$[V^{5+}] + [V^{A+}] = 1. \quad (3)$$

The meaning of the parameters k_r, λ_r, a_r and λ_0 is formally the same as in Part I, but since here they characterize the catalytic steps themselves, their numerical values may be different.

According to the redox mechanism, the reaction rate (r_{st}) in the steady state is equal to the rate of each step

$$r_{st} = r_r = r_o, \quad (4)$$

and therefore, substituting for V^{5+} and V^{A+},

$$r_{st} = \frac{\lambda_r \lambda_0 P_E P_{O_2}}{\lambda_r P_E + \lambda_0 P_{O_2}(1 + a_r P_E)}. \quad (5)$$

To compare with Part I, r_{st} will be expressed in gram atoms of oxygen per minute per gram involved in the reactions. If r_E is the formation rate of (AcH + AcOH) as deduced from Figs. 3 and 4, the relation between r_{st} and r_E is obtained by means of the experimental stoichiometric coefficient γ given in Figs. 5c and d: $r_{st} = \gamma r_E$ (the mean value of γ is 1.5).

Equation (5) can be put in a well-known linear form:

$$\frac{1}{r_{st}} = \frac{1}{\gamma r_E} = \frac{1}{\lambda_0 P_{O_2}} + \frac{1}{\lambda_r P_E} + \frac{a_r}{\lambda_r}. \quad (6)$$

From Fig. 7, we can see that Eq. (6) satisfactorily fits the experimental data of Figs. 3 and 4, when plotting $1/r_{st}$ versus $1/P_E$ or $1/P_{O_2}$, respectively, for P_{O_2} or P_E maintained constant. From the slopes p of the straight lines, we obtain $\lambda_r = 600$ and $\lambda_0 = 66$ g · atoms of oxygen $\min^{-1}$ g^{-1} atm^{-1}. From the intersection with the y axis, the values of y_0 for $1/P_E = 0$ and for $1/P_{O_2} = 0$, give two equations, from which two independent values of a_r can be calculated, when λ_0 and λ_r are known. The close agreement between the two results, $a_r = 22$ and 29 atm^{-1}, confirms the formal validity of kinetic equations (5). We must point out that the use of the simpler equation $r_r = \lambda_r P_E[V^{5+}]$ instead of (1) for the reduction step would lead to incoherent results.

The values of kinetic constants obtained respectively from the catalytic and gas–solid (*3*) experimental results are recalled in Table 2.

In both cases, the reduction reactivity is higher than the oxidation reactivity, but to a lesser degree from catalytic than from gas–solid data. We must note that in both cases too, the higher values of λ_r than of λ_0 are due to the influence of Pd. In addition,

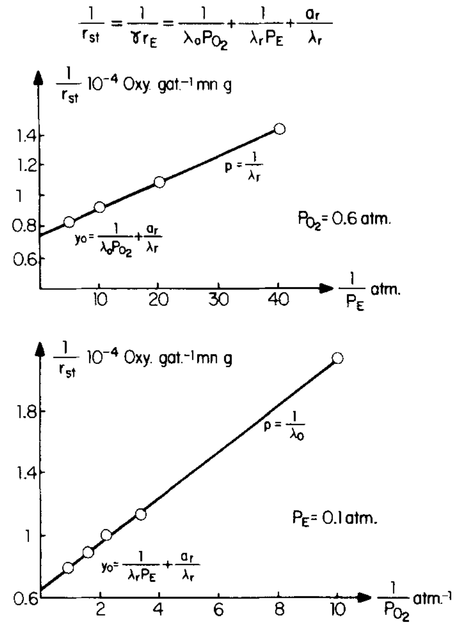

FIG. 7. Linear forms of the rate equation.

the increase in the catalytic reaction rate, when λ_r increases (by adding Pd), appears clearly in Eq. (5). On the other hand, the reactivities deduced from the catalytic reaction are higher than those deduced from the gas–solid reaction. This does not invalidate the redox surface mechanism but supports the fact that it is more complex than the one which would simply associate each step of the catalytic reaction with the initial gas–solid reduction and oxidation of, respectively, the oxidized or reduced catalyst.

The simplest elementary redox mechanisms leads to the same steady state for the catalyst composition whether we start from its oxidized or reduced form. In our case however, this does not appear to be so (cf. Fig. 1 in this paper and Fig. 4 in Part I if the steady state has really been attained), which may denote some factor of complexity. But having no certainty about the intervention of such a complexity or about its nature or its degree of magnitude, we have felt it would be interesting to apply the simplest theory for calculating the theoretical catalyst composition, so as to compare it with experimental results.

TABLE 2

Kinetic Constants for Pd–V_2O_5 at 250°C

	Reduction reactivity $10^5\,\lambda_r$	Oxidation reactivity $10^5\,\lambda_o$	a_r (atm^{-1}) from P_E	a_r (atm^{-1}) from P_{O_2}
	(oxygen g · atom min^{-1} g^{-1} atm^{-1})			
From catalytic reaction	600	66	32	29
From gas–solid reactions	75	5.4	7.8	

C. Catalyst Composition: Theory and Experiment

At steady state, Eqs. (1), (2), (3), and (4) are valid, so that the superficial fraction $[V^{5+}]$ or $[V^{A+}]$ can be calculated:

$$[V^{A+}] = \frac{\lambda_r P_E}{\lambda_r P_E + \lambda_o P_{O_2}(1 + a_r P_E)}. \quad (7)$$

Since experimental results concern the bulk composition of the catalyst, any attempt to make a comparison is based on the assumption that surface and bulk compositions are not different.

By using the values of parameters deduced from catalysis in Table 2, the theoretical curve of the transformation of $[V^{A+}]$ has been drawn as dashed lines in Figs. 3

and 4 versus either P_E or P_{O_2} when, respectively, P_{O_2} or P_E are maintained constant. We can observe the right direction of the change, but no exact coincidence between theoretical and experimental curves.

The same calculation was made for the experiment depicted in Fig. 5 of Part I. Figure 8 then presents:

(i) the experimental curve for the final bulk composition, when the ratio P_{O_2}/P_E varies, for $P_{O_2} + P_E$ maintained constant.

(ii) the theoretical curve according to Eq. (7) by using the values of parameters in Table 2 deduced from gas–solid reactions.

(iii) the theoretical curve according to Eq. (7) by using the values of parameters in Table 2 deduced from catalysis.

Although not perfect, the coincidence is better in this last case. Formally this is due to the fact that the ratio λ_r/λ_0 obtained from the catalytic data is lower than when calculated from the gas–solid experiments. Indeed, it is reasonable to find better agreement using the catalytic data, because they take into account the complexity of the reaction mixture.

The discrepancies which remain between theory and experiment may come from the excessive approximation made when assuming that the surface and bulk compositions were the same. It would be interesting to try to characterize the catalytic surface by physical methods. On the other hand, it would be better to consider separately the AcH and AcOH formations; this would need a much more complete kinetic investigation. Moreover, our calculation does not take into account the influence of reaction products and the influence of the degradation reactions into CO_2 + CO, which may also play a role in the attainment of the steady state of the catalyst. Considering all these factors of complexity, the agreement between experiment and theoretical calculation appears reasonably satisfying.

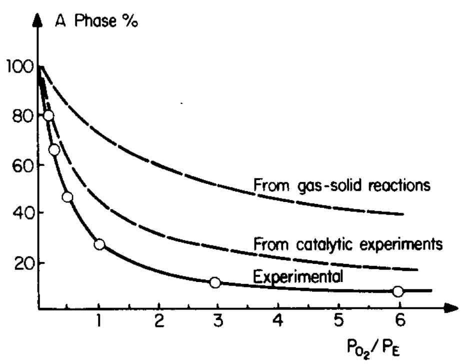

FIG. 8. Comparison between experimental (-O-) and theoretical (---) curves for the catalyst steady-state composition, as a function of reactant partial pressures, at 230°C for $P_{O_2} + P_E = 0.7$ atm and N_2 as diluent. Starting phase Pd–V_2O_5 (cf. Fig. 5 in Part I).

V. CONCLUSIONS

The redox mechanism proposed for the catalytic oxidation of ethylene into acetic acid, demonstrated by the study of gas–solid reactions, has enabled us to explain all the kinetic results observed. The influence of adding Pd to V_2O_5 is interpreted, within the scope of this mechanism, by the acceleration of the reduction step which makes possible high conversions and selectivity to acetic acid, at a temperature as low as 230°C. The simultaneous formation of acetic acid and acetaldehyde, under the initial kinetic conditions, can easily be understood on the basis of the proposed "rake" type of kinetic scheme in which the consecutive process of the oxidation of ethylene into acetaldehyde and then into acetic acid takes place directly in the adsorbed phase. The steady state of the catalyst composition is governed, albeit in a complex way, by the two inverse reactions of oxidation and reduction.

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