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The Mechanism of Vinyl Acetate Formation by Gas-Phase Catalytic Ethylene Acetoxidation*

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The synthesis of vinyl acetate by vapor phase oxidation of ethylene–acetic acid mixtures has been studied using catalysts prepared by palladium deposition on silica or alumina supports. The kinetic study of this reaction served to determine the influence of palladium dispersion, the partial pressures of acetic acid, oxygen, ethylene, and water vapor, and the role of alkaline acetates usually recommended for catalyst activation.

The results obtained, with or without water vapor in the gas mixture, enable a mechanism suggested which explains the influence of the various parameters studied.

INTRODUCTION

After the research results obtained by Moiseev *et al.* (*1*) concerning the catalytic synthesis of vinyl acetate in the homogeneous phase from ethylene, oxygen, acetic acid, and sodium acetate using palladium chloride as a catalyst in the presence of a redox system, a great many studies (*2*) concerning this reaction have been published. The reaction takes place in two stages:

(i) Synthesis of vinyl acetate:

$$Pd^{2+} + C_2H_4 + 2AcO^{\ominus} \rightarrow AcO\text{—}CH{=}CH_2 + Pd^0 + AcOH.$$

The presence of sodium acetate considerably increases the rate of this reaction.

(ii) Oxidation of the palladium by means of a redox system, e.g., with the pair Cu^+–Cu^{2+}:

$$Pd^0 + 2Cu^{2+} \rightleftarrows 2Cu^+ + Pd^{2+}.$$

The mechanism involved in the formation of vinyl acetate is not known with certainty. Van Helden *et al.* (*3*) propose the following scheme:

$$Pd(OAc)_2 + AcO^{\ominus} \rightleftarrows Pd(OAc)_3^{\ominus}$$
$$Pd(OAc)_3^{\ominus} + C_2H_4 \rightleftarrows C_2H_4Pd(OAc)_3^{\ominus}$$
$$C_2H_4Pd(OAc)_3^{\ominus} \rightarrow CH_2{=}CH\text{—}OAc + Pd^0 + AcO^{\ominus} + AcOH$$

with the last step being limiting.

At the same time as these investigations, it has been reported (*4*) that the synthesis of vinyl acetate can be carried out in the vapor phase with a palladium-base catalyst deposited on a support. The presence of activators of the alkaline-metal acetate type increases performance. Except for patent literature, there are no publications on this subject other than those by Krekeler *et al.* (*5*), Kunugi *et al.* (*6*), and Nakamura and Yasui (*7*).

I. EXPERIMENTAL

A. Analysis Equipment and Technique

Investigations have been made under dynamic conditions at atmospheric pressure in a Pyrex reactor thermostatically controlled at temperatures varying from

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100 to 150°C by oil circulation. A thermometric well fitted with a thermocouple enabled the temperature of the catalytic bed to be controlled.

Acetic acid was introduced either in a liquid state by a pump or by entrainment in an ethylene flow. The three reagents (oxygen, ethylene, and acetic acid) were preheated prior to their arrival in the reactor. The ratio *W/F*, in which *W* represents the catalyst weight in grams and *F* the total gaseous flow in moles/hr, varied between 0 and 100.

After passing over the catalyst, the liquid products (surplus acetic acid, vinyl acetate, and water) were collected in two traps in series, the first being cooled to 0°C and the second to —78°C. The only products of the reaction were vinyl acetate, carbon dioxide, and water. No acetaldehyde was formed, even in the presence of water.

Quantitative analyses of the reagents and products were made by gas chromatography.

Products analyzed	Column	Gauge
CO_2–C_2H_4 →	Poropak Q	→ Thermal conductance
O_2–N_2 →	Molecular sieve 13 X	→ Thermal conductance
CH_3COOH $CH_3COO—CH{=}CH_2$ →	Poropak T	→ Flame ionization

B. Preparation and Characterization of Catalyst

Two supports (alumina and silica) were pretreated so as to eliminate as much sodium as possible. After treatment the amounts were respectively less than 10 and 200 ppm.

Impregnation was achieved by means of a palladium nitrate acid solution 2 moles/liter of HNO_3 in an amount corresponding to the retention volume of the support. After being allowed to stand for 3 to 4 hr, the solution was evaporated and the catalyst was dried. Roasting at 400°C during 1 hr produced supported palladium oxide which was then reduced to a metal state by a flow of pure hydrogen at 150°C.

The specific surface area was measured by the BET method using a sorptometer. From the structural density and the grain density, the total pore volume was deduced. Then mercury porosimetry was used to determine pore distribution. The dispersion of the metal on the surface of the catalyst was obtained by measuring the volumes of CO irreversibly adsorbed at ambient temperature which were reduced to a catalyst unit mass (1 g) according to a dynamic volumetric method described by Brooks (*8*). The stoichiometry of the adsorption reaction of CO on metallic palladium is not very well-defined, and so we have preferred to give the results in volume of CO adsorbed per gram of catalyst.

The characteristics of the catalyst were as follows:

Carrier	m^2 (*S*/g)	V_p (cm^3/100 g)	Pore ϕ (Å)	% Pd weight	V_{CO} (cm^3/g)
SiO_2	230	110	120	0.5	0.03
				1.125	0.07
				2	0.17
Al_2O_3	190	58	180	1.33	0.7

Among the different activators claimed in patents, we chose to use sodium acetate. For silica, this could be deposited on the palladium-impregnated support either directly by means of a sodium acetate solution or in the form of a precursor by means of a sodium hydroxide solution. For alumina, only depositing by means of sodium hydroxide enable suitable catalytic activities to be obtained.

C. *Expressing the Results*

The conversion of ethylene to vinyl acetate (V.A.) cannot be measured directly because it is quite small under the conditions chosen. We have defined this conversion as follows:

$$C(\%) = \frac{\text{No. of moles of V.A. produced} + \frac{1}{2}\text{ No. of moles of CO}_2\text{ produced}}{\text{No. of moles of ethylene introduced}} \times 100.$$

This assumes carbon dioxide formation to originate solely via ethylene. We will justify this assumption later on. The other symbols (yield and selectivity) are expressed as:

$$Y(\%) = - \frac{\text{No. of moles of V.A. produced}}{\text{No. of moles of ethylene introduced}} \times 100,$$

$$S(\%) = - \frac{\text{No. of moles of V.A.} \times 100}{\text{No. of moles of V.A.} + \frac{1}{2}\text{ No. of moles of CO}_2} = \frac{Y}{C}.$$

For the kinetic study, the initial rates V_i are expressed in moles per gram of catalyst per hour and the partial pressures in atmospheres.

II. RESULTS

A. *Kinetic Study*

For the catalytic reaction to be studied kinetically, the activity of the catalyst must be stable. In the present reaction system, the activity remained constant after about the first 5 hr.

The results described below mainly have to do with silica-base catalysts. We were led to investigate the effect of the following parameters:

(a) The amounts of sodium acetate and palladium on the surface of the support;
(b) the contact time;
(c) the partial pressure of each gaseous reagent (oxygen, ethylene, and acetic acid) in the absence and presence of water vapor, in the initial kinetics;
(d) the temperature in the initial kinetics.

(*a*) *Effect of Sodium Acetate and Palladium Contents*

The experimental conditions were exactly the same from one experiment to another. The only variation was in the amount of sodium acetate and palladium.

$$\begin{aligned} P_{C_2H_4} &= P_E = 0.715 \text{ atm;} \\ P_{AcOH} &= P_A = 0.159 \text{ atm;} \\ P_{O_2} &= P_O = 0.126 \text{ atm;} \\ W/F &= 49 \text{ g-cat/mole/hr;} \\ T &= 140°\text{C.} \end{aligned}$$

Figure 1 shows the influence of the sodium acetate deposited on the surface of the catalyst. The activity is very low in the absence of an activator, and although the activator causes a marked increase in activity, the effect of incremental increases in activator concentration soon becomes small, especially at the lower level of palladium concentration.

If the sodium acetate content is maintained constant (5%), catalytic activity increases with the palladium content (Fig. 2).

(*b*) *Effect of the Contact Time*

Figure 3 shows the variation of performance vs contact time at 140°C, with W/F varying from 0 to 100. The catalyst contained 2% Pd and 15% sodium acetate. The yield of vinyl acetate first increases linearly with W/F, then the effect

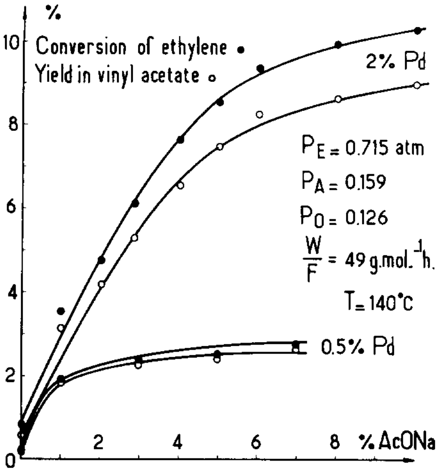


FIG. 1. Effect of sodium acetate on catalytic performance.

of the incremental increase of the W/F becomes small, but there is no maximum within the range studied.

(c) *Effect of the Partial Pressure of the Original Reagents in Initial Kinetics*

The partial pressure of the one of the reagents varied as the result of dilution with nitrogen, while the other partial pressures and total flow remained constant. The degrees of conversion of each reagent were kept low so as to work in a range where catalytic activity remained proportional to W/F. The catalyst used contained 2% Pd and 15% AcONa so as to be beyond the range of acetate concentration influencing the rate. The temperature was 120°C.

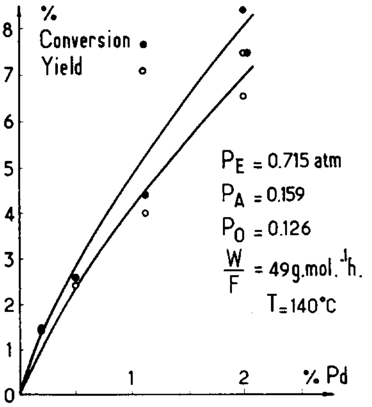


FIG. 2. Effect of palladium on catalytic performance.

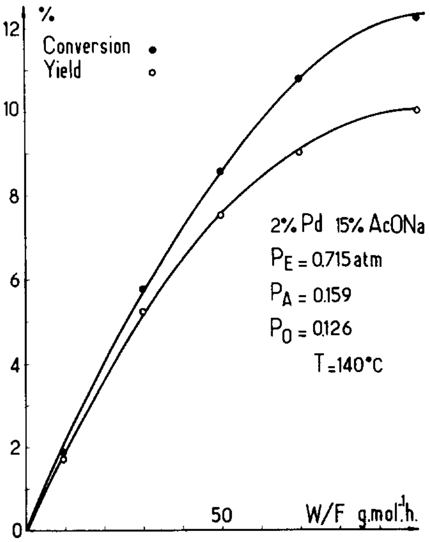


FIG. 3. Effect of W/F on catalytic performances.

(1) Effect of acetic acid partial pressure. Figure 4 contains the results involving acetic acid partial pressure under the following conditions: In the absence of water vapor:

$$\begin{aligned} P_O &= 0.101 \text{ atm}; \\ P_E &= 0.56 \text{ atm}; \\ W/F &= 24 \text{ g-cat/mole/hr}. \end{aligned}$$

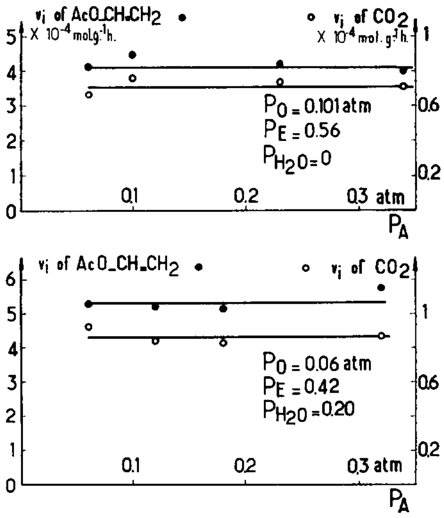


FIG. 4. Effect of acetic acid partial pressure on initial rates of reaction.

In the presence of water vapor:

$$\begin{aligned} P_O &= 0.06 \text{ atm;} \\ P_E &= 0.42 \text{ atm;} \\ P_{H_2O} &= 0.20 \text{ atm;} \\ W/F &= 18 \text{ g-cat/mole/hr.} \end{aligned}$$

The rate at which vinyl acetate is formed is independent of the acetic acid partial pressure in the absence or presence of water. The same is true for the reaction forming carbon dioxide. It can be seen that the rate of the reaction for both vinyl acetate and carbon dioxide increases with the presence of water.

(2) **Effect of oxygen partial pressure.** Figure 5 gives the effect of oxygen partial pressure under the following conditions: In the absence of water vapor:

$$\begin{aligned} P_A &= 0.16 \text{ atm;} \\ P_E &= 0.56 \text{ atm;} \\ W/F &= 24 \text{ g-cat/mole/hr.} \end{aligned}$$

In the presence of water vapor:

$$\begin{aligned} P_A &= 0.06 \text{ atm;} \\ P_E &= 0.42 \text{ atm;} \\ P_{H_2O} &= 0.20 \text{ atm;} \\ W/F &= 18 \text{ g-cat/mole/hr.} \end{aligned}$$

For increasing oxygen partial pressure up to 0.15 atm in the presence of water, the rate of formation of vinyl acetate reaches a plateau, whereas in the absence of water it increases throughout, though less so in the upper part of the range. The acetic acid partial pressure is not the same with and without water, but this fact does not seem important because we observed zero order with respect to this reagent.

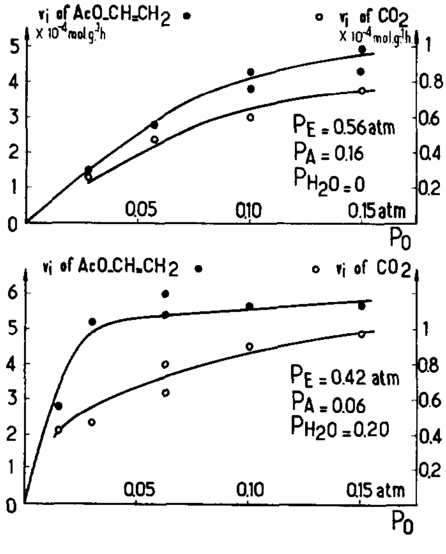


Fig. 5. Effect of oxygen partial pressure on initial rates of reaction.

Likewise, the formation of carbon dioxide increases with oxygen partial pressure.

(3) **Effect of ethylene partial pressure.** The effect of ethylene partial pressure is presented in Fig. 6, with the experimental conditions being as follows: In the absence of water vapor:

$$\begin{aligned} P_O &= 0.15 \text{ atm;} \\ P_A &= 0.16 \text{ atm;} \\ W/F &= 24 \text{ g-cat/mole/hr.} \end{aligned}$$

In the presence of water vapor:

$$\begin{aligned} P_O &= 0.11 \text{ atm;} \\ P_A &= 0.06 \text{ atm;} \\ P_{H_2O} &= 0.20 \text{ atm;} \\ W/F &= 18 \text{ g-cat/mole/hr.} \end{aligned}$$

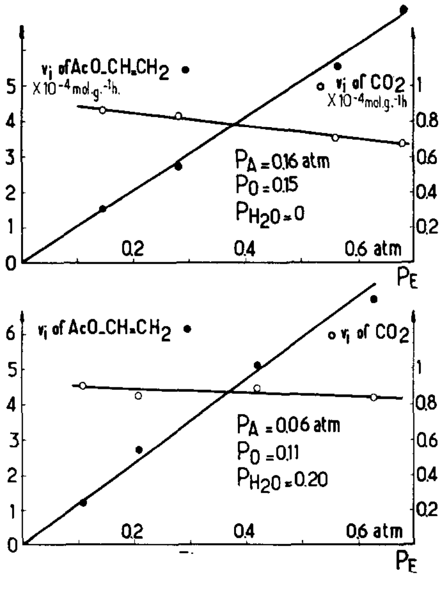


Fig. 6. Effect of ethylene partial pressure on initial rates of reaction.

The rate of the reaction forming vinyl acetate varies linearly with ethylene partial pressure, while the rate at which carbon dioxide is formed remains constant

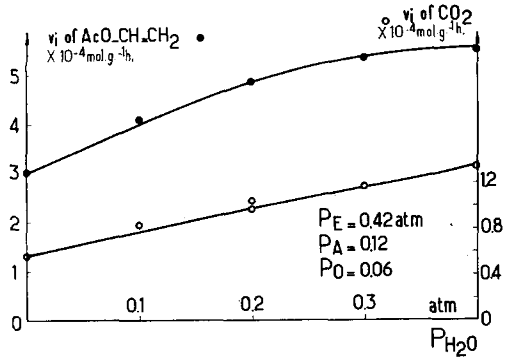


FIG. 7. Effect of water vapor partial pressure on initial rates of reaction.

or decreases slightly when ethylene partial pressure rises.

(4) **Effect of water vapor partial pressure.** The following conditions were employed: $P_E = 0.42$ atm; $P_A = 0.12$ atm; $P_O = 0.06$ atm; $W/F = 18$ g-cat/mole/hr.

When water vapor partial pressure varied from 0 to 0.4 atm, there was an increase in the rates at which vinyl acetate and carbon dioxide were formed (Fig. 7). These effects have already been indicated.

The same kinetic study with an alumina-base catalyst revealed many points that are just the same:

The presence of an activator is necessary at the surface of the catalyst in order to obtain suitable catalytic activities, with the activator being deposited in this case by means of a sodium hydroxide solution.

The effect of different partial pressures of the gaseous reagents is similar. The experiments were made with a 1.33% Pd catalyst on which was deposited an amount of sodium corresponding to 13% acetate.

When the oxygen partial pressure is increased, the rate at which vinyl acetate is formed increases to a saturation plateau that is reached faster in the presence of water vapor.

The rate increases linearly with ethylene partial pressure and is nearly independent of acetic acid partial pressure.

The presence of water causes an increase in the rate at which vinyl acetate is formed. This increase appears to be less than in the case of silica.

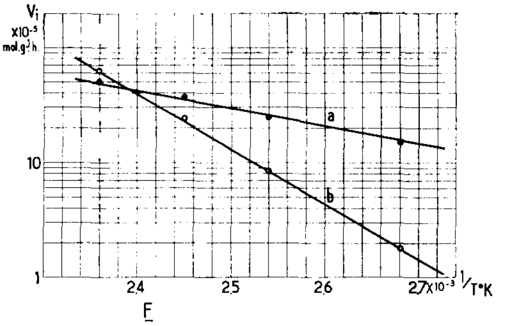


FIG. 8. Activation energies for (a) vinyl acetate and (b) carbon dioxide formation.

(d) *Effect of Temperature*

Figure 8 shows log V_i vs $1/T$ with an alumina-base catalyst in the presence of water vapor for reactions forming vinyl acetate and carbon dioxide. The apparent activation energies obtained are respectively:

$$E_A = 7.3 \text{ kcal} \pm 1.5 \text{ kcal} \qquad P_A = 0.138 \text{ atm}, \quad P_E = 0.52 \text{ atm}$$

$$E_{CO_2} = 20.1 \text{ kcal} \qquad P_O = 0.142 \text{ atm}, \quad P_{H_2O} = 0.20 \text{ atm}$$

The apparent activation energy of the reaction forming vinyl acetate is the same in the absence and presence of water vapor for both silica and alumina supports. The formation of CO_2 follows exactly the same law in the absence and presence of water vapor.

The fact that the apparent activation energies of the vinyl acetate and carbon dioxide forming reactions are quite different suggests the existence of two parallel reactions.

The activation energy obtained for the reaction of ethylene with oxygen in the absence of acetic acid is the same as that obtained for CO_2 formation when acetic acid is present, thus also suggesting that the carbon dioxide comes mainly from the combustion of ethylene. This hypothesis is confirmed by experiments at high acetic acid conversion for which precise measurement of acid conversion is possible. At temperatures lower than 120°C, the acetic acid that has disappeared is entirely transformed into vinyl acetate within the accuracy limitations of measurements, revealing the additional fact that the degradation of vinyl acetate is negligible under the conditions chosen.

B. Effect of Dispersion of Palladium

On the basis of the assumption generally accepted in heterogeneous catalysis that catalytic activity increases with metal dispersion, we searched for a method of preparing the catalyst in such a way as to obtain good metal dispersions.

Echigoya and Furuoya (*9*) have described a method of depositing palladium on silica–alumina by means of an ammonia-containing solution of palladium chloride. In the presence of ammonia, palladium chloride forms Pd $(NH_3)_mCl_2$ complexes. Upon contact with this solution the support adsorbs the solute, thus causing a decrease in the palladium concentration in the solution. The adsorption phenomenon is interpreted by a cationic exchange having the form:

$$2SA\ominus NH_4^+ + Pd(NH_3)_m^{2+} \rightleftarrows (SA\ominus)_2Pd(NH_3)_m^{2+} + 2NH_4^+,$$

with the symbol SA indicating silica–alumina.

We applied this method in the case of silica.

(*a*) *Procedure*

The silica support was left in contact with an ammonia-containing solution of palladium chloride during 72 hr, washed, and then dried for 12 hr at 120°C. The support, which was white prior to impregnation, became yellow. Finally, the solid was calcined at a temperature varying from 300 to 800°C for 1 hr in an air flow, followed by a 1-hr reduction at 150°C in a pure hydrogen flow.

(*b*) *Experimental Results*

(γ) **Measuring dispersion.** The dispersion of palladium on the surface of the silica varied with the calcining temperature. Figure 9 gives the results obtained for different concentrations of palladium, i.e., 0.5, 2, and 4%. The examination by X-ray diffraction of the state of crystallinity of the metal for 2% and 4% has been done with respect to the calcining temperature. Figures 10 and 11 show that, for 500°C only, the (1,1,1) line of palladium appears and increases with the temperature of calcination. By differential thermal analysis and pore-distribution measurement, we found that during heating at 800°C the support underwent no structural transformation.

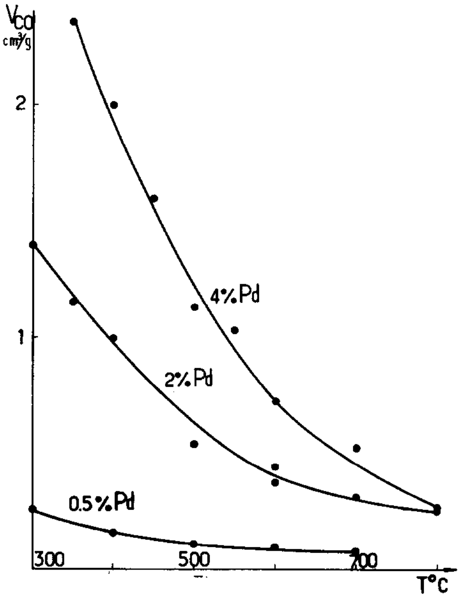


FIG. 9. Effect of calcination temperature on dispersion of palladium.

(β) **Relation with catalytic activity.** After deposition of the activator in the following proportions

Pd (%)	NaOAc (%)
0.5	4.35
2	15
4	15

the catalysts were tested under the same experimental conditions in the absence and presence of water vapor:

$P_E = 0.56$ atm
$P_O = 0.12$ atm
$P_A = 0.32$ atm
$W/F = 24$
$P_E = 0.408$ atm
$P_O = 0.087$ atm
$P_A = 0.117$ atm
$P_{H_2O} = 0.388$ atm
$W/F = 17.5$

Figures 12 and 13 contain the results obtained. Contrary to what might be expected, the activity is very low for high dispersions of palladium. It increases initially when this dispersion decreases, and after going through a maximum it then decreases. The only effect of the presence of water is to increase catalytic activity (similar yields for different contact times).

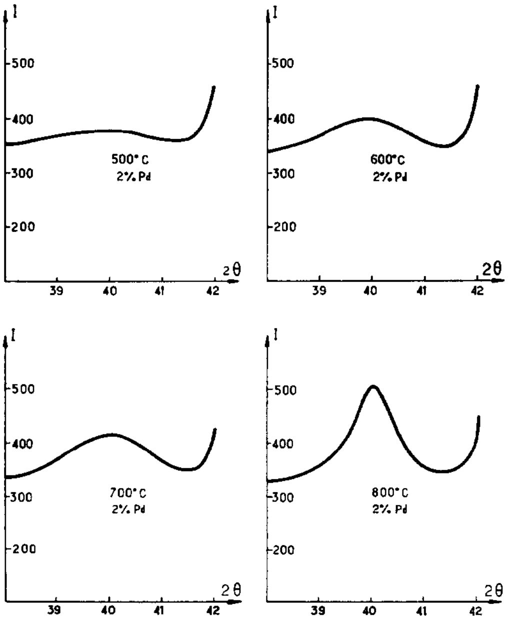


FIG. 10. X-Ray diffraction patterns of palladium. Variation of (1,1,1) line with calcination temperature ($d = 2.242$, Cu K_α: 1.54 Å). (Figures 10 and 11: Vertical axis, intensity in counts per second; horizontal axis, spectrometer angle.)

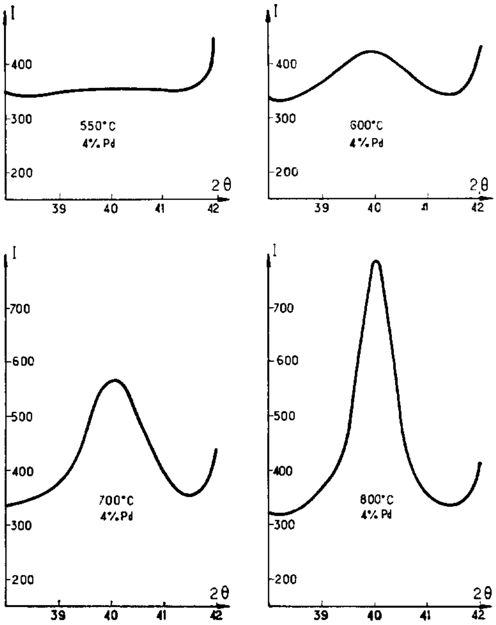


FIG. 11. X-Ray diffraction patterns of palladium. Variation of (1,1,1) line with calcination temperature ($d = 2.242$, Cu K_α: 1.54 Å).

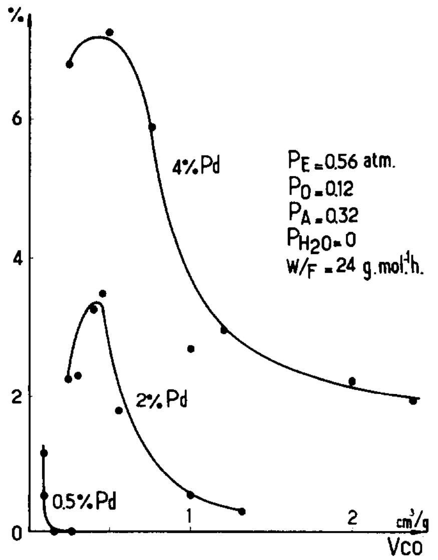


FIG. 12. Effect of dispersion of palladium on yield of vinyl acetate in the absence of water vapor.

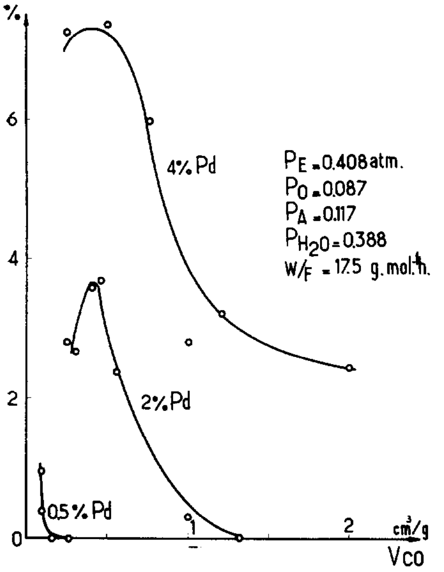


FIG. 13. Effect of dispersion of palladium on yield of vinyl acetate in the presence of water vapor.

C. Interaction of Support With Acetic Acid and Water

The equipment used included a chromatography column filled with silica or alumina of the same type used in the support. This was followed by a thermal conductance gauge connected to a recorder. The entire apparatus was maintained at 140°C by a thermostat, and helium was used as the carrier gas (60 cm³/min). The mass used was approximately 1 g. Acetic acid and water (10 μl) were injected at the head of the chromatography column in a spray form. We verified that the vaporization of acetic acid and water was extremely fast.

The retention times for water and acetic acid were large, with that for acetic acid being the greater both for silica and alumina. Consequently, there is a high degree of interaction between the support and both products, with the interaction involving acetic acid being greater than that with water. The recorded curves rise to peaks and then descended more slowly, thus revealing a slow desorption of the products. No interaction could be detected between the supports and ethylene or oxygen.

III. DISCUSSION OF RESULTS

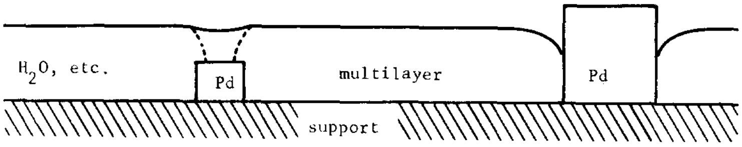
A. Effect of Support

An examination of catalytic activity vs palladium dispersion on the surface of silica reveals the harmful effect of good dispersion. An interpretation of this might be that the metallic nature of the palladium needs to be well-developed for activation, and is not obtained in the region where catalytic activity is low. However, experiments with an alumina-base catalyst have shown that it is possible to obtain suitable catalytic activity with a much greater palladium dispersion than that required by silica-base catalysts. A realm exists where, with equal dispersion, the silica-base catalyst is inactive as opposed to an alumina-base catalyst. Therefore, the influence of the support must be considered in order to explain this phenomenon. This influence may be exerted in at least two different ways:

(1) Either by modifying the properties of the palladium itself as the result of interaction with the support, with this solid–solid interaction clearly differentiating alumina from silica.

(2) Or by the intervention of the adsorption properties of supports with regard to acetic acid and water. Actually, we have already seen (§ II C) that both acetic acid and water are strongly adsorbed on the surface of silica or alumina supports at 140°C. Capillary condensation under the chosen conditions cannot explain this adsorption, which appears due to the chemical properties of alumina and silica. During the catalytic reaction, therefore, we must assume that on the surface of the catalyst, in addition to sodium acetate, there is a certain concentration of constantly renewed acid during the vinyl acetate synthesis.

It is this fact which may be responsible for the harmful effect of dispersion, because too finely dispersed palladium is not accessible for gaseous reagents such as ethylene or oxygen as the result of the presence of adsorbed layers of acetic acid and water according to the simplified and illustrative scheme:



In the case of alumina, this sort of inhibition is probably absent or much less effective on account of a smaller degree of adsorption of acetic acid or water.

B. Determining the Kinetic Equation from the Proposed Mechanism

Not counting the effect of the support, the kinetic results obtained with silica or alumina-base catalysts are similar, thus enabling a common interpretation to be made.

The proposed mechanism assumes, first of all, the existence of two parallel reactions. The first reaction is the direct combustion of ethylene catalyzed by metallic palladium

$$C_2H_4 + 3O_2 \xrightarrow{Pd} 2CO_2 + 2H_2O.$$

The second reaction is the synthesis of vinyl acetate, and we will attempt to determine its mechanism. Direct experience shows that vinyl acetate can be formed from metallic palladium in two separate steps.

The first step is the oxidation of metallic palladium to form palladium acetate. If a catalyst containing only metallic palladium deposited on silica is submerged in acetic acid at boiling temperature, palladium acetate is formed in the solution if an oxygen flow is passed through it. In an inert atmosphere (N_2 or He) no reaction occurs. This result has also been found on unsupported palladium (*3*).

The second step is the reaction of ethylene on the palladium acetate thus formed. This leads to the formation of vinyl acetate with the simultaneous precipitation of metallic palladium. This second step requires the presence of sodium acetate. We have verified this well-known result (*1*).

As the result of the presence of acetic acid together with sodium acetate on the surface of the catalyst, we have adopted this reaction sequence to explain the synthesis of vinyl acetate and to check whether this gives an agreement with experimental kinetic results.

1. Oxidation of palladium:

$$(1)\ Pd + \tfrac{1}{2}O_2 + 2AcOH \xrightarrow{k_1} Pd(OAc)_2 + H_2O$$

2. Synthesis of vinyl acetate:

$$(2)\ Pd(OAc)_2 + AcO^{\ominus} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Pd(OAc)_3^{\ominus}$$

$$(3)\ Pd(OAc)_3^{\ominus} + C_2H_4 \xrightarrow{k_3} AcO{-}CH{=}CH_2 + AcOH + AcO^{\ominus} + Pd^0$$

k_1, k_2, k_{-2}, and k_3 represent the rate constants for each of the reactions, and K_2 is the equilibrium constant for reaction (2).

The following assumptions are made for the purpose of calculating:

The elementary steps of reaction (1) are not known. However, because strong adsorption of acetic acid occurs on the support, we assumed that the support always remains saturated with this reagent (physical adsorption) and that if chemisorbed molecules come from the physical adsorption, this chemisorption does not vary with the partial pressure of acetic acid. This enables us to write:

$$r_1 = k_1(\text{free Pd})(P_{O_2})^n$$

Equilibrium (2) is attained no matter what the experimental conditions may be. Reaction (3) is the limiting step:

$$\frac{d[\text{V.A.}]}{dt} = k_3[Pd(OAc)_3^{\ominus}]P_{C_2H_4}.$$

The balance for the distribution of surface palladium enables the following relationship to be written:

(a) (Total accessible Pd)
$= (\text{free Pd}) + [Pd(OAc)_2] + [Pd(OAc)_3^\ominus]$.

The principle of the stationary state applied to $[Pd(OAc)_2]$ is expressed as follows:

(b) $k_1(\text{free Pd})P_{O_2}^n + k_{-2}[Pd(OAc)_3^\ominus] = k_2[Pd(OAc)_2][AcO^\ominus]$.

The assumption of constantly achieved equilibrium in step (2) makes it possible to write:

$$(c)\ K_2 = \frac{[Pd(OAc)_3^\ominus]}{[Pd(OAc)_2][AcO^\ominus]}.$$

From the three preceding equations the following is deduced:

(d) $(\text{Total accessible Pd}) = [Pd(OAc)_3^\ominus] \times \{[(k_2/K_2) - k_{-2}]/k_1P_{O_2}^n + 1/K_2[AcO^\ominus] + 1\}$.

Referring to the value of $Pd(OAc)_3^-$ in the expression for the rate of vinyl acetate formation, the following relation (Eq. (e)) is deduced:

$$r = k_3(\text{total accessible Pd}) \frac{K_2k_1P_{O_2}^nP_{C_2H_4}[AcO^\ominus]}{\left(\frac{k_2}{K_2} - k_{-2}\right)K_2[AcO^\ominus] + k_1P_{O_2}^n + k_1K_2P_{O_2}^n[AcO^\ominus]}$$

This mechanism assumes that ethylene reacts from the gas phase with the complex $Pd(OAc)_3^-$. If an adsorption step is made to occur prior to the decomposition of the complex formed, then:

$$Pd(OAc)_3^\ominus + C_2H_4 \rightleftarrows C_2H_4Pd(OAc)_3^\ominus,$$

$$C_2H_4Pd(OAc)_3^\ominus \xrightarrow{k_4} Pd^0 + AcO{-}CH{=}CH_2 + AcOH + AcO^\ominus.$$

Assuming that this last step is the limiting one, the rate of reaction then becomes:

$$r = k_4[C_2H_4Pd(OAc)_3^-].$$

Then, for the calculation of r, using the same expressions as before and writing the thermodynamic equilibrium for Eq. (4), we obtain a new relation (Eq. (e′)) of rate; (e′) only differs from (e) by the addition to its denominator of the term $AP_{O_2}^n[AcO^\ominus]P_{C_2H_4}$ which is not revealed by experimental results. This is the reason why the adsorption step was not introduced.

C. Comparison With Experimental Kinetic Results

At the level of the catalyst, the experimental results reveal the need to have sodium acetate in addition to palladium. Since the partial pressures of each reagent are maintained constant, the kinetic Eq. (e) is reduced to an expression having the form:

$$r = \frac{A[Pd][AcO^\ominus]}{1 + B[AcO^\ominus]}.$$

This expression gives an idea of the linear variation of performance vs the palladium content (Fig. 2) as well as the hyperbolic rate of catalytic activity versus the sodium acetate content (Fig. 1), with the concentration of AcO^- varying in the same way as the AcONa deposited or the catalyst.

If the sodium acetate and palladium contents are fixed, the kinetic Eq. (e) vs the partial pressure of the different reagents can be reduced to:

$$r = \frac{KP_{C_2H_4}P_{O_2}^n}{C + DP_{O_2}^n}.$$

The rate is proportional to the ethylene partial pressure and is independent of the acetic acid partial pressure. Depending on oxygen partial pressure, the rate expression implies a saturation plateau at high pressures. This is confirmed by the experimental results in the absence and presence of water vapor.

Furthermore, the diagram of the reverse rate vs reverse oxygen partial pressure is approximately a straight line, thus suggests that the palladium oxidation step is a first-order reaction compared with oxygen (Fig. 14).

In the presence of water, the kinetic results are similar, but two new facts

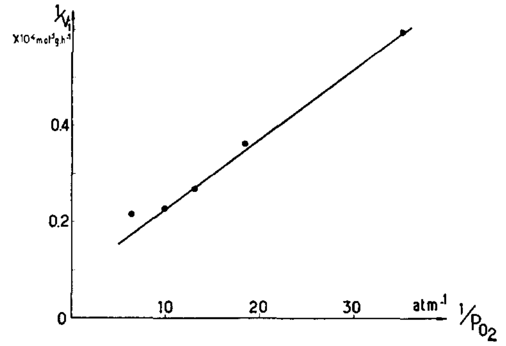


FIG. 14. Determination of the order with respect to oxygen.

appear. The rate increases vs water partial pressure; versus oxygen partial pressure, it reaches a saturation plateau faster than in the absence of water. The exact cause of these phenomena has not yet been entirely explained.

The water does not appear to intervene chemically in the different reaction steps, because no competitive products such as acetaldehyde appear. Nevertheless, water is capable of interacting with the support, although to a much lower degree than acetic acid, and this may bring about a modification in the layer adsorbed on the surface of the catalyst. The number of active sites may increase, which explains the higher level of activity in the presence of water.

The fact that, in the presence of water, the initial slope of the curve giving V_i vs P_O is increased and that the rate-saturation plateau vs P_O appears more quickly may be due, as shown by Eq. (e), to the increase in the constant k_1. This would mean that, in the first step of the mechanism, the presence of water increases the rate of the palladium-oxidation step.

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