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Gas-Phase Acetoxylation of Ethylene: Palladium-on-Carbon Catalyst Stability

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The gas-phase acetoxylation of ethylene has been studied on a palladium-on-carbon catalyst, using a fixed-bed flow reactor in the temperature range 415 to 455 K. The extent of deviation in the lattice constant of palladium from expected values correlated with the decrease in the activity of a catalyst.

INTRODUCTION

Two different processes are being employed in the manufacture of vinyl acetate. The conventional method is to make vinyl acetate from acetylene and acetic acid over a zinc catalyst. The other process involves the reaction of ethylene, oxygen, and acetic acid in a heterogeneous phase over a palladium catalyst. The reaction proceeds according to the equation,

$$CH_2{=}CH_2 + CH_3COOH + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CH \cdot O \cdot C \cdot O \cdot CH_3 + H_2O.$$

The information available on the process is mostly in the patents. In these patents, a slow decline in the activity of catalysts when used in the reaction for about 100 hr has been reported (*1*). The aim of the present study is to correlate this aging of the catalysts with changes in the structure of the palladium metal present in them.

EXPERIMENTAL

Reactions were carried out in a fixed-bed flow reactor, heated by a fluidized sand bath. Reaction temperatures were maintained by a high thermal capacity electrical furnace, which could be held at a selected temperature to ±1°C by a nickel-Alumel/nickel-Chromel thermocouple and control unit. The reactor itself was a stainless-steel tubing of 1.25 cm inner diameter and 60-cm length. The reactor assembly and the experimental procedure were identical to those described elsewhere (*2*). Analysis of the products was made by a flame ionization gas chromatograph (Perkin–Elmer F-II) using a 1-m-long column of Carbowax 1540 on AW-DMCS Chromosorb and nitrogen as a carrier gas. Ethylene and acetaldehyde were found to separate out at 323 K and vinyl acetate and acetic acid at 433 K.

X-Ray diffraction patterns of catalysts in air, were obtained with a Norelco counter-diffractometer using Ni-filtered Cu–K α radiations. The apparent lattice constants were calculated from the centroid of the individual peaks, while the lattice parameter was derived by extrapolating the diffraction angle to 90°, using the Nelson–Riley function (*3*). The Scherrer equation (*3*) was used to calculate the average metal crystallite size.

Acetic acid in vapor form was added to the reaction feed by passing nitrogen through a glass bubbler containing the liquid in order to saturate the gas with acid vapor. All the connecting tubing was lagged with heater tapes and maintained at 350 K. Scanning electron microscopy was performed with a Cambridge Instruments Stereoscan 600.

Reagents. The gases in high-pressure cylinders were supplied by British Oxygen Company and the purities of these gases were: nitrogen not less than 99.9%; oxygen

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not less than 99.9%; ethylene not less than 98.0%. Acetic acid of analytical grade was used. The carbon support (surface area 1050–1150 m^2/g; pore volume 0.8 cm^2/g; bulk density of 0.5 g/cm^3; size 6 × 8 mesh; average pore diameter 2 nm) was obtained from Pittsburgh Activated Carbon Company.

Calculation. Feed rates were calculated on the basis of rotameter readings and analysis of the feed. The effluent rates were calculated on the basis of the product stream and computation of the olefin consumed. The amount of olefin reacted was calculated on the analysis of the effluent stream. Selectivity was calculted on the basis of the olefin reacted. Quantitative estimation of the chromatographic analyses was obtained from the peak area determination.

Procedure. The reactor was packed with 20–40 g of the catalyst sample. For all the experiments catalyst particles were diluted with inert ceramic spheres in the ratio of 1 : 1. The reactor was operated at a small positive pressure. At the shutdown, it was flushed in an atmosphere of nitrogen.

Catalyst preparation. The catalysts were prepared by impregnating the carbon support with solutions containing the required amount of palladium chloride and dilute hydrochloric acid. For a typical catalyst batch, carbon (40 g) was immersed for 24 hr in an aqueous HCl solution (200 ml) containing palladium chloride. Palladium chloride solution was made by heating the salt in a small quantity (5 ml) of concd HCl till it dissolved, and then diluting it with distilled water. The catalyst was allowed to drain for a further 12 hr before being dried and reduced in a flow of hydrogen gas (0.1 liter/min) at 475 K for 4 hr. The catalyst was then activated in nitrogen at 575 K for a further 10 hr to occlude out the hydrogen absorbed in the palladium metal.

Feed composition. Two reaction mixtures were employed for the determination of the aging behavior of catalysts. Reaction mixture 1 was lean in acetic acid concentration, whereas reaction mixture 2 had a high acetic acid concentration. The composition of these reaction mixtures is shown in Table 1.

RESULTS

X-Ray Diffraction

For the determination of the changes in the structure of the catalyst during the reaction, a sample of the catalyst containing 10% palladium on carbon (w/w) was examined before and after the reaction in reaction mixtures 1 and 2. A comparison of the structural changes in the palladium metal and the activity of the freshly prepared catalyst with that of the catalyst after use in reaction mixture 2 for 104 hr is given in Table 2.

Electron Microscopy

The electron micrographs of the catalyst containing 10% palladium on carbon before and after use in reaction mixture 1 for 30 hr are shown in Figs. 1 and 2.

Thermal Treatment

In order to determine the extent of deviation in the interplanar distance of palladium metal, a sample of the catalyst was heated at 1075 K for 24 hr. The lattice constant for this sample was found to be 0.38872 ±0.00005 nm. As the metal crystal size, i.e., 35.1 nm, appeared to be too large for the lattice discrepancy to be explained by the small crystallite size (4 nm) alone (*4*), it thus seems probable that the support affects the metal lattice dimension. Henceforth a lattice parameter value of 0.38872 ±0.00005 nm was taken as reference for the

TABLE 1

Composition of the Reaction Mixtures

Reaction mixture	Partial pressure (kN/m^2)				Total feed (ml/min)
	C_2H_4	CH_3COOH	O_2	N_2	
1	53.32	1.55	4.83	48.48	220
2	25.99	18.13	9.47	54.51	400

TABLE 2

The Effect of Processing Time on the Activity of 10% Palladium-on-Carbon Catalyst

Reaction mixture	Processing time hr,	Temperature K	% Yield		Lattice constant	
			Vinyl acetate	CO_2	α-hydride (nm)	β-Hydride (nm)
1	5	415	1.1	—	0.38895	—
	30	415	0.2	—	0.3895[a]	0.3963[a]
2	5	435	0.93	5.41	0.38895	—
	104	435	1.1	5.0	0.3894[a]	0.3986[a]

Note. Reaction mixture 1: Space velocity, 85.1 hr^{-1}—N_2- dilution. Reaction mixture 2: Space velocity, 270 hr^{-1}—Na_2- dilution.

[a] Determined from (1,1,1) plane. $a_0 = 0.38872 \pm 0.00005$ (For bulk palladium, in the palladium-supported catalyst—refer to text).

bulk palladium in the carbon-supported palladium catalysts.

Treatment of Catalyst Surface with Reactants

Samples of the 10% palladium-on-carbon catalysts were separately treated in a flow of ethylene and hydrogen (0.1 liter/min) at 475 K for 1 hr. In both cases the diffraction angle (2θ) changed from the higher angle to a lower angle ($2\theta = 39.0$ for hydrogen; $2\theta = 39.5$ for ethylene). This indicates an easy abstraction of hydrogen from ethylene and a stable palladium hydride formation by hydrogen absorption in the metal.

Treatment of a sample of catalyst under the above conditions with acetic acid vapors and oxygen, however showed no other diffraction lines, except those for palladium and carbon.

In the case of a deactivated catalyst sample heated in a flow of oxygen for 10 min, the palladium hydride phase which was present before heating, seemed to be only partly removed and was still apparent in the X-ray diffraction profiles. The apparent lattice parameter value derived for the catalyst heated in oxygen for 3 hr was 0.38897 ±0.00003. This value was in close agreement with the lattice parameter value of the fresh batch of the same catalyst, i.e., $a = 0.38895 \pm 0.00003$. No other diffraction lines, except those for palladium metal and carbon, were detected in the catalyst.

Catalyst Aging

The stability of a freshly prepared catalyst and a vacuum-regenerated sample of deactivated catalyst (aged for 30 hr in reaction mixture 1 at 415 K) was examined in reaction mixture 1, containing a lower concentration of acetic acid (pp 1.55 kN/m^2) than reaction mixture 2 (pp 18.13 kN/m^2). The vacuum-regenerated catalyst was obtained by heating a sample of deactivated catalyst at 475 K under vacuum for 24 hr. The effect of catalyst aging was clearly apparent in both of the catalysts when used in reaction mixture 1 at 415 K. The rate of the progressive deactivation of a freshly prepared catalyst and a vacuum-regenerated catalyst for vinyl acetate formation is shown in Table 3. Although the effect of aging was not observed when a 10% palladium-on-carbon catalyst was used in reaction mixture 2, and the catalyst was found to maintain its activity with time over a period during which its activity declined when employed with reaction mixture 1, this aging effect was once again apparent when the catalyst was used continuously for 104 hr in the process. A comparison of the activity of the freshly prepared catalyst with that of the catalyst after use in reaction for 104 hr is given in Table 2.

The Effect of Feed Composition

The influence of the partial pressures of oxygen and acetic acid on conversion and selectivity is shown in Figs. 3–6. An aged catalyst which had been exposed in reaction mixture 2 for 70 hr at 415 K was also examined for its conversion rates at various oxygen/ethylene ratios.

As the mass velocity of the fluid past the catalyst particles was high, the external mass transfer was assumed to be insignificant. The influence of internal diffusion on reaction rate was not determined.

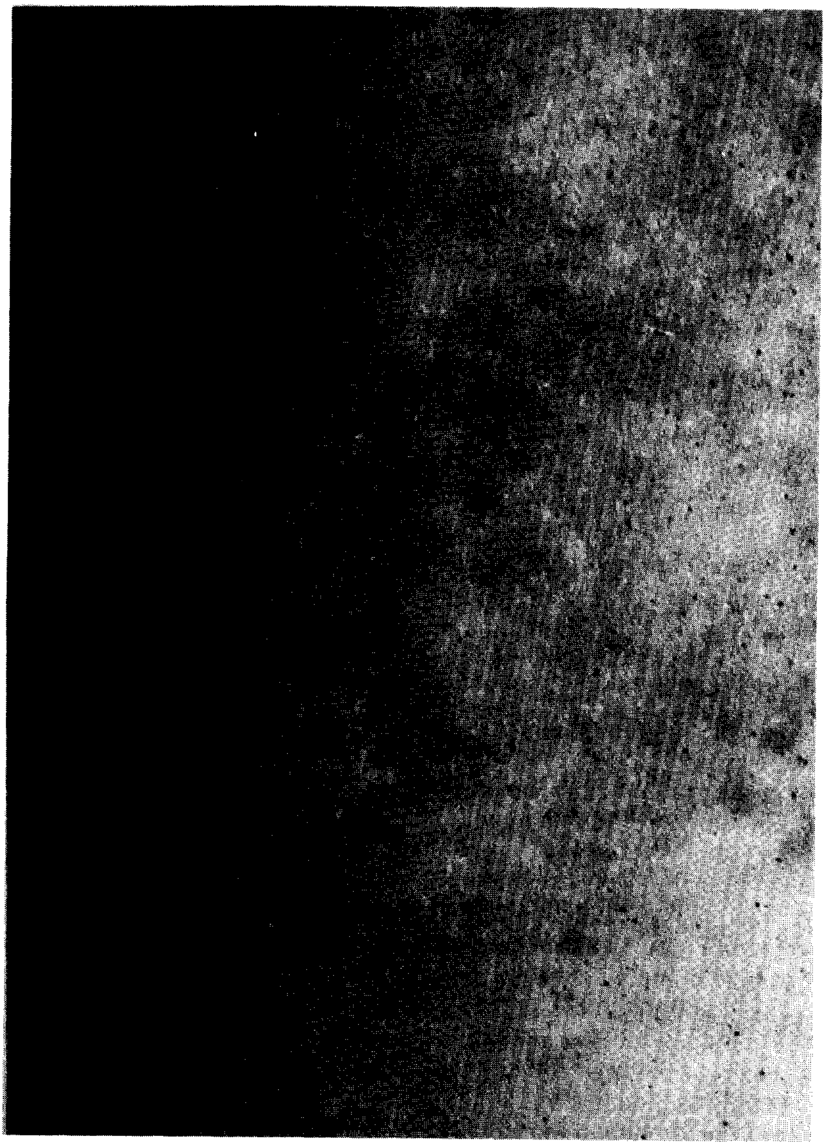

FIG. 1. Electron micrograph of the freshly prepared 10% palladium-on-carbon catalyst; magnification 10^5.

DISCUSSION

A number of structures like, diadsorbed σ-bonded Pd—CH═CH—Pd, π-bonded Pd—CH_2═CH_2, and monoadsorbed CH_2═CH—Pd species for ethylene chemisorption on palladium have been proposed (*5*). At a temperature lower than 273 K, ethylene is predominantly associatively adsorbed (*6*, *7*(*a*)) though a part of ethylene is dissociated. At temperatures higher than 273 K, ethylene is more extensively dissociated than at 273 K, and the extent of dissociation depends upon the experimental conditions. Results in the literature on related systems like adsorption of ethylene on platinum also show similar results (*7*b)). At higher temperatures (300 K), the existence of an intermediate of a type such as the vinylidene (:C═CH_2) radical, leading to the formation of a stable species ethylidyne (:C–CH_3) on the surface of the catalyst has been proposed (*8*).

Available data on heat of adsorption of

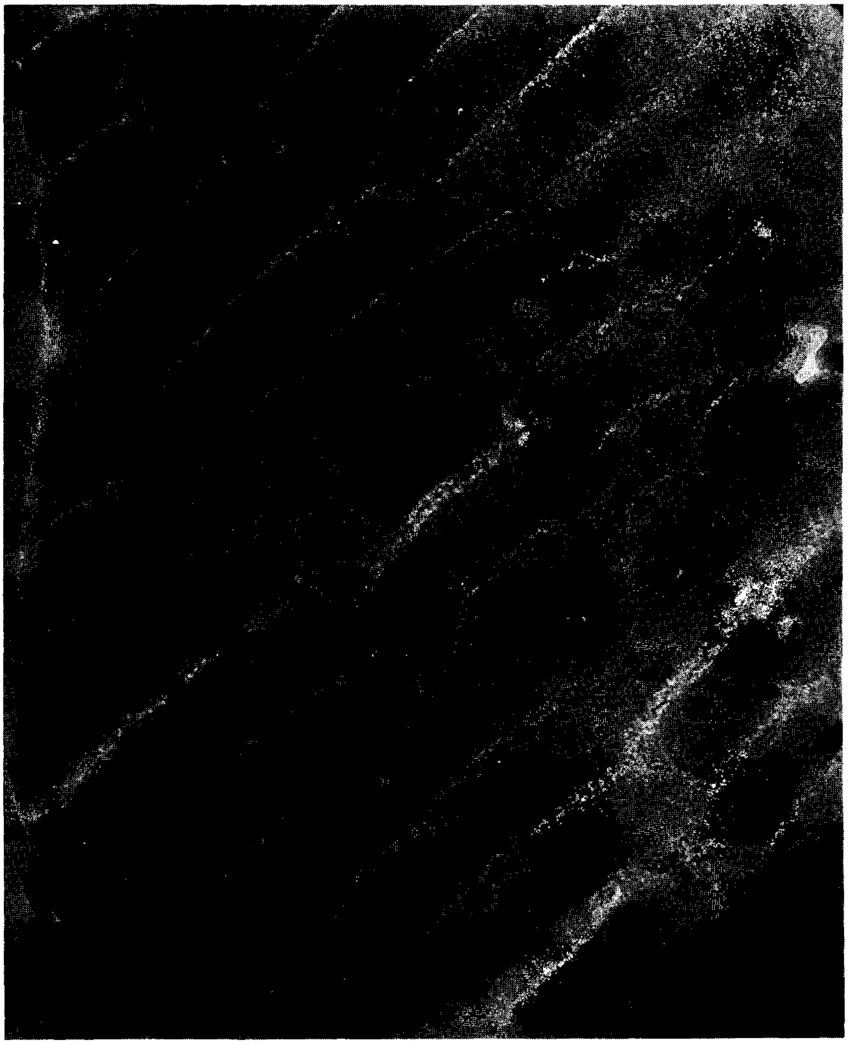

FIG. 2. Electron micrograph of the aged catalyst used for 30 h in reaction mixture 1; magnification 10^5.

TABLE 3

Aging Behavior of Freshly Prepared And Vacuum-Regenerated Catalysts in Reaction Mixture 1 at 415 K

Freshly prepared catalyst		Vacuum-regenerated catalyst	
Catalyst age (hr)	% yield vinyl acetate	Catalyst age (hr)	% yield vinyl acetate
5.0	0.09	0.5	0.11
7.0	0.11	1.0	0.09
12.0	0.15	3.0	0.05
16.0	0.10	6.0	0.02
31.0	0.02	20.0	0.01

oxygen at low coverages indicate that oxygen is more strongly adsorbed than olefins on the metal surface (*9*). On the other hand, at higher ethylene partial pressures, the kinetic data indicate that ethylene is more strongly adsorbed than oxygen on the surface of the catalyst (*10*). This indicates that heats and coverages of oxygen and ethylene on palladium vary with the mechanism of adsorption of the two species in the presence of each other on the surface of the catalyst. The data on the heat of adsorption of oxygen or ethylene in the presence of acetic acid are not available. Acetic acid, itself is dissociatively adsorbed on palladium in the presence of oxygen (*11*). From the experimental results obtained, it appears that both the reactants, i.e., oxygen and acetic acid, compete for adsorption sites which preferentially adsorb ethylene. A large part of the metal surface seems to be covered with ethylene (or residues of ethylene), the concentration of which decreases with an increase in acetic acid coverage at high acetic acid partial pressures.

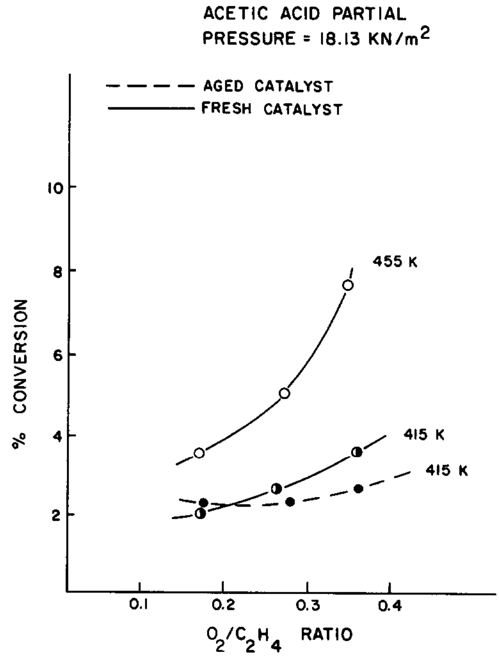

FIG. 3. Effect of oxygen/ethylene ratio on conversion at different temperatures.

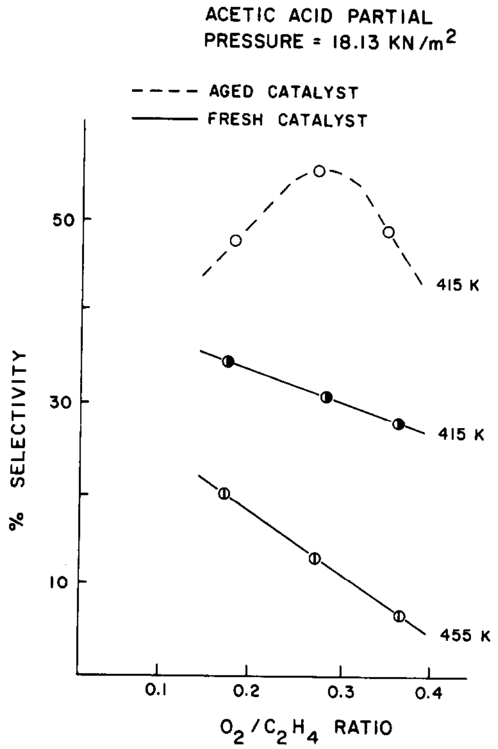

FIG. 4. Effect of oxygen/ethylene ratio on selectivity at different temperatures.

X-Ray studies of all the catalysts examined after use in the reaction showed a continuous increase in the lattice parameter of the palladium metal till a new phase

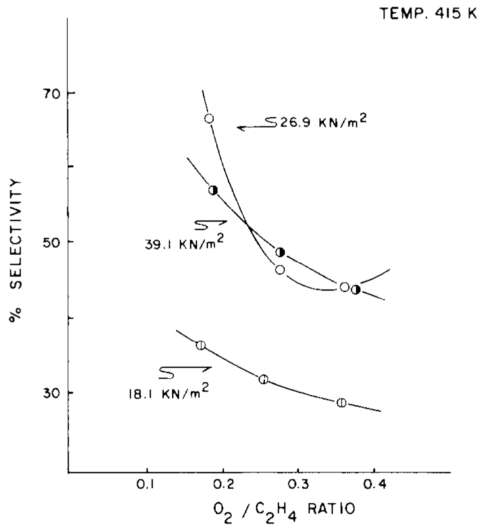

FIG. 5. Effect of oxygen concentration on selectivity at different acetic acid partial pressures.

appeared and diffraction lines for both the α-hydride and β-hydride palladium phases were simultaneously present (*12*). The formation of a palladium hydride phase in the fresh catalyst may arise in the first place during the catalyst preparation by the diffusion into the palladium lattice of the hydrogen used to reduce palladium chloride, thus causing an expansion of the lattice parameter. The continuous increase in the lattice parameter during the process suggests on this basis, a further diffusion of hydrogen into the palladium metal. Moreover, the catalysts after treatment with hydrogen (diffraction angle, 2θ, of (1,1,1) plane = 39.0) and ethylene (2θ = 39.5) showed similar increases in the interplanar distance of the palladium metal. A lattice stretch of 0.001 and 0.01 nm at 1 atm of hydrogen pressure has been reported on the uptake of H_2 by palladium films at 373 and 473 K, respectively (*13*).

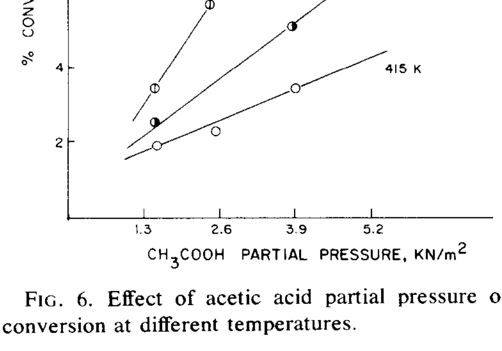

FIG. 6. Effect of acetic acid partial pressure on conversion at different temperatures.

During the reaction process, it appears that the hydrogen dissolution into palladium metal forms new catalytic "sites" as palladium hydrides.

No palladium acetate or palladium oxide was evident in the samples of catalyst, when treated with oxygen or acetic acid. This is in contrast with the studies (*14, 15*) where an acetate or an oxide formation is reported. However, it is expected as supported catalysts are more stable than the catalysts in the form of films (*15*) or as powder (*14*). The incomplete removal of palladium hydride phase from a deactivated catalyst sample by oxygen treatment (475 K, 10 min) also indicates the stable nature of such catalysts and also, that a long vacuum treatment and a high temperature are required for the complete removal of hydrogen from finely divided metal crystallites impregnated on a support. The removal of desorbable hydrogen from the catalyst is not unexpected in view of the known ability of the palladium metal for hydride formation. This long period of time taken for desorption can be due to the slow diffusion of the adsorbed hydrogen to the surface of the metal.

The absence of any evidence of palladium hydride phase in the deactivated catalyst sample when examined after treatment in oxygen for 1 hr at 475 K, suggests that a milder treatment is needed for the regeneration of deactivated, supported metal catalysts.

The electron micrographs showed a wide

variation in metal particle sizes. The sizing of metal particles showed a bimodal size distribution in all the catalysts. In the catalyst heated at 1075 K the particle diameter corresponding to maximum population was at 20 nm. The other population maximum which corresponded to fewer particles was found to be near 100 nm.

The micrograph of the aged 10% palladium-on-carbon catalyst sample showed a substantial number of finely dispersed metal particles gathered together in the form of round masses.

The formation of these round masses of very small crystallites (10 nm) was also observed in the different parts of the catalyst. The appearance of metal particles in round masses can be caused by the stretching of the lattice and due to the separation of palladium hydride phases in the catalyst. The splitting of palladium metal due to distortion of lattice and grain boundary cracking occurs in passing around the area of coexistence of the α and β hydride phases (*13*).

The decline of catalyst activity with reaction time was mainly associated with the formation of a palladium hydride phase during the reaction. A decrease in the rate of growth of this phase in catalysts when used in reaction mixture 2 indicates the adsorption of acetic acid molecules competing for the active "sites." Also the activity of the catalyst fell more rapidly (0.02% in 31 h) when used in the hydrocarbon-rich reaction mixture 1 in comparison to its active life in a hydrocarbon-lean reaction mixture 2. This slow decline in catalyst activity in the presence of additional oxygen in reaction mixture 2 indicates the desorption of hydrogen as water molecules competing with the dissolution of hydrogen in the bulk metal.

An increase in the selectivity of vinyl acetate formation with processing time suggests a decrease in the population of active sites responsible for the complete combustion of ethylene into carbon dioxide.

It is suggested that palladium sites saturated with hydrogen seem to be inactive in the formation of a dehydrogenated species from the olefin to act as an intermediate in the partial oxidation of olefin. Ethylene adsorbed dissociatively on sites less saturated with hydrogen appears to be responsible for vinyl acetate formation, whereas complete combustion of ethylene occurs on palladium sites.

Catalyst Stability, and Chemical Aspects of the Reaction System

During the first 40 hr of catalyst life at 415 K, it was observed that, at a constant acetic acid partial pressure of 18.13 kN/m^2, the conversion increased and selectivity decreased with the increase in oxygen partial pressure in the reaction feed. The conversion was also increased by an increase in the acetic acid partial pressure.

The same general pattern of influence of ethylene-oxygen ratio and acetic acid partial pressure upon conversion and selectivity at a fixed residence time was observed at 435 and 455 K with the same batch of catalyst. At fixed ethylene–oxygen ratios and acetic acid partial pressure, a rise in temperature increased the conversion and reduced the selectivity. This regularity of behavior in a single batch of catalyst exposed successively to different temperatures and reaction conditions might be taken to suggest that no significant catalyst aging occurred. However, an effect of catalyst aging was apparent when the catalyst batch was returned to the original reaction conditions; in addition, the effect of catalyst age was clearly demonstrated in the experiments conducted with reaction mixture 1, specifically designed to investigate this matter.

After 70 hr of operation in reaction mixture 2 the activity of the catalyst when examined in original conditions at 415 K was found to be lower than before. As expected the behavior of fresh and aged catalysts for the vinyl acetate formation in the reaction were different. On the aged catalyst, evidently some of the palladium sites were partially saturated with hydrogen. The selectivity for vinyl acetate thus depending on the degree of hydrogen saturation in the sites was influenced by the oxygen concentration in the feed. The selectivity increased with the increase in the oxygen concentration and reached a maximum at a C_2H_4/O_2 ratio of 1:0.27. This behavior contrasts with that of the fresh catalyst where no such sites were present. The selectivity decreased with a further increase in oxygen concentration, as with the fresh catalyst.

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