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Formation of Palladous Acetate and Stability of Catalyst in Palladium-Metal-Catalyzed Synthesis of Vinyl Acetate from Ethylene

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Palladium-catalyzed synthesis of vinyl acetate (VAc) from ethylene was investigated especially in the light of the formation of palladium(II) acetate in the working state. Palladium(II) acetate was thought to be formed only under higher partial pressures of acetic acid and oxygen and at lower temperatures and to facilitate the formation of acetaldehyde. The aggregation of palladium was connected with the formation of palladium(II) acetate on the surface of a catalyst. The catalytic activity was maintained for prolonged times under those conditions in which palladium(II) acetate was not formed.

INTRODUCTION

The palladium-metal-catalyzed process of VAc from ethylene has been commercialized since 1968. The mechanism of this reaction has been recently proposed. We have also studied this reaction and assumed that the catalytically active species was dissociatively adsorbed acetic acid (Pd(I)acetate) on palladium in industrially important reaction conditions (*1*). Kunugi *et al.* reported that palladium(II) acetate was not present in usual reaction conditions (*2*). Adversely, Samanos *et al.* offered the mechanism in which palladium(II) acetate was the catalytically active species (*3*). The existence of palladium(II) acetate in the working state is of interest from the view of the mechanism but it has remained unclear.

In this paper we reexamined this reaction in the light of the formation of palladium(II) acetate in the working state. The stability of the catalyst has also been discussed.

EXPERIMENTAL

Catalyst Preparation

The catalyst was prepared by the same method as previously reported, and Neobead calcined at 1050°C for 3 hr was used as a carrier (*1*). The particle diameter of the catalysts was 3 mm ϕ–~4 mm ϕ.

Procedure and Analysis

All experiments were performed by using a flow system. A reactor consisting of a 12-mm i.d. hard glass tube was used under atmospheric pressure, and a 100 mm (length), 21.2 mm i.d. stainless-steel tube was used as a reactor when the reaction was carried out under superatmospheric pressure (2–~7 atm). Acetic acid was fed into an evaporator with a feeding pump. Ethylene (purity over 99.8%) and oxygen were passed through the evaporator into the reactor.

Products were quantitatively analyzed by gas chromatography using the internal standard method. Surface structures of catalysts and adsorbed species were examined with X-ray and infrared measurements. A Rigaku Denki X-ray diffractometer with Ni-filtered Cu K_α radiation was used to obtain X-ray diagrams. Infrared spectra were obtained by the KBr disk techniques with a Hitachi infrared spectrometer EPI-G_2. The aggregation of palladium was observed with Shimazu-ARL Electron Microprobe X-ray Analyzer (Type

TABLE 1
PRODUCTS IN ACETOXYLATION OF ETHYLENE WITH PALLADIUM METAL CATALYST IN PRESENCE OF WATER[a]

Expt No.	Gas composition (%)				Temp (°C)	Products (mole/hr)		
	C_2H_4	O_2	CH_3COOH	H_2O		Acetaldehyde	VAc	Carbon dioxide
1	58	7	15	20	98	0.015	0.58	0.02
2	68	7	10	15	130	0.008	1.00	0.08
3	72	7	6	15	130	0.003	0.78	0.10
4	75	5	5	15	150	trace	0.75	0.24

[a] Catalyst; Pd 1.0 wt % and $KOCOCH_3$ 3 wt % on Al_2O_3 (0.601):SV; 1000(hr^{-1}), total pressure; 5 atm.

2A, acc voltage; 30 kV, sample current; 0.1 mA).

RESULTS AND DISCUSSION

Formation of Acetaldehyde

When a mixture of ethylene, acetic acid, water, and oxygen was exposed to palladium metal catalyst at 98–~150°C, vinyl acetate was formed selectively together with small amounts of carbon dioxide. It is quite clear from Table 1 that appreciable amounts of acetaldehyde are formed only under higher partial pressures of acetic acid and at lower temperatures. It is well known that acetaldehyde is produced from the combinations of ethylene:water (*4*), vinyl acetate:water (*5*) and vinyl acetate: acetic acid (*6, 7*) when palladous salt is used as a catalyst. On the other hand, no acetaldehyde was detected in those reactions catalyzed by palladium metal catalyst (*8*). Kunugi *et al.* have also shown this point (*2, 9*). It is conceivable from these observations that acetaldehyde shown in Table 1 is derived from one of the above reactions catalyzed by palladium(II) acetate which is formed on the surface of a catalyst.

Detection of Palladium(II) Acetate

It is quite difficult to directly detect the presence of palladium(II) acetate in the case of vinyl acetate synthesis because of its small amounts. In order to support this point, palladium black was used in the following experiments. When a mixture of acetic acid and oxygen was passed over palladium black at 105°C, palladium(II) acetate was formed as shown in Table 2

TABLE 2
X-RAY DIFFRACTION PATTERNS OF PALLADIUM BLACK[a]

Expt No.	Pd black	Gas composition (%)				Temp (°C)	Time (hr)	X-ray lines (2θ = 10–~14°)
		CH_3COOH	O_2	N_2	C_2H_4			
5	Pd	14	23	63	0	105	40	10.0, 10.5, 11.0 12.0, 12.5, 13.0 13.5
6	Pd	50	10	0	50	95	40	11.0, 12.4
7	Pd	10	10	0	80	130	20	Not detected
8	Pd-K[b]	19	21	65	0	105	5	11.0, 11.8, 12.0 12.5
9	Pd-K[b]	14	21	65	0	105	21	11.0, 11.8, 12.0
10	Pd-K[b]	14	21	65	0	130	20	Not detected

[a] Pd black; 2g, flow rate of gas; 3(l/hr).
[b] Pd:$KOCOCH_3$ = 50:1 (mole/mole).

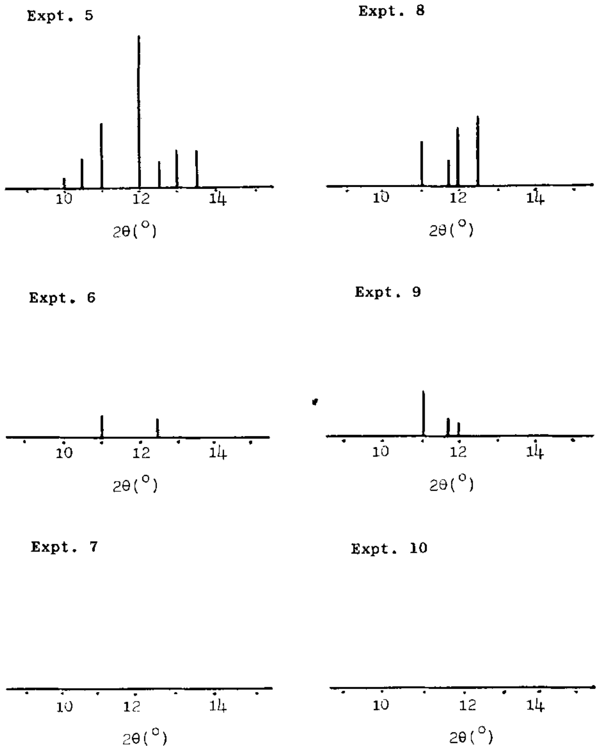

FIG. 1. X-Ray diffraction patterns of palladium black corresponded to Table 2.

and Fig. 1 (Expt. 5).* Even if ethylene was mixed in above gas, palladium(II) acetate was still detected under the lower partial pressure of ethylene (Expt. 6). Potassium acetate did not essentially disturb the formation of palladium(II) acetate, if man considered that potassium acetate could accelerate the thermal decomposition of palladium(II) acetate especially at higher temperature (Expt. 10 cf. Expt. 9). The presence of palladium(II) acetate in these reactions was also confirmed by ir spectra (620, 650, 695, 1420, 1575, and 1600 cm^{-1}) of Expts. 5 and 6. It is conclusive from these observations that palladium(II) acetate is surely produced under higher partial pressure of acetic acid and the lower partial pressure of ethylene as well as at lower temperature. As shown in Table 1, acetaldehyde was formed preferably under those conditions in which palladium(II) acetate was produced easily.

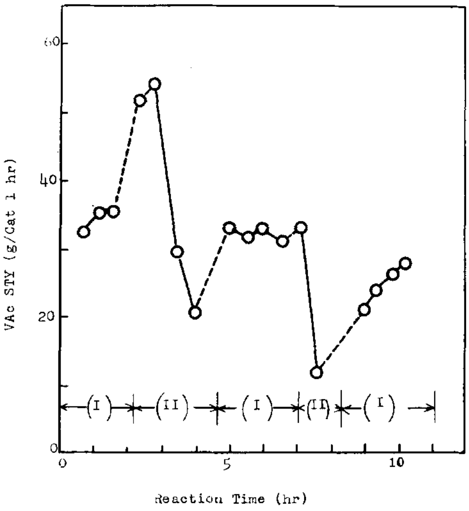

FIG. 2. Effect of partial pressure of acetic acid on catalytic activity: Catalyst; Pd, 1.5 wt % and $KOCOCH_3$, 3 wt % on Al_2O_3, SV; 1000(hr^{-1}), $C_2H_4:O_2:CH_3COOH$ = 80:10:10 (I), 50:10:40 (II), 100°C.

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* Stephenson *et al.* obtained the X-ray lines at $2\theta = 11.05$, 12.5 and 13.6 (10–~14°) as palladous acetate (*10*). Palladous acetate shows different X-ray diffraction patterns according to its preparation (*11*).

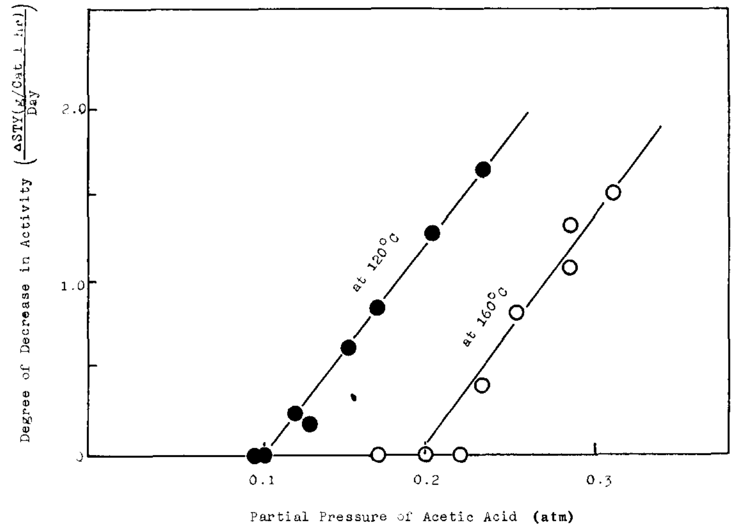

FIG. 3. Relation between partial pressure of acetic acid and decrease in catalytic activity. Catalyst; Pd, 1.0 wt % and $KOCOCH_3$, 3 wt % on Al_2O_3. $p\text{-}C_2H_4 + p\text{-}CH_3COOH + p\text{-}O_2 = 1\text{–}\sim 7$(atm), $p\text{-}O_2$; 0.08–∼0.10(atm) at 120°C, 0.15–∼0.20(atm) at 160°C.

Stability of Catalyst

Catalytic activity remarkably decreased with time when partial pressures of acetic acid and oxygen were higher as indicated in Figs. 2, 3, 4, and 5. The reaction temperature also greatly influenced the stability of a catalyst which could be maintained for a prolonged time at a higher temperature even under the higher pressure of acetic acid (Fig. 3). The decreased catalytic activity could be recovered by lowering the partial pressure of acetic acid or oxygen as shown in Figs. 2 and 4 at the initial stage of the reaction. On the other hand, when the reaction was carried out for a long time the decreased catalytic activity could not be recovered (Figs. 3 and 5). In this case the aggregation of palladium on the surface of the catalyst was observed as shown in Fig. 6 (A and B, however, it was not observed on C in contrast with D). Moreover, the aggregation of palladium on the surface of the catalyst was predominated when the catalyst was treated with

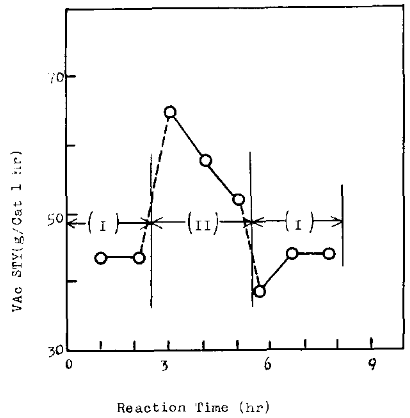

FIG. 4. Effect of partial pressure of oxygen on catalytic activity (short reaction time). Catalyst; Pd, 1.5 wt % and $KOCOCH_3$, 3 wt % on Al_2O_3, SV; 1000(hr^{-1}), $C_2H_4:O_2:CH_3COOH$ = 75:10:15 (I), 66:19:15 (II), 110°C.

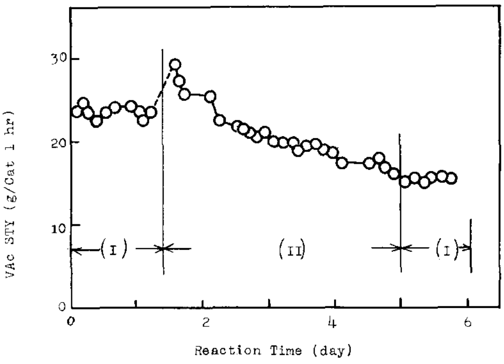

FIG. 5. Effect of partial pressure of oxygen on catalytic activity (long reaction time): Catalyst; Pd, 1.0 wt % and $KOCOCH_3$, 3 wt % on Al_2O_3, SV; 1000(hr^{-1}), $C_2H_4:O_2:CH_3COOH$ = 80:10:10 (I), 71:19:10 (II).

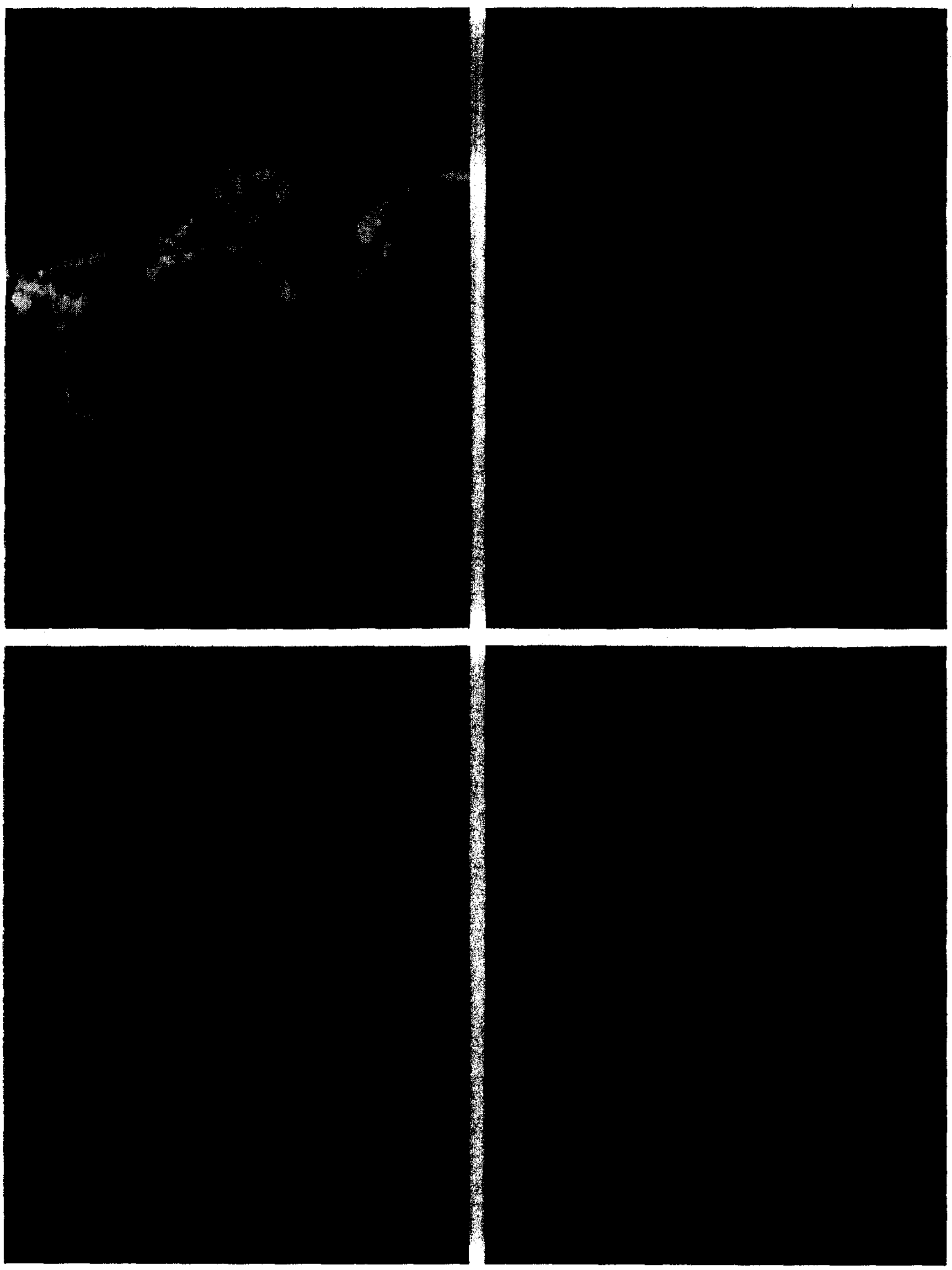

FIG. 6. Characteristic X-ray image of reacted catalyst. Catalyst; Pd, 1.0 wt % and $KOCOCH_3$, 3 wt % on Al_2O_3, SV; 1000(hr^{-1}), (a) after 12 days, total pressure; 5 atm; $C_2H_4:O_2:CH_3COOH = 85:5:10$, temp (av) 160°C; (b) after 15 days, total pressure; 6 atm; $C_2H_4:O_2:CH_3COOH = 89:5:6$, temp (av); 160°C; (c) after 20 days, total pressure; 5 atm; $C_2H_4:O_2:CH_3COOH = 90:5:5$, temp (av); 160°C; (d) before reaction.

a mixture of acetic acid and oxygen. It is suggested from these results that the formation of palladium(II) acetate may cause the aggregation of palladium and once the aggregation has occurred, the recovery of catalytic activity is difficult only by the change of the gas composition. Sirasaki *et al.* have reported that the aggregation of palladium easily occurs in the presence of palladium which is the higher oxidation state (*12*, *13*).

Our conclusion is that the catalytic activity in the production of vinyl acetate from ethylene is maintained only in those reaction conditions in which palladium(II) acetate does not exist, i.e., lower partial pressures of acetic acid and oxygen and at higher temperatures as well as the addition of large amounts of potassium acetate to a catalyst.

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