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SELECTIVE OXIDATION OF HYDROGEN IN CARBON MONOXIDE OVER PALLADIUM CATALYST

Part 1: Effect of Hydrogen Chloride

By

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(Received May 28, 1958)

Introduction

HORIUTI and WATANABE[1] found that the activity of palladium catalyst on the selective oxidation of hydrogen in carbon monoxide was remarkably enhanced by the addition of the small amount of hydrogen chloride into the reactant gas. HORIUTI *et al.*[2] also found by means of radioactive chlorine that hydrogen chloride readily reacted with the evapolated palladium film at the temperature of oxidation. Such results may suggest that a new active surface was created by the reaction of hydrogen chloride with palladium. It is the purpose of the present work to study at what state chlorine is deposited on the surface of the working catalyst and how it promotes the reaction. For this purpose, the present authors observed the promoter action of hydrogen chloride more in detail and investigated the working catalysts by means of the chemical analysis and electron diffraction.

§ 1 Experimental

Two kinds of the catalysts were used: one was "palladium black" prepared by the usual method.[3] To stabilize its catalytic activity, it was heated for five hours in the stream of hydrogen at 400°C and then preserved in a desiccator. Surface area of this catalyst measured by the BET method was 3.0 m^2/g. It was used for the activity test described later either without further treatment or after reducing it for four hours at 250°C in hydrogen. This palladium black without pretreatment is called "Pb-black-1" and that reduced "Pb-black-2".

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The other catalyst was "alkali free palladium catalyst", which was prepared by passing H_2 at 90°C through 1N-hydrochloric acid solution dissolving c. p. $PdCl_2$ until the solution became transparent and then by washing the precipitate with distilled water. The same heat treatment at 400°C and the same reduction at 250°C before use, as in the case of Pd-black-2, were performed also with this catalyst. Surface area of this catalyst was 0.2 m^2/g.

The activity of the catalyst was observed by the flow method in the presence or absence of hydrogen chloride. The reactant gas was the mixture of H_2, O_2 each from cylinder and CO prepared by the decomposition of formic acid. The gas mixture was passed through caustic soda solution, chemically pure hydrochloric acid in the case when mixed with hydrogen chloride and then through concentrated sulphuric acid in succession. The composition of the reactant gas and the gaseous product was determined by the Orsat method.

The content of Cl^-, Pd^{++} and K^+ on the surface of the working catalysts was chemically analysed as follows: as soon as the flow of the reactant gas was stopped, the catalysts were dropped into distilled water. Allowing it to stand overnight, as did by HORIUTI *et al.*,[2] the quantity of Cl^- and Pd^{++} leached out was determined colorimetrically using mercuric thiocyanate[4] and p-nitrosodimethylaniline[5] as the reagents, respectively, and K^+ volumetrically by means of hexanitrodiphenylamine sodium.[6] Trace of Pd^{++} was determined by order of magnitude by the spot analysis using p-dimethylaminobenzylidenrhodanine.[7]

Samples of catalyst for the investigation by electron diffraction were prepared by evacuating the catalyst for one hour after the reaction, cooling it down to room temperature and then immersing in benzene without bringing it into contact with air.

The reduction rate of $PdCl_2$ was determined by allowing the above mentioned reactant gas to flow through $PdCl_2$ at the similar condition as in the activity test of palladium catalyst, passing the resultant gas including HCl through 4–5 cc of 0.1 N caustic soda solution dissolving methyl red as indicator, until the color of methyl red changes from yellow to red.

§ 2 Experimental Results

1) The promoter action of hydrogen chloride

Fig. 1 and Fig. 2 show the results obtained with 0.3 g Pd-black-1

and 0.3 g Pd-black-2, respectively. The sign, (+) or (−), on the dotted verticals of the figures indicates the addition of HCl to reactant gas or its interruption. ΔCO or ΔH_2 on the ordinate is the percentage of oxidized CO or H_2. It is clearly seen from the figures that the addition of HCl accelerates the oxidation of H_2 and retards that of CO while

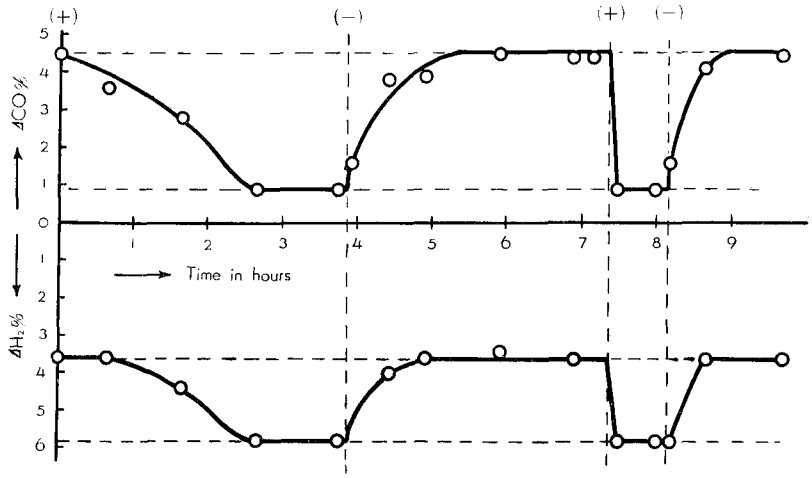

Fig. 1 Results of the activity test on Pd-black-1.
Weight of the catalyst, 0.300 g; length of the catalyst bed, 10 mm; reaction temperature, 250°C; flow rate of the reactant gas, 30 cc/min; composition of the reactant gas: H_2, 5.8%; O_2, 4.2%; CO, 90.0%.

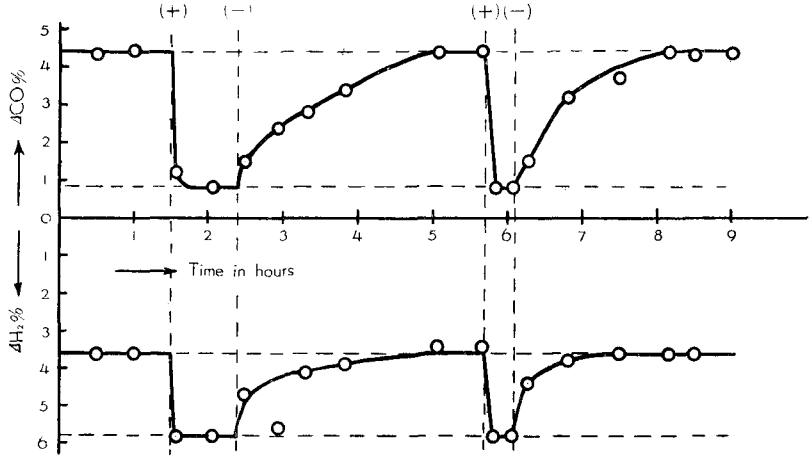

Fig. 2 Results of the activity test on Pd-black-2.
The conditions of the reaction are the same as in Fig. 1.

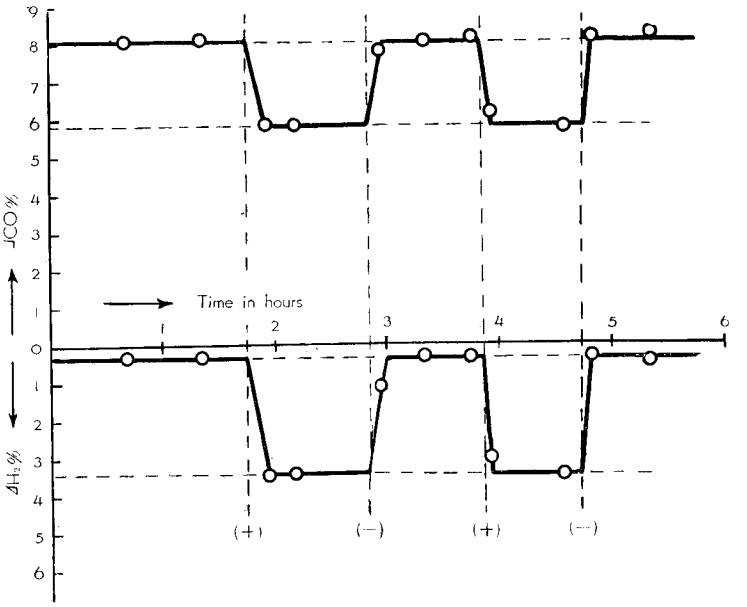

Fig. 3 Results of the activity test on the alkali free palladium catalyst. The composition of the reactant gas: H_2, 6.2%; O_2, 4.5%; CO, 89.3%. The other conditions are the same as in Fig. 1.

its interruption gives rise to the complete reversion to the original catalytic activity and that the activities of these two catalysts are appreciably the same at the stationary states of reaction attained respectively afetr the addition and interruption of HCl. However, it takes longer time for the activity of Pd-black-1 after the first addition of HCl to attain the stationary state than for that of Pd-black-2; *i.e.*, about two and half hours are required for Pd-black-1 while less than several minutes for Pd-black-2. In the second addition of HCl, there exists apparently no such difference. It is remarkable that these two palladium black catalysts, before the addition of HCl, give a similar catalytic activity irrespective of the pretreatment described before.

The results obtained with the alkali free palladium catalyst are illustrated in Fig. 3. The effect of HCl is distinctly observed in this case, too. The selectivity of this catalyst and the time required for the reversion of its activity, however, is much less than that of Pd-black-1 or Pd-black-2.

2) The results of chemical analysis

Table 1 shows the results of chemical analysis of Cl^-, Pd^{++} and K^+ in the catalysts used in experiments in the foregoing section. The latter catalysts were likewise treated as in the above experiments in the stream of N_2 or H_2 and similarly analysed in the respective cases. The analysis was performed after four hours of the reaction or the similar treatment, which is sufficient for the reaction to attain the stationary state. "Coverage by Cl^-" or "Coverage by K^+" in the Table is the ratio of the number of Cl^- or K^+ to that of the surface palladium atoms calculated from the assumption that (100), (110) and (111) plane are exposed on the surface, respectively, by the same amount. It follows from the result with Pd-black-2 that:

TABLE 1 Analytical results of Cl^-, Pd^{++} and K^+ on the surface of the catalysts

Experimental number	Catalyst	Reaction temperature °C	Weight of the catalyst (g)	Atmosphere	Add. of HCl (+) or its interrupt. (−)	Cl^- (mg)	Pd^{++} (mg)	K^+ (mg)	Coverage by Cl^-	Coverage by K^+
1	Pd-black-2	100	0.3	Reactant gas	+	1.0	0	—	1.7	—
2	〃	250	0.3	〃	+	0.5	0	—	0.9	—
3	〃	350	0.3	〃	+	1.0	0	—	1.7	—
4	〃	250	0.3	〃	−	0.3	0	—	0.5	—
5	〃	〃	0.3	〃	−	0.3	0	—	0.5	—
6	〃	〃	2.0	〃	+	25	10^{-2}	3.5	6.3	0.8
7	〃	〃	2.0	〃	+	25	10^{-2}	2.8	6.3	0.6
8	〃	〃	1.5	〃	+	5.0	0	0.7	1.7	0.2
9	〃	〃	1.5	〃	−	1.0	0	0.5	0.3	0.15
10	〃	〃	1.5	H_2	+	24	10^{-2}	—	8.0	—
11	〃	〃	0.3	〃	−	1.7	0	—	0.9	—
12	〃	〃	0.3	N_2	+	1.0	0.2	—	1.7	—
13	〃	〃	0.3	〃	−	0.6	0	—	1.0	—
14	Alkali free Pd catalyst	〃	0.3	Reactant gas	+	0	0	—	—	—
15	〃	〃	0.3	〃	−	0	0	—	—	—

i) The quantity of Cl^- amounts, in the presence of HCl, to the coverage from monoatomic to several atomic layer but decreases after interruption.

ii) The quantity of Pd^{++} is much less than that of Cl^- on the catalysts treated in the reactant gas and in H_2, but it amounts ca. ten times as much as in the latter cases when treated in N_2.

iii) A small amount of K^+ (0.17–0.03%) is always present in the catalyst.

iv) Even after the interruption of HCl, Cl^- is detected to comparable amount to that of K^+ in the catalyst.

No chlorine was detected in the alkali free catalyst within the accuracy of the analysis in both the cases of the presence and absence of HCl.

3) The observation by electron diffraction

The formation of palladium chloride as well as potassium chloride were confirmed directly through the observation of the catalyst by means of electron diffraction. Typical results obtained are shown in Fig. 4 and Table 2. The Debye-Scherrer rings obtained from Pd-black-2

TABLE 2 The observed values of the interplanar spacing and the relative intensities

Pd-black-2				Alkali free palladium catalyst				References[8]		
Sample 1		Sample 2		Sample 3		Sample 4		Pd	KCl	$PdCl_2$
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0			
—	—	—	—	—	—	—	—	—	—	5.3
(3.59)	v.w.	(3.54)	v.v.w.	—	—	3.54	v.w.	—	—	3.29
—	—	3.12	v.s.	—	—	—	—	—	3.14	—
(3.05)	v.w.	—	—	—	—	3.10	m.	—	—	3.11
—	—	—	—	—	—	—	—	—	—	2.39
—	—	—	—	—	—	—	—	—	—	2.25
2.22	s.	—	—	2.22	v.s.	—	—	2.23	—	—
—	—	2.22	v.s.	—	—	2.18	v.v.w.	—	2.22	—
1.97	w.	—	—	1.94	s.	—	—	1.94	—	—
—	—	—	—	—	—	—	—	—	—	1.93
—	—	—	—	—	—	1.88	v.s.	—	—	1.87
—	—	—	—	—	—	—	—	—	—	1.82
—	—	1.81	s.	—	—	—	—	—	1.81	—
—	—	—	—	—	—	1.77	v.v.w.	—	—	1.77
—	—	—	—	—	—	1.63	s.	—	—	1.64
—	—	—	—	—	—	—	—	—	—	1.61
—	—	1.57	m.	—	—	1.56	v.v.w.	—	1.57	1.57

Pd-black-2				Alkali free palladium catalyst				References[8]		
Sample 1		Sample 2		Sample 3		Sample 4		Pd	KCl	PdCl
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0			
—	—	—	—	(1.53)	v.w.	—	—	—	—	1.54
—	—	—	—	—	—	—	—	—	—	1.50
—	—	—	—	—	—	—	—	—	—	1.43
—	—	1.41	s.	—	—	—	—	—	1.40	—
1.39	w.	—	—	1.37	s.	1.35	w.	1.37	—	1.37
—	—	—	—	—	—	—	—	—	—	1.33
—	—	—	—	—	—	—	—	—	—	1.308
—	—	1.28	m.	(1.29)	v.w.	—	—	—	1.28	—
—	—	—	—	—	—	1.24	w.	—	—	1.250
—	—	—	—	—	—	—	—	—	—	1.208
1.18	w.	—	—	1.17	s.	1.16	v.v.w.	1.17	—	—
—	—	—	—	1.12	v.w.	—	—	1.120	—	1.124
—	—	1.11	v.w.	—	—	—	—	—	1.11	—
—	—	1.05	w.	—	—	—	—	—	1.05	—
—	—	0.990	v.w.	—	—	—	—	—	0.992	—
—	—	—	—	—	—	—	—	0.970	—	—
—	—	0.947	v.w.	—	—	—	—	—	0.947	—
—	—	—	—	—	—	—	—	—	0.906	—
0.887	v.w.	—	—	0.894	w.	—	—	0.891	—	—
—	—	0.867	v.v.w.	—	—	—	—	—	0.870	—
—	—	—	—	—	—	—	—	0.869	—	—
—	—	—	—	0.795	w.	—	—	0.793	—	—

relative intensities: v.s.>s.>m.>w.>v.w.>v.v.w.

are interpreted as being mainly of metallic palladium (Sample 1 in Table 2) and KCl crystal (Sample 2 in Table 2 and Fig. 4 (a)). The presence of $PdCl_2$ could not be definitely confirmed on this catalyst, although some unidentifiable weak rings were often observed, as shown by the interplanar spacing in parentheses in Table 2. In the case of the alkali free palladium catalyst, $PdCl_2$ was distinctly observed as illustrated in Sample 4 in Table 2 and Fig. 4 (b). However, there were sometimes observed in this case the patterns of metallic palladium alone or those of unknown substances besides palladium (Sample 3 and Fig. 4 (c)). Furthermore, very diffuse patterns were seldom observed as shown in Fig. 4 (d).

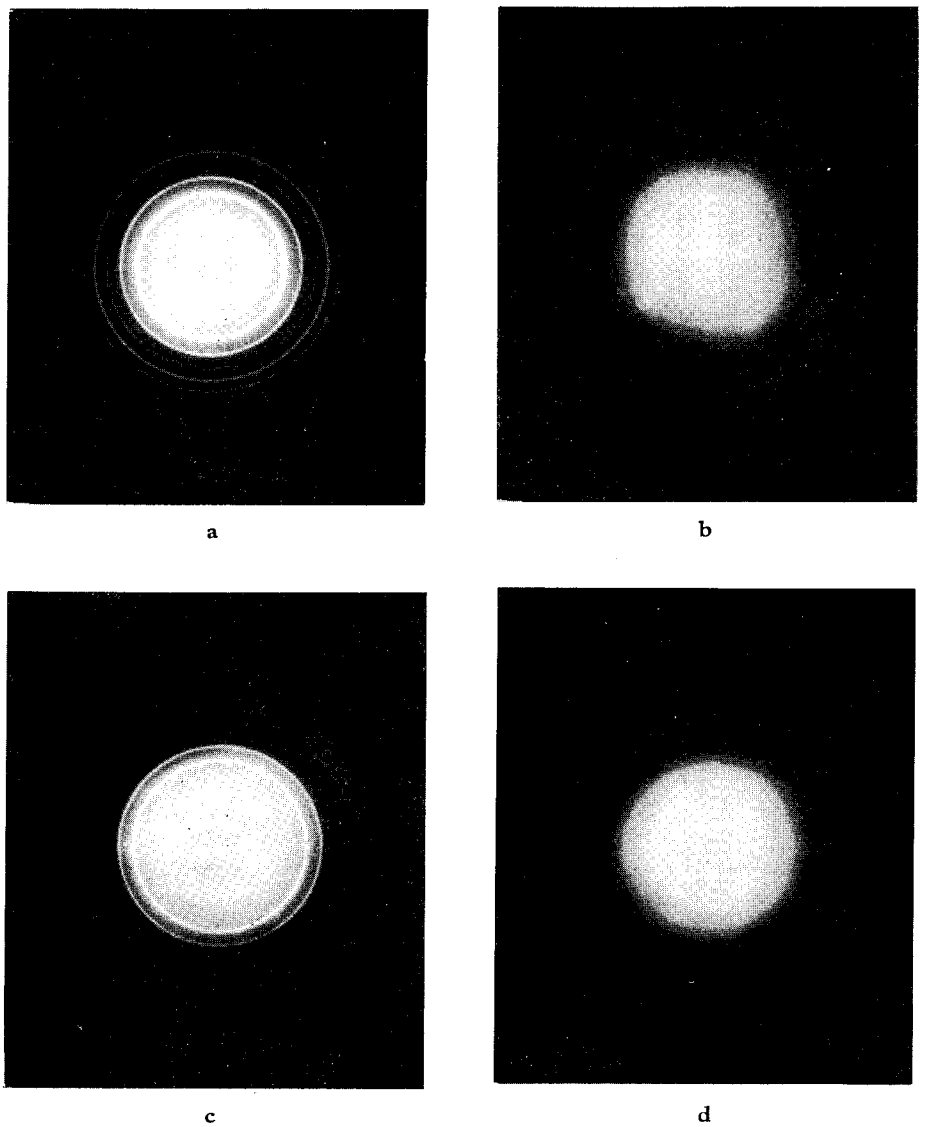

Fig. 4 Electron diffraction photographs of the catalysts.
(a): Photograph corresponding to Sample 2 in Table 2.
(b): " " " Sample 3 "
(c): " " " Sample 4 "
(d): Diffuse pattern obtained from the alkali free palladium catalyst.

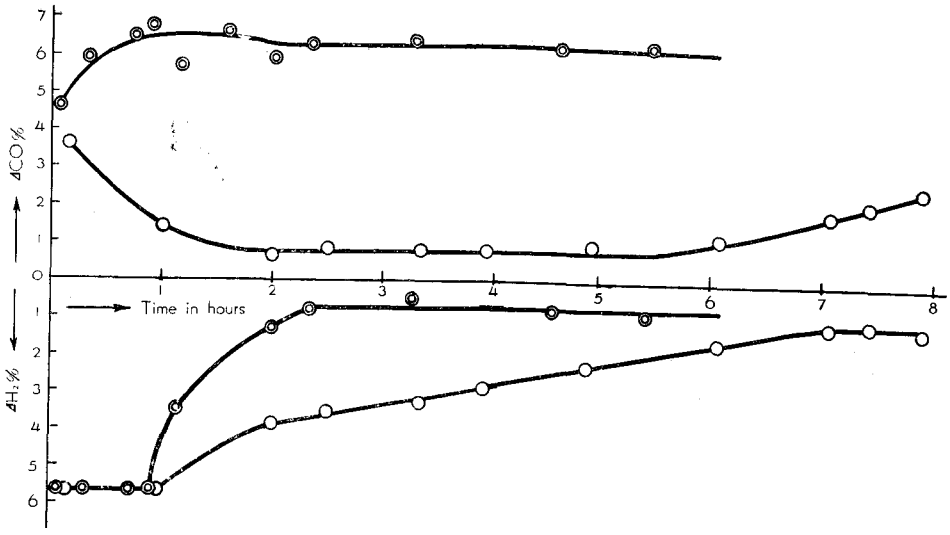

Fig. 5 Results of the activity test on pure $PdCl_2$.
Weight of $PdCl_2$, 0.500 g; reaction temperature, 250°C, flow rate of the reactant gas, 30 cc/min; composition of the reactant gas: H_2, 5.7%; O_2, 3.8%; CO, 90.5%; ○, in the presence of HCl; ◎, in the absence of HCl.

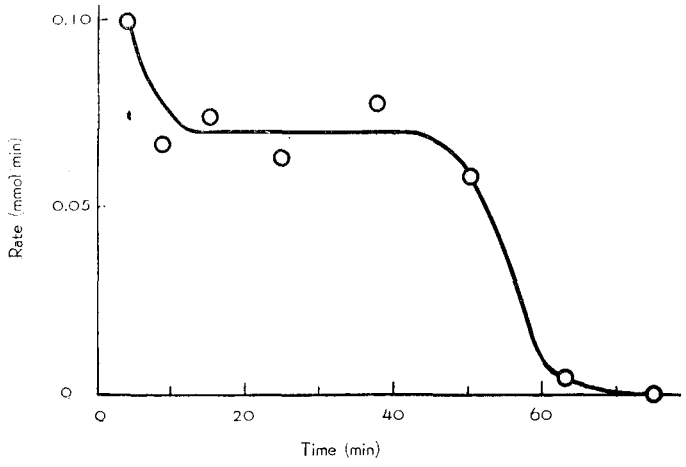

Fig. 6 Rate of the reduction of $PdCl_2$ (in HCl mmol/min) by the reactant gas.
The conditions of the reaction are the same as in Fig. 5.

4) Activity test on pure palladium chloride

Pure palladium chloride shown present on catalysts in the above observation was now investigated for its catalytic activity of the selective oxidation. Fig. 5 shows the results. H_2 was completely consumed for the first one hour of the reaction, but incompletely later, with an abrupt change in hydrogen consumption at the end of the first period irrespective as to whether HCl was present or not. The abrupt change was concerted by that of the formation rate of HCl by the reduction of $PdCl_2$ shown in Fig. 6 as observed separately under the same condition. It was found that the catalytic oxidation of H_2 occured concurrently for this first one hour as deduced from the observed formation rate of HCl always smaller than twice of the consumption rate of H_2 (0.14 mmol hydrogen atoms/min) and qualitatively also from water condenced on the wall of the reactor, despite that $PdCl_2$ was preliminarily dried at the reaction temperature in the stream of N_2 immediately before the above experiments.

After this initial one hour, the rate of the consumption of H_2 decreased gradually depending on the reaction condition as shown in Fig. 5: in the absence of HCl the catalytic activity attained to stationary value after about two hours from the beginning, whereas in its presence it takes much longer time to approach the stationary value. It should be noted that the selectivity of the catalyst continued to vary further, the rate of the oxidation of CO increasing after six hours even in the presence of HCl.

After the reaction shown in Fig. 5, Pd^{++} and Cl^- in the black product (metallic palladium) from palladium chloride used was chemically analysed with the same method described before. No Pd^{++} and Cl^- was detected whether HCl was added to the reactant gas or not. This may suggest that the surface area of the above product is small as well as that of alkali free palladium catalyst.

§ 3 Discussion

The formation of $PdCl_2$ on the catalyst was confirmed with the alkali free palladium catalyst, as observed by electron diffraction. This result is concerted by that of the chemical analysis that the amount of Cl^- on palladium black in working state is sufficient to form monoatomic or even several atomic layer. The latter result is apparently inconsistent with the deficiency of Pd^{++} found by chemical analysis.

This might be ascribed to the reduction of palladium chloride to metal during the chemical analysis by hydrogen sorbed in the catalyst, since $PdCl_2$ is, as well-known, readily reduced and moreover much more Pd^{++} is found when the catalyst was treated in N_2 than in H_2 or in the reactant gas. The small surface area ($0.2\,m^2/g$) of the alkali free palladium catalyst might be responsible for the result that Cl^- was not detected in this catalyst by the chemical analysis, although Cl^- must be present on account of the observed presence of $PdCl_2$ described above.

From these results and the interpretation it can safely be said that there exists generally $PdCl_2$ or adsorbed chlorine on the surface of the palladium catalyst in working state. It should be noted, however, that the stability of $PdCl_2$ on palladium surface is quite different from that of bulky $PdCl_2$, which is reduced at the same condition as mentioned before.

It was found that Cl^- was present on the surface of Pd-black-2 after the interruption of HCl. The amount of Cl^- thus present was approximately equal to that of K^+, while the presence of KCl crystal was confirmed by means of the electron diffraction. These results indicate that Cl^- except that combined with K^+ readily leaves palladium surface in the form of HCl, being reduced by H_2 in the reactant gas.

From these results, there may be no doubt that the following reaction occurs in either direction at least on a part of the catalyst surface at the working state,

$$Pd + 2HCl \rightleftarrows PdCl_2 + H_2$$

On the basis of this information and the result that the addition of HCl or its interruption causes the increase or decrease in the selectivity of the present catalysts, it may safely be said that H_2 is oxidized effectively on $PdCl_2$ formed or chlorine adsorbed on the catalyst surface.

However, the oxidation rate of CO is lower with Pd-black-1 or -2 than with the alkali free palladium catalyst in both the cases of the presnce and absence of HCl, despite that the total surface area of the former is much larger than that of the latter. Furthermore, the oxidation rate of CO, as seen in Fig. 5, increases, whereas that of H_2 decreases. These general feature on the selectivity of the catalysts would suggest that surface heterogeneity is playing an important part

in the selectivity of palladium catalyst on the present reaction.

It was found that there existed small amount of potassium ion in palladium black. The effect of potassium ion on the catalytic activity will be discussed in Part 2 of this report.

Summary

To elucidate the promoter action of hydrogen chloride on the palladium catalyst used for the selective oxidation of H_2 in CO, activities of two kinds of the catalysts, *i.e.*, "palladium black" and "alkali free palladium catalyst" were measured in the presence or absence of HCl and the properties of the working catalysts were investigated by means of electron diffraction and chemical analysis. From these experiments, the following results were obtained:

1) The quantity of Cl^- in the palladium black catalyst amounts, in the presence of HCl, to the coverage from monoatomic to several atomic layer, but decreases after the interruption of HCl.

2) The formation of $PdCl_2$ was directly confirmed with the alkali free palladium catalyst by means of electron diffraction.

3) The addition of HCl or its interruption caused the increase or decrease in the selectivity of the catalysts.

Acknowlegement

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