



# HOKKAIDO UNIVERSITY

Title	SELECTIVE OXIDATION OF HYDROGEN IN CARBON MONOXIDE OVER PALLADIUM BLACK : Part 2: Effect of Alkali
Author(s)	SATO, Toshio; ISHIZUKA, Kazuhiko
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 6(2), 138-145
Issue Date	1958-10
Doc URL	<a href="https://hdl.handle.net/2115/24677">https://hdl.handle.net/2115/24677</a>
Type	departmental bulletin paper
File Information	6(2)_P138-145.pdf



# SELECTIVE OXIDATION OF HYDROGEN IN CARBON MONOXIDE OVER PALLADIUM BLACK

## Part 2: Effect of Alkali

By

Toshio SATO and Kazuhiko ISHIZUKA <sup>\*)</sup>

(Received September 12, 1958)

### Introduction

As reported in Part 1,<sup>1)</sup> palladium black prepared by the usual method<sup>2)</sup> contains a small amount of potassium (0.17 to 0.03%) as an impurity. Since its catalytic activity was found to be much higher than that of "alkali free palladium catalyst" described in Part 1, it seems very likely that a trace of alkali which is difficult to be removed by the usual washing markedly enhances the activity of palladium black. The present investigation was carried out to confirm this by means of the activity test of the catalysts containing various amounts of alkali.

### § 1. Experimental

The apparatus and experimental procedures are the same as those reported in Part 1. The preparation of the catalysts are as follows.

*Catalyst No. 1:* After reducing palladium chloride by formaldehyde in KOH solution, the precipitate was washed by decantation until no more chlorine became detectable.<sup>2)</sup> Palladium black thus obtained was heated for five hours at 150, 400, 650°C, and for two hours at 1100°C, respectively, in hydrogen before use.

*Catalyst No. 2:* Catalyst No. 1 was immersed in 1N hydrochloric acid overnight, washed 4-5 times by decantation using 1N hydrochloric acid and then washed by distilled water. The precipitate was heated for five hours at 400°C in hydrogen before use. This procedure was adopted to remove alkali in Catalyst No. 1.

*Catalyst No. 3:* Catalyst No. 2 was treated as follows after its

---

\*) T. S. and K. I.: Research Institute for Catalysis, Hokkaido University.

activity test in the flow of reactant gas described below with a small amount of HCl. The addition of HCl to the reactant gas was interrupted leaving the catalyst in the flow of reactant gas for four hours later. The catalyst was then immersed into distilled water overnight and washed by distilled water. The catalyst thus freed from a trace of KCl,<sup>1)</sup> was dried and heated for five hours at 350°C in hydrogen before use.

*Catalyst No. 4:* Catalyst No. 2 was heated for fourteen hours more at 350°C in hydrogen.

*Catalyst No. 5:* "Alkali free palladium catalyst", which was prepared by reducing pure palladium chloride dissolved in 1N hydrochloric acid solution by passing hydrogen through it, was heated before use for five hours at 400°C in hydrogen.

*Catalyst No. 6:* Catalyst No. 1 was immersed in 1N KOH solution overnight, just filtered without washing by distilled water and heated for five hours at 200°C in hydrogen before use.

*Catalyst No. 7:* The catalyst was prepared under the same condition as in Catalyst No. 6, except immersed in 2N KOH solution instead.

## § 2. Results

Fig. 1-7 show the temperature dependency of the catalytic activity on the selective oxidation of H<sub>2</sub> in CO with the present catalyst. The dotted and solid lines in the figures indicate the activity data in the presence and absence of HCl in the reactant gas, respectively. In all cases, the weight of the catalyst used is 0.300 g, the flow rate of the reactant gas 30 cc/min and the composition of the reactant gas 5.0-6.2% of H<sub>2</sub>, 4.0-4.5% of O<sub>2</sub> and 91.0-89.9% of CO.

The results on Catalyst No. 1 treated at 150°C are illustrated in Fig. 1. In the absence of HCl, the reaction was perceptible at *ca.* 60°C and H<sub>2</sub> was completely oxidized at *ca.* 90°C. Further increase of the reaction temperature, however, resulted the decrease of selectivity of the reaction: the rate of the oxidation of H<sub>2</sub> decreased and that of CO increased. When HCl was added, the reaction started at higher temperature<sup>\*)</sup> and the selectivity increased remarkably. The effects of

\*) The similar tendency was also observed on palladium black preliminarily immersed in KOH solution (Catalyst No. 6 and No. 7) as shown in Fig. 6 and 7, while the opposite tendency on the catalysts of less or free from alkali (Catalyst Nos. 2, 4 and 5) as shown in Figs. 3, 4 and 5.

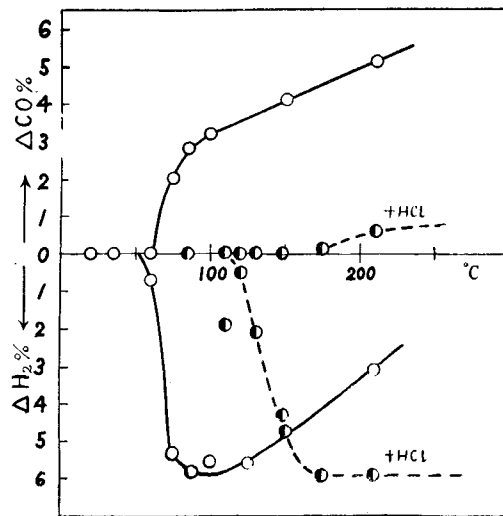


Fig. 1. The results on the activity test with Catalyst No. 1.

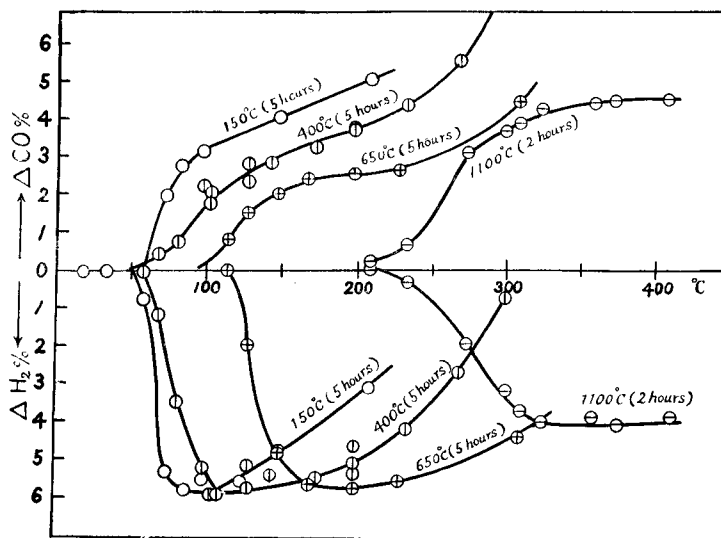


Fig. 2. The effect of the heat treatment on the activity of Catalyst No. 1.

the heat treatment with Catalyst No. 1 are shown in Fig. 2. The higher the temperature of the heat treatment, the lower was the catalytic activity. However, it should be remarked that the catalyst treated at 1100°C has, as described below, a comparable or even larger activity than the catalysts free from alkali, i. e., Catalysts from No. 2 to No. 5, which have been treated at much lower temperatures.

The results on Catalyst No. 2 and No. 3 are illustrated in Fig. 3 and those on Catalyst No. 4 and No. 5 in Fig. 4 and 5. As mentioned before, Catalyst No. 2 was prepared by washing Catalyst No. 1 with hydrochloric acid to remove potassium and then by heating it for five hours at 400°C in H<sub>2</sub>. The activity of this catalyst was definitely much less than that of Catalyst No. 1: H<sub>2</sub> was not oxidized completely even above 400°C in the absence of HCl. Catalyst No. 4, which was prepared by additional heat treatment of Catalyst No. 2 for a long time at 350°C, had much lower activity: H<sub>2</sub> could not be oxidized completely below 400°C even when HCl was added. Chemical analysis indicated that Catalyst No. 2 contained 3.6 mg Cl<sup>-</sup>/g-catalyst immediately after treated in the flow of reactant gas containing a small amount of HCl and 0.2 mg Cl<sup>-</sup>/g-catalyst after treated further in the flow without HCl addition

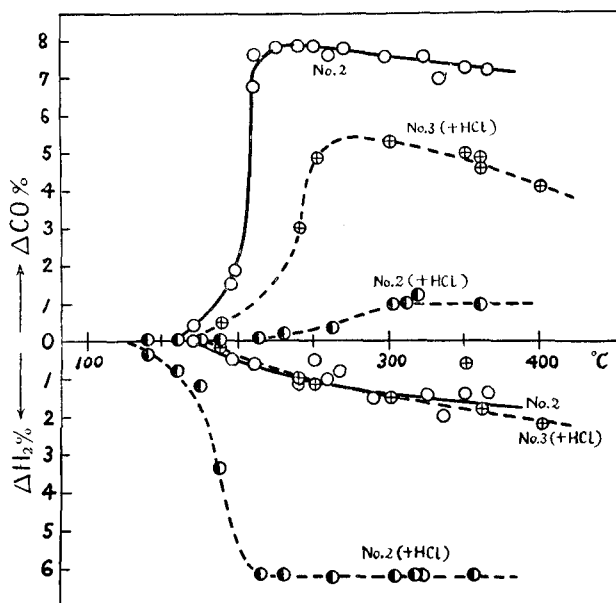


Fig. 3. The results on the activity test with Catalyst No. 2 and 3.

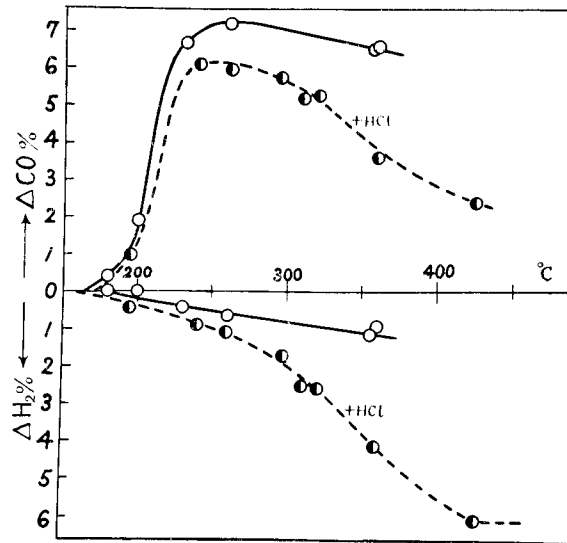


Fig. 4. The results on the activity test with Catalyst No. 4.

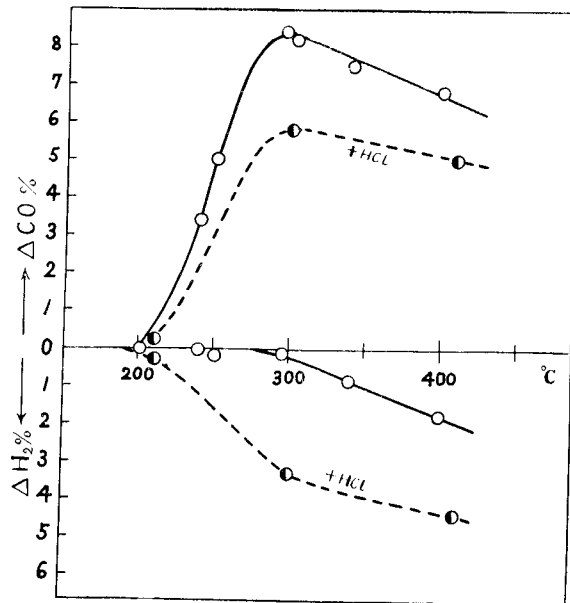


Fig. 5. The results on the activity test with Catalyst No. 5.

to the reactant gas for four hours. According to the results in Part 1,  $\text{Cl}^-$  detected in the latter case is  $\text{Cl}^-$  fixed as  $\text{KCl}$  by the reaction between  $\text{HCl}$  and potassium remained in the catalyst. This result may show that alkali in palladium black is difficult to be removed completely even by washing it with hydrochloric acid.\*) Catalyst No. 3 freed from the trace of  $\text{Cl}^-$  as described above was of much less activity than Catalyst No. 4:  $\text{H}_2$  could not be oxidized completely even when  $\text{HCl}$  was added and the reaction temperature was raised above  $400^\circ\text{C}$ . The alkali free palladium catalyst (Catalyst No. 5) had as low activity as Catalyst No. 3 (Fig. 5). It is clear from the inspection of the relation between the activity and the preparation of Catalyst No. 1-5 that the catalyst activity depends sensitively on the amount of potassium present.

For contrast with the above-mentioned experiments, potassium was deliberately added to palladium black. The results obtained on such catalyst are illustrated in Fig. 6 and 7. Palladium black immersed in 1N  $\text{KOH}$  solution (Catalyst No. 6) was slightly of less activity than Catalyst No. 1, that immersed in 2N  $\text{KOH}$  solution (Catalyst No. 7) was found of far less activity than Catalyst No. 1. The following Table shows the lowest temperature at which the oxidation of  $\text{H}_2$  in  $\text{CO}$  is perceptible without  $\text{HCl}$  as well as the magnitude of the specific surface area of the present catalysts.

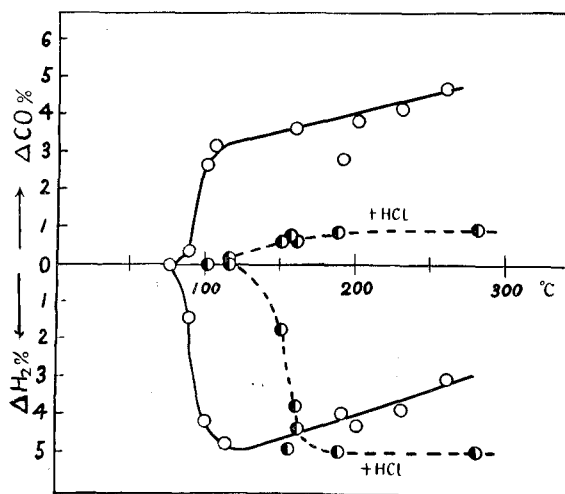


Fig. 6. The results on the activity test with Catalyst No. 6.

\*) Alkali can still be detected spectroscopically also in platinum black washed with hydrochloric acid and then by water for several days (Ref. 3).

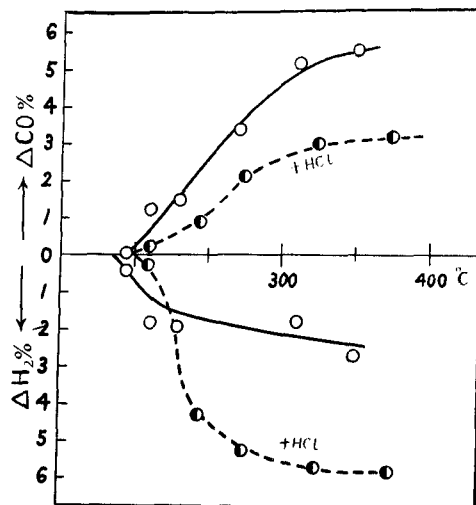


Fig. 7. The results on the activity test with Catalyst No. 7.

TABLE. The lowest temperature of oxidation of H<sub>2</sub> in CO and specific surface area of the catalysts.

Kind of palladium black catalyst No.	Condition of the heat treatment		Surface area m <sup>2</sup> /g	Temp. of the reaction °C
	Time (hours)	Temp. (°C)		
1 (usual)	5	150	—	55
1 "	5	400	2.6	60
1 "	5	650	—	110
1 "	2	1100	—	210
2 (of less alkali)	5	400	1.2	160
4 "	5 (14) *)	400 (350) *)	—	180
5 (alkali free)	5	400	0.2	230
6 (alkali rich)	5	200	—	80
7 "	5	200	—	180

\*) Figures in parentheses indicate the time interval or temperature of the additional heat treatment on Catalyst No. 2.

It is seen from this Table that the surface area decreases along with decrease of alkali content.

### § 3. Concluding Remarks

It was found that the activity as well as the surface area of pal-

ladium black markedly decreases along with decrease of potassium content. It is concluded, therefore, that one of the important effects of alkali in palladium black is to retard the sintering of the palladium particles.

It was found, furthermore, that the activity of palladium black also decreases by addition of excess alkali. This may be attributed to the coverage of surface by non-active alkali. It is therefore concluded that a certain trace of potassium introduced unintentionally during the usual preparation is essential to maintain the high activity and stability of palladium black.

### Summary

In order to elucidate the effect of a trace of alkali in palladium black, catalysts containing various amounts of alkali were subjected to activity test with respect to the selective oxidation of  $H_2$  in CO. It was thus found that the activity of palladium black decreased markedly in case of alkali either added in excess or exhaustively removed. It was also found that the surface area of the catalysts decreased along with decrease of alkali content. From these results, it is concluded that alkali keeps palladium black from sintering although catalytically inactive itself.

### Acknowledgement

Present authors wish to express their sincere thanks to Prof. J. HORIUTI, Director of Institute and Prof. T. KWAN for their valuable discussion in the present study.

### References

- 1) T. SATO and K. ISHIZUKA, this Journal **6**, 1 (1958).
- 2) A. FARKAS and H. W. MELVILLE, *Experimental Methods in Gas Reaction*, p. 338 (1939).
- 3) G. B. TAYLOR, G. B. KISTIAKOWSKY and H. H. PERRY, *J. Phys. Chem.* **34**, 748, 799 (1930).