Partial Hydrogenation of 1, 4-Butynediol. II. On the Role of Calcium Carbonate as a Carrier of the Palladium Catalyst

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As previously reported[1], when palladium–calcium carbonate catalyst was poisoned by lead acetate, the activity for the hydrogenation of 1,4-butenediol decreased with increasing amount of lead acetate, but was not suppressed completely. When it was poisoned by quinoline, the activity for the hydrogenation of 1,4-butenediol disappeared almost completely, while that for the hydrogenation of 1,4-butynediol decreased only slightly. On the other hand, when Pd-$CaCO_3$ catalyst was poisoned by pyridine or piperidine, the activity for the hydrogenation of 1,4-butenediol decreased only to some extent and did not disappear. When the Pd-$CaCO_3$ catalyst poisoned by lead acetate was poisoned furthermore by quinoline, similar results were obtained. Consequently, it has been shown that the partial hydrogenation of 1,4-butynediol can be achieved by using the Pd-$CaCO_3$ catalyst with quinoline.

However, it is well-known that the properties of a catalyst occasionally depend upon the kind of the carrier on which it is deposited[2]. Accordingly, the selectivity of the catalyst would also be associated with the kind of the carrier. Therefore, the effect of calcium carbonate as a carrier was studied in the hydrogenation of 1,4-butynediol. This paper describes the experimental results and the consideration on the role of calcium carbonate as a carrier of Pd-$CaCO_3$ catalyst.

Experimental

The same apparatus as previously described was employed[1].

1,4-Butynediol was recrystallized several times from ethyl acetate. Commercial hydrogen was used. Calcium carbonate, active charcoal, alumina, silica gel, and Kieselguhr were all obtained from the commercial products. Barium carbonate and barium sulfate were prepared from barium chloride and sodium carbonate and sulfuric acid, respectively.

Various catalysts were prepared from aqueous solutions of palladium (II) chloride by H. Lindler's method[3].

Twenty cc. of an aqueus solution of 0.34 g. of 1,4-butynediol was used. The hydrogenation experiments were carried out at 25°C and at about the atmospheric pressure, with 200 turns oscillation, using 0.3—0.6 g. of the catalyst.

Results and Discussion

With various catalysts the whole hydrogenation of 1,4-butynediol took place in two distinct steps at room temperature. The first step is the hydrogenation of 1,4-butynediol to 1,4-butenediol and the second is that of the latter to 1,4-butanediol, as shown in the previous paper[1].

The absorbing velocity of hydrogen depended upon the kind of the carrier

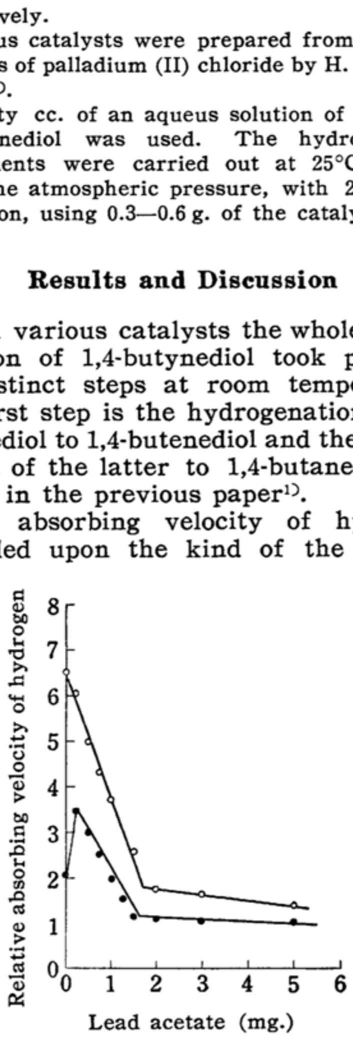

Fig. 1. The poisoning effect of lead acetate on the activities of Pd-$CaCO_3$ catalyst, at 25°C.

Pd-$CaCO_3$ catalyst (Pd, 5%) 0.3 g.
1,4-butynediol solution 20 (1,4-butynediol, 0.34 g.)

●: the effect on the hydrogenation of 1,4-butynediol
○: the effect on the hydrogenation of 1,4-butenediol

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[1] T. Fukuda and T. Kusama, This Bulletin **31**, 339 (1958).

[2] N. D. Zelinsky and A. A. Balandin, *Z. Phys. Chem.*, **126**, 267 (1927); T. Sabalitschka and K. Moses, *Ber.*, B. **60**, 786 (1927); J. T. McCartney, W. K. Hall and L. T. E. Hofer, *Ind. Eng. Chem.*, **39**, 1618 (1947); A. Wheeler, "Catalysis", Vol. 2, p 110 (1950).

[3] H. Lindler, *Helv. chim. Acta*, **35**, 446 (1952).

used, as shown in Table I. The activity of Pd-$CaCO_3$ catalyst was not the highest.

When 1.0 cc. each of aqueous solutions of lead acetate, containing various amounts of lead acetate, was added to the reactant prior to hydrogenation, the activity of Pd-$CaCO_3$, Pd-$BaCO_3$, Pd-alumina, and Pd-$BaSO_4$ catalyst decreased with increasing amount of lead acetate, as shown in Figs. 1~4. That is, when Pd-$CaCO_3$ and Pd-$BaCO_3$ catalyst were poisoned by increasing amount of lead acetate, the activity for the hydrogenation of 1,4-butynediol increased at first, and then decreased as the poisoning proceeded. On the other hand, that for 1,4-butenediol monotonously

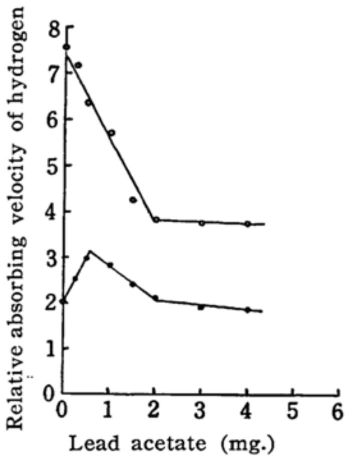

Fig. 2. The poisoning effect of lead acetate on the activities of Pd-$BaCO_3$ catalyst, at 25°C.
Pd-$BaCO_3$ catalyst (Pd, 3%) 0.3 g.
1,4-butynediol solution 20 cc. (1,4-butynediol, 0.34 g.)
●: the effect on the hydrogenation of 1,4-butynediol
○: the effect on the hydrogenation of 1,4-batenediol

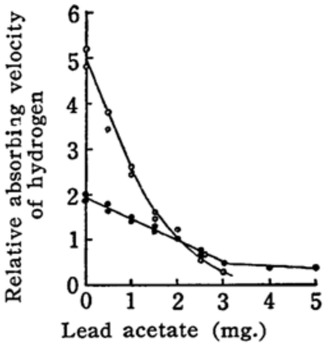

Fig. 3. The poisoning effect of lead acetate on the activities of Pd-alumina catalyst, at 25°C.
Pd-alumina catalyst (Pd, 5%) 0.3 g.
1,4-butynediol solution 20 cc. (1,4-butynediol, 0.34 g.)
●: the effect on the hydrogenation of 1,4-butynediol
○: the effect on the hydrogenation of 1,4-butenediol

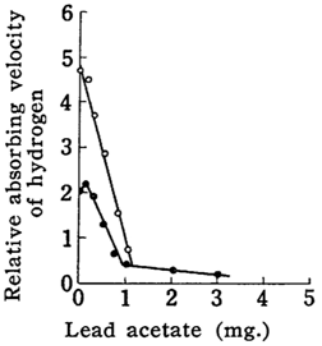

Fig. 4. The poisoning effect of lead acetate on the activities of Pd-$BaSO_4$ catalyst, at 25°C.
Pd-$BaSO_4$ catalyst (Pd, 5%) 0.3 g.
1,4-butynediol solution 20 cc. (1,4-butynediol, 0.34 g.)
●: the effect on the hydrogenation of 1,4-butynediol
○: the effect on the hydrogenation of 1,4-butenediol

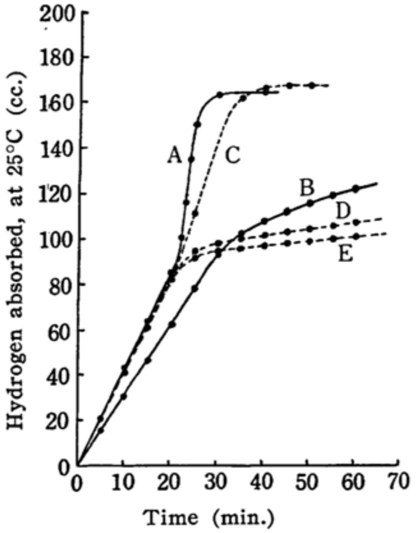

Fig. 5. The poisoning effect of quinoline on the activity of Pd-$BaCO_3$ catalyst, at 25°C.
Pd-$BaCO_3$ catalyst (Pd, 3.5%)
1,4-butynediol solution
A: no poison was added
B: quinoline (0.3 cc.) was added
C: lead acetate (3 mg.) was added
D: lead acetate (3 mg.) and quinoline (0.3 cc.) was added
E: lead acetate (5 mg.) and quinoline (0.3 cc.) was added

TABLE I

THE ABSORBING VELOCITY OF HYDROGEN, AT 25°, IN THE HYDROGENATION OF 1,4-BUTYNEDIOL ON THE VARIOUS CATALYSTS

Catalysts	Pd-content (% by wt.)	Used amt. (g.)	Absorbing velocity of hydrogen, per 10 min. (at 25°C)	
			1st step (cc., N.T.P.)	2nd step (cc., N.T.P.)
Pd-CaCO$_3$	5	0.3	18∼20	46∼ 59
〃	2	0.6	17∼19	75∼ 91
Pd-BaCO$_3$	3.5	0.3	36∼37	163∼174
〃	2	0.6	32∼34	156∼169
Pd-Alumina	5	0.3	16∼20	35∼ 46
〃	2	0.6	12∼14	27∼ 31
Pd-Charcoal	5	0.3	26∼28	92∼101
Pd-Kieselguhr	5	0.6	14∼16	38∼ 39
Pd-BaSO$_4$	5	〃	18∼20	38∼ 40
〃	3.5	〃	15∼16	33∼ 35
Pd-Silica-gel	3.5	〃	17∼18	35∼ 37

TABLE II

THE VOLUME OF HYDROGEN ABSORBED IN THE HYDROGENATION OF 1,4-BUTYNEDIOL ON THE VARIOUS CATALYSTS

Catalysts*	(Pd-content)	Poisons	(amt.)	Absorbing volume of hydrogen per 0.3 g. of 1,4-butynediol, at 25°C			
				1st step (cc., N.T.P.)	2nd step (cc., N.T.P.)	total volume (cc., N.T.P.)	%**
Pd-CaCO$_3$	(5%)	none	—	83	68	151	85.4
〃	〃	lead-acetate	(1 mg.)	85	83	168	95.0
〃	〃	〃	(5 〃)	〃	〃	〃	〃
〃	〃	piperidine	(0.3 cc.)	〃	〃	〃	〃
〃	〃	quinoline	〃	87	—	—	49.6
Pd-BaCO$_3$	(3.5%)	none	—	84	67	151	85.4
〃	〃	lead-acetate	(1 mg.)	85	69	154	87.0
〃	〃	〃	(5 〃)	〃	〃	〃	〃
〃	〃	piperidine	(0.3 cc.)	87	72	159	89.9
Pd-Charcoal	(5%)	none	—	76	69	145	82.0
〃	〃	lead-acetate	(1 mg.)	78	67	〃	83.1
〃	〃	piperidine	(0.3 cc.)	70	88	158	89.3
Pd-Alumina	(5%)	none	—	82	74	156	88.2
〃	〃	lead-acetate	(1 mg.)	〃	〃	〃	〃
〃	〃	piperidine	(0.3 cc.)	78	90	168	95.0
Pd-BaSO$_4$	(5%)	none	—	84	79	163	92.1
〃	〃	lead-acetate	(1 mg.)	88	82	170	96.0
Pd-Kieselguhr	(5%)	none	—	85	73	158	89.3

* 0.3 g. of the catalyst was used in all the experiments.

** Calculated adsorption (177 cc., N.T.P.) was taken as 100%.

decreased with increasing amount of lead acetate. When Pd-alumina catalyst was poisoned by lead acetate, its catalytic activity for both steps of the hydrogenation decreased monotonously. Pd-charcoal catalyst (Pd, 1∼5% by weight) was not affected by lead acetate in the experimental range (1∼5 mg. of lead acetate to 0.3 g. of the catalyst).

When 0.3 cc. of piperidine or quinoline was added to the reactant, the hydrogenation proceeded as shown in Figs. 5∼7 with Pd-BaCO$_3$, Pd-charcoal, and Pd-alumina catalyst, respectively. The activity of Pd-CaCO$_3$ catalyst was diminished by quinoline, but the effect of quinoline was small for the hydrogenation of 1,4-butynediol and relatively great for that

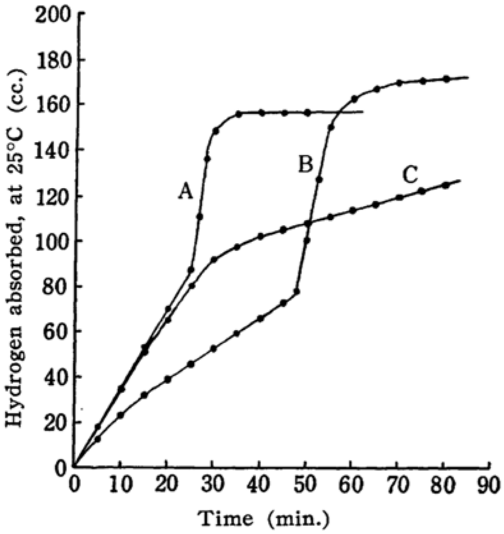

Fig. 6. The poisoning effect of piperidine and quinoline on the activity of Pd-charcoal catalyst, at 25°C.

Pd-charcoal catalyst (Pd, 5%)	0.3 g.
1,4-butynediol solution	20 cc. (1,4-butynediol, 0.34 g.)

A: no poison was added
B: piperidine (0.3 cc.) was added
C: quinoline (0.3 cc.) was added

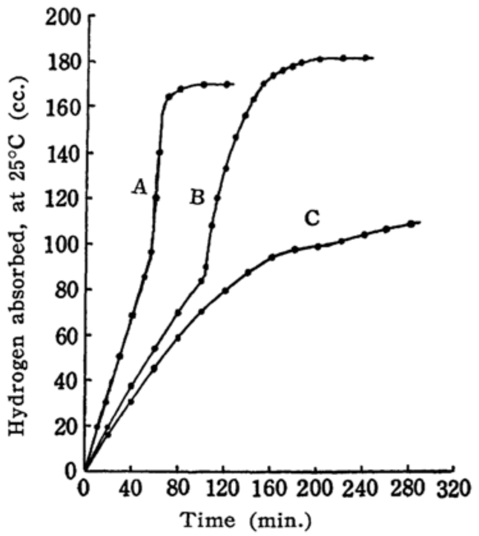

Fig. 7. The poisoning effect of piperidine and quinoline on the activity of Pd-alumina catalyst, at 25°C.

Pd-alumina catalyst (Pd, 5%)	0.3 g.
1,4-butynediol solution	20 cc. (1,4-butynediol, 0.34 g.)

A: no poison was added
B: piperidine (0.3 cc.) was added
C: quinoline (0.3 cc.) was added

of 1,4-butenediol. On the other hand, the activity of Pd-$BaCO_3$ catalyst was not diminished by piperidine. The activity of Pd-alumina catalyst for the hydrogenation of 1,4-butynediol was more markedly diminished by piperidine and by quinoline, and that for the hydrogenation of 1,4-butenediol was markedly diminished, especially by quinoline. When Pd-charcoal catalyst was poisoned by piperidine, the activity for the hydrogenation of 1,4-butynediol markedly decreased, and that for the hydrogenation of 1,4-butenediol remained almost unchanged. When it was poisoned by quinoline, however, the former was not changed much on the contrary, while the latter decreased markedly.

When Pd-$BaCO_3$ catalyst was used with lead acetate and quinoline, the hydrogenation proceeded as shown by dotted lines in Fig. 2. Its activity for the hydrogenation of 1,4-butenediol was suppressed much remarkably than when quinoline alone was used, while that for the hydrogenation of 1,4-butynediol did not change substantially.

As the properties of the catalyst depend upon the kind of the carrier, it is considered that the effect of the poisons varies complicatedly with the kind of the carrier. But it should be noticed that the partial hydrogenation of 1,4-butynediol might also be achieved by using the Pd-$BaCO_3$ catalyst poisoned by both lead acetate and quinoline, though it would not be in the same manner as in the case of Pd-$CaCO_3$ catalyst.

The volume of hydrogen absorbed during the hydrogenation depended upon the kind of the carrier and the poison added to the catalyst. The results are shown in Table II. The volume absorbed was relatively large in the case of the poisoned Pd-$CaCO_3$ catalyst.

According to the previous research, the catalytic hydrogenation of acetylene always causes the acetylene polymerization as its side reaction.[4] The polymerization may be depressed if the catalyst is poisoned[5]. The polymerization may be accompanied with the decrease of the absorbing volume of hydrogen. It is thus considered that 1,4-butynediol also polymerizes during the hydrogenation. Accordingly, the variation of the absorbed volume of hydrogen as observed may be

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[4] K. Tamaru, This Bulletin, **23**, 64, 180, 184 (1950).
[5] M. Sato and N. Ota, *Catalyst*, **12**, 45 (1955); T. Yamanaka; *J. Scientific Research Institute*, **29**, 319 (1948).

attributed to 1,4-butynediol polymerization. It seems that the role of calcium carbonate as a carrier consists in suppressing the polymerization with the poisons, but not in increasing the hydrogenating activity, nor in giving the selectivity for the hydrogenation.

Summary

1. The role of calcium carbonate as carrier of the palladium catalyst was studied in the hydrogenation of 1,4-butynediol.

2. The hydrogenation velocity on Pd-$CaCO_3$ catalyst was not the highest among various palladium catalysts. And the partial hydrogenation of 1,4-butynediol might also be achieved by using the Pd-$BaCO_3$ catalyst poisoned by both lead acetate and quinoline. On the poisoned Pd-$CaCO_3$ catalyst, however, the 1,4-butynediol porimerization, a side reaction of the hydrogenation, was suppressed largely.

3. Consequently, it seems that the role of calcium carbonate as a carrier is to decrease the polymerization as a side reaction of the hydrogenation, but not to increase the activity for the hydrogenation, nor to give the selectivity for the hydrogenation.

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