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Palladium–Carbon Hydrogenolysis Catalysts: The Effect of Preparation Variables on Catalytic Activity

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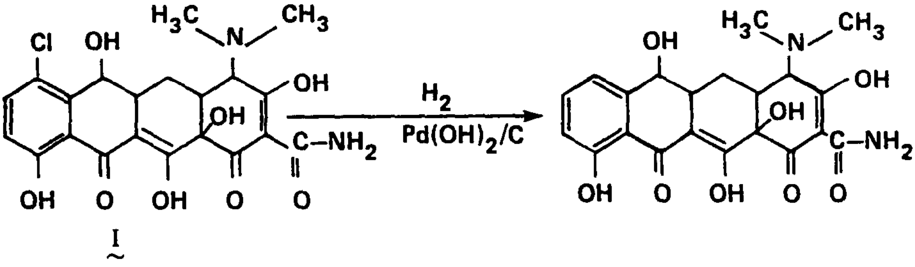
Supported palladium hydroxide has been identified as the active component (or its shelf-stable precursor) of a palladium/carbon catalyst used in the hydrogenolysis of aryl halides. The most conclusive evidence comes from a combination of thermogravimetric analysis and radiotracer experiments using tritium. A designed study indicates that the Pd source and control of the preparation temperature are the most important catalyst fabrication variables with the relative importance of the other variables depending on the Pd salt used. Deposition of aqueous Pd species onto the carbon support prior to formation of $Pd(OH)_2$ is accompanied by some reduction of Pd^{II} to inactive Pd^0. This can be minimized by the use of low fabrication temperatures, use of Pd^{IV} rather than Pd^{II} salts and/or by minimizing the time of contact of Pd and carbon prior to addition of base.

I. INTRODUCTION

Although it is widely recognized that the properties of heterogeneous catalysts are greatly dependent on the method of catalyst preparation, few systematic studies of the effect of preparation variables on activity have been reported for noble metal systems (*1*, *2*). A notable exception is the recent work by Palmer and Vannice on supported platinum catalysts (*3*).

In the work described here, we have demonstrated that $Pd(OH)_2/C$ is an active catalyst (or its precursor) for the selective hydrodechlorination of 6-demethylchlorotetracycline under mild reaction conditions.



Because of the nature of this catalyst, complete characterization by routine methodology was not possible but the rate of hydrogenolysis is sufficiently sensitive to the method of catalyst preparation so that a direct correlation of activity and catalyst preparation variables could be obtained. These results are presented here.

II. METHODS

All reagents were obtained commercially and were used without further purification. The powdered carbon used for all catalysts was prepared as described in Ref. (*4*). It had a N_2 BET surface area of ~450 m^2/g, a pore volume of 0.85 cm^3/g, and a particle

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size of less than 149 μm.

TEM work was performed on catalyst samples which had been embedded in epoxy resin and sectioned. An RCA EMA 37 transmission electron microscope was used. Additional analyses were performed using a DuPont 950 thermogravimetric analyser coupled with a DuPont 990 thermal analyser, an ORTEC TEFA EDX apparatus, a Rigaku computerized X-ray diffractometer, and a Packard 3375 liquid scintillation spectrometer.

Preparation of $Pd(OH)_2/C$. $Pd(NO_3)_2$ (1.3 g, 5.6 mmol, 0.6 g Pd) was added to 300 ml deionized water at 23°C. The solution was cooled to 5°C and 20 g C support was added. Aqueous KOH (10%) was added dropwise until the pH reached 9. The resulting slurry was filtered through sintered glass and the catalyst cake was washed with several 150 ml portions of 80°C water. The catalyst was air dried to 50% wetness and stored in a tightly capped container until use.

The catalysts used in the factorial design series were prepared in a similar manner using the conditions listed in Table 1. EDX analyses indicated a 3 wt% loading of palladium (*5*).

Hydrogenolysis of 6-demethylchlorotetracycline (I). The $Pd(OH)_2/C$ catalyst (1.7 g, 50% wet; 0.24 mmol Pd) was added to 5 ml ethyleneglycol monomethyl ether in a 500 ml Parr bottle. To this catalyst slurry was added a solution containing 23 g I-HCl (46 mmol) in 89 ml ethyleneglycol monomethyl ether and 21 ml triethylamine. The Parr bottle was then attached to a Parr hydrogenation apparatus. The water-jacketed bottle was purged with hydrogen, pressurized to 45 psig, and the consumption of hydrogen at 30°C was monitored with time. The pressure was maintained between 30 and 45 psig during this procedure and catalysts were compared on the basis of total hydrogen consumption over a 20-min reaction period. Typical data are presented in Table 1. The resulting solutions were also analyzed by HPLC. Greater than 95% selectivity to the dechlorinated product was always observed.

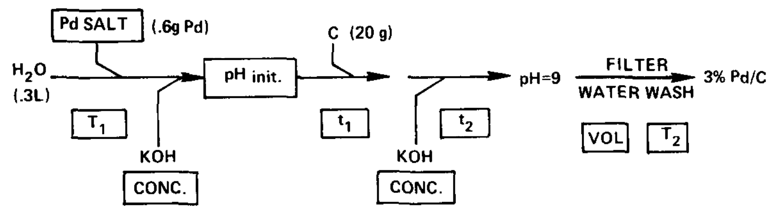
Thermogravimetric analysis. The palladium–carbon catalyst (50–60 mg, ~50% wet) was placed in the thermogravimetric analyser and allowed to dry under flowing N_2 (~10 cm³/min) overnight. TGA was conducted in a N_2 atmosphere at a heating rate of 10°C/min.

TABLE 1

Effect of Preparation Conditions on the Activity of 3% Pd/C Catalysts Prepared from $Pd(OAc)_2$ and K_2PdCl_4

Run	Variables							Hydrogenolysis activity	
	Temperature	$pH_{init.}$	Adsorption time (t_1)	Time at pH 9(t_2)	Wash vol.	Wash temp.	KOH conc.	$Pd(OAc)_2$ 20 min H_2 uptake (psig)	K_2PdCl_4 20 min H_2 uptake (psig)
A	−	−	−	+	+	+	−	7	14
B	+	−	−	−	−	+	+	17	22
C	−	+	−	−	+	−	+	1	3
D	+	+	−	+	−	−	−	20	30
E	−	−	+	+	−	−	+	9	20
F	+	−	+	−	+	−	−	22	27
G	−	+	+	−	−	+	−	5	2
H	+	+	+	+	+	+	+	17	34
Variable	+ 5°C	2	5 min	5 min	0.5 liter	80°C	10%		
Values	− 80°C	5	30 min	30 min	1.0 liter	5°C	50%		

SCHEME 1



(V=VOLUME, T=TEMPERATURE, t=TIME)

Radiotracer experiments. Using a humidity chamber controlled at 47% relative humidity, an active 6% Pd/C catalyst was exposed to tritiated water vapor of known specific activity for 48 hr. This material was then stored in a desiccator over anhydrous calcium sulfate in a nitrogen atmosphere for 100 hr and the residual tritium determined by liquid scintillation measurements. As a control, a sample of the carbon support was treated in an identical manner. The catalyst sample contained 27% of the theoretical maximum amount of tritium based on an assumed structure of 6% $Pd(OH)_2/C$ (5.56 μg HTO/mg catalyst). The carbon support gave a total tritium incorporation of 0.42 μg HTO/mg carbon.

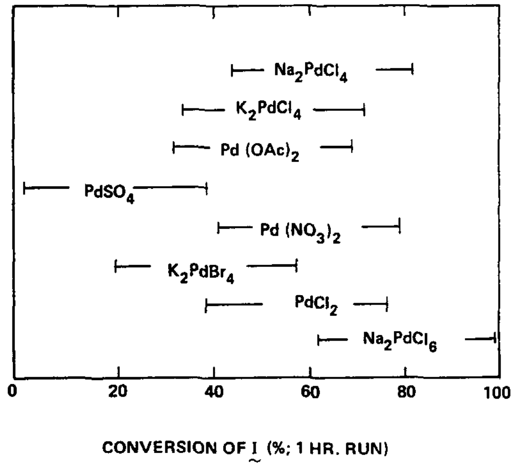


FIG. 1. Summary of the data obtained from the 2^{7-4} factorial series of catalyst preparations.

III. RESULTS AND DISCUSSION

A. *Factorial Study of Catalyst Preparation Variables*

The sequence of steps used in the preparation of $Pd(OH)_2/C$ resulted from initial orienting experiments and is illustrated in Scheme 1. The seven variables examined in detail are enclosed in boxes. A 2^{7-4} factorial design was used (*6*). The conditions for this series of preparations and results obtained with two Pd salts are summarized in Table 1.

Figure 1 shows the range of activities obtained in this series for each Pd salt used. Of the salts tested, $PdCl_2$, $Pd(NO_3)_2$, Na_2PdCl_4, and Na_2PdCl_6 gave the highest activities. The poor results obtained for $PdSO_4$ are due, at least in part, to its low solubility under the conditions used. Complete Pd deposition on the support was not obtained for this salt. $PdBr_2$ and PdI_2 are not usable under these conditions for the same reason.

The data in Table 2 summarize the relative importance of each of the procedural variables for each Pd compound tested. From these data it is clear that temperature is the single most important variable. Lower preparation temperatures are preferred in all cases. The relative importance of the remaining variables depends on the choice of Pd species.

It is reasonable that two factors are important in obtaining active catalysts: the ef-

TABLE 2

Relative Importance of Catalyst Preparation Variables

Palladium salt	Correlation coefficients						
	Temp	pH	t_1	t_2	Wash vol.	Wash temp.	KOH conc.
Na_2PdCl_4	0.9	−0.2	0.2	0.3	−0.2	0.1	−0.1
K_2PdCl_4	0.8	−0.2	0.1	0.5	−0.1	0	0.1
$Pd(OAc)_2$	0.4	0.2	0.3	−0.3	0.4	0.2	−0.6
$PdSO_4$	0.9	−0.1	−0.2	−0.1	−0.1	−0.2	−0.2
$Pd(NO_3)_2$	0.4	−0.4	0.5	0.4	−0.5	0.3	−0.2
K_2PdBr_4	0.7	−0.2	−0.2	0.1	0.4	0	0.5
$PdCl_2$	0.8	−0.3	0.1	0.5	0.0	0	0.1
Na_2PdCl_6	0.8	−0.2	0.4	0.1	−0.3	0.2	−0.1
Average	+0.7	−0.2	+0.2	+0.2	−0.2	0	−0.1

ficiency of formation and the dispersion of the active species on the support. The fabrication procedure used for these catalysts suggests that $Pd(OH)_2$ could be the active phase and the characterization data presented below strongly support this contention.

B. Spectroscopic and X-Ray Diffraction Results

Table 3 presents results from X-ray diffraction (XRD) and energy dispersive X-ray fluorescence spectroscopic (EDX) analyses of 6% Pd/C catalysts of known activity prepared from $PdCl_2$.

TABLE 3

Characterization of 6% Pd/C Catalysts

Sample number	Relative activity by hydrogen uptake (psig)	Chlorine[a] content (%)	XRD[b] fraction Pd seen	"PdO"[c]
A	3	2	0.52	No
B	4	1	0.62	No
C	17	1	0.60	No
D	21	1	0.42	No
E	28	1	0.27	Yes
F	32	1	0.29	Yes
G	36	0	0.11	Yes

[a] Determined by EDX.

[b] Determined by XRD using magnesium oxide as an internal standard (*7*).

[c] See text for details.

The EDX data clearly demonstrate that the presence of chlorine is not necessary for high catalytic activity. Thus, (chloro)-palladium complexes are unlikely to be the active catalytic species. The residual chloride is probably a measure of the efficiency of the reaction of palladium chloride with hydroxide (*8*).

XRD data must be interpreted with care because well-dispersed or amorphous materials are not observable (*7*). XRD data from a number of 4% Pd catalysts are presented in Table 4. From these and the data in Table 3, it appears that a necessary but not sufficient condition for high catalytic activity is that the level of observable Pd^0 must be low (<10%). This result indicates that either Pd^0 is not the active species or it must be well dispersed in order to be active. The former explanation is supported by the observation that prereduction of the catalyst by either hydrogen or sodium borohydride decreases catalytic activity, but the latter explanation cannot be conclusively eliminated.

From the XRD data, it appears that a species containing palladium–oxygen bonds is conducive to high catalytic activity. The XRD peak attributed to "PdO" in the tables appears as a very broad absorption in the general region expected for pal-

TABLE 4

Analysis of XRD Data for 4% Pd/C Catalysts

Sample number	Relative activity by hydrogen uptake (psig)	Percentage Pd observed as	
		Pd^0	"PdO"
H	23	5	5–10
I	21	7	5–10
J	20	7	5–10
K	18	5	5–10
L	18	7	5–10
M	16	2	23
N	14	13	10
O	12	1	Trace
P	6	39	10
Q	3	8	Trace
R	1	39	Trace

ladium oxide or a variety of $Pd(OR)_2$ type species (*9*). The broadness of the absorption also introduces considerable uncertainty to quantitative analysis of the data.

C. Radiolabeling and Thermogravimetric Analysis

One potential method for differentiating palladium oxide from palladium hydroxide is based on the fact that only palladium hydroxide has hydrogen–oxygen bonds. This offers the potential to study the catalyst by tritium labeling experiments.

i. Radiotracer study. The radiotracer experiment was conducted by exposing an active 6% Pd/C catalyst to tritiated water in the vapor phase, drying, and determining the residual tritium by liquid scintillation counting. As a control, a sample of the carbon support was treated in an identical manner. The catalyst sample contained 27% of the theoretical maximum amount of tritium based on an assumed structure of 6% $Pd(OH)_2/C$ (5.56 μg HTO/mg catalyst) while the fresh carbon support treated similarly exhibited only a trace of tritium incorporation (0.42 μg HTO/mg C).

$$Pd(OH)_2/C + H^*_2O \leftrightarrows Pd(OH^*)_2/C + H_2O$$

Palladium oxide is not hygroscopic and no tritium incorporation is expected. (This is supported by thermogravimetric data, *vida infra.*)

These results demonstrate that the drying conditions used are sufficient to dehydrate the carbon support and, therefore, the remaining tritium must be associated with the palladium, most reasonably in the form of palladium hydroxide. The formation of a palladium tritide is not expected in the absence of gaseous tritium and, even if formed, would not be stable to the drying conditions used (*10, 11*).

The fact that only ~30% of the theoretical tritium incorporation is detected could be due to several factors. The possibility of a slow, incomplete, initial tritium incorporation into the supported $Pd(OH)_2$ is eliminated by the observation that >90% of the tritium is lost on exposure of the tritiated catalyst to the atmosphere (~50% relative humidity) overnight.

The method of analysis is such that the detected tritium incorporation is almost certainly less than the actual tritium incorporation. In the liquid scintillation analysis, energy of the emitted radiation is absorbed by scintillator molecules, phosphors, which in turn emit photons which are detected and counted. Most of the palladium, and, therefore, most of the tritium lies within the porous structure of the carbon particle. Thus, a significant fraction of the emitted β radiation will be absorbed by phosphor located in the pore structure of the support. The support is opaque to the light emitted by the phosphor and, therefore, this fraction of events will not be detected.

In addition, decomposition of some of the palladium hydroxide to palladium oxide may have occurred during the drying procedure. Thus, the ~30% observed tritium incorporation under these conditions is quite substantial and provides strong evidence for the identification of supported palladium hydroxide as the active species.

ii. Thermogravimetric analysis. Additional support for the presence of $Pd(OH)_2$ is provided by thermogravimetric analysis

(TGA). (All TGA analyses were performed in a nitrogen atmosphere.)

The TGA curves for palladium hydroxide and the dry active catalyst both show a discrete weight loss at ca. 250°C which is not present on repeated analysis of these same samples. This peak most reasonably corresponds to the dehydration of palladium hydroxide to palladium oxide. By contrast, TGA of palladium oxide shows it to be stable to at least 500°C.

TGA analyses of three 6% Pd/C catalysts of varying activity are summarized in Table 5. The good and fair catalysts show a discrete weight loss at ca. 250°C, while the poor catalyst does not. As shown in the table, the difference in weight loss between the good and poor catalysts is 0.8 ± 0.1% and occurs exclusively in the 200–300°C range. Conversion of 6% $Pd(OH)_2$/C to 6% PdO/C would involve a weight loss of 1%.

The combination of radiolabeling experiments and TGA analyses provides conclusive evidence that the active catalytic species is palladium hydroxide. The thermal stability of palladium oxide observed by TGA demonstrates that palladium oxide does not physically adsorb moisture and, therefore, cannot be responsible for the tritium incorporation observed in the radiolabeling work. The data in Table 5 demonstrate that the weight loss observed at ~250°C is not due to either the carbon support or to catalytically inactive palladium species. And, the magnitude of the weight loss is consistent with the palladium hydroxide hypothesis.

D. Pd–Carbon Interaction

The t_1 correlation coefficients for $Pd(NO_3)_2$ and Na_2PdCl_6 (Table 1) suggest that interaction of the Pd salt with the carbon support prior to formation of $Pd(OH)_2$ is detrimental to catalytic activity. This is demonstrated more clearly by the following experiments. In this series, we attempted to convert $PdCl_2$ to $Pd(OH)_2$ *after* the Pd had been adsorbed onto carbon. To start, carbon was added to a stirred, homogeneous aqueous solution of $PdCl_2$ at pH 1 under the reaction conditions shown in Table 6. The theoretical maximum Pd loading was 4.7 wt%. Catalyst I, the low-temperature, short adsorption time sample, contained 1.7 wt% Pd; catalyst II, the high-temperature, long adsorption time sample, contained 3.5% Pd. Relatively high levels of Pd^0 were observed by XRD in each case: ca. 15% for catalyst I and ca. 30% for catalyst II. Neither catalyst showed any hydrogenolysis activity.

The resultant catalysts I and II were then treated chemically as indicated in Scheme 2. Activity data for both wet and dry aliquots of these catalysts are presented in Table 7. Although treatment with base does result in some hydrogen uptake in the standard hydrogenolysis test, these results are much poorer than expected for catalysts

TABLE 5

Thermogravimetric Analysis of 6% Pd/C Catalysts

Catalyst	Cumulative weight loss (%) at					
	150°C	200°C	250°C	300°C	350°C	400°C
S (Good)	1.3	1.7	2.5	3.3	3.9	4.7
T (Fair)	1.2	1.6	2.6	3.4	4.1	4.6
U (Poor)	1.2	1.6	2.0	2.5	3.2	3.8
Δ (S-U)	0.1	0.1	0.5	0.8	0.7	0.9

SCHEME 2

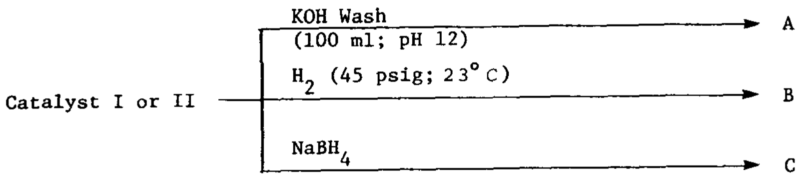


TABLE 6

Conditions for the Adsorption of Palladium Chloride on Carbon

Variable	Catalyst I	Catalyst II
Palladium chloride concentration	4.17 g/2 liters	4.17 g/0.5 liters
Temperature	15°C	70°C
Time	15 min	150 min
Weight C	50 g	50 g
Wash	0.3 liter @ 80°C	0.5 liter @ 15°C
Final palladium loading (wt%)	1.7	3.5
XRD observable Pd^0 (% of total Pd)	15	30

TABLE 7

Activity of Catalysts Prepared as Described in Scheme 2

Catalyst	40 min H uptake (psig)	
	Wet (2 g)	Dry (1 g)
I	1	1
IA	3	0
IB	4	0
IC	0	0
II	1	1
IIA	12	4
IIB	4	0
IIC	0	0

prepared by the normal procedure (a 1.5% Pd/C catalyst prepared by the standard technique would give a H_2 uptake of 12–15 psig compared to only 3 psig for catalyst IA). These results demonstrate that Pd–carbon interaction prior to deposition of $Pd(OH)_2$ is detrimental to catalytic activity.

This detrimental effect of the Pd–carbon interaction could be due to either poor dispersion or to a decreased efficiency of formation of $Pd(OH)_2$. Transmission electron microscopic (TEM) examination of these catalysts favors the latter explanation.

Since most of the palladium of an active catalyst is not observable by XRD, TEM is the only facile method for at least qualitative evaluation of the state of Pd aggregation. TEM examination of various catalysts from the factorially designed series revealed that those samples showing palladium aggregates ≥50 Å were always poor catalysts. Better catalysts always showed well-dispersed, small (≤20 Å) Pd aggregates (presumably these aggregates contain $Pd(OH)_2$). Thus, well-dispersed Pd appears to be necessary, but not sufficient, for high catalytic activity.

TEM photos of the poor catalyst IIA showed small, well-dispersed Pd aggregates. We therefore hypothesize that the Pd–carbon interaction must decrease the ease of $Pd(OH)_2/C$ formation. This may involve a reduction of Pd^{II} to Pd^0, and is consistent with the relatively high levels of Pd^0 observed in samples I and II. It may also explain why Na_2PdCl_6 appears to be a better catalyst precursor than $PdCl_2$: reduction of Pd^{IV} to Pd^0 should be less likely/extensive than reduction of Pd^{II} to Pd^0.

It also appears that this reduction process is facilitated at higher catalyst preparation temperature (Tables 6 and 7).

IV. CONCLUSIONS

This work has utilized a series of factorially designed experiments to evaluate the relative importance of preparation variables in determining the activity of $Pd(OH)_2$/C catalysts for the hydrogenolysis of an arylchloride. The results indicate that temperature is the single most important variable and that optimal conditions must be developed for each palladium salt used. We have presented evidence which suggests that the preparation variables are important in determining the efficiency of $Pd(OH)_2$ formation and in controlling palladium dispersion on the carbon support.

We have also shown that interaction of the palladium salt with the carbon support prior to formation of palladium hydroxide results in reduction of the palladium and decreased catalyst activity. It should be interesting to conduct similar studies on catalysts used for other hydrogenation or hydrogenolysis processes.

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