JOURNAL OF CATALYSIS 44, 271-280 (1976)

The Composition of Reduced Palladium Oxide and Its Behavior as a Catalyst for Liquid Phase Hydrogenation

I. T. CAGA, E. SHUTT,[1] AND J. M. WINTERBOTTOM

*Department of Chemical Engineering, University of Birmingham, P. O. Box 363,
Birmingham B15 2TT, England; and [1] Johnson, Matthey Research Centre,
Blount's Court, Sonning Common, Reading RG4 9NH, England*

Received February 4, 1976

The behavior of reduced palladium oxide as a catalyst for the liquid phase hydrogenation of 1-octyne and phenylacetylene has been studied in C_1- to n-C_4-alcohols and n-C_6- to n-C_8-alkanes as solvents, at 1 atm and at 30°C.

When the palladium oxide was reduced *in situ* it gave rise to better activities in alcoholic solvents than in the *n*-alkanes, and nonlinear rate-catalyst weight relationships were observed. If the catalyst was prereduced in the solvent before alkyne addition, linear rate vs catalyst-weight plots were observed, and the catalyst not only gave better activity in *n*-hexane than in the alcohols, but the activity passed through a maximum value over a particular range of prereduction times. Hydrogen concentrations in solution were measured under different reaction conditions in order to assess the likelihood of hydrogen mass transfer limitation being responsible for the nature of the rate vs catalyst weight plots in the case of *in situ* reduced PdO. The reduced PdO was X-rayed in its solvent for different prereduction times and a brief X-ray study was made of catalyst taken from a reacting system.

In part the behavior of reduced palladium oxide can be explained by hydrogen solubility differences in the various solvents and upon agglomeration of small catalyst particles. The X-ray diffraction studies of the reduced PdO reveal the presence of PdO, Pd, and β-$PdH_{0.6}$, the latter being produced rapidly from PdO prereduced in alcohols. An activity maximum observed with PdO prereduced in *n*-hexane is attributed to PdO, with a surface that has been converted to Pd. Incomplete reduction of the PdO during *in situ* reductions is probably a main cause of nonlinear rate-weight relationship. It is also thought that the behavior of reduced PdO may be influenced by the presence of a small quantity of Pt (0.1% w/w).

INTRODUCTION

The hydrogenation of an unsaturated compound in the liquid phase is very much more complex than the analogous gas phase process, and the number and nature of the parameters involved have been discussed (*1–3*). Satterfield (*4*) discusses in some detail the influence of mass transfer and pore diffusion, while other workers (*3*) report apparent solvent effects in liquid phase hydrogenations. In systems involving complex molecules, both mass transfer (*5*) and catalyst structure (*6*) have considerable influence upon reaction rate and nature of the reaction products. Because many investigations have employed supported catalysts, with the attendant problems of metal distribution and support structure, this study has sought to avoid such issues by employing unsupported palladium oxide, which is of low area and easily reducible.

EXPERIMENTAL METHODS

Materials. The palladium oxide [Batch 101, 84.77% (w/w) Pd] was kindly sup-

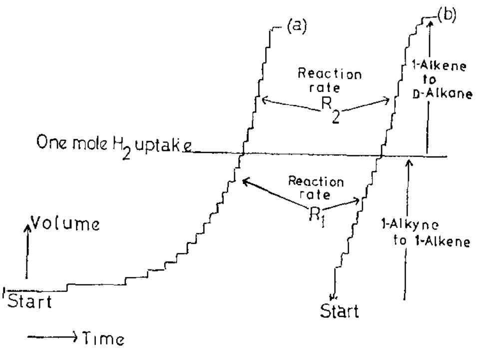

FIG. 1. Volume hydrogen uptake vs time traces for (a) *in situ* and (b) prereduced systems.

plied by Johnson, Matthey & Co., Ltd., along with a further batch of oxide [Batch 2, 84.93% (w/w) Pd], the latter being used mainly as a comparison with Batch 101 in the X-ray studies. 1-Octyne (Koch-Light, Ltd.) was used as supplied but phenylacetylene (Kodak, Ltd.) was distilled once (bp range, 141–143°C) before use. Solvents were either of "Analar" grade or in the case of *n*-alkanes $\geqslant$ 99% purity; *n*-propanol (G.P.R. grade) was distilled once before use (bp range 97–99°C).

Hydrogenations. Reactions were carried out in a thermostatted 80-ml round-bottomed flask fitted with a purge and, when necessary, with a side arm allowing sample withdrawal for analysis. The flask, which was agitated by a calibrated variable speed shaker, was connected to an automatic hydrogenation unit which maintained the reaction at ambient pressure (higher working pressures could be selected) and recorded a continuous trace of volume hydrogen uptake vs time (Fig. 1), from which reaction rates were calculated.

Hydrogen solubility measurements. Hydrogen concentration in solution during reaction was measured using a gas chromatographic technique, after the method of Swinnerton *et al.* (7). A liquid sample (0.25 ml) was withdrawn from the vessel and injected into the gas chromatograph, previously calibrated for hydrogen. Because small quantities of catalyst were drawn into the syringe, thus causing rapid depletion of the hydrogen (in$<$10 sec), thereby giving rise to low or zero hydrogen concentrations, the reaction was poisoned by addition of 1 ml of tetrahydrothiophen (THT), agitation being stopped immediately after injection of the latter. Even this technique could only be employed during the second mole hydrogen uptake (Fig. 1; see later for explanation of the volume-time curve), because the alkynes compete with the poison for the catalyst and the reaction does not stop. However, alkenes involved in the second stage do not compete and the reaction was completely stopped by poison addition. It was established that the absorption coefficient (β_{30}) at 30°C for hydrogen was virtually identical for 5% (v/v) 1-octyne/solvent and 5% (v/v) 1-octene/solvent; furthermore, the addition of 1 ml of THT to such solutions had no effect upon β_{30}, the latter being defined as milliliter of H_2 (STP) per milliliter of solution. Samples were withdrawn from the stagnant, poisoned system as rapidly as possible (at $\frac{1}{2}$- to 1-min intervals initially, but later at 1- to 2-min intervals) for up to 10 min after poisoning and were injected into the gas chromatograph for hydrogen content analysis.

Gas chromatography. Hydrogen concentration in solution was analyzed by direct sample injection into a 6-ft × $\frac{1}{4}$-in. o.d. column packed with 60–80 mesh silica gel, operated at 30°C, with a nitrogen flow of 40 ml min^{-1}. The silica gel was activated at 120°C before use and overnight between operations to remove accumulated solvents. The estimated error involved in any given result is probably ±2% with a reproducibility of ±10%.

Reaction products were analyzed on a 15-ft × $\frac{1}{4}$-in. o.d. column packed with Carbowax 1500 on 60–80 mesh Silocel operated at 120°C; the latter was suitable for both phenylacetylene and 1-octyne systems. Analyses were checked only periodically, as the selectivity for 1-alkene production always lay in the range $0.94 \leqslant S \leqslant 0.98$; i.e., the first mole hydrogen uptake concerned the conversion of 1-alkyne to 1-alkene (reaction rate = R_1, Fig. 1) and the second mole hydrogen uptake concerned the conversion of 1-alkene to *n*-alkane (reaction rate = R_2, Fig. 1). It is estimated that the probable error involved in these analyses was ±2% with a rep o-ducibility of the same order.

Characterization of the catalyst. The surface area of unused and reduced PdO was determined in this laboratory using a dynamic method of nitrogen adsorption developed from the methods of Nelson and Eggertsen (*8*) and Daeschner and Stross (*9*). Mean particle size was calculated from the surface area and the value obtained was in good agreement with those determined by Johnson, Matthey, and Company Ltd., from X-ray and electron microscopy studies (see Table 2).

X-ray powder diffraction studies were carried out in the Department of Physical Metallurgy on palladium oxide samples that had been exposed to hydrogen under various solvents for different lengths of time. The catalyst sample (10–20 mg) was withdrawn in its solvent and stored in a stoppered capillary tube (still in the solvent) from which a sample of catalyst and solvent was drawn into a fine capillary tube for X-ray studies.

EXPERIMENTAL RESULTS AND DISCUSSION

Unless otherwise stated, all results are expressed at 1 standard atm total pressure (1.013×10^2 kN m^{-2}), 30°C, and 1600 vibrations min^{-1} shaking speed, with 20 ml of 5% (v/v) 1-alkyne in solvent.

Hydrogen Uptake vs Time Traces

Figure 1a is typical of the traces obtained during an *in situ* reduction, in which the alkyne-solvent-PdO system was made up before hydrogen was introduced. Figure 1b is typical of a prereduced system, in which the PdO-solvent system was shaken with hydrogen for a given length of time before the alkyne was introduced.

R_1 and R_2 values were easily calculated from the slopes of the linear volume-time traces in the case of prereduction. Similarly the measurement of R_2 presented no problem in the *in situ* case, since the rate was constant after the acceleration at 1 mole hydrogen uptake. R_1 was determined by drawing a straight line through the last one-third of the trace up to 1 mole hydrogen uptake; this represents the fastest rate attainable since addition of further 1-alkyne just before 1 mole hydrogen uptake resulted in a linear volume vs time trace for a further 1 mole uptake, whereupon the rate accelerated giving a normal R_2 value.

Rate vs Catalyst Weight Studies

For *in situ* reduced systems, the reaction rate (R_1 or R_2) did not vary linearly with catalyst weight, as shown in Fig. 2a. The latter is entirely representative of the behavior of 1-octyne and phenylacetylene in a number of alcohols (C_1- to *n*-C_4-) and *n*-alkanes (*n*-C_6 to *n*-C_8). The R_1 and R_2 values in Fig. 2a were obtained using methanol as solvent and for the alcohols the R_1 and R_2 values at any catalyst weight decrease in the order $CH_3OH > C_2H_5OH >$ *n*-$C_3H_7OH >$ *n*-C_4H_9OH. In the case of the *n*-alkane solvents, the R_1 and R_2 values were comparable but slightly lower than those obtained with *n*-butanol as solvent.

Nonlinear rate vs catalyst weight (W) curves (Fig. 2a) are unusual compared with our own (*10*) and other workers, (*1*) experience with supported catalysts, although they have been reported on occasions (*2, 3*); the likely causes in the latter cases were probably agglomeration of colloidal particles and failure to keep

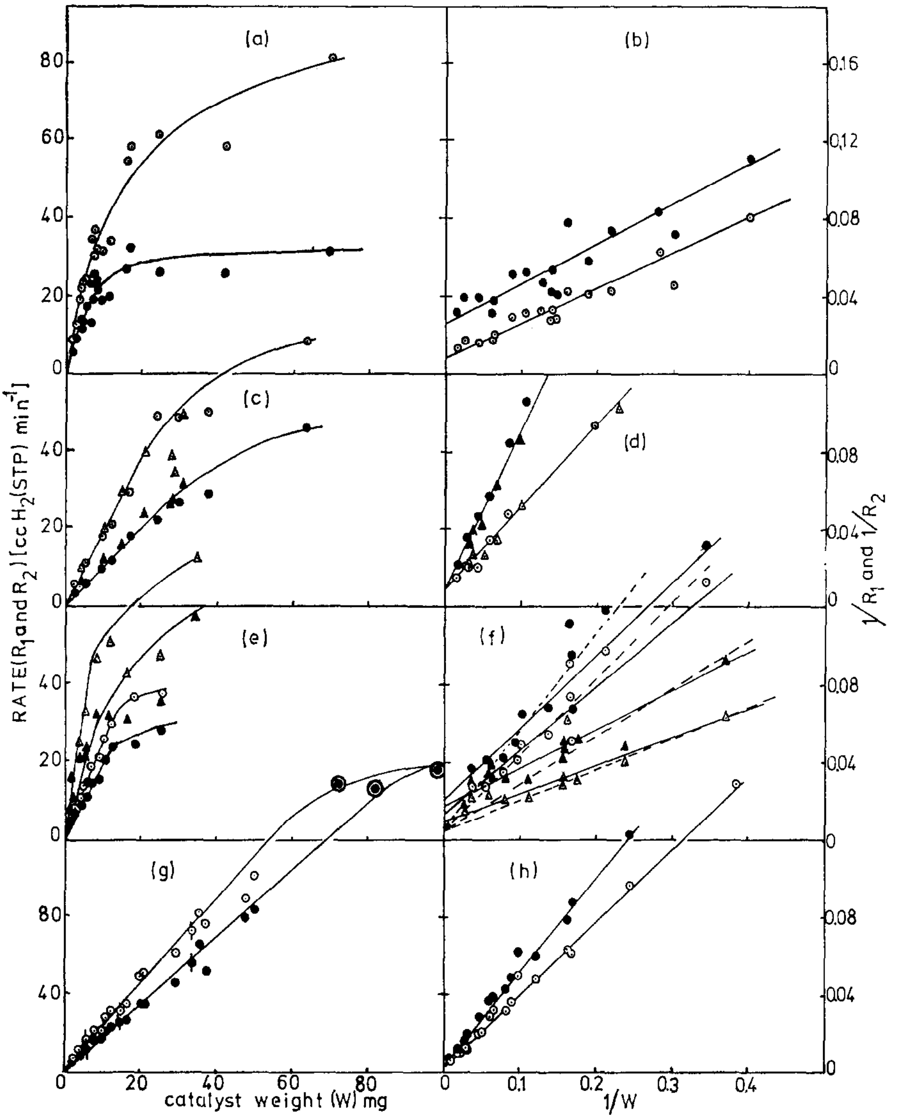

Fig. 2. Rate vs catalyst weight (w) and reciprocal rate vs reciprocal catalyst rate plots for: (a) and (b) *in situ*-reduced PdO/1-octyne/CH_3OH (● R_1, ⊙ R_2); (c) and (d) prereduced PdO/1-octyne/CH_3OH (● R_1, ⊙ R_2), /C_2H_5OH (▲ R_1, △ R_2); (e) and (f) prereduced PdO/1-octyne/*n*-C_6H_{14} (▲ R_1, △ R_2, 5 min prereduction; ● R_1, ⊙ R_2, 30 min prereduction); (g) and (h) 30 min prereduced PdO/1-octyne/*n*-C_6H_{14} + 100 μl H_2O (● R_1, ⊙ R_2; ϕ R_1, ϕ R_2, 5 min prereduction).

catalyst particles in suspension, respectively. However, the existence of different limiting values of R_1 and R_2 at high weights in the same solvent indicates that the low limiting value of R_1 is certainly not genuine. This is confirmed by plotting the results for methanol in reciprocal form ($1/R$ vs $1/W$; Fig. 2b), a well-known way of expressing such data (*4*). At large catalyst loadings $1/W \rightarrow 0$ and the value of $1/R$ at this value should be that due to liquid film resistance, due to hydrogen diffusion through the gas–liquid interface; for a given solvent the limiting values of $1/R_1$ and $1/R_2$ should be identical and Fig. 2b indicates that this is not so (kinetic

TABLE 1

Equilibrium Values of β_{30} Measured by the Gas Chromatographic Method

Solvent	CH_3OH	C_2H_5OH	$n—C_3H_7OH$	$n—C_4H_9OH$	$n—C_6H_{14}$
β_{30} (solvent)	0.096	0.088	0.080	0.074	0.128
β_{20} (solvent)	0.083 (0.083[a])	0.071 (0.066[a])	—	—	—
β_{30} † 5% (v/v) 1-octyne in solvent	0.093	0.084	0.074	0.068	0.118
β_{30} † 5% (v/v) 1-octyne + 1 ml T.H.T.	0.092[b]	—	—	0.072[b]	0.114

[a] Literature values.

[b] Average of direct measurements and poisoned reaction systems, repurged with hydrogen.

† Very similar results are obtained using 1-octene instead of 1-octyne.

studies showed that the rate of hydrogenation $R_1 \propto P_{H_2}^{1.0}[\text{Alkyne}]^0$ and $R_2 \propto P_{H_2}^{1.0}[\text{Alkene}]^0$).

A further indication that the limiting value of R_1 was not genuine was obtained by measuring the hydrogen concentration in the reacting solution by the technique already described. Table 1 shows the measured equilibrium values of β_{30} for solvents and solutions, along with some literature values; the latter indicate the value of this technique as a rapid comparative method, despite the reproducibility problem involved. Figure 3 shows the value of β_{30}, measured under reaction conditions and at high shaking speeds and low catalyst weights, the values of β_{30} for n-hexane and methanol systems are very similar to the measured equilibrium values, as might be expected. At high catalyst weights and high shaking speed, β_{30} is only a little smaller for both solvents than its equilibrium values. It is suggested that this is due to the THT taking fractionally longer to stop the reaction, thus resulting in hydrogen loss and depressed values of β_{30}. Only at very low shaking speeds and high catalyst weights were very low initial hydrogen concentrations observed, and on standing, β_{30} slowly increased to approach its equilibrium value. Since very low values of β_{30} would be expected with

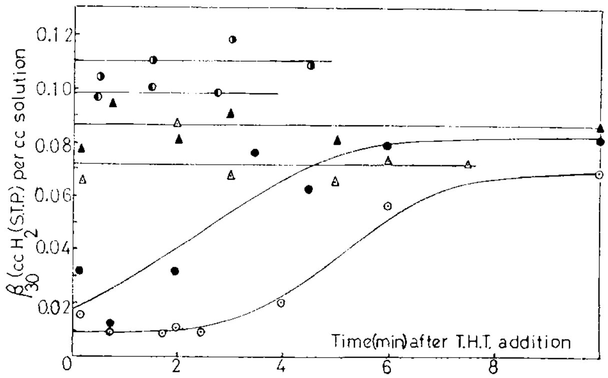

FIG. 3. Variation of absorption coefficient (β_{30}) with time for 1-octyne hydrogenation. ◑ (n-C_6H_{14}, 6 mg PdO, 1600 min^{-1}); ◐ (n-C_6H_{14}, 34 mg PdO, 1600 min^{-1}); ▲ (CH_3OH, 6 mg PdO, 1600 min^{-1}); △ (CH_3OH, 30 mg PDO, 1600 min^{-1}); ● (CH_3OH, 30 mg PdO, 600 min^{-1}); ⊙ (CH_3OH, 30 mg PdO, <200 min^{-1}).

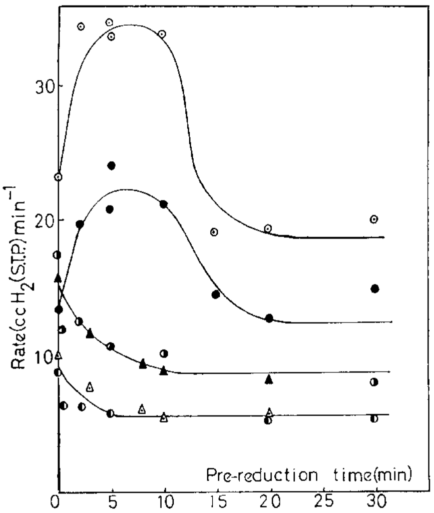

FIG. 4. Variation of rate with prereduction time in different solvents. ◐ (R_1), ◑ (R_2) (1-octyne/CH_3OH/5 mg PdO); △ (R_1), ▲ (R_2) (1-octyne/C_2H_5OH/4.5 mg PdO); ● (R_1), ⊙ (R_2) (1-octyne/n-C_6H_{14}/6 mg PdO).

a diffusionally controlled process, it is concluded that at high catalyst weights and high shaking speeds, where the rate levels off (Fig. 2a), the limiting value of R_1 is not due to the onset of diffusional control.

Prereduction of the catalyst for various times gave rise in alcohols (CH_3OH and C_2H_5OH) to R_1 and R_2 values that decreased with increasing prereduction time, but at times >5 min became constant and time-independent (Fig. 4). In addition, the rate vs catalyst weight plot for reactions in methanol (5 min prereduction) and in ethanol (15 min prereduction) is linear up to about 30 mg PdO (Fig. 2c), and the corresponding reciprocal plot (Fig. 2d) gives identical limiting values of R_1 and R_2 (in the region of 120–150 ml min^{-1}). No distinction can be made between methanol and ethanol, although the latter should give slightly lower limiting rates.

Prereduction of PdO in n-hexane gave rise to a maximum activity between 2 and 10 min prereduction times, after which the activity declined to give virtually constant rates from 15 to 30 min prereduction times (Fig. 4). Furthermore, rate vs catalyst weight plots for 5 and 30 min prereduction times (Fig. 2e) are in accord with the above activity pattern. However, the corresponding reciprocal plots (Fig. 2f) still exhibit different limiting values for R_1 and R_2 (solid lines), but it is also apparent that $1/R$ values at low $1/W$ values are virtually constant, which is a symptom of catalyst agglomeration (*4*). If lines are constructed (broken lines in Fig. 2f) ignoring points for which $1/W < 0.1$, then both sets of results give a common limiting R_1 and R_2 value, which lies in the range 300–500 ml min^{-1}.

It was also observed that addition of up to 100 μl of water to the standard charge of solvent had no effect upon the rates obtained in the prereduced system, apart from one phenomenon peculiar to n-hexane (see below); added water caused severe inhibition of reaction for *in situ* reduced PdO in alcohol systems. Figure 2g shows that 100 μl of water in the system gives identical rates for both 5 and 30 min prereduction times, and the linearity of the rate vs catalyst weight plot is extended to much greater catalyst weights. The corresponding reciprocal plot (Fig. 2h) does not show symptoms of agglomeration and the limiting values of R_1 and R_2 are identical and lie in the range 300–500 ml min^{-1}; this value is expected to be greater than that for alcohols because of the lower viscosity of n-hexane and the larger diffusion coefficient for hydrogen in the latter. It was also obvious that catalyst agglomeration was much reduced because the water prevented the particles from clumping together. Since agglomeration is a property of small particles, a number of methods were used to determine the mean particle diameter ($\bar{d}_p$). The latter was calculated from surface area measurements on both used and unused PdO samples,

TABLE 2

Mean Particle Size for PdO (Batch 101)

Method	Material	Parameters used in calculation		Mean particle diameter ($\bar{d}_p$) (nm)
		ρ (g cm^{-3})	S (cm^2 g^{-1})	
Surface area	PdO (unused)	8.7	7.5×10^{4a}	92^a
Surface area	PdO (used)	8.7^b	9.5×10^4	73
X-ray[c]	PdO (unused)	—	—	63
Electron diffraction[c]	PdO (unused)	—	—	100
Surface area	PdO (unused) (Batch 2)	—	7.0×10^4	—

[a] This laboratory and Johnson Matthey.

[b] ρ(PdO) = 8.7 g cm^{-3}. If the material was largely Pd then $\rho \sim 12$ g cm^{-3}. This does not significantly alter the conclusions.

[c] Johnson Matthey.

using a spherical particle model from

$$\bar{d}_\text{p} = \frac{6}{\rho S},$$

where ρ = catalyst density, and S = surface area.

The results of these and X-ray and electron diffraction studies are summarized in Table 2, all three methods confirming that the mean particle diameter $\leqslant$ 100 nm (0.1 μm).

X-Ray Diffraction Studies of Prereduced PdO

These studies were carried out in order to see whether or not the activity patterns for PdO prereduced for different lengths of time in three solvents could be related to the composition of the catalyst. It must be borne in mind that for ease of sampling, a larger quantity of PdO was required (100–200 mg), compared with the amount used in a reaction (usually 5–10 mg and rarely >50–60 mg).

Samples were obtained by reducing PdO (100–200 mg) for a given length of time ($\frac{1}{2}$ to 60 min) in the solvent (H_2O, CH_3OH, and n-C_6H_{14}) under a hydrogen atmosphere with shaking. The shaking was stopped and a sample (10–20 mg) was withdrawn in its solvent, via a hypodermic syringe and stored for X-ray analysis. Sometimes samples were taken at the different times from one initial charge of catalyst, and at other times a separate run was used for each time of prereduction. In one case, samples were taken from a reacting system.

The results of X-raying prereduced PdO are shown qualitatively in Table 3, which indicates the species detected and, when appropriate, whether or not they were the major or minor component. A number of well-known phases was identified from their lattice parameters, namely PdO, Pd, and β-$PdH_{0.6}$. Indeed, in water the reduction appears to proceed in distinct stages from PdO to Pd to β-$PdH_{0.6}$.

In methanol, the production of β-$PdH_{0.6}$ is fairly rapid and since it is relatively inactive in hydrogen activation (*11*), the observed activity pattern for PdO reduced in alcoholic solvents (Fig. 4) is easily understood. The situation in n-hexane is more complex and PdO can exist as the dominant phase for 10–15 min prereduction time. It may at first appear anomalous that PdO is linked with the time sequence in which the activity maximum is obtained, since the latter might be expected to occur with a system dominated by Pd.

TABLE 3

Phases Detected by X-Ray Examination of Prereduced PdO[a]

Time (min)	Phases detected from X-ray diffraction pattern for															
	PdO (Batch 101) in											PdO (Batch 2) in				
	W+	M+	M+	M+	M*	M*	H+	H+	H+	H*	H*	W*	M+	M*	H+	H*
½	PdO (Pd)	PdO Pd	(PdO) Pd	—	—	—	—	—	—	—	—	—	-	—	—	—
¾	—	—	—	PdO (Pd)	—	—	—	—	PdO	PdO	—	PdO	PdO	PdO	PdO	PdO
2	PdO Pd	β Pd	Pd	—	—	—	—	PdO	PdO	—	PdO	—	—	—	PdO	—
2½	—	—	—	Pd	—	β	—	PdO	—	PdO	—	PdO Pd	—	PdO	—	PdO
5	(PdO) Pd	β	β	β Pd	β	β	PdO (Pd)	PdO (PD)	PdO	PdO	PdO β	(PdO) Pd	β	β	PdO	PdO
10	—	β	—	β	—	—	PdO (Pd)	β	PdO	—	β	—	β	—	PdO	—
15	β	β	β	β (Pd)	β	β	—	β	β	β	β	Pd β	β	β	PdO	PdO
20	—	—	—	β	—	—	—	—	β	—	—	—	β	—	—	—
25	—	—	—	—	—	—	—	β	—	—	—	—	—	—	—	—
30	—	—	—	β	—	β	—	—	β	β	β	β	β	β (Pd)	Pd β	Pd
45	—	—	—	β	—	β	—	—	β	β	—	β	β	β	β	β
60	—	—	—	—	—	β	—	—	β	β	—	β	β	—	β Pd	β
Catalyst weight (mg)	108	104	201	100	100	100	100	202	100	100	200	100	100	100	100	100

[a] Reduction temperature = 30°C; pressure = ambient; shaking speed = 1200 vibrations min^{-1}; solvent volume = 20 ml. + Samples from same initial charge; * individual experiments; ( ), minor component; W, water; M, methanol; H, *n*-hexane; β, β-$PdH_{0.6}$.

TABLE 4

X-Ray Studies of Catalyst from a Reacting System (*in Situ* Reduced)

Catalyst weight = 100 mg (PdO, batch 2*);
Solution = 20 ml 5% (v/v) 1-octyne/CH_3OH
Pressure = ambient
Temperature = 30°C
Shaking speed = 1600 vibrations min^{-1}

Time after start of reaction (min)	14	16	17	19	21	60
Phase observed	PdO	PdO	Pd	β	β	β

* Surface area = 7.0×10^4 cm^2 g^{-1}. $\beta = \beta - PdH_{0.6}$.

The results shown in Table 4 provide evidence that helps to explain this situation. The samples were taken during the second mole hydrogen uptake of an *in situ* reduced system, which was apparently catalyzed by PdO for much of the time. However, X-ray analysis only reveals the bulk composition of such small particles and not that of the surface. Hence, when PdO is indicated, following prereduction, it is highly probable that the surface layer is already Pd, and this is supported by the fact that the existence of bulk Pd as the major component is not only rare but does not coincide with the activity peak. It is further concluded that, when bulk Pd is detected, the surface of the particles is already converted to β-$PdH_{0.6}$.

The polarity of the alcohol solvents, along with their reasonably large equilibrium hydrogen concentration, facilitates the rapid reduction of PdO to β-$PdH_{0.6}$. *n*-Hexane will dissolve slightly more hydrogen than the alcohols under similar conditions but its lack of polarity inhibits the reduction of bulk PdO to β-$PdH_{0.6}$, enabling Pd to exist as a surface layer, giving greater activity. Water is of interest since, although it is more polar than the alcohols, its equilibrium concentration of hydrogen is five to six times smaller than methanol and *n*-hexane under comparable conditions, and its use as a prereduction medium is being further investigated.

The PdO (Batch 101) was found to contain 0.1% (w/w) Pt while PdO (Batch 2) contained <100 ppm Pt, and small differences in their reduction behavior may be attributable to this, particularly if surface enrichment of Pt occurs, and current investigations are concerned with the behavior of "pure" PdO and samples of PdO "doped" with increasing quantities of Pt. It is hoped that X-ray studies may provide evidence regarding the change in lattice parameter as it is added to the system and whether or not the latter metal suppresses the formation of β-$PdH_{0.6}$ by closing the palladium–hydrogen miscibility gap.

The behavior of catalysts derived from PdO can be explained partly in terms of (i) agglomeration effects and (ii) incomplete reduction of the PdO for *in situ* reduced systems, leading to nonlinear rate vs catalyst weight plots (this is supported by the results given in Table 4). Agglomerates will be greater in a low dielectric constant solvent such as *n*-hexane, where the electrostatic charge on the particles cannot be dispersed easily; the addition of small quantities of water facilitates this. In alcohols, with which water is miscible, its addition does not facilitate charge dispersion. Greater rates of reaction in *n*-hexane compared with methanol for prereduction times that produce β-$PdH_{0.6}$, i.e., when R_1 and R_2 are independent of prereduction time can probably be explained in terms of the greater hydrogen concentration in *n*-hexane. For *in situ* reduced systems the use of alcohols gives more rapid reduction of the PdO than does *n*-hexane, and the reaction rates are therefore faster in the former solvents.

Superimposed on all the above considerations are the phase composition changes occurring during PdO reduction. These changes are strongly solvent influenced and may also be influenced by traces of other metals in the host material.

ACKNOWLEDGMENTS

The authors are grateful to Johnson Matthey & Co., Ltd., for their support, and one of us (E. S.) is particularly grateful to them for the provision of a research studentship. The authors also thank Mr. A. J. Bird of Johnson, Matthey & Co., Ltd., for his kind assistance in obtaining particle size measurements, and to Professor G. C. Bond and Dr. D. E. Webster for their valuable comments on the work. A special debt of gratitude is due to Dr. I. R. Harris, Mrs. B. Morris, and Mr. S. Harwood (Department of Physical Metallurgy, Birmingham University) for their advice and assistance in obtaining and interpreting the X-ray diffraction data.

REFERENCES

1. Acres, G. J. K., and Bond, G. C., *Platinum Met. Rev.* **10**, 122 (1966).
2. Yao, H. C., and Emmett, P. H., *J. Amer. Chem. Soc.* **81**, 4125 (1959).
3. Price, R. H., and Schiewetz, D. B., *Ind. Eng. Chem.* **49**, 807 (1957).
4. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis." M. I. T. Press, Cambridge, Mass., 1970.
5. Coenen, J. W. E., "Proceedings of the Symposium of The Mechanism of Heterogeneous Catalysis" (Amsterdam, 1959), p. 126, Elsevier, Amsterdam, 1965.
6. Coenen, J. W. E., Boerma, H., Linsen, B. G., and De Vries, B., "Third Congress on Catalysis," **2**, 1387 (1964).
7. Swinnerton, J. W., Linnenbom, V. G., and Cheek, C. H., *Anal. Chem.* **34**, 1509 (1962).
8. Nelson, F. M., and Eggertsen, F. T., *Anal. Chem.* **30**, 1387 (1958).
9. Daeschner, H. W., and Stross, F. H., *Anal. Chem.* **34**, 1150 (1962).
10. Ahmad, M. M., Ph.D. thesis, University of Birmingham, England (1973).
11. Couper, A., and Eley, D. D., *Discuss. Faraday Soc.* **8**, 172 (1950).