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The Behavior of Mixed Metal Adams Oxide Catalysts in the Liquid Phase Hydrogenation of 1-Octyne

I. Platinum–Palladium Oxides

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Adams Pt–Pd oxide catalysts containing 0–15 atom% Pt have been prepared and studied for the hydrogenation of 1-octyne in the solvents methanol and *n*-hexane at 1 atm and 30°C. In methanol, activity declined with increasing prereduction time and eventually reached a limiting value, whereas in *n*-hexane most catalysts gave an activity maximum before activity declined and became constant. X-Ray diffraction revealed that for catalysts containing <6 atom% Pt, β-PdH$_{0.6}$ was formed, with the expected loss of activity. Catalysts containing more than 10 atom% Pt did not form β-PdH$_{0.6}$, but still lost activity at longer prereduction times. Reduced catalysts had substantially greater areas than the unreduced oxides and such measurements were used in conjunction with selectivity and rate measurements to calculate turnover numbers at zero or short prereduction times and at long prereduction times. Some Auger studies of reduced catalysts indicated that Pd enrichment occurred at the surface in the catalysts containing most Pt.

The X-ray results indicate that alloying had occurred, since at higher Pt contents β-PdH$_{0.6}$ was not formed. However, catalyst activity still declined with hydrogen pretreatment and it would seem that the surface is capable of hydridation because of the Pd enrichment. Nevertheless, Adams PtO$_2$ also deactivated and does not form a bulk hydride, so the surface may be subject to hydridation and activity loss irrespective of the bulk properties of the system. The turnover numbers do not reveal any trend in activity with Pt content but they do support the hypothesis of an initial surface consisting of metal on unreduced oxide, followed either by complete or surface hydridation. The ease or otherwise of hydride formation was observed, using methanol, *n*-hexane, and water as reduction media, to depend upon solvent polarity and hydrogen concentration.

INTRODUCTION

The liquid phase hydrogenation of some 1-akynes over reduced Adams PdO was shown by Caga *et al.* (*1*) to be strongly influenced by the phase composition of the reduced or partially reduced catalyst and the process of catalyst reduction was influenced by the polarity of the reaction solvent. Furthermore, activity loss after prolonged reduction by hydrogen was shown to be associated with the formation of β-PdH$_{0.6}$. It has been reported that the Pd–H miscibility gap is closed by alloying platinum (18 atom%) with palladium (*2*), thus preventing formation of β-PdH$_{0.6}$. The preparation techniques for Adams palladium oxide and Adams platinum oxide have been subjected to numerous modifications since the original method was reported (*3*) and Nishimura (*4*) later

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TABLE 1

Platinum Content and Surface Area of Catalysts

Catalyst	Pt (% w/w)	Atom% Pt in reduced catalyst	Surface area (m^2 g^{-1})		
			a[a]	b[a]	c[a]
A1	0.7	0.4	16	53	—
A2	18.3	10.0	23	37	63
A3	8.4	5.6	11	60	131
A4	1.2	0.8	10	66	85
A5	20.5	14.5	8	66	98
PdO B60663	0.1	0.06	41	113	50
PtO_2 (H226)		100	85	135	—

[a] a, unreduced oxide; b, reduced catalyst (N_2 adsorption); c, reduced catalyst (X-ray line broadening).

adapted the technique to produce mixed metal catalysts. Subsequently, Bond and Webster (*5*) and Rylander (*6*) reported the preparation and behavior of a large number of mixed metal systems by Adams' methods, some of which exhibited activity enhancement at certain catalyst compositions. However, few of the systems appear to have been characterized extensively and the degree of true alloying is probably not known. Indeed, most evidence for true alloying seems to have been obtained for Pd–Au and Pt–Au systems (*7*). This study has sought to alloy platinum with palladium to see whether or not the Pd–H miscibility gap can be closed, thus preventing activity loss via β-$PdH_{0.6}$ formation.

EXPERIMENTAL METHODS

(*a*) *General.* The methods used to measure the rate of hydrogenation of 1-octyne (R_1) and of 1-octene (R_2) and to analyze the reaction products were described earlier (*1*), along with the techniques employed for X-ray studies of the catalysts. Again, results are expressed at 1 standard atmosphere total pressure (1.013×10^2 kN m^{-2}), 30°C, and 1600 vibrations min^{-1} with 20 ml of 5% v/v 1-octyne in solvent.

(*b*) *Preparation and characterization of the catalyst.* It is reported that 18 atom% platinum in palladium will close the Pd-H miscibility gap. Consequently, the objective was to prepare a series of Adams Pt–Pd oxides covering the composition range up to 18 atom% platinum in the reduced catalyst.

Appropriate quantities of the isomorphous salts ammonium chloroplatinite (52.31% w/w Pt) and ammonium chloropalladite (37.5% w/w Pd) were mixed as aqueous solutions. The water was evaporated off, leaving the mixed salts, which were dried and powdered.

Sodium nitrate (200 g) was melted in a stainless-steel beaker and heated to 380 to 400°C and the mixed salts were added carefully in small quantity (approx. 10 mg for each addition) to the mechanically stirred melt (400–600 rpm). When the addition was complete, the temperature was raised to 460 to 480°C and maintained there for 10 min. The melt was allowed to solidify and was leached with distilled water while still hot. The product was washed several times by decantation with distilled water and finally by filtration until the filtrate was chloride free. The scale of the preparation was such that the total metal content of the mixed metal was about 1 g. The metal assay is given in Table 1.

The catalyst surface area was measured for the unreduced oxide and the reduced catalyst using the same dynamic adsorption method reported previously (*1*). In the case of the reduced catalyst, the reduction was effected in methanol under flowing hydrogen for about 0.5 hr, after which the hydrogen was replaced by nitrogen and the methanol was removed by gentle heating, leaving a dry, reduced catalyst; thereafter the surface area was measured in the usual way. When the X-ray diffraction patterns contained palladium lines only, X-ray line broadening measurements were carried out in order to determine mean

TABLE 2

Phases Observed following Prereduction of Catalysts for Various Times[a]

Time (min)	A1			A2			A3			A4			A5	B60663			PtO_2 H22 W, M, and H
	W	M	H	W	M	H	W	M	H	W	M	H	W	W	M	H	
0.75	O Pd	β Pd	O	O Pd	Pd	O (Pd)	O Pd	β	O	O Pd	Pd	O	O	O	Pd	Pd	Pt
2	O Pd	β	O	O Pd	Pd	O Pd	O Pd	β	O (Pd)	O Pd	β	O	O Pd	(O) Pd	Pd β	Pd	Pt
5	O Pd	β	O	Pd	Pd	Pd	Pd	β	Pd	O Pd	β	Pd	Pd	(O) Pd	(Pd) β	Pd	Pt
10	β	β	β	Pd	Pd	Pd	β	β	Pd	β	β	β	Pd		β	β	Pt
15	β	β	β	Pd	Pd	Pd	β	β	Pd	β	β	β (Pd)	Pd	β	β	β	Pt
20	β	β	β	Pd	Pd	Pd	β	β	Pd	β	β	β (Pd)	Pd		β	(Pd) β	Pt
30	β	β	β	Pd	Pd	Pd	β	β	Pd	β	β	β (Pd)	Pd	β	β	β	Pt
45	β	β	β	Pd	Pd	Pd	β	β	Pd	β	β	β (Pd)	Pd	β	β	(Pd) β	Pt
60	β	β	β	Pd	Pd	Pd	β	β	Pd	β	β	β (Pd)	Pd	β	β	(Pd) β	Pt
Atom% Pt in reduced catalyst		0.4			10.0			5.6			0.8		14.5		0.06		100

[a] O, PdO; Pd, palladium metal; β, β-$PdH_{0.6}$; minor phase indicated in parentheses.

crystallite size and, hence, surface area of the reduced catalyst.

Auger electron spectroscopy (AES) studies were carried out using a Vacuum Generators model with a hemi-cylindrical mirror analyzer using operating conditions consisting of a 3-V peak-to-peak modulation signal, a sweep time of 2.3 eV s^{-1} and a lock-in amplifier time constant of 300 ms. The 2.5-keV 50-μA primary electron beam irradiated a 1-mm-diameter spot and was incident at an angle of 75° to the sample surface. The catalysts were reduced in methanol, which was removed eventually by the hydrogen stream, leaving a dry, reduced catalyst, which was mounted on a duralumin rod using "Aquadag" and placed in the Auger spectrometer. The latter was ion pumped for 1 to 2 days, with frequent titanium sublimation to produce a vacuum of the order of 1.3×10^{-7} Pa. The heights of the Pd (330 eV) and Pt (64 eV) peaks were compared with that of carbon, which remained essentially constant due to the "Aquadag" and those were then used as a measure of the proportion of those elements in the surface. Some depth distributions were determined by successive applications of AES and bombardment with 300 eV argon ions. Such distributions were determined after bombardments of 10 min (7 layers), 30 min (20 layers), and 60 min (40 layers).

In addition to the catalysts prepared, two other catalysts (Johnson, Matthey and Co. Ltd.) were investigated, these being PdO B60663 (0.1% w/w Pt) prepared by a low-temperature route and Adams PtO_2 (H226).

RESULTS AND DISCUSSION

In an earlier paper Caga *et al.* (*1*) examined the phase composition of two Adams palladium oxide catalysts and it was apparent that their activity and phase composition were related. In particular, loss of catalyst activity, following prolonged hydrogen prereduction, was observed to be connected with the formation of β-$PdH_{0.6}$. In consequence an attempt was made to

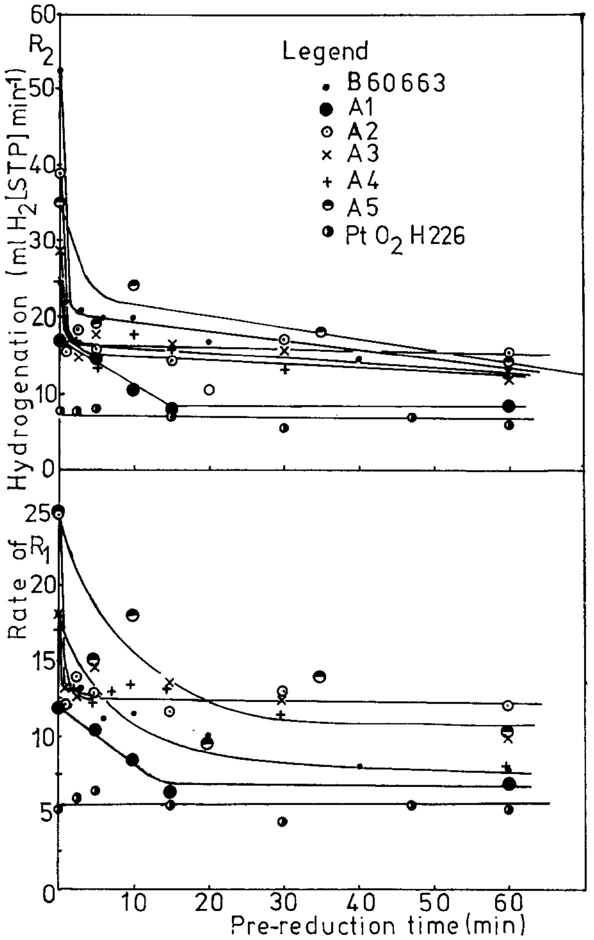

FIG. 1. Variation of rate with prereduction time in methanol.

prevent formation of the latter by addition of platinum to the system.

Table 1 gives the assays and surface areas of the catalysts measured by various techniques. It was intended to cover a range of platinum contents up to 18 atom%, but the latter was not obtained, perhaps due to volatilization of some of the salt during the catalyst preparation. The reduced catalyst was always significantly greater in surface area than the original oxide, which is not too surprising since the latter will undoubtedly break up on reduction. The nitrogen adsorption and X-ray line broadening results are in broad agreement, but it is suggested (*8*a) that the latter method can be in error by as much as 30% and more reliance is placed on the nitrogen adsorption results.

Phase Composition as a Function of Prereduction Time

The phases obtained, following prereduction for times varying between 0.75 and 60 min were examined using X-ray powder diffraction techniques and the phases detected are given in Table 2. The catalysts containing small quantities of platinum (A1, A4, and PdO B60663) behaved in the same way as those reported earlier by Caga *et al.* (*1*) and the phase formed

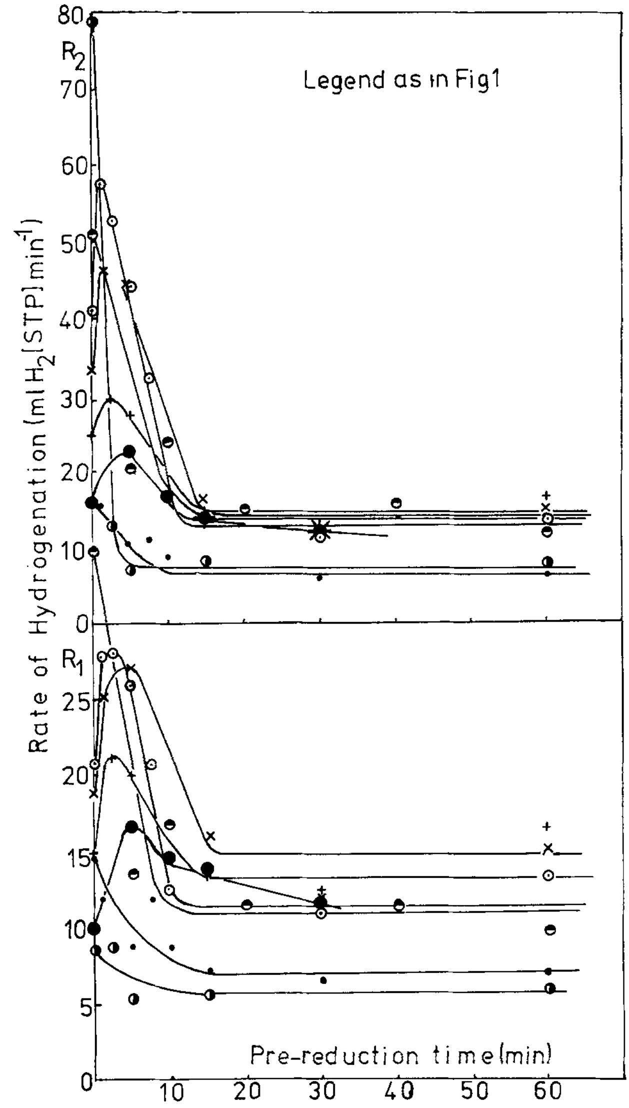

FIG. 2. Variation of rate with prereduction time in *n*-hexane.

finally was β-$PdH_{0.6}$, the latter being formed most rapidly in methanol. In *n*-hexane, the oxide and/or Pd phase were stable for a longer period of time and the stepwise changes were again apparent, if water was used as the catalyst reduction medium. The non-Adams oxide PdO B60663 appeared to reduce very rapidly and this must be due largely to its high initial surface area (41 m^2 g^{-1}). This is also the case for Adams PtO_2 (H226), for which an oxide phase was never observed, even in water at the shortest prereduction time, and its initial surface area was 85 m^2 g^{-1}, which would facilitate rapid reduction.

The three catalysts containing significant quantities of platinum (A2, A3, and A5) behaved somewhat differently. First, A3 with 5.6 atom% platinum behaved as expected in methanol and water by forming β-$PdH_{0.6}$. In *n*-hexane, the final phase observed was Pd, but it is thought that if sufficiently

TABLE 3

Surface Compositions of Some Reduced Adams Pt–Pd Oxides by Auger Spectroscopy

Catalyst	Atom% Pt at				
	Surface	Layer 7[a]	Layer 20[a]	Layer 40[a]	In bulk
A2	3.9	5.0	6.8	8.1	10.0
A3	6.7	6.7	—	6.9	5.6
A5	6.4	4.1	6.9	10.0	14.5

[a] Approximate.

long prereduction times been employed (>60 min), β-PdH$_{0.6}$ would have been formed since 5.6 atom% platinum is insufficient to close the Pd–H miscibility gap. Even so, it would seem that the presence of about 6 atom% platinum, in conjunction with a nonpolar solvent, probably served to inhibit the expansion of the palladium lattice so that hydrogen dissolution could not occur. Second, A2 and A5, although containing less platinum than required to close the Pd–H misibility gap, did not form β-PdH$_{0.6}$. It is thought that the above observations provide reasonable grounds for proposing that alloying of platinum and palladium had occurred, since β-PdH$_{0.6}$ would surely have been formed had palladium been present as a separate phase from platinum. Unfortunately, the powder diffraction lines were of low angle only (due to the small particle size) and the latter, while permitting phase identification, did not allow accurate *d*-spacing determination; in any case the *d*-spacings of palladium and platinum are very similar, so that it would be very difficult even with high-angle lines to detect accurately a change of lattice spacing as a function of alloy composition. If the inability of A2 and A5 to form β-PdH$_{0.6}$ can be regarded as evidence in favor of alloying then the Pd–H miscibility gap was closed by the respective addition of 10 and 14.5 atom% platinum. This apparent anomaly may be the result of the small particles of the material requiring less platinum to close to Pd–H miscibility gap than when the metal is in more massive form.

Catalyst Activity as a Function of Prereduction Time

The catalysts were prereduced in the reaction solvent for a given length of time, 1-octyne was injected, and the rates R_1 (1-octyne → 1-octene) and R_2 (1-octene → *n*-octane) were measured. In methanol, all catalysts behaved as reported previously (*1*) and the catalyst activity declined initially as prereduction time increased, eventually attaining a constant, limiting value (Fig. 1). The activities of the various catalysts were not simply related to surface area and although in the case of A2 and A5, β-PdH$_{0.6}$ was not formed in the bulk, decline in catalyst activity was not prevented by addition of platinum.

In *n*-hexane, catalysts A1, A2, A3, and A4 gave activity maxima for a prereduction time in the range 0 to 5 min (Fig. 2) and this behavior is similar to that reported by Caga *et al.* (*1*) for other Adams palladium oxide catalysts. Rather surprisingly, A5 and PdO B60663 behaved in the same way as in methanol, but the use of water as a prereduction medium along with low hydrogen partial pressures for the prereduction of PdO B60663 provides some explanation of the apparent anomaly (see below). Again, the closing of the Pd–H miscibility gap did not prevent loss of catalyst activity as prereduction time increased.

The behavior of Adams PtO$_2$ (H226) is interesting, since its activity was low at all times in methanol, with no variation as a function of prereduction time (Fig. 1). In *n*-hexane, a very high R_2 value was observed at zero time (Fig. 2), followed by a rapid decline to a constant value as prereduction time increased. Platinum is not reported to absorb hydrogen as does

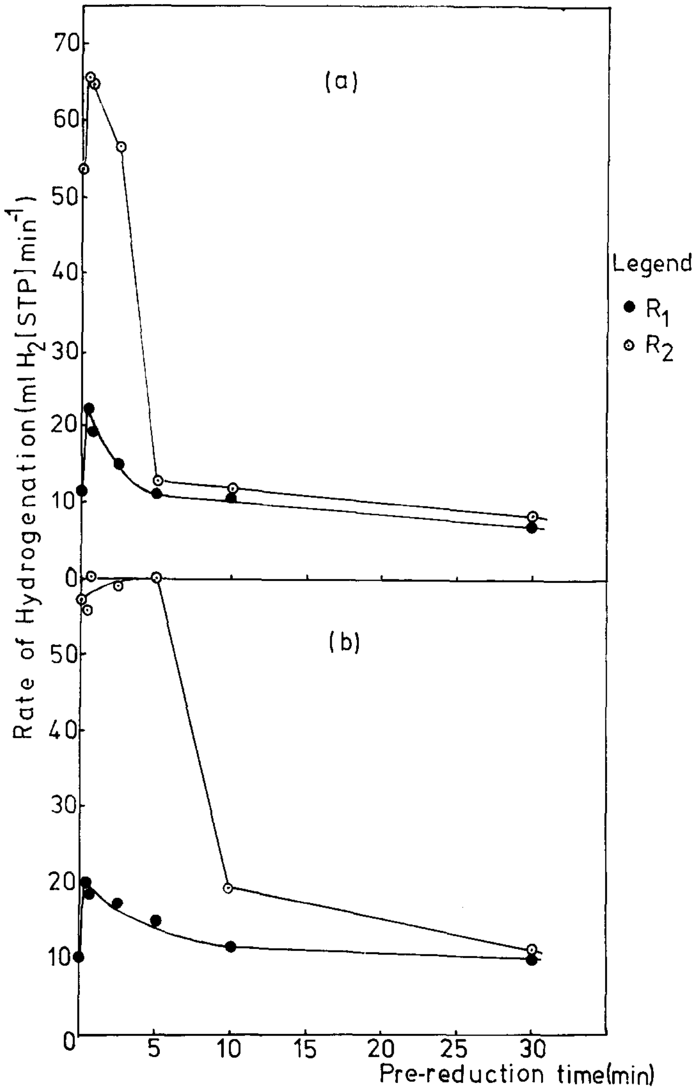

FIG. 3. Variation of rate in n-hexane with prereduction time for PdO B60663. (a) Prereduction in H_2O using H_2 only; (b) prereduction in H_2O using $H_2/Ar = 0.1$.

palladium, but the surface is obviously deactivated by hydrogen treatment. In the case of the three Adams Pt–Pd oxides (A2, A3, and A5) containing significant quantities of platinum, it might be expected (*8*b) that surface enrichment in palladium occurs and for A2 and A5 the Auger spectra confirm this (Table 3). First, catalyst A3 gives a platinum content which is slightly greater than that measured for the bulk but the result can be regarded as the same within experimental error. Indeed, the 64-eV Pt peak, being at the low-energy end of the spectrum, is difficult to measure accurately. The results for A2 and A5 certainly indicate that palladium enrichment of the surface occurred and, as deeper layers are exposed, the platinum content approaches that of the bulk. Such results provide a good explanation for the loss of activity in two systems that did not form bulk β-$PdH_{0.6}$. However, hydridation of

TABLE 4

Reaction Rate as a Function of Mole Fraction H_2 for Prereduction in Water followed by Reaction in n-Hexane[a]

Mole fraction H_2	R_1	R_2
0.1	15.3	60.2
0.3	15.4	58.8
0.5	17.0	63.1
1.0	11.1	13.0

[a] Catalyst, PdO B60663; prereduction time, 5 min.

the surface due to palladium enrichment cannot be the only reason for loss of activity as platinum alone behaves in the same way and the surface obviously possesses properties not shared by the bulk.

Use of Water as a Prereduction Medium

Because the reduction of Adams palladium oxide occurred in stages in water, it was decided to prereduce a catalyst in the latter in order to produce a PdO/Pd system, transfer the catalyst by decantation to methanol or *n*-hexane, and measure the rate of reaction.

Adoption of the above procedure using methanol as reaction solvent resulted in behavior similar to prereduction and reaction in methanol alone (Fig. 1). Prereduction in water, followed by transfer to *n*-hexane, also resulted in activity decline with approach to a constant rate at longer prereduction times for catalysts A1–A5. An activity maximum was obtained with PdO B60663 (Fig. 3a) and if, in addition, a hydrogen/argon mixture was used for prereduction in water ($H_2/Ar = 0.1$, Fig. 3b), a more pronounced maximum was observed after transfer of the catalyst to *n*-hexane. Finally, Table 4 shows the effect of varying the mole fraction of hydrogen in the H_2/Ar mixture for a constant prereduction time of 5 min. For hydrogen mole fractions <0.5, enhanced R_1 and R_2 values were observed and again, it is suggested that the activity maximum corresponds to the catalyst being in the oxide form with a palladized surface. This situation probably occurs in methanol, but too rapidly to be detected by the methods adopted in this work.

Catalyst Selectivity

The selectivity for 1-octene formation was measured for each of the catalysts and Table 5 gives the average selectivity for the first mole of hydrogen uptake. There is a gradual decrease in selectivity as platinum is added to the system.

An interesting observation was made in the case of catalyst PdO B60663, when a relatively large quantity of catalyst (0.85 g) was reduced for 10 min in methanol to produce β-$PdH_{0.6}$. The catalyst and solvent were then purged for 30 min using argon, so that the only available hydrogen present was in the form of β-$PdH_{0.6}$. One milliliter of 1-octyne was added and samples of the reacting solution were removed and analyzed at various times. The average selectivity was only 0.65 (Table 5) and corresponded to 87% 1-octyne remaining. This observation is in broad agreement with that of Borodzinski *et al.* (*9*) and it is clear that hydrogen reacting atomically via diffusion to the catalyst surface from within the catalyst does so less selectively than hydrogen arriving at the surface via an external route. The contribution via the

TABLE 5

Average Initial Selectivities for 1-Octene Production

Catalyst	S	At percentage Pt
PdO B60663	0.98 (0.65[a])	0.06
A1	0.96	0.04
A2	0.90	10.0
A3	0.91	5.6
A4	0.94	0.08
A5	0.90	14.5
PtO_2 (H226)	0.77	100

[a] For β-$PdH_{0.6}$.

former route will be negligible normally, but hydrogen atoms generated in this way may contribute in a very significant way to the double bond migration and *cis–trans* isomerization of olefins, for which palladium is much more efficient than other Group VIII metals.

Calculation of Turnover Number (N)

Turnover number was calculated (a) as moles 1-octyne reacting/min m^2 from the hydrogenation rate R_1, the selectivity, and the surface area at zero or short prereduction times (N_{1a}) and at long prereduction times (N_{1b}) and (b) as moles 1-octene reacting/min m^2 from the hydrogenation rate R_2 and the surface area, also at zero or short (N_{2a}) and long (N_{2b}) prereduction times.

Obviously, the value obtained for N, particularly at short prereduction times, is very sensitive to the surface area measurement. In the case of methanol the highest activity was obtained at zero prereduction time, when the area was presumably similar to that of the unreduced oxide (Table 1). In the case of n-hexane, maximum activity was usually observed between 0 and 5 min prereduction time, when the catalyst surface area lay somewhere between that of the unreduced oxide and the fully reduced catalyst. For this reason some modified N_a values were calculated arbitrarily on the basis of an area based on that of the original oxide plus 20% of the difference between the fully reduced system and the original oxide (see Table 1 for data used). This approach assumes that all catalyst areas will have changed by about the same amount at the activity maximum, which is very unlikely.

TABLE 6

Turnover Numbers for Long Prereduction Times

Catalyst	Turnover number × 10^{-20} in CH_3OH and in n-C_6H_{14}	
	N_{1b}	N_{2b}
PtO_2 (H226)	2	3
A1, A2, A3, A4, A5, and PdO B60663	11 ± 6	13 ± 9

TABLE 7

Turnover Numbers at Zero or Short Prereduction Times

Catalyst	Turnover number × 10^{-20} in CH_3OH and in n-C_6H_{14}	
	N_{1a}	N_{2a}
PtO_2 (H226)	3–5	5–50[a]
A1, A2, A3, A4, A5, and PdO B60663	19–208 (14–85)[b]	56–335 (39–137)[b]

[a] In n-hexane.

[b] Modified values based upon adjusted surface area.

Because of the problems stated above and the assumptions made results have not been quoted in detail and only averages or ranges are given to indicate the order of magnitude of the values calculated.

Table 6 shows the turnover numbers for long prereduction times for Adams PtO_2 (H226) and average values for the catalysts containing palladium and they are smaller than those for zero or short prereduction times (Table 7). In the latter case, ranges of values are given and it is noticeable that modification of the surface area (results in parenthesis) do not vary as widely and more accuracy may be obtained by measuring the catalyst surface area at a series of prereduction times in order to relate these to the measured activities at those times.

The N values obtained support the idea that the reaction surface changes, presumably as a result of hydridation from short to longer prereduction times, and this appears to happen for platinum as well as for palladium-based catalysts; there is a suggestion of a different surface for the Adams PtO_2 (H226) catalyst in n-hexane when $N_{2a} = 50 \times 10^{-20}$ mol 1-octyne/min m^2 but if anything a platinum catalyst surface appears to deactivate more quickly than a palladium surface and it is concluded that some kind of surface hydridation can occur independently of the possibility or otherwise of bulk hydridation.

There was no detectable trend in turnover number with increasing platinum content and although alloying probably occurred, and formation of bulk β-$PdH_{0.6}$ can be prevented by platinum contents >10 atom%, surface hydridation occurs independently and causes loss of catalyst activity. The behavior of the surface and subsurface will require study by more refined techniques than those applied to date.

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