JOURNAL OF CATALYSIS 78, 188–196 (1982)

Preparation of $Pd/AlPO_4$, $Pd/AlPO_4–SiO_2$, and $Pd/AlPO_4–\gamma\text{-}Al_2O_3$ and Study of Their Catalytic Activity for the Reduction of Nitrobenzene by Hydrogen Transfer

M. A. ARAMENDIA, V. BORAU, C. JIMÉNEZ, J. M. MARINAS,[1] AND J. A. PAJARES*

*Departamento de Química Orgánica, Universidad de Córdoba, Av. Medina Azahara, Córdoba, Spain and *Instituto de Catálisis y Petroleoquímica, C.S.I.C., Serrano 119, Madrid-6, Spain*

Received February 24, 1982; revised June 11, 1982

The preparation and catalytic activity for the hydrogen-transfer reduction of nitrobenzene of new metallic systems obtained by supporting palladium on $AlPO_4$, $AlPO_4–SiO_2$, and $AlPO_4–\gamma\text{-}Al_2O_3$ are reported. Metal dispersion decreases in the order $Pd/AlPO_4–SiO_2$ > $Pd/AlPO_4$ > $Pd/AlPO_4–\gamma\text{-}Al_2O_3$, and, according to the method of preparation, cationic exchange > impregnation > anionic exchange. Catalysts prepared by cationic exchange on $AlPO_4–SiO_2$ show high dispersion values ($D = 0.63$, $\bar{d} = 1.8$ nm mean particle size). The catalysts have different activities for the reduction of nitrobenzene to aniline at the reflux temperature of the nitrobenzene–cyclohexene mixture (383 K), with a selectivity near 100% and without poisoning. No influence of the acidity of the different metal systems was found, the activity depending only on the dispersion of the active metal phase.

INTRODUCTION

Most of the papers in the literature on supported metallic catalysts refer to the use of silica, alumina, silica–alumina, carbon, or zeolites as supports. We have recently reported (*1*) the activity of new catalysts obtained by supporting palladium on $AlPO_4$, $AlPO_4–SiO_2$, and $AlPO_4–\gamma\text{-}Al_2O_3$, used in the reduction of aromatic derivatives.

In the present paper, different preparation methods of such systems are reported, together with their physicochemical characterization and measurement of catalytic activity for the hydrogen-transfer reduction of nitrobenzene using cyclohexene as hydrogen donor.

Hydrogenation–dehydrogenation by hydrogen transfer between a donor and a different acceptor molecule

$$DH_x + nA \rightarrow nAH_x + D$$

is a process studied long ago by Braude and Linstead (*2*). These authors (*3*) ran the reduction of nitrobenzene over heterogeneous supported palladium catalysts. With noble metals (*4–8*), iron and cobalt-phthalocyanines (*9*) and other catalysts (*10*) have been used in this process. Cyclohexene and cyclohexadiene have been preferentially used as donors, although formic acid (*6*) and triethylammonium formiate (*1, 8*) have also been successfully employed.

EXPERIMENTAL

Materials

Supports. Three different supports have been used: support AP corresponds to pure aluminum orthophosphate; support APA has a composition $AlPO_4–\gamma\text{-}Al_2O_3$ (75 : 25 wt) and was prepared by gelling the phosphate on a suspension of $Al(OH)_3$ precipitated with ammonia from an aluminium nitrate solution; and support APS was obtained by gelling aluminium orthophosphate on commercial silica gel (70–230 mesh), thus leading to colloidal $AlPO_4$: SiO_2 (20 : 80 wt). In all three cases the gellification process was carried out in ethylene oxide using particle sizes between 70 and 230 mesh.

[1] To whom correspondence should be addressed.

0021-9517/82/110188-09$02.00/0

The synthesis and textural properties of these supports have been published elsewhere (*11–13*).

Catalysts. Three series of catalysts have been prepared: I, II, and III.

Series I. Samples of this series were obtained by impregnation of the support with an aqueous solution of $PdCl_2$ slightly acidified with HCl to facilitate dissolution of the palladium salt. In all cases, the pH was kept close to 4, in order to avoid dissolution of the aluminium orthophosphate. The impregnated supports were dried at 100–110°C for 24 h, and subsequently reduced in a static reactor under $P_{H_2} \simeq 800$ Torr (1 Torr = 133.3 N m^{-2}), at several times and temperatures.

The catalysts are named with a set of letters and figures: the chemical symbol of the metal is followed by a letter indicating the type of support and a subscript for the percentage metal loading, followed by the reduction temperature in degrees Celsius and the number of hours of reduction.

Series II. The impregnating aqueous solution was $PdCl_2$ or $[Pd(NH_3)_4]^{2+}$. The preparation of these samples was the same as for series I, but, after drying, part of the samples were calcined in a flow-reactor at a previously programmed heating rate, followed by reduction in hydrogen stream (60 ml min^{-1}) in the same thermal conditions as for calcination. Another set of samples was reduced immediately after drying, without calcination.

Samples are named with the chemical symbol of the metal, followed by a letter indicating the type of support, subscript for the percentage metal loading, impregnating salt (M for $PdCl_2$ and N for $Pd(NH_3)_4Cl_2$), heating rate (°C min^{-1}), and final temperature reached during reduction. C and NC indicate, respectively, whether the sample was calcined or not before reduction.

Series III. These samples were prepared by ionic exchange of the supports with an aqueous solution of $[Pd(NH_3)_4]^{2+}$ (*14*) or $PdCl_4^{2-}$ (*15*), taking into account the zero point of charge of the support (*16, 17*). The solids were dried *in vacuo* (30 Torr, 24 h) and calcined before reduction in hydrogen stream, by linearly raising the temperature up to 300°C.

Naming of the samples was similar to those of series I and II, but + (plus) or − (minus) signs were used to indicate the impregnating salt ($[Pd(NH_3)_4]^{2+}$ or $PdCl_4^{2-}$, respectively).

Procedures

Specific surface area and pore volume. Specific surface area—S_{BETN_2}, A_{N_2} = 16.2 $Å^2$—of the supports was determined in a volumetric adsorption apparatus. The pore volume was obtained from the desorption branch of the nitrogen adsorption isotherm, by following the method of Innes as modified by Lippens *et al.* (*18*). An average pore diameter ($\bar{d}$, Table 1) was obtained directly from the experimental plots.

Zero point of charge of the supports. Following Brunelle (*17*), we have determined the pH which remains unaltered by addition of the solid. Changes of pH (mV) were determined as a given amount of solid is added at a series of aqueous solutions originally at different pHs. In this way, the zpc corresponds to the pH of the solution that shows no pH change when the solid is added. Monochloroacetic acid 0.01 *N* and ammonia 0.01 *N* were used over 0.40 g of sample.

Metal loading. Chemical analysis of the metal content was made by atomic absorption spectrometry using a Perkin-Elmer 370 instrument with a hollow cathode lamp, at λ = 247.8 nm. In order to eliminate the aluminium interference, an aqueous solution (5%) of lanthanum oxide was added.

Acidity. A spectrophotometric method based on the chemisorption of amines on the surface acid sites on the solids has been followed (*19, 20*), with cyclohexylamine (pK_a = 10.6) as titrating reagent. A Bausch & Lamb Spectroscopic 21 apparatus, at λ = 225 nm, was used.

Metal surface area. The active metallic surface area has been measured by CO che-

misorption at room temperature (*21*) either thermogravimetrically with a Cahn RG electrobalance, or volumetrically in a conventional adsorption static apparatus. A stoichiometric factor of 1.15 was chosen (*22*). The average size of the metallic crystallites has been calculated assuming a spherical shape.

Transmission electron microscopy (TEM) was carried out in a Philips EM-300 instrument working at 100 kV with a resolution of 3 Å. Samples were prepared by an extractive replica method, and metallic size distribution was determined by counting 600–800 particles. The average diameter ($\bar{d}$) was obtained from the volume/surface ratio.

XR diffractograms were taken in a Philips 1130/00/60 apparatus, by using the Cu$K\alpha$ radiation, λ = 1.5418 Å. The measurement of the half peak width was made graphically, at an angle $2\theta = 40.10°$ corresponding to plane (111) of Pd, and a value 0.89 was taken for the constant C of the Debye–Scherrer equation.

Catalytic activity. Nitrobenzene reduction experiments have been carried out in a three-necked flask equipped with a thermometer, a refluxing refrigerant, and a rubber subaseal that permits periodical withdrawal of samples. The flask was immersed in a silicon oil bath and operates at reflux (383 ± 2 K) while magnetically stirred at 360 rpm. Previous work indicated that the reaction rate is constant between 200 and 700 rpm. Blank tests did not show any reaction product in the presence of the support alone after 8 h. Disproportionation of cyclohexene was completely inhibited by nitrobenzene. In all cases, 1.46×10^{-2} mol nitrobenzene, 6.90×10^{-2} mol cyclohexene, and an amount of catalyst equivalent to 2.40×10^{-2} g Pd were used.

GC analysis of the reaction products was made with a Hewlett–Packard 5830 A apparatus. Polyphenilether and u.c.c. columns were used, with nitrogen as the carrier gas. The injection chamber and detector temperatures were 210–250 and 220–250°C, respectively. The nature of the products was confirmed by combining the GC apparatus with a mass spectrometer Hewlett–Packard 5992 B.

RESULTS AND DISCUSSION

Catalysts Characterization

Physical properties of the supports employed in this work are given in Table 1. Although high, the specific surface area of $AlPO_4$ (S_{BET} = 256 $m^2\ g^{-1}$) has a lower value than those reported by Kearby (*23*) and Alberola and Marinas (*11*) using the same preparation method. The higher values of the specific surface of $AlPO_4$–γ-Al_2O_3 (S_{BET} = 263 $m^2\ g^{-1}$) and $AlPO_4$–SiO_2 (S_{BET} = 327 $m^2\ g^{-1}$) are more in accord with the results found by Hall and co-workers (*24*) for calcium phosphate than with the trend reported by Moffat (*25*) and Tada *et al.* (*26*) that the surface area of $AlPO_4$ decreases with decreasing P/Al ratio. In any case, it must be taken into account that the correspondence of these prepared *mixed* systems with usual P/Al preparations cannot be straightforward. The pore volumes—V_p = 0.60–0.46 $cm^3\ g^{-1}$—remain acceptable for a support, but the average pore diameter—$\bar{d}$ = 30–40 Å—is relatively low.

Results for the surface acidity of the supports and some samples of the three series of catalysts are given in Table 2. The acidity of the aluminium phosphate falls quite near that found in previous work (*23, 26, 27*); its higher value by specific surface unit could be related to its larger pore size, traduced in a better accessibility of the

TABLE 1

Textural Properties of the Supports

Support	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	$\bar{d}$ (Å)
AP($AlPO_4$)	256	0.60	40
APA ($AlPO_4$–γ-Al_2O_3)	263	0.53	30
APS ($AlPO_4$–SiO_2)	327	0.46	30

TABLE 2

Surface Acidity (Cyclohexylamine Titration)

System	Total acid concentration (mmol g^{-1})	System	Total acid concentration (mmol g^{-1})
APS	0.69	Pd $APS_{5.0}$M-300C	0.40
AP	0.71	Pd $APS_{1.0}$M-300C	0.47
APA	0.62	Pd $APS_{1.0}$N-300C	0.53
Pd $APS_{0.50}$300-3	0.43	Pd $APS^{+}_{0.56}$1-300C	0.36
Pd $APS_{1.0}$300-3	0.41	Pd $AP^{+}_{0.91}$1-300C	0.39

amine. The strength of the acid centers falls in the sequence APA > AP > APS (*1*). A decrease of acidity is generally observed upon incorporation of the metallic phase. Neither the preparation method used nor the metal content seems to have a clear correlation with this decrease.

Knowledge of the isoelectrical point of a solid is fundamental in the application of the modern theory of ionic exchange to the preparation of supported catalysts from adsorption in solution (*16, 17*). The experimental determination of this point for all three supports can be seen in Fig. 1. The pH values found for the zpc for supports AP and APA, 3.2 and 4.25, respectively, suggest the possibility of exchange with cationic precursors above these values, and anionic ones below them. Also support APS, zpc = 3.4, permits the use of cationic exchange at higher pH; but the shape of the neutralization curve for this support indicates a polarization of the solid near zero at lower pH, implying a difficult anion exchange. This finding has been fully confirmed, as no exchange at all between support APS and $PdCl_4^{2-}$ has been experimentally detected.

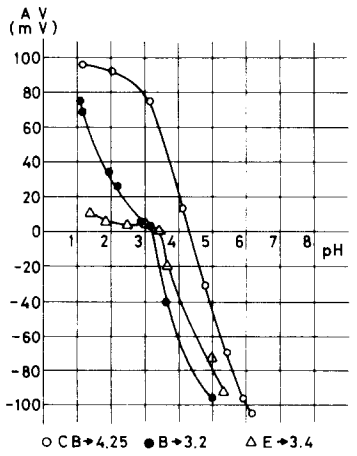


FIG. 1. Zero point charge determination of the supports.

Results on metal dispersion for a part of the three series of prepared catalysts are given in Table 3. The particle diameters obtained from TEM micrograph counting practically coincide with those calculated from CO chemisorption; only for the lowest sizes ($\bar{d}$ < 2.0 nm) TEM gives slightly higher values (0.4–0.5 nm) probably due to errors in counting for choosing of the larger crystal sizes (for these catalysts the dispersion value in Table 3 is that calculated from gas adsorption). The experimentally obtained dispersion follows the sequence

support APS > support AP > support APA

Therefore more data are reported on the catalysts prepared on support APS.

Catalysts corresponding to Series I are very badly dispersed, with metal surface areas in the order of 10 m^2/g Pd, showing the deleterious effect of the water vapor presence when using the static system of reduction. The correct reduction treatment in hydrogen flow is clearly demonstrated for the dispersion results of catalysts of Series II

TABLE 3

Metal Dispersion

System	Sp. metal surface (m^2/g Pd)	Dispersion (D)	Mean particle size (Å)
Series I			
Pd $APS_{0.5}$200-3	24	0.05	208
Pd $APS_{1.0}$200-3	13	0.03	374
Pd $APS_{1.0}$200-4	9	0.02	558
Pd $APS_{1.0}$300-3	7	0.02	721
Pd $APS_{1.0}$300-4	10	0.02	492
Series II			
Pd $AP_{1.0}$M1-200C	58	0.13	86
Pd $AP_{1.0}$M3-200NC	59	0.13	85
Pd $AP_{1.0}$M4-200NC	46	0.10	110
Pd $AP_{1.0}$N-300NC	43	0.09	116
Pd $APS_{1.0}$N1-200C	39	0.13	88
Pd $APS_{1.0}$M1-300C	63	0.14	80
Pd $APS_{1.0}$N-300NC	35	0.08	141
Pd $APS_{1.0}$N1-300C	57	0.13	88
Pd $APS_{1.0}$N2-300C	38	0.08	132
Pd $APS_{1.0}$N3-300C	27	0.06	186
Pd $APS_{5.0}$M-300C	32	0.07	155
Pd $APS_{5.0}$M-300C	26	0.06	194
Series III			
Pd $APA_{0.57}$1-300C	3	0.01	1671
Pd $AP^{+}_{0.91}$1-300	39	0.09	129
Pd $AP^{+}_{0.45}$1-300C	8	0.02	627
Pd $APS^{+}_{0.56}$1-300C	280	0.63	18
Pd $APS^{+}_{0.82}$1-300C	280	0.63	18
Pd $APS^{+}_{0.60}$-200NC[a]	68	0.15	74
Pd $APS^{+}_{0.60}$-300NC[a]	46	0.10	108

[a] Reduced at constant temperature.

(metal surface areas in the order 30–60 m^2/g Pd). Better dispersion values were obtained when the impregnating solution started from $[Pd(NH_3)_4]^{2+}$ (N), and data are preferentially referred to these preparations. For the same reduction temperature (300°C) a detrimental effect for the higher heating rates of reduction is clear: the metal surface area decreases, $57 > 38 > 27$ m^2 g^{-1} when the heating rate raises from 1 to 3°C min^{-1}. The previous calcination treatment does not seem to affect the state of dispersion, the phosphate supports having a behavior more similar to a support as SiO_2, with low water content and weak interaction with the metal.

Adsorption from solution was the best method to develop a high metal area. As could be expected from the zpc data, cationic exchange at higher pH gives the best results (280 m^2/g Pd for the catalysts with 0.5–1.0% Pd). Similar results with this procedure have been obtained with other metals (Rh, Pt)/support (*17, 28*) and nonmetals (MoO_3)/support (*29*) catalytic systems. As can be seen in Fig. 2 the metal is fairly homogeneously dispersed on the support. From the collected data it seems that a calcination treatment may improve the dispersion of palladium.

Nitrobenzene Reduction

Catalytic activity runs were made over more than 50 catalysts. Representative results are given in Table 4. Data are referred to conversion to aniline per hour (column 3) and specific activity per surface atom of palladium or turnover number (column 4). All the activity data were taken at the reflux temperature of the nitrobenzene–cyclohexene mixture, 383 K.

Cyclohexene behaves as a good hydrogen donor, as expected (4). A previous comparative experimental study, with the same catalyst (Pd $APS^{+}_{0.82}$-1-300 C) and several hydrogen donors at their respective reflux temperatures, gave conversions to aniline in the sequence

cyclohexene > 1.3 cyclohexadiene > methylcyclohexene > tetralin

limonene and α-phellandrene giving very low activity values (<0.2%).

Among the Series I catalysts none gave a noticeable activity for nitrobenzene reduction with cyclohexene as hydrogen donor. Catalysts of Series II showed a moderate activity. The percentage of conversion to aniline seems to be related to the degree of dispersion of the metal, as can be deduced from the data for the Pd $APS_{1.0}$ N 300 C series. Consequently the highest conversion rates correspond to the catalysts of Series III, prepared by ionic exchange, with

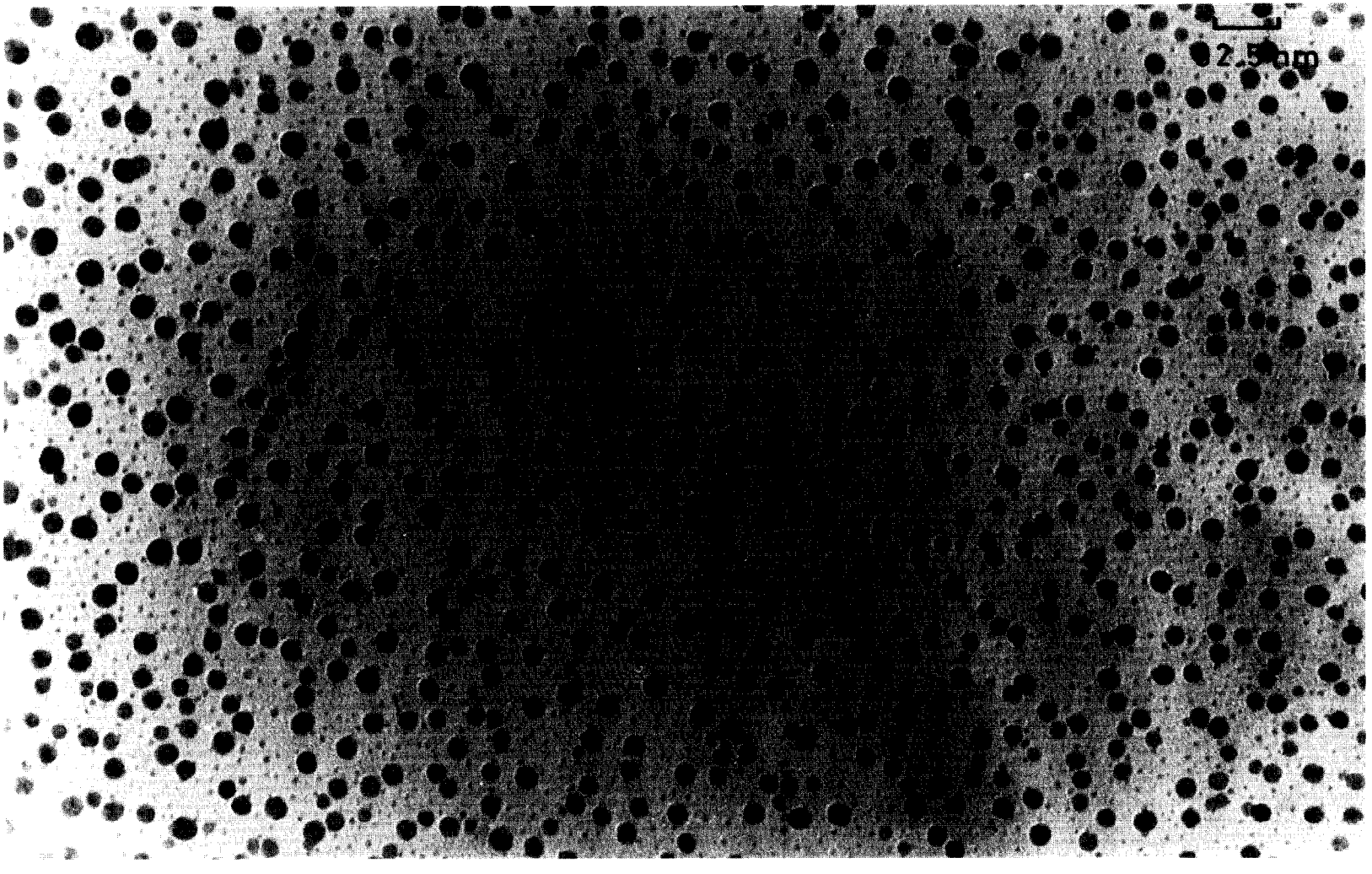


FIG. 2. TEM micrograph of Pd $AP^{+}_{0.91}$ 1-300 C ($Pd/AlPO_4$, cationic exchange).

TABLE 4

Nitrobenzene Reduction by Hydrogen Transfer from Cyclohexene on Several Pd/Aluminium Phosphate Catalysts[a]

System	Dispersion (*D*)	Percentage anilin/hour	Turnover number (h^{-1})
Series I			
Pd $APS_{1.0}$200-3	0.03	<0.1	—
Pd·$APS_{1.0}$300-3	0.02	<0.1	—
Pd $APS_{1.0}$300-4	0.02	<0.1	—
Series II			
Pd $AP_{1.0}$M1-200C	0.13	1.4	71
Pd $APS_{1.0}$M1-300C	0.14	6.0	290
Pd $APS_{1.0}$N1-300C	0.13	6.1	328
Pd $APS_{1.0}$N2-300C	0.08	3.5	281
Pd $APS_{1.0}$N3-300C	0.06	2.5	281
Series III			
Pd $AP^{+}_{0.91}$1-300	0.09	7.7	600
Pd $AP^{-}_{0.45}$1-300C	0.02	1.8	670
Pd $APA^{-}_{0.57}$1-300C	<0.01	1.5	1526
Pd $APS^{+}_{0.56}$1-300C	0.63	18.0	195
Pd $APS^{-}_{0.82}$1-300C	0.63	18.0	195
Fluka Pd/carbon		3.0	
Fluka Pd/Al_2O_3		11.7	
Merck Pd/CO_3Ca		0.6	

[a] T = 383 K.

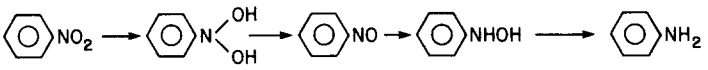
the highest values of specific metallic area and dispersion.

The specific rate of conversion per active site, turnover number, is very similar for the catalysts of Series II and III, prepared over ($AlPO_4$–SiO_2). Therefore the reaction seems to belong to the group of *structure insensitive* or *facile* reactions although results are not conclusive. The higher specific rates found in some palladium catalysts over the supports AP, and APA, may be due to an increase of the exposed metal area under reaction conditions which would produce erroneously high values of the turnover number. In fact some decomposition to metal of unreduced metal precursor under electron beam impinging during TEM examination has been observed. In any case, work in progress on more recent Pd/$AlPO_4$ preparations gave higher dispersion with higher reduction temperatures up to 450°C. This indicates that the metal precursor is not easily decomposed, the system apparently showing a stronger metal–support interaction than previously expected (*30*).

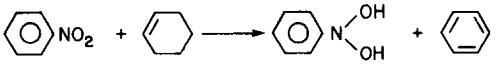
Some experiments over the catalyst Pd $APS_{1.0}$ N 2-200 C in benzene solution gave unit-slope plots log r vs log concentration, from which an order 1 for the dependence of the rate of reaction on the concentrations of cyclohexene and nitrobenzene may be obtained. In the range of conditions studied, the rate depends also linearly on the weight of catalyst, with slope 1. Therefore a kinetic expression

$$r = k[\text{cat}][\text{nitrobenzene}][\text{cyclohexene}]$$

may be inferred, similar to that found by Bar Ilan and Manassen (*9*) when an oxydative dehydrogenation mechanism is considered. Probably the reaction begins, as suggested by Brieger and Nestrick (*4*), by the easier dissociative adsorption of cyclohexene on palladium with the formation of palladium hydride, followed by the reaction of this hydride with the nitrobenzene chemisorbed through a π-bond. The process follows the sequence (*3, 10*)



As the nitrosobenzene and phenyl-hydroxylamine reduction are quicker steps (*3*), the kinetics of the whole process is practically dependent on the reduction of nitrobenzene, step 1:



It seems that the acidity of the catalysts has no relation with their activity for nitro-

benzene reduction. Although obviously the acid centers on the aluminium phosphate can easily adsorb amines (*4, 31*) probably the effect of the reflux suffice for an easy products desorption. Alcohol dehydrogenation on hydroxyapatite following a concerted mechanism has been reported by Kibby and Hall (*32*), the acid sites for adsorption being surface cations or protons from HPO_4^{2-} groups and the basic sites surface OH^- or PO_4^{3-} groups; but in our work such a mechanism does not seem to be important, the reaction being carried out mainly over the metal component. Some activity of $AlPO_4$ in the transfer of hydrogen from isopropanol to methylethylketone to produce acetone and 2-butanol begins at a higher temperature range, above 150°C (*25, 33*).

Comparison with some commercial preparations shows a better performance for the well-dispersed $Pd/AlPO_4$–SiO_2 catalysts (Table 4). The selectivity to aniline was always near 100%, the conversion being kept constant, without the progressive poisoning, mainly due to carbon deposits, so typical of many hydrogen-transfer catalytic processes.

CONCLUSIONS

(1) Different preparation procedures—ion exchange, impregnation—have been used to deposit palladium on $AlPO_4$, $AlPO_4$–SiO_2, and $AlPO_4$–γ-Al_2O_3 as catalyst supports. Cationic exchange is superior to impregnation, metal dispersion decreasing in the sequence $Pd/AlPO_4$–SiO_2 > $Pd/AlPO_4$ > $Pd/AlPO_4$–γ-Al_2O_3. Materials prepared following this method on $AlPO_4$–SiO_2 show dispersion values as high as 0.63 ($\bar{d}$ = 1.8 nm mean particle size). A calcination treatment seems to have a beneficial effect on metal dispersion.

(2) The different Pd/support preparations have different activities for reduction with hydrogen transfer of nitrobenzene to aniline with cyclohexene as the donor molecule; selectivity was near 100% in all cases. The percentage of conversion to aniline seems to be related to the degree of dispersion of the metal. The acidity of the catalysts does not have a noticeable effect on their activity for this reaction.

REFERENCES

1. Aramendia, M. A., Ph.D. Thesis, University of Cordoba, 1980; Aramendia, M. A., Climent, M. S., Jimenez, C., and Marinas, J. M., *React. Kinet. Catal. Lett.* **14,** 489 (1980).
2. Braude, E. A., and Linstead, R. P., *J. Chem. Soc.* 1954, 3544.
3. Braude, E. A., Linstead, R. P., and Wooldridge, K. R. H., *J. Chem. Soc.* 1954, 3586.
4. Brieger, G., and Nestrick, T. J., *Chem. Rev.* **74,** 567 (1974).
5. Entwistle, I. D., Johnstone, R. A. W., and Povall, T. J., *J. Chem. Soc. Perkin I* 1979, 1300.
6. Entwistle, I. D., Johnstone, R. A. W., and Telford, R. P., *J. Chem. Res.* 1977, 1382.
7. Entwistle, I. D., Gilkerson, T., Johnstone, R. A. W., and Telford, R. P., *Tetrahedron* **34,** 213 (1978).
8. Cortesse, N. A., and Heck, R. F., *J. Org. Chem.* **22,** 3491 (1977).
9. Bar-Ilan, A., and Manassen, J., *in* "Proc. Vth Int. Symposium on Catalysis" (J. W. Hightower, Ed.), Vol. II, p. 1149. Elsevier, Amsterdam, 1973.
10. Iwasawa, T., Mori, H., and Ogasawara, S., *J. Catal.* **61,** 366 (1980).
11. Alberola, A., and Marinas, J. M., *An. Quim.* **65,** 1001 (1969).
12. Campelo, J. M., Marinas, J. M., and Pérez-Ossorio, R., *An. Quim.* **72,** 698 (1976); *in* "Proc. Vth Iberoamerican Symposium on Catalysis" (P. F. Portela and C. Pulido, Eds.), Vol. 2, p. 155. Lisbon, 1978.
13. Jiménez, C., Marinas, J. M., Pérez-Ossorio, R., and Sinisterra, J. V., *An. Quim.* **73,** 1164 (1977).
14. Gonzo, E. E., and Boudart, M., *J. Catal.* **52,** 462 (1978).
15. Fuentes, S., and Figueras, F., *J. Chem. Soc. Faraday Trans. I* **74,** 174 (1978).
16. Parfitt, G. D., *Pure Appl. Chem.* **48,** 415 (1976).
17. Brunelle, J. R., *Pure Appl. Chem.* **50,** 1211 (1978).
18. Lippens, B. C., Linsen, B. G., and de Boer, J. H., *J. Catal.* **3,** 32 (1967).
19. Benesi, H. A., *J. Catal.* **28,** 176 (1973).
20. López González, J. D., and Valenzuela, C., *An. Quím.* **74,** 220 (1978).
21. Scholten, J. J. F., and Van Monfoort, A. V., *J. Catal.* **1,** 83 (1962).
22. Farrauto, R., *AIChE Symp. Ser.* 70 (N. 143) 9 (1974).

23. Kearby, K., *in* "Proc. IInd Int. Symposium on Catalysis," p. 2567. Technip., Paris, 1961.
24. Bett, J. A. S., Christner, L. G., and Hall, W. K., *J. Amer. Chem. Soc.* **89,** 5535 (1967).
25. Moffat, J. B., *Catal. Rev. Sci. Eng.* **18,** 199 (1978).
26. Tada, A., Yoshida, M., and Hirai, M., *Nippon Kagaku Kaishi* 1973, 1379.
27. Aramendia, M. A., Campelo, J. M., Boráu, V., Jiménez, C., Luna, D., and Marinas, J. M., *in* "Proc. VIIth Iberoamerican Symposium on Catalysis," p. 79. La Plata (Argentina), 1980.
28. Reyes, P., Ph.D. Thesis, University Complutense, Madrid, 1980; Reyes, P., and Pajares, J. A., *Rev. Real Acad. Cienc. Exact. Fís. Nat. (Madrid)* **75,** 306 (1981).
29. Wang, L., and Hall, W. K., *J. Catal.* **66,** 251 (1980).
30. Martín, M. A., González Tejuca, L., and Pajares, J. A., unpublished results.
31. Haber, J., and Szybalsa, U., *Disc. Faraday Soc.*, Preprint 16, 1981, in press.
32. Kibby, C. L., and Hall, W. K., *J. Catal.* **29,** 144 (1973); **31,** 65 (1973).
33. Freidlin, L. Kh., Sharf, V. Z., German, E. N., Vorob'eva, N. K., and Shcherbakova, S. I., *Izv. Akad. Nauk SSSR, Ser. Khim.* **9,** 2130 (1970).