JOURNAL OF CATALYSIS 57, 516–521 (1979)

Atomically Dispersed Palladium as a Borderline Case between Heterogeneous and Homogeneous Hydrogenation of Olefins

INTRODUCTION

Very active hydrogenation catalysts can be prepared by reduction with saline hydrides or molecular hydrogen of (allyl)-Pd(II) derivatives anchored to inorganic supports (*1, 2*). The high catalytic activity has been related to the high degree of dispersion of the Pd metal which has been described as Pd dispersed at "atomic level." A small-angle X-ray investigation carried out on these materials confirmed the extreme dispersion of the metal; in fact the Pd particle diameters fall for the most active catalysts in the range 2 to 20 Å (*3*). In the framework of this study, we thought it may be promising to investigate the catalytic behavior of these materials toward the hydrogenation of a variety of olefins and dienes under mild experimental conditions.

Indeed heterogeneous hydrogenation of olefins has often been interpreted analogously to the homogeneous counterpart, i.e., involving the same elementary steps (*2, 4, 5*), whatever the physical status of the catalyst. This parallelism seems to be very appropriate in this case where an extreme dispersion has been verified.

EXPERIMENTAL SECTION

Olefinic compounds were commercially purchased and purified by filtration through grade 1 neutral alumina, distilled and stored under N_2. $[Pd(C_3H_5)_2]$ was prepared according to the literature procedure (*6*). The catalysts were synthesized as previously described on reacting $[Pd(C_3H_5)_2]$ with the vitreous supports and reducing with molecular H_2 (*2*). The supports were obtained with the described procedures (*2, 7*).

Kinetics

The hydrogenation of the olefins to the corresponding alkanes was performed in a round bottomed flask equipped with a sidearm fitted with a silicone septum to allow olefin injection and sampling for g.l.c. analysis. Two stopcocks allowed connection to a vacuum rack and to a standard gas absorption apparatus operating at constant H_2 pressure. Temperature was maintained constant (25 ± 0.1°C) with the aid of a jacket connected to the external circulation of a thermostat. Stirring was performed by a teflon coated bar driven externally by a magnetic stirrer. To the reaction vessel containing a standard weight of catalyst prepared *in situ* (0.5 g of support with the appropriate amount of Pd) 10 ml of dried degassed THF was added and the suspension was allowed to stand under H_2 with vigorous stirring for 2 hr. Kinetic runs were commenced upon injection of 0.3 ml of the appropriate olefin. The percentages of conversion calculated from the ratio v_t/v_∞, were plotted vs time. From the slopes of

0021-9517/79/060516-06$02.00/0

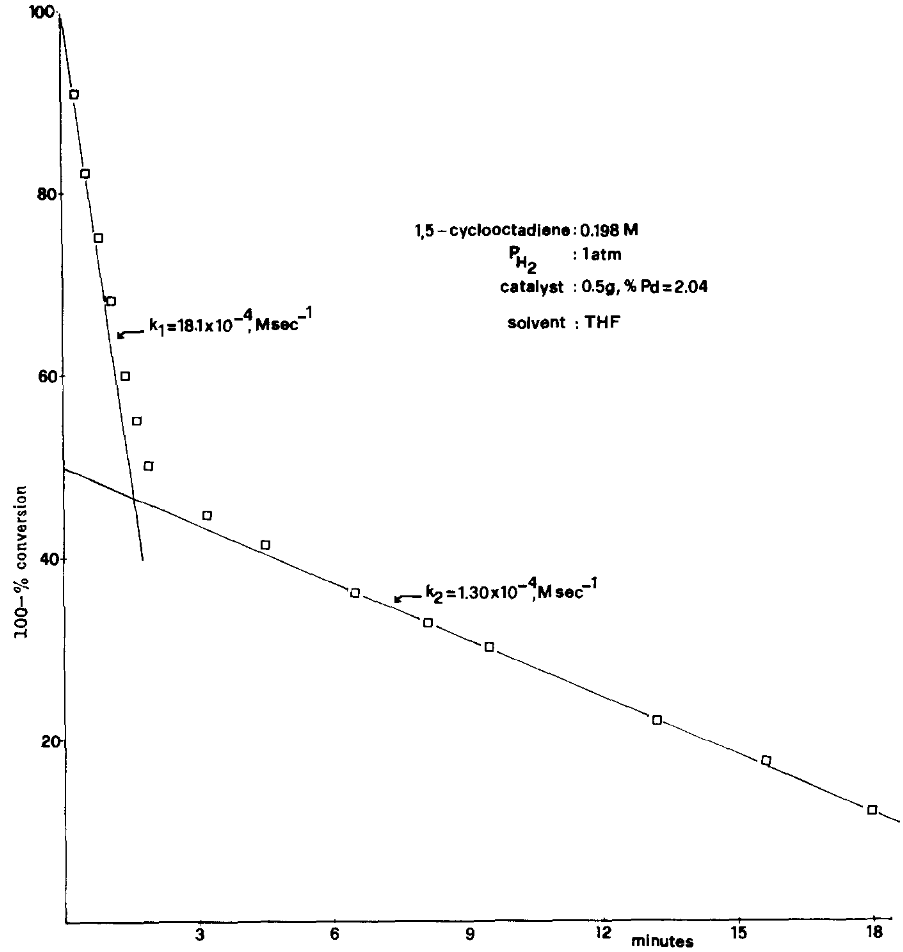

FIG. 1. Typical plot for the hydrogenation of dienes.

the obtained plots the pseudozero-order rate constants were calculated on multiplying the slopes by $C_o/100$, where C_o is the initial olefin concentration.

In the case of the hydrogenation of dienes a marked deviation from the linearity of the plots of percentages vs time has been observed in agreement with a two step reaction. Figure 1 reproduces a typical plot for the diene hydrogenation experiments. The Guggenheim method (*8*) was used to calculate the k_{obs} values for both steps, k_1 and k_2, i.e., the first third of the overall trend to calculate k_1 and the last third to obtain k_2. When the ratio k_1/k_2 was less than 10 an iterative least-squares program was used to obtain the best k_1 and k_2 values to fit the percentage of conversion vs time curves.

Kinetic runs for different dienes have been carried out under identical experimental conditions in order to provide the best homogeneity in the data collection. Where specified (Table 1) kinetic runs were also followed with an HP 5730A gas-chromatograph equipped with an automatic integrator, and the obtained rate constants were in good agreement with the data from volumetric measurements. The reproducibility of the kinetics was also

TABLE 1

Pseudozero-Order Rate Constants ($10^4 \times k, M$ sec^{-1}, volumetric) for the Hydrogenation of Various Olefins[a]

		0.12% Pd	0.5% Pd	1.02% Pd	2.04% Pd
1-Hexene		1.02	4.53	9.92	19.6
1-Heptene		0.62[b]	3.10	6.21	13.3
1-Octene		—	1.10	2.41	4.90
2-Methyl-2-butene		—	0.31[b]	0.68	1.42
Cyclohexene		0.82[b]	2.94	4.80	12.5
Cyclooctene		—	0.27	0.51	1.04
1,5-Cyclooctadiene	k_1	1.05[b]	3.87	—	18.1
	k_2	0.08[b]	0.24	—	1.30
1,3-Cyclooctadiene	k_1	—	4 02	8.90	18.4
	k_2	—	0.26	0.47	0.96
Dicyclopentadiene	k_1	1.25	4 54	—	21.8
	k_2	0.19	0.75	—	4.22
1,4-Octadiene	k_1	—	4.34[b]	10.7	22.3
	k_2	—	1.20[b]	2.53	4.71
1,7-Octadiene	k_1	1.20	4.51	9.97	—
	k_2	0.35	1.21	2.36	—

[a] Experimental conditions: catalyst 0.5 g, olefin 0.3 ml; solvent THF 10 ml; p_{H_2} 1 atm.

[b] Duplicated by g.l.c.

checked by duplicate experiments and the k_{obs} were found to fall within a standard deviation of ±4–±9%.

RESULTS AND DISCUSSION

The catalysts constituted of Pd metal dispersed on vitreous supports have been demonstrated to have a different catalytic activity in the hydrogenation reactions depending on the degree of dispersion of the metal (*2*, *3*). For the purpose of this study, the one having the highest catalytic activity was chosen, since in this case the activity was found to be linearly dependent on the percentage of Pd. Moreover, the physical properties of this particular material were previously investigated (*3*) and the Pd particle diameter was found to fall in the interval 2 to 20 Å so that the percentage of exposed metal is very close to 100%.

Hydrogenation of Monoolefins

The linear dependence of the percentage of conversion on time indicates that the rate of hydrogenation is independent of the olefin concentration. This fact is typical of the hydrogenation of olefins catalyzed by heterogeneous catalysts (*9–11*) and indicates that the activation of molecular hydrogen is the rate-determining step of the overall process. The pseudozero-order rate constants are collected in Table 1. The catalytic activity was studied using catalysts having different percentages of Pd and the k_{obs} values obtained for each olefin have been plotted vs the percentage of Pd. The resulting trends are shown in Fig. 2, where the linear dependence of the catalytic activity on the percentage of Pd is evident for all the olefins used. Clearly, the same type of relationship obtained for different olefins indicates that the same mechanism can be applied to all cases. This allows a direct comparison among the different olefin hydrogenation rate constants which is strongly affected by the nature of the olefin.

Owing to the large degree of dispersion of Pd, the hydrogen sorbed by Pd results essentially from a chemisorption process, since the solubility of hydrogen tends to zero as the dispersion of the metal approaches 100% (*12*). Thus, the activation of the molecular hydrogen is given by the reaction:

$$\underset{\mathbf{1}}{Pd} + H_2 \rightarrow \underset{\mathbf{2}}{PdH_2}. \qquad (1)$$

The presence of small clusters of Pd makes this catalyst more properly comparable, with respect to hydrogen activation, to homogeneous Pd(O)/Pd(II) systems, rather than to the usual Pd blacks having a large number of nonsurface atoms where an important role is played by the hydrogen dissolved in the body of the metal particle. Reaction (1) is therefore interpreted as an overall oxidative addition reaction which implies the assumption of a homolytic H_2 activation process.

It is noteworthy that species of type **2** should be very unstable and reactive—as a matter of fact very few Pd(II) hydrides have been isolated thus far (*13*)—so that

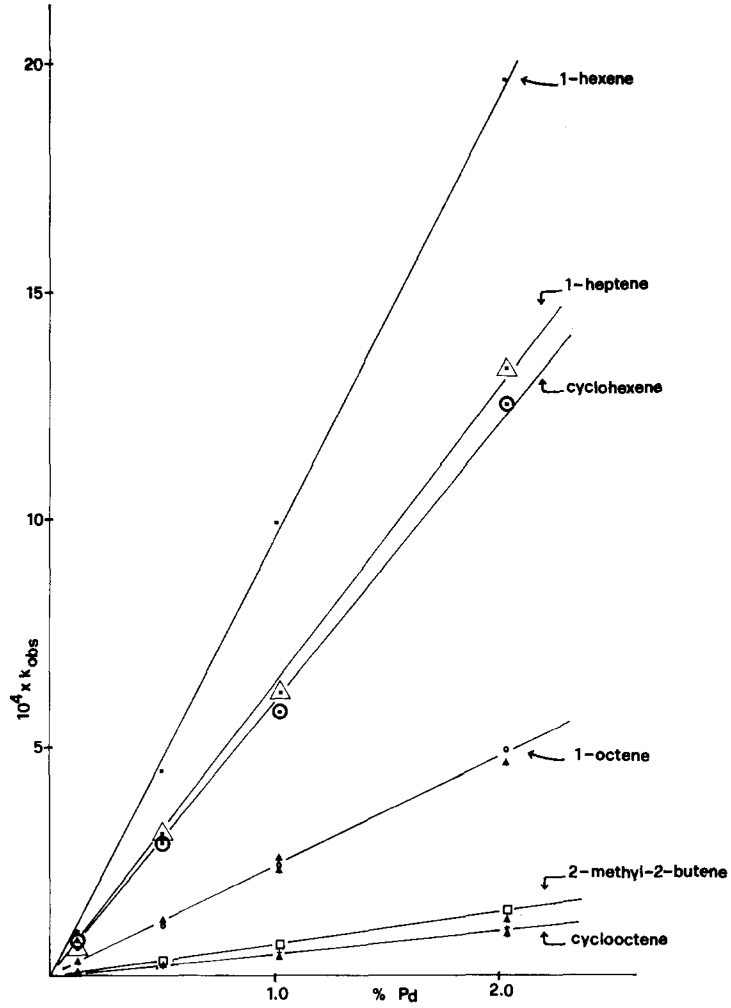

FIG. 2. Linear dependence of the catalytic activity on the Pd content for various olefinic systems; solid triangles refer to k_2 for the hydrogenation of dienes.

the insertion of the olefin into the Pd–H bond to give the half-hydrogenated state **3** can be reasonably not considered as the rate determining step of the hydrogenation reaction.

$$\underset{\mathbf{2}}{H_2Pd} + \text{olefin} \rightarrow \underset{\mathbf{3}}{\text{H–Pd–}R}. \qquad (2)$$

The independence of the catalytic activity on the olefin concentration agrees with these considerations.

Species of type Pd–*R* have been demonstrated to be key intermediates in the heterogeneous hydrogenation over Pd catalysts (*14*), whereas the hydrogen transfer to the Pd–*R* moiety is generally regarded as being the slow step of the reaction. At variance in our case, owing to the assumed homolytic H_2 splitting, the reaction:

$$\underset{\mathbf{3}}{\text{H–Pd–}R} \rightarrow \underset{\mathbf{1}}{\text{Pd}} + \text{alkane}$$

should be fast in consideration of the large instability of species of type **3**. On the other hand, the dependence of the catalytic activity on the nature of the olefin (see Fig. 2) indicates that bond formation between substrate and metal must precede hydrogen activation, therefore the overall hydrogenation mechanism can be described according to the following scheme:

$$\begin{tikzcd}
\underset{\mathbf{1}}{\mathrm{Pd}^0 + \text{olefin}} \arrow[r, "\text{fast}"] & \underset{\mathbf{4}}{\mathrm{Pd}^0\text{–olefin}} \arrow[d, "(+\mathrm{H}_2)"', "\text{slow}"] \\
\underset{\mathbf{3}}{R\text{–Pd–H}} \arrow[u, "\text{fast}", "(\text{-alkane})"'] & \underset{\mathbf{2}}{\mathrm{H}_2\mathrm{Pd}^{\mathrm{II}}\text{–olefin}} \arrow[l, "\text{fast}"']
\end{tikzcd}$$

Thus while reaction **4** → **2** accounts for the activation of H_2 as the rate-determining step, the equilibrium **1** → **4** justifies the observed changes of the catalytic activity on changing the substrate. As written the above scheme is analogous to the "unsaturate route" for the homogeneous hydrogenation of olefins catalyzed by Rh(I) complexes (*15*).

The effect of the substrate on the hydrogenation rate has been thoroughly investigated both for homogeneous (*15*) and heterogeneous (*16*) processes where it was interpreted in terms of the stability and reactivity of species of type **4**. Our results are in agreement with these views. Thus internally or sterically hindered olefins, such as 2-methyl-2-butene or cyclooctene, are hydrogenated more slowly than terminal olefins. This result suggested that we extend our investigation to the hydrogenation of dienes in order to test the possibility of achieving selective hydrogenations.

Hydrogenation of Dienes

The pseudozero-order rate constants for the first and second hydrogenation steps are also reported in Table 1. Gaschromatographic experiments indicate that no isomerization occurs during the first step of the reaction in agreement with the high hydrogenation activity of the catalyst which overwhelms the possible isomerization ability.

The equivalence between the k_2 values of 1,5-C_8H_{12}, 1,3-C_8H_{12}, and 1,7-octadiene and the k values obtained for the corresponding monoenes, i.e., cyclooctene and 1-octene, confirms a two-step hydrogenation process for the dienes.

Recently Wells (*17*) reported that in the hydrogenation of dienes, selectivity is inversely dependent on the extent of H_2 occlusion on the metal and in this respect a prominent factor is the presence of cavitated zones on the surface. It seems difficult to apply these results to our case where the maximum diameter of the Pd particles was never found to exceed 15–20 Å. Consequently the present palladium catalyst can be regarded in this perspective as the one having the best selectivity in the hydrogenation of dienes. In fact it does not suffer from the limitation due to the physical state of the surface. Hence the k_1/k_2 ratio can be considered as a typical factor intrinsic of each diene/monoene system. These observations are confirmed by the higher k_1/k_2 values obtained for cyclic diolefins than for linear diolefins independently on the relative position of the two double bonds. This reflects the more effective chelating ability of 1,5- or 1,3-cyclooctadiene relative to cyclooctene, compared to 1,4- or 1,7-octadiene with respect to the corresponding monoenes.

REFERENCES

1. Yermakov, Yu. I., *Catal. Rev.* **13**, 77 (1976).
2. Carturan, G., and Gottardi, V., *J. Mol. Catal.* **4**, 349 (1978).
3. Cocco, G., Fagherazzi, G., Carturan, G., and Gottardi, V., *J. Chem. Soc. Chem. Commun.*, 979 (1978).
4. Siegel, S., *J. Catal.* **30**, 139 (1973).
5. Ugo, R., *Catal. Rev.* **11**, 225 (1975).
6. Becconsall, J. K., Job, B. E., and O'Brien, S., *J. Chem. Soc. A*, 423 (1967).
7. Carturan, G., Gottardi, V., and Graziani, M., *J. Non-Cryst. Solids* **29**, 41 (1978).
8. Frost, A. A., and Pearson, R. G., "Kinetics and Mechanism." Wiley, New York, 1961.

9. Kieboon, A. P. G., and VanBekkum, H., *J. Catal.* **25**, 342 (1973).
10. Caga, I. T., Shutt, E., and Winterbottom, J. M., *J. Catal.* **44**, 271 (1976).
11. Fuji, Y., and Bailar, J. C., Jr., *J. Catal.* **52**, 342 (1978).
12. Boudart, M., and Hwang, H. S., *J. Catal.* **39**, 44 (1975).
13. Hosokawa, T., and Maitlis, P. M., *J. Amer. Chem. Soc.* **95**, 4927 (1973); Matsumoto M., Yoshioka, H., Yoshida, T., and Otsuka, S., **96**, 3322 (1974); Kramer, A. V., and Osborn, J. A., **96**, 7832 (1974).
14. Siegel, S., and Smith, G. V., *J. Amer. Chem. Soc.* **82**, 6082, 6087 (1960).
15. James, B. R., "Homogeneous Hydrogenation," Chap. 11 and references therein. Wiley-Interscience, New York, 1973.
16. Bond, G. C., "Catalysis by Metals." Academic Press, New York 1962; Mitsui, S., Shionoya, M., Gohke, K., Watanabe, F., Imaizumi, S., and Senda, Y., *J. Catal.* **40**, 372 (1975); Tanaka, K., Takagi, Y., Nomura, O., and Kobayashi, I., *J. Catal.* **35**, 24 (1974).
17. Wells, P. B., *J. Catal.* **52**, 498 (1978) and refs. therein.

G. Carturan
G. Strukul

Centro di Chimica Metallorganica del C.N.R.,
c/o Istituto di Chimica Industriale,
Università di Padova
and Istituto di Chimica Generale,
Università di Venezia, Italy

Received September 14, 1978