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Pumice-Supported Palladium Catalysts

II. Selective Hydrogenation of 1,3-Cyclooctadiene

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Two series of pumice-supported palladium catalysts (W and U) have been tested in the liquid-phase selective hydrogenation of 1,3-cyclooctadiene (1,3-COD) to cyclooctene (COE). The two series of catalysts, obtained via organometallic precursors, differ in the preparation procedure. In the W series the reduced metal derives only from Pd intermediates anchored to pumice; in the U series the metal originates also from unreacted $Pd(allyl)_2$ species in solution. The U catalysts present agglomerated metal particles. The hydrogenations, free of any diffusion problems, were performed at constant pressure of hydrogen (1 atm). Analysis of the data suggests that the rate-determining step is a surface reaction involving activated 1,3-COD. Selectivity is very high since cyclooctane (COA) is detected only when all 1,3-COD is consumed. The turnover frequencies (TOF_1) of the first semihydrogenation do not change with palladium dispersion, determined from the Porod diameter D_p up to $D_x < 35\%$, but thereafter they slowly decrease. Experimental evidence, such as the absence of oxidation when exposed to air and the negative shift of binding energy of the Pd 3*d* level in XPS measurements, indicate a different behavior of the present catalysts in comparison with other supported palladium catalysts. These differences are attributed to the presence of alkali metal ions (Na^+, K^+) on the pumice surface and are explained on the basis of the change in electron density and/or in the ensemble size of the supported palladium. Several interesting features and differences in activity and selectivity between the two series of catalysts can be accounted for by the presence of agglomerated palladium particles in the U series and are discussed in terms of the evolution of parameters with dispersion. © 1994 Academic Press, Inc.

1. INTRODUCTION

Selective hydrogenation of alkynes and alkadienes is a process used for the purification of alkenes in the petrochemical industry (1). Extensive and comparative studies (2) on catalysts based on group VIII metals have proven that palladium is the most active and selective metal in these hydrogenations.

Several studies on the hydrogenation of alkynes to alkenes (3–5) as well as of alkadienes to alkenes (6, 7) over palladium supported on alumina or silica or carbon have shown a marked sensitivity to particle size variation (8). In fact, an antipathetic dependence (9), i.e., a decrease in the specific activity with increasing Pd dispersion, is usually found.

The continuing quest for purer products has addressed the attention of researchers to find more selective processes, and further progress has been achieved by using bimetallic palladium catalysts (1, 5, 10) and/or liquid phase hydrogenation (10). So far the characteristics of the support have not received much attention. A series of studies involving characterization and surface and structural analyses of pumice and pumice-supported palladium and platinum catalysts have been published (11–17).

Pumice from different caves in Lipari, Italy, after treatment with dilute HNO_3, shows reproducible features. XPS analyses on Pd and Pt catalysts supported on pumice (15) determined a negative chemical shift in the Pd 3*d* and Pt 4*f* binding energies relative to energies of the same levels in the pure metals, suggesting an increase in electron density in the supported metals. The electron donation to the metal has been confirmed by comparing the XPS spectra of the valence band and the X-ray excited OKLL Auger transition of the pumice-supported Pd and Pt catalysts with those of pumice alone (16). Moreover, stacking faults in the palladium particles supported on pumice were detected by wide-angle X-ray line-broadening (WAXS) as previously reported (11–13). The presence of stacking faults can be attributed to the interaction with the support or, more likely, to the chemical preparation (18). Therefore it is possible that these planar defects are a general feature of other supported catalysts prepared under very mild conditions.

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The above outlined structural and electronic characteristics could be correlated with the interesting behavior that palladium supported on pumice shows when used as a hydrogenation catalyst.

In this paper we report a kinetic study of the selective hydrogenation in liquid phase of 1,3-cyclooctadiene in the presence of pumice-supported palladium catalysts. The catalytic activities were calculated as turnover frequencies (TOF), on the basis of palladium dispersions (percentages of exposed Pd atoms), D_X, obtained by the small-angle X-ray scattering (SAXS) technique, as described in the previous paper (Part I) (13).

For comparison purposes we report, for three catalysts, also the metal dispersion, D_h, obtained by chemisorption with H_2 followed by H_2–O_2 titration.

2. EXPERIMENTAL

Two series of catalysts (W and U) were prepared and their dispersions D_X determined following the procedures outlined in Part I (13). Furthermore, the dispersion D_h of the catalysts W_2, W_6, and W_7 was determined by chemisorption of H_2 and H_2–O_2 titration in a pulse system. An unusual stoichiometry has been considered

$$4Pd + 2H_2 \rightarrow 4\,PdH \quad 4PdH + O_2 \rightarrow 4Pd + 2H_2O$$

since no formation of PdO has been detected in the titration with oxygen. Moreover, no desorption peak is found in thermal desorption experiments experiments of Pd catalysts exposed to air for a long time (18), and no change is noted in their XPS spectra. Therefore, the ratio $H_2/O_2 > 2$ is indicative of partial dissolution of H_2 in Pd and the D_h values here reported are corrected to account for this well-known phenomenon in palladium catalysts (19).

1,3-Cyclooctadiene (1,3-COD) and cyclooctene (COE) (Aldrich) were purified by fractional distillation from potassium, passed over activated alumina and stored at −5°C under dinitrogen. Purity was tested by GC analysis. THF distilled from $LiAlH_4$ was distilled from potassium under dinitrogen just before use.

The hydrogenations of 1,3-COD and COE were performed in a stirred tank reactor similar to that described by Santacesaria and co-workers (20), operating in batch conditions. The stirrer develops very high gas–liquid interface areas. A side arm closed by a silicone septum allowed olefin injection and withdrawal of the samples for GC analyses. The reactor was connected by stopcocks to a vacuum line and to a gas adsorption system operating at atmospheric pressure of hydrogen. Temperature was maintained constant (25 ± 0.1°C) with the aid of a thermostat.

The dependence of the catalytic hydrogenation rate on stirring rate was determined for the most active catalyst (Fig. 1) and all reactions were performed at a constant stirring of 2500 rpm.

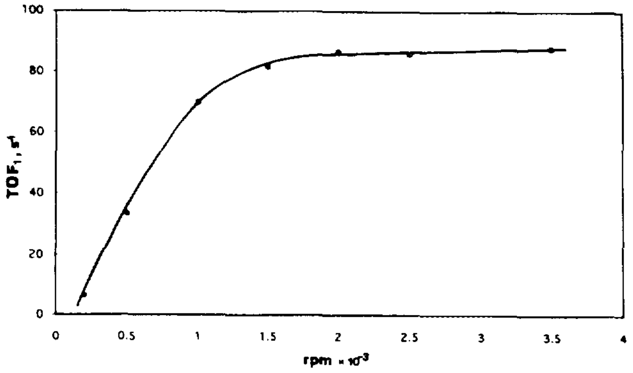

FIG. 1. Dependence of the catalytic hydrogenation rate on stirring for the W_2 catalyst.

In all the experiments the molar ratio olefin/palladium (olefin = 1,3-COD or COE) was 5000 : 1 and the olefin concentrations in THF were 0.25 *M*. Figure 2 shows that the hydrogenation rate for the most active catalyst is proportional to the amount of catalyst. Therefore in our system diffusive effects are absent and a chemical surface reaction is the rate-controlling step (21). After the hydrogenation reactions, the catalysts retained the same activity.

Before starting the reaction, the catalyst–THF system was kept for 2 h under hydrogen or half an hour with the diene with vigorous stirring. From now on these time periods are called "hydrogen preconditioning" and "diene preconditioning" periods, respectively. Kinetic analyses were performed by a GC, Dani 3800 HR PTV equipped with a Supelco capillary column SPB1701 and by a DANI 68/10 FID detector. The system was linked to a Shimadzu C-RIB Chromatopac automatic integrator.

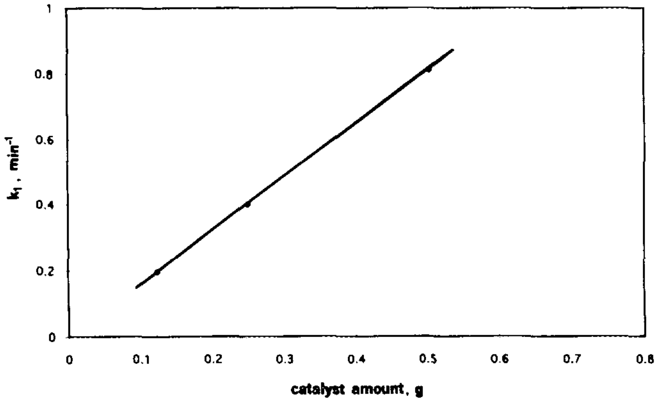

FIG. 2. Dependence of the rate constant k_1 (percentage 1,3-COD transformed per minute) on catalyst amount for the W_2 catalyst. Solvent volume and 1,3-COD concentrations were kept constant.

TABLE 1

Elementary Steps (S) and Mechanisms (M) for the Reaction $1,3\text{-COD} + H_2 \rightleftarrows \text{COE}^a$

$S_1 = H_2 + 2^* \rightleftarrows 2H^*$	$M_1 = S_4 - S_6 + S_8 + S_9$
$S_2 = H_2 + * \leftrightarrows H_2^*$	$M_2 = S_4 - S_5 + S_7 + S_9$
$S_3 = 1,3\text{-COD} + * \rightleftarrows 1,3\text{-COD}^*$	$M_3 = S_3 + S_4 + S_9$
$S_4 = 1,3\text{-COD}^* + H_2 \rightleftarrows \text{COE}^*$	$M_4 = S_2 + S_8 + S_9$
$S_5 = 1,3\text{-COD}^* + 2H^* \rightleftarrows \text{COE}^* + 2^*$	$M_5 = S_2 - S_5 + S_6 + S_7 + S_9$
$S_6 = 1,3\text{-COD}^* + H_2^* \rightleftarrows \text{COE}^* + *$	$M_6 = S_1 + S_7 + S_9$
$S_7 = 1,3\text{-COD} + 2H^* \rightleftarrows \text{COE}^* + *$	$M_7 = S_1 + S_5 - S_6 + S_8 + S_9$
$S_8 = 1,3\text{-COD} + H_2^* \rightleftarrows \text{COE}^*$	$M_8 = S_1 + S_3 + S_5 + S_9$
$S_9 = \text{COE}^* \rightleftarrows \text{COE} + *$	$M_9 = S_2 + S_3 + S_6 + S_9$

[a] $*$ represents a catalytic site and X^* a chemical species X adsorbed on the same site.

The results obtained in repeated experiments showed deviations less than 5%.

3. RESULTS AND DISCUSSION

As discussed in the previous paper (Part I) (13), the low specific surface area (about 5 m^2/g) of pumice increases the efficiency coefficient of a supported metal catalyst and minimizes the effects of mass and heat transfer (22) referred to intraparticle diffusion so that a study of the catalyzed reaction can be performed on the basis of a pure chemical regime, when other diffusion processes are not operative. Figures 1 and 2 show that in our experiments a chemical regime is operative and therefore drawbacks from transport of reactants (hydrogen and cyclooctadiene) and products (cyclooctene and cyclooctane) are overcome.

A possible reaction mechanism for the catalyzed reaction was obtained following a procedure similar to that employed by Happel and Sellers (23). We determined, by a Fortran program developed by us, the possible pathways for the catalytic hydrogenation of a diene (1,3-COD) to a monoene (COE), neglecting further hydrogenation of COE to cyclooctane (COA) and excluding isomerization of 1,3-COD. These conditions are correct since selectivity remains 100% until all the 1,3-COD is consumed.

With reference to Table 1, the possible reaction steps (S) for the catalyzed reaction $1,3\text{-COD} + H_2 \leftrightarrows \text{COE}$ give rise, according to Happel and Sellers (23), to nine algebraically possible mechanisms (M). Among the reported mechanisms only M_3, M_4, M_6, M_8 and M_9 are reasonable. In the others, a logical sequence of steps cannot be found. Five concurrent mechanisms are suggested also by application of the Horiuti–Polanyi equation (24), modified according to Temkin (25),

$$P = S + W - J,$$

Here P is the number of basic rates (or mechanism), S the number of stages (or steps), W the number of balance equations, and J the number of intermediates. In our case $S = 9$, $W = 1$, and J [the cataytic site ($*$) and the surface adsorbed species (X^*)] is 5. Therefore it follows again that there are five basic routes (or mechanisms ($P = 5$) which concur to the hydrogenation of 1,3-COD to COE. Since diffusion processes have been eliminated, as pointed out above, the following are the rate-determining steps in the selected mechanisms:

(a) $1,3\text{-COD}^* + H_2 \rightleftarrows \text{COE}^*$ (M_3)
(b) $H_2^* + 1,3\text{-COD} \rightleftarrows \text{COE}^*$ (M_4)
(c) $2H^* + 1,3\text{-COD} \rightleftarrows \text{COE}^* + *$ (M_6)
(d) $1,3\text{-COD}^* + 2H^* \rightleftarrows \text{COE}^* + 2^*$ (M_8)
(e) $1,3\text{-COD}^* + H_2^* \rightleftarrows \text{COE}^* + *$ (M_9)

At a constant pressure of H_2, the rate-controlling steps (a), (d), and (e) are indistinguishable. Since dehydrogenation of COE^* is unlikely, the differential form

$$-dc_{1,3}/dt = k\theta_{1,3} \qquad (1)$$

accounts well for the hydrogenation rate; k is a constant that depends only on the pressure of H_2 and $\theta_{1,3}$ is the fractional occupancy of active sites by 1,3-COD. According to Langmuir–Hinsehelwood-type kinetic behavior, $\theta_{1,3}$ can be expressed (21) as

$$\begin{aligned}\theta_{1,3} &= (k_{1,3}c_{1,3})/(1 + k_{1,3}c_{1,3} + k_E c_E)\\ &= c_{1,3}/(1/k_{1,3} + c_{1,3} + Qc_E)\end{aligned} \qquad (2)$$

where $c_{1,3}$ represents the 1,3-COD concentration in the liquid phase, $k_{1,3}$ and k_E are the adsorption constants on the catalyst surface, respectively, for 1,3-COD and COE, $Q = k_E/k_{1,3}$, and c_E is the concentration of COE in the liquid phase.

The selectivity S(%) of the hydrogenation of 1,3-COD

$$S(\%) = 100(\text{mol COE})/\text{mol } 1,3\text{-COD converted}$$

is always 100, and assuming a unitary initial concentration of 1,3-COD, $c_E = 1 - c_{1,3}$ and (2) becomes

$$\theta_{1,3} = c_{1,3}/[1/k_{1,3} + c_{1,3} + Q(1 - c_{1,3})]. \qquad (3)$$

Substitution of Eq. (3) in Eq. (1) and integration give the equation

$$t = [(1 - Q)(1 - c_{1,3}) - (Q + 1/k_{1,3}) \ln c_{1,3}]/k \qquad (4)$$

which has been used to fit the experimental data (t vs $c_{1,3}$) using Q, k, and $1/k_{1,3}$ as nonlinear parameters. Since, however, $1/k_{1,3}$ is about two orders of magnitude lower

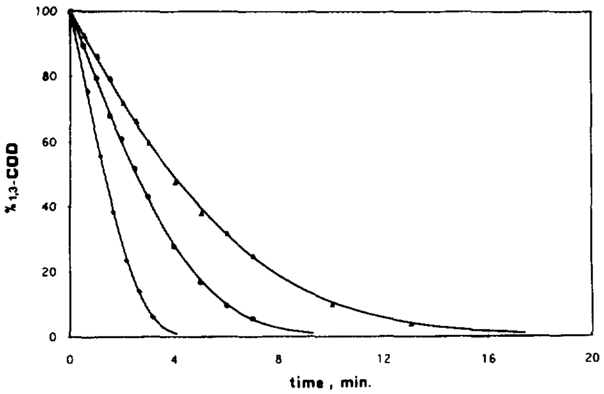

FIG. 3. Percentage of 1,3-COD transformed vs time for the W_2 (◆), U_3 (●), and W_7 (△) catalysts. The solid lines correspond to the fitted theoretical values calculated with Eq. (4′).

than Q and the fitting gives an error for $1/k_{1,3}$ larger than one order of magnitude of its own value, we have neglected this term in Eq. (2):

$$\theta_{1,3} = c_{1,3}/(c_{1,3} + Qc_E). \qquad (2')$$

This simplification, already applied in other liquid-phase hydrogenations when the catalyst surface is always covered by reactants (26), is suitable in our study especially in the case of "diene preconditioning." Consequently, the new integrated equation

$$t = [(1 - Q)(1 - c_{1,3}) - Q \ln c_{1,3}]/k \qquad (4')$$

was used to fit the experimental data (t vs $c_{1,3}$) using Q and k as nonlinear parameters. Theoretical curves obtained with Eq. (4′) fit quite well the experimental points, as shown in Fig. 3 for the hydrogenation of 1,3-COD with W_2, W_7, and U_3 catalysts when "diene preconditioning" is performed. Data for the other catalysts are reported in Table 2 together with relevant structural data. From inspection of the curves in Fig. 3 it appears that the reaction follows a zero-order kinetic behavior up to relatively high extents of conversion (pseudo-zero-order kinetics), depending on the value of Q (21).

We have also considered the possibility that (b) and (c) were the rate-controlling steps. However, the analysis according to first-order kinetics,

$$-dc_{1,3}/dt = k_1c_{1,3},$$

which accounts for mechanisms M_4 and M_6, does not give curves that fit the experimental data, suggesting that adsorption of 1,3-COD on the surface is relevant to our reaction. This is not surprising since when hydrogenation of 1,3-COD was performed with hydrogen preconditioning, an induction period was always detected. After this time, probably to form surface activated 1,3-COD, hydrogenation proceeds at a rate simmilar to that of diene preconditioning. A similar induction period is obtained by concomitant introduction of both 1,3-COD and H_2.

When "diene preconditioning" is settled, i.e., the surface is covered by the organic reactant, the conditions for hydrogenation of 1,3-COD via mechanisms M_8 and M_9 require the formation of activated surface hydrogen (H_2^* or H^*). The absence of an induction period does not rule out the possibility that very rapid activation of hydrogen occurs on the surface. In fact, since 1,3-COD is a large molecule, even at full coverage as in the case of "diene preconditioning," hydrogen can find some access to the palladium surface. In a similar study preformed with pumice-supported Pd–Pt catalysts (27), owing to the reduced rate of hydrogenation of 1,3-COD, an induction period was also detected with "diene preconditioning," suggesting that molecular hydrogen has no great influence, if any, in the rate-controlling step of the hydrogenation of 1,3-COD. Although we have no indication, we think that the rate-controlling step (d) is more probable than (e) and, accordingly, that M_8 should be the mechanism of choice.

In Fig. 4 the turnover frequencies (TOF_1) for the hydrogenation of 1,3-COD to COE (the turnover frequencies relative to the hydrogenation of COE to COA will be labeled, from now on, TOF_2) are reported vs D_X. It is interesting to note (Table 2) that the D_X values are similar (even if systematically lower) to the corresponding D_h values. The slightly lower hydrogenation rate of the U series of catalysts may be attributed, at least in part, to agglomeration. This occurrence has been documented by TEM micrographs (13) and is indicative of some accumulation of the metal not anchored to the hydroxyls of pumice during the reduction. Since the SAXS determination does not distinguish agglomerated particles (28, 29), the dispersion of the unwashed catalysts, calculated by SAXS, could be overestimated with respect to that of the washed catalysts, thus accounting for the reduced TOF_1. Owing to the errors in TOF_1 and D_X measurements, TOF_1 can be considered invariant, with dispersion increasing up to $D_x < \sim 35\%$, for both W and U series catalysts. At higher dispersions TOF_1 starts to decrease slowly.

The hydrogenation of dienes with other conventional supported Pd catalysts (Pd/Al_2O_3, Pd/SiO_2, and Pd/C), in both liquid (3, 6) and gas (7, 30) phases, shows a drastic decrease in the specific rate of hydrogenation on increasing dispersion from 20–25% to higher values. These results have been explained (3, 6, 30) by a higher strength of adsorption of the diene on the small particles. Support for this interpretation is provided by XPS data which show an increase in the binding energy in the 3*d* core level of small Pd particles supported on alumina or silica

TABLE 2

Structural and Kinetic Data for the Catalysts Investigated

Catalyst	Pd (%)	D_P[a] (A)	D_X (%)	D_h[b] (%)	k_l[c] (min^{-1})	k_l*[d] (mol/g)	k_2[e] (min^{-1})	k_2*[d] (mol/g)	k_1/k_2	Q[c]	TOF_1 (s^{-1})	TOF_2 (s^{-1})
U_1	0.114	24	47	n.d.	0.364(7)	3.25×10^{-4}	1.8×10^{-4}	1.6×10^{-7}	2022	0.15(2)	64.5	3.2×10^{-2}
U_2[f]	0.27	31	36	n.d.	0.35(3)	7.40×10^{-4}	1.7×10^{-4}	3.6×10^{-7}	2011	0.21(3)	81.0	3.9×10^{-2}
U_3[f]	1.14	50	22	n.d.	0.22(3)	1.96×10^{-3}	1.2×10^{-4}	1.1×10^{-6}	1833	0.29(1)	83.3	4.5×10^{-2}
U_4[f]	2.42	73	15	n.d.	0.152(4)	2.88×10^{-3}	1.0×10^{-4}	1.9×10^{-6}	1520	0.45(7)	84.4	5.6×10^{-2}
W_0	0.05	18	62	n.d.	0.24(1)	9.39×10^{-5}	2.9×10^{-4}	1.1×10^{-7}	827	0.16(2)	32.3	3.9×10^{-2}
W_1	0.2	22	51	n.d.	0.38(4)	5.95×10^{-4}	2.6×10^{-4}	4.1×10^{-7}	1461	0.17(4)	62.1	4.2×10^{-2}
W_2	0.108	29	39	41	0.40(6)	3.38×10^{-4}	2.9×10^{-4}	2.5×10^{-7}	1379	0.18(1)	85.4	6.2×10^{-2}
W_3[f]	0.39	35	32	n.d.	0.338(2)	1.03×10^{-3}	2.7×10^{-7}	8.2×10^{-7}	1251	0.20(3)	88.0	7.0×10^{-2}
W_4[f]	0.61	35	32	n.d.	0.343(1)	1.63×10^{-3}	2.8×10^{-4}	1.3×10^{-6}	1214	0.21(2)	89.5	7.3×10^{-2}
W_5[f]	0.86	40	28	n.d.	0.31(2)	2.02×10^{-3}	2.6×10^{-4}	1.8×10^{-6}	1153	0.26(1)	91.3	7.7×10^{-2}
W_6	0.37	50	22	29	0.24(1)	6.96×10^{-4}	2.1×10^{-4}	6.1×10^{-7}	1143	0.34(6)	90.9	8.0×10^{-2}
W_7	1.05	81	14	20	0.15(4)	1.23×10^{-4}	1.9×10^{-4}	1.6×10^{-6}	790	0.44(5)	89.4	1.1×10^{-1}

[a] Porod diameters determined by SAXS, from which the metal dispersions D_x were obtained [see Ref. (13)].

[b] Palladium dispersions obtained by chemisorption with H_2, followed by H_2–O_2 titration.

[c] Parameter obtained by fitting Eq. (4′) to the experimental data (t vs $c_{1,3}$).

[d] Hydrogenation constant referred to grams of catalyst.

[e] Initial slope of the COE concentration in the COE-to-COA hydrogenation.

[f] For the complete microstructural features of these catalysts, see the previous paper (Part I) (13).

(31–34) and carbon (35) with respect to pure Pd powder. As a consequence of the lower electron density on the metal, the strength of the adsorption of electron-rich dienes should increase, and accordingly, the hydrogenation rates should decrease (3, 6, 30).

Although dispersion values obtained by different techniques can be different, there is other evidence that pumice-supported Pd catalysts behave differently than other supported Pd catalysts. As mentioned in the Introduction, our XPS studies on pumice-supported palladium catalysts have shown a decrease in the binding energy (15) in the Pd 3d core level with respect to pure Pd, suggesting a donation of electron density to the supported metal. This occurrence has been confirmed by comparing XPS spectra of the valence band region and OKLL Auger spectra of the pumice-supported Pd catalysts with those of pumice alone (16). Based on previous XPS studies of Pd supported on silica doped with alkali metal ions (36), this effect could be due to small amounts [turning out to be about 3% of the surface atoms (14)] of ionic alkali metals still present even after treatment of pumice with dilute HNO_3 (13). An electron-donating alkali metal–oxygen composite could account for the increased electron density on the supported metal (36).

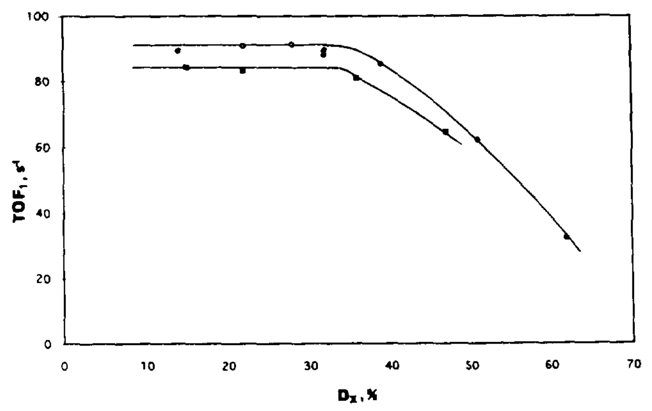

FIG. 4. Dependence of turnover frequencies (TOF_1) on dispersion D_X for the hydrogenation of 1,3-COD to COE. Catalysts: washed (●), unwashed (■).

Assuming comparable dispersions of palladium supported on the different oxides, the maintenance of a constant value of TOF_1 at $D_x > 20\%$ in the hydrogenation of 1,3-COD to COE with our catalysts could be a consequence of the increasing electron density on the metallic particles, which reduces the strength of the diene–metal interaction. Analogously, increased activity and selectivity in the hydrogenation of acetylene to ethylene have been found for Pd/Al_2O_3 catalysts doped with potassium (37). Although our previous XPS studies (15) were not directed to find a correlation between particle size and shift in the binding energy of Pd 3d core level, it seems reasonable that the transfer of electron density from the support to the metal is more pronounced in smaller particles. The enhanced electron density could be counterbalanced by the well-known decrease in the metallic character of supported Pd particles (8, 31–34) as their size decreases to less than about 20–30 Å. Ryndin *et al.* (31,

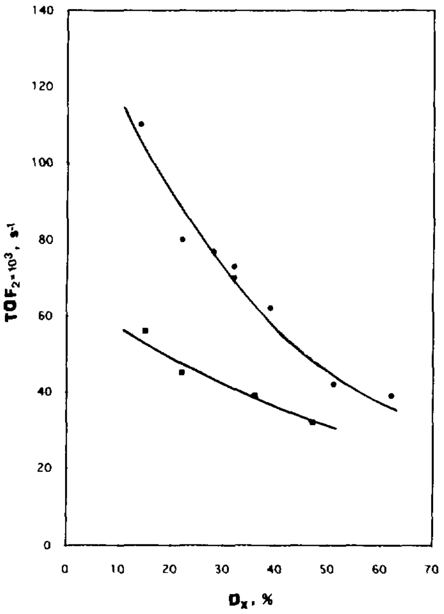

FIG. 5. Dependence of turnover frequencies (TOF_2) on dispersion D_X for the hydrogenation of COE to COA. Catalysts: washed (●), unwashed (■).

35) found by XPS a decrease in electron density for particle sizes smaller than 30 Å. The constant value of TOF_1 shown in Fig. 4 could be the outcome of the above outlined opposite trends, and the slow decrease in activity at $D_X > 35\%$ could be indicative of an insufficient supply of electron density on the metal to counterbalance the decrease in the metallic character.

Moreover, the transfer of electron density from the support to the metal can drive alkali metal ions onto palladium. In this case, an alternative explanation of the invariant TOF_1 up to $D_X < \sim 35\%$ could be linked with the presence of Na^+ and K^+ which decrease the Pd ensemble size (38), giving optimal adsorption of 1,3-COD. At present we cannot exclude that our catalysts will exhibit an increase in electron density with increasing dispersion; in such a case the decrease of TOF_1 could be ascribed to too high an electron density on the metal or to excessive coverage of the Pd crystallite surface by Na^+ and K^+. Both situations would account for the reduced hydrogenation rate of 1,3-COD at $D_X > 35\%$.

To the best of our knowledge, only one case of hydrogenation of 1,3-COD has been reported using Pd on a synthetic vitreous support (39) as catalyst. Our catalysts appear to have an activity at least one order of magnitude higher; however, the magnetic stirring used in the above-cited work could, at least in part, be responsible for the lower rate.

In the second semihydrogenation (COE → COA) the decrease in activity (TOF_2) with increasing dispersion is evident for both the W and U series of catlysts (Fig. 5). The difference between the corresponding curves, which is higher than for TOF_1, becomes lower and lower with increasing dispersion, confirming the diminished probability of formation of agglomerated metal particles in the U series when diluted solutions of diallyl palladium are used in the preparation of the catalysts. The turnover frequencies TOF_2 (Table 2) are about three orders of magnitude lower than TOF_1. Furthermore, there is no difference in the rate of direct hydrogenation of COE or of the monoene originating from the hydrogenation of 1,3-COD in the same reaction vessel. As mentioned before, the selectivity of the hydrogenation of 1,3-COD is 100% until all 1,3-COD is converted and this remarkable behavior is mostly attributable to the low activity of our catalysts in the hydrogenation of monoene. It is, however, interesting to follow the evolution of k_1/k_2 (selectivity ratio) with dispersion (Fig. 6). A net maximum is found at $D_X \sim 45\%$ but the selectivity ratio is always better in the U series. These results are remarkable, especially if compared with other trends obtainable from the data listed in Table 2. Palladium catalysts are known to be the most selective in the hydrogenation of dienes (2, 10) and, among the various interpretations of this behavior, the higher ratio of adsorption of dienes vs monoenes appears convincing (40).

In the two series of catalysts, k_1/k_2 vs Q (the adsorption constant ratio $k_E/k_{1,3}$) (Fig. 7) follows two different lines, with comparable slope. Again k_1/k_2 is more favorable in the U series. However, the variation of Q with dispersion appears to be independent of agglomeration phenomena

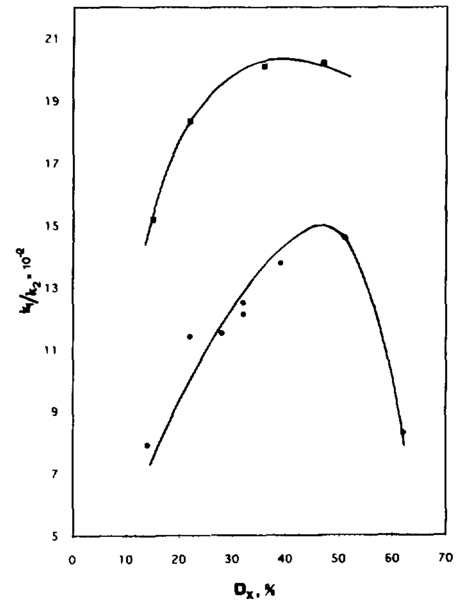

FIG. 6. Dependence of selectivity ratio (k_1/k_2) on dispersion D_X. Catalysts: washed (●), unwashed (■).

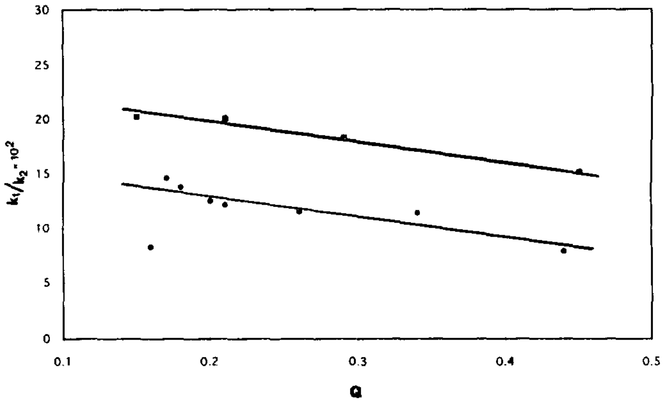

FIG. 7. Dependence of selectivity ratio (k_1/k_2) on the ratio of adsorption constants ($Q = k_E/k_{1,3\text{-COD}}$) of cyclooctene and 1,3-cyclooctadiene. Catalysts: washed (●), unwashed (■).

(Fig. 8), suggesting that the difference in activity and selectivity in the two series of catalysts reported here is linked to different strengths of adsorption. This observation is most likely to be explained in terms of different electron density on the supported metal. The U series is expected to be less influenced by any transfer of electron density, because some of the agglomerated particles are not in direct contact with the support.

4. CONCLUSIONS

Kinetic analyses of the hydrogenation of 1,3-COD to COE in the liquid phase over a series of pumice-supported palladium catalysts have suggested that the surface reaction

$$1{,}3\text{-COD}^* + 2\text{H}^* \rightleftarrows \text{COE}^* + 2^*$$

is very probably the rate-determining step.

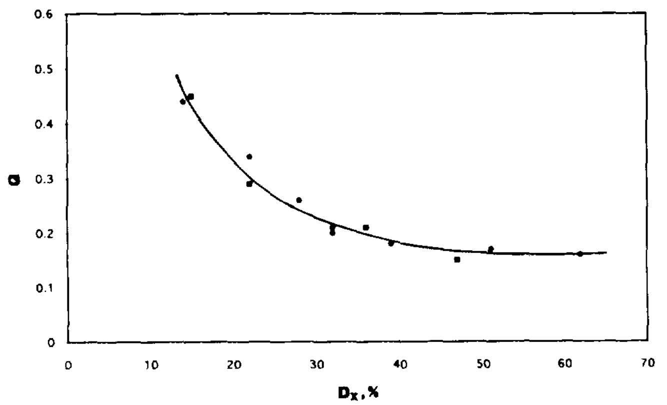

FIG. 8. Dependence of the ratio of adsorption constants ($Q = k_E/k_{1,3\text{-COD}}$) of cyclooctene and 1,3-cyclooctadiene, on dispersion D_X. Catalysts: washed (●), unwashed (■).

The experimental data are in accord with a zero-order reaction up to very high conversion as shown by fitting the equation

$$-dc_{1,3}/dt = kc_{1,3}/[c_{1,3} + Q(1 - c_{1,3})]$$

with the experimental data.

The high selectivity [$S(\%) = 100$ up to complete conversion of 1,3-COD] is due to a very low hydrogenation rate of the second process COE + $H_2 \rightleftarrows$ COA.

The same low rates are obtained in the direct hydrogenation of COE on the same catalysts.

The invariance of TOF_1 with metal dispersions up to about 35% is attributed to an enhanced electron density on the metal. This effect, which was detected by XPS (15) and Auger (16) studies, should decrease the strength of the adsorption of the electron-rich dienes on supported Pd, thus favoring its hydrogenation rate. A plausible explanation of the transfer of electron density on the metal is provided by the effect of alkali metal ions present on the pumice surface. Indeed, a similar electronic effect has been evidenced by XPS for Pd supported on SiO_2 doped with alkali metal ions (36). The decrease in TOF_1 with dispersion which occurs for $D_X > 35\%$ can be related to the dominant effect of the progressive loss of metallic character or to a too high an electron density on the metal, on decreasing the crystallite sizes. The range of good activity in the pumice-supported Pd catalysts seems to be larger than that of Pd on other conventional supports. Although further investigation must be performed to confirm these conclusions, it is likely that pumice behaves as a natural alkali-doped support and Pd on pumice may be of some utility in selective hydrogenations used for the purification of alkene compounds.

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REFERENCES

1. Derrien, M., *in* "Catalytic Hydrogenation" (L. Červeny, Ed.), p. 613. Elsevier, Amsterdam, 1986.
2. Bond, G. C., and Wells, P. B., *Adv. Catal.* **15,** 92 (1964).
3. Boitiaux, J. P., Cosyns, J., and Vasudevan, S., *Appl. Catal.* **6,** 4 (1983).
4. Gigola, C. E., Adruiz, H. R., and Bodnariuk, P. *Appl. Catal.* **27,** 133 (1986).

5. Aduriz, H. R., Bodnariuk, P., Dennehy, M., and Gigola, C. E., *Appl. Catal.* **58,** 227 (1990).
6. Boitiaux, J. P., Cosyns, J., and Vasudevan, S., *in* "Preparation of Catalysts" (G. Poncelet, P. Grange, and P. A. Jacobs, Eds.), p. 123. Elsevier, Amsterdam, 1983.
7. Tardy, B., Noupa, C., Leclercq, C., Bertolini, J. C., Hareau, A., Treilleux, M., Faure, J. P., and Nihoul, G., *J. Catal.* **129,** 1 (1991).
8. Bond, G. C., *Chem. Soc. Rev.* **20,** 441 (1991).
9. Che, M., and Bennett, C. O., *Adv. Catal.* **36,** 55 (1989).
10. Boitiaux, J. P., Cosyns, J., Derrien, M., and Leger, G., *Hydrocarbon Process.* **64,** 51 (1985).
11. Fagherazzi, G., Benedetti, A., Martorana, A., Giuliano, S., Duca, D., and Deganello, G., *Catal Lett.* **6,** 263 (1990).
12. Martorana, A., Deganello, G., Duca, D., Benedetti, A., and Fagherazzi, G., *J. Appl. Crystallogr.* **25,** 31 (1992).
13. Fagherazzi, G., Benedetti, A., Deganello, G., Duca, D., Martorana, A., and Spoto, G., *J. Catal.* **150,** 117 (1994).
14. Venezia, A. M., Floriano, M. A., Deganello, G., and Rossi, A., *Surf. Interface Anal.* **18,** 532 (1992).
15. Venezia, A. M., Duca, D., Floriano, M. A., Deganello, G., and Rossi, A., *Surf. Interface Anal.* **19,** 548 (1992).
16. Venezia, A. M., Duca, D., Floriano, M. A., Deganello, G., and Rossi, A., *Surf. Interface Anal.* **18,** 619 (1992).
17. Floriano, M. A., Venezia, A. M., Deganello, G., Svensson, E. C., and Root, J. H., *J. Appl. Crystallogr.* **27,** 271 (1994).
18. Duca, D., Martorana, A., Parmaliana, A., and Deganello, G., unpublished results.
19. Chou, P., and Vannice, M. A., *J. Catal.* **104,** 1 (1987).
20. Santacesaria, E., Wilkinson, P., Babini, P., and Carra, S., *Ind. Eng. Chem. Res.* **27,** 780 (1988).
21. Gut, G., Kut, O. M., Yucelen, F., and Wagner, D., *in* "Catalytic Hydrogenation" (L. Červeny, Ed.), p. 517. Elsevier, Amsterdam, 1986.
22. Ruiz, P., Criné, M., Germain, A., and L'Homme, G., *in* "Chemical and Catalytic Reactor Modelling" (M. P. Dudukovic and P. L. Mills, Eds.), p. 15, ACS Symposium Series 237. Am. Chem. Soc., Washington, DC, 1984.
23. Happel, J., and Sellers, P. H., *Adv. Catal.* **32,** 273 (1983).
24. Horiuti, J., and Nakamura, T. Z., *Z. Phys. Chem.* (Frankfurt am Main) [N.S.] **11,** 358 (1957).
25. Temkin, M. I., *Adv. Catal.* **28,** 173 (1979).
26. Jungers, J. C., "Cinétique Chimique Appliquée." Soc. Ed. Technique, Paris, 1958.
27. Deganello, G., Duca, D., Martorana, A., Venezia, A. M., Benedetti, A., and Fagherazzi, G., *J. Catal.*, in press.
28. Borodzinsky, A., Dus, R., Frak, R., Janko, A., and Palczewska, W., *in* "Proceedings, the 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 150. Chemical Society, London, 1977.
29. Matyi, R., Schwartz, L. H., and Butt, J. B., *Catal Rev. Sci. Eng.* **29,** 41 (1987).
30. Aduriz, H. R., Bodnariuk, P., Coq, B., and Figueras, F., *J. Catal.*, **129,** 47 (1991).
31. Ryndin, Yu. A., Nosova, L. V., Boronin, A. I., and Chuvilin, A. L., *Appl. Catal.* **42,** 131 (1988).
32. Hub, S., Hilaire, L., and Touroude, R., *Appl. Catal.* **36,** 307 (1988).
33. Takasu, Y., Unwin, R., Tesche, B., Bradshaw, A. M., and Grunze, M., *Surf. Sci.* **77,** 219 (1978).
34. Mason, M. G., *Phys. Rev. B* **27,** 748 (1983).
35. Ryndin, Yu. A., Stenin, M. V., Boronin, A. I., Bukhtiyarov, V. I., and Zaikovskii, V. I., *Appl. Catal.* **54,** 277 (1989).
36. Pitchon, V., Guenin, M., and Praliaud, H., *Appl. Catal.* **63,** 333 (1990).
37. Park, Y. H., and Price, G. L., *J. Chem. Soc. Chem. Commun.*, 1188 (1991).
38. Guczi, L., *J. Mol. Catal.* **25,** 13 (1984).
39. Carturan, G., and Strukul, G., *J. Catal.* **57,** 516 (1979).
40. Ouchaib, T., Massardier, J., and Renouprez, A., *J. Catal.* **119,** 517 (1989).