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Selective Hydrogenation of Phenylacetylene on Pumice-Supported Palladium Catalysts

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The liquid phase, selective hydrogenation of phenylacetylene on pumice-supported palladium catalysts has been studied for a large range of metallic dispersions (14% $\leq D_x \leq$ 62%). The kinetics were analyzed by a five-parameter mathematical model. The mechanism was determined by the contribution of three basic routes involving only surface species in the rate-determining steps. The hydrogenation of phenylacetylene to styrene is "structure insensitive." The disappearance rate constant of styrene produced from phenylacetylene is slightly lower than that of phenylacetylene and does not change in the case of the direct hydrogenation of styrene on the same Pd/pumice catalyst. However, Q_3 (the ratio of adsorption constants K_{Eb}/K_{St}, where Eb is ethylbenzene and St is styrene), which is typical of a zero-order reaction ($Q_3 \rightarrow 0$) in the case of the direct hydrogenation, is practically constant ($Q_3 \cong 2$) in the case of hydrogenation of styrene produced from phenylacetylene. This is explained by the formation, in the latter case, of polymeric species or other species which are difficult to hydrogenate and by the consequent occupation of active sites so that the adsorption of styrene is inhibited. These species are also thought to be responsible for a flattening effect in the catalytic activity. Activity and selectivity data are critically analyzed and compared with those reported for other supported palladium catalysts. Since Pd/pumice catalysts also show high activity and selectivity at high metal dispersions, they could be of interest for industrial applications. © 1995 Academic Press, Inc.

1. INTRODUCTION

The complete elimination of alkynes from alkene feedstocks is an important process in the polymer industry (1, 2). Since palladium catalysts supported on low surface area alumina are usually employed in the industrial process (3), there has been extensive research on supported palladium catalysts (4–12) to find more selective processes (13). Some success has been obtained by the addition of carbon monoxide, organic bases, sulphides, and metal ions (14, 15) and by alloying palladium with copper, platinum, and other metals (9, 14–16). A number of papers have dealt with the influence of metal dispersion (6–9, 12) on selectivity but controversial results have been reported (5, 8, 9, 11), mostly due to the different experimental conditions employed but also to different interpretations of the experimental results (6).

We have recently reported a study of the liquid phase selective hydrogenation of 1,3-cyclooctadiene, on pumice-supported palladium catalysts (17–20). The use of pumice (21, 22) could have some advantage related (17) to the presence of alkali metal ions in the support (23, 24).

With the aim of extending our results we have studied the behaviour of our Pd/pumice catalysts in the selective hydrogenation of phenylacetylene in the liquid phase, which is described in this paper, and that of acetylene in the gas phase (25).

As pointed out in a recent review (26), "the minimal information that a mechanistic statement should aspire to ...," is "(i) identification of the principal adsorbed species ... (ii) specification of the principal routes ... (iii) nomination of the rate-determining step." This is reflected in the kinetic study reported in the present paper.

2. EXPERIMENTAL

All the reagents used (Aldrich) were of analytical grade. Phenylacetylene and styrene were purified before use and stored at −10°C under N_2. Purity was always tested by GC analyses before the compounds were used.

Tetrahydrofuran (THF) was distilled from $LiAlH_4$ and redistilled from K under N_2 just before use.

2.1. Catalysts

Pumice is a natural alumino-silicate glass of volcanic origin with a very low surface area (less than 5 m^2/g). The powder used as support for our catalysts is a waste product from the production of Pumex SpA-Lipari, with a particle size smaller than 45 μm. Its characteristics are standardized by treatment for half an hour with boiling

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25% nitric acid, successive cleaning with water up to neutrality, and final drying under a nitrogen flux for 7 h at 250°C (21). This treatment reduces the atomic percentage of K^+ (1.4%) and Na^+ (1.3%) (21), but the aluminosilicate structure remains unaltered (22).

The Pd catalysts were prepared as already reported (20), using a modified Yermakov method (27). The catalysts were synthesized in pentane by anchorage of $[Pd(C_3H_5)_2]$ to PUM-OH groups of the support (PUM) and successive reduction by H_2 of the Pd anchored species (20). Although stable in air (17), the catalysts were stored under nitrogen.

Particle dimensions, studied by SAXS (small angle X-ray scattering) (20), WAXS (wide angle X-ray scattering) (18–20), TEM (transmission electron microscopy) (20), and BET surface area (20), are easily reproducible in these catalysts so that the desired particle sizes can be obtained by suitably changing parameters such as temperature, concentration of $[Pd(C_3H_5)_2]$ in solution, and metal/support ratio. Catalysts with different metal loading and equal dispersion show the same kinetic properties (17). The metal crystallites show stacking faults in the piling up of the (111) layers (19). A donor effect from support to metal particles is always found, as documented from XPS spectra by a shift towards lower binding energies of the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ peaks of the supported palladium with respect to the corresponding peaks of unsupported Pd powder (23).

The catalysts used in long-term activity studies and with much higher concentrations of 1,3-cyclooctadiene appeared fairly stable to sintering [by SAXS analysis (20)].

Some structural data of the catalysts are listed in Table 1.

TABLE 1

Some Characteristics of the Pumice-Supported Palladium Catalysts

Catalyst[a]	%Pd	S_{sp}[b] (m^2/g)	D_p[c] (Å)	D_x[d] (%)
W_7	1.05	62	81	14
W_6	0.37	100	50	22
W_3	0.38	143	35	32
W_2	0.11	172	29	39
U_1	0.12	208	24	47
W_0	0.05	278	18	62

[a] These catalysts have been described previously (17, 20); we retained the original symbols for immediate comparison.

[b] Specific surface of the metallic phase as determined by SAXS (20, 28).

[c] Pore diameter, obtained from S_{sp} hypothesizing spherically shaped particles (17, 20, 28).

[d] Percentage of exposed metallic atoms (17, 20, 29). This parameter is used to calculate TOF_1.

2.2. Kinetic Studies

The reactions were performed in a mechanically stirred tank reactor similar to that described by Santacesaria *et al.* (30). The reactor was connected to an inert gas–vacuum line and to a gas absorption system operating at a constant atmospheric pressure of H_2. A side arm closed by a silicone septum allowed the injection of reagents and withdrawal of samples for GC analyses. Constant temperature (25.0 ± 0.1°C) was ensured by a thermostat.

We studied the hydrogen-diffusion effects in our system with the macroscopically most active catalyst (W_7). We observed that the TOF (turnover frequency) did not change when the stirring rate was higher than 2000 rpm. Moreover, the TOF was always directly proportional to the catalyst amount when temperatures and/or catalyst amounts were changed. According to Madon and Boudart (31), the above tests are sufficient to consider the reported catalytic data as being free from transport influences. In other words, at 2500 rpm the chemical regime of the reaction is ensured. The initial reagent concentration (phenylacetylene or styrene) in THF was always 2.5×10^{-1} *M* and the catalyst amount was arranged so but the initial ratio reagent moles/metal atoms was equal to 1000. Before the start of the reactions, the THF-catalyst system was subjected to an organic substrate or hydrogen preconditioning period, by being thoroughly stirred for half an hour with the organic reagent or hydrogen, respectively. In both cases of preconditioning with a reaction, sufficiently slow (i.e., reagent moles/metal atoms = 10,000) induction periods were detected (see later discussion).

Kinetic analyses were performed by a Dani 3800 HRPTV GC equipped with a Supelco capillary column SPB1701 and with a DANI68/10 FID detector. This system was linked to a Shimadzu C-R1B Chromatopac integrator.

The results obtained in duplicated experiments showed less than 5% deviation.

Activation energies were measured in the temperature range 15–35°C on the W_0 and W_6 catalysts.

3. RESULTS AND DISCUSSION

The hydrogenation of alkynes to alkanes is considered to occur by two successive reactions, involving alkenes as intermediates, but several papers have shown that alkanes can be formed also directly from alkynes (8, 32, 33):

$$R{-}C{\equiv}C{-}R \xrightarrow{k_1} R{-}CH{=}CH{-}R \xrightarrow{k_3} R{-}CH_2{-}CH_2{-}R. \qquad (R{-}C{\equiv}C{-}R \xrightarrow{k_2} R{-}CH_2{-}CH_2{-}R)$$

Therefore, to improve yields in alkenes, not only must the successive hydrogenation to alkanes be minimized but also the direct hydrogenation of alkynes to alkanes.

3.1. Activity

A correct approach to solve this problem requires detailed knowledge of the reaction mechanism, and with this aim, the following eight elementary steps have been considered:

s_1 $H_2 + 2* \rightleftarrows 2H*$

s_2 $Ph + 2* \rightleftarrows Ph*_2$

s_3 $Ph*_2 + H* \rightleftarrows Alk*_3$

s_4 $Ph*_2 + 2H* \rightleftarrows St*_2 + 2*$

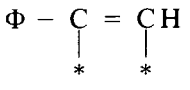
s_5 $St*2 \rightleftarrows St + 2*$

s_6 $St*_2 + 2H* \rightleftarrows Eb*_n + (4 - n)*$

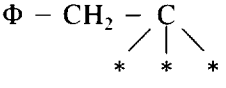
s_7 $Alk*_3 + 3H* \rightleftarrows Eb*_n + (6 - n)*$

s_8 $Eb*_n \rightleftarrows Eb + n*$,

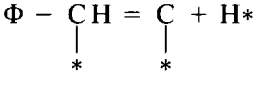
where Ph, Alk, St, and Eb represent phenylacetylene, alkylidene, styrene, and ethylbenzene, respectively, the asterisk represents a catalytic site, and $X*_n$ is a generic reactant adsorbed on n catalytic sites. Therefore, $Ph*_2$ is a phenylacetylene molecule adsorbed as



and $Alk*_3$ is an adsorbed alkylidene species



(8) which could derive (32) from



Steps s_1, s_2, s_5, and s_8 represent the adsorption (or desorption) of the reactants and the remaining steps are the surface reactions usually considered in the hydrogenation of acetylenic species (4, 8, 10). Steps s_4, s_6, and s_7 are not simple stages (34); however, the reported analysis is not affected by their inclusion. Although we do not think that different catalytic sites (4, 35) are present on the surface for the adsorption of hydrogen and organic species, in consideration of the fact that organic species (particularly $Ph*_2$ and $Alk*_3$) are adsorbed more strongly than hydrogen (31–33), the sites accessible to hydrogen should be those which, for steric reasons, are not occupied by the organic species.

These steps contribute to the balance equation

$$(\alpha + \beta + 2\gamma)H_2 + (\beta + \gamma)Ph + (\alpha - \beta)St = (\alpha + \gamma)Eb, \quad [1]$$

where the expressions in parentheses are the stoichiometric coefficients, which vary during the reaction. Considering the number of steps ($S = 8$), balance equations ($W = 1$), and surface intermediates ($J = 6$), we find (by Eq. [2]) (34) the number ($P = 3$) of basic routes

$$P = S + W - J. \quad [2]$$

Moreover, if in the balance equation the total number of species ($B = 4$), as well as the number of independent ones ($C = 3$), is considered, we obtain from Eq. [3] (35) the number of mechanisms ($N = 1$)

$$N = B - C. \quad [3]$$

Using a Fortran program developed by us (17), the basic routes are obtained by a procedure similar to that employed by Happel and Sellers (36),

$$m_1 = s_1 + s_2 + s_4 + s_5, \quad \text{that is, } Ph + H_2 \rightarrow St$$

$$m_2 = 2s_1 + s_2 + s_3 + s_7 + s_8, \quad \text{that is, } Ph + 2H_2 \rightarrow Eb$$

$$m_3 = s_1 - s_5 + s_6 + s_8, \quad \text{that is, } St + H_2 \rightarrow Eb.$$

The reaction mechanism is determined by a combination of the above basic routes

$$M = \alpha m_1 + \beta m_2 + \gamma m_3, \quad [4]$$

where α, β, and γ are the same parameters already used in the balance equation.

As pointed out under Experimental, diffusion processes should be ineffectual, so steps s_1, s_2, s_5, and s_8, which are related to the adsorption (or desorption) of the reactants, cannot be rate-determining steps in the reaction if Langmuir–Hinshelwood conditions are assumed. Therefore s_4 in the basic route m_1 and s_6 in the basic route m_3 are easily identified as rate-determining steps; for the basic route m_2, both steps s_3 and s_7 must be considered. However, if s_3 were the rate-determining step of m_2, the $Alk*_3$ species would be much less important than generally stated (8, 32, 33). Therefore, since the formation of $Alk*_3$ is expected to be fast, s_7 is very likely to be the rate-determining step for m_2.

If diffusion does not affect the adsorption equilibria, the concentrations of the different species in solution are proportional to their fractional occupancies on the catalyst surface. The importance of the surface species is evident when conditions for a sufficiently slow reaction are used (reactant moles/metal atoms = 10,000) and preconditioning experiments are carried out. In both cases (organic reactants or hydrogen preconditioning) an induction period is found, confirming the necessity of adsorbed organic species in the mechanism in one case and suggesting the participation of adsorbed hydrogen in the other case.

The dependence on hydrogen can be taken as $\theta_{H_2} = C_{H_2}/(1 + k_A C_{H_2})$, where C_{H_2} is the concentration of hydrogen in the liquid phase; θ_{H_2}, in any case, is constant under our reaction conditions. Therefore the kinetic model, on the basis of steps s_4, s_7, and s_6 as rate-determining steps, can be reduced to the following system of differential equations

$$d\mathrm{Ph}/dt = -(k_1 + k_2)\theta_{\mathrm{Ph}} \quad [5]$$

$$d\mathrm{St}/dt = k_1\theta_{\mathrm{Ph}} - k_3\theta_{\mathrm{St}} \quad [6]$$

$$d\mathrm{Eb}/dt = k_2\theta_{\mathrm{Ph}} + k_3\theta_{\mathrm{St}} \quad [7]$$

where k_1, k_2, and k_3 are the reaction rate constants for step s_4, s_7, and s_6, respectively, expressed as the percentage of conversion of the relative species per minute and

$$\theta_{\mathrm{Ph}} = K_{\mathrm{Ph}}\mathrm{Ph}/(1 + K_{\mathrm{Ph}}\mathrm{Ph} + K_{\mathrm{St}}\mathrm{St} + K_{\mathrm{Eb}}\mathrm{Eb})$$
$$= \mathrm{Ph}/[1/K_{\mathrm{Ph}} + \mathrm{Ph} + (K_{\mathrm{St}}/K_{\mathrm{Ph}})\mathrm{St} + (K_{\mathrm{Eb}}/K_{\mathrm{Ph}})\mathrm{Eb}] \quad [8]$$

and

$$\theta_{\mathrm{St}} = K_{\mathrm{St}}\mathrm{St}/(1 + K_{\mathrm{Ph}}\mathrm{Ph} + K_{\mathrm{St}}\mathrm{St} + K_{\mathrm{Eb}}\mathrm{Eb})$$
$$= \mathrm{St}[1/K_{\mathrm{St}} + (K_{\mathrm{Ph}}/K_{\mathrm{St}})\mathrm{Ph} + \mathrm{St} + (K_{\mathrm{Eb}}/K_{\mathrm{St}})\mathrm{Eb}] \quad [9]$$

represent the fractional occupancy of surface active sites (37, 38) for phenylacetylene and styrene, respectively. Ph, St, and Eb are the percentage concentrations of the reactants in the liquid phase and the K_X (X = Ph, St, Eb) are the adsorption constants of the X species on the catalyst surface.

If the relative ratio between the adsorption constants of the various species in the three basic routes are considered

$$Q_1 = K_{\mathrm{St}}/K_{\mathrm{Ph}}, \quad Q_2 = K_{\mathrm{Eb}}/K_{\mathrm{Ph}}, \quad \text{and}$$
$$Q_3 = K_{\mathrm{Eb}}/K_{\mathrm{St}} = Q_2/Q_1$$

and introduced in Eqs. [8] and [9], we have

$$\theta_{\mathrm{Ph}} = \mathrm{Ph}/(1/K_{\mathrm{Ph}} + \mathrm{Ph} + Q_1\mathrm{St} + Q_2\mathrm{Eb}) \quad [10]$$

and

$$\theta_{\mathrm{St}} = \mathrm{St}/(1/K_{\mathrm{St}} + \mathrm{Ph}/Q_1 + \mathrm{St} + Q_3\mathrm{Eb}). \quad [11]$$

When, as in the present case, the coverage of the metal surface by the organic species is large, $1/K_{\mathrm{Ph}}$ and $1/K_{\mathrm{St}}$ in Eqs. [10] and [11] become very small (38) in comparison to the other terms of the denominator and can be omitted, so that

$$\theta_{\mathrm{Ph}} = \mathrm{Ph}/(\mathrm{Ph} + Q_1\mathrm{St} + Q_2\mathrm{Eb}) \quad [12]$$

$$\theta_{\mathrm{St}} = \mathrm{St}/(\mathrm{Ph}/Q_1 + \mathrm{St} + Q_2/Q_1\mathrm{Eb}). \quad [13]$$

The five parameters k_1, k_2, k_3, Q_1, for the different catalysts (Table 2) are obtained by fitting the kinetic model above described to the kinetic data. The calculation was performed by a Fortran program, written by us, using the Bulirisch–Stoer method (39) to calculate the time dependent functions Ph, St, and Eb, and the continuous minimization by simulated annealing procedure (39) to fit the parameters. An example of fitting is shown in Fig. 1. The numerical and data analyses indicate a pseudo-zero-order reaction which agrees well with the Langmuir–Hinshelwood mechanism considered here. Moreover, the above coincidence of data analysis and experimental results and the direct proportionality between reaction rate and catalyst amount could have not been realized if H_2 diffusion limitation was not negligible.

The turnover frequencies TOF_1, calculated from k_1 and D_x, are practically constant (Fig. 2), with the differences falling within experimental error, and are at least two

TABLE 2

Kinetic Parameters

Catalyst	Q_1[a]	Q_2[b]	Q_3[c]	k_1[d] (min−1)	k_2[e] (min^{-1})	k_3[f] (min^{-1})	k_2/k_1	k_3/k_1	TOF_1[g] (s^{-1})
W_7	0.052	0.11	2.1	6.4	0.37	3.5	0.06	0.54	7.6
W_6	0.076	0.17	2.2	7.8	0.32	4.5	0.04	0.58	5.9
W_3	0.057	0.15	2.6	13.1	1.00	8.9	0.08	0.68	6.8
W_2	0.052	0.11	2.1	14.0	0.84	9.8	0.06	0.70	6.0
U_1	0.051	0.11	2.1	13.3	0.95	9.5	0.07	0.72	4.7
W_0	0.053	0.10	1.9	19.2	0.75	14.3	0.04	0.75	5.2

[a] Ratio of styrene/phenylacetylene adsorption constants.
[b] Ratio of ethylbenzene/phenylacetylene adsorption constants.
[c] Calculated from Q_2/Q_1.
[d] Phenylacetylene to styrene rate constant.
[e] Phenylacetylene to ethylbenzene rate constant.
[f] Styrene to ethylbenzene rate constant.
[g] Turnover frequency for phenylacetylene conversion, calculated from k_1 and D_x.

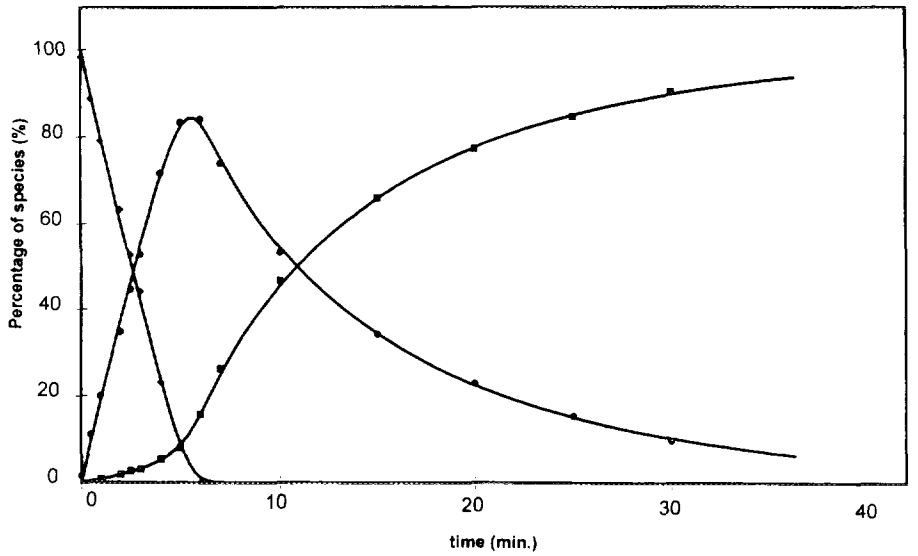


FIG. 1. Hydrogenation of phenylacetylene (percentage of reactants vs time): experimental points and relative theoretical curves, using the W_0 catalyst. Phenylacetylene (◆), Styrene (●), and Ethylbenzene (■).

orders of magnitude higher than those calculated from the data reported by Carturan *et al.* (9) for a similar reaction system. Since the diffusion of hydrogen, if magnetic stirring is used (40), usually affects hydrogenation in the liquid phase, the large difference in activity between the two reactions could be mostly due to insufficient stirring by the magnetic apparatus (9).

Moreover, the structure insensitivity (41), for the whole range of metal dispersion considered ($14\% \leq D_x \leq 62\%$), is unusual in the hydrogenation of alkynes. As suggested in other articles by our groups (17, 42), the electron density transfer from pumice to palladium, documented by XPS measurements (23, 24), could also explain the activity of these catalysts at high metal dispersions.

It is well known (43) that the turnover frequency for the semihydrogenation of alkadienes (6, 13, 17) with supported Pd catalysts is at least 20 times higher than the TOF for the semihydrogenation of alkynes (2, 6, 43); in our opinion this experimental result cannot be explained exclusively by the difference in bond strength of the two adsorbed species to palladium. Related to this fact is the hydrogenation of styrene with pumice-supported Pd catalysts, which shows a rate constant similar to that obtained in the hydrogenation of styrene produced from phenylacetylene. However, the curve (Fig. 3) is typical of a zero-order reaction with $Q_2/Q_1 = Q_3 \rightarrow 0$, but Q_3 in the hydrogenation of styrene produced from phenylacetylene is practically constant ($Q_3 \simeq 2$). Therefore, it appears that

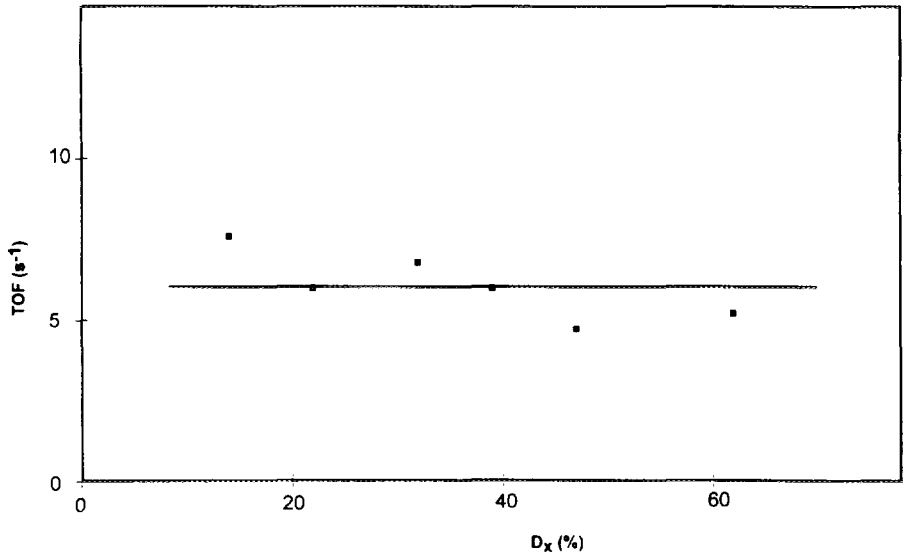


FIG. 2. Catalytic activity of pumice-supported catalysts in phenylacetylene hydrogenation (TOF_1 vs D_x).

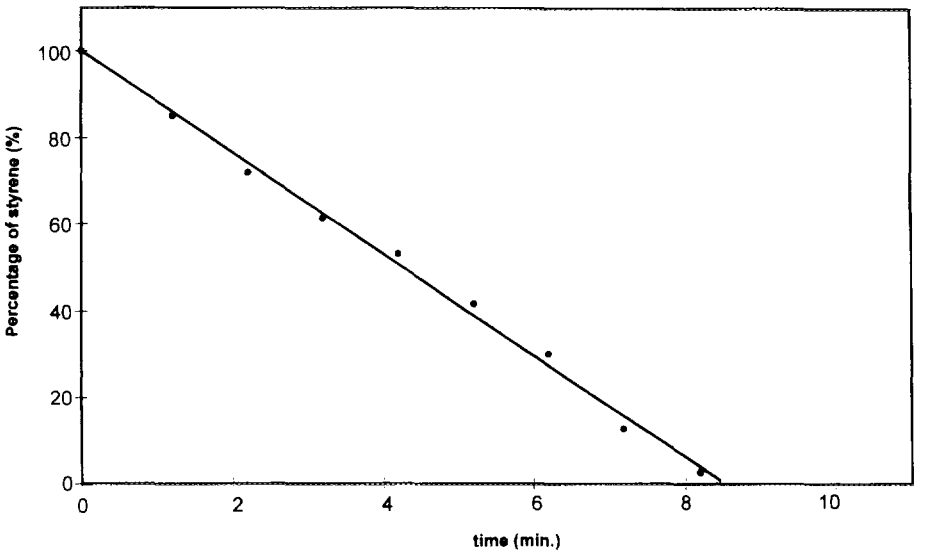


FIG. 3. Hydrogenation of styrene (percentage vs time); experimental points and relative theoretical curve, using the W_0 catalyst.

the catalyst surface available for the direct hydrogenation of styrene is different from that available to styrene derived from hydrogenation of phenylacetylene. Since, however, hydrogenation of phenylacetylene, added to the reaction mixture when the first semihydrogenation is complete follows the same curve as the original phenylacetylene, the modification of the surface catalyst responsible for the different adsorption ratio Q_3 cannot be due to persistent and increasing impurities such as carbonaceous residues (4, 10) but to reaction intermediates (8, 44). The surface appears to be modified in such a way that the interaction with styrene is decreased whereas the ability to hydrogenate the styrene remains unaltered.

We have considered the possibility of poisoning effects by adding to the original eight elementary steps another step,

$$s_9 \quad * \rightarrow \bigcirc,$$

where $\bigcirc$ represents a poisioned catalytic site.

If θ is the fraction of active sites on the metallic surface, its dependence on time is easily obtained

$$\theta = [k^{\bigcirc} + k^*\exp - (k^{\bigcirc} + k^*)t]/(k^{\bigcirc} + k^*), \quad [14]$$

where k^* and $k^{\bigcirc}$ are the rate constants for the disappearance of active sites and poisoned sites, respectively. If both Eqs. [12] and [13] are multiplied by [14] in the system of eqs. [5]–[7], the hydrogenation of phenylacetylene can be followed under conditions of continuous decrease in catalytic sites. However, the calculations according to

$$d\mathrm{Ph}/dt = [-(k_1 + k_2)\theta_{\mathrm{Ph}}]\theta \quad [15]$$

$$d\mathrm{St}/dt = [k_1\theta_{\mathrm{Ph}} - k_3\theta_{\mathrm{St}}]\theta \quad [16]$$

$$d\mathrm{Eb}/dt = [k_2\theta_{\mathrm{Ph}} + k_3\theta_{\mathrm{St}}]\theta \quad [17]$$

do not change the value of the parameters of Table 2, because θ is always about 1, since $k^{\bigcirc} \gg k^*$.

In light of the experiments which compare the direct hydrogenation of styrene with that of styrene derived from phenylacetylene, and considering that hydrogenation of added phenylacetylene does not change when it is added to the reaction mixture after the original phenylacetylene has been consumed, the agreement of parameters of Table 2 with those obtained by the Eqs. [15]–[17] could be explained by a very fast initial poisoning of the catalyst surface. This effect should be a consequence of the large adsorption constant of phenylacetylene and alkylidene species and the origin of the constant values of Q_1, Q_2, and K_2/K_1 (Table 2 and Fig. 5) for the different catalysts.

The poisoning intermediates which have originated from phenylacetylene can be polymeric species (4, 10) or other species which are difficult to hydrogenate such as Alk^*_3 (8). The latter should be important at least when phenylacetylene is present (4, 8). The trace amounts of unidentified products which are found in the chromatograms of the reaction samples, and which show an increasing retention time with the progress of the reaction, could be an indication of polymeric species.

The poisoning effects which are present in the semihydrogenation of alkynes, together with the different strengths of the Pd-alkyne and Pd-alkadiene interactions, contribute, therefore, to the difference in TOF between the two hydrogenations. In addition, on the poisioned surface, geometric or better decoration (45) effects could modify the relative reactant interactions and therefore

have a direct influence on the selectivity. Indeed the ethylbenzene adsorption constant K_{Eb} on the catalytic sites could become competitive or even greater than that of styrene K_{St} ($Q_3 = Q_2/Q_1 \approx 2$), thus increasing selectivity. Owing to the strong adsorption of phenylacetylene and alkylidene, and to the reduced rate in the hydrogenation of alkenes on Pd/pumice (17), ethylbenzene is probably produced mostly by the hydrogenation of Alk*$_3$.

The effect of temperature on phenylacetylene hydrogenation has been considered by experiments carried out in the temperature range 15–35°C with two catalysts of different metal dispersions (W_0 and W_6). The results, which are listed in Table 3, were used to calculate the activation energy of the three processes occurring in the hydrogenation of phenylacetylene, namely m_1, m_2, and m_3. The Arrhenius plots are reported in Fig. 4. We have no plausible explanation for the low value of the activation energies of the reactions Ph → St and St → Eb. The low temperatures of the experiments, the low surface area of the support, the very high rate of mechanical stirring, the introduction of hydrogen inside the reaction mixture in our system (see Ref. 30), and the direct proportionality of the reaction rates with the catalyst amount and/or the temperature indicate, in our opinion, that diffusion limitations are not important. Moreover, we did not find any important change in Q_1, Q_2, and consequently Q_3 in the range of temperatures considered.

3.2. *Selectivity*

As shown in Fig. 5, the selectivity ratio k_2/k_1 is practically constant, while k_3/k_1 increases slightly with D_x. This is not surprising since the same trend was found with the same catalysts in the selectivity ratio $k_{COE}/k_{1,3\text{-}COD}$ (17) (COE = cyclooctene, 1,3-COD = 1,3-cyclooctadiene). More interesting are the observations that at least one order of magnitude separates k_2 and k_3 and that k_3 never exceeds k_1, in contrast to that reported under apparently identical experimental conditions (9). On the other hand, the supply of electron density to palladium in the pumice-supported Pd catalysts has the same effect of a decrease in dispersion in conventional supported Pd catalysts. Accordingly, on the basis of the characteristic "volcano" curve obtained by relating the activity of supported Pd catalysts (6) with the adsorption coefficients of unsaturated hydrocarbons in hydrogenation processes, larger particles increase the activity of hydrogenation of alkynes and alkadienes but deplete that of alkenes. However, since the decrease in k_1 is expected to be less pronounced than the increase in k_3, the overall trend of k_3/k_1 is expected to increase with metal dispersion; this is exactly what our data show.

Three different expressions of selectivity have been considered:

$$S_{\%} = 100(\text{moles of styrene})/(\text{moles of converted phenylacetylene})$$

$$S_H = 100(\text{moles of styrene})/(\text{moles of unconverted phenylacetylene})$$

$$S_N = 100(d\text{St}/|d\text{Ph}|).$$

$S_{\%}$ is the selectivity usually reported in the literature (43), S_H is reported by Hub *et al.* (6) and allows one to determine the maximum congruous ratio between styrene and phenylacetylene for a catalytic system. S_N, suggested by us, represents the instantaneous selectivity of a catalyst, where dSt is an infinitesimal change in styrene and $|d\text{Ph}|$ is the absolute value of the corresponding infinitesimal change in phenylacetylene. These different selectivities are reported vs percentage of phenylacetylene conversion in Figs. 6–8, respectively; the parameters of Table 2 were used to calculate the plotted curves.

Figures 6–8 do not show any particular correlation between selectivity and dispersion. On the basis of these results, it appears that pumice-supported Pd catalysts show good activity and selectivity. Both activity and selectivity appear to be independent of metal dispersion. However, if we consider that when industrial conditions are employed (7) (phenylacetylene in the reaction mixture

TABLE 3

Turnover Frequencies (TOF) and Activation Energies (E_a^0) for Hydrogenation Reactions 1, Ph → St; 2, Ph → Eb; 3, St → Eb[a]

Catalyst	Temperature (°C)	TOF_1 (s^{-1})	TOF_2 (s^{-1})	TOF_3 (s^{-1})	E_{a1}^0 ($kJmol^{-1}$)	E_{a2}^0 ($kJmol^{-1}$)	E_{a3}^0 ($kJmol^{-1}$)
W_0	35	6.6	0.3	5.0			
W_0	25	5.2	0.2	3.8			
W_0	15	4.0	0.1	2.6	18.5	40.6	24.2
W_6	35	7.6	0.4	4.5			
W_6	25	5.9	0.2	3.4			
W_6	15	4.8	0.1	2.0	16.9	51.1	30.0

[a] Ph, phenylacetylene, St, styrene, Eb, ethylbenzene.

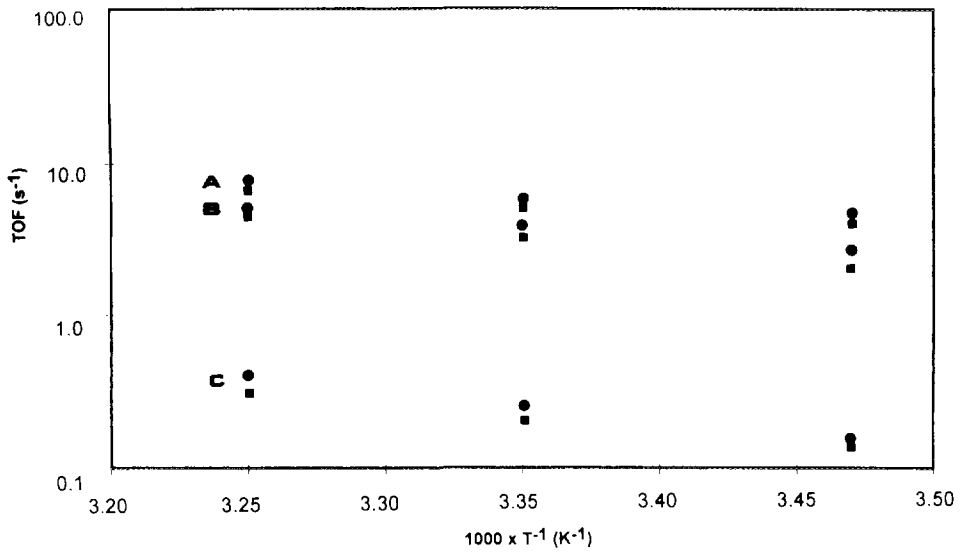


FIG. 4. Arrhenius plots for phenylacetylene hydrogenation. (A) Ph → St; (B) St → Eb; (C) Ph → Eb. Data for the W_6 (●) and W_0 (■) catalysts.

≤10 ppm), $\theta_{Ph} \ll \theta_{St}$, and the values of k_2 for each catalyst are on the order of experimental error of k_1 (<10%), the expression for S_N, namely

$$S_N = 100\frac{dSt}{|d\mathrm{Ph}|} = 100\frac{k_1\theta_{Ph} - k_3\theta_{St}}{|-(k_1 + k_2)\theta_{Ph}|}$$

can be simplified to

$$S_N = 100\frac{-k_3\theta_{St}}{|-k_1\theta_{Ph}|} = -100\,Q_1\frac{k_3\,\mathrm{St}}{|-k_1\,\mathrm{Ph}|}.$$

Therefore, for equal St/Ph ratios, S_N becomes proportional to $Q_1 \times k_3/k_1$, for each catalyst. Since for all the catalysts Q_1 is almost constant and S_N, under the industrial conditions, is lower than zero (Fig. 9), selectivity decreases as k_3/k_1 and D_x increase.

The literature on the matter of the influence of metal dispersion on the selectivity for alkyne hydrogenation shows opposite trends: an increase (5, 6, 8, 12) as well as a decrease (11) in selectivity have been reported with increasing dispersion. Direct comparisons, however, are difficult, owing to different conditions and sometimes different substrates (6).

Several authors (7, 12, 46) have attributed much importance to β-Pd–H formation during hydrogenation processes with supported Pd catalysts. However, WAXS analyses on the W_7 catalyst reemployed several times

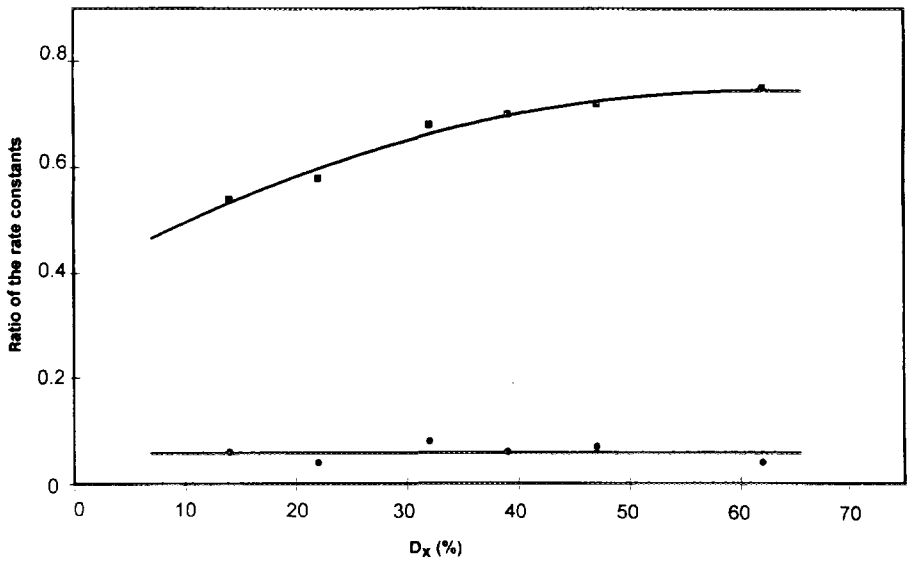


FIG. 5. Dependence of rate constant ratios [k_2/k_1 (●) and k_3/k_1 (■)] on metal dispersion (D_x).

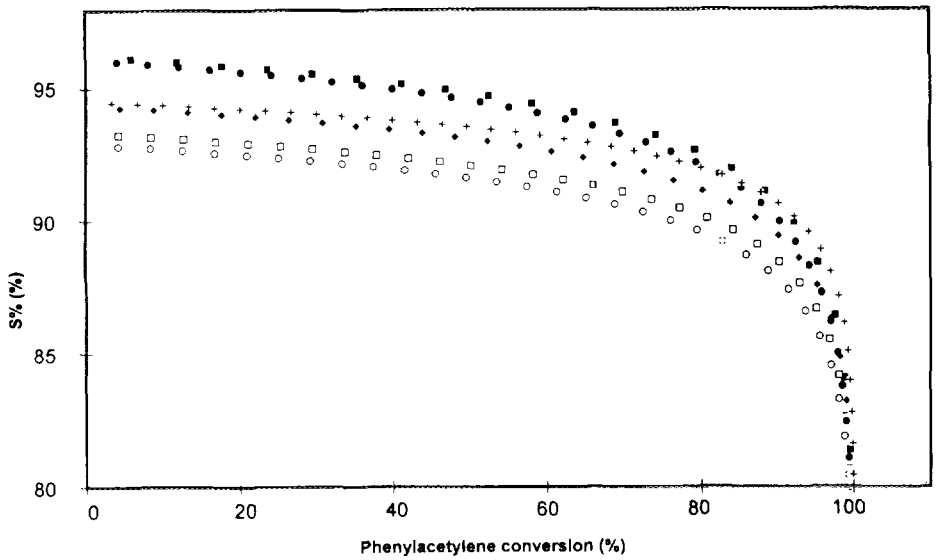


FIG. 6. $S_{\%}$ selectivity for the different catalysts ($S_{\%}$ vs percentage of phenylacetylene conversion): W_7 (+); W_6 (●); W_3 (○); W_2 (◆); U_1 (□); W_0 (■).

under our kinetic conditions did not show any increase in intensity in the reflection peak (111). The absence of this effect, which is expected when reconstruction of palladium crystallites occurs because of β-Pd hydride formation, suggests that β-Pd hydride is not very important in the hydrogenation of phenylacetylene with pumice-supported Pd catalysts, at least under our kinetic conditions.

4. CONCLUSIONS

This kinetic study of the hydrogenation of phenylacetylene in the liquid phase on pumice-supported Pd catalysts shows that three basic routes contribute to the mechanism of the reaction. The rate-limiting steps of the three routes involve only surface species:

$$\mathrm{Ph}*_2 + 2\mathrm{H}* \rightarrow \mathrm{St}*_2 + 2*$$

$$\mathrm{Alk}*_3 + 3\mathrm{H}* \rightarrow \mathrm{Eb}*_n + (6 - n)*$$

$$\mathrm{St}*_2 + 2\mathrm{H}* \rightarrow \mathrm{Eb}*_n + (4 - n)*.$$

Comparison with similar reactions on other supported Pd catalysts shows an increased activity for Pd/pumice catalysts and also, more interestingly, that pumice-supported Pd catalysts are still active at very high metal dispersions.

The formation of polymeric species or other species difficult to hydrogenate (4, 8, 10) at the initial stage of the reaction produces a "flattening" effect in the catalytic activity, due to coverage of active sites. However, the involvement of a positive effect in the activity, due to an electron density supply from the support to the metal

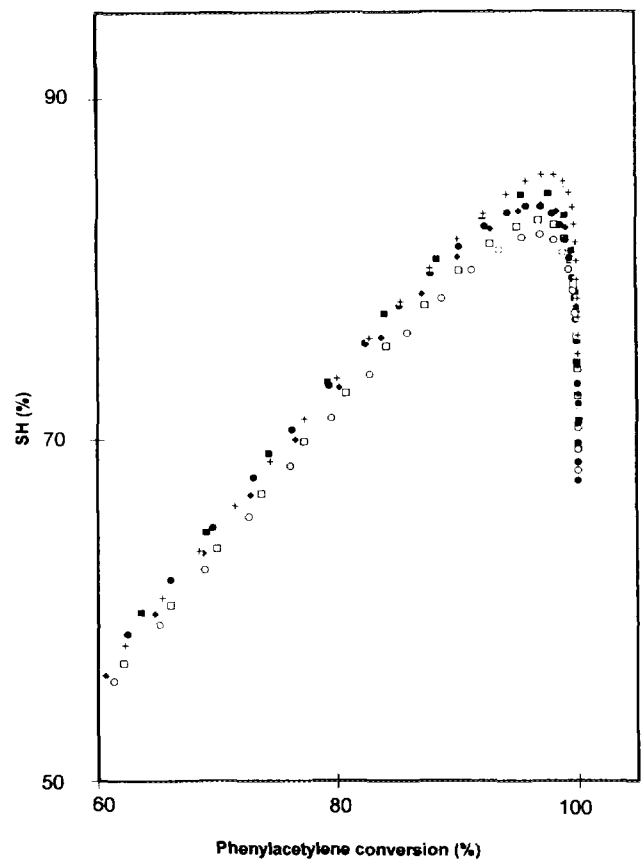


FIG. 7. S_H selectivity for the different catalysts (S_H vs percentage of phenylacetylene conversion). W_7 (+); W_6 (●); W_3 (○); W_2 (◆); U_1 (□); W_0 (■).

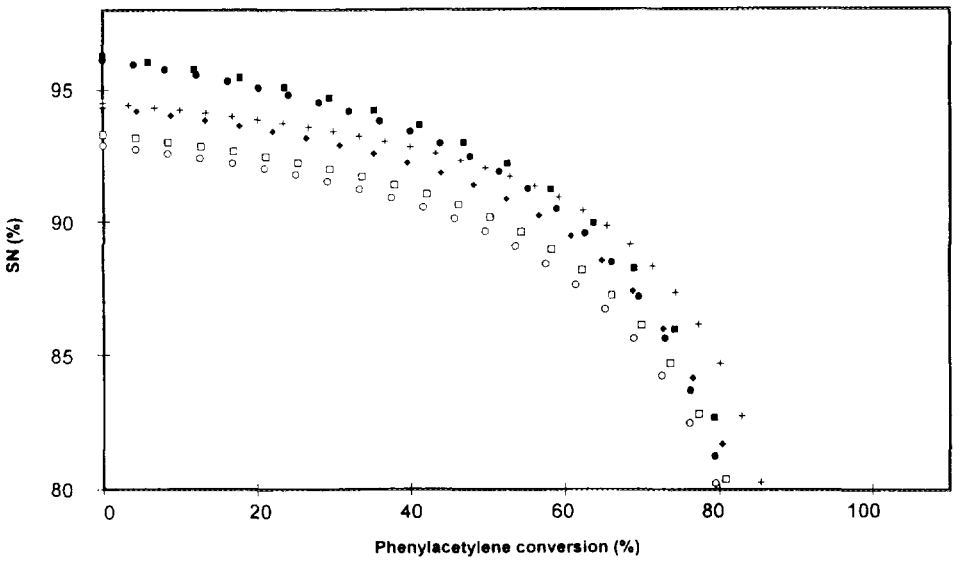


FIG. 8. S_N selectivity for the different catalysts (S_N vs percentage of phenylacetylene conversion). W_7 (+); W_6 (●); W_3 (○); W_2 (◆); U_1 (□); W_0 (■).

particles (23), could be responsible for the increased range of activity of Pd/pumice at higher metal dispersions. Further studies on the Pd/pumice catalysts used in this work show that the transfer of electron density to the metal, determined by the Auger parameter (47), increases with dispersion. This behaviour is different from the normally found decrease in metallic properties with particle dimensions (43), documented by an increase of binding energy in the small particles (48).

Although selectivity does not appear to be influenced by dispersion, the decrease in the activity of pumice-supported Pd catalysts in the hydrogenation of alkenes improves the selectivity of our catalysts to styrene. In addition, the flattening effect could be essentially due to the very high adsorption coefficient of phenylacetylene and consequently to decoration of the metal surface (45) by species difficult to hydrogenate. This occurrence, causing a change in the ratio of the adsorption coefficients of ethylbenzene and styrene, would generate, independently of dispersion, a high constant selectivity up to unusually large phenylacetylene conversions.

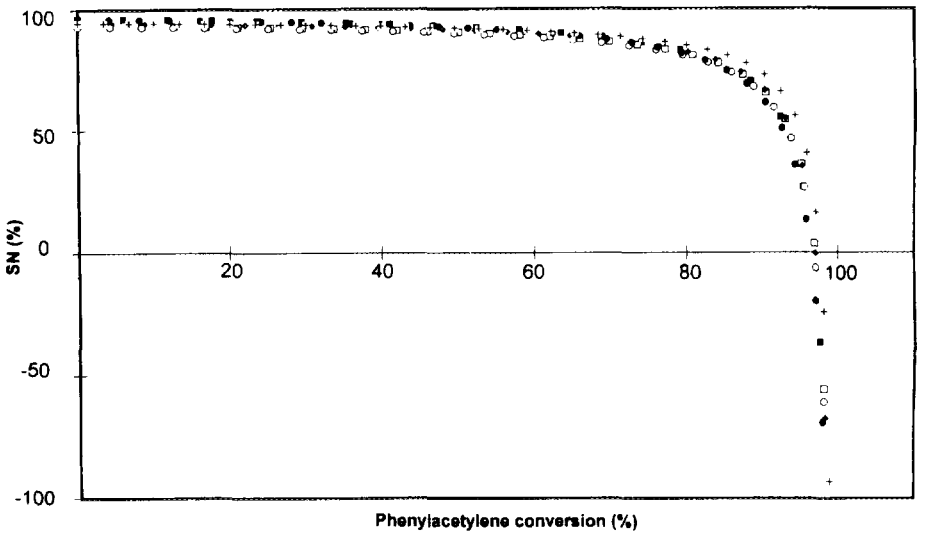


FIG. 9. Influence of dispersion (D_x) on S_N, under conditions close to those of industrial operations. W_7 (+); W_6 (●); W_3 (○); W_2 (◆); U_1 (□); W_0 (■).

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