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# Liquid phase hydrogenation of phenylacetylene on pumice supported palladium catalysts

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**Abstract**

The liquid phase hydrogenation of phenylacetylene on pumice supported palladium catalysts with a large range of metallic dispersions ($14\% < D_x < 62\%$) has been carried out in a mechanically stirred glass reactor where any mass transfer effects are eliminated. A five parameters mathematical model has been used to analyze the kinetics. Three basic routes, involving only surface species in the rate determining steps, contributed to the mechanism of the reaction. The hydrogenation of phenylacetylene to styrene, with the pumice supported palladium catalysts, shows good activity and selectivity. The reaction is structure insensitive in the whole range of the considered dispersions, in contrast to that with other Pd catalysts on more traditional supports, which show a marked decrease in activity and selectivity when dispersion of the metallic phase is higher than 20%.

## 1. Introduction

Supported palladium catalysts find several applications in the petrochemical industry [1] specially in the hydrogenation of highly unsaturated hydrocarbons. The catalyst of choice for the reduction of alkynes in the front-end and tail-end cuts of alkenes for the production of polymers is palladium on $\alpha$-alumina [2,3]. These supported palladium catalysts manifest a decrease in activity of about one order of magnitude when the metal dispersion becomes higher than 20–25%. Moreover, selectivity decreases as well. Among the various attempts to improve the catalyst performances in the above process, addition of carbon monoxide, organic bases, sulphides and metal ions [4,5], and alloying palladium with other transition [6,7] and non-transition metals [8] have achieved some success. Our interest in the field is based on a different approach which deals with the characteristics of the supporting oxide. Recent studies have shown that pumice supported palladium catalysts, in the selective hydrogenation of conjugated dienes, in liquid phase [9], maintain a good activity and selectivity also when highly dispersed catalysts are used. Here we report a kinetic study of the liquid phase hydrogenation of phenylacetylene over pumice supported catalysts and comment on some different behaviours of our pumice supported palladium catalysts with respect to palladium catalysts on other traditional supports.

## 2. Experimental

All the used reagents (Aldrich) were of analytical grade. Phenylacetylene and styrene were

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Table 1
Some characteristics of the pumice supported palladium catalysts

| Catalyst[a] | Pd (%) | $S^{b}_{sp}$ ($m^2/g$) | $D^{c}_{p}$ (Å) | $D^{d}_{x}$ (%) | $\Delta\alpha$(cat.–Me)[e] (eV) | $\Delta q^{f}$ (a.u.) |
|---|---|---|---|---|---|---|
| $W_7$ | 1.05 | 62 | 81 | 14 | −0.1 | 0.000 |
| $W_6$ | 0.37 | 100 | 50 | 22 | −0.2 | −0.015 |
| $W_3$ | 0.38 | 143 | 35 | 32 | −0.5 | −0.020 |
| $W_2$ | 0.11 | 172 | 29 | 39 | −0.9 | −0.070 |
| $U_1$ | 0.12 | 208 | 24 | 47 | n.d. | n.d. |
| $W_0$ | 0.05 | 278 | 18 | 62 | −2.0 | −0.148 |

[a] These catalysts have been reported previously [9,13]; they have the original symbols for immediate comparison.
[b] Specific surface of the metallic phase determined by SAXS [13,17].
[c] Porod diameter.
[d] Percentage of exposed metallic atoms (parameter used to calculate $TOF_1$).
[e] $\Delta\alpha$(cat.–Me) [19] has been evaluated as Auger parameter of the catalyst minus Auger parameter of metallic Pd equal to 662.9 eV [20].
[f] Electronic charge variation of $W_n$ catalyst with respect to $W_7$; n.d., not determined.

purified and stored at − 10°C under $N_2$, and tested by GC analyses before use. Tetrahydrofuran was distilled from $LiAlH_4$ and then from K under $N_2$ just before use.

The pumice is a waste of the production of Pumex SpA-Lipari (Messina) with sizes smaller than 45 μm. Its characteristics are standardized by a treatment of half an hour with boiling 25% nitric acid, consecutive cleaning with water up to neutrality and final drying in a nitrogen flux for 7 h at 250°C [10]. This treatment eliminates all the oxides with an original concentration lower than 1%, reduces to traces iron oxides and decreases the atomic percentage of $K^+$ (1.4%) and $Na^+$ (1.3%) [11]. The alumino-silicate structure, however, remains inalterate [12].

The Pd catalysts were prepared as already reported [13], using a modified Yermakov method [14]. Although stable in air [9], the catalysts were stored in nitrogen.

Particle dimensions were studied by SAXS (small angle X-ray scattering) [13], WAXS-LB (wide angle X-ray scattering, line-broadening) [13,15–17], and TEM (transmission electron microscopy) [13]. A donor effect from the support to the metal particles was always found, as documented 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 the Pd powder in the XPS spectra [12,18]. The transfer of the electronic density to palladium has been recently confirmed by calculation of Auger parameter shifts (combination of the photoelectron and Auger shifts), which showed that the electron density on the metal particles increased as the particle size decreases [19].

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

### 2.1. Kinetic studies

The reactions were carried out in a mechanically stirred tank reactor (Fig. 1), connected to an inert gas-vacuum line and to a gas adsorption system operating at a constant atmospheric pressure of $H_2$. A side arm closed by a silicone septum allowed injection of reagents and withdrawing of samples for GC analyses. The constant temperature (25.029 ± 0.1°C) was ensured by a thermostat. $TOF_1$ (turnover frequency) did not change when the stirring rate was higher than 2000 rpm, and it was directly proportional to the catalyst amount, when temperature and/or catalyst amount were changed, suggesting that mass transfer limitations were negligible [21]. All the reactions were carried out using an initial ratio (reagent moles)/(metal atoms) equal to 1000; the initial reagent concentration in THF was always $2.5 \cdot 10^{-1}$ M. The reaction mixture was stirred for half an hour with the organic reagent before addition of hydrogen.

Kinetic analyses were performed by a GC DANI 3800 HRPTV equipped with a SUPELCO capillary column SPB1701 and with a DANI 68/10 FID detector. This system was linked to a SHIMADZU C-R1B CHROMATOPAC integrator.

## 3. Results and discussion

To preserve the catalyst in the polymerization processes, pure alkene feedstock is needed. It is well known that deactivation of the catalyst is due, among others, to the presence of alkynes and/or alkadienes in the alkene cut. Reduction of alkynes or alkadienes to less than 10 ppm is necessary. The 'industrial tolerance' of formation of the alkane in this process is 1%. According to the well known hydrogenation Scheme 1 [6,21,22] the balance equation is:

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

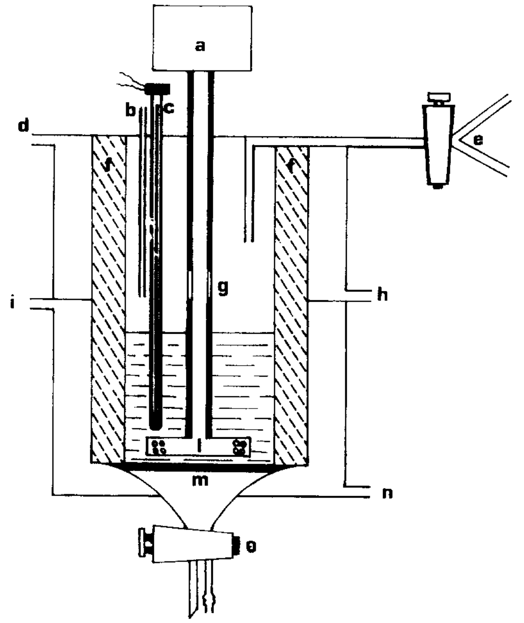
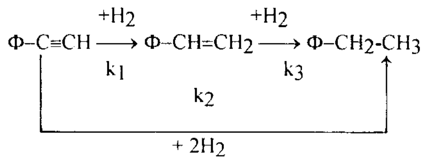


Fig. 1. Scheme of the reactor: (a) stirrer (5000 rpm); (b) injection and withdrawing of reactants; (c) thermometer connected to thermostat; (d) water out; (e) three ways stopcock for gas fluxing and vacuum operations; (f) baffles; (g) gas inside the stirrer; (h) water in; (i) thermostat liquid out; (l) gas in the reaction; (m) gas frit; (n) thermostat liquid in; (o) three ways stopcock for solution recovery and gas introduction.



Scheme 1. Hydrogenation scheme.

An improvement of the hydrogenation to alkenes, without production of alkane, and a minimization of the direct hydrogenation of alkynes to alkanes must be performed, or in other words an increase of $k_1$ and/or a decrease of $k_2$ and $k_3$ should be achieved. To solve this problem a detailed knowledge of the reaction mechanism is necessary [23]. The following eight elementary steps, considering a Langmuir–Hinshelwood (L.H.) mechanism, have been proposed:

$$H_2+2* \rightleftharpoons 2H* \quad (s_1)$$

$$Ph+2* \rightleftharpoons Ph*_2 \quad (s_2)$$

$$Ph*_2+H \rightleftharpoons Alk*_3 \quad (s_3)$$

$$Ph*_2+2H* \rightleftharpoons St*_2+2* \quad (s_4)$$

$$St*_2 \rightleftharpoons St+2* \quad (s_5)$$

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

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

$$Eb*_n \rightleftharpoons Eb+n* \quad (s_8)$$

where Ph, Alk, St and Eb represent phenylacetylene, alkylidene, styrene and ethylbenzene, '$*$' a catalytic site and $X*_n$ is a reactant adsorbed on $n$ catalytic sites. Therefore $Ph*_2$ represents phenylacetylene adsorbed onto two catalytic sites, whereas $Alk*_3$ is alkylidene adsorbed onto three sites at one carbon atom.

The steps $s_3$, $s_4$, $s_6$, and $s_7$ represent the surface reactions usually considered in the hydrogenation of alkynes [6,24] whereas $s_1$, $s_2$, $s_5$, and $s_8$ are the steps involving adsorption (or desorption) of reactants (or products). As pointed out in the Experimental Section, the design of the reaction vessel (Fig. 1) and the high rpm value of the mechanical stirring make negligible any mass transport limitation. Moreover, considering the L.H. mechanism, it is legitimate to exclude the

Table 2
Kinetic parameters

| Catalyst | $Q_1^a$ | $Q_2^b$ | $Q_3^c$ | $k_1^d$ ($\mathrm{min^{-1}}$) | $k_2^e$ ($\mathrm{min^{-1}}$) | $k_3^f$ ($\mathrm{min^{-1}}$) | $k_2/k_1$ | $k_3/k_1$ | $\mathrm{TOF}_1^g$ ($\mathrm{s^{-1}}$) | $\mathrm{TOF}_2^g$ ($\mathrm{s^{-1}}$) | $\mathrm{TOF}_3^g$ ($\mathrm{s^{-1}}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $W_7$ | 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 | 0.2 | 3.4 |
| $W_3$ | 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 | 0.2 | 3.8 |

[a] Styrene/phenylacetylene adsorption constant ratio.
[b] Ethylbenzene/phenylacetylene adsorption constant ratio.
[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 frequencies were calculated from the corresponding $k_n$ and $D_x$.

adsorption (or desorption) steps as rate determining ones, owing also to the very low surface area of the support (ca. 5 $\mathrm{m^2\,g^{-1}}$). By a combination of the possible elementary steps, following a procedure similar to that employed by Happel and Sellers [25], using a FORTRAN program developed by us [9], we obtained the following reaction mechanism:

$$M = \alpha m_1 + \beta m_2 + \gamma m_3 \qquad (2)$$

where $\alpha$, $\beta$, and $\gamma$ (changing during the reaction) represent the same stoichiometric coefficients of the balance equation, and $m_x$ are basic routes obtained from the computational procedure:

$m_1 = s_1 + s_2 + s_4 + s_5$ that is $Ph + H_2 \rightarrow St$

$m_2 = 2s_1 + s_2 + s_3 + s_7 + s_8$ that is

$Ph + 2H_2 \rightarrow Eb$

$m_3 = s_1 - s_5 + s_6 + s_8$ that is $St + H_2 \rightarrow Eb$

The solution of a series of differential equations:

$$\mathrm{dPh}/\mathrm{d}t = (-k_1 + k_2)\,\Theta_{Ph}$$

$$\mathrm{dSt}/\mathrm{d}t = k_1\Theta_{Ph} - k_3\Theta_{St}$$

$$\mathrm{dEb}/\mathrm{d}t = k_2\Theta_{Ph} + k_3\Theta_{St}$$

which describe the changes of Ph, St, and Eb with time, and where $Q_{Ph}$ and $Q_{St}$ (the fractional occupancy of the active sites [26,27] for phenylacetylene and styrene, respectively) are independent variables, gives the kinetic parameters (Table 2).

When, as in the present case, the coverage of the metal surface by the organic species is large (see Experimental), simplified expressions of $\Theta_{Ph}$ and $\Theta_{St}$, can be used:

$$\Theta_{Ph} = Ph/(Ph + Q_1 St + Q_2 Eb) \qquad (3)$$

$$\Theta_{St} = St/(Ph/Q_1 + St + Q_3 Eb) \qquad (4)$$

where Ph, St, and Eb are the percentage concentrations of the reactants in the liquid phase, $Q_n$ are the ratios between the adsorption constants $K_X$ of the various species (Table 2).

The five parameters obtained are $k_1$, $k_2$, $k_3$, (rate constants of the surface reactions of the basic steps $m_1$, $m_2$, and $m_3$) and $Q_1$, and $Q_2$ (adsorption constants ratio $K_{St}/K_{Ph}$ and $K_{Eb}/K_{Ph}$). $Q_3$ ($K_{St}/K_{Eb}$) is obtained from $Q_2/Q_1$. The fitting of the experimental results with theoretical curves is quite good (Fig. 2).

The first semihydrogenation appears to be structure insensitive, at least in the range of the metal dispersion considered ($14\% < D_x < 62\%$) (Fig. 3).

Although a direct comparison of the activity with other palladium catalysts on conventional supports (3) is difficult, owing to different pressure of hydrogen (when comparison is feasible (7) the activity of our catalysts is much higher, but probably in that case (7) diffusion limitations

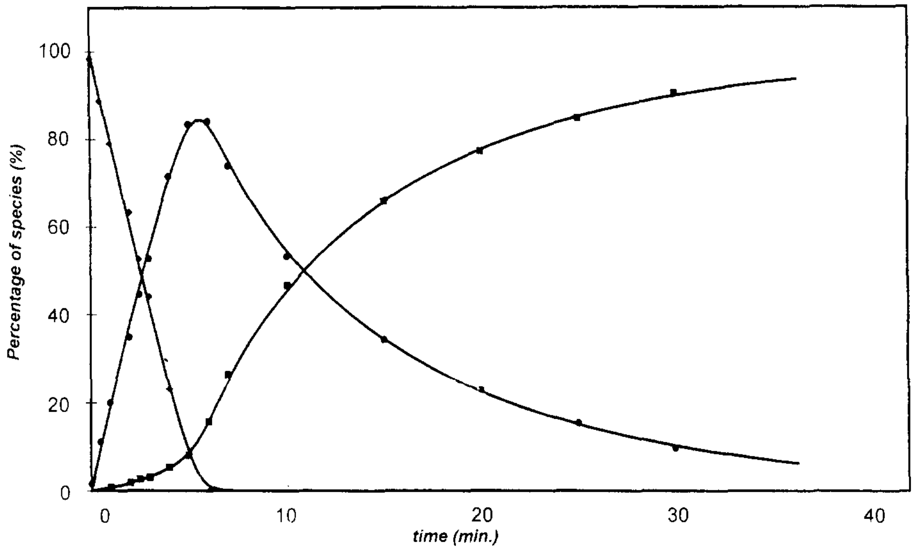


Fig. 2. Hydrogenation of phenylacetylene (percentage of reactants vs. time); experimental points and theoretical curves, using the $W_0$ catalyst: Ph (◆), St (●), Eb (■).

are important), the range of metal dispersion which appears suitable for the employment of the catalyst is larger in Pd/pumice than in other supported palladium catalysts. Usually the activity decreases drastically at metal dispersions higher than 20%; this limitation is not present in Pd/pumice at least till 62% dispersion.

The hydrogenation of styrene on pumice supported Pd catalysts (Fig. 4) shows a constant rate similar to the rate of the hydrogenation of styrene as intermediate of the hydrogenation of phenylacetylene. However while $Q_3$ for the direct hydrogenation tends to zero, in the case of hydrogenation of styrene produced from pheny-

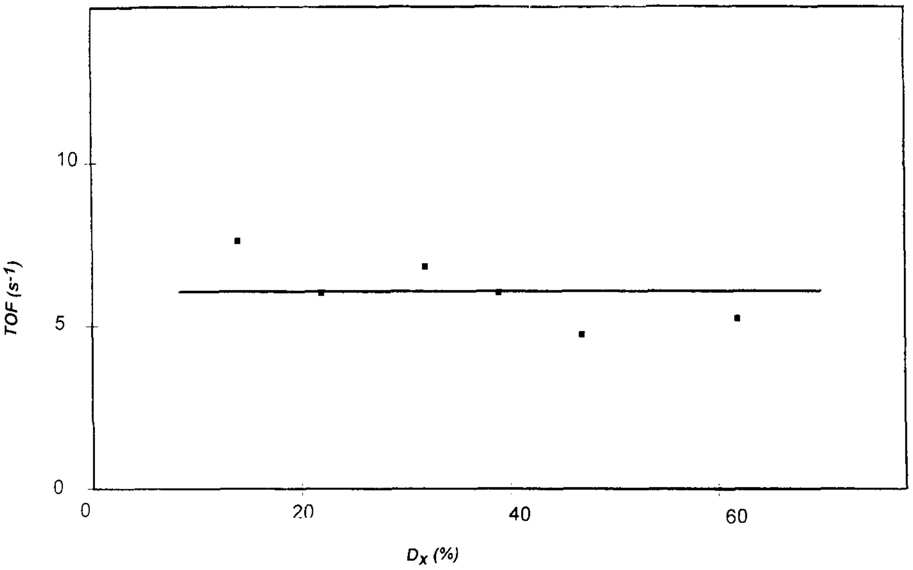


Fig. 3. Catalytic activity of pumice supported catalysts in phenylacetylene hydrogenation ($TOF_1$ vs. $D_x$).

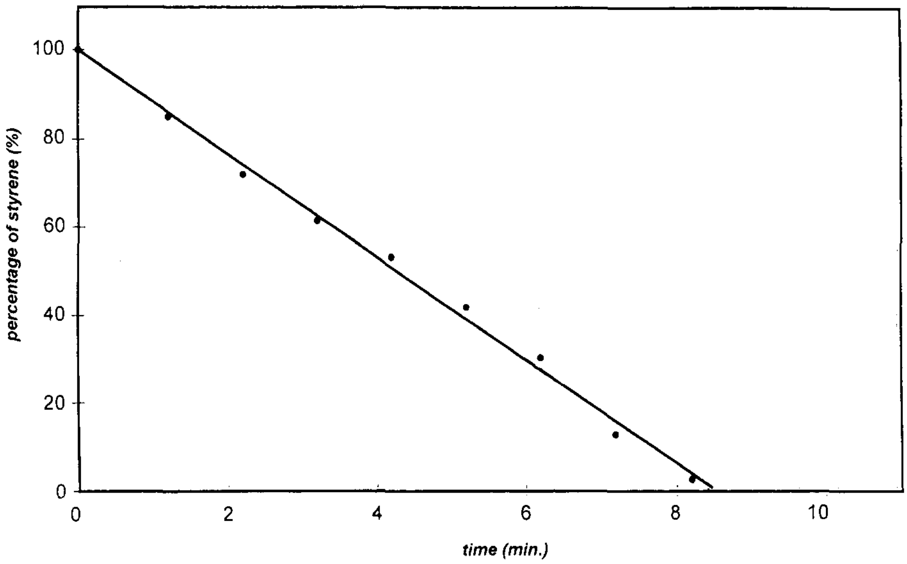


Fig. 4. Hydrogenation of styrene (percentage vs. time) on the $W_0$ catalyst.

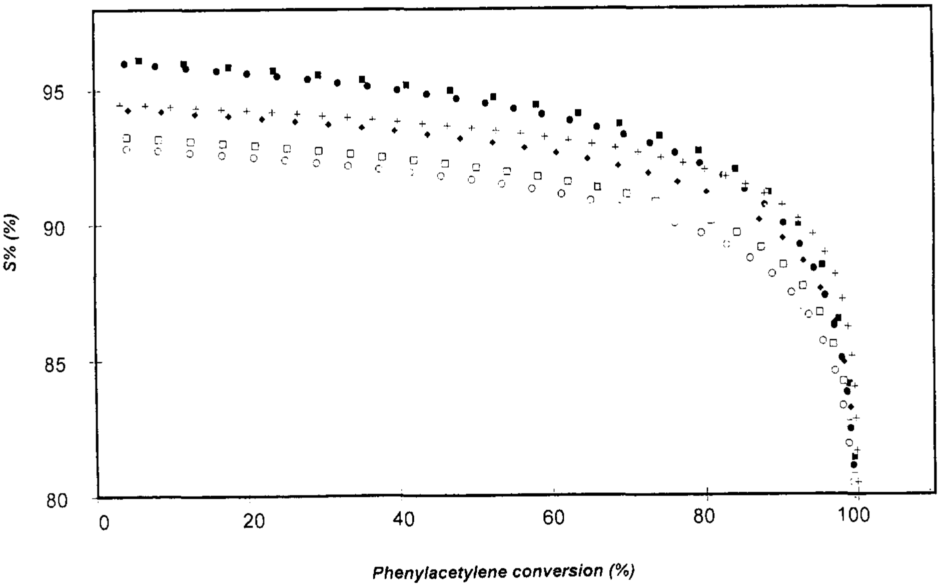


Fig. 5. Dependence of selectivity ($S\%$) on phenylacetylene conversion (%). Catalysts: $W_7$ ( + ); $W_6$ (●); $W_3$ (○); $W_2$ (♦); $U_1$ (□); $W_0$ (■).

lacetylene $Q_3$ is practically constant (ca. 2), thus indicating that the catalyst surface available in the two cases is different. Addition of phenylacetylene to the reaction mixture, when the first phenylacetylene has been consumed, does not produce changes in its hydrogenation rate, suggesting the occurrence of a very fast poisoning of the catalysts as consequence of the high value of the adsorption constant of phenylacetylene and the low value of $k_2$. The formation of polymeric species or of other species difficult to hydrogenate produces a flattening effect consequent to the coverage of active sites when phenylacetylene is hydrogenated. The enhanced electron density on the metal can be important in maintaining good activity at high metal dispersion.

Selectivity also appears higher than that shown by other conventional palladium catalysts, particularly at very high conversion, i.e. at the conditions usually employed in industrial processes (Fig. 5).

The flattening effect, consequent to the strong adsorption of phenylacetylene, reduces the active sites for the contemporaneous hydrogenation of styrene and generate, independently from metal dispersion, a constant and high selectivity up to unusually large phenylacetylene conversion.

## 4. Conclusions

Comparison of these Pd/pumice catalysts with other supported Pd catalysts shows a higher activity but, more interesting, the possibility of using Pd/pumice also at high dispersions. The decrease in activity of pumice supported Pd catalysts in the hydrogenation of alkenes improve the selectivity to styrene up to large phenylacetylene conversions.

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