

Palladium catalysts supported on oligomeric aramides in the liquid-phase hydrogenation of phenylacetylene

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Abstract

The catalytic behaviour of palladium supported on oligomeric aramides has been investigated in the liquid phase selective hydrogenation of phenylacetylene to styrene, by comparison with conventional Pd-supported systems, such as Pd/carbon, Pd/Al₂O₃ and Pd/SiO₂. The influences of the reduction temperature and metal loading on the activity/selectivity behaviour of the title reaction are explained in terms of different reducibility patterns of the catalysts, as well as in the light of a peculiar support effect of the organic matrix on Pd particles.

Keywords: Palladium catalysts; Organic matrices; Aromatic oligoamides; Phenylacetylene hydrogenation; Metal dispersion; Turnover frequency

1. Introduction

The selective hydrogenation of alkynes to alkenes has fundamental importance in the fine chemicals production and industrial polymerization processes. Although Pd catalysts supported on conventional carriers (i.e., alumina, silica, carbon, etc.) exhibit a satisfactory performance in the above reactions [1–3], a remarkable research interest focus up on the development of more selective catalysts. Moreover, the factors controlling the catalytic behaviour of selective hydrogenation catalysts as well as the role of the various surface adsorbed C-containing species in the reaction pathways are still under debate. Generally, thermodynamic effects,

specificity of the interaction of different catalytic sites with carbon–carbon multiple bonds and structure properties of the catalysts have been invoked to explain the activity-selectivity pattern in selective hydrogenation reactions [4–6]. In fact, it was ascertained that the electronic and/or morphological properties of metal particles affect the selectivity pattern of Pd catalysts in the hydrogenation of acetylene compounds driving to different extents the occurrence of two parallel reaction surface paths which lead to the formation of ethane and ethene as intermediate [7]. Since small metal particles strongly adsorb acetylene compounds, highly dispersed catalysts usually exhibit a lower activity along with a higher selectivity to partial hydrogenation products [3,6–9]. On this account, various methods for tuning the morphological and/or electronic properties of the Pd-based catalysts

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by allowing palladium with Cu, Pt, Pb [6,10–12] or by selectively ‘poisoning’ active Pd sites with CO [8,11] or ammonia [13] have been successfully proposed in order to improve their selectivity. Besides, it has been found that the support too plays an important role in determining the activity-selectivity pattern of Pd catalysts [1,4,6,13,14]. Namely, taking into account that high surface area carriers generally cause deactivation by carbon deposition, then affecting the selectivity during time on stream [1,4,6,13], low specific surface area supports ensure immediately the steady-state catalytic performance and result the most appropriate ones [1,6,14]. Recently, Pd catalysts on low surface area pumice have been effectively tested in partial hydrogenation reactions [15,16]: no effects of metal dispersion (14–65%) were found on the above systems, neither in terms of specific activity nor of selectivity in the liquid-phase phenylacetylene hydrogenation [16].

A peculiar method to improve the reactivity and/or the selectivity of the catalytically active species is to ‘immobilize’ transition metal derivatives on organic matrices. In an attempt to overcome the limitations related to the known chemical, mechanical and thermal properties of organic matrices, we made to interact some palladium derivatives with the existing chain terminal groups of the *oligo-p-phenylene-terephthalamide* (OPTA) obtaining a system with unique catalytic properties [17,18]. In fact, such ‘heterogenized’ systems were successfully tested in some model reactions such as hydrogenation [19] and oxidation [20] of carbon–carbon and carbon–oxygen multiple bonds, achieving high activity and specificity with respect to conventional catalytic systems. A TPR investigation of PdCl₂ catalysts supported on oligomeric amides [21] provided evidence of the ‘unusual’ *strong metal–support interaction* which markedly depresses the reducibility of Pd²⁺ in such systems.

This paper is aimed to provide insights into the catalytic behaviour of Pd-derivatives supported on oligomeric aramides in the liquid

phase hydrogenation of phenylacetylene to styrene by a comparative study with conventional Pd-supported catalysts (i.e., Pd/Al₂O₃, Pd/SiO₂, Pd/C).

2. Experimental

2.1. Catalysts

Palladium was added to the OPTA support [20] by wet impregnation for 6 h with a water:acetic acid (9:1) solution of PdCl₂ in the appropriate quantities for obtaining catalysts of different metal contents. Pd/Al₂O₃ and Pd/SiO₂ systems were prepared by a wet impregnation of γ -Al₂O₃ (Akzo Product, cod. 000-1.5E E) or SiO₂ (Akzo product, cod. Si 4-5P) supports with a hydrochloric acid solution of PdCl₂. After impregnation the latter samples were dried at 110°C, calcined at 400°C for 6 h in air and then reduced at 400 and 800°C, respectively, for 1 h in flowing H₂. Pd/C catalysts (Chimet Product, Italy) were commercial products.

The list of investigated samples together with their main physico-chemical properties are reported in Table 1.

2.2. Metal dispersion (*D*, %)

Metal dispersion of Pd catalysts were determined by performing H₂/O₂ titration tests in pulse mode using Ar as carrier gas flowing at 30 STP cm³ min⁻¹. In order to avoid formation of bulk Pd hydrides, H₂ uptake measurements were carried out at 75°C, while the titration of adsorbed hydrogen was performed at 25°C. Several H₂/O₂ titration cycles (3–5) were run according to the above procedure until constant H₂/O₂ uptake values were attained [22]. Titration stoichiometries of O₂:Pd_s = 4:3 and H₂:Pd_s = 2:3 were used for the calculation of the number of surface Pd atoms (Pd_s). Before measurements, dried catalyst samples were reduced in situ for 1 h in H₂ flow, at *T* ranging between 70 and 300°C.

Table 1
Physico-chemical properties of the catalysts

Catalyst	T_{red} (°C)	α^a (%)	Pd_s^b ($\mu\text{g atoms/g}_{\text{cat}}$)	MSA ^c ($\text{m}^2_{\text{Pd}}/\text{g}_{\text{cat}}$)	D^d (%)	d_s^e (Å)
1%Pd/C	70/130	100	16.8	0.80	18.0	63
5%Pd/C	70/130	100	114.0	5.40	24.3	47
10%Pd/C	70/130	100	226.0	10.70	24.0	47
0.3%Pd/ γ -Al ₂ O ₃	130	100	9.3	0.44	33.0	35
0.05%Pd/SiO ₂	130	100	0.2	0.01	4.0	270
0.2%Pd/OPTA	70	n.d.	0.13	0.01	—	—
1%Pd/OPTA	70	10.0	3.5	0.17	37.5	30
2%Pd/OPTA	70	14.5	6.9	0.33	25.3	45
6%Pd/OPTA	70	32.0	19.1	0.92	11.5	100
0.2%Pd/OPTA	130	8.0	0.85	0.04	56.5	20
1%Pd/OPTA	130	27.0	8.6	0.40	33.9	34
2%Pd/OPTA	130	45.0	12.5	0.60	14.8	77
6%Pd/OPTA	130	73.5	36.8	1.75	8.9	128

^a α = degree of reduction of Pd²⁺, calculated by TPR measurements.

^b Pd_s = surface Pd atoms.

^c MSA = Pd_s × 47.425 m²/g_{Pd}.

^d D (metal dispersion, %) = Pd_s/Pd.

^e d_s (surface mean particle size, Å) = 1140/ D (%).

2.3. Catalytic activity measurements

Liquid-phase hydrogenation tests were carried out in a 250 cm³ jacketed pyrex flask. The required amount of distilled solvent (75 cm³, ethanol) was added to the catalyst under a flow of hydrogen at 70°. After 45 min the system was cooled to 5° and the distilled phenylacetylene (0.5 cm³ in 5 cm³ of ethanol) was added by a dropping funnel. The activity data were obtained by analysing microsamples withdrawn from the reaction mixture and introduced in a gas-chromatograph (Fractovap 4160, C. Erba) equipped with a Supelco SPB-1 capillary column (30 m, 0.25 mm i.d.) operating at 333 K.

3. Results and discussion

Typical results of phenylacetylene hydrogenation over 2% PdCl₂/OPTA reduced at 70°C are reported in Fig. 1. Under the adopted experimental conditions, styrene and ethylbenzene were the only products detected.

Results of Fig. 1 also show that the hydrogenation reaction of phenylacetylene is zero order with respect to the substrate, as also con-

firmed by runs carried out at different substrate concentrations. Furthermore, the trend of reaction rate with the partial pressure of H₂, shown in Fig. 2, indicates a reaction order close to one with respect to P_{H_2} .

The influence of Pd loading of Pd/OPTA (0.2–6 wt% Pd) and Pd/C (1–10 wt% Pd) catalysts, reduced at 70 and 130°C, on the apparent kinetic constant (k_{app} , mol_{C₈H₆} s⁻¹ g_{Pd}⁻¹) in phenylacetylene hydrogenation at 5°C is shown in Fig. 3. It is evident that the k_{app} value of Pd/C catalysts is not affected by the reduction temperature (T_{red}) while it increases with the Pd loading according to a straight-line relationship from ca. 8 to 14 mol_{C₈H₆} s⁻¹ g_{Pd}⁻¹. By contrast, a rise in the reduction temperature from 70 to 130°C causes a significant increase of activity in different Pd/OPTA catalysts. Namely, for $T_{\text{red}} = 70^\circ\text{C}$ the k_{app} increases of ca. four times going from 0.2 to 2% Pd/OPTA catalysts, thereafter it decreases at higher loading levelling off to a value of ca. 4.5×10^{-4} mol_{C₈H₆} s⁻¹ g_{Pd}⁻¹. Meanwhile, the trend of k_{app} with metal loading is featureless for $T_{\text{red}} = 130^\circ\text{C}$.

The selectivity to styrene ($S_{\text{C}_8\text{H}_8}$, % = mol styrene/(mol styrene + mol ethylbenzene) ×

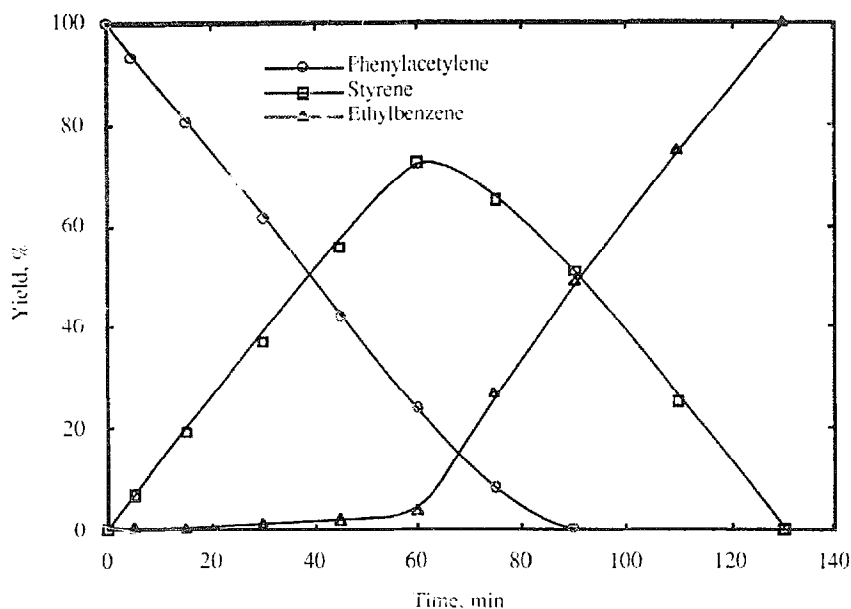


Fig. 1. Selective liquid-phase hydrogenation of phenylacetylene over 2% PdCl₂/OPTA, reduced at 70°C.

100) as a function of phenylacetylene conversion for various catalysts is compared in Fig. 4. It decreases very slowly with conversion and only after almost all phenylacetylene has reacted ($\approx 95\%$), styrene is further hydrogenated to ethylbenzene. However, these data show that the nature of the support does not cause remarkable differences in the selectivity pattern of Pd

based catalysts in the reaction investigated. In particular, apart from minor differences in the trends, it is noticeable that for all Pd/C systems the selectivity falls from 100 to ca. 90%, while conversion rises from 10 to ca. 100. For low loaded ($\leq 2\%$) Pd/OPTA catalysts reduced at 70°C the selectivity tends to a limit value of 94–96%, whilst for the same systems reduced at

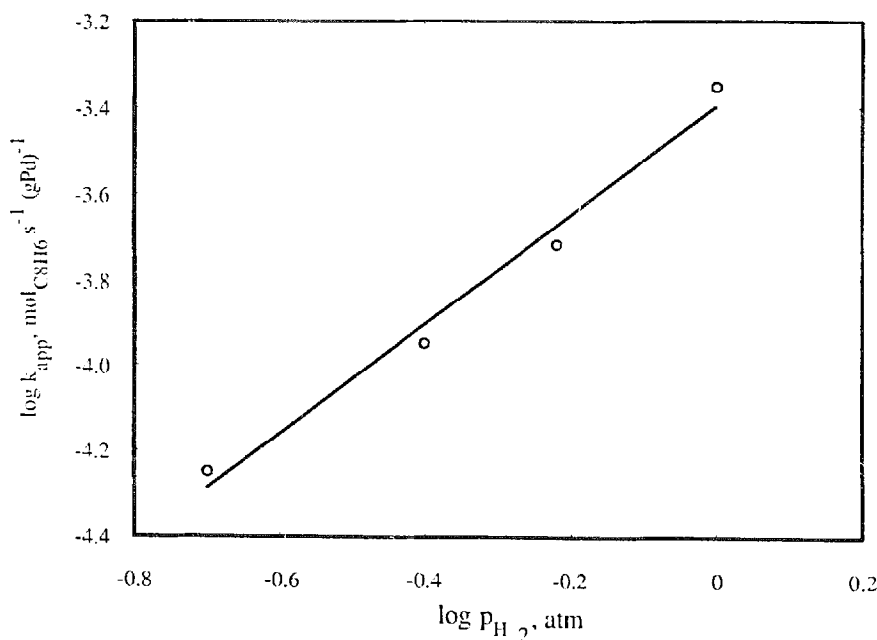


Fig. 2. Effect of H₂ partial pressure on phenylacetylene hydrogenation with 1% PdCl₂/OPTA catalyst, reduced at 70°C.

130°C and for the 6% Pd/OPTA catalyst reduced both at 70 and 130°C the lower selectivity values range between 92 and 88%.

Then, in order to shed light into the peculiar catalytic properties of Pd/OPTA catalysts, characterization data reported in Table 1 must be taken into account. First, according to our previous TPR findings [21], indicating a strong metal–support interaction which inhibits the reduction of oligoaramides-supported Pd catalysts at lower temperature, the above data show that the fraction of reduced Pd increases with both loading and reduction temperature (T_{red}) though in no case the overall reduction of the supported Pd is attained. The positive influence of the loading and reduction temperature on the degree of reduced Pd leads as a general rule to an increase of about two orders of magnitude in the amount of exposed Pd atoms on such catalysts when the loading increases from 0.2 to 6 wt%. However, to the positive effects of loading and T_{red} on the amount of exposed Pd atoms, it generally corresponds a negative influence of such parameters on the metal dispersion (Table

1). In particular, on varying the loading and T_{red} , D values ranging between 9 and ca. 60% are observed for Pd/OPTA catalysts (Table 1). In contrast with the singular behaviour of such heterogenized catalysts, conventional Pd/C, Pd/ γ -Al₂O₃ and Pd/SiO₂ catalysts exhibit a quite regular pattern in that an overall reduction of Pd²⁺ is observed at $T \geq 70^\circ\text{C}$ (TPR results not reported here). The metal dispersion of Pd/C catalysts remains practically unchanged (18–24%) on varying the Pd loading between 1 and 10 wt%, while the metal dispersion results to be 33 and 4% for 0.3% Pd/ γ -Al₂O₃ and 0.05% Pd/SiO₂ catalysts, respectively.

Therefore, in order to find out whether the metal dispersion and/or the nature of the support affect the specific activity of supported Pd, the values of turnover frequency (TOF, s⁻¹) for all the studied samples are compared in Table 2. These data essentially indicate that the TOF (0.5 s⁻¹) keeps practically unchanged for differently loaded (1–10 wt%) Pd/C catalysts, resulting equal to that of 0.05% Pd/SiO₂, while the TOF value is quite lower for the 0.3% Pd/ γ -Al₂O₃

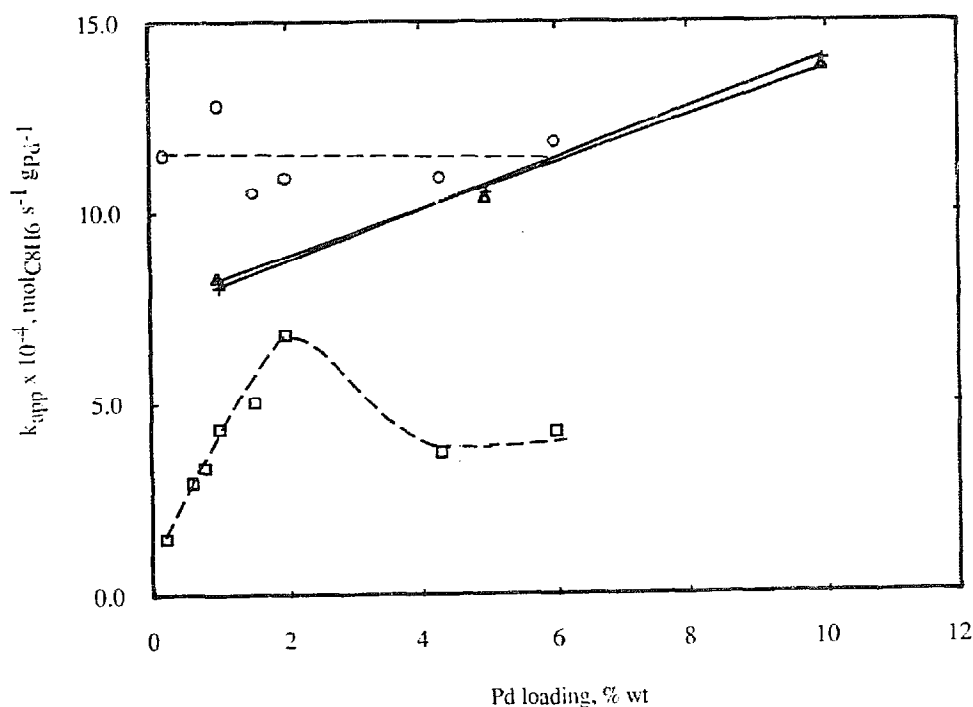


Fig. 3. Influence of the Pd loading on the apparent kinetic constant of Pd/C and PdCl₂/OPTA catalysts, reduced at 70 and 130°C: + Pd/C 70°C. Δ Pd/C 130°C. □ PdCl₂/OPTA 70°C. ○ PdCl₂/OPTA 130°C.

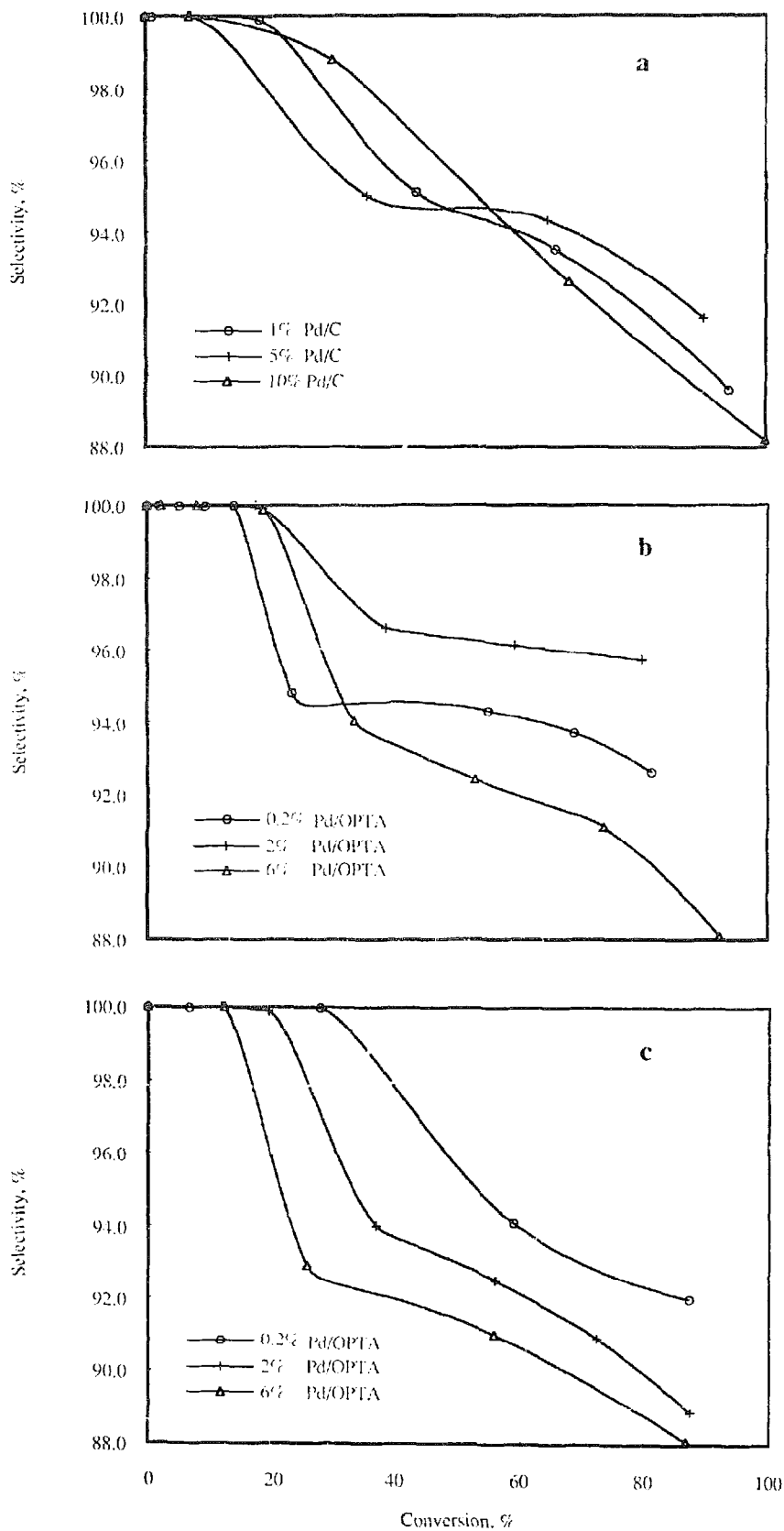
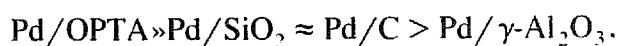


Fig. 4. Selectivity to styrene as a function of phenylacetylene conversion for differently loaded Pd/C catalysts (a) and PdCl₂/OPTA catalysts, reduced at 70°C (b) and 130°C (c).

Table 2
Kinetic parameters in liquid phase Ph–C≡C hydrogenation

Catalyst	T_{red} (°C)	k_{app} ($10^4 \text{ mol}_{\text{C}_6\text{H}_5} / \text{s}^{-1} \text{ g}_{\text{Pd}}$)	D (%)	TOF (s^{-1})
0.2%Pd/OPTA	70	1.5	—	2.3
1%Pd/OPTA	70	4.3	37.5	1.3
2%Pd/OPTA	70	6.8	25.3	2.0
6%Pd/OPTA	70	4.2	11.5	1.3
0.2%Pd/OPTA	130	11.5	56.5	2.7
1%Pd/OPTA	130	12.8	33.9	1.5
2%Pd/OPTA	130	10.9	14.8	1.8
6%Pd/OPTA	130	11.8	8.9	1.9
1%Pd/C	70/130	8.0	18.0	0.5
5%Pd/C	70/130	10.5	24.3	0.5
10%Pd/C	70/130	14.0	24.0	0.6
0.3%Pd/ γ -Al ₂ O ₃	130	6.0	33.0	0.2
0.05%Pd/SiO ₂	130	2.0	4.0	0.5

system. For the series of Pd/OPTA catalyst no significant trend of TOF values (1.3 – 2.7 s^{-1}) with the metal dispersion is found, even when D ranges between 9 and 60% (Table 2). On this account the trends in k_{app} (Fig. 3) with Pd loading are a consequence of the changes produced by such parameter on the reducibility [21] and metal dispersion (Table 1). The fact that TOF is insensitive to Pd dispersion is in good agreement with the findings of Duca et al. [16] pointing out to a *structure insensitive* character of the title reaction on Pd/pumice catalysts, with metal dispersion ranging from 0.65 to 0.14. Such a catalytic pattern of Pd/pumice catalysts, was related to the peculiar electron-donor character of the support which confers enhanced metallic features also to small Pd particles [16]. Then, considering that the average TOF value of Pd/OPTA catalysts is 2 ± 0.7 , on the whole the latter catalysts result to be much more reactive ($0.2 < \text{TOF} < 0.5 \text{ s}^{-1}$), at least at the same level of selectivity, than conventional systems. Indeed, the reactivity scale, drawn on the basis of TOF values reported in Table 2:



clearly indicates the occurrence of a support effect on the reactivity of Pd in the liquid-phase phenylacetylene hydrogenation. Such an effect,

as well as the structure insensitive character of the above reaction on Pd/OPTA catalysts, can be ascribed to an electron enrichment of Pd particles induced by the OPTA support similar to that observed for Pd/pumice catalysts [16]. Indeed, the presence of either unsaturated aromatic rings as well as of $-\text{NH}_2$ groups in the OPTA structure [17–19] should induce an electron transfer to the metal surface [13] which favours a rapid desorption of styrene molecules and consequently ensures high activity and selectivity. By contrast, SiO₂, C and to the largest extent γ -Al₂O₃ supports, could exert an opposite electron acceptor effect, which results in a stronger metal–support interaction and in turn depresses the specific activity of Pd particles.

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