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Palladium on pumice: new catalysts for the stereoselective semihydrogenation of alkynes to (Z)-alkenes

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Abstract—High selectivities (93-99%) and excellent stereoselectivities (>99%) in the semihydrogenation of C–C triple bonds were achieved using palladium on pumice with a metal loading of 0.5, 1.5 or 3.0% wt as catalyst. The reactions were carried out in ethanol or tetrahydrofuran with only 2.5% of ethylenediamine allowing a self-terminating semihydrogenation independently on the C–C triple bond. © 2001 Elsevier Science Ltd. All rights reserved.

Catalytic semihydrogenation of alkynes to (Z)-alkenes constitutes a very important process in organic chemistry.^{1,2} Indeed, the production of highly pure (Z)-alkenes is often a key-step during the synthesis of important substances such as pheromones³ or other natural products.⁴ Among the catalysts reported as being efficient in performing selective semihydrogenations of alkynes, the most common is the well-known Lindlar palladium⁵ (used in the presence of quinoline) and P-2 nickel⁶ (used in the presence of ethylenediamine). In addition to these, new catalysts have been developed such as palladium foil,7 interlamellar montmorillonite-diphenylphosphinepalladium(II) complexes,⁸ Pdc⁹ (used in the presence of quinoline) and, as recently reported, Pd or nickel boride on borohydride exchange resin¹⁰ and Pd colloidal catalysts.¹¹ In a previous communication¹² we have reported several examples of efficient semihydrogenation of the C-C triple bond using palladium on pumice with a metal loading of 3.0% wt as catalyst. Here we report new examples of the semihydrogenation of the C–C triple bond using other two new Pd/pumice catalysts with a different metal loading (1.5, 0.5%).¹³

Preliminary investigations were carried out with compound 1a, by using absolute ethanol or tetrahydrofuran as solvent and checking how the other parameters such as metal loading, hydrogen flow, molar ratio substrate/ Pd, stirring rate, nitrogen base (pyridine, triethylamine, or ethylenediamine in 2.5-20% with respect to the substrate) may influence the selectivity (Scheme 1). The best results, without base, were obtained when we used a hydrogen flow of 40 N mL/min,¹⁴ a stirring rate of 1300 rpm¹⁵ and a molar ratio substrate/Pd equal to 110.¹⁶ However, these results were not satisfactory because the selectivity¹⁷ was not excellent (ca. 80%), whereas the stereoselectivity was found to be high (93-96%). In EtOH good results were obtained with 10% of ethylenediamine (eda) using Pd/pumice 0.5%(Table 1, entry 1).



Scheme 1.

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Entry	Cat. (% Pd) ^a	Base (%)	Solvent	t (min)	2 (%)	3 (%)	4 (%)
1	0.5	Eda 10	EtOH	12	96	0	4
2	1.5	Eda 10	EtOH	200	96	0	4
3	3.0	Eda 10	EtOH	200	0	0	0
4	0.5	Eda 10	THF	80	99	0	1
5	0.5	Eda 2.5	THF	60	99	0	1
6	0.5	Ру 2.5	THF	15	62	1	37

Table 1. Reaction times and selectivities for the hydrogenation of 1a with Pd/pumice

^a (% Pd) refers to different metal loading.

Pd/pumice (3%) did not catalyze the reaction (Table 1, entry 3). The different behavior of the three catalysts (Table 1, entries 1–3) is, in our opinion, ascribed to the different dispersion of the metal particles on the surface. Palladium/pumice with the highest metal content (3.0%), shows a very low dispersion $(Dx = 8\%)^{18}$ as a consequence of the low specific surface area $(5 \text{ m}^2/\text{g})^{12}$ of pumice that determines the growth of large metal particles, producing a few neighboring catalytic sites. Using the latter catalyst the nitrogen base will cover all the catalytic sites blocking the adsorption of the alkyne. Palladium/pumice (1.5 and 0.5%) have a higher dispersion (25 and 40%, respectively)¹⁸ and so nitrogen base is not able to cover all the catalytic sites and competes only with the re-adsorption of the alkene, blocking or displacing it. In tetrahydrofuran excellent results were obtained when we added 10% ethylenediamine (Table 1, entry 4). The reaction was slower than those carried out in ethanol, probably because in the less polar solvent (THF) the nitrogen base competes more efficiently for the catalytic sites. In order to achieve high selectivity with shorter reaction times we added only 2.5% of base (Table 1, entry 5). We were delighted by the excellent results. It must be noted that hydrogenation reaction with Pd/pumice (0.5%) in tetrahydrofuran with 2.5% pyridine was not selective and it could not be stopped at the semihydrogenation stage (Table 1, entry 6). The different behavior between pyridine and ethylenediamine is probably due to the presence of two nitrogen atoms that interact more efficiently with the catalytic sites.

On the basis of these results we then carried out the hydrogenation reactions on substrate 1b-g (Table 2). Diphenylacetylene (1b) was selectively and stereoselectively hydrogenated in ethanol with 2.5% base (Table 2,

entry 1). With tetrahydrofuran as solvent the reaction was too slow. Hydrogenation of compound 1c was stopped at the semihydrogenation stage when we used Pd/pumice (1.5%) in tetrahydrofuran (Table 2, entry 2).

The addition of a larger amount of base did not improve the selectivity (Table 2, entry 3). Using the less active Pd/pumice (3.0%) with 2.5% ethylenediamine we also obtained a good selectivity (Table 2, entry 4). Compounds 1d-g were excellently hydrogenated with Pd/pumice (0.5%) in tetrahydrofuran with 2.5% base (Table 2, entries 5-8). The results obtained in the semihydrogenation of alkynes with Pd/pumice catalysts are comparable and in some cases better than those reported in the literature.^{7a,8,9,19} Moreover, they are quite interesting since by an appropriate choice of the metal dispersion in the catalyst, solvent and nitrogen base added, high selectivities (93-99%) and stereoselectivities (>99%) can be achieved. The best concentration of ethylenediamine is 2.5% for any substrate. When the substrate is less reactive, such as **1b**, the most dispersed metal catalyst, Pd/pumice (0.5%), in ethanol gives the best results. For slightly more reactive substrates change of the solvent is sufficient to give good selectivity (1a, 1d-g). When reactive substrate like 1c are used, the less active Pd/pumice (1.5 or 3.0%) catalysts in tetrahydrofuran are preferred to achieve good selectivity.

In contrast with several literature reports^{5,6,9} where the nitrogen base is used in large amounts, in the hydrogenation of C–C triple bonds on the Pd/pumice catalysts only a catalytic amount of base is necessary, allowing a self-terminating semihydrogenation. Finally Pd on pumice catalysts, differently from other catalysts, ^{8,9} do not need any reduction pretreatment, due to their stability to oxidation.

Table 2. Reaction times and selectivities for the hydrogenation of 1b-g with Pd/pumice

Entry		Cat. (%Pd) ^a	Solvent	Base (eda%)	t (min)	2 (%)	3 (%)	4 (%)
1	1b	0.5	EtOH	2.5	90	93	0	7
2	1c	1.5	THF	2.5	30	94	0	6
3	1c	1.5	THF	10	30	93	1	6
4	1c	3.0	THF	2.5	50	93	0	7
5	1d	0.5	THF	2.5	100	98	0	2
6	1e	0.5	THF	2.5	50	99	0	1
7	1f	0.5	THF	2.5	30	98	0	2
8	1g	0.5	THF	2.5	30	98	0	2

^a (% Pd) refers to different metal loading.

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- 13. The synthesis of pumice supported palladium catalysts was performed following Yermakov's method.²⁰ In a typical experiment, a pumice suspension in pentane was

treated at -10° C with a pentane solution of $[Pd(C_3H_5)_2]$ of known concentration, under nitrogen. After 30 min the suspension turned yellow-brown as a result of the anchoring reaction. The mixture was then stirred at 0°C for 1 h. Reduction to metallic Pd was obtained using hydrogen (10%)/argon at low temperature (from -20 to 0°C within 30 min, then from 0 to 25°C within 60 min, then 25°C for 120 min). Compounds 1 (0.40 mmol) in absolute ethanol or tetrahydrofuran (20 mL) were stirred with Pd/pumice catalyst (molar ratio substrate/Pd = 110) for the time indicated in the tables. Hydrogenation reactions were performed in a three-necked glass reactor with jacket. The reactor was connected to a line operating at a constant atmospheric pressure of H₂ by using the first two necks. The last neck, closed by a silicone septum, allowed withdrawing of samples for GC-MS analysis. The suspension was magnetically stirred. All the products were identified and quantified by comparison with known samples.

- 14. We performed hydrogenations using an hydrogen flow in the range 40-200 N mL/min.
- 15. At 1300 rpm the reactions were found to be under kinetic control.
- 16. We also performed the hydrogenation with a molar ratio substrate/Pd equal to 55 or 220, in the former case the reactions cannot be stopped at the semihydrogenation stage while in the latter case the reactions were very slow.
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- 18. The metal dispersion (Dx%), i.e. the percentage of metallic atoms exposed, was calculated by means of the mean crystallite sizes D (Å) of Pd estimated by using the Scherrer equation; (Klug, H. P.; Alexander, L. E. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials; Wiley: New York, 1954).
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