

On the mechanism of Pd-catalyzed low pressure gas–solid hydrogenation

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Abstract

A palladium-catalyzed, low pressure hydrogenation of phenylalkynyl derivatives in a gas–solid reaction in the absence of a solvent was studied. The distinctive initiation step was found to be related to the catalyst activation stage and was directly affected by the treatment of the metallic catalyst: deoxygenating of the catalyst helped to diminish the initiation step, while partial poisoning of the catalyst resulted in extending the slower initial step.

In the following propagation step, triple bonds are being hydrogenated to give initially a phenylalkenyl and phenylalkanyl products mixture.

The chemoselectivity of the hydrogenation depends both on hydrogen pressure and on the mode of preparation of the reacting phenylalkynyl/catalyst powder.

A mechanism, which is based on hydrogen mobility in the phenylalkynyl lattice, is suggested and a direct measurement of hydrogen mobility in the lattice was demonstrated.

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1. Introduction

Alkynes hydrogenation over Pd supported catalysts is well established [1] both in liquid and in gas phase hydrogenations.

The acetylene group is readily hydrogenated to form a saturated carbon–carbon bond. Palladium catalysts have been intensely used for triple bond hydrogenation and the effects of metal dispersion, catalyst surface area, carbon deposits, etc., have been reported [2].

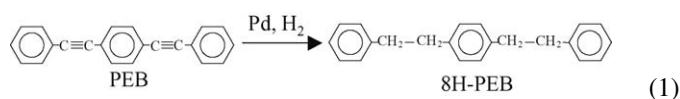
Catalyzed hydrogenations of alkynes in the solid phase have been scarcely studied and reported.

However, there is an increasing interest in solid-phase chemistry as a result of its potential applications in high technology industries [3].

Since there is also some confusion in using the term solid-state or gas–solid catalyzed reaction, we have to distinguish between: (a) gas–solid hydrogenation where only the catalyst is in the solid phase and both the alkyne and hydrogen are in

the gas phase [4] and (b) gas–solid hydrogenation where both alkyne substrate and the catalyst are in solid phase and only the hydrogen is in the gas phase [5].

The catalyzed reaction of hydrogen gas with phenylalkynyl solid substrates deposited on a palladium catalyst, in the absence of a solvent, is shown to proceed giving high yields of saturated products [6]. A relatively fast reaction takes place at ambient temperature and low hydrogen pressure [6]. Even with a molar ratio of over 50:1 of the metal catalyst to 1,4-di(phenylethynyl)benzene (PEB) the reaction proceeds to give almost quantitative yield of the saturated product (Eq. (1)).



Such a reaction of H₂ gas with solids is being used commercially as a means for trapping hydrogen, produced by batteries, in sealed cavities of devices like flash lights and cameras [7].

The mechanism of transition metal initiated reaction between hydrogen gas and an organic substrate involves a preliminary step of H₂ activation by the catalyst followed by a hydrogen transfer to an adjacent unsaturated organic molecule.

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The lack of molecular mobility, in the solid phase, would prevent any subsequent hydrogenation of molecules which are not accessible to the metal. However, the existence of a catalytic reaction in these systems points to a mechanism in which a hydrogen transfer in the solid organic lattice took place [8].

The mechanism of this reaction could be easily understood by adopting the idea of the existence of active hydrogen mobility throughout the aromatic hydrocarbons matrix [8].

The concept of a mobile hydrogen species is well-known as hydrogen spillover, which is usually taking place in metals, oxides and carbon matrix [9].

Oxygen functional groups have also shown to play a role in H spillover on activated carbon by stabilizing the H species [10].

However, recent study on hydrogen spillover on carbon gave no indication that hydroxyl groups are necessary to accept spillover hydrogen [11].

The current study on the catalytic hydrogenation in the solid state shed more light on the initial activation step and on the mobility of hydrogen in the unsaturated substrate lattice which take place along the propagation step.

2. Experimental

2.1. Methods and materials

1,4-Diphenylethynylbenzene (PEB) was synthesized according to a known procedure [6,8]. Commercially available Pd/C (5 wt.% of Pd) was used as a catalyst.

Mixing of PEB and catalyst (2:1 wt.%) was done either by milling the two solids in a ball milling machine, or by adding the powdered catalyst to a solution of PEB in tetrahydrofuran (THF), followed by low pressure THF evaporation [8]. THF of analytical grade (99.5%) was distilled over potassium metal right before its use, unless otherwise stated.

2.2. Instrumentation

The hydrogenation kinetics was determined by recording hydrogen pressure decrease during the reaction, using a computer controlled volumetric system with 0.01–100 Torr pressure transducers as previously described [6,8].

Hydrogenation products were analyzed by GC (Varian GC/MS model Saturn 2100D) using CP-Sil5 CB LOW BLEED/MS 60 m column. Triphenyl phosphine oxide was used as internal standard for quantitative analysis.

Ball milling of powders by a planetary milling machine (Fritsch's pulverisette 6) was performed using an agate vessel and balls (600 rpm, 25 min, powder to the balls weight ratio 0.25).

3. Results and discussion

A reaction mechanism was proposed [6,8], based on a supramolecular phenomena of a hydrogen transfer in a well organized PEB lattice, in which strong π -interactions exist between the aromatic molecules.

In the study of the hydrogenation kinetics of PEB at low hydrogen pressures, two diverse steps were detected: a slow primary activation step followed by a faster propagation process.

When hydrogen gas was introduced into the reaction vessel in several consecutive portions, each containing 10% of the theoretical hydrogen capacity of the PEB sample, the first portion was consumed significantly slower than the following one. The following hydrogen loadings reacted faster, however, a gradual decrease in the hydrogenation rate was found as the reaction proceeds toward its conclusion [6,8].

3.1. Kinetic study at the initiation step

There are several indications that the initial slower step could be related to the activation of the transition metal catalyst.

The duration of the initial step was found to be dependent on preparation method and on pretreatment of the catalyst: when a 5% Pd/C catalyst was exposed to hydrogen prior to the preparation of the solid PEB/catalyst mixture, almost no initiation step was detected, probably as a result of removal of oxide layer from the metallic catalyst particles (Fig. 1, open squares). While the use of the catalyst without hydrogen pretreatment resulted in somewhat reduced initial rate and a delayed propagation (Fig. 1, full circles).

Preparation the catalyst/PEB mixture by THF vaporization, resulted in extending the initiation step (Fig. 1, open circles), most likely as a result of further oxidation of the catalyst surface caused by residual peroxides in the THF.

Finally, exposure of the solid PEB/catalyst mixture prepared by THF evaporation to carbon monoxide gas prior to the introduction of hydrogen induces a significant extension of the initial activation step (Fig. 1, full squares); the competing poisoning by carbon monoxide of solid phase catalytic hydrogenation is well-known, and a 10-fold drop in hydrogenation rate was previously demonstrated [6].

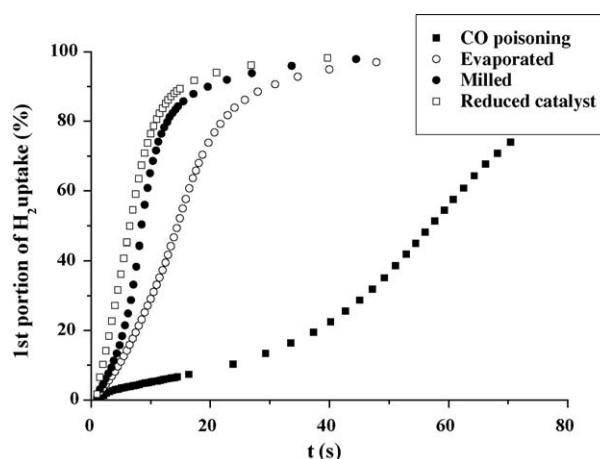
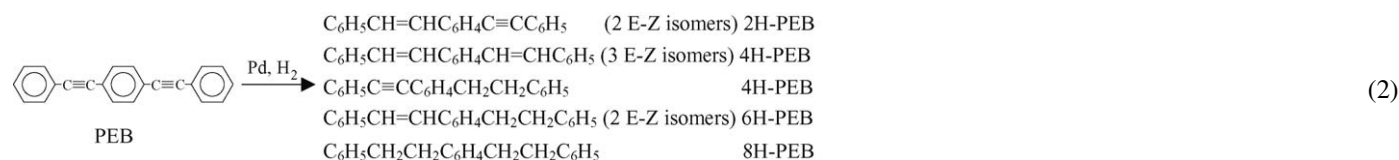


Fig. 1. Hydrogen uptake at the initiation step as a function of time for different solid samples: (1) catalyst pretreated with hydrogen (open squares), (2) sample prepared by milling (full circles), (3) sample prepared by vaporization of THF (open circles) and (4) sample pretreated (poisoned) by carbon monoxide (full squares).

These results indicate that the initial slower initiation step is most probably related to the activation of the metallic catalyst.

3.2. Hydrogen mobility during the propagation step

An incomplete hydrogenation of PEB produces a variety of partially hydrogenated products (Eq. (2)). In addition to the fully hydrogenated PEB, to which eight hydrogen atoms were added (8H-PEB), partially saturated products were separated and analyzed by GC–MS (Fig. 2).



Eight of the nine possible intermediates shown in Eq. (2) were separated by GC–MS (Fig. 2). The composition of the products mixture was found to be affected by the initial partial pressure of the reacting hydrogen (Fig. 2a–c).

Hydrogenations of PEB samples to 10% of their theoretical hydrogen capacity were performed under various hydrogen initial pressures: reacting PEB under hydrogen with an initial pressure of 150 Torr, gave 8H-PEB as the main product (Fig. 2c); performing hydrogenation with a reduced hydrogen partial pressure (12 Torr) resulted in a products mixture containing 8H-PEB and 4H-PEB at approximately 1:1 ratio (Fig. 2b); further drop

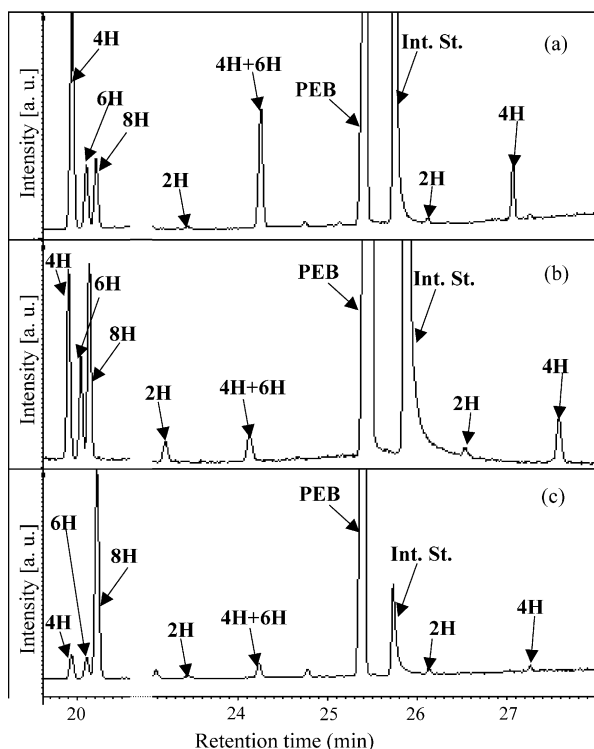


Fig. 2. GC–MS chromatograms of products mixtures obtained by hydrogenation of PEB (to 10% of theoretical capacity) under various initial hydrogen pressures: (a) 0.1 Torr, (b) 12 Torr and (c) 150 Torr. The labels 2H, 4H, 6H and 8H represent various isomers of 2H-PEB, 4H-PEB, 6H-PEB and 8H-PEB accordingly. The peak at 24.3 min consists of both 4H and 6H.

of H₂ partial pressure to about 0.1 Torr resulted in 4H-PEB as the main product (Fig. 2a).

The changes in the products' distribution, at the same extent of reduction, reflect modifications in the reduction kinetics: when a higher hydrogen pressure was applied, PEB molecules adjacent to catalytic sites were fully hydrogenated to give mainly 8H-PEB. Such fast hydrogenation process resulted therefore in fully saturated lattice around the catalyst sites where the process of hydrogen mobility is retarded.

Hydrogenation at lower hydrogen pressures and lower uptake

rates, presumably allow also a slow process of hydrogen mobility, which enable the formation of partially saturated 6H-PEB and 4H-PEB. The combination of a slow uptake and slow spillover processes allow also hydrogen transport to less accessible PEB molecules.

The percent distribution of hydrogenated products as a function of hydrogen pressure is summarized in Table 1.

In order to further demonstrate the mechanism of hydrogen migration in the solid powder, a time-dependent study of the products distribution was performed by comparing the changes in products' distributions following a partial hydrogenation of PEB at 12 Torr: in this experiment, one half of the reduced sample was dissolved and analyzed by GC–MS immediately after the hydrogenation and a second half was dissolved and analyzed only 40 days later.

This experiment was performed three times, with three different hydrogenated samples: one sample was reduced up to 4% of its theoretical hydrogen capacity.

The second sample was hydrogenated similarly to 10% H-capacity and the third sample was hydrogenated up to 13% of its theoretical hydrogen capacity.

The results are summarized in Table 2, demonstrating that hydrogen migration occurred in the three solid samples, which were kept at room temperature for 40 days. The hydrogen migration resulted in a systematic decrease of the 8H-PEB abundance accompanied by an increase of the 4H-PEB concentration.

The results of these experiments confirm the trend of hydrogen migration in the organic lattice: hydrogen is transferred from the 8H-PEB or 6H and 6H-PEB to form 4H-PEB.

Table 1

Distribution of partially hydrogenated products formed at various initial hydrogen pressures for hydrogenation to 10% of theoretical capacity uptake

Fraction of	Hydrogen initial pressure (Torr)		
	0.1	12	150
2H-PEB (%)	–	1	–
4H-PEB (%)	71	40	22
6H-PEB (%)	22	20	5
8H-PEB (%)	7	39	73

Note: These values were calculated by summing the isomers' fractions for each of the hydrogenated products.

Table 2
Products distribution changes in time in partially hydrogenated PEB

Hydrogen content in partially reduced PEB sample	Hydrogenated product	Fraction of hydrogenated product (%)	
		1 Day following hydrogenation	40 Days following hydrogenation
4% of theoretical hydrogen capacity	8H-PEB	23	21
	6H-PEB	16	12
	4H-PEB	59	66
10% of theoretical hydrogen capacity	8H-PEB	40	35
	6H-PEB	20	19
	4H-PEB	39	45
13% of theoretical hydrogen capacity	8H-PEB	48	37
	6H-PEB	19	19
	4H-PEB	33	44

Note: Initial hydrogen pressure for all samples was 12 Torr.

As expected, the abundance of 8H-PEB is increasing with the amount of hydrogen consumed. Moreover, higher hydrogen mobility was found for the samples with higher percentage of 8H-PEB.

3.3. Kinetic profile of the propagation step: effect of the sample's method of preparation

During the propagation step of PEB hydrogenation a gradual decrease in the reaction rate could be observed.

Fig. 3 shows the transformation of the hydrogenation rate during the propagation. The reaction progress (on the x axis) is expressed in terms of percent saturation of PEB.

For a PEB/catalyst mixture, prepared by ball milling, the hydrogenation rate decreases almost in a linear slope throughout the reaction (Fig. 3, full circles).

However, the hydrogenation rate of material prepared by THF evaporation decreases sharply in the range of 30–50% of the PEB saturation (Fig. 3, open triangles).

The third curve in Fig. 3 describes the ratio of hydrogenation rates of these two samples (Fig. 3, full squares). This ratio emphasizes the fact that the sample prepared by milling is fairly reactive even behind 50% saturation range. While, the sam-

ple prepared by evaporation is reacting rather sluggishly at this range. The rates ratio curve also shows that the ball milled sample reacts up to about 50 times faster at this range.

A plausible explanation for the higher rate in the ball milled powder is the higher homogenization of the metal catalyst in the PEB powder.

When the catalyst is not perfectly homogenized there is a greater possibility for the existence of isolated “pockets” of pure PEB with low catalyst concentration. Such pockets will undergo a slow hydrogenated ion, only by a sluggish hydrogen migration process.

The slower hydrogenation process taking place with PEB/catalyst mixture prepared by solvent vaporization proceeds to 90% of hydrogen uptake capacity (Table 3); however, rates at higher conversions are extremely low.

Choosing ball milling as the preparation method also resulted in achieving the same degree of hydrogenation in a shorter reaction time (Table 3). For example, loading hydrogen to rise the hydrogenation level from 80 to 90% saturation, will take 4.4 h for a sample prepared by milling and 39.3 h for a sample prepared by THF vaporization.

3.4. Kinetic profile of the propagation step: effect of solvent impurities

When a non-distilled THF was used for the sample preparation the hydrogenation rate became considerably slower. Reaction rates were compared for two samples: a sample prepared with freshly distilled THF versus a sample prepared by a non-distilled THF (Table 4).

The difference in hydrogenations rates could be explained by the presence of peroxides in the non-distilled THF which slow down the rate by interaction with the hydrogen species.

3.5. Kinetics and products distribution

To further investigate the relation between hydrogenation kinetics and products distribution, the reaction was performed under low initial pressure (0.1 Torr) and stopped at low hydrogen uptake (3.1% of the theoretical capacity) with samples prepared either with freshly distilled THF or with non-distilled THF.

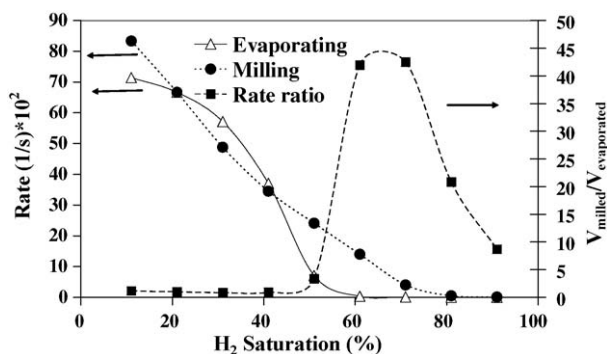


Fig. 3. Changes in hydrogenation rate for two different powder mixtures: (a) sample prepared by solvent vaporization (open triangle) and (b) sample prepared by ball milling (full circles). The curve describing the ratio of these rates (full squares) shows an enhancement of the reaction rate of the ball milled sample in the range 50–80% of hydrogen saturation.

Table 3

Times needed to complete 10% saturation intervals in a stepwise PEB hydrogenation: (a) for a ball milled sample (t_M) and (b) for a sample prepared by vaporization of predistilled THF (t_D)

	Fraction (%) of theoretical hydrogen capacity of solid sample					
	40–50	50–60	60–70	70–80	80–90	90–96
t_M (h)	0.07	0.1	0.2	0.8	4.4	16.0
t_D (h)	0.08	1.0	4.5	16.0	39.3	Not cont.

Notes: Initial hydrogen pressure at each step 150 Torr.

Table 4

Times needed to complete 10% saturation intervals in a stepwise PEB hydrogenation: (a) for a sample prepared with freshly distilled THF (t_D) and (b) for a sample prepared by a non-distilled THF (t_{ND})

	Fraction (%) of theoretical hydrogen capacity of sample				
	10–20	20–30	30–40	40–50	50–60
t_D (min)	0.8	0.7	0.7	1.5	7.0
t_{ND} (min)	5.8	10.0	15.5	25.2	35.0

Notes: Initial hydrogen pressure at each step was 150 Torr.

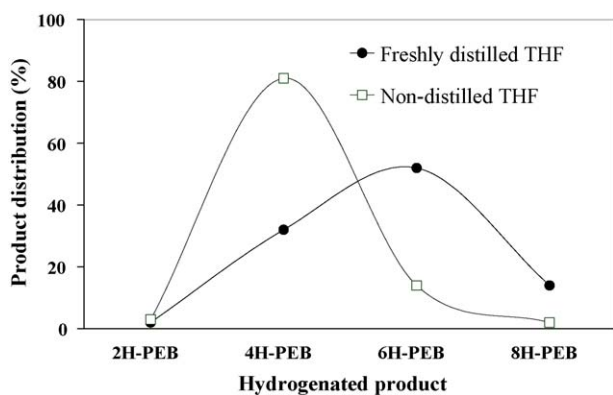


Fig. 4. Distribution of hydrogenated products following PEB hydrogenation to 3.1% of full capacity at 0.1 Torr of hydrogen pressure: (a) sample prepared with distilled THF (full circles) and (b) sample prepared with non-distilled THF (open squares).

As shown in Fig. 4, there is a tendency for formation of higher hydrogenated products (6H-PEB and 8H-PEB) in the case of the faster reaction (sample prepared with freshly distilled THF); whereas with the slower reaction kinetics (sample prepared with non-distilled THF) the main product is 4H-PEB.

This effect of reaction rate on the distribution of partially hydrogenated products is similar to the previously described results where various hydrogen initial pressures were studied (Table 1).

In the previously described experiments higher hydrogenated products were also obtained by using higher hydrogen pressures which, in turn, means higher reaction rates.

4. Conclusions

Low pressure catalyzed hydrogenation of the powders mixture of PEB and Pd/C involves two steps: a slow initial step which is related to the activation of the metallic catalyst, followed by a faster propagation step.

The propagation step is engaged with the mobility of hydrogen inside the reacting solid lattice.

Hydrogen reaction rate dictates both the reaction hydrogen mobility and the distribution of partially hydrogenated products.

Hydrogenation of two solid samples using the same quantity of hydrogen but with different rates results in different distribution of partially hydrogenated products: fast hydrogenation rate (e.g. due to higher hydrogen pressure) lead to product distribution with highly hydrogenated intermediates. While a slower hydrogenation rate will result in intermediates of lower hydrogen content.

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