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Unravelling the effect of Lewis acid properties of the support on the performance of palladium based catalyst in hydrogenation and hydrogenolysis reactions

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ABSTRACT

A catalyst, $Pd/B(OH)_3$, based on the cheap and environmentally friendly support, was synthesized by using the impregnation method with the aim of investigating the Lewis acid effect on hydrogenation and hydrogenolysis reactions. The sample was reduced at 353 K under hydrogen flowing and characterized by various physico-chemical techniques, such as BET, TPR, XRD, TEM, FESEM and XPS. Its catalytic performance, in hydrogenation reactions of carbonyls and hydrogenolysis of aromatic alcohols, carried out at 0.1 MPa H_2 pressure and 323 K, was investigated. It was demonstrated that $Pd/B(OH)_3$ is active using cyclohexane as solvent and the reactivity depends on the steric hindrance of the substrate. Conversely, in ethanol, boric acid dissolves and does not influence catalytic reactions.

1. Introduction

The increasing knowledge of chemical factors involved in a catalytic reaction points to the most appropriate choice of a metal support, in order to: (i) drive the selectivity towards a preferred product; (ii) make possible a process, otherwise unlikely, such as reduction of aliphatic carbonyls, in presence of palladium systems, only possible by using Pd/CoO, Pd/NiO or Pd/Fe_2O_3 co-precipitated catalysts [1].

Lewis acids catalyze organic reactions such as the Friedel–Crafts process or the Fries rearrangement, as well as petrochemical processes aimed to produce bulk and base chemicals. Use of Lewis acids supported on "inert" carriers of large surface area is an useful procedure since the system is heterogeneous and facilitates the catalyst recovery, reactivation and reuse [2]. The hard and soft acids and bases (HSAB) general theory, formulated by R. Pearson, offers, in the case, the basic principles to interpret the behaviour of Lewis acids in catalytic reactions [3].

There is, however, another route for highlighting the contribution of a strong solid Lewis acid in catalysis: to use it directly as support, so taking advantage of both the activation activity of the metal and the properties of the acidic support. On this regard, boric acid, $B(OH)_3$, is a typical support to be used, because of its commercial availability, environmental compatibility, cheap cost and facility to handle. It forms white needle-like crystals in which $B(OH)_3$ units, linked together by hydrogen bonds, form layers of nearly hexagonal symmetry, stable until 448 K, when $B(OH)_3$ transforms to HBO_2. It is moderately soluble in water and hydroxylic solvents and insoluble in apolar or hydrocarbon solvents and has been also used as green, selective and recyclable catalyst [4–6]. It behaves as very strong Lewis acid so that, in aqueous solution, the low acidity observed stems from the acceptor properties of boron [7].

Heterogeneous palladium based catalysts have been widely investigated in hydrogenation [8,9] and hydrogenolysis [10–12] reactions. However, studies focused on the role of Lewis acidity of the support, with the exception of zeolites [13,14], on the catalytic properties of palladium have been much less explored.

Therefore, in the present work, a $Pd/B(OH)_3$ catalyst was prepared by incipient wetness impregnation method and tested in catalytic hydrogenation and hydrogenolysis reactions, involving organic molecules bearing oxygen containing groups: carbonyls or aromatic alcohols. In order to highlight the acidic properties of $B(OH)_3$ ethanol and cyclohexane were used as solvents and results compared. In ethanol $B(OH)_3$ dissolves and the acidic properties of the support vanish since alcohol remains linked to the central boron, affording an inactive tetrahedral structure so that the catalytic activity depends only on the bare palladium. A detailed investigation of the physico-chemical properties of the catalyst by nitrogen adsorption (BET), temperature-programmed reduction

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(TPR), X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS) is also included.

2. Experimental

2.1. Catalyst preparation

5% Pd/$B(OH)_3$ was prepared by incipient wetness impregnation of the commercial support $B(OH)_3$ (Aldrich, purity 99.99%, $S_{BET} = 1.9\,m^2/g$) with an acetone solution of palladium (II) acetylacetonate, $Pd(acac)_2$, (Aldrich, purity 99%). After impregnation, the sample was dried under vacuum at 353 K for 1 day and then reduced for two hours, at the same temperature, under flowing hydrogen.

2.2. Catalyst characterization

BET surface area was determined by N_2 adsorption desorption isotherms at the liquid nitrogen temperature by using a Micromeritics Chemisorb 2750 instrument. The composition of the flow gas was N_2:He = 30:70. Samples were outgassed under flowing nitrogen for 1 h at 473 K, before measurements.

Temperature-programmed reduction (TPR) was employed to evaluate the reduction profile of the catalyst. 50 mg of the dried sample were placed in a quartz tube reactor and heated from 298 to 700 K with a constant heating rate of 10 K/min and exposed to a flow of 5 vol.% H_2/Ar mixture (20 cm^3/min). H_2 consumption was monitored by using a thermal conductivity detector (TCD). A molecular sieve cold trap (maintained at 193 K) and a tube filled with KOH, placed before the TCD, were used to block water and CO_2, respectively. The calibration of signals was made by injecting in the carrier a known amount of H_2.

Powder X-ray diffraction (XRD) patterns were acquired, at room temperature, on a Philips X-Pert diffractometer, by using the Ni β-filtered Cu-Kα radiation (λ = 0.15418 nm). Data were collected in the 2θ range 10°–80° with a scanning rate of 0.5°/min. Diffraction peaks were compared with those of standard compounds reported in the JPCDS Data File.

Field Emission Scanning Electron Microscopy (FESEM) pictures of the reduced sample were collected on a High Resolution FESEM instrument (LEO 1525) equipped with a Gemini Field Emission Column. The catalyst particles size and the relative morphology were analyzed by transmission electron microscopy (TEM), using a JEOL 2000 FX instrument operating at 200 kV and directly interfaced with a computer for real-time image processing. Particles size distribution was obtained by counting several hundred particles visible on the micrographs of the sample. The average value of the metal particles size was calculated by the following equation:

$$\bar{d} = \frac{\sum n_i d_i}{\sum n_i}$$

where n_i is the number of particles of diameter d_i.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Physical Electronics GMBH PHI 5800-01 spectrometer, equipped with a monochromatic Al Kα X-ray source. Binding energies (BE) values were referred to the carbon C 1s peak at 284.8 eV.

Table 1
Main characteristics of $B(OH)_3$ supported palladium catalyst.

Catalyst	Pd loading (wt%)		BET surface area (m^2/g)	Mean particle size (nm)[a]
	Nominal	XRF		
Pd/$B(OH)_3$	5	3.8	2.2	7.5

[a] Mean particles size from TEM.

2.3. Catalytic tests

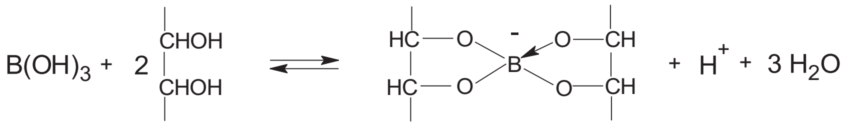
Liquid phase hydrogenation of both aliphatic and aromatic carbonyls and hydrogenolysis of aromatic alcohols were carried out at 0.1 MPa partial hydrogen pressure in a 100 ml five-necked batch reactor fitted with a reflux condenser. The reaction temperature was maintained at a constant value (323 K) by circulation of silicone oil in an external jacket connected with a thermostat. The temperature of the reaction mixture was monitored by placing a thermocouple inside the vessel. The catalyst (~300 mg), previously activated under H_2 at 353 K for 2 h, was added to 25 ml of ethanol (Fluka, 99.8% analytical grade) or cyclohexane (Sigma–Aldrich, 99% analytical grade), and reduced in "situ" at 323 K for 1 h under H_2 flow. Then, a solution of the organic compound (carbonyl or aromatic alcohol) in ethanol or cyclohexane (0.6 M, 15 ml), containing tetradecane as internal standard, was added through one arm of the flask. The reaction mixture was stirred with a magnetic stirrer head coupled with a gas stirrer at a rate of 500 rpm. A TPR measurement, carried out after reduction of the catalyst at 353 K, demonstrated that palladium was completely reduced.

Preliminary runs, performed with different amounts of catalyst and stirring rate, indicate that, under the experimental conditions adopted, the reaction was carried out in absence of external and internal mass-transfer limitations.

The progress of the reaction was followed by analyzing a sufficient number of samples, withdrawn periodically from the reaction mixture. Products analysis was performed with a gas chromatograph (HP model 5890), equipped with a wide-bore capillary column (CP-WAX 52 CB, 50 m, i.d. = 0.53 mm) and a flame ionization detector. Quantitative analysis was carried out by calculating the areas of the chromatographic peaks with an electronic integrator (HP model 3396).

2.4. Analytical determination of boric acid in ethanol solution

In order to verify the complete dissolution of boric acid in ethanol, 300 mg of catalyst were poured in 40 ml of C_2H_5OH and maintained at 323 K for 30 min. Then, after filtration of the solid, 2.5 g of sorbitol, dissolved in water, were added and the proton concentration ensuing from the reaction:



was determined by means of a conductometric titration, using a standard solution 0.1 M of NaOH [15].

3. Results and discussion

3.1. Catalyst characterization

Physical and chemical properties of Pd/$B(OH)_3$ were analyzed by several techniques, including BET, TPR, XRD, XRF, TEM, FESEM and XPS.

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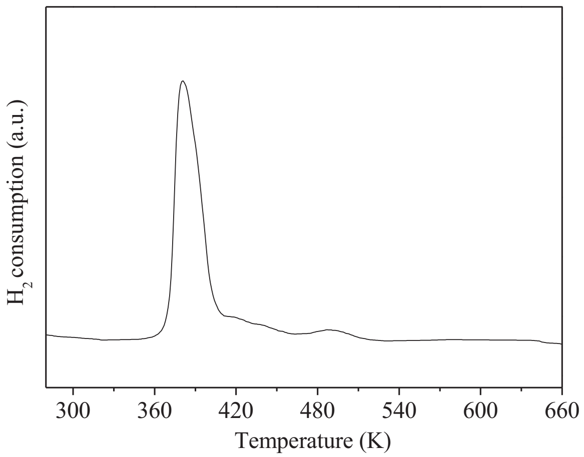

Fig. 1. H_2-TPR profile of $B(OH)_3$ supported palladium catalyst.

Table 1 reports the real wt% of palladium, determined by X-ray fluorescence analysis, the surface area and the mean particle size value.

The TPR profile of the fresh $Pd/B(OH)_3$ catalyst is illustrated in Fig. 1. A single peak, centred at ~380 K (value close to the reduction temperature of $Pd(acac)_2$, used as precursor in the catalyst preparation), referring to the $Pd^{2+} \rightarrow Pd^{\circ}$ reduction, is detected.

Fig. 2 shows the XRD patterns of the reduced $Pd/B(OH)_3$ catalyst. In addition to diffraction peaks related to the support structure, a diffraction pattern at $2\theta = 40.1°$, corresponding to the most intense diffraction line of the (1 1 1) plane of metallic palladium is observed. Furthermore, diffraction patterns at $2\theta = 46.8°$ and 68.2° are clearly noticed and ascribed to diffraction lines relative to the (2 0 0) and (2 2 0) plane of Pd°, respectively.

TEM microphotographs of the catalyst reveal that palladium particles are not homogeneously distributed and are poorly contrasted with respect to the matrix (Fig. 3). Therefore a reliable size distribution cannot be obtained whereas an approximate average metal particle size is calculated and reported in Table 1. FESEM micrograph (Fig. 4) of reduced $Pd/B(OH)_3$ shows a “star shape” structure of the sample, depending on strong intermolecular hydrogen bonds that symmetrically link boric acid molecules.

Fig. 5 reports XPS plots, in the Pd 3d and B 1s binding energy (BE) region, of the fresh and reduced $Pd/B(OH)_3$ catalyst. The Pd $3d_{5/2}$ BE value, on the reduced $Pd/B(OH)_3$ sample, is found at 335.0 eV, as expected for metal Pd particles not interacting with the support [16,17] and is in accordance with TPR and XRD data. The binding energy value of 193 eV (B 1s) is found, as expected, for an oxidated boron in a trigonal structure [18].

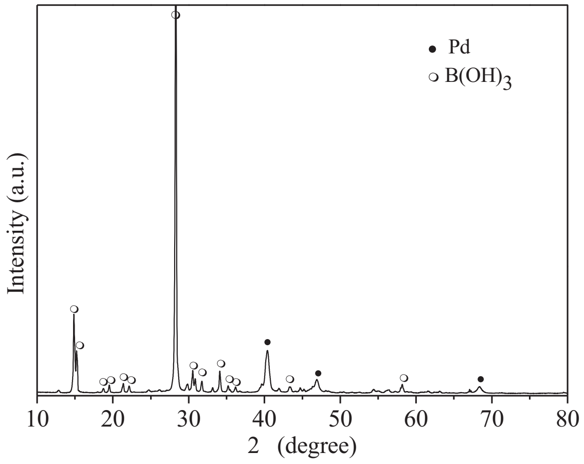

Fig. 2. XRD patterns of reduced $B(OH)_3$ supported palladium catalyst.

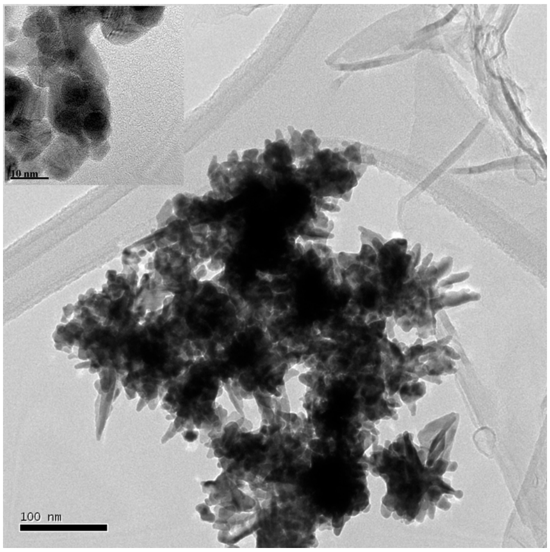

Fig. 3. TEM microphotographs of reduced $B(OH)_3$ supported palladium catalyst.

Characterization data point to the following features:

(i) metal-support interactions in $Pd/B(OH)_3$ are scarce and, in any case, of poor importance;

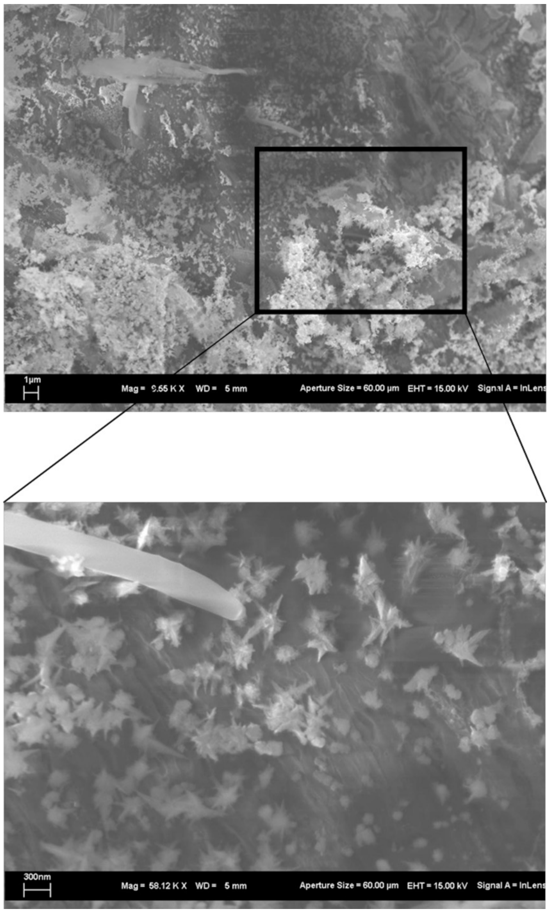

Fig. 4. FESEM images of reduced $B(OH)_3$ supported palladium catalyst.

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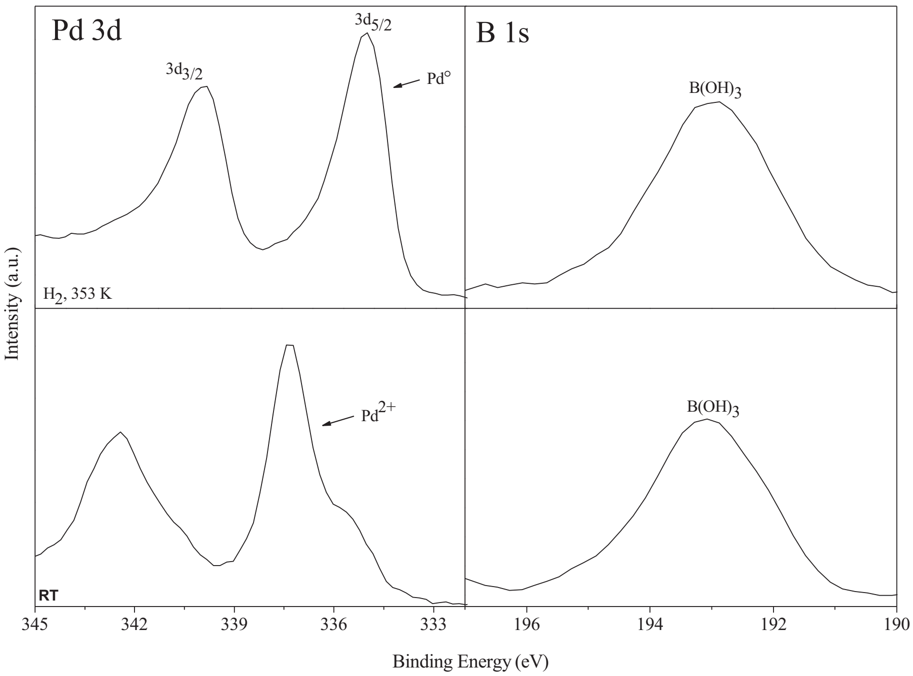


Fig. 5. XPS plots, in the Pd 3d and B 1s binding energy region, of 5% Pd/$B(OH)_3$ specimens: (down) fresh sample; (up) sample after reduction at 353 K for 2 h under H_2.

(ii) agglomerates of palladium particles occur on the surface, as expected from the very low surface area of $B(OH)_3$;

(iii) the symmetric distribution of boric acid molecules (star shape structure), linked together through hydrogen bonds, makes the support, through the trigonal central boron, suitable for Lewis interactions with hard bearing groups reacting molecules. This point is of remarkable interest, since, as XPS data confirm, in solid $B(OH)_3$ the trigonal structure is maintained so that the Lewis acidity can be effectively expressed.

3.2. *Catalytic activity*

3.2.1. *Reduction of carbonyl compounds*

The reduction of carbonyl compounds (see Scheme 1) was carried out in ethanol and cyclohexane at 323 K and 0.1 MPa H_2 pressure. Preliminary results indicate that no reaction occurs by using $B(OH)_3$ alone.

A typical composition against time plot for the hydrogenation reaction of 1-phenylethanone is shown in Fig. 6. Further hydrogenolysis of the corresponding reduction products, aromatic alcohols, does also occur. Initial reaction rates, r_i, expressed as moles of substrate/grams of palladium per second, are reported in Table 2. It clearly appears that, in ethanol, benzaldehyde reacts faster than 1-phenylethanone, whereas, in cyclohexane, the activity of both carbonyls is levelled. Indeed, in alcohol $B(OH)_3$ completely dissolves, as inferred from a conductometric acid–base titration (see Section 2.4), carried out on a typical solution, obtained after filtration of the solid, added with an excess of sorbitol, dissolved in an equal volume of water. Furthermore, the Lewis activity should be drastically reduced, in the case, since C_2H_5OH should coordinate the central boron of $B(OH)_3$ as an analogous reaction in water suggests [7].

On the other hand, as expected, no hydrogenation reaction occurs on using the filtered solution containing only boric acid and carbonyl molecules.

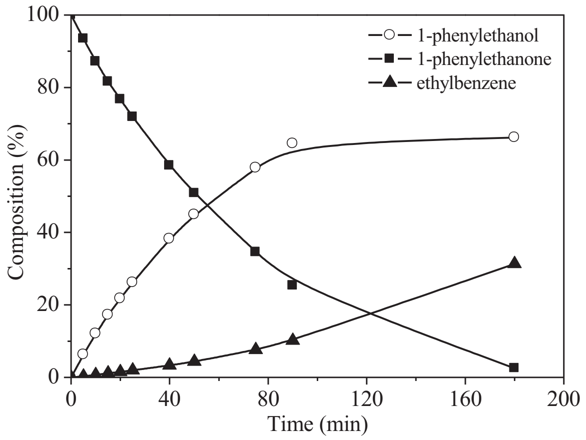
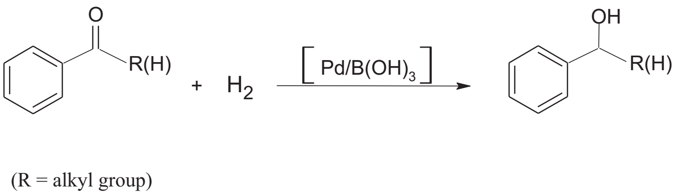


Fig. 6. Composition-time plot of the hydrogenation reaction of 1-phenyethanone over 5% Pd/$B(OH)_3$ at 323 K and 0.1 MPa H_2 pressure, using ethanol as solvent.

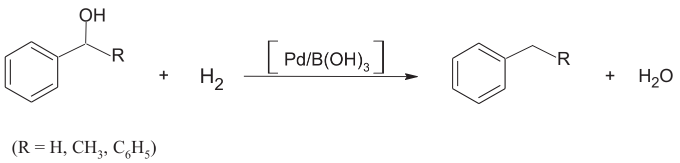


Scheme 1. Reaction pathway of carbonyl compounds hydrogenation on Pd/$B(OH)_3$.

Table 2
Activity of 5% Pd/$B(OH)_3$ catalyst in carbonyl compounds hydrogenation at 323 K and 0.1 MPa of H_2 pressure, using ethanol and cyclohexane as solvent.

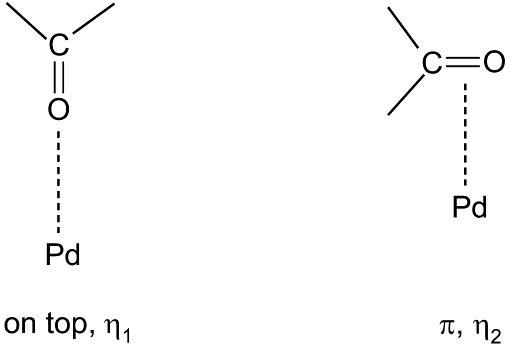
Substrate	r_i (mol/g_{Pd} s) × 10^5	
	Ethanol	Cyclohexane
Pentanal	u.d.	u.d.
Benzaldehyde	27.2	11.6
Pentan-2-one	u.d.	u.d.
1-Phenylethanone	10.9	10.8

u.d. = undetectable value.



Scheme 2. Reaction pathway of aromatic alcohols hydrogenolysis on Pd/B(OH)$_3$.

In principle carbonyls adsorption modes on a palladium surface mainly occurs through the following configurations



[19]: and the π structure should be involved in catalytic reduction [1]. Therefore, in ethanol, the activity can be attributed to the intrinsic steric hindrance of benzaldehyde lower than that of 1-phenylethanone. Conversely, in cyclohexane, the Lewis interaction of boric acid with the carbonylic oxygen is the main factor that contributes to level the reactivity. Data included in Table 2, and referring to cyclohexane, indicate that no reduction occurs with aliphatic carbonyls, pentanal or pentan-2-one. It is well known that transition metals, such as Pt, Ru and Rh hydrogenate both C=C and C=O double bonds and Os and Ir are the most active catalysts towards carbonyl hydrogenation [20–23]. Furthermore, oxidated metal species (Sn^{2+}, Fe^{2+}, Fe^{3+}, Ge^{4+}) on a surface of a noble metal, acting as Lewis acids, may promote activation of the C=O bond “via” the lone pair of oxygen [24–26]. The behaviour of palladium systems is completely different since they generally catalyze hydrogenation of aromatic carbonyls but lack to reduce the analogous aliphatic [19,27]. Only recently bimetallic species Pd–Co or Pd–Ni and Pd/Fe_3O_4 systems were found able to promote reduction of both aromatic and aliphatic aldehydes and ketones and a theory, looking to the mechanism of activation of carbonyl compounds on a palladium surface, was proposed in order to explain the particular behaviour of palladium catalysts [1]. Data, reported in Table 2, clearly suggest that aliphatic carbonyls are not reduced, thus indicating that the strong hard acidity of B(OH)$_3$ is not sufficient to properly modify the electronic properties of the carbonyl bond (π bonding and π^* antibonding energy levels) so that C=O activation of aliphatic carbonyls on the palladium surface is not allowed.

3.2.2. *Reduction of aromatic alcohols*

Scheme 2 reports the reaction pathway of aromatic alcohols hydrogenolysis carried out, both in ethanol and cyclohexane, at 323 K and 0.1 MPa H_2 pressure. Preliminary results indicate that no hydrogenolysis occurs in presence of boric acid alone.

Table 3
Activity of 5% Pd/B(OH)$_3$ catalyst in aromatic alcohols hydrogenolysis at 323 K and 0.1 MPa of H_2 pressure, using ethanol and cyclohexane as solvent.

Substrate	r_i (mol/g_{Pd} s) $\times 10^5$	
	Ethanol	Cyclohexane
Benzyl alcohol	9.2	51.6
1-Phenylethanol	6.4	0.9
Diphenylmethanol	1.0	0.2

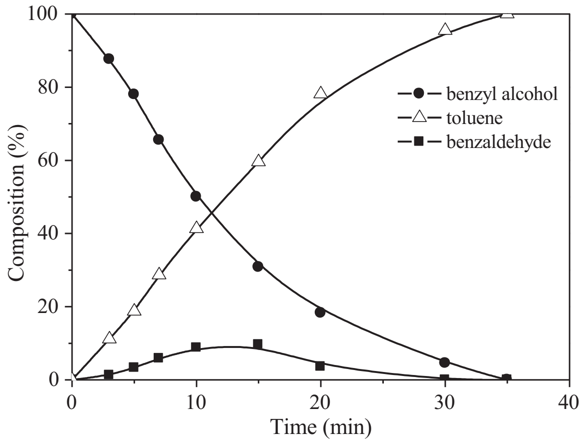


Fig. 7. Composition-time plot of the hydrogenolysis reaction of benzyl alcohol over 5% Pd/B(OH)$_3$ at 323 K and 0.1 MPa H_2 pressure, using cyclohexane as solvent.

Table 3 and Fig. 7 report initial reaction rates, r_i, and a typical composition against time plot, respectively. In both solvents activity values follow the order benzyl alcohol > 1-phenylethanol > diphenylmethanol, as it would be expected if the steric hindrance of alcohols plays a role in determining the activity. However, in order to highlight the effect of B(OH)$_3$, by itself, on the reactivity of aromatic alcohols, a comparison between rate values in ethanol (where no boric acid rate effect operates, as previously discussed) and cyclohexane, where the Lewis acid effect is particularly important, is considered. In this context data in ethanol are to be regarded only as ancillary information to understand the boric acid influence in hydrogenolysis reactions in cyclohexane. Data of Table 3 indicate that r_i (cyclohexane) > r_i (ethanol) for benzyl alcohol and r_i (cyclohexane) < r_i (ethanol) for the more sterically hindered 1-phenylethanol and diphenylmethanol. In principle, hydrogenolysis of aromatic alcohols can occur through one of two possible paths [28]: (i) a S_{N2}-type mechanism, in which the surface palladium bonded hydrogen displaces the hydroxyl group bonded to the carbon atom, or (ii) a more stepwise mechanism starting with the dissociation of the C—OH bond and temporary bonding of the OH group and the hydrocarbon residue on the Pd surface, followed by the transfer of a metal-bonded H atom to the unsaturated hydrocarbon intermediate. Therefore, the higher activity of the less hindered benzyl alcohol, in cyclohexane, has to be attributed to a beneficial effect due to a possible coordination of the hydroxyl moiety to boric acid that highlights the electrophilic ability of the alcoholic carbon. The same interaction abundantly slows down the reactivity of the more sterically hindered 1-phenylethanol and diphenylmethanol acting as an additional steric hindrance factor. Conversely, in ethanol, the boric acid contribution to the steric effect, in aromatic alcohol hydrogenolysis, is absent. Therefore, a better balance between steric and electronic factors occurs. Generally speaking, this is perfectly on line with the view that radical substitutions, in catalytic reactions, depend both on electronic and steric effects and activity values depend on the relative importance of the one and/or the other factor.

4. Conclusions

A 5 wt% palladium catalyst supported on the low cost, commercial and environmentally compatible carrier, boric acid, was prepared by impregnation method and characterized by BET, TPR, XRD, FESEM, TEM and XPS. The catalytic performance of Pd/B(OH)$_3$ was investigated in the reduction of carbonyl

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compounds and aromatic alcohols, carried out at 323 K and 0.1 MPa H_2 pressure, using ethanol and cyclohexane as solvents. The reported results indicate that the substrate structure affects the reactivity of the catalyst in cyclohexane, whereas is abundantly reduced in ethanol where boric acid dissolves and should coordinate an alcohol molecule. Furthermore, the strong hard Lewis acid $B(OH)_3$ is not able to contribute to activate the C=O group of aliphatic carbonyls on the palladium surface, whereas the $Pd/B(OH)_3$ system is very active in the hydrogenation of benzyl alcohol in cyclohexane. The high reactivity has to be attributed to a beneficial effect due to coordination of the hydroxyl moiety to boric acid that highlights the electrophilic ability of the alcoholic carbon.

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