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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A B S T R A C T

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.

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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$_2$O$_3$ 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

(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

$$B(OH)_3 + 2 \begin{array}{c} CHOH \\ | \\ CHOH \end{array}$$

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.
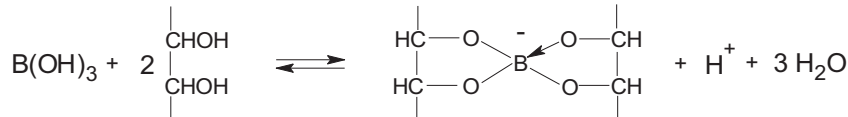
2.3. Catalytic tests

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$_2$H$_5$OH 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:

$$\begin{array}{c} HC-O \\ | \\ HC-O \end{array} \overset{-}{B} \begin{array}{c} O-CH \\ | \\ O-CH \end{array} + H^+ + 3 H_2O$$

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.