



## Short Communication

## Boron nitride as an alternative support of Pd catalysts for the selective oxidation of lactose

Nathalie Meyer, Kevin Bekaert, Damien Pirson, Michel Devillers, Sophie Hermans\*

Université Catholique de Louvain, Institut de la Matière Condensée et des Nanosciences (IMCN), Place Louis Pasteur 1/3, B-1348 Louvain-la-Neuve, Belgium

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## ABSTRACT

The potential of boron nitride as innovative support for the selective oxidation of carbohydrates has been evaluated. Pd/h-BN catalysts as well as Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> have been synthesized by two different methods for comparison: dry impregnation and deposition–precipitation. It is shown that BN is a suitable alternative to alumina and carbon for sugar oxidation in liquid phase. Very active and selective Pd/h-BN catalysts were obtained by the two synthetic methods under consideration.

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## 1. Introduction

Carbohydrates represent an important source of renewable raw materials because of their large availability, high framework complexity and independency from fossil energies. The industrial chemo-catalytic processes that convert sugars into specialty chemicals imply most often fermentation or enzymatic steps. The use of supported catalysts for these transformations is less widespread because of a lack of reliable catalytic methods to transform carbohydrates into high added value compounds. This is due to the fact that the transformation of sugars gives rise to rapid deactivation of the catalysts. For example, lactose is oxidized into 2-keto-lactobionic acid with a 5%Bi–5%Pt/C catalyst, but the latter deactivates rapidly because of the formation of platinum oxide at the catalyst surface [1]. Ideally, these transformations should be carried out in water, the catalysts should be very stable to permit recycling and the conversion and selectivity should be as high as possible.

However, many compounds interesting for fine chemistry can be produced from sugars [2,3]. For example, it is possible to oxidize glucose into gluconic acid, a chelating biodegradable agent, with Bi–Pd/C and Au–Pd/C catalysts [4–7].

The present work deals with the catalytic oxidation of lactose in lactobionic acid using supported palladium catalysts. Lactobionic

acid finds applications in cosmetics and as an antioxidant [8,9]. It is also the major constituent of organ preservation fluids used during transplantation [10]. The heterogeneous catalysts reported so far to carry out this reaction are based on noble metals (Au, Pd, Bi–Pd, Pt) and supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, carbon or zeolites [1,8–14].

Boron nitride is isoelectronic to carbon and its hexagonal h-BN form is isostructural to graphite with covalent bonds in the planes and very weak attractions between the planes. Its strong mechanical and corrosion resistance, its high stability against thermal shock, chemical attacks [15] and oxidation [16–18] make BN a promising catalyst support for all applications in which stability is a key point. A further interest of BN as an alternative to carbon comes from the possibility to characterize the BN-supported catalysts by vibrational spectroscopy.

Examples of uses of BN as catalyst support are quite scarce in the literature and are essentially restricted to processes requiring relatively high temperatures. BN-supported noble metal catalysts have been used to abate volatile organic compounds [19]. Pt/BN has been applied in deep oxidation of methanol and benzene [20]. Postole et al. studied the influence of the preparation methods of Pd/BN catalysts on the activity for methane oxidation [16,21,22]. They also studied the characteristics of BN and BN-supported oxide systems and their use in the reduction of NO<sub>x</sub> [23]. BN has also been used as support for the hydrogenation of crotonaldehyde with Pt–Fe catalysts [24] or alkynes using Pd/BN catalysts [25] for example.

\* Corresponding author. Tel.: +32 10 472810; fax: +32 10 472330.

E-mail address: [sophie.hermans@uclouvain.be](mailto:sophie.hermans@uclouvain.be) (S. Hermans).

In this work, the potential of boron nitride as a new support for lactose selective oxidation was evaluated: Pd/h-BN catalysts have been synthesized, and compared to Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The influence of several parameters, such as the synthesis method, the nature of the precursor or reducing agent, on the structural characteristics and the catalytic performances has been investigated.

## 2. Experimental

### 2.1. Starting materials

The supports were commercially available alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Sigma-Aldrich,  $S_{\text{BET}} \approx 173 \text{ m}^2 \text{ g}^{-1}$ ) and hexagonal boron nitride (h-BN, Sigma-Aldrich,  $S_{\text{BET}} \approx 24 \text{ m}^2 \text{ g}^{-1}$ ). A batch of the alumina support was calcined in air at 1000 °C for 24 h to give  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $S_{\text{BET}} \approx 17 \text{ m}^2 \text{ g}^{-1}$ ). The textural properties of the supports are given in Supplementary data (Table S1). The palladium precursors were sodium tetrachloropalladate(II) (Na<sub>2</sub>PdCl<sub>4</sub>, Sigma-Aldrich, 99.99%) and diacetatobis(diethylamine) palladium(II) (Pd(OAc)<sub>2</sub>(NHET<sub>2</sub>)<sub>2</sub>) synthesized as described elsewhere [26].

### 2.2. Catalyst synthesis

The palladium loading of each catalyst prepared in this work is 5 wt.%.

#### 2.2.1. Dry impregnation method (DI)

This method consists in using the amount of solvent needed to obtain incipient wetness. This amount has been determined by visual observation of the formation of a homogeneous wetted paste for 1 g of each support:  $V_{\text{methanol}} = 700 \text{ }\mu\text{L}$  for 1 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and 1.1 mL for 1 g h-BN. It corresponds in both cases to about ten times the porous volume of the supports (pore volume of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> = 0.1127 cm<sup>3</sup>/g and of h-BN = 0.1419 cm<sup>3</sup>/g). Pd(OAc)<sub>2</sub>(NHET<sub>2</sub>)<sub>2</sub> was dissolved in the corresponding methanol volume and added dropwise to the support under constant stirring at room temperature. The catalyst was then reduced by thermal decomposition under hydrogen flow in a tubular oven (2 h, 200 °C). For some catalysts, the reduction step was preceded by calcination (under air flow, 500 °C, 12 h).

#### 2.2.2. Deposition–precipitation method (DP)

Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Pd/h-BN catalysts were prepared by a deposition–precipitation method following a literature procedure [11]: 5 g of support dispersed in 100 mL of a Na<sub>2</sub>CO<sub>3</sub> 2.5 wt.% aqueous solution were stirred 15 min at room temperature. The calculated amount of Na<sub>2</sub>PdCl<sub>4</sub> or Pd(OAc)<sub>2</sub>(NHET<sub>2</sub>)<sub>2</sub> dissolved in 50 mL of distilled water was added dropwise to the suspension within 30 min. After 15 additional minutes of stirring, 5 g of NaBH<sub>4</sub> in 50 mL of distilled water were added. The suspension was stirred for 1 h at room temperature. Finally, the catalyst was filtered, washed with distilled water and dried for 12 h at 80 °C. The filtrates were analyzed by atomic absorption spectrometry and no losses of Pd were observed. In addition, all the solid samples were analyzed by ICP and the Pd wt.% was found to be 4.37–4.71 in all cases except one (DP-8, Pd = 3.85 wt.%).

The catalysts were characterized after activation by XPS, SEM, TEM, powder XRD and Raman spectroscopy. In situ Raman measurements were carried out for some catalysts prepared by DI to study the activation step (see Supplementary data S2 for more details).

### 2.3. Oxidation of lactose

All catalytic tests were performed in a thermostated double-walled glass reactor. The pH of the lactose solution was measured continuously by a combined AgCl/Ag Beckman electrode. An automatic titration device Metrohm 842 Titrando was used to neutralize the acids formed over time with KOH (Riedel-de-Haën,  $\geq 85\%$ ). Constant

**Table 1**

Experimental conditions used for lactose oxidation.

Parameter	Lactose oxidation
Starting substrate solution	500 mL lactose 10 mmol L <sup>−1</sup>
Temperature	40 °C
Stirring rate	1000 rpm
pH	9
Basic solution to fix the pH	KOH 0.1 mol L <sup>−1</sup>
Oxygen flow	0.5 L min <sup>−1</sup>
Mass of catalyst	500 mg
Duration of a catalytic test	4 h

stirring was ensured by a mechanical stirrer (Heidolph RZR 2051 electronic). The experimental conditions used for lactose oxidation are summarized in Table 1. The catalyst was recovered by filtration and the filtrate was analyzed by HPLC. Because selectivity was found to be 100% in all cases, the lactose conversion always equals the yield in lactobionic acid. The other carbohydrates were tested in exactly the same conditions and also gave 100% selectivity.

## 3. Results and discussion

### 3.1. Catalysts synthesized by dry impregnation (DI)

The catalytic results in lactose oxidation and XPS characterization data of the Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Pd/h-BN catalysts synthesized by dry impregnation are displayed in Table 2.

The catalysts calcined in air before activation under H<sub>2</sub> are more active than without calcination. This observation can be correlated to XRD and microscopy results, while XPS surface atomic intensity ratios are similar. In the XRD analysis of the DI-1 catalyst (Fig. 1), the molecular precursor is clearly visible after DI (Fig. 1(a)), PdO appears after calcination (Fig. 1(b)), and metallic Pd after reduction (Fig. 1(c)). The last diffractogram (d) refers to the same catalyst activated without prior calcination and shows thinner Pd peaks than in Fig. 1(c), indicating larger crystallites. SEM analyses of DI-1C point in the same direction and reveal smaller Pd particles at the surface of the support and a more homogeneous distribution in the case of the pre-calcined sample (Fig. S3(a) and (b)). The same observation can be made by XRD (Fig. 2) and SEM (Fig. S3) analyses of BN-supported catalysts.

It also appears that the catalysts prepared on boron nitride are much more active in the oxidation reaction than their homologues supported on alumina. Experimental Pd/support XPS intensity ratios were higher than the calculated values for BN, indicating better surface accessibility to active sites for the sugar transformation. SEM images of the BN-supported catalysts (Fig. S3) showed metallic Pd particles to be smaller and better spread on BN than on alumina. Because BN is more hydrophobic than alumina, the former takes more time to sedimentate in CH<sub>3</sub>OH than in water. This probably increases the interactions between the support and the precursor improving the Pd dispersion on the surface in the final catalyst.

**Table 2**

Catalysts prepared by dry impregnation: Pd(OAc)<sub>2</sub>(NHET<sub>2</sub>)<sub>2</sub> as precursor.

Catalyst	Name	XPS		Lactobionic acid yield (%) at t = 4 h
		Calc.	Exp.	
<i>Pd/Al (×100)</i>				
DI-1	Pd/α-Al <sub>2</sub> O <sub>3</sub>	2.4	1.7	11.7
DI-1C <sup>a</sup>	Pd/α-Al <sub>2</sub> O <sub>3</sub>	2.4	1.6	29.5
<i>Pd/B (×100)</i>				
DI-2	Pd/h-BN	1.2	2.2	27.4
DI-2C <sup>a</sup>	Pd/h-BN	1.2	2.5	48.6

<sup>a</sup> Catalysts calcined under air flow at 500 °C for 12 h before reduction.

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