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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

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Keywords: Boron nitride Lactose Palladium Oxidation Alumina 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/α -Al₂O₃ 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 Al₂O₃, SiO₂, TiO₂, 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_x [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 (S. Hermans).

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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/ α -Al₂O₃ 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 (γ -Al₂O₃, Sigma-Aldrich, S_{BET} \approx 173 m²g⁻¹) and hexagonal boron nitride (h-BN, Sigma-Aldrich, S_{BET} \approx 24 m²g⁻¹). A batch of the alumina support was calcined in air at 1000 °C for 24 h to give α -Al₂O₃ (S_{BET} \approx 17 m²g⁻¹). The textural properties of the supports are given in Supplementary data (Table S1). The palladium precursors were sodium tetrachloropalladate(II) (Na₂PdCl₄, Sigma-Aldrich, 99.99%) and diacetatobis(diethylamine) palladium(II) (Pd(OAc)₂(NHEt₂)₂) 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: $V_{methanol} = 700 \ \mu L$ for 1 g α -Al₂O₃ 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 α -Al₂O₃ = 0.1127 cm³/g and of h-BN = 0.1419 cm³/g). Pd(OAc)₂(NHEt₂)₂ 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/α-Al₂O₃ and Pd/h-BN catalysts were prepared by a depositionprecipitation method following a literature procedure [11]: 5 g of support dispersed in 100 mL of a Na₂CO₃ 2.5 wt.% aqueous solution were stirred 15 min at room temperature. The calculated amount of Na₂PdCl₄ or Pd(OAc)₂(NHEt₂)₂ 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 NaBH₄ 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 thermostatized doublewalled 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

|--|

Experimental conditions used for lactose oxidation.

Parameter	Lactose oxidation
Starting substrate solution Temperature Stirring rate pH Basic solution to fix the pH Oxygen flow Mass of catalyst Duration of a catalytic test	500 mL lactose 10 mmol L ⁻¹ 40 °C 1000 rpm 9 KOH 0.1 mol L ⁻¹ 0.5 L min ⁻¹ 500 mg 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/α -Al₂O₃ and Pd/h-BN catalysts synthesized by dry impregnation are displayed in Table 2.

The catalysts calcined in air before activation under H_2 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_3OH 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.

fable 2	
Catalysts prepared by dry impregnation: $Pd(OAc)_2(NHEt_2)_2$ as precursor.	

Catalyst	Name	XPS		Lactobionic acid	
		Calc.	Exp.	yield (%) at $t=4$ h	
		Pd/Al (×100)			
DI-1	Pd/α - Al_2O_3	2.4	1.7	11.7	
DI-1C ^a	$Pd/\alpha\text{-}Al_2O_3$	2.4	1.6	29.5	
		Pd/B (×10	0)		
DI-2	Pd/h-BN	1.2	2.2	27.4	
DI-2C ^a	Pd/h-BN	1.2	2.5	48.6	

^a Catalysts calcined under air flow at 500 °C for 12 h before reduction.



Fig. 1. XRD diffractograms of Pd/α -Al_2O_3 catalysts: (a) after DI, (b) after calcination, (c) after reduction, and (d) activated without prior calcination.

The samples obtained via this preparation method can be analyzed by in situ Raman spectroscopy in order to study the activation step. The Raman spectrum of the precursor shows a few sharp peaks for Pd(OAc)₂(NHEt₂)₂, while that of the alumina is featureless (Fig. S4(a) and (b)). The spectrum of h-BN shows one main peak at 1400 cm⁻¹ (Fig. S4(c)). The spectrum of the DI-1 catalyst before reduction is clearly the superimposition of the complex and the support (Fig. S5(a)). Concerning the catalyst DI-2 (Fig. S5(b)), the Raman shift range 4000–2000 cm⁻¹ was selected to monitor the precursor peaks useful to study the activation step. The latter was achieved (Fig. 3) by heating the catalyst under nitrogen, and it was found that the activation corresponds to a ligand abstraction phenomenon leading to the reduction of Pd(II) to Pd(0) as confirmed by XPS. The same study was carried out for the Al₂O₃-supported catalyst, leading to the same observation (Fig. S6).

3.2. Catalysts synthesized by deposition-precipitation (DP)

Catalytic performances of catalysts prepared by deposition– precipitation are illustrated in Table 3. It comes out that Pd/Al₂O₃ catalysts reduced with formalin (DP-1 and DP-2) are less active than their homologues reduced with NaBH₄ (DP-3 and DP-4). In addition, a solvent effect can be observed when these two catalysts are analyzed one step further. Indeed, the DP-2 catalyst prepared in the H₂O/ CH₃OH mixture is slightly less active than the DP-1 catalyst prepared in water. Alumina, being more hydrophilic, is better dispersed in water than in a water/methanol mixture. Hence, the precursor/support



Fig. 2. XRD diffractograms of Pd/h-BN catalysts: (a) after DI, (b) after calcination, (c) after reduction, and (d) activated without prior calcination.



Fig. 3. DI-2: Raman spectra of Pd(OAc)₂(NHEt₂)₂/h-BN heated in situ under N₂ flow.

interaction is better in water. The catalysts prepared on α -Al₂O₃ with two different precursors but activated with NaBH₄ (DP-3 and DP-4) exhibit a higher activity and are characterized by much higher XPS Pd/Al ratios, indicating more palladium available for the sugar at the surface of the support. SEM images of DP-3 and DP-4 show particle sizes comprised between 15 and 30 nm (Fig. S7). XRD analyses of these two systems are quite similar with very broad peaks for Pd.

The samples prepared on boron nitride also reveal the influence of the solvent: the activity of DP-6 is almost twice that of DP-5. In a water/methanol mixture, BN gives rise to a homogeneous suspension which increases the contact between the precursor and the support, contrary to water alone. This is confirmed by an XPS Pd/B ratio higher for DP-6 than for DP-5.

In the BN-supported catalysts reduced with NaBH₄ (DP-7 and DP-8), it comes out that the chlorinated precursor has a negative influence on the activity. A neutral precursor seems better adapted for the synthesis of supported boron nitride catalysts.

The most competitive BN-based catalyst in this table is DP-8 prepared from $Pd(OAc)_2(NHEt_2)_2$ and activated with NaBH₄. It is the only one that contained slightly less Pd (3.85 wt.%) as determined by ICP analysis of the solid. XRD analysis shows very broad Pd peaks meaning small Pd crystallites (Fig. 4), while TEM images show particle sizes in the range of 2–30 nm (Fig. 5). This result can be correlated with literature observations quoting that having a particle size around 3 nm makes the catalyst more active and selective for sugar oxidation [2,27].

DP-5 and DP-6 synthesized with the same precursor and the same reducing agent in respectively water and in a mixture of water/ CH_3OH are less active than DP-8 probably because of the presence

Table 3Catalysts prepared by deposition-precipitation method (DP).

Catalyst	Precursor	Name	Reducing agent	XPS		Lactobionic	
				Calc.	Exp.	acid yield (%) at t=4 h	
				Pd/Al (×100)			
DP-1	$Pd(OAc)_2(NHEt_2)_2$	Pd/α - Al_2O_3	Formalin	2.4	5.9	10.7	
DP-2 ^a	$Pd(OAc)_2(NHEt_2)_2$	Pd/α - Al_2O_3	Formalin	2.4	6.4	7.8	
DP-3	Na ₂ PdCl ₄	Pd/α - Al_2O_3	NaBH ₄	2.5	11	42.9	
DP-4	$Pd(OAc)_2(NHEt_2)_2$	$Pd/\alpha\text{-}Al_2O_3$	NaBH ₄	2.4	12	38.1	
				Pd/B (x100)			
DP-5	$Pd(OAc)_2(NHEt_2)_2$	Pd/h-BN	Formalin	1.2	1.2	14.3	
DP-6 ^a	$Pd(OAc)_2(NHEt_2)_2$	Pd/h-BN	Formalin	1.2	2.0	26.8	
DP-7	Na ₂ PdCl ₄	Pd/h-BN	NaBH ₄	1.2	2.7	21	
DP-8	$Pd(OAc)_2(NHEt_2)_2$	Pd/h-BN	NaBH ₄	1.2	2.3	64	

Synthesized in $H_2O-Na_2CO_3 + CH_3OH 50/50$.



Fig. 4. XRD diffractogram of DP-8: Pd/BN catalyst.

of bigger Pd aggregates, as evidenced by TEM (Fig. S8). It is also due to the reducing agent since NaBH₄ is more efficient than formaldehyde. Indeed, the Pd XPS spectrum of DP-8 shows only Pd(0), which is claimed in the literature as the active phase for sugar oxidation [2], while for DP-5 and DP-6, XPS 3d peak can be decomposed in two doublets for Pd(II) and Pd(0) (Fig. S9).

Except for DP-7, there is a correlation between XPS results and the yield in lactobionic acid for the BN-supported catalysts. Indeed, the higher the Pd/B ratio, the higher the activity in this reaction.

The preparation method has also a clear influence on the catalytic performances. On alumina as well as on BN, the catalysts are more active when the deposition–precipitation method is used instead of dry impregnation. The former method permits to obtain smaller Pd particles at the surface of the support as shown by microscopy and XRD analyses. However, when a catalyst prepared by DI is calcined and then activated under hydrogen, its catalytic performances are greatly increased and reach the activity of its counterpart prepared by DP.

Mirescu and Pruesse showed that very active and selective Au/ alumina catalysts were obtained for the oxidation of lactose in lactobionic acid. However, when palladium is supported on alumina [11] or on carbon [14], it gives a lower selectivity. In our case, when palladium is supported on boron nitride, 100% selectivity is reached. We believe that the high selectivity of BN-supported catalysts is due to the absence of surface functional groups, the small surface area, the absence of micropores and probably also to the particle sizes obtained (which, if too small, promote overoxidation). A control experiment was carried out by preparing a catalyst by DP on a porous



Fig. 5. TEM image of DP-8: Pd/h-BN catalyst.

 γ -Al₂O₃ and it indeed displayed half the activity of α -Al₂O₃ and selectivity below 100%.

Pd/h-BN was also tested in maltose and glucose oxidation. In both reactions, Pd/h-BN was active: yields of 43% and 55% in maltobionic acid and gluconic acid, respectively, were obtained after a 4 h reaction. The selectivity was 100% in both cases.

XPS analyses carried out after every catalytic test confirmed that there was no change in the Pd(0) oxidation state (Fig. S10). Pd losses during catalytic tests were always <1% as verified by ICP on catalysis filtrates. The recyclability of the catalysts was also studied. For both the BN and α -Al₂O₃-supported catalysts, there is a loss of about 50% of activity in the second run but no further decrease in the next run.

4. Conclusions

We have shown that BN is a promising alternative support to replace alumina and carbon for sugar oxidation in the liquid phase. Lactose was the most studied but BN could also be used as support for other sugar conversions. It is a robust and non-porous material, which seems advantageous to avoid internal diffusion limitations when carrying catalysis in water. In addition, the absence of surface hydroxyl groups is expected to limit side reactions which should guarantee high selectivity and stabilizes the metal in its reduced form. Finally, it allows spectroscopic in situ characterization. Very active Pd/h-BN catalysts were obtained by either dry impregnation or deposition–precipitation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.10.007.

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