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Noble metal supported catalysts for lactose transformations in liquid phase

1. Introduction and objectives

This thesis was realized under the supervision of Michel Devillers and Sophie Hermans within the general framework of heterogeneous catalysis. The goal was to study noble metal catalysts supported on boron nitride for sugar transformations. For nearly a century, oil has constituted the reference resource in our society for fuel and as raw material for the synthesis of many compounds essential to our daily life. However, the abundant supply of cheap oil will decrease because of the known reserves depletion [1, 2]. To overcome this problem, chemicals derived from available biomass should be used. In particular, sugars are an interesting source of raw materials because they are renewable and many compounds interesting for fine chemistry can be produced from them [3-6]. Most of the chemo-catalytic processes that convert sugars into specialty chemicals in the

industry imply mainly fermentation or enzymatic steps [7-9]. Ideally, these transformations should be carried out in water, with recyclable catalysts. The present work is focused on one particular sugar: lactose. Two transformations have been studied: the selective oxidation of lactose into lactobionic acid and the selective hydrogenation of lactose into lactitol (Figure 1).

The former has already been widely studied in the literature but the main problems encountered are a non-optimal selectivity in the desired product and the noble metal leaching during catalytic tests preventing the application of heterogeneous catalytic lactose transformation at industrial scale [9-16]. Lactobionic acid presents several interesting applications as an antioxidant. Indeed, it is used in cosmetic industry but also in the medical sector because it can replace formol as an organ preservation

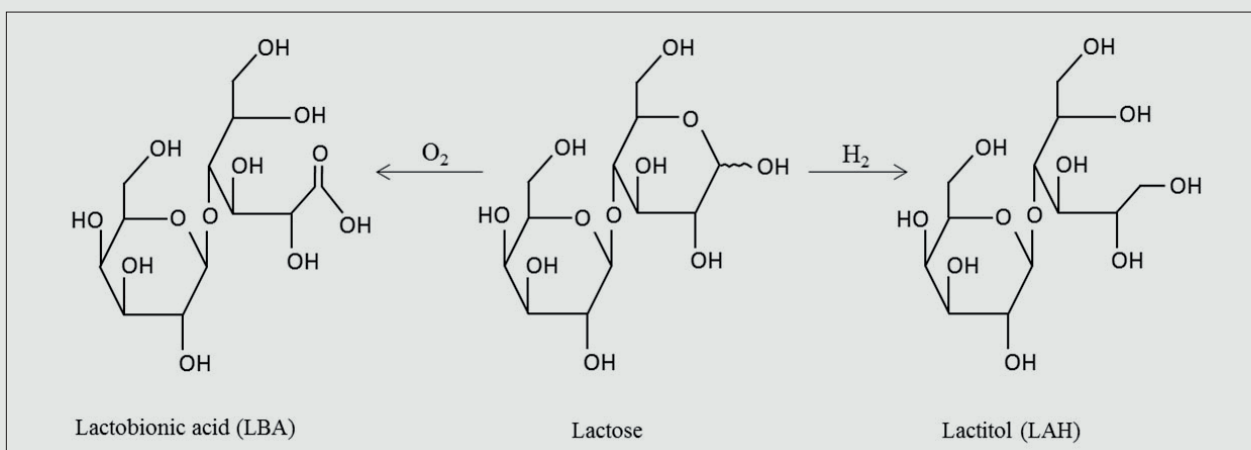


Figure 1: Lactose oxidation into lactobionic acid (LBA) and lactose hydrogenation into lactitol (LAH)

liquid [6]. Concerning lactose hydrogenation, Ru/C catalysts have been essentially used, in the literature [17- 20], to carry out this transformation and a low selectivity implying the formation of undesired products was often observed. In addition, most of the studies are devoted to the influence of the conditions employed during the catalytic tests but the reasons for deactivation, noble metal poisoning or structure-reactivity relationships are rarely mentioned. In this thesis, we have explored the structural properties of the catalysts needed to carry out both oxidation and hydrogenation of lactose. The main emphasis was made on the former reaction.

2. Results and discussion

2.1. Oxidation of lactose into lactobionic acid

In each of the following sections, several synthesis methods used to prepare catalysts will be described. In each case, the prepared catalysts have been tested in lactose oxidation using a thermostated double-walled glass reactor and by controlling parameters such as temperature, stirring rate, pH and gas flow rate. The catalysts were characterized by XPS, TEM, powder XRD and CO chemisorption. The reaction mixtures were analyzed by HPLC using two columns in order to detect and separate all the possible by-products.

2.1.1. Impact of chemical functions at support surface [21]

In heterogeneous catalysis, it is known that an ideal supported catalyst should exhibit a homogeneous distribution of metallic particles of controlled sizes

[22, 23] and particularly for sugars transformations that are structure-sensitive [12, 16, 24]. The support plays an important role in the final distribution of these particles on the catalyst surface [25] and the chemical functions at the surface are generally preferred to ensure high dispersion (Figure 2).

Hence, we have varied the supports nature and metallic active phase precursors. Several preparation methods were implemented in order to obtain different catalysts with varying characteristics. Palladium supported catalysts have been prepared by grafting and anchoring on alumina or carbon xerogels (Figure 3).

In the literature, the majority of processes described to fix the metal precursor onto the support are not well defined [26-29]. In addition, when grafting is concerned, no experimental evidence that a covalent grafting bond occurred is given. In general, the precursor is reduced at the surface of the support which makes it difficult to obtain the grafting proof. The first objective here was to develop a methodology to prove that grafting or anchoring actually occurred at a molecular level on the supports surface. This was carried out mainly by Raman and XPS spectroscopy and allowed to prove the direct grafting of Pd complexes onto hydroxyl functions present at the surface of γ -Al₂O₃. Grafting was successful for [Pd(CF₃CO₂)₂(bipy)] on calcined alumina and for [PdCl₂(PhCN)₂] on two different treated aluminas. Pd^{II} was present at the surface after the syntheses. Anchoring via two different amine-bearing silanes previously grafted on the γ -Al₂O₃ support was also successful. The anchoring was proven to take place for catalysts prepared in acetone. The catalysts prepared on carbon xerogels

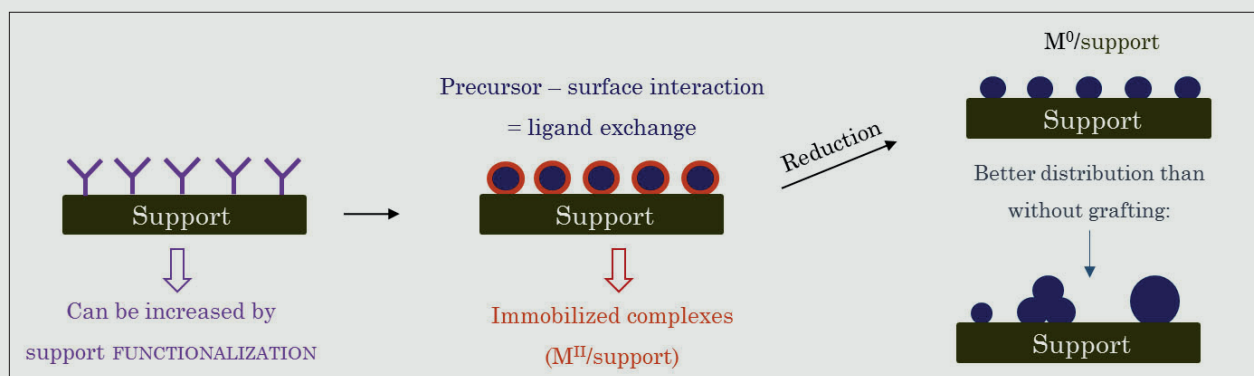
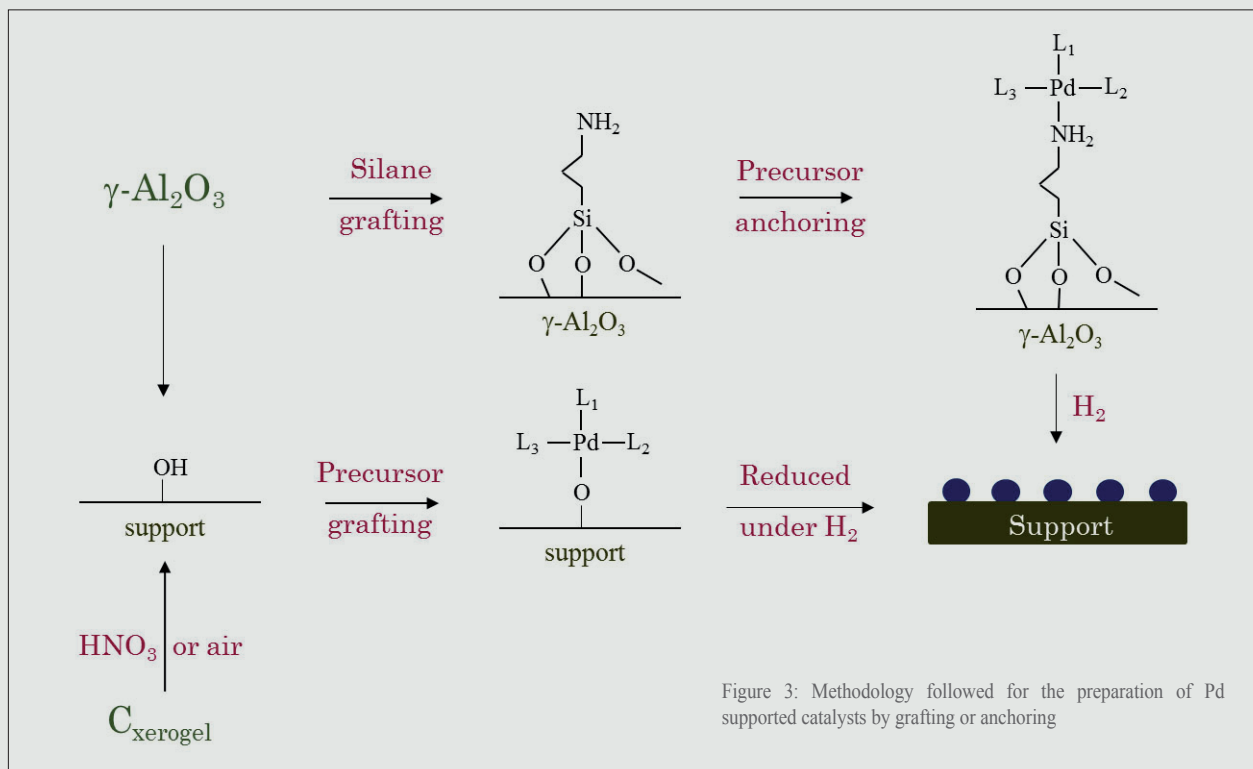


Figure 2: Preparation of an ideal supported catalyst with homogeneous particles distribution at the surface



demanded a first step of functionalization to increase the number of oxygenated groups at their surface. This was carried out by HNO_3 oxidation in liquid phase. The $\text{Pd}(\text{OAc})_2(\text{NHEt}_2)_2$ complex was grafted on five functionalized xerogels with different porosity, by using the surface oxygen groups as anchors. Again, the grafting was shown to occur by a ligand exchange mechanism keeping Pd in its +II oxidation state on the support surface.

The second objective was to study the influence of the physico-chemical characteristics of the reduced catalysts and prior supports functionalization on the catalytic performances in lactose oxidation. Table 1 presents some catalytic results: for the two supports considered, the catalysts prepared on unmodified supports always exhibited the highest activity and selectivity in lactobionic acid (LBA).

Catalyst	Pd loading (wt.%) AAS	X_{Lactose} (%) ^a	Y_{LBA} (%) ^b	S_{LBA} (%) ^c
Pd/ $\text{C}_{\text{xerogel}}$ unmodified	3.66	30	30	100
Pd/ $\text{C}_{\text{xerogel}}$ functionalized in liquid phase	4.49	28.3	26	92
Pd/ $\gamma\text{-Al}_2\text{O}_3$ unmodified	3.24	15.3	15	98.3
Pd/ $\gamma\text{-Al}_2\text{O}_3$ functionalized with silane	3.95	12.1	2.22	18.4

^a: $X_{\text{Lactose}} = n_{\text{lactose transformed}}/n_{\text{lactose engaged}}$
^b: $Y_{\text{LBA}} = n_{\text{LBA}}/n_{\text{lactose engaged}}$
^c: $S_{\text{LBA}} = n_{\text{LBA}}/n_{\text{lactose transformed}}$

Table 1: Catalytic performances of catalysts prepared on unmodified and functionalized supports

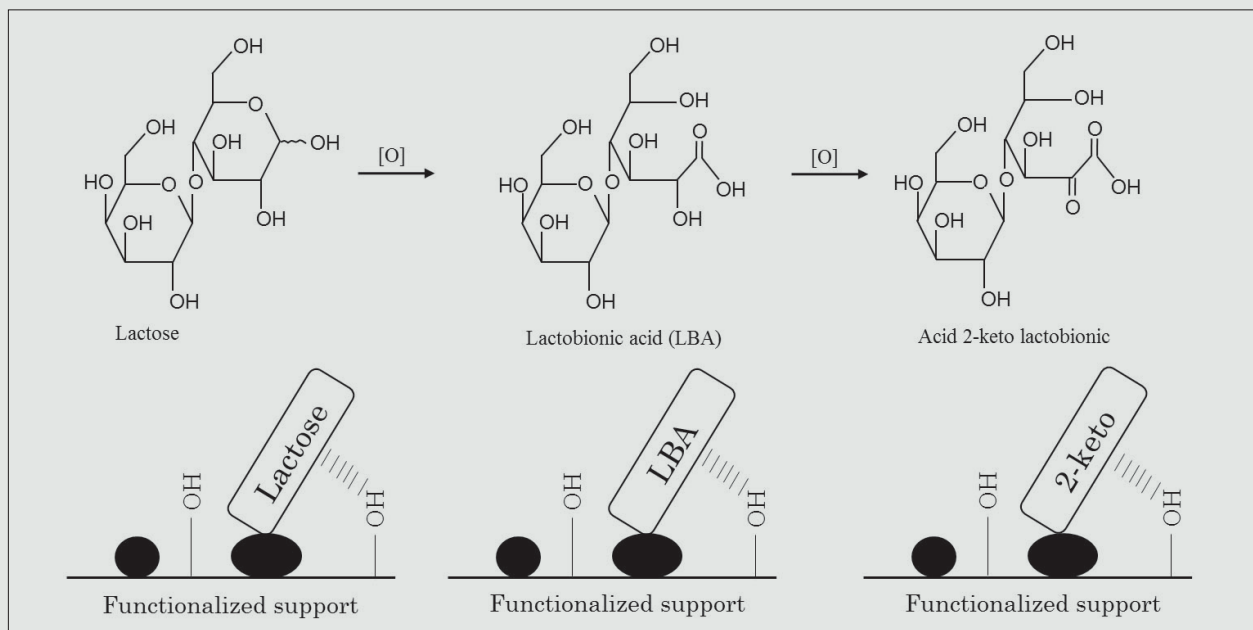


Figure 4: Model of the influence of $-OH$ functions on S_{LBA}

An explanation of such observation concerning the selectivity can be found in Figure 4. Indeed, the $-OH$ functions present on alumina or xerogels surface could be implied in hydrogen-bridge bonding with the adsorbed sugar. This “stabilization” could prevent desorption before the subsequent oxidation product (2-keto lactobionate) is formed. A low amount of surface acid functions was shown to influence positively the selectivity in LBA. Even though support functionalization is often used in heterogeneous catalysis to increase metallic dispersion, it does not have a positive impact in lactose oxidation.

2.1.2. Boron nitride as an alternative support [30]?

Given that selectivity is a key point in heterogeneous catalysis in both fundamental research and industrial applications, the support selected next to carry out oxidation of lactose, in light of the observations described above, was chosen to be more inert and presenting no functions at its surface. Boron nitride is isoelectronic to carbon and is found mainly in hexagonal h-BN form (α -BN) isostructural to graphite [31] (Figure 5). Examples of uses of BN as catalyst support are quite scarce in the literature and essentially restricted to processes requiring relatively high temperatures [32].

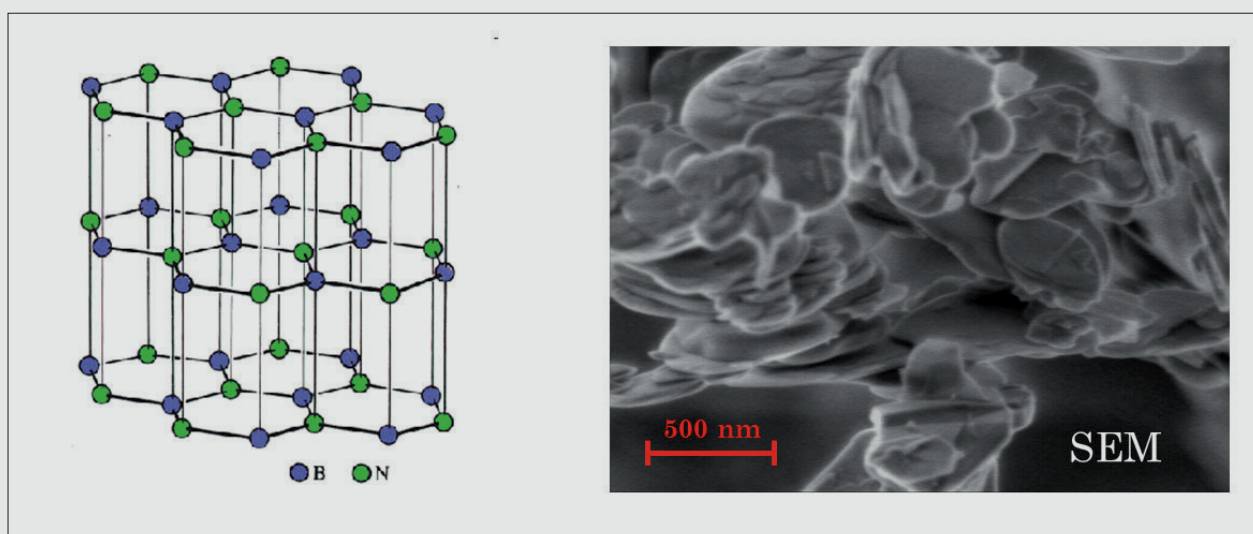


Figure 5: Hexagonal form of boron nitride (left) and SEM image of h-BN (right)

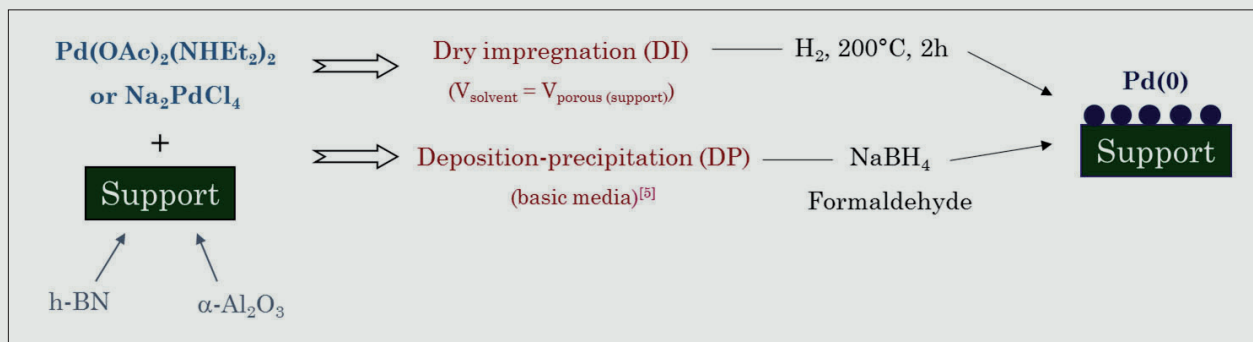


Figure 6: Methodology followed for the preparation of Pd/h-BN and Pd/ α -Al₂O₃ catalysts

The objective was to study the impact of using a very inert support in liquid phase transformations in terms of catalyst preparation, activity, selectivity and stability. Pd/h-BN catalysts have thus been synthesized, and compared to Pd/ α -Al₂O₃ catalysts. The influence of several parameters such as the synthesis method, the nature of precursor or reducing agent, on the structural characteristics and the catalytic performances was investigated following the methodology presented in Figure 6.

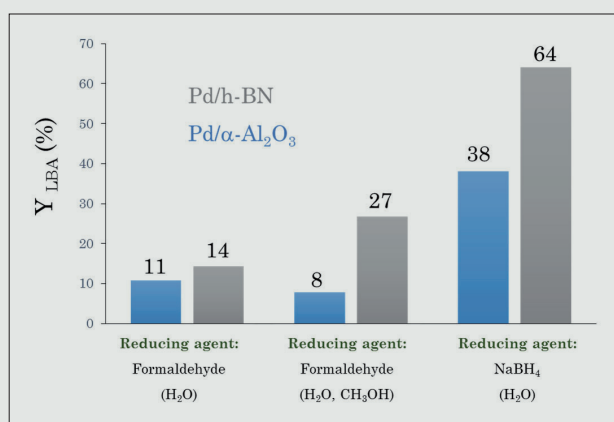


Figure 7: Catalytic results with Pd/h-BN and Pd/ α -Al₂O₃ catalysts prepared by deposition-precipitation with Pd(OAc)₂(NHET₂)₂ as precursor

Some catalytic results are presented in Figure 7. These catalysts were prepared by deposition-precipitation with Pd(OAc)₂(NHET₂)₂ as precursor. In all cases, the selectivity in lactobionic acid was 100 % and Pd/h-BN catalysts presented a yield in LBA superior to their homologues prepared on α -Al₂O₃. Thus we have shown that BN is a promising support to replace alumina or carbon for lactose oxidation. This robust and non-porous support was also shown to be advantageous to avoid internal diffusion limitations when carrying out catalysis in water. Moreover, the absence of hydroxyl groups on its surface permits to

limit side-reactions and guarantees high selectivity together with stabilization of the metal in its reduced form. The activation step could be followed in situ using Raman spectroscopy, which would be much more difficult with carbon used commonly as support in this reaction.

2.1.3. Optimal particle size distribution of Pd/h-BN catalysts [33]

Boron nitride has demonstrated its potential as support for lactose oxidation but the inertia of this support surface makes it difficult to obtain a narrow particle size distribution because no anchoring points are present. Here, the optimal range of particle size and Pd dispersion within Pd/h-BN catalysts for high activity and selectivity in lactose oxidation was investigated. Several parameters in the preparation of Pd/h-BN catalysts were varied in order to obtain samples presenting different ranges of palladium particle sizes. Two synthesis methods were employed: wet impregnation and aqueous impregnation which differ essentially by the impregnation solvent, the precursor nature, and the reducing agent. Indeed, optimizing support/precursor interactions will produce a better distribution of metallic particles on the support.

Very active and selective catalysts were obtained by wet impregnation (WI) and aqueous impregnation (AI) using respectively Pd(OAc)₂(NHET₂)₂ and Pd(NO₃)₂.H₂O as precursors. It was shown for WI catalysts loaded with 5 wt.% Pd, that the hydrophobic/philic character of the impregnation solvent influences greatly the particle size obtained after activation. The higher the hydrophobicity of the solvent, the lower the Pd particle size obtained. When preparing the catalyst in toluene,

lots of particles inferior to 3 nm were obtained, by opposition to the case of water/methanol (Figure 8).

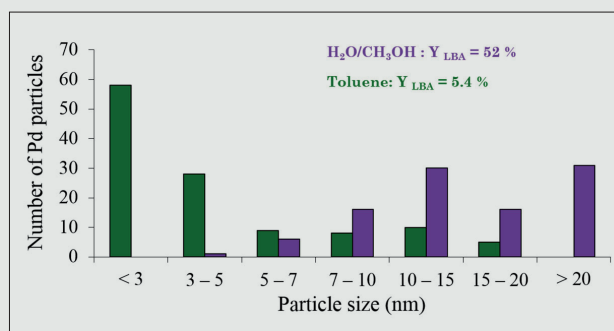


Figure 8: Particle size distribution of catalysts prepared in toluene and in water/methanol mixture

This played a direct impact on the catalytic performances because the yield in LBA was very low in the first case. As shown in Figure 9, the impregnation solvent influences greatly the yield in LBA. The ideal catalyst for this reaction was found to present metallic particle sizes between 3 and 15 nm and no particles inferior to 3 nm. These, when present in more than 10 % of the total, were shown to be detrimental for lactose oxidation. The metallic dispersion has to be comprised between 4 and 8 %, confirming the structure-sensitivity of this reaction.

Several hypotheses can be formulated regarding the fact that particles smaller than 3 nm are detrimental. Indeed, to decrease the particle size implies a variation in electronic and geometric properties of the metallic particles. They present more edges and

corners and are more sensitive to impurities which tend to accumulate on those more reactive sites. In addition, too small metallic particles could prevent a good adsorption of lactose, which is a large molecule.

2.1.4. Au/h-BN for lactose oxydation [34]

After unravelling the structural needs of Pd/h-BN catalysts for the selective oxidation of lactose, gold was chosen as active phase. Gold is known for its surprisingly high activity in heterogeneous catalysis [35], therefore the objective was to combine the high activity of gold with the promising h-BN support in order to optimize the catalytic performances in this reaction. Pd and Au might not function with the same mechanisms hence the conclusions reached for Pd/h-BN cannot be transposed as such to Au/h-BN catalysts.

Au/h-BN catalysts have been prepared by the wet impregnation method (Table 2). After 1h reaction, these Au/h-BN materials were more active than all the Pd/h-BN catalysts described before [30, 33]. The standard tests have shown that we were not in diffusional regime. Several supports have been compared to h-BN: α -Al₂O₃, γ -Al₂O₃ and C_{black}. The catalyst prepared on α -Al₂O₃ is the most active and competitive with the best Au supported catalysts described in the literature (Figure 10) [12].

During their first run, they have all demonstrated 100 % selectivity towards LBA. After a 2nd run, a non-negligible loss of activity was observed except

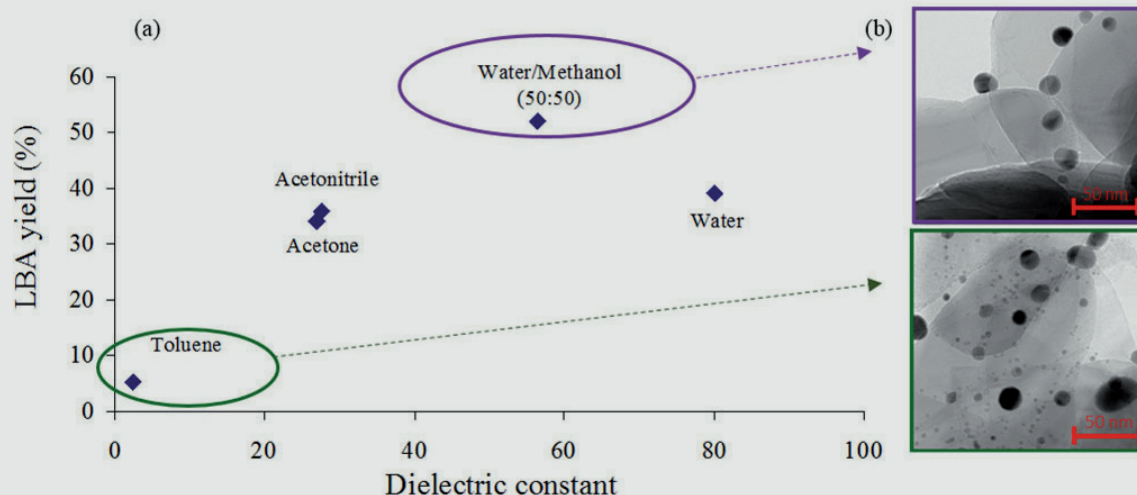


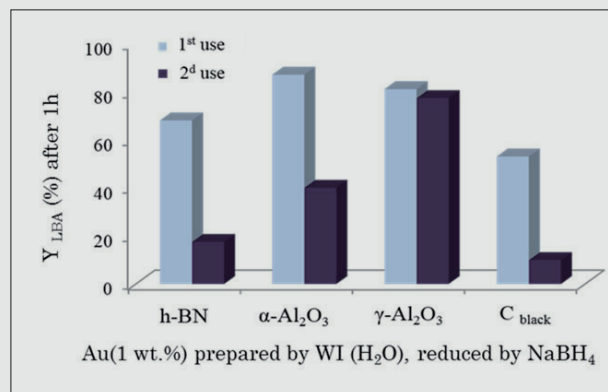
Figure 9: (a) Influence of the impregnation solvent on the catalyst activity and (b) TEM images of catalysts prepared in toluene and in water/methanol

Name	Synthesis solvent	Reducing agent	Au (wt.%)	Time at 100% conversion
Au/h-BN	H ₂ O	NaBH ₄	4.92	2h36
Au/h-BN	H ₂ O	NaBH ₄	1.02	2h

Table 2: Time needed to convert 100% of lactose with Au/h-BN catalysts prepared in water with 5 and 1 wt.% Au.

Figure 10: 1st and 2nd use of Au(1 wt.%) catalysts supported on several supports in lactose oxidation after 1h reaction

for γ -Al₂O₃ (Figure 10). However, the selectivity with this catalyst was not 100% anymore. The causes of deactivation were studied for Au/ α -Al₂O₃ and Au/h-BN. XPS characterization data have shown that a probable poisoning of metallic phase takes place during the catalytic reaction because the atomic O as well as O/B or O/Al ratios increased after one run. The poisoning is more consequent for Au/ α -Al₂O₃ given that the atomic C % also increased after one run. In order to retrieve the effectiveness of the fresh catalysts, thermal and chemical regenerations have been investigated for α -Al₂O₃ and h-BN supported catalysts. Even though the catalysts were not as active as during their first run, the regeneration still allowed catalyzing the reaction with 100 % selectivity in LBA. The thermal regeneration was the most appropriate because it allows cleaning the surface of the actives sites previously poisoned. The Au⁰ oxidation state being relatively non-affected by the reaction, the chemical regeneration failed to restore lost performance, as expected. After thermal regeneration, the catalyst supported on boron nitride presented the highest activity (Figure 11). This could be explained by the presence of oxygenated functions on α -Al₂O₃ which stabilize surface poisons and might hinder cleaning during regeneration.



2.2. Lactose hydrogenation [36]

Boron nitride supported Pd catalysts were prepared by wet impregnation (WI) in various solvents or by aqueous impregnation (AI) followed by thermal activation. The catalysts were characterized by XPS, TEM, powder XRD and CO chemisorption. They were tested in a batch reactor from Parr in lactose hydrogenation (Pressure H₂: 50 bar, T° = 130°C). The reaction mixtures were analyzed by HPLC using two columns in order to detect and separate all the possible by-products.

In this last part, the lactose hydrogenation reaction was studied. Again, the use of boron nitride as support in this reaction was new. Its potential as a catalyst support was evaluated and we have tried to understand the needs in terms of structural properties to obtain good activity and selectivity in lactitol. This study was conducted in direct comparison with the oxidation of lactose in order to assess if a same Pd/h-BN catalyst is able to carry out both transformations. It has to be noted that the major challenge for this reaction is the selectivity. Indeed, as shown in Figure 12, many products can be

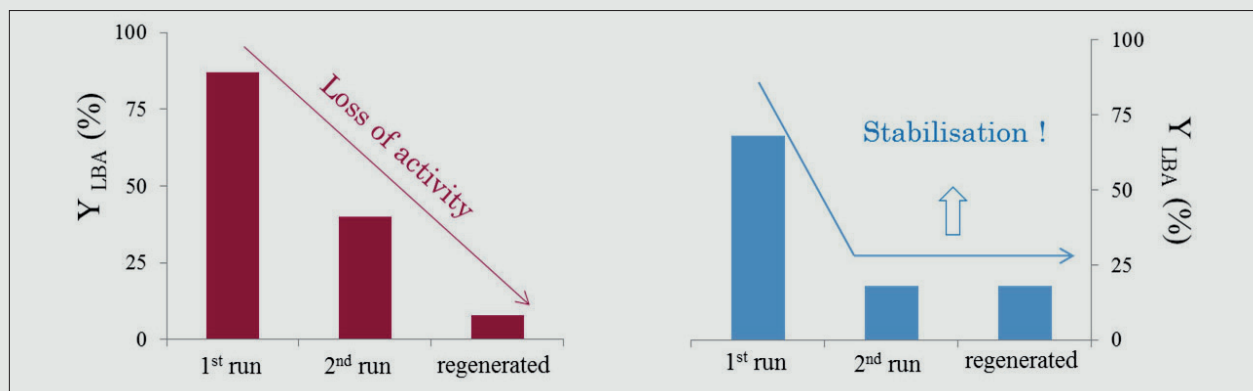


Figure 11: Yield in LBA along the thermal regeneration process for Au/ α -Al₂O₃ (left) and Au/h-BN (right)

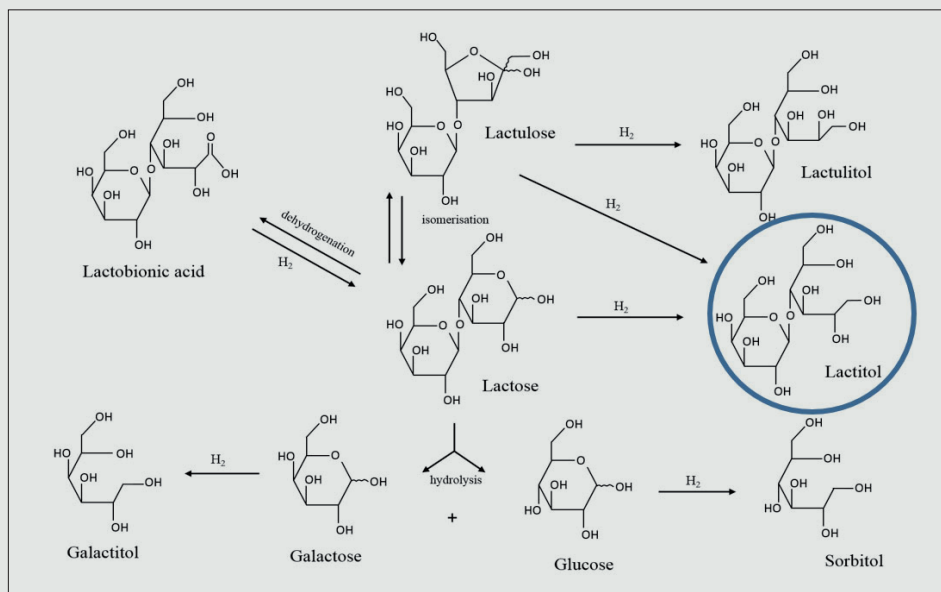


Figure 12: Reactions network of lactose transformations

obtained from lactose. In our case, it is lactitol that we are interested in, finds application principally in the food industry as a sweetener but also in the pharmaceutical industry [17-20].

Lactose conversions were in general higher for the AI catalysts but lactose was preferentially transformed into lactulose followed by lactitol instead of lactitol. Lactulose is interesting as well: it has many applications in food and pharmaceutical industries and moreover, it can be extracted from the reaction mixture and then purified [37, 38]. In all cases, the selectivity in lactitol is higher at low lactose conversion level. It was also shown that the activity and selectivity in lactitol are influenced by the Pd loading, the particle shape and size on the

surface of the support. Indeed, a higher Pd loading is more suitable to obtain higher lactitol selectivity. The palladium dispersion has to be lower than 5 % to obtain a good selectivity.

Previously, it was shown that too small particles were detrimental for the lactose oxidation reaction. In the case of lactose hydrogenation, these particles are also undesired because they present many defects at the surface rendering them more reactive towards H atoms chemisorption. Thus, these small particles are poisoned and become non-reactive. In addition, we discovered for this reaction an influence of the particle shape, triangular pyramid particles being more adapted to obtain selective catalysts than spherical ones, as shown in Figure 13.

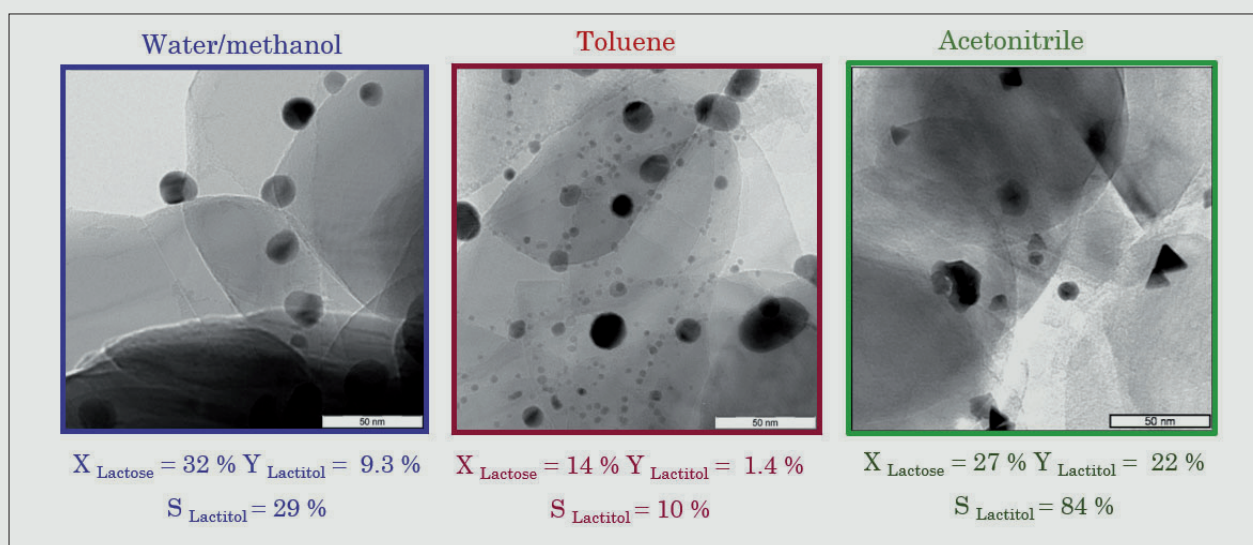


Figure 13: TEM images and catalytic performances in lactose hydrogenation of catalysts prepared in water/methanol, toluene and acetonitrile

The proximity of sugar (adsorbed on the flat terraces) and H atoms (formed on corner and edges) on these particular shaped particles could play a positive role for obtaining lactitol. Finally, the best catalysts obtained in oxidation reaction do not stand out in hydrogenation reaction. This is related to the different mechanisms of both reactions. Indeed, even though similarities exist because lactose oxidation is an oxidative dehydrogenation reaction, this latter is clearly reversible, while lactose hydrogenation is not. Moreover the reaction scheme and in particular the competitive reactions governing selectivity are different.

3. Conclusions

Several important points were unravelled for catalysts applied to lactose transformations. For lactose oxidation, the support employed does not need to be functionalized. Indeed, the support has to be inert, non-porous and without any functional groups at the surface. Boron nitride was shown to be a suitable support for this reaction, even though it is carried out in liquid phase, because it avoids diffusional limitations and side-reactions. Palladium as active phase was able to selectively transform lactose but the particle size distribution has to be comprised between 3 and 15 nm without particle smaller than 3 nm. Gold permits to obtain higher activity than palladium. However, strong deactivation of Au/h-BN catalysts was observed, which could be partially suppressed by regeneration. For hydrogenation, similar particle sizes are needed together with a pyramidal particle shape to obtain high selectivity in lactitol. In conclusion, Pd or Au/h-BN catalysts can transform in water a renewable substrate, lactose, into high added value products: lactitol and lactobionic acid with very high selectivity and reusability.

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