

Faculté des sciences

Synthesis of Gold Nanoparticles Catalysts Supported On Nanostructured Silica

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“ Mettre des citations c’est joli,

mais au final personne ne les lit. »

(A.Engel)

C'est désormais officiel mon mémoire est terminé et me voilà arrivé à la fin de mon cursus en chimie. 5 années se sont écoulées depuis mes débuts à l'université ; 5 années faites de rencontres, d'amitiés et de soirées qui resteront à jamais de bons souvenirs. C'est la fin d'une aventure et, espérons-le, le début d'une autre tout aussi palpitante. Dans les quelques lignes qui suivent, j'aimerais remercier tous ceux qui m'ont aidé pour ce mémoire et tout au long de ces 5 années.

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RÉSUMÉ

L'intérêt porté à la valorisation de la biomasse s'est fortement amplifié depuis quelques décennies. Notamment, le lactose, produit en grande quantité par l'industrie fromagère, est très peu voire pas du tout valorisé. En effet, il existe peu d'applications directes dû à son faible potentiel en tant qu'édulcorant et l'intolérance d'une part importante de la population à ce composé. En revanche, plusieurs produits dérivés du lactose trouvent des applications concrètes, dont l'acide lactobionique. Celui-ci est issu de l'oxydation du lactose et est d'intérêt pour les industries pharmaceutiques, cosmétiques, chimiques et alimentaires. Ainsi, dans cette étude, la synthèse de matériaux à base d'or (connu pour son pouvoir oxydant) permettant de catalyser cette réaction d'oxydation a été entreprise.

Trois morphologies de supports de silice telles que les sphères pleines, les sphères creuses et les nanofibres creuses ont été synthétisées et caractérisées. Mis à part pour les nanofibres, les SEM/TEM ont permis de prouver que ces matériaux ont été obtenus avec la morphologie souhaitée.

Ensuite, de l'or a été déposé sur les sphères pleines de silice via diverses méthodes afin d'obtenir un large panel de taille de particules (de 9-12 à 34 nm). Les imprégnations humides ont donné lieu à des particules de 9-12 nm, l'imprégnation humide suivie d'un lavage à l'ammoniac a donné des particules de 34 nm et la méthode colloïdale des particules de 11 nm. De plus, des catalyseurs de type Au/h-BN ont également été préparés afin d'évaluer l'effet du support. En parallèle de ces synthèses, une nouvelle méthode HPLC a été développée afin de séparer et de quantifier correctement le lactose de l'acide lactobionique et également de pouvoir identifier les différents produits secondaires obtenus lors de la réaction.

Les performances catalytiques de l'ensemble de ces catalyseurs Au/support ont été évaluées. Comparé aux sphères pleines de silice, h-BN s'est révélé être le support le plus approprié pour cette réaction. En effet, une très faible quantité d'acide lactobionique a été produite en utilisant les catalyseurs Au/SiO₂, et ce malgré l'utilisation de particules d'or de tailles variées et la modification des conditions de réaction (masse de catalyseur et température). Cependant, le produit majoritaire, obtenu de manière sélective ($\geq 80\%$), a été identifié comme étant le lactulose, issu de l'isomérisation du lactose en milieu basique. Ce produit a également des applications pharmaceutiques ce qui en fait un produit d'intérêt et ouvre des perspectives futures à ce travail.

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Table of Abbreviations and Units:

AAS	atomic absorption spectroscopy
a.u.	arbitrary unit
BET	Brunauer–Emmett–Teller
BOD	biochemical oxygen demand
°C	celsius degree
CB	carbon black
CNF	carbon nanofibers
CTAB	hexadecyltrimethylammonium bromide
DLS	dynamic light scattering
EtOH	ethanol
equiv.	equivalent
eV	electron-volt
g	gram
h	hour
h-BN	hexagonal boron nitride
HMS	hexagonal mesoporous silica
HPLC	high-performance liquid chromatography
IEP	isoelectric point
IUPAC	international union of pure and applied chemistry
L	litre
LBA	lactobionic acid
MCM	mobil composition of matter
MeOH	methanol
mHSN	mesoporous hollow silica nanofibers
mHSS	mesoporous hollow silica spheres
min	minute
MSNs	mesoporous silica nanoparticles
MSU	Michigan state university
n.d.	not determined
nm	nanometer
NP(s)	nanoparticle(s)

pH	potential of hydrogen
PVA	polyvinyl alcohol
rpm	rotation per minute
RT	room temperature
SBA	Santa Barbara amorphous
SEM	scanning electron microscopy
T	temperature
TEM	transmission electron microscopy
TEOS	tetraethyl orthosilicate
TGA	thermogravimetric analysis
wt.	weight
XPS	X-ray photoelectron spectroscopy
XRPD	X-ray powder diffraction

INTRODUCTION

1.1 Valorisation of Lactose

Since few decades, the use of biomass as raw material has become of great interest from a sustainable development perspective for its renewability, abundance and worldwide distribution capacity. From a source of energy to intermediate building blocks for the synthesis of high value-added products, biomass has a wide range of possible applications ^[1]. Biomass is characterized by a high carbohydrate content. These compounds represent one of the most important sources of renewable materials for their large availability, high framework complexity and independency from fossil energies ^[2-3]. Sometimes, conversion of biobased carbohydrates into value-added molecules requires pre-treatment of the biomass due to chemical, structural, or physiochemical hindrance. In such cases, biological (enzymes), chemical (alkaline, acid, oxidising agent or solvent extraction), physical (milling, irradiation or pyrolysis) and physico-chemical (steam explosion, hydrothermolysis or wet oxidation) pre-treatments can be applied ^[4-5]. Then, selective oxidation or hydrogenation of isolated sugars, such as fructose, cellobiose, glucose and lactose, have been the subject of much investigation ^[6]. In this context, the use of lactose as starting material for high value-added products is of high industrial interest.

Indeed, the dairy industry produces huge amounts of whey with 190 million tonnes of whey wastewater each year worldwide ^[7]. Whey is a liquid by-product generated from cheese manufacturing which represents 85-95% of the milk volume and 55% of the milk components ^[8]. The cheese whey contains, among other things, 5% of lactose. Therefore, it is approximatively 8 million tonnes of lactose produced each year from cheese whey, of which only about 400,000 tonnes are processed further ^[9]. Lactose in itself has some applications such as diluent in tablets and carrier of medicines in the pharmaceutical industry or as food additive, beverages and confectionery products ^[10-11]. However, because of its low sweetness and solubility, as well as the intolerance of some population segment to it, the use of lactose is limited in many applications ^[2, 9, 11-12]. Moreover, the biochemical oxygen demand (BOD) of

cheese whey is very high (52-56 g/kg) mainly due to its lactose content ^[8, 13]. This means that 52-56 g of dissolved oxygen is consumed by aerobic biological organisms per kilogram of cheese whey to break down the organic molecules it contains. Hence, it is a major environmental problem if it is disposed of as a waste ^[8]. As a consequence, due to its large-scale production and its few possible applications, lactose is a low-cost product. Therefore, the research of innovative processes for transforming lactose into value-added derivatives in the food and pharmaceutical industries is of great interest ^[2, 9-10, 12, 14]. Some of the valuable derivatives which can be obtained from lactose are epilactose, galacto-oligosaccharides, lactitol, lactobionic acid, lactosucrose, lactulose, sialyllactose and tagatose (Processes detailed in Figure 1.1) ^[2, 10, 14]. Lactulose (isomerization), lactitol (hydrogenation) and lactobionic acid (oxidation) are the industrially most important lactose derivatives ^[9].

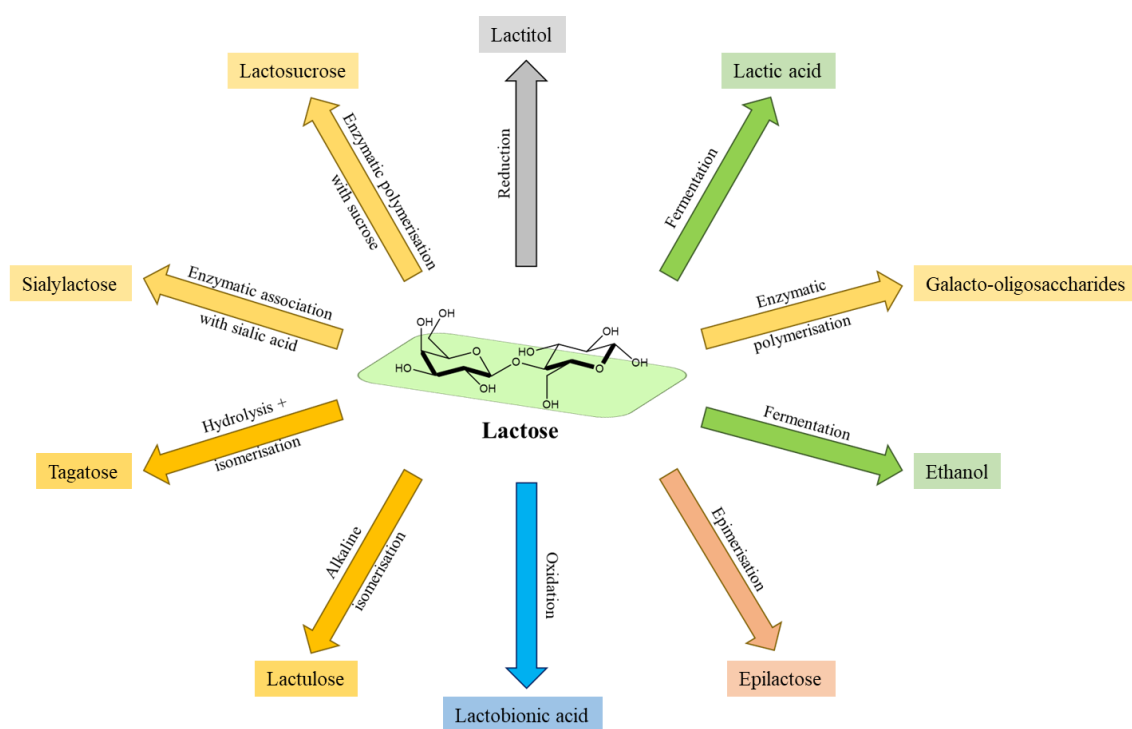


Figure 1.1 Scheme of lactose derivatives and their related production processes: fermentation (green), oxidation (blue), reduction (grey), epimerisation (red), enzymatic (gold), isomerisation (orange). Adapted from ^[11].

Among the lactose derivatives presented in Figure 1.1, lactobionic acid (4-O- β -D-galactopyranosyl-D-gluconic acid) (LBA) is the one with the highest added value and the second one regarding the market share (Figure 1.2). This organic acid is a disaccharide formed from gluconic acid and galactose units which can be produced from lactose by oxidation of the aldehyde group of its glucose moiety ^[10, 12]. All of this supports the idea of converting lactose into LBA from an economic point of view. Moreover, from a more practical perspective, LBA has applications in food, medicine, pharmaceutical, chemical and in cosmetic industries due to its antioxidant, chelating, humectant, biocompatibility, nontoxicity, biodegradability and amphiphilic properties ^[2, 12, 15-16]. The first synthetic production of LBA was conducted in 1889 by Fisher and Meyer by oxidising lactose with bromine ^[17]. Since then, many different processes such as biocatalytic, chemical, electrochemical and heterogeneous catalytic oxidations have been implemented for the production of LBA ^[11-12, 16].

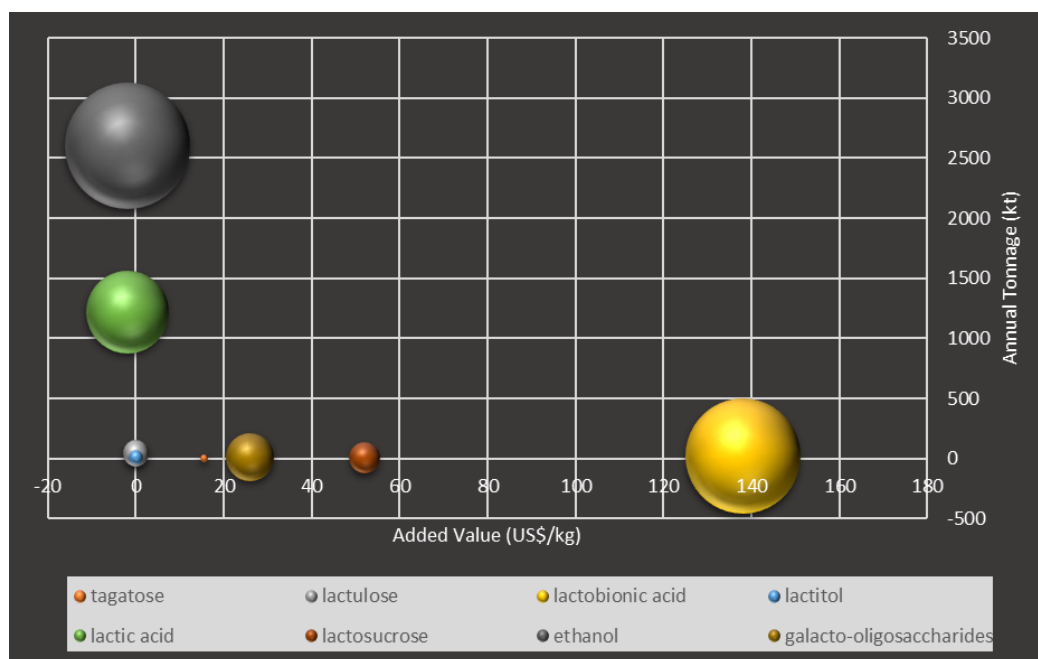


Figure 1.2 Plot of annual tonnage (kt) versus added value (US\$/kg) of the different derivatives manufactured from lactose. The size of the spheres is proportional to the market share of the different derivatives. Price data are based on the API reference prices ^[18] and prices advertised on the Alibaba website ^[19]. Annual tonnage data are compiled from ^[20-22].

1.1.1 Biocatalytic Oxidation

The biocatalytic production of LBA is based on the oxidation of lactose by using specific enzymes or microorganisms as biocatalysts. The production of LBA by bacteria was first discovered in 1947 by Stodola and Lockwood after a wide screening for LBA-producing ability in *Pseudomonas* species. Since then, many different microorganisms have been tested for LBA production. Nevertheless, microbial production of LBA results in a difficult purification process compared to enzymatic methods. Therefore, industrial implementation of microbial methods faces strong challenges, which may delay the application of these processes ^[16, 23]. Several enzymes such as lactose dehydrogenase from *Pseudomonas graveolens*, cellobiose dehydrogenase from *Sclerotium rolfsii*, glucose-fructose oxidoreductase from *Zymomonas mobilis* and hexose oxidases from red algae can serve as biocatalysts for the oxidation of lactose ^[15, 24]. The main reaction mechanism involves the formation of lactobiono- δ -lactone as an intermediate product followed by hydrolysis of this intermediate to form LBA (Figure 1.3) ^[11, 15-16, 23-24].

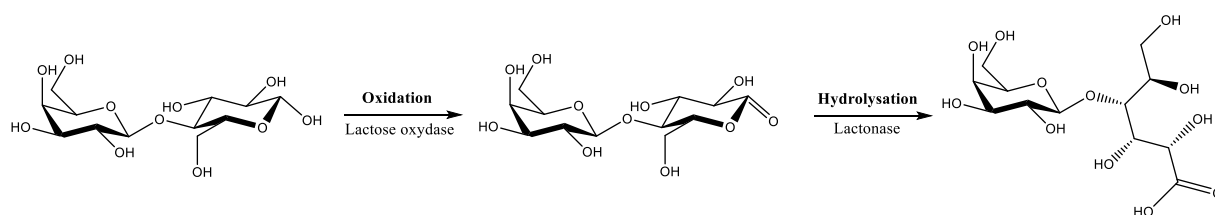


Figure 1.3 Schematic pathway for biocatalytic oxidation of lactose into LBA.

The process is generally managed between 25 and 50 °C at a constant pH value (pH ~ 6) and can yield 75-100% LBA using enzymes from *Pseudomonas*, *Zymomonas* and *Burkholderia* species ^[11, 16].

1.1.2 Electrochemical Oxidation

In 1934, Isbell patented production of calcium lactobionate by using graphite electrodes in the presence of bromide and calcium carbonate ^[25]. Thereafter, this patent has been improved by Magariello and Islip by approaching 98% yield using graphite electrodes, iodine or bromine as catalysts and calcium carbonate to maintain the solution at a pH above 5.2 to reduce side reactions and decomposition of lactose ^[26]. Since then, studies performed by Druliolle's group identified lactone as the primary reaction product, which further undergoes hydrolysis in aqueous medium to give LBA ^[27]. This group demonstrated that high yields and selectivities

(close to 100% for both) can be attained toward LBA using platinum, lead-adatoms modified platinum and gold electrodes in alkaline media. They suggested that gold could be the best electrocatalyst for the oxidation of sugars since it reaches higher current densities, suffers less from poisoning than platinum and exhibits high catalytic activity in alkaline media ^[27-28]. A more recent publication by Kokoh and Alonso-Vante in 2006 confirmed that the use of electrodes modified by gold nanoparticles ensures good selectivity and yield toward LBA (yield of 91%) ^[29]. Nonetheless, publications regarding the electrochemical production of LBA are still scarce ^[11].

1.1.3 Heterogeneous Catalytic Oxidation

Heterogeneous catalysts have the advantage to be easily separated from the reaction mixture, while the disadvantages are often connected to limited activity and selectivity. In 1990, Hendriks *et al.* performed the first successful heterogeneous catalytic oxidation of lactose on palladium and bismuth-palladium supported catalysts. They studied the selectivity of sodium lactobionate at 80% conversion under different pH (6-11) and temperature (40-70 °C) conditions. The optimum (with 100% selectivity) was found to be between pH 7-10 and at a temperature of 40-60 °C ^[23]. Since then, platinum, palladium and bismuth-palladium catalysts have been investigated for the oxidation of lactose with conversions and selectivities close to 100% ^[11, 30]. Nevertheless, bismuth-containing catalysts are not suitable for the production of chemicals for the food and pharmaceutical industries since bismuth is prone to leaching ^[12]. Another main problem encountered in oxidation reactions is deactivation by over-oxidation of these catalysts. Indeed, the poisoning of the catalyst is attributed to a side relaxation process in which oxygen adatoms are slowly transformed into inactive subsurface oxygen ^[31-32]. This is why it is important to control the oxygen concentration in the reaction media. Moreover, undesirable by-products such as lactulose and 2-keto LBA can be produced in function of the activity and selectivity of the catalysts employed and of the reaction operation conditions (Figure 1.4).

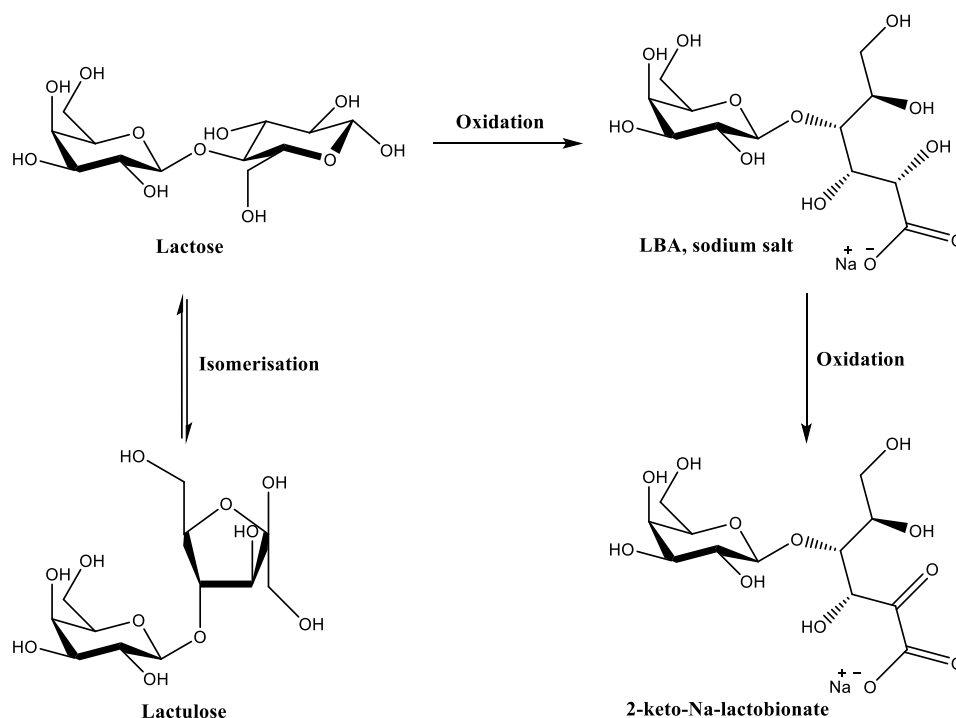


Figure 1.4 Schematic catalytic oxidation of lactose to LBA under basic conditions (using NaOH as base).

In order to obtain LBA selectively, the reaction must be conducted at atmospheric pressure in a temperature range of 50-70 °C and in an alkaline medium (pH between 8.0 and 9.0) using air or oxygen as oxidant. Higher pH values decrease the selectivity since isomerization of lactose to lactulose is then favoured whereas lower pH values increase the risk of poisoning of the catalyst by adsorption of the reaction products on its surface ^[11, 30].

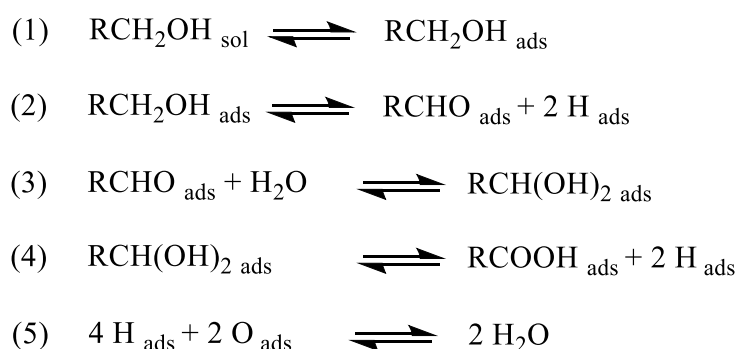
Recently, the oxidation of lactose has been investigated over gold catalysts ^[2, 6, 9, 14, 30, 33-34]. Gold catalysts exhibit very high stability against over-oxidation and exceptional activity and selectivity toward LBA, outperforming palladium or platinum-based catalysts ^[9, 11]. However, only a few papers about oxidation of lactose over gold catalysts have been published. The catalytic performances obtained with several gold catalysts are summarized in Table 1.1.

Table 1.1 Production of LBA by oxidation of lactose over gold supported catalysts.

Catalyst	Conversion (%)	Selectivity in LBA (%)	Reaction time (min)	References
2% Au/CeO ₂	100	~ 95	~ 150	[9]
0.7% Au/SiO ₂ -CeO ₂	100	100	100	[30]
0.7% Au/SiO ₂	100	100	100	[14]
1% Au/TiO ₂	100	~ 90	200	[33]
1.0% Au/h-BN	100	100	120	[2]
1.0% Au/ α -Al ₂ O ₃	100	100	93	[2]
1.0% Au/ γ -Al ₂ O ₃	100	100	106	[2]
2% Au/ γ -Al ₂ O ₃	100	n.d.	125	[6]
1.0% Au/CB	100	100	162	[2]
0.5% Au/ZnO	98.7	97	492	[34]
2% Au/MgO	99.8	99	600	[34]

1.2 Mechanism of Catalytic Oxidation of Sugars over Noble Metal Catalysts

Since 1957, it is generally accepted that liquid-phase oxidation on noble metal catalysts proceeds via an oxidative dehydrogenation mechanism [30, 32, 35-36]. The proposed reaction steps are the following:



The first step corresponds to the adsorption of the sugar on the surface of the catalyst; more specifically on the metal atoms with low coordination numbers (1) followed by transfer of two hydrogen atoms to the metal which leads to formation of the lactone (2) [32, 37]. The resulting lactone is subsequently hydrolysed to give the corresponding geminal glycol (3) [37]. Then, a second transfer of hydrogens leads to the aldonic acid (4) [32, 36-37]. Finally, the activated

hydrogens are oxidised by dissociatively adsorbed oxygen, forming water (5) ^[35-36]. In this mechanism, oxygen is not directly oxidizing the sugar molecule, but serves to regenerate the active catalytic surface. As mentioned above (section 1.1.3), noble metal catalysts such as platinum and bismuth are vulnerable to overoxidation due to oxygen atoms forming subsurface oxygen by penetrating the most external layers of the metal crystals ^[31-32]. Although the oxidative dehydrogenation mechanism is widely accepted, the precise mechanism is still under debate due to the doubt that hangs over the nature and concentration of the adsorbed species ^[32, 36]. Indeed, the nature of the adsorbed species mainly rely on the pH value of the reaction medium, the rate of oxygen supply and the acidity of the catalyst ^[32, 36-38]. Alternative mechanisms such as a pure auto-oxidation involving a peroxide intermediate ^[35], a spontaneous dehydrogenation ^[39] and the direct involvement of the oxidizing species in the rate determining step of dehydrogenation ^[37] have been proposed.

As far as we know, only one report (third line in Table 1.1) uses silica as support, even if it gives excellent results. Promoting silica support by gold seems to be an interesting alternative to avoid the kind of drawbacks described previously ^[9, 11]. Therefore, there is room for fundamental investigations to study mechanisms and structure/activity relations of this particular class of catalysts in this reaction, and this will be the topic of this Master Thesis. In particular, introducing mesoporosity in silica supports is worth examining. Indeed, owing to their high surface area, great thermal stability, highly ordered structure and excellent mechanical properties, mesoporous silicas are considered very attractive as supports ^[14, 40]. Moreover, the mesoporosity is known to improve the diffusion performance of catalysts ^[41]. Several morphologies of support and methods of deposition of gold on silica will therefore be presented in the next section of this Introduction chapter, even if these materials were most of the time designed for other reactions.

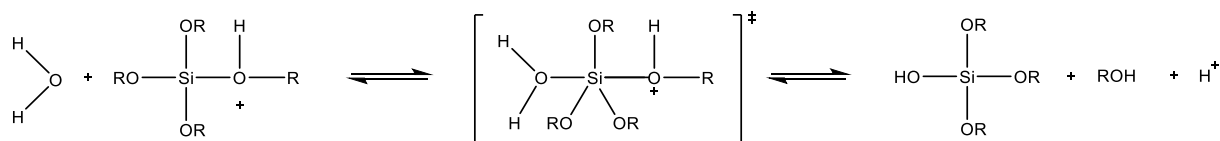
1.3 Characteristics and Synthesis Methods for Mesoporous Silica Supports

In this section, general aspects of silica materials will be described. The sol-gel method as well as the mechanism involved in this particular synthesis will be presented. It will be followed by a discussion about the introduction of mesoporosity in silica materials and finally a description of some possible ways to control the size and shape of the silica particles.

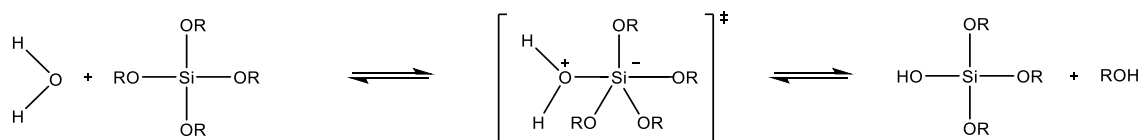
1.3.1 Silica Synthesis by the Sol-Gel Method

Silica is a simple solid inorganic oxide, of chemical formula SiO_2 , that is ubiquitous in nature but can also be prepared in the laboratory, with control over grain sizes, shape and/or porosity. Several methods exist to form metal oxide nanoparticles (NPs), among which the sol-gel process permits the preparation of monodisperse nanometric silica particles with a controlled size and morphology^[42]. Ways to control the porosity in the mesoporous range will be covered in the next section (1.2.2). The sol-gel method applied for silica NPs involves hydrolysis and subsequent condensation of a silicon alkoxide precursor under acid or basic conditions. It is carried out in solution (forming a *sol* with reactants and intermediates) and the product solidifies by forming a 3D-connected network of Si entities (*gel*) that can be further dried or calcined (heated under air) to give the final oxide powder. This method has the advantage of producing monodisperse particulate suspensions which avoids biased evaluation and interpretation of the characterization data based on shape distributions^[43]. The reaction mechanism is very different under acid, neutral or basic conditions and leads to products that are structurally different (Figure 1.5)^[42, 44-45].

a)



b)



c)

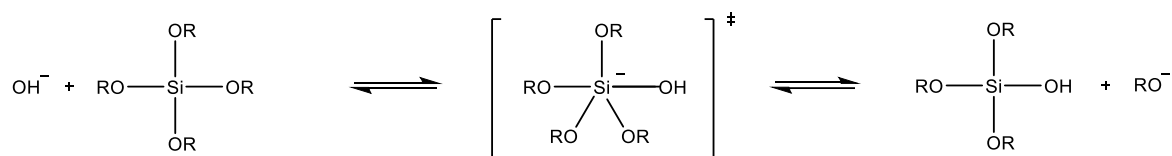
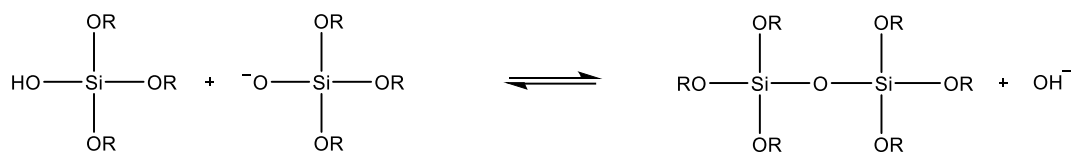


Figure 1.5 Hydrolysis mechanism of silicon alkoxide under (a) acidic; (b) neutral and (c) basic conditions ^[45-47].

Under acid conditions (Figure 1.5a), the silicic precursor is protonated and then the hydrolysis is speeded up due to the formation of an alkoxonium which is a good leaving group ^[47]. However, the rate of the hydrolysis reaction will slow down as the number of hydroxyl groups carried by the precursor is increasing since the silicon atom becomes more electrophilic ^[47]. Without acid or basic catalyst (Figure 1.5b), the gelation occurs slowly as a result of the extremely slow rate of hydrolysis at neutral pH ^[46]. This is due to the fact that water is a weak nucleophilic agent and alkoxy a poor leaving group ^[48]. Under basic conditions (Figure 1.5c), the hydrolysis is also speeded up since hydroxyl ions are more effective nucleophiles compared to water molecules ^[48-49]. In contrast to acidic conditions, the reactivity of the precursor increases after each hydrolysis step thanks to the increase in its electrophilic nature ^[45].

a)



b)

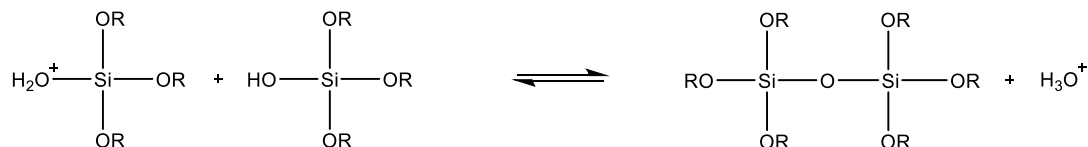


Figure 1.6 Condensation mechanism of alkoxy silane under (a) basic and (b) acidic conditions [50].

Under basic conditions, the silanol proton is abstracted by hydroxide ion leading to the formation of water and siloxide ion. In a second step, a $\text{S}_\text{N}2$ attack of the siloxide ion on the silicon center of silanol takes place forming a siloxane linkage and regenerating the hydroxide ion (Figure 1.6a). When an acid is used as catalyst, the condensation consists in a protonation of the silanol group, followed by the formation of a siloxane bridge between a protonated silanol group and an unprotonated one via the loss of a hydronium cation (Figure 1.6b) [50]. Condensation results in the formation of small oligomeric species which can condense with each other to give a polymer-like network [47].

As a consequence of all the aspects mentioned above, the hydrolysis of the precursor is linearly proportional to acid and base concentration and has a minimal rate at neutral pH (Figure 1.7) [46].

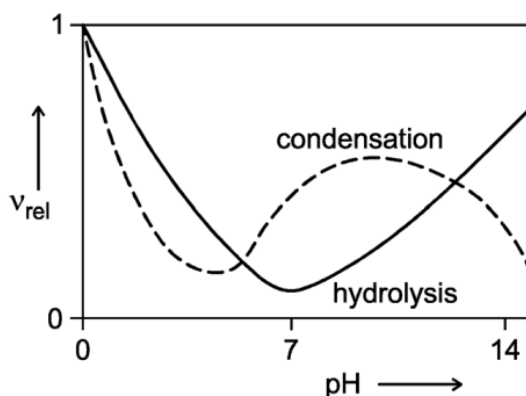


Figure 1.7 Relative rates of silicon alkoxide hydrolysis and condensation as a function of the pH value.

Moreover, the condensation rate of silicon alkoxides is also pH sensitive with a minimal value at pH 1.5-4.5 which corresponds to the isoelectric point of silica. Silica is not very reactive in this pH range since it is therefore neutral [42, 45, 47, 50-51]. By comparing hydrolysis and condensation, we notice that at pH < 5 the hydrolysis is favoured and the condensation is the rate-determining step, whereas at pH > 5 the condensation is favoured and the hydrolysis becomes the rate-determining step [47]. Therefore, at pH < 5 a large number of monomers or small oligomers are simultaneously formed presenting reactive terminal Si-OH groups allowing the condensation of clusters among each other and then the formation of a polymer-like network [47]. On the opposite, at pH > 5 hydrolysed species are immediately consumed to form larger silica NPs by reaction with existing clusters which favours large, bulky and ramified structures (i.e. more highly condensed structures) [42, 47]. Under strongly alkaline conditions (pH > 10), silica particles tend to redissolve by Si-O-Si bond cleavage [47, 51].

1.3.2 Introducing Mesoporosity in Silica Supports

According to the IUPAC definition, pores with widths not exceeding 2 nm are called micropores, intermediate ones comprised between 2 and 50 nm are mesopores and those larger than 50 nm are macropores [52].

Even if the discovery of mesoporous silica nanoparticles (MSNs) dates back to the late 1970's, their first synthesis was achieved in 1992 by Mobil Research and Development Corporation from aluminosilicate gels using a liquid crystal template mechanism. The material obtained with a hexagonal arrangement of the mesopores was designated as MCM-41 (mobil composition of matter No. 41). Based on the sol-gel process and by using ionic surfactants to create porosity, various other mesoporous materials have been synthesized, such as MCM-48 (with a cubic arrangement) and MCM-50 (with a lamellar arrangement) giving rise to the M41S family. The synthesis of the M41S materials is based on the sol-gel process with the use of ionic surfactants as soft-template to control the pore morphology [45, 53]. Specifically, a cationic surfactant such as hexadecyltrimethylammonium bromide (CTAB) is needed to prepare M41S materials [53]. As mentioned above (section 1.3.1), the nature of the silica solid surface is pH sensitive (with an isoelectric point at around pH 2) and therefore the electrostatic interactions between the surfactant and the silica precursor differ depending on the pH value. At pH below 2, the silica precursor is positively charged whereas at pH above 2 it is negatively charged. Hence, it is important to adapt the pH value to the surfactant used [45, 53]. After this breakthrough, numerous MSNs families have been conceived such as the SBA (Santa Barbara amorphous) (which

includes SBA-1, SBA-2, SBA-3, SBA-6, SBA-8, SBA-11, SBA-12, SBA-14, SBA-15, SBA-16), the HMS (hexagonal mesoporous silica), the MSU (Michigan state university) and many others, by varying the starting precursor (TEOS, TMOS, *etc.*), the surfactant (anionic, cationic or neutral) and reaction conditions (pH, temperature, concentrations, *etc.*). The most commonly used types of MSNs are MCM-41, MCM-48 and SBA-15 (Table 1.2 and Figure 1.8) with possible applications as drug carriers, biosensors, catalysts, adsorbents and energy storage devices due to their highly ordered structure, large pore size, and high surface area [11, 45, 50, 54-57].

Table 1.2 List the most used MSNs and their textural properties: pore symmetry, pore size (nm) and total pore volume (cm³/g).

MSN family	MSN type	Pore Symmetry	Pore size (nm)	Total pore volume (cm ³ /g)	References
M41S	MCM-41	2D hexagonal <i>P6mm</i>	2-10	0.7-1.56	[11, 55, 58-60]
	MCM-48	3D cubic <i>Ia3d</i>	2-5	0.5-0.8	[55-56, 58, 60]
SBA	SBA-15	2D hexagonal <i>P6mm</i>	5-30	0.56-2.5	[58-59, 61]

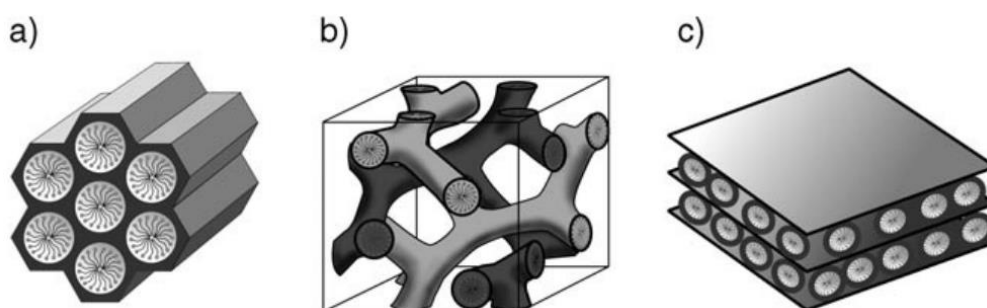


Figure 1.8 Structures of (a) MCM-41/SBA-15; (b) MCM-48; (c) MCM-50 [53].

Fine tuning of the pore size and shape can be controlled by using different surfactants as soft templates [45, 53]. For instance, by the use of pluronics, larger pores are obtained giving rise to the SBA-15 MSN [53, 61]. The micelle shape in solution and therefore the resulting material mesophase can be predicted by the stacking parameter (*g*) which is calculated by the following equation:

$$g = \frac{v}{l_0 \times a_0} \quad (\text{Equation 1.1})$$

where V represents the volume occupied by the hydrophobic head of the surfactant, a_0 the surface occupied by the hydrophilic head and l_0 the kinetic length of the hydrophobic tail ^[45, 57, 62]. Table 1.3 highlights the relationship between the shape of the micelles, the mesophases and the MSNs produced as a function of the range of values of the g parameter ^[45, 57].

Table 1.3 Link between the stacking parameter g and the resulting mesophase.

Stacking parameter	Micelle shape	Mesophase	Examples of MSNs
$g < 1/3$	spherical	cubic	SBA-1, SBA-6
$1/3 < g < 1/2$	cylindric	2D hexagonal	MCM-41, SBA-3, SBA-15
$1/2 < g < 2/3$	3D cylindric	cubic	MCM-48
1	lamellar	lamellar	MCM-50

It should be mentioned that in aqueous solution, surfactants can also adopt different mesophases depending on their concentration ^[45, 53, 57] and that the necessary micelles are only formed above a certain critical value of concentration.

1.3.3. Control of Silica Particle Sizes and Shapes

Now that we have seen how to use the sol-gel method to form silica particles, and how to introduce porosity thanks to the addition of surfactants, we will now focus on variations of particles sizes but also shapes and possible introduction of void spaces in their cores. This latter idea allows diminishing even more diffusional limitations as the support particles would be made only of a mesoporous shell.

1.3.3.1 Synthesis of Full-Spheres with Controlled Sizes

The Stöber process was developed in 1967 by Werner Stöber, Arthur Fink and Ernst Bohn which were able to obtain spherical silica particles ranging from 50 nm to 2 μ m in size using this method ^[43]. This chemical synthesis is a sol-gel reaction involving a mixture of water and low-molecular-weight alcohol (methanol, ethanol, n-propanol or n-butanol) as solvent, a tetra-alkyl silicate as silica precursor and ammonium hydroxide as base catalyst ^[43]. Tetraethyl orthosilicate (TEOS) is one of the most used silica precursor for this synthesis ^[50]. The final size and shape of the silica NPs depends on the ammonium hydroxide to alcohol ratio, the reaction time, the temperature, the nature of the silica precursor and alcohol chosen ^[42-44]. As just mentioned, the ammonia to alcohol ratio is an important parameter: the higher the ammonia

concentration, the bigger the particles. Furthermore, the rate of the reaction is sensitive to the nature of the alcohol used. Indeed, the rate is faster with methanol whereas it is slower with n-butanol as solvent. The size of the silica nanoparticles is also influenced by the choice of alcohol, the nanoparticles being smaller with methanol than with n-butanol under the same synthesis conditions. A similar relationship is observed between tetramethyl ester and tetrapentyl ester as silica precursors with a slower rate and bigger particles obtained with the latter ^[43]. Due to their uniform size, spherical shapes and the possibility of fine-tuning their size by changing the experimental parameters, these kinds of NPs have been valorized in many applications such as in ceramics, catalysis, chromatography, paint and pharmaceutical industries, optical imaging and in high-tech computers ^[49].

In this work, we will use the Stöber process for the synthesis of monodispersed full-filled spherical silica NPs (Figure 1.9) ^[42-43, 49]. These SiO₂ particles mainly comprise micropores and mesopores together with some macropores ^[63-64].

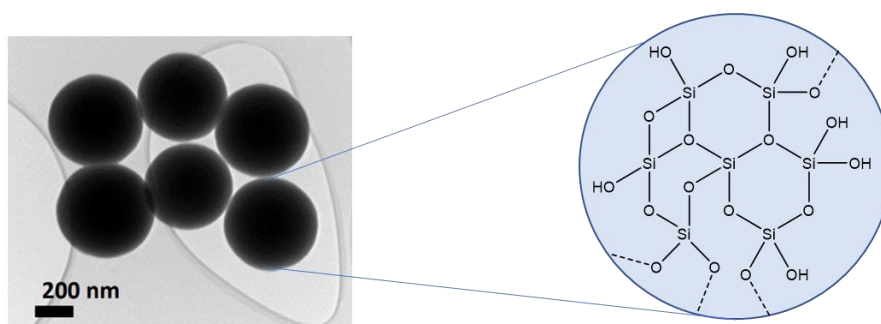


Figure 1.9 TEM image of silica NPs produced using the Stöber method and schematic representation of the silica network. Adapted from ^[65].

1.3.3.2 Synthesis of Hollow Mesoporous Structures

Hollow nanostructures, which consist in an interior void cavity separated from atmospheric air by a solid shell, have many possible applications in electronics, energy, biomedical and catalysis fields due to their exceptional properties such as lightweight, high specific surface, low thermal conductivity, high rate of mass transfer, *etc.* ^[66-67]. Hollow structures are also relevant for electrocatalysis, enzymatic, heterogeneous and homogeneous catalysis as catalyst supports or nanoreactors. Since it is possible to isolate by compartmentalisation catalytic functions that would normally be incompatible, this type of catalyst has excellent prospects for carrying out cascade reactions. Most of the studied hollow materials are spherical but this

morphology is not mandatory for many applications ^[67]. The interest in this type of materials has grown significantly over the past decade (Figure 1.10). In this project, we aim to synthesize mesoporous hollow silica spheres (mHSS) and mesoporous hollow silica nanofibers (mHSN) with a mesoporosity of M41S type and a mixture of M41S and SBA-15/16 phases respectively in the shell.

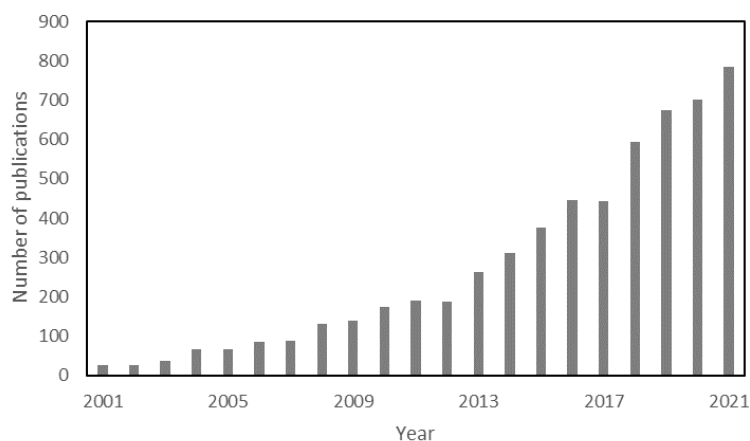


Figure 1.10 Evolution of the number of publications containing the words “hollow” and “catalyst” over the last 20 years. Data compiled from Scopus database.

Hollow structures of silica can be prepared by different strategies, which very often involve using the sol-gel method in the presence of a sacrificial nano-object that will be removed in the end to liberate the inner void. The nano-object plays therefore the role of a hard template and is coated by silica in the first steps. By adding a surfactant to the silica precursor, this coating can easily be made mesoporous, but the surfactant soft template has then to be removed as well.

The method that we have considered in this Thesis is using carbon black (CB) or carbon nanofibers (CNF) as hard-template to produce mesoporous hollow silica spheres (mHSS) or mesoporous hollow silica nanofibers (mHSN), respectively (Figure 1.11). This synthesis, based on the PhD thesis work of Tommy Haynes, developed in our lab at UCLouvain, consists in three main steps as follow ^[45]:

- (i) CB/CNF serves as anchoring site for developing a mesoporous silica layer.
- (ii) The soft-template (CTAB) is removed by heating the material under refluxing conditions.
- (iii) The hard-template (CB/CNF) and the remaining surfactant are removed by means of calcination at high temperature (600/800 °C).

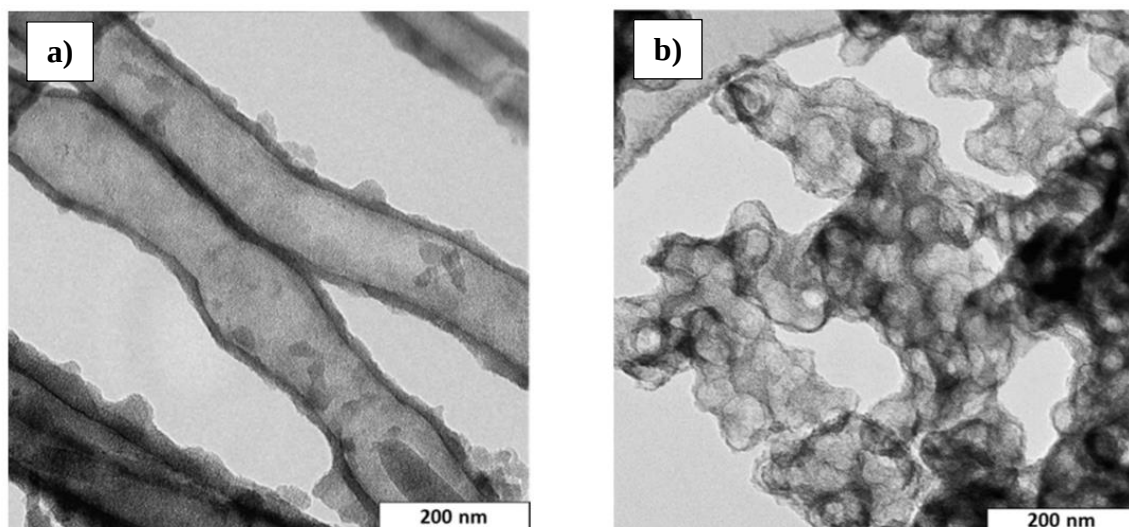


Figure 1.11 TEM images of the mesoporous hollow structures obtained by Tommy Haynes: (a) mHSN; (b) mHSS ^[45].

In the last section of this Introduction, we will now cover methods to decorate silica supports with small gold particles, as active sites for catalytic transformations. In heterogeneous catalysis, supported particles usually have to be below 10 nm in sizes to be active, and this is particularly true for gold ^[68].

1.4 Synthesis of Gold on Silica Catalysts

1.4.1. Interactions Between the Silica Surface and Gold Species

It has been recognized by several authors that the formulation Au/SiO₂ is particularly challenging to obtain ^[14, 69-71]. Indeed, gold has a tendency to form larger particles on silica than on other oxide supports such as titania. It has been demonstrated that interaction between any oxide support and HAuCl₄ (a very common gold precursor, and the one used in this work) proceeds via anionic adsorption. Therefore, the isoelectric point (IEP) of the support is crucial to determine the conditions for the preparation of the gold supported catalysts ^[69]. Given that for SiO₂ IEP $\approx$ 2, this support is positively charged at pH < 2 and negatively charged at pH > 2 ^[11, 42, 47, 51, 72]. Since the gold species are negatively charged whatever the pH value, the silica must be positively charged to ensure good interactions. This means that the synthesis of silica-supported gold catalysts must be carried out at pH < 2 (Figure 1.12) ^[73].

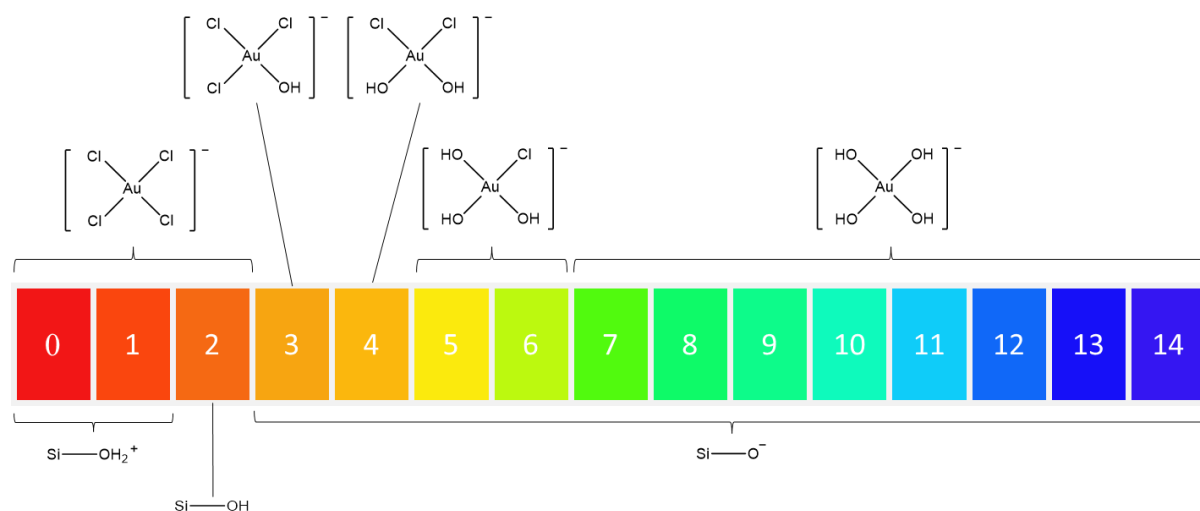


Figure 1.12 Effect of the pH value on the silica and gold species in aqueous solution ^[51, 69].

In the resulting catalyst, it has been proposed that the gold atoms at the boundary between the support and the gold nanocrystals are in a cationic form: Au^+ or Au^{3+} ^[32, 72, 74-75]. The formation and stabilisation of these $\text{Au}^{\delta+}$ species is dependent of the size of the silica NPs: the smaller they are, the more stable the $\text{Au}^{\delta+}$ species are ^[75]. Au^{3+} ions can enter the oxide lattice of the support and create anion vacancies close to the gold nanocrystals which can serve to adsorb and activate oxygen. However, this oxygen activation mechanism is not true for ceramic oxides like silica since they are not reducible and therefore cannot follow a Mars-van Krevelen type mechanism ^[74]. Regarding the gold atoms in the bulk and on the surface, these are of Au^0 nature provided that the particle is larger than 3 nm ^[32, 76]. Studies made on gold deposited on silica NPs underlines the thermal stability and resistance to sintering of this kind of catalysts after UHV annealing to 600 K ^[75].

1.4.2 Gold Deposition Methods

Gold NPs can be synthesised via different methods such as deposition-precipitation (DP), direct anionic exchange (DAE), chemical and physical vapor deposition (CVD and PVD), preparation of colloidal gold NPs and impregnation ^[77]. This section aims to present the latter two methods, which will be both used in this work.

1.4.2.1 Impregnation

This preparation technique is divided into two different methodologies: (i) dry impregnation (DI) also called incipient wetness impregnation (IWI) and (ii) wet impregnation (WI). In the first one, the volume of the metallic precursor solution is equivalent of the total porous volume of the support. For the latter, the support is dispersed in an excess volume of precursor solution. Once more, we must underline that the respective charge of the gold species present in solution and the silica surface are important to ensure favourable electrostatic interactions and subsequent fine dispersion and distribution of the active phase on the support. The reduction of the gold takes place via thermal or chemical reduction (involving reducing agents such as NaBH_4 , formate, citrate, *etc.*) (Figure 1.13) ^[30, 77-78]. Gold crystallites size are comprised between 3 and 20 nm depending on the synthesis conditions ^[14, 77].

The impregnation method using HAuCl_4 as gold precursor is known to induce gold sintering ^[71]. This sintering is triggered during the activation procedure (particularly under thermal treatment) by the high amount of chlorine residues present on the support after impregnation. This mechanism yields to larger gold particles, which can affect the performances of the catalyst ^[71, 79]. Therefore, the addition of a washing step in the procedure to get rid of the chlorine residues could be a beneficial option. The procedure developed by Delannoy *et al.* has been selected for the washing of the silica full spheres support ^[71]. This procedure consists in washing the catalyst twice with an ammonia solution and twice with deionized water. The gold NPs are expected to be around 4 nm in size by following this method ^[71]. Both DI and WI with a washing step methodology will be tested in this work.

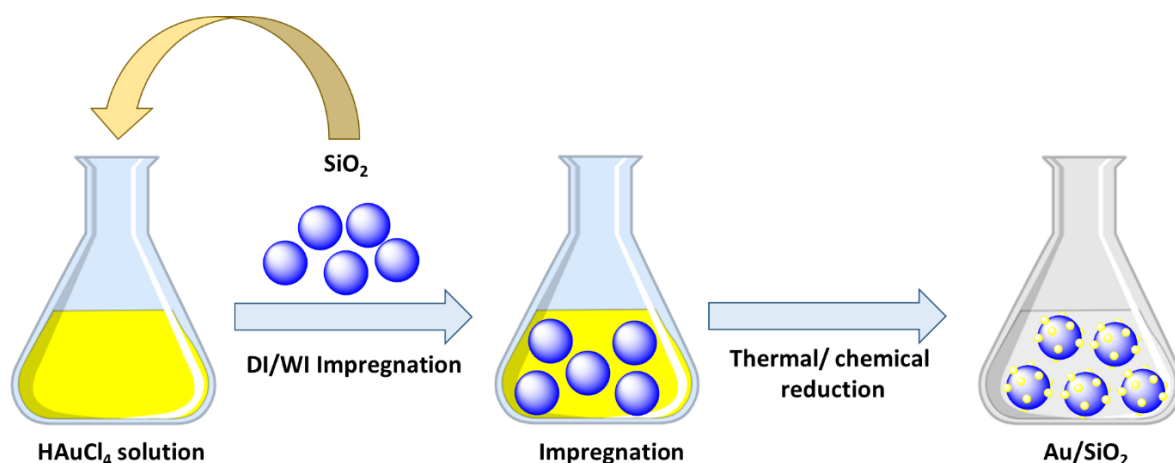


Figure 1.13 Schematic representation of the general procedure for DI and WI impregnation of gold on silica.

1.4.2.2 Production and Protection of Gold Colloids

In this method, small gold nanoparticles are formed separately and protected from agglomeration by a surfactant before being deposited on the silica support ^[73, 80]. The gold precursor and the surfactant (such as PVA, PAMAM, PVP, *etc.*) are generally mixed at room temperature for several minutes. Then, a certain amount of freshly prepared NaBH₄ solution is quickly added into the solution. This solution must be fresh due to the strong reducibility ability of NaBH₄. The colour variation of the solution indicates the formation of gold colloids. In a second step, the gold colloids are deposited on a support by impregnation, by adding the support powder to the colloidal suspension, and the resulting solid is filtered out to recover the gold catalyst (Figure 1.14) ^[77, 81].

Polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) are two commonly used polymeric stabilisers for this synthesis ^[73, 82-83]. PVA-stabilized gold NPs have been widely investigated in the selective oxidation of alcohols and sugars which makes them attractive for our research ^[73]. The synthesis method of the PVA-stabilized gold NPs used in this work is based on the method of Porta *et al.* ^[80] with few modifications inspired by the article of Zhao *et al.* ^[81]. The gold NPs produced by this modified method are expected to be of spherical morphology and with a size distribution of 3.0 ± 0.6 nm ^[81, 84]. Particles ranging from 3 to 10 nm can be obtained by varying the concentration of PVA as Au colloid stabiliser ^[73]. This procedure is of interest because it allows to obtain relatively small gold NPs with a narrow size distribution without suffering from agglomeration. Moreover, the catalytic performance of the small gold NPs can be compared afterwards with the performance of the larger gold nanoparticles obtained differently.

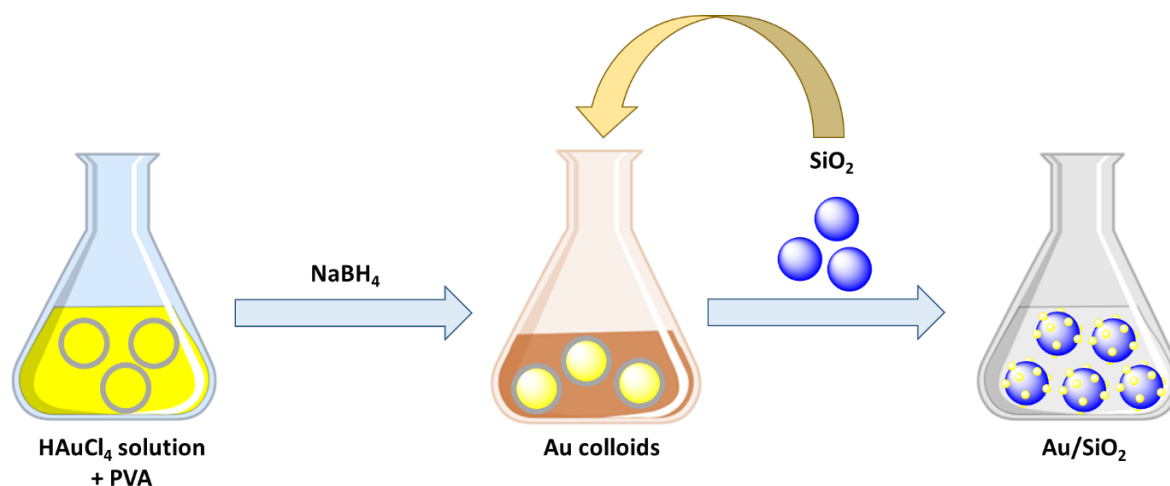


Figure 1.14 Schematic representation of the production of gold colloids and their anchoring onto silica with PVA as polymeric stabiliser and NaBH₄ as chemical reducing agent.

1.5 Influence of the Gold Particle Size

The size of the gold nanoparticles (NPs) appears to be the most important parameter with respect to activity and selectivity in reactions catalyzed by Au. A wide range of Au NPs diameters can be achieved by varying different parameters such as the metal loading, the support, the pH, the temperature, the concentration of the Au solution and many more [3, 30, 32, 74, 85]. It is generally accepted that gold NPs below 10 nm and with a narrow particle size distribution are the most active [30, 32]. It has been reported that for gold NPs, the optimum size is 2-5 nm for the oxidation of CO [30, 85] and 2-6 nm for the oxidation of sugars [3, 32, 86]. Since carbohydrates are adsorbed on the gold atoms with low coordination numbers and the number of low-coordinated atoms has a maximum value in particles of around 2 nm, the catalysts usually have a maximum activity around this value of particle sizes [32]. Concerning specifically the selective oxidation of lactose into LBA, the influence of the size of gold NPs on the catalytic performances has been investigated by Gutierrez *et al.* with mesoporous silica as support. This study shows that the initial rate of lactose conversion is highly sensitive to the size of the gold crystallites (7-14 nm) with a maximum catalytic activity obtained for particles of 7 ± 1 nm (measured by transmission electron microscopy) (Figure 1.15a). A catalyst with particles of 7 ± 1 nm allowed to obtain conversion of almost 100% in 100 minutes with a selectivity of 100% towards LBA. This study also underlines the high sensitivity of the particle size to gold loading as prepared by the reported procedure (modification of mesoporous silica by bis-[3-(triethoxysilyl)propyl] tetrasulfide before addition of Au) (Figure 1.15b). This allows very fine control of the size and therefore the activity of the resulting catalysts by tuning the gold loading

^[14]. However, the authors did not study the influence of the shape or porosity of the silica support in this reaction.

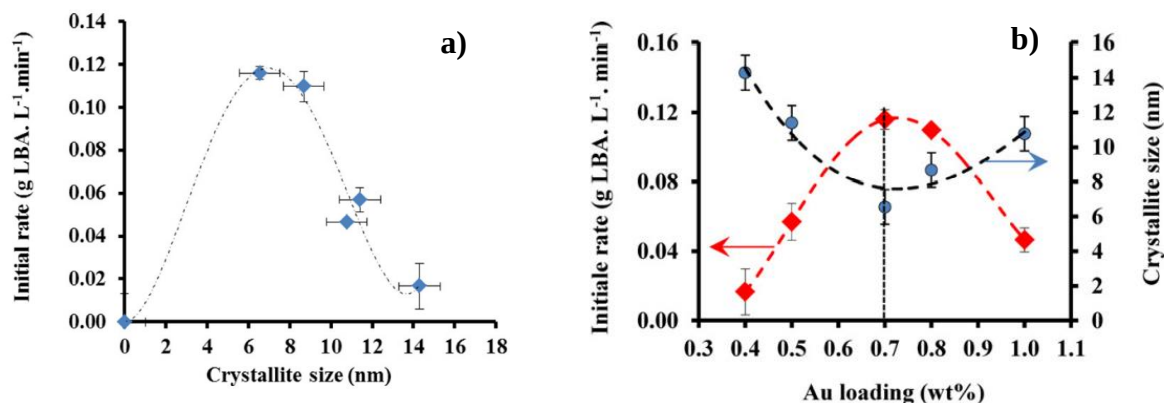


Figure 1.15 (a) Evolution of the initial rate of lactose oxidation versus the gold crystallite size (nm); (b) Evolution of the initial rate and the gold crystallite size (nm) versus the gold loading (wt.%). Dashed line represents the general tendency. The bars stand for the standard deviation for two repetitions for each catalyst synthesis ^[14].

1.6 Objectives of the Project

The main objective of this work consists in preparing gold catalysts supported on silica. To achieve this goal, we will first synthesize mesoporous silica supports. We have selected three different support morphologies: full spheres, hollow spheres and hollow nanofibers, as these might impact the performance in the final application. Once these supports have been synthesised, we will be able to deposit gold on them. We will use different gold deposition methods to obtain gold NPs of different sizes. By varying the size of these gold particles, we hope to modify the activity of the resulting catalysts. We will evaluate the activity of the obtained catalysts using a reference reaction: the oxidation of lactose to lactobionic acid. This reaction has the advantage of having already been extensively studied with catalysts based on noble metals, including gold. Hence benchmarking of our new materials will be facilitated. In parallel, we will develop a new HPLC method to be able to quantify the products with a completely new column. We will study the influence of catalytic tests parameters such as the temperature and catalyst mass on the conversion and selectivity. Finally, the effect of the support will be studied using Au/h-BN catalysts in comparison with SiO₂.

1.7 Methodology

In order to achieve the objectives, this work is divided into three parts. The first part consists in preparing mesoporous silica supports, the second part in depositing gold on silica to obtain Au/SiO₂ catalysts and the last part involves testing these catalysts in the oxidation of lactose to lactobionic acid.

As mentioned above, three different morphologies of mesoporous silica supports will be selected: full spheres, hollow spheres and hollow nanofibers.

The full spheres will be prepared following the Ströber method with some modifications compared to the original protocol. The time and ammonia/alcohol ratio are the two main parameters that will be modified. Dynamic light scattering (DLS) will be used systematically for each batch to evaluate the hydrodynamic diameter of the obtained NPs. In addition, nitrogen physisorption measurements will be performed in order to determine the BET surface area of the materials. X-ray diffraction will also be used to obtain a reference spectrum of the silica support to be able to analyse the gold-on-silica catalysts later on.

The synthesis of the hollow materials is based on the work carried out during Tommy Haynes' PhD thesis. This synthesis method consists in a sol-gel process with the use of a surfactant as a soft-template (to ensure the mesoporosity) and CB or CNF as hard-template (to obtain the hollow core). We aim to make some modifications to this synthesis in order to diminish the number of steps and consequently the time required to obtain the final products. In order to verify the morphology of the products, multiple transmission electron microscopy (TEM) images will be recorded. Thermogravimetric analysis (TGA) will also be needed to prove the necessity of adding (or not) a reflux step to wash the material and get rid of most of the surfactant. As for the full spheres, nitrogen physisorption measurements will be performed in order to determine the BET surface area of the materials and XRD diffraction patterns will be measured to determine the reference spectra of the hollow structures.

The second part of this project involves the production of gold supported on mesoporous silica catalysts by diverse methods. These methods are either wet impregnation or the production of gold colloids prior to immobilisation onto the solid surface. Most of the catalysts will be studied by TEM or scanning electron microscopy (SEM) to be able to see how the gold is deposited and measure the size of the loaded gold particles. XRD measurements will systematically be carried out in order to calculate the gold crystallites size by means of the Scherrer formula.

Atomic absorption spectroscopy (AAS) will also be used to determine the real quantity of gold deposited.

The analysis of the products formed during the catalytic tests will be achieved by HPLC analysis. As said above, a new HPLC method has to be developed before any test to be able to obtain a good separation between lactose and lactobionic acid, and to detect and ideally quantify any by-product formed.

Finally, catalytic tests will be performed for the selective oxidation of lactose into lactobionic acid, using the different catalysts prepared. This will allow to make comparisons between the synthesized materials and to assess the influence of the support and gold particle sizes.

This manuscript is divided into 5 different parts. Following the introduction part, an experimental section will be developed giving details on the experimental methods and chemicals used in this work as well as on the characterization techniques.

The results about the silica supports and the gold supported on silica materials syntheses are discussed in the third part. The size, morphology and impact of the changes in procedure will be detailed for the supports. Concerning the catalysts, the discussion will focus on the influence of the methodology and the solvent used on the gold crystallites size.

The fourth part discusses the development of the HPLC method, the attribution of the different HPLC peaks, and the results obtained for the catalytic tests. Concerning the catalytic tests, the activity of the catalysts and the influence of the temperature and catalyst mass parameters will be discussed.

Finally, the last part aims to conclude on the work carried out throughout this year and to give some perspectives to this project. This document ends with the reference section and some annexes.

EXPERIMENTAL SECTION

This chapter aims to give detailed information on the materials and methods used to synthesize and characterize the different compounds and solids obtained during this Master project.

2.1 Solvents and Chemicals

All the chemical reagents and solvents used during this project are listed below in alphabetic order with their supplier and purity under brackets.

Acetonitrile ($\geq 99.9\%$ for HPLC, HiPerSolv CHROMANORM®, VWR Chemicals), Ammonium chloride ($>99.8\%$ for laboratory use, ACS, ISO, Ph. Eur., Chem-Lab NV), Ammonium hydroxide (extra pure, 25% solution in water, Acros Organics), Carbon black (IMERYS GRAPHITE & CARBON), Carbon nanofibers (PYROGRAF®), D-Lactose monohydrate ($\geq 98.0\%$ for HPLC, Sigma-Aldrich), Ethanol (99%, EURO DENATURATED Techni Solv®, VWR Chemicals), Ethanol absolute (AnalaR NORMAPUR® Reag. Ph. Eur., VWR Chemicals), Hexadecyltrimethylammonium bromide ($\geq 98.0\%$, Sigma-Aldrich), Hexagonal boron nitride (h-BN, Sigma-Aldrich, $S_{\text{BET}} \approx 23 \text{ m}^2 \text{ g}^{-1}$), Lactobionic acid (97%, Sigma-Aldrich), Hydrochloric acid (ACS reagent, 37%, Sigma-Aldrich), Lactulose ($\geq 98.0\%$ for HPLC, Sigma-Aldrich), Methanol ($\geq 98.5\%$ technical, VWR Chemicals), Oxygen ($\geq 99.5\%$, Air Liquide), Polyvinyl alcohol (Mw 89,000-98,000, 99+% hydrolyzed, Sigma-Aldrich), Potassium hydroxide ($>85\%$ for laboratory use, Ph. Eur., Chem-Lab NV), Sodium borohydride ($\geq 98.0\%$, Sigma-Aldrich), Sodium formate (for analysis, EMSURE® ACS, Reag. Ph. Eur., Merck), Sodium hydroxide (99%, AnalaR NORMAPUR® Reag. Ph. Eur., VWR Chemicals), Sulfuric acid (98% for HPLC, LiChropur®, VWR Chemicals), Tetrachloroauric (III) acid trihydrate (99.999%, Acros Organics), Tetraethyl orthosilicate ($\geq 99.0\%$ for GC, Sigma-Aldrich), Urea (ACS reagent, 99.0-100.5%, Sigma-Aldrich).

2.2 Synthesis of the Silica Nanoparticles

2.2.1 Synthesis of Full Spheres Silica Particles

This synthesis involves the hydrolysis of the silica precursor, namely tetraethyl orthosilicate (TEOS), followed by condensation to form the silica network (Figure 2.1) ^[43].

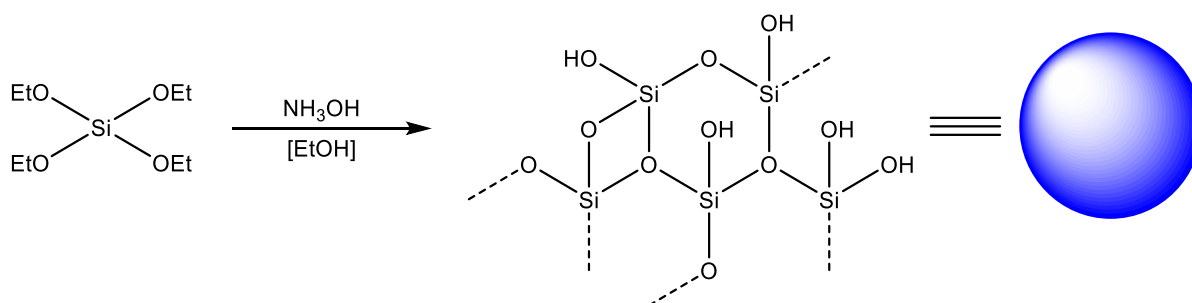


Figure 2.1 Schematic representation of the synthesis of full spheres silica nanoparticles.

150 mL of denatured EtOH and 6 mL of 25% NH₃OH aqueous solution were added in a 500 mL Erlenmeyer under vigorous stirring (400 rpm) for 5 min, then 10 mL of TEOS were added within 10 min. The Erlenmeyer was covered with parafilm and the solution stirred for 6 h under reduced stirring (200 rpm) giving a white and opaque solution. The mixture was diluted in 100 mL of EtOH and a small portion of this mixture was set aside for DLS analysis. The resulting mixture was centrifugated (Biofuge Stratos®, Heraeus instruments, 10 000 rpm, 45 minutes, Corning® 50 mL centrifuge tubes, CentriStar Cap), washed with EtOH and then centrifugated again. The resulting solid was dried at 100 °C overnight leading to a white powder (515 mg on average) (see annexe A.1 for the XPS spectrum and A.2 for the image of the powder).

2.2.2 Synthesis of Hollow Spheres and Hollow Nanofibers

The preparation of the hollow silica materials takes place in 3 steps: (i) anchoring of the silica layer on the hard template, (ii) washing of the material to remove the CTAB surfactant used as porogen agent and (iii) calcination to remove the hard template and the remaining CTAB (Figure 2.2).

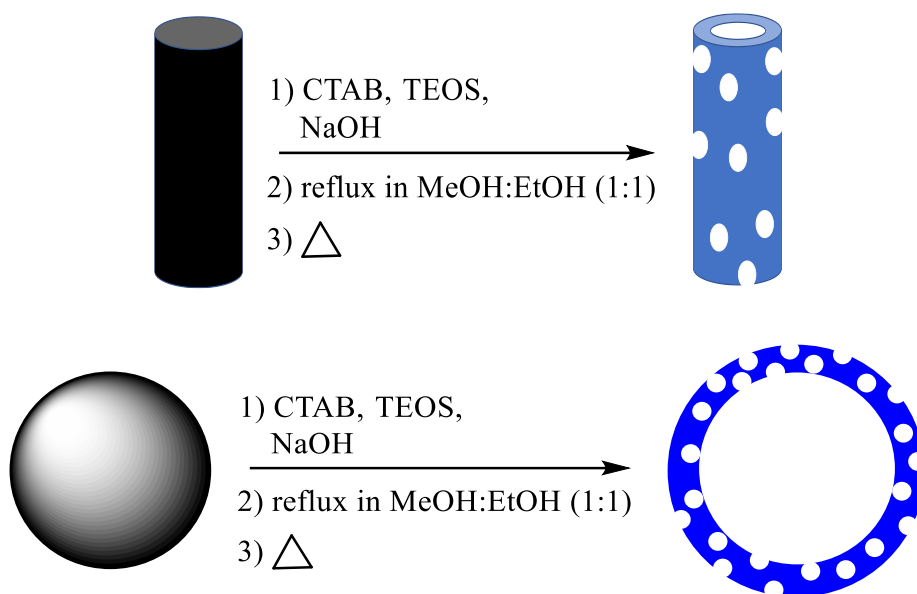


Figure 2.2 Schematic representation of the hollow silica structures synthesis.

Typically, 1 g of carbon black/carbon nanofibers was added in a 250 mL triple-neck flat-bottom flask containing 100 mL of distilled water and 40 mL of sodium hydroxide solution (0.1 M). The mixture was sonicated for 10 min, using a VWR Ultrasound cleaner (power level 3) leading to a black suspension. To this suspension, 2.284 g of CTAB were added and the resulting mixture was heated at 60 °C. 2.8 mL of TEOS were added dropwise within 30 min and the mixture was further stirred (300 rpm) for 3 h and 30 min at 60 °C. The solution was charged into a propylene bottle, which was closed tightly and heated at 100 °C for 3 days. The product was washed with EtOH, centrifugated (ALC® centrifuge PK 120, 6000 rpm, 5 minutes, Corning® 50 mL centrifuge tubes, CentriStar Cap) and dried overnight at 100 °C. The CTAB template was removed by refluxing (400 rpm) the solid material in 250 mL EtOH/MeOH (1:1; v:v) overnight. The product was filtrated out and dried overnight at 100 °C. The remaining CTAB template and the carbonaceous template were removed by calcination at 250 °C for 2 h

and then at 600 °C (for carbon black) or 800 °C (for carbon nanofibers) for 5 h to obtain silica hollow nanospheres/nanofibers as white/pink powders (500/400 mg), respectively.

2.3 Synthesis of Gold Supported on Silica Catalysts

The names of the different catalysts are codified as follows: name of the chemical reducing/additional agent, solvent(s) and support used, as detailed in Table 2.1 below.

Table 2.1 Codes related to the chemical reductor/additional agent, solvent(s) and support used.

Chemical reducing/additional agent	Sample code
NaBH ₄	Na
Formate	UF
Ammoniac	NH ₃
PVA	PVA
Solvent(s) used	Sample code
Water	W
Acetonitrile	A
Water/Acetonitrile	W/A
Support	Sample code
Silica	SiO ₂
Hexagonal boron nitride	h-BN

For example, a catalyst prepared on silica in water with NaBH₄ as chemical reducing agent is named NaW SiO₂.

An exception to this coding system exists. Indeed, the catalyst prepared following the exact same procedure as Nathalie Meyer (N.M.) is codified as NM h-BN ^[2].

2.3.1 Influence of Solvent for Au Impregnation

Several catalysts were prepared by wet impregnation method in two different solvents or mixture of both, with NaBH_4 as reducing agent (Figure 2.3).

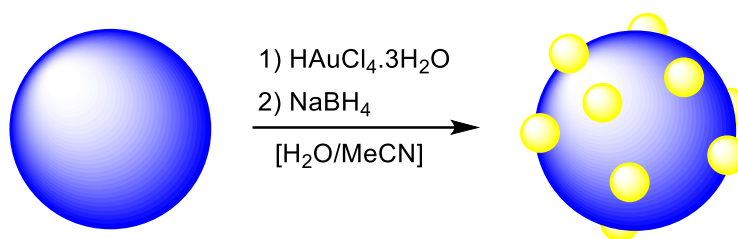


Figure 2.3 Schematic representation of the Au/SiO_2 and $\text{Au}/\text{h-BN}$ catalysts prepared by WI with NaBH_4 as reducing agent.

Typically, 250 mg of full-spheres silica or h-BN particles were added under stirring (300 rpm) in a 50 mL round bottom flask containing 15 mL of acetonitrile (for preparing NaA SiO_2 , NaW/A SiO_2 and NaA h-BN materials) or distilled water (for NaW SiO_2). 10 mL of chloroauric acid in solution in acetonitrile (NaA SiO_2 and NaA h-BN) or water (NaW SiO_2 and NaW/A SiO_2) (0.5 g/L) were added dropwise within 20 min to this solution giving a white opaque (NaW SiO_2 and NaA h-BN) or light-yellow (NaA and NaW/A SiO_2) mixture. 1.00 g of NaBH_4 was added to this mixture forming a dark purple (SiO_2 catalysts) or purple (NaA h-BN) solution. This solution was stirred for 20 min (300 rpm) and filtrated under vacuum (Filter membranes, Durapore® PVDF pore size 0.45 μm , diameter of 47 mm). The catalyst was washed with distilled water to produce a dark purple (SiO_2 catalysts) or blue-grey (NaA h-BN) solid and a colourless filtrate. The solid was dried overnight at 100 $^\circ\text{C}$ leading to a black or blue-grey powder for SiO_2 or NaA h-BN supported catalysts, respectively. The filtrate containing potentially non-adsorbed gold was analysed by atomic absorption spectrometry.

2.3.2 Influence of the Deposition Method and the Support

2.3.2.1 UFW SiO₂ Catalyst

The UFW SiO₂ catalyst was obtained by WI method using urea to generate hydroxides and sodium formate as reducing agent (Figure 2.4).

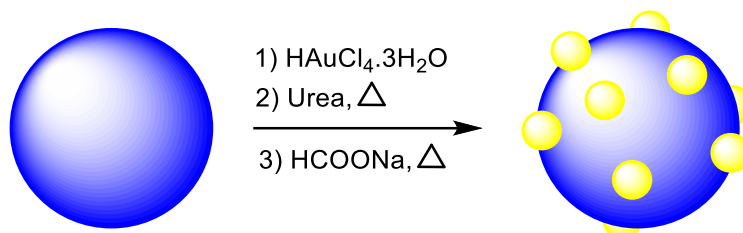


Figure 2.4 Schematic representation of the WI preparation of UF SiO₂ catalyst with sodium formate as reducing agent.

Typically, 250 mg of full-spheres silica nanoparticles were added to 300 mg of urea in 40 mL of distilled water. The mixture was stirred (300 rpm) for 15 minutes forming a slightly cloudy solution. 10 mL of an aqueous chloroauric acid solution (0.5 g/L) were added to this solution leading to a light-yellow mixture. After 15 minutes of stirring (300 rpm) the solution was heated to 120 °C for 1 h and then the solution was cooled down to RT. 3.5 g of sodium formate were added and the solution was heated to 130 °C for 1 h. The solution was cooled down to RT prior to filtration under vacuum (Filter membranes, Durapore® PVDF pore size 0.45 µm, diam. 47 mm). The catalyst was washed with distilled water giving a dark purple solid and a colourless filtrate. The powder was dried overnight at 100 °C to produce a dark purple powder.

2.3.2.2 NH₃W SiO₂ Catalyst

The NH₃W SiO₂ catalyst synthesis consists in a WI followed by a washing with ammonia. The gold is reduced by thermal treatment (Figure 2.5).

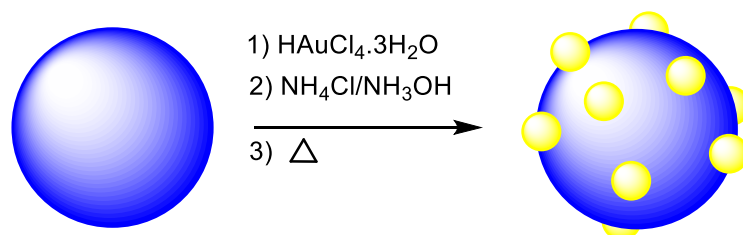


Figure 2.5 Schematic representation of the synthesis of the NH₃W SiO₂ catalyst.

10 mL of an aqueous chloroauric acid solution (0.5 g/L) were added to 250 mg of full-spheres silica nanoparticles in 15 mL of distilled water. The mixture was stirred (300 rpm) for 15 minutes yielding a light-yellow solution. The solid was washed two times with an ammonium chloride buffer solution (2.588 g NH_4Cl + 2.8 mL NH_3OH 25%) and two times with distilled water and centrifugated between each washing (ALC® centrifuge PK 120, 6000 rpm, 5 minutes, Corning® 50 mL centrifuge tubes, CentriStar Cap). The resulting white powder was dried overnight at 100 °C leading to a light-pink powder which was then calcinated at 300 °C for 4 h to generate a pink powder.

2.3.2.3 PVAW SiO_2 Catalyst

The production of the PVAW SiO_2 catalyst is based on the preparation of protected gold colloids and subsequent deposition of these pre-formed gold nanoparticles on the silica support (Figure 2.6).

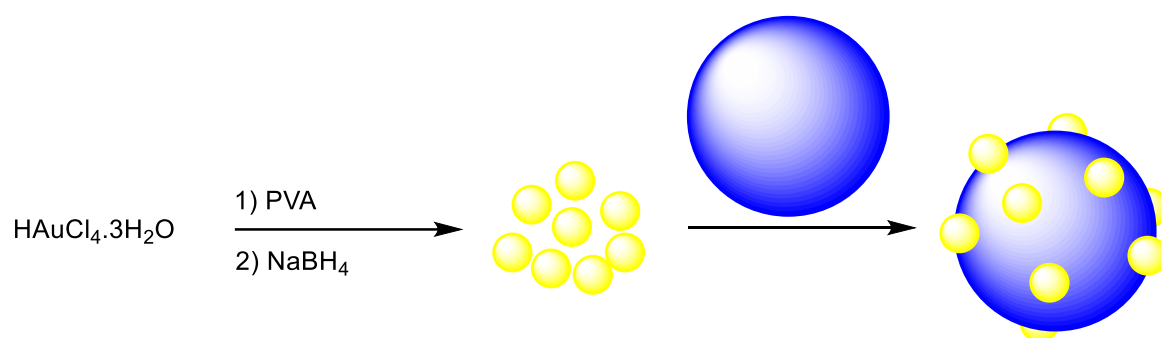


Figure 2.6 Schematic representation of the PVAW SiO_2 catalyst preparation.

2 wt% aqueous solution of polyvinyl alcohol (PVA) was heated to 70 °C for 1 h in order to dissolve the PVA. 1 mL of this solution was added to a 200 mL aqueous chloroauric acid solution (100 mg/L). The resulting light-yellow solution was stirred for 1 h (400 rpm). 5 mL of a freshly prepared solution of NaBH_4 (0.1 M) was added within 30 min leading to a red solution. This solution was further stirred for 2h (400 rpm). 250 mg of full-spheres silica nanoparticles were added to 50 mL of the so-prepared gold NPs suspension set at pH 1.5 by addition of a few drops of HCl (37%) and the mixture was stirred for 2 h (500 rpm). The catalyst was filtered (Filter membranes, Durapore® PVDF pore size 0.10 μm , diam. 47 mm) under vacuum and washed with hot water at 70 °C (3 times; 70 mL) and absolute ethanol (120 mL). The black powder was dried overnight at 100 °C giving a red powder.

2.3.2.4 PVAW h-BN Catalyst

The production of the PVAW h-BN catalyst is based on the same principle than in section 2.3.2.3 (Figure 2.7).

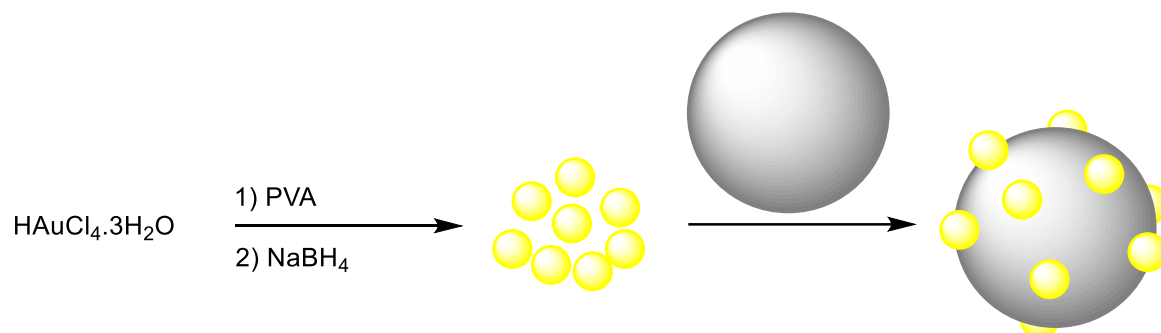


Figure 2.7 Schematic representation of the PVAW h-BN catalyst preparation.

500 mg of h-BN particles were added to 100 mL of the gold NPs suspension prepared as described in Section 2.3.2.3 and set at pH 1-2 by addition of few drops of HCl (37%) and the pink mixture was stirred for 2 h (500 rpm). The powder was filtered (Filter membranes, Durapore® PVDF pore size 0.10 μm , diam. 47 mm) under vacuum and washed with 70 °C hot water (3 times; 130 mL) and absolute ethanol (120 mL). The solid was dried overnight at 100 °C to give a pink powder.

2.3.2.5 NM h-BN Catalyst

This catalyst serves as a reference and therefore has been synthesized by following strictly the procedure developed by N. Meyer^[2]. This procedure consists in a WI followed by a reduction with NaBH_4 (Figure 2.8).

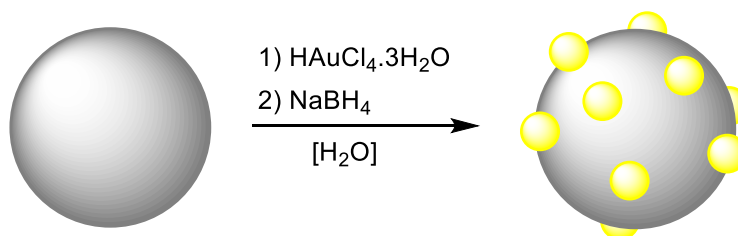


Figure 2.8 Schematic representation of the NM h-BN catalyst production.

2.5 g of h-BN particles were added in a 250 mL triple-neck flat-bottom flask containing 50 mL of distilled water and stirred for 15 min (400 rpm). 25 mL of an aqueous chloroauric acid

solution (2 g/L) were added dropwise within 30 min to this solution forming a white opaque mixture. This mixture was further stirred for 15 min (400 rpm) and then 6 mL of NaBH₄ solution (0.1 g/mL) were added to it leading to a purple solution. This solution was stirred 10 min (500 rpm) and then filtrated under vacuum (Filter membranes, Durapore® PVDF pore size 0.45 µm, diam. 47 mm) and the catalyst was washed with distilled water forming a purple slurry and a colourless filtrate. The slurry was dried overnight at 100 °C leading to a purple powder.

2.4 Catalytic Tests

All the catalytic tests were performed using the experimental set-up described in Figure 2.9.

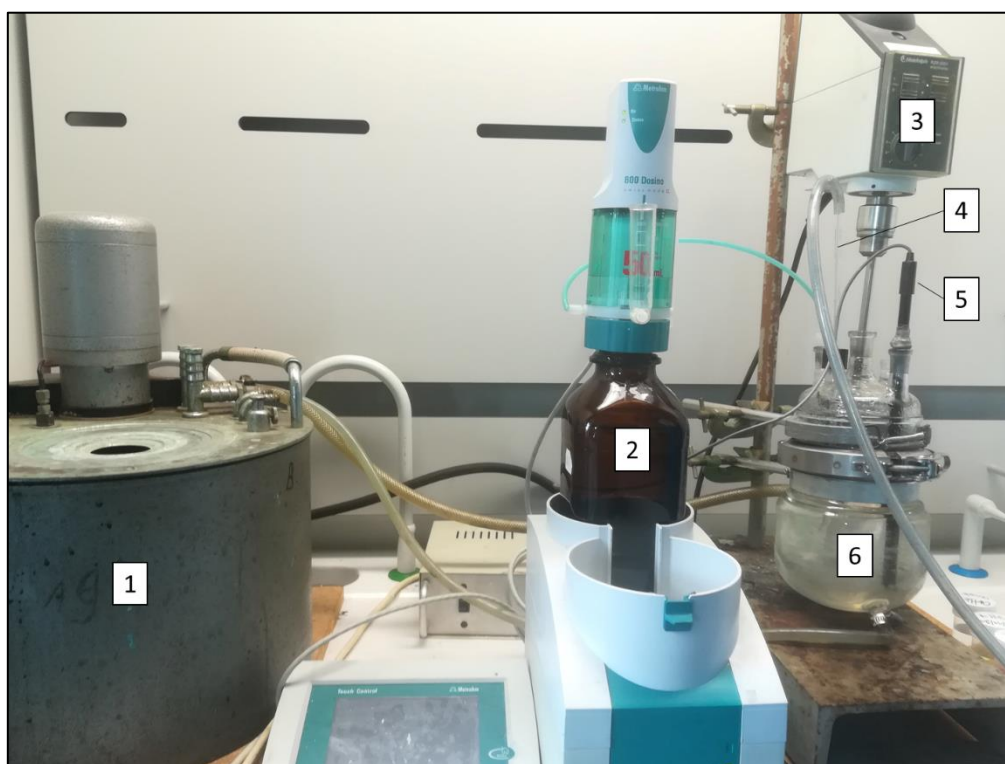


Figure 2.9 Experimental set-up for the catalytic tests: (1) heating tank; (2) automatic titration device; (3) mechanical stirrer; (4) oxygen supply pipe; (5) electrode and (6) double-walled glass reactor.

In a thermostated double-walled glass reactor, 1.8 g of lactose was dissolved in 500 mL of milliQ water and the pH of the lactose solution was measured continuously by a combined AgCl/Ag Beckman electrode calibrated with Specpure® buffer solutions of pH 4.00 ($\pm 0.01@25\text{ }^{\circ}\text{C}$), 7.00 ($\pm 0.01@25\text{ }^{\circ}\text{C}$) and 10.00 ($\pm 0.01@25\text{ }^{\circ}\text{C}$). An automatic titration device Metrohm 842 Titrando was used to neutralize the acids formed over time with KOH aqueous solution (0.1 M) so that the pH is maintained at a constant value of 9 during all the catalytic

test. Constant stirring was ensured (1000 rpm) by a mechanical stirrer (Heidolph RZR 2051electronic). The temperature was fixed by water circulation in the outer compartment of the reactor. Oxygen was introduced into the solution at a constant flow rate of 0.5 L/min. A known mass of catalyst was introduced in the reactor after 5 min, which allows the system to stabilize at pH 9. The test started when the catalyst was added. The experiments were stopped after 4h. The catalyst was recovered by filtration and the filtrate was diluted by two and then analyzed by HPLC.

Table 2.2 Experimental conditions used for lactose oxidation.

Parameter	Lactose oxidation
Starting substrate solution	500 mL lactose 10 mmol.L ⁻¹
Temperature	40, 52.5, or 65 °C
Stirring rate	1000 rpm
pH	9
Basic solution to fix the pH	KOH 0.1 mol.L ⁻¹
Oxygen flow	0.5 L.min ⁻¹
Mass of catalyst	100, 250, or 400 mg
Duration of a catalytic test	4 h

2.5 Characterization Techniques

2.5.1 High-Performance Liquid Chromatography (HPLC)

HPLC analyses were performed using a Waters system equipped with a Waters 2414 refractive index detector (detector temperature = 35 °C). For a good separation of our products, 10 μ L of sample were injected in a Transgenomic ICSep ICE-ION-300 column using 0.45 mM H₂SO₄ as eluent (0.5 mL/min) and at 75 °C. The HPLC method development will be discussed in Chapter 4.

2.5.2 Dynamic Light Scattering (DLS)

DLS analysis was performed for the full-spheres obtained with the Stöber method using a CGS-3 Compact Goniometer System (ALV, Germany) equipped with a correlator (LSE-5003 light scattering electronics and multiple tau digital correlator). The sample collected at the dilution step in EtOH (see section 2.2.1) was introduced in the machine by means of an appropriate glass test tube. The measurements were carried out three times at a wavelength fixed at 632.8 nm and at an angle of 90.0°. Data were analyzed using the ALV-5000 & 60X0 software (ALV, Germany).

2.5.3 X-Ray Powder Diffraction (XRPD)

X-ray diffraction patterns of powders were recorded on a D8 Advance (Bruker, USA) diffractometer with a Bragg Brentano geometry using a power of 1200 W (40 kV, 30mA), equipped with a copper source ($\lambda_{K\alpha} = 0.15409$ Å) and a LynxEye XE-T detector. About ten milligrams of each sample were deposited on an epoxy sample holder, previously covered with a very thin layer of commercial moisturizer (Nivea®). Data were collected in the 2 θ range from 5° to 80°, with a step of 0.015° and a time/step of 0.15 s at room temperature. The obtained 2D diffractograms were analyzed using DIFFRAC.EVA software (Bruker, USA). The Au particles sizes (d_{XRD}) were extracted from XRPD measurements by using the Scherrer equation ^[87]:

$$d_{XRD} = k \lambda / (B \cos \theta) \text{ (Equation 2.1)}$$

where k is a constant taken as 0.9 here, λ is the wavelength of X-ray radiation ($\lambda_{K\alpha} = 0.15409$ Å), θ is the diffraction angle and B is the line width at half maximum height. The (111) diffraction line of gold crystallites was used to determine the B and θ values.

2.5.4 BET (Brunauer–Emmett–Teller)

The BET specific surface area of the nanomaterials was calculated using the BET equation based on nitrogen physisorption measurements that were performed by Jean-François Statsyns on a Micromeritics ASAP 2020 instrument at -196 °C. Prior to analysis, about a hundred milligrams of solid sample were degassed at 120 °C during 10 h with a heating rate of 10 °C/min under 0.133 Pa pressure.

2.5.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was performed on a Field Emission Scanning Electron Microscope JEOL JSM-7600F equipped with an energy dispersive X-ray system operating at 30.0 kV when using the STEM mode. The sample preparation consisted in suspending a few milligrams of the sample in EtOH under ultrasonic treatment (VWR Ultrasound cleaner, power level 3, few minutes). Then, a few drops of the supernatant were deposited on a holey carbon film deposited on a copper grid (CF-1.2/1.3-2 Cu-50, C-flat™, Protochips, USA). The grid was then carefully deposited on a filter paper and dried overnight under vacuum at room temperature. This sample preparation will also be used in characterizations by transmission electron microscopy.

2.5.6 Transmission Electron Microscopy (TEM)

TEM images were recorded by Tommy Haynes, Nathalie Body or Fabien Drault on a LEO 922 OMEGA Energy Filter Transmission Electron Microscope operating at 120 kV. The sample preparation is similar to the one used for SEM analysis (section 2.5.5).

2.5.7 Atomic Absorption Spectroscopy (AAS)

The quantification of gold in the synthesis filtrates was performed by atomic absorption spectroscopy, using a Perkin-Elmer 3110 spectrometer equipped with an air-acetylene flame atomizer. The calibration curve (from 2 to 10 mg/L Au) was realized with standard solutions obtained by dilution of a commercial gold solution (1 g/L, Sigma-Aldrich).

2.5.8 X-Ray Photoelectron Spectroscopy (XPS)

XPS analyses were carried out by Nathalie Body at room temperature with a SSI-X-probe (SSX 100/206) photoelectron spectrometer from Surface Science Instruments (USA), equipped with

a monochromatized microfocus Al X-ray source. A few milligrams of each sample were stuck onto small sample holders with double-face adhesive tape and then placed on an insulating ceramic carousel (Macor®, Switzerland). Charge effects were avoided by placing a nickel grid above the samples and using a flood gun set at 8 eV. The binding energies were calculated with respect to the C-C component of the C1s peak fixed at 284.8 eV. Data treatment was performed using the CasaXPS program (Casa Software Ltd., UK). The peaks were decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley-type baseline.

2.5.9 Thermogravimetric Analysis (TGA)

Thermograms were recorded using a TGA/SDTA 851e instrument from Mettler Toledo. Samples (2-10 mg) were heated at 10.00 °C/min under an air flux (100.0 mL/min) from 25 to 850 °C in alumina containers.

RESULTS AND DISCUSSION: MATERIALS SYNTHESIS

3.1 Synthesis of the Mesoporous Silica Nanoparticles

In this section, the synthesis of three different silica supports and their characterization will be studied. At first, the full-spheres are discussed followed by the hollow spheres and hollow nanofibers.

3.1.1 Synthesis of Full Spheres Silica Particles

The full sphere silica NPs were produced in 15 batches as described in section 2.2.1. As mentioned above (section 1.3.3.1), this synthesis was inspired from the Stöber method which consists in using an alcohol (methanol, ethanol, n-propanol or n-butanol) as solvent, a tetra-alkyl silicate as silica precursor and ammonia as base catalyst to obtain spherical monodispersed silica NPs ^[43]. Werner Stöber was able to obtain particles ranging from 50 nm to 2 μ m in size using this original process ^[43].

The synthesis used for this work differs from the original one in terms of reaction time (6h vs 2h) and ratio of ammonium hydroxide to ethanol in order to obtain particles of ~ 40 nm ^[88]. These conditions were already tested in the past in the lab by N. Body and L. Lejeune. The size distribution (Figure 3.1) of the freshly formed silica NPs was evaluated using DLS analysis.

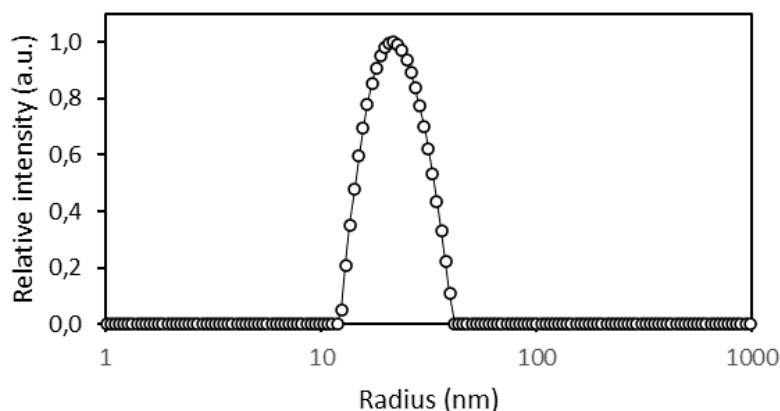


Figure 3.1 Hydrodynamic radius size distribution (nm) of silica NPs obtained by modified Stöber method before centrifugation of the sample.

The modified Stöber synthesis method produced silica NPs with hydrodynamic diameters of 41.6 nm ($\sigma = 3.1$). This result is consistent since it is close to the particles size (38.4 nm) obtained by L. Lejeune in her work using the same parameters ^[88].

The BET specific surface area of the spherical silica NPs is 371 m²/g, which is also in accordance with previous results obtained in our lab for the same synthesis (380 m²/g). The curve of nitrogen adsorption-desorption obtained (Figure 3.2) is of type IV (according the IUPAC classification of adsorption isotherms) suggesting a mesoporous structure ^[50]. However, the DFT average pore width of 1-2 nm (vs 0.8 nm in the past) and the BET pore volume (0.7 cm³/g for both) indicates that this silica material is also microporous. Therefore, both types of porosity are present in the spheres. The similarity between the old and new results underline the reproducibility of this synthesis procedure.

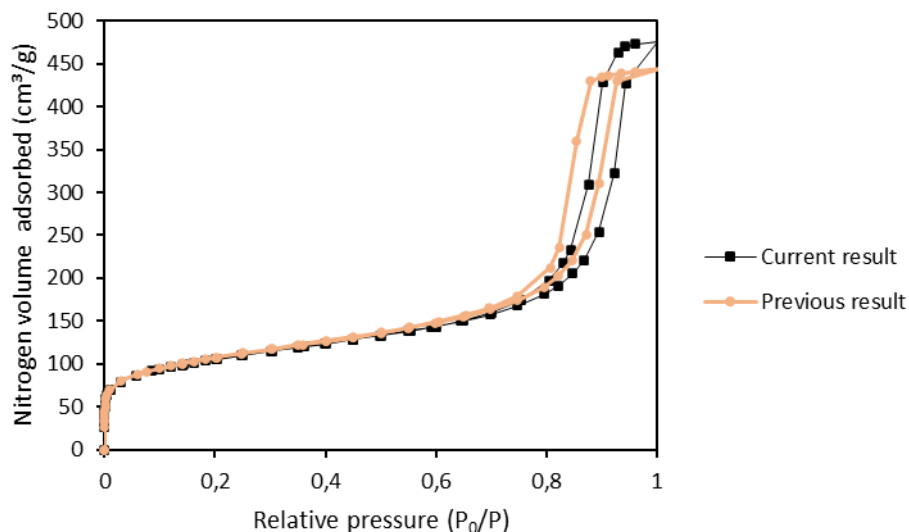


Figure 3.2 Current (black) and previous (orange) nitrogen adsorption-desorption isotherms at 77 K for the silica full-spheres NPs.

The XRD pattern of the silica NPs (Figure 3.3) shows a broad peak at around $2\theta = 25^\circ$ which reveals the amorphous nature of the silica nanoparticles, as expected. Indeed, this peak broadening is thought to be correlated with the formation of a porous structure^[89]. This assumption is in accordance by the BET measurements which indicates a mesoporous network in the silica NPs. Furthermore, the powder diffraction pattern confirms the absence of any ordered crystalline structure^[90].

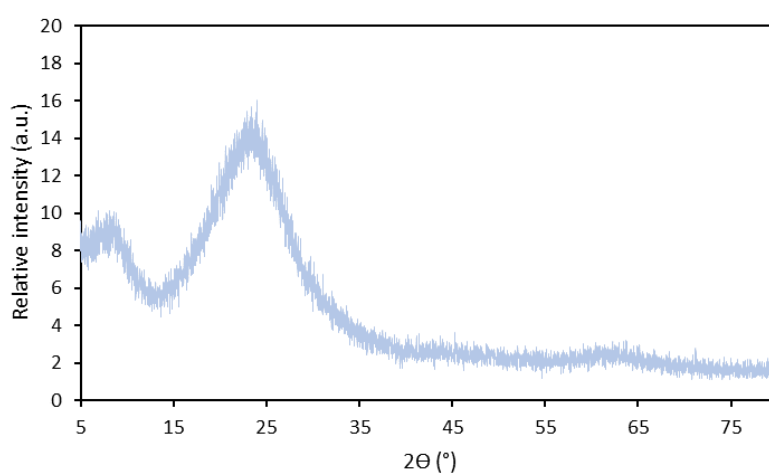


Figure 3.3 XRD diffractogram of silica NPs obtained via the modified Stöber method.

3.1.2 Synthesis of Hollow Nanofibers and Hollow Spheres

In this section, it is described how the procedure developed by Tommy Haynes was adapted to optimize the time and number of steps needed to obtain the hollow structures (spheres and nanofibers) ^[45]. A summary of the path followed in order to obtain the products with the desired morphologies is given below (Figure 3.4).

The synthesis of the mesoporous silica hollow spheres (mHSS) and hollow nanofibers (mHSN) consists in using respectively carbon black (CB) or carbon nanofibers (CNF) as hard-template, TEOS as silica precursor, deionised water as solvent, NaOH as base catalyst and CTAB as soft-template to obtain carbonaceous template coated with mesoporous silica. In a second step, the carbonaceous template is removed by calcination at 600°C for CB and at 800°C for CNF ^[91-92]. The control of silica mesoporosity is ensured by CTAB, which forms micelles in the aqueous solution. By following this method, it was expected to obtain the MCM-41 phase for mHSS and a mixture of MCM-41 and SBA-15/16 phases for mHSN ^[92].

In our case, the first step, which consist in the functionalisation the carbon template with APTES, ^[91-92] has been considered not necessary since the carbon support will be calcined in order to obtain the hollow structures. This hypothesis allowed us to eliminate two steps (chlorination and functionalisation with APTES of the hard template) in the synthesis of the material and thus save time. In addition, to save even more time, the reflux washing step (24 hours) of the product was replaced with a centrifugation (5 minutes) to get rid of most of the CTAB. A schematic representation of the old and new synthesis routes is represented in Figure 3.4.

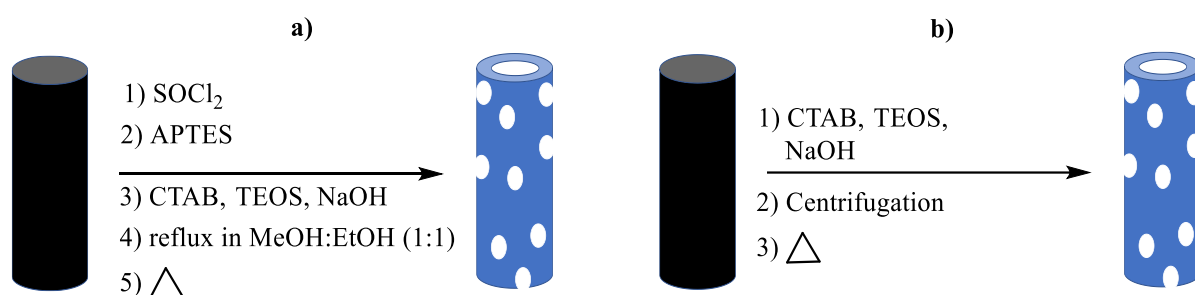


Figure 3.4 Schematic representation of (a) the old and (b) the new synthesis route for hollow silica nanostructures synthesis.

In order to verify the impact of these changes in the procedure, the “silica hollow nanofibers” and the “silica hollow spheres” obtained by this new synthetic route were analysed by SEM and BET (Figure 3.5). Concerning SEM analysis, the “silica hollow materials” had to be coated with gold following the procedure described in section 2.5.5 to avoid charging effects.

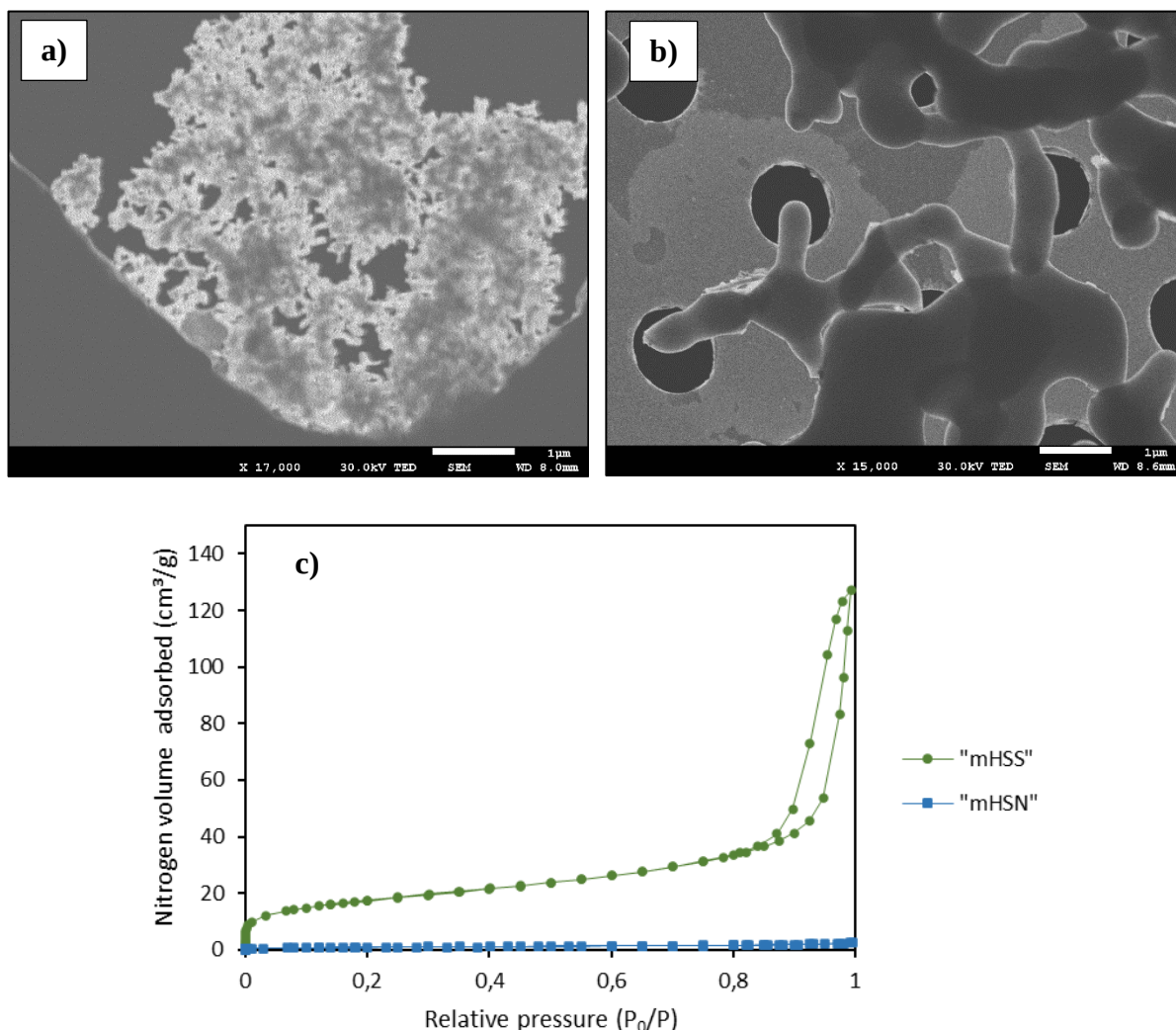


Figure 3.5 STEM images of (a) the “mHSS”; (b) the “mHSN” materials and (c) their respective nitrogen adsorption-desorption isotherms at 77 K.

In Figure 3.5a and b, as can be seen, the silica hollow spheres and hollow nanofibers were not obtained with the method employed, but rather a branched and a silica-stone structure, respectively. The N₂ adsorption curves obtained for the “hollow-spheres” and “hollow-nanofibers” (Figure 3.5c) are both representative of type II according to IUPAC classification, which is typical for nonporous materials ^[50]. This is confirmed by the measurement of a very

low specific surface area: $63 \text{ m}^2/\text{g}$ for the “hollow spheres” and $4 \text{ m}^2/\text{g}$ for the “hollow nanofibers”. Interestingly, the “mHSS” show exactly the same surface area and the same morphology as CB^[91]. This method might be a way to prepare non-porous silica that reproduces the morphology of CB. This type of silica was already used 30 years ago by Michelin in its “green-tire” formulation to improve the level of abrasion resistance of the tire compared to the traditional carbon black filled tire treads^[93].

These strange morphologies and porosities are probably due to the fact that centrifugation does not allow to get rid of most of the CTAB. Therefore, during the calcination step, all the CTAB that is left is burned and could affect the structured silica to form a “stony” structure for the “mHSN” and a branched structure for the “mHSS”.

In response to these results, a washing step in refluxing MeOH/EtOH (50:50 v:v) was added in the procedure after centrifugation, prior to calcination. In order to study the effect of this reflux step, it has been decided to compare by TGA analysis the thermograms obtained after the centrifugation (Figure 3.6a), the reflux (Figure 3.6b) and the calcination (Figure 3.6c) steps for the hollow spheres synthesis.

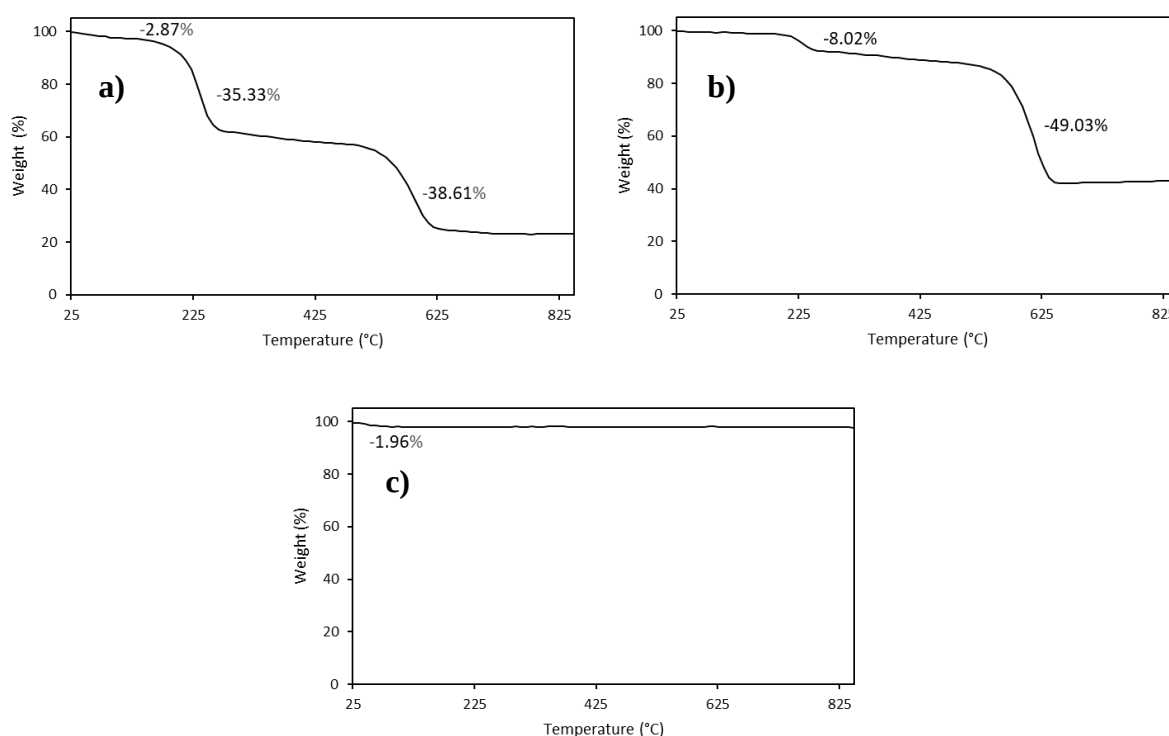
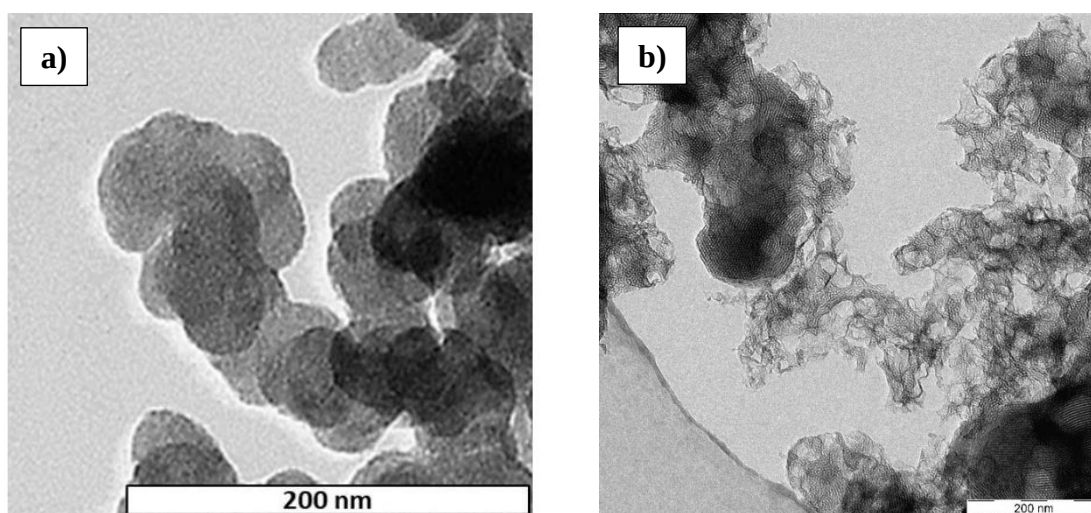


Figure 3.6 Thermograms recorded under air of the material obtained after (a) centrifugation; (b) reflux and (c) calcination.

On Figure 3.6a, as can be seen, three major weights losses have been recorded. The first one of 2.87 % is due to the loss of water which is known to be a degradation product of CTAB at low temperatures (20-150 °C) ^[94]. This loss can also be attributed to water physically adsorbed on the surface of the material ^[94]. The second weight loss is representative of the decomposition of CTAB which begins approximately at 200 °C and ends at 250 °C according to the literature ^[45, 94]. The third and last one is due to the combustion of the carbon template which takes place at around 600 °C for CB ^[45]. Regarding the material obtained after the reflux step (Figure 3.6b), the weight loss due to the decomposition of CTAB is strongly reduced compared to that obtained after the centrifugation (from 35.33 % to 8.02 %) which proves the effectiveness of this washing step. Finally, Figure 3.6c shows that, after the calcination, everything has been removed, from the carbonaceous template to the CTAB, as expected. As said above, the remaining weight loss of 1.96 % is probably due to water which was previously adsorbed on the surface of the material ^[94]. Similar results have been obtained for the hollow nanofibers. Based on these results, it is clear that the centrifugation is not enough to get rid of most of the CTAB. From now on, the reflux step will be added to our initial procedure to wash most CTAB prior to calcination.

Furthermore, the calcination step has been modified, based on the TGA results. The materials will be calcined for 2 h at 250 °C and then for 5 h at 600/800 °C (CB/CNF) instead of one step at 600/800 °C for 24 h. By making this adjustment, the residual CTAB is expected to be removed in a more controlled way and thus will not damage the structure of the silica material. In order to study the effect of these adjustments, some characterisations have been performed by TEM (Figure 3.7) and BET (Figure 3.8).



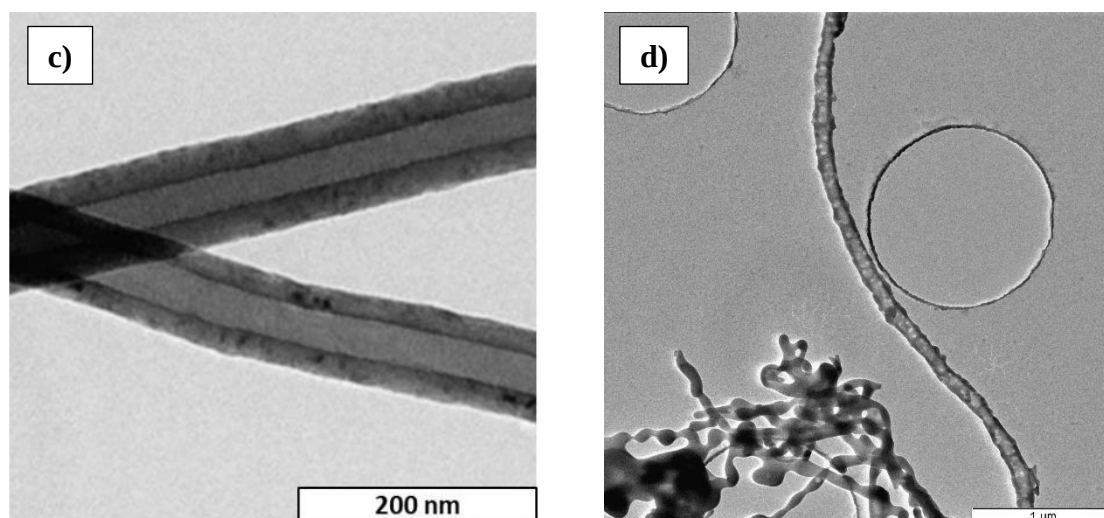


Figure 3.7 TEM images of (a) CB; (b) mHSS; (c) CNF and (d) mHSN. TEM images of CB and CNF are taken from ^[45].

Thanks to these changes in the procedure, the mHSS were successfully produced. However, the preparation of the mHSN was still not conclusive (Figure 3.7d).

As can be seen in Figure 3.7b and d, the obtained silica materials maintain more or less the initial CB or CNF structures. Nevertheless, after calcination, only the mHSS are produced with a void present where the hard-template was previously located. Concerning the “mHSN”, this material has been obtained with a heterogeneous structure. Some “stony” material as well as some mHSN with large holes (around 30 nm) are present in the sample analysed.

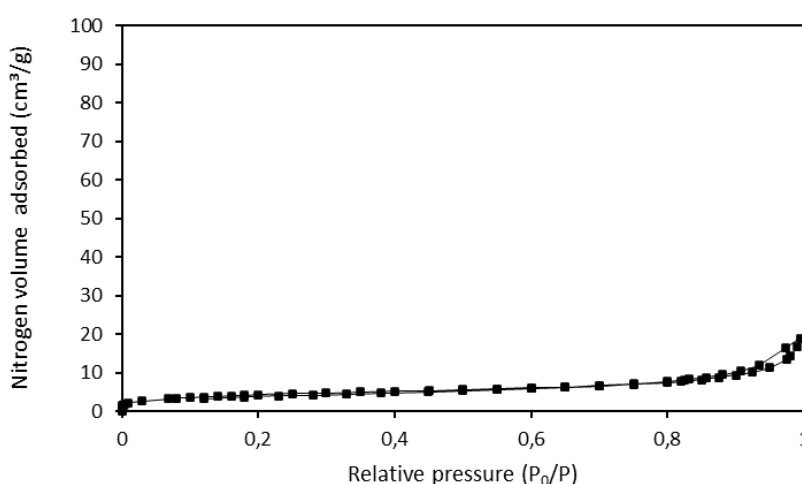


Figure 3.8 Nitrogen adsorption-desorption isotherm at 77 K of the “mHSN”.

The silica material prepared with CNF as hard template exhibits a specific surface of only 16 m²/g (Figure 3.8b). The curve belongs to type II which confirms the absence of porosity. This low specific surface area value is not surprising considering the heterogeneity observed on the TEM image given above. This sample was analysed by XRD in order to understand this strange result (Figure 3.9). From this analysis, it turns out that the crystalline polymorph obtained corresponds to α -cristobalite. Indeed, both experimental and reference XRD patterns give rise to similar peaks. Astonishingly, this phase is supposed to be formed when silica is heated at 1400 °C [95], but it can exist as a metastable phase at room temperature. This means that overheating happened during the calcination step. This problem may come from the oven used for the calcination step with a bad control of the temperature due to its inertia. Another explanation could be that the residual Na coming from the NaOH used in the sol-gel process promotes the formation of this silica phase. Indeed, it is well-known that the presence of alkali metals can reduce the formation temperature of cristobalite to as low as 900 °C [96].

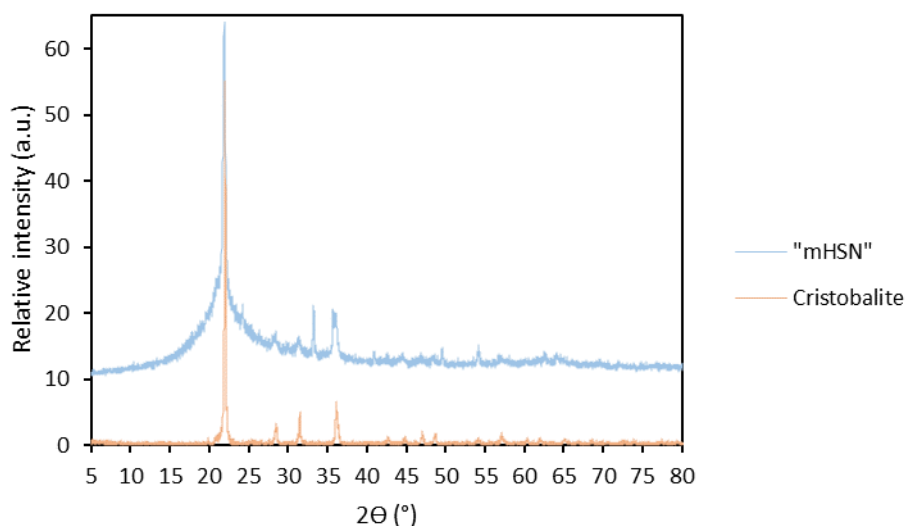


Figure 3.9 Diffraction pattern obtained for the “mHSN” (blue) and reference diffraction pattern for cristobalite (orange) [95].

Therefore, synthesis of the hollow silica materials turned out to be more complicated than expected. Further experimentations, with different experimental parameters, need to be carried out to prepare this material more homogeneously and to avoid the obtention of “stony” structures. Nevertheless, the mHSN obtained with large pores might be interesting for catalytic applications.

3.2 Synthesis of Gold Supported on Silica Catalysts

This section aims at discussing the effectiveness and the influence of the methodology on the preparation of gold NPs supported on silica. First, the Au/SiO₂ reference catalyst will be discussed, followed by the influence of the synthesis parameters with SiO₂ and h-BN as supports.

3.2.1 Preparation and Characterization of the Reference Catalyst (NaW SiO₂)

3.2.1.1 Evaluation of Gold Loading

Since this work is a continuation of the work carried out by Nathalie Meyer in the Hermans group, the first catalyst (NaW SiO₂) synthesised is based on the procedure developed during her PhD thesis ^[2]. The quantity and nature of the support (250 mg of SiO₂ instead of 2.5 g of h-BN) as well as the concentration and volume of the gold precursor (0.5 g/L vs 2.0 g/L HAuCl₄) and of the reductor (1g vs 0.6 g NaBH₄) were modified (see section 2.3.1) to target an Au(1.0 %)/SiO₂ catalyst. As described in section 2.3.1, the catalyst was filtered out and the filtrate analysed by AAS. Based on the calibration curve shown in Figure 3.10, a slight loss of gold has been observed in the catalyst.

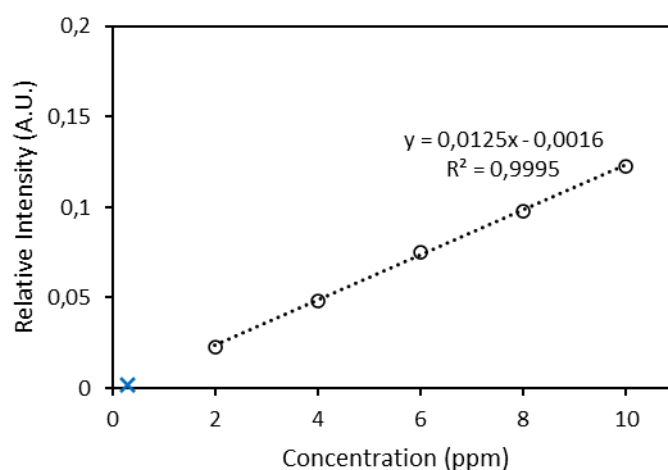


Figure 3.10 Calibration curve of gold solutions from 2 to 10 mg/L with result obtained for the reference catalyst (blue cross).

Indeed, for a nominal value of 0.99 wt.% gold, the catalyst contained up to 0.97 wt.% gold at the end of the synthesis according to the AAS analysis. N. Meyer reported similar results

concerning slight gold loss (for 1.02 wt.% gold engaged, 1.0 wt.% remaining at the end) [2]. However, this method enables to effectively deposit most of the gold on the support whether it is silica or h-BN.

3.2.1.2 Analysis of the Gold Crystallite Size and Reproducibility

The NaW SiO₂ catalyst was analysed by XRD measurement (Figure 3.11). The peaks at around 38, 44, 64 and 77° of the obtained diffraction pattern match very well with the reference XRD pattern (04-0784) (38.1, 44.4, 64.5 and 77.4°) of crystalline gold. This reference pattern consists in four peaks corresponding to standard Bragg reflections (111), (200), (220), and (311) of face-centered cubic lattice [97]. The (220) and (311) plane peaks are not prominent and blend in with the background noise. Like the AAS analysis, the XRD measurement confirm that the synthesis method used allows the gold NPs to be effectively deposited onto the silica support.

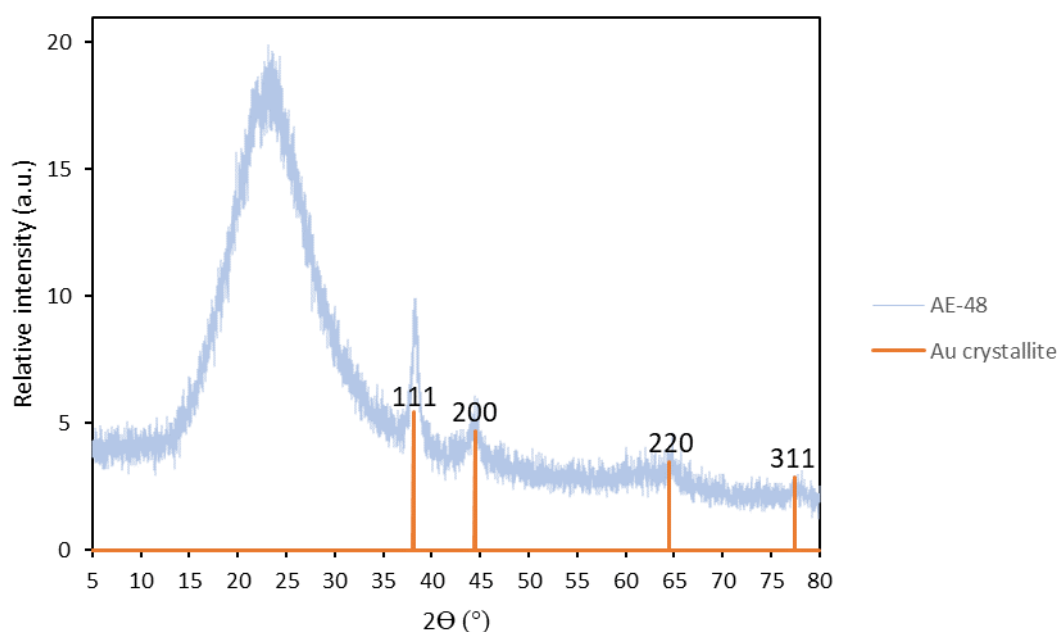


Figure 3.11 Diffraction pattern obtained for the NaW SiO₂ catalyst (blue) and reference diffraction pattern for gold crystallite (04-0784) (orange).

Given the facility and efficiency of the synthesis of this catalyst, it has been selected as reference to test the impact of the temperature and the mass of the catalyst on the activity in the test reaction (as described in the next Chapter). Therefore, nine batches of the NaW SiO₂ catalyst were prepared following the procedure as described in section 2.3.1. The size of the gold

crystallites (d_{XRD}) in the nine batches (Table 3.1) was determined by means of the Scherrer formula (Equation 2.1) using the parameters described in section 2.5.3 and the (111) plane to determine the B and θ values. The calculated d_{XRD} of the gold supported on silica NPs is 12.0 nm on average ($\sigma = 2.2$). The characteristic peaks ($2\theta \approx 25, 38$ and 44°) of the catalyst show up at the same angle from one sample to another (Figure 3.12). This underlines the reproducibility of this synthesis. Only the AE-72 catalyst is relatively inconsistent with the other results obtained (Table 3.1).

Table 3.1 Gold crystallite size in the different NaW SiO₂ catalysts synthesised.

Sample Code	d_{XRD} (nm)
AE-16	8.9
AE-48	13.6
AE-58	10.4
AE-60	12.4
AE-61	13.6
AE-65	10.2
AE-68	10.6
AE-69	11.9
AE-72	16.7

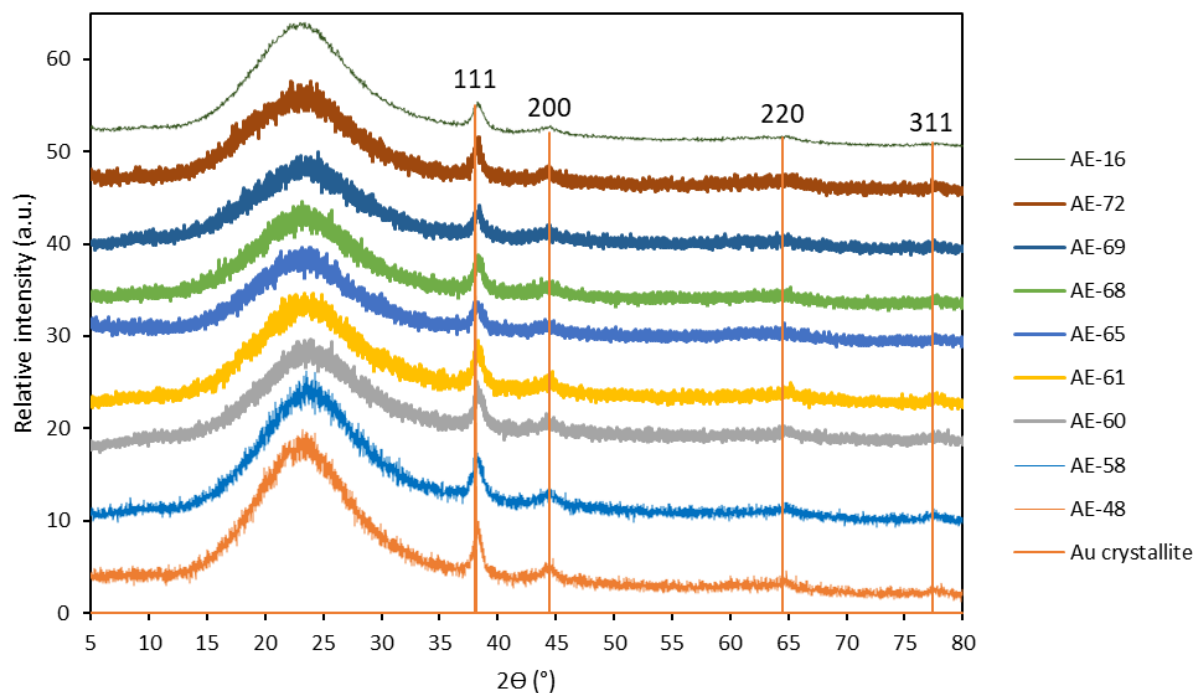


Figure 3.12 Diffraction patterns of the nine different batches of the NaW SiO₂ catalyst and reference diffraction pattern for gold crystallite (04-0784) (orange).

The NaW SiO₂ catalyst was also analysed by TEM. Surprisingly, as can be seen in Figure 3.13, the gold particles are not really visible. Nevertheless, based on the XRD measurements, we are certain to have gold deposited on the silica support. It is also possible that smaller particles than those observed in XRD were obtained and not detected because of their non-crystallinity.

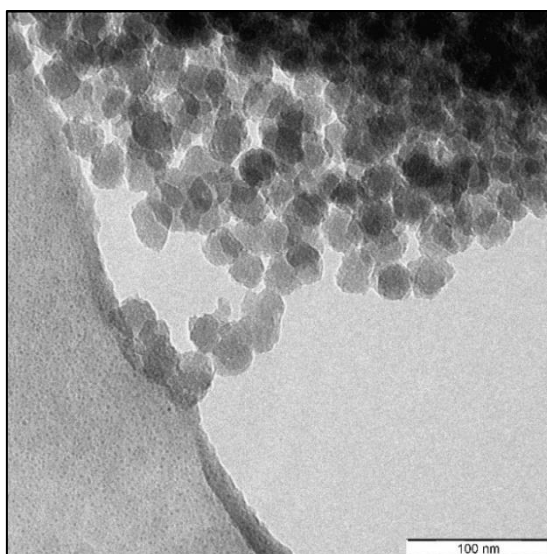


Figure 3.13 TEM image of the NaW SiO₂ catalyst (AE-16).

3.2.2 Influence of the Synthesis Parameters on the Gold Crystallites Sizes

As mentioned in section 1.5, the influence of the gold particle size on its catalytic performance is well established for CO, sugars and more specifically for LBA oxidation [3, 30, 32, 85-86]. Therefore, it is of particular interest to study the influence of the size of the gold crystallites on the catalytic activity. And through this study find the optimal size of gold nanoparticles for the oxidation of lactose under the conditions used in this work (section 2.4). In this section, the effect of the solvent(s) used and the methodology adopted on the size of the gold nanoparticles obtained will be studied.

3.2.2.1 Influence of the Impregnation Solvent(s) Used

N. Meyer demonstrated in her publication that the impregnation solvent (Table 3.2) has a major impact on the size of the gold crystallites obtained via her synthesis route (section 2.3.2.5) [2].

Table 3.2 Influence of the impregnation solvent(s) on the gold particle size in Au/h-BN catalysts [2].

Impregnation solvent	Gold (wt.%)	d _{XRD} (nm)
H ₂ O	1.02	34
CH ₃ CN	1.00	12
CH ₃ OH-H ₂ O (50:50 v/v)	0.99	38

The smallest gold particles were obtained with acetonitrile as solvent while the largest are observed using the water-methanol mixture as solvent.

Based on these results, we tested the following solvents using our own procedure (section 2.3.1): water, acetonitrile, a water-acetonitrile mixture (40 v/v %) (Table 3.3 and Figure 3.14).

Table 3.3 Influence of the impregnation solvent(s) on the gold particle size in Au/SiO₂ catalysts.

Catalyst Code	Impregnation solvent	Gold (wt.%)	d _{XRD} (nm)
NaW SiO ₂	H ₂ O	1.00	12.0
NaA SiO ₂	CH ₃ CN	1.00	8.9
NaW/A SiO ₂	H ₂ O-CH ₃ CN (40 v/v %)	1.00	9.2

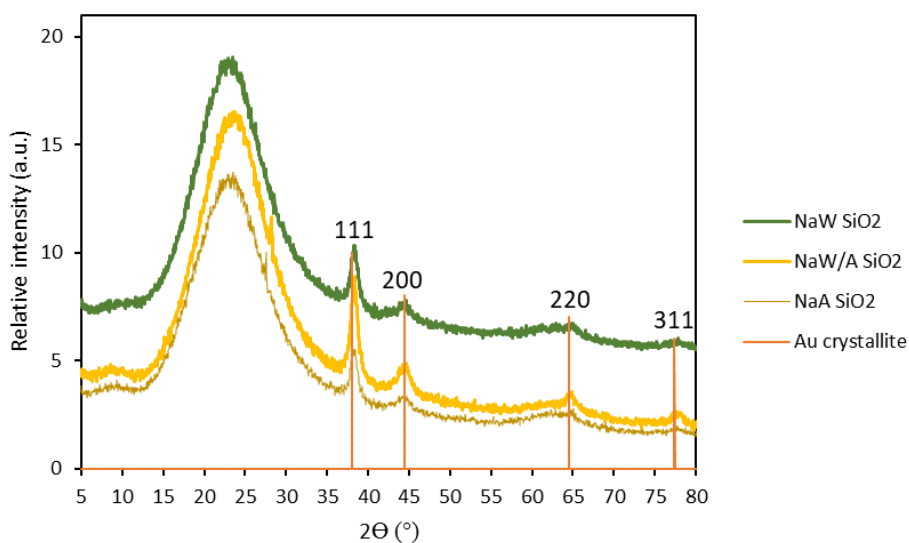


Figure 3.14 Diffraction patterns of NaW (green), NaW/A (gold) and NaA (brown) SiO₂ catalysts and reference diffraction pattern for gold crystallite (04-0784) (orange).

As expected, the trend remains the same, with the smallest gold particles being obtained using acetonitrile (8.9 nm) as solvent and the largest with water (12.0 nm). Those obtained in the water-acetonitrile mixture have an intermediate size (8.9 nm). However, the extent to which the nature of the solvent influences the size of the gold particles is not as important as in the case of h-BN. In addition, the particles obtained are systematically smaller than those obtained by N. Meyer (Tables 3.2 and 3.3). This difference is mostly due to the different support used. Indeed, silica is hydrophilic (thanks to the silanol groups on its surface), which favours the impregnation of gold species. In contrast, a solvophobic effect is observed with h-BN as support, which disfavours the impregnation of gold on its surface. Therefore, silica yields to smaller particles than h-BN with water as solvent (12 vs 34 nm). Also, the modifications introduced in the synthesis developed by N. Meyer, which mainly consist in a higher concentration of the chemical reductant (NaBH₄) and a lower amount of support (section 2.3.1) can also affect the gold particles size.

3.2.2.2 Influence of the Methodology

As described in the introduction part (section 1.4.2), the gold deposition method also influences the size of the gold particles obtained. More Au/SiO₂ catalysts were prepared following two different methodologies: the wet impregnation and the prior preparation of gold colloids. XRD

diffraction patterns of the UFW, NH₃W, PVAW and NAW SiO₂ catalysts are shown below (Figure 3.15) as well as their calculated d_{XRD} (Table 3.4).

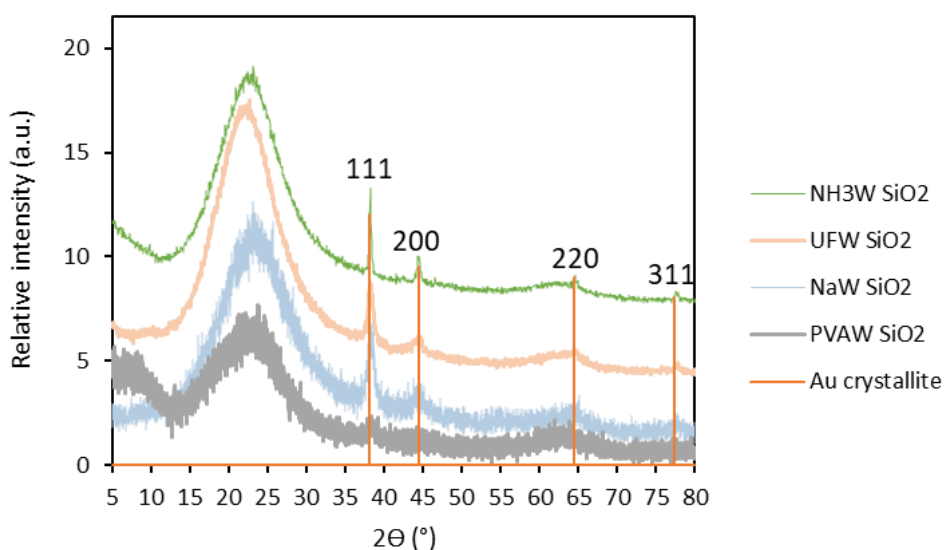


Figure 3.15 Diffraction patterns of NH₃W (green), UFW (pink), NaW (blue) and PVAW (grey) SiO₂ catalysts and reference diffraction pattern for gold crystallite (04-0784) (orange).

Table 3.4 Influence of the gold deposition methodology on the gold particle size in Au/SiO₂ catalysts.

Au/SiO ₂ materials	d_{XRD} (nm)
NH ₃ W SiO ₂	34.2
UFW SiO ₂	11.8
NaW SiO ₂	12.0
PVAW SiO ₂	11.3

The UFW SiO₂ catalyst synthesis consists in a urea-assisted sodium formate homogeneous deposition process. From the literature, it was assumed that this method (applied for Pd) would yield relatively small gold NPs ^[45]. Using this method, the authors were able to obtain Pd particles of around 3 nm. These small particles are promoted by the slow pH rise due to the gradual urea hydrolysis under heating (90 °C) which avoids precipitation of the metal hydroxide in solution ^[98]. Chemical reduction of the metal species present in solution is ensured by sodium formate. Based on the XRD measurements (Figure 3.14) and using the Scherrer formula with

the (111) plane at $2\theta = 38^\circ$, the gold crystallite size calculated is 11.8 nm. This discrepancy in size compared to literature probably comes from the use of a silica instead of CB as support ^[45]. Indeed, the specific surface area of 63 m²/g for CB vs 371 m²/g for SiO₂, as well as the chemical functions present at the surface are drastically different, which may affect the size of the resulting NPs ^[45].

As mentioned in section 1.4.2.1, it has been decided to use the procedure developed by Delannoy *et al.* consisting in washing with ammonia the silica full spheres support after gold impregnation ^[71]. Furthermore, a thermal reduction of the gold precursor was performed in the same conditions as in this publication ^[71]. The (111) plane peak of the so-obtained NH₃W SiO₂ catalyst (Figure 3.14) is sharp and narrow, which means that the size of the gold crystallites is quite large. Indeed, the d_{XRD} calculated using Scherrer formula is equal to 34.2 nm. Therefore, the gold particles obtained are much larger than expected (4 nm; as determined by TEM in the publication) (Table 3.5) ^[71]. There are several possible explanations for this result. The first one is that another type of silica support was used in the publication. Even if the BET specific surface area is nearly equivalent (250 vs 371 m²/g for our silica support), the particle size is drastically different with 40 μm vs 40 nm in diameter, respectively (Table 3.5) ^[99]. As a result of the slightly larger surface area of our SiO₂ support, a larger amount of chlorinated residues from the precursor can adsorb to its surface. Thus, the washing step may be insufficient by keeping the same parameters as in the publication ^[71]. The choice of the deposition method might be another explanation. Indeed, a wet impregnation method was used in this work (with an excess of solvent) whereas it was an incipient wetness impregnation (same amount of solvent than the total pore volume) in the publication (Table 3.5) ^[71].

Table 3.5 Comparison of the method developed in this work and the method from the reference publication ^[71].

	Method described in [71]	NH ₃ W SiO ₂ method
Gold particle sizes (nm)	4	34
SiO ₂ particles size (nm)	40 000	40
BET specific surface area (m ² /g)	250	371
Impregnation method	IWI	WI

However, the obtention of large particle sizes is not a dramatic issue, as we wanted to make gold-on-silica catalysts with a range of gold particle sizes. By this method, we succeeded in obtaining relatively large gold nanoparticles that might be interesting for comparison purpose.

The colloidal gold NPs used in the synthesis of PVAW SiO₂ catalyst were first characterised by TEM in order to determine the morphology and size of the NPs. As shown in Figure 3.16, gold NPs possess a spherical morphology with a calculated (over 100 different NPs) average diameter of 3.6 ± 0.7 nm. This result is consistent with the expected morphology and size mentioned above (section 1.4.2.2) by using PVA as polymeric stabiliser ^[81].

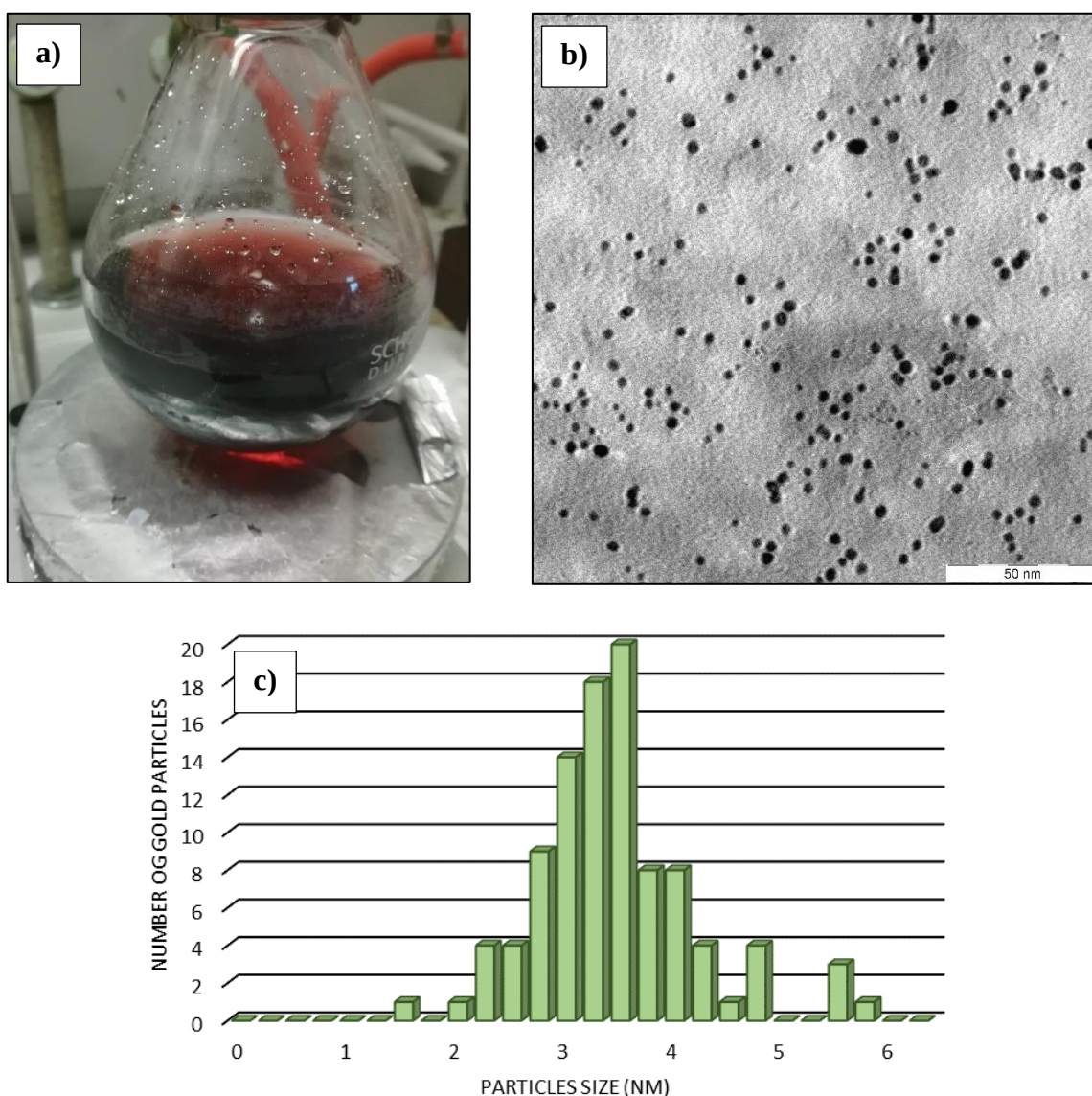


Figure 3.16 (a) Suspension obtained after the synthesis of gold NPs; (b) TEM image of the gold NPs and (c) Particle size distribution (over 100 particles) in the gold NPs obtained using the PVA method.

Once the colloidal gold suspension was prepared, the gold particles were deposited on silica (section 2.3.2.3). The presence of residual polymeric stabiliser is considered to have a negative effect on the catalytic performance, due to the hindered access of reactants to the catalyst surface^[100]. A washing step was therefore added, with hot water (70 °C) and ethanol to dissolve the remaining PVA on the catalyst surface. Indeed, PVA is known to be soluble in hot water and slightly soluble in ethanol while it is insoluble in most organic solvents^[101].

TEM images of the so-obtained PVAW SiO₂ catalyst were recorded (see Figure 3.17). The calculated (over 40 different particles) average size of PVA-free gold NPs is equal to 8.1 nm ($\sigma = 3.7$). This result is consistent with the calculated d_{XRD} of 11.3 nm (Table 3.4). This growth of the gold NPs compared to the PVA-protected gold colloids has been also observed in the work of Shi *et al.* (from 3 nm to 16 nm of diameter)^[73]. They proved that even after intensive washing (with deionised water) of the catalyst, PVA bound to gold NPs was still remaining. However, they found no evidence of surface modification due to PVA interaction with gold NPs^[73]. Therefore, this sintering is probably due to the tendency of the gold particles to decrease their surface energy, once released from their protective PVA layer.

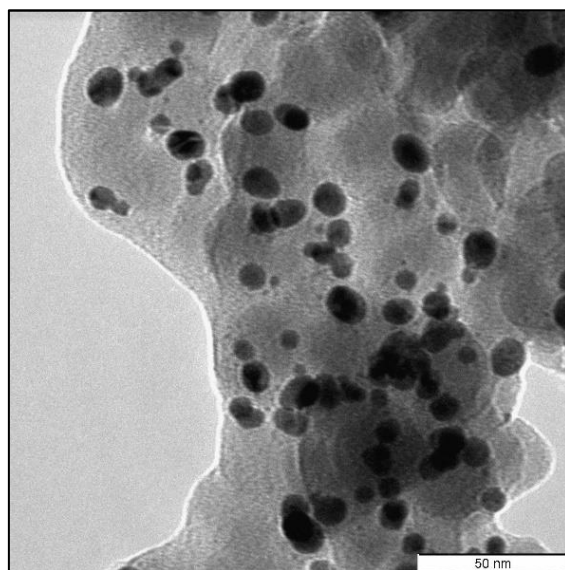


Figure 3.17 TEM image of the PVAW SiO₂ catalyst.

3.2.3 Gold Supported on h-BN Catalysts

It has been decided to reproduce the N. Meyer Au/h-BN catalyst synthesis to use it as a reference for the selective oxidation of lactose to LBA. With this catalyst (named NM h-BN), 100 % conversion of lactose and 100 % selectivity toward LBA are expected after 4 h of

reaction under the conditions described in section 2.4 with a mass of catalyst of 500 mg and a temperature of 40 °C ^[2]. This catalyst was analysed by TEM (Figure 3.18). The calculated (over 50 different particles) average size of gold NPs is equal to 7.2 nm ($\sigma = 1.8$). N.M. obtained similar particle sizes (around 10 nm) proving the reproducibility of this synthesis ^[2].

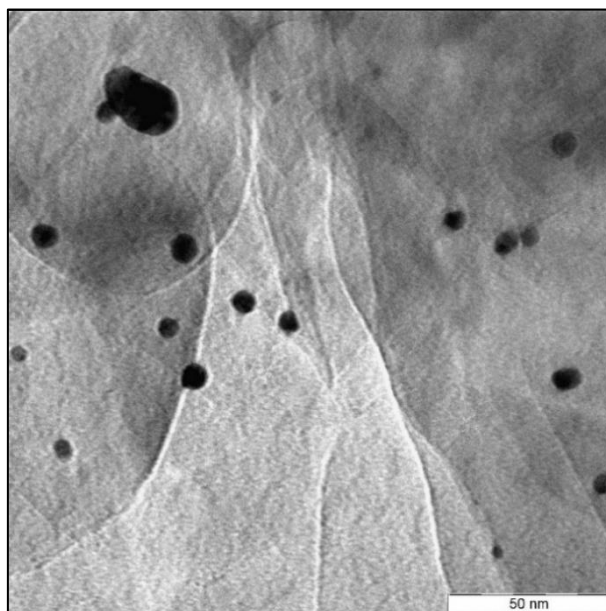


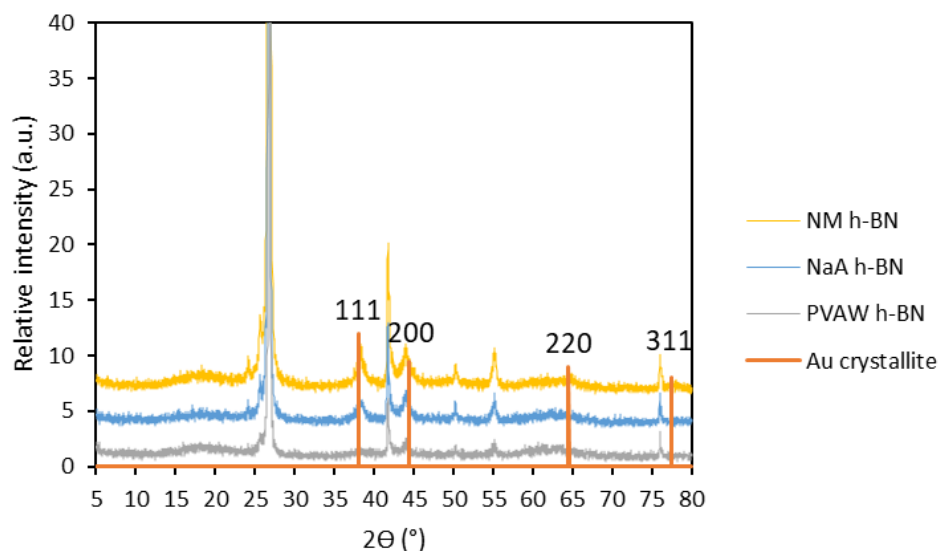
Figure 3.18 TEM image of the NM h-BN catalyst.

One of the objectives of this work was to produce also Au/h-BN catalysts via the methods developed in the sections 2.3.1 (NaA h-BN) and 2.3.2.4 (PVAW h-BN). The activity in the oxidation of lactose of these catalysts may then be directly compared to that achieved with the NM h-BN catalyst. From this, it would be possible to deduce which method of synthesis is the most suitable for the reaction.

The three h-BN catalysts so produced were analysed by XRD measurements (Figure 3.19) and the gold crystallite size was calculated using the Scherrer formula with the (111) plane at $2\theta = 38^\circ$ (Table 3.6). The NM and NaA h-BN catalysts contain gold crystallites equivalent in size (14.0 vs 13.3 nm). In contrast, gold NPs obtained via the colloidal method (PVAW h-BN) do not lead to any peak at $2\theta = 38^\circ$, which means that the particles size is approximatively under 3 nm. Indeed, the smallest nanoparticles are usually not detected by XRD since they are amorphous ^[45]. Based on the red colour of the material, the hypothesis that the gold was not deposited on the h-BN was rejected. This means that no sintering of the colloidal gold NPs is observed with h-BN as support, unlike with silica (section 3.2.2.2). Therefore, we expect the gold particles size to be around 3-4 nm in this sample.

Table 3.6 Gold crystallites sizes in the h-BN catalysts.

Catalyst	d_{XRD} (nm)
NM h-BN	14.0
NaA h-BN	13.3
PVAW h-BN	≤ 3 nm

**Figure 3.19** Diffraction patterns of the NM h-BN (yellow), NaA (blue) and PVAW h-BN (grey) catalysts and reference diffraction pattern for gold crystallite (04-0784) (orange).

3.3 Conclusions of the chapter

The main aim of this chapter was to produce materials made of gold particles supported on silica. Three different silica supports morphologies were studied: full spheres, hollow spheres and hollow nanofibers.

For the full spheres, their preparation via the modified Stöber method was a real success with an average hydrodynamic diameter of 40 nm. Concerning the hollow structures, the addition of a washing step turned out to be essential and enabled to obtain the hollow spheres. TEM analysis of the hollow spheres confirmed the formation of an inner cavity. Regarding the preparation of the hollow nanofibers, heterogeneous structures (nanofibers with holes and “stony” structures) have been observed by TEM. Based on XRD, the silica phase obtained

corresponds to α -cristobalite. The formation of this phase is probably catalysed by the remaining Na present in the material during the calcination step.

The silica full spheres were selected for the next step, namely gold deposition. We aimed at producing gold particles with a large size range, which has been achieved by producing NPs with sizes ranging from 9-12 to 34 nm, as confirmed by XRD and TEM measurements.

Au/h-BN catalysts were also prepared for comparison, in order to study the effect of the support on the catalyst properties. Of these catalysts, N. Meyer's catalyst was successfully replicated and will be used as a reference for the catalysis of lactose oxidation reaction in LBA.

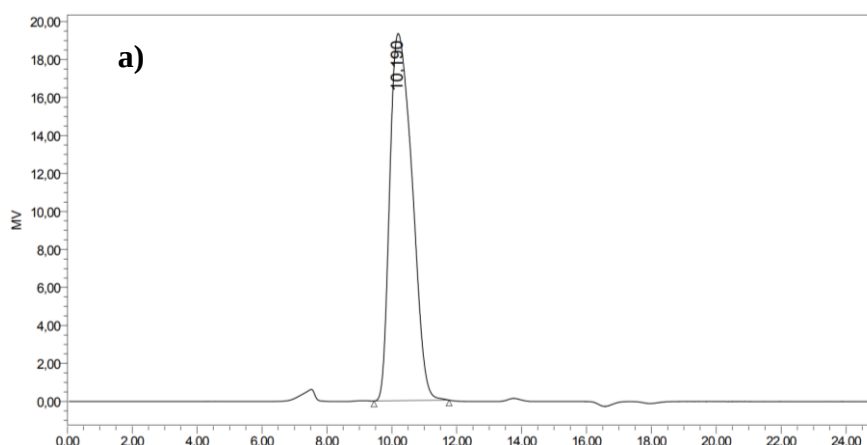
RESULTS AND DISCUSSION: CATALYTIC TESTS

4.1 HPLC Method Development

In this section, the development of an HPLC method in order to separate acidic sugars formed from lactose oxidation will be studied. The assignation of the different peaks obtained is also discussed.

4.1.1 Quantification of Lactose and LBA

Since the Hermans group had not worked with acidic sugars for a few years and the column used to perform the analysis by HPLC was no longer functional, the first attempt was to test the Carbohydrate Transgenomic CarboSep CHO682 column to determine if lactose and lactobionic acid (LBA) were separated. Based on the parameters from a previous publication of N. Meyer, injections (10 μ L) were performed using mQ water as eluent with a flow of 0.4 mL/min, a column temperature of 80 °C (Figure 4.1) [2].



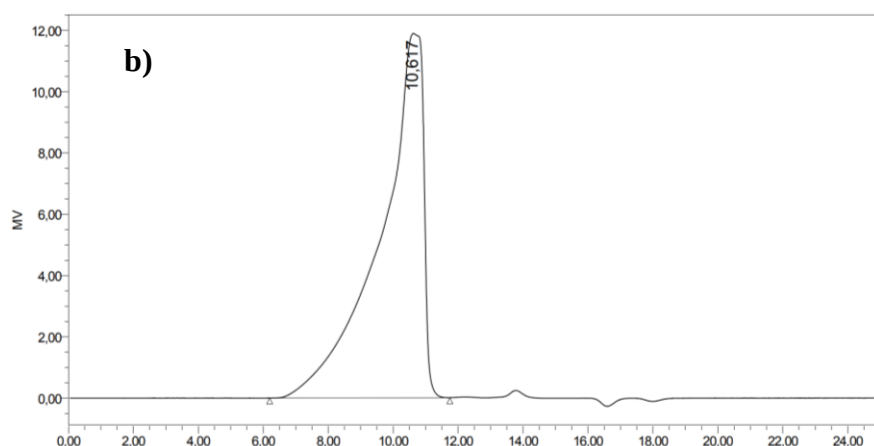


Figure 4.1 Chromatogram of (a) lactose and (b) LBA on Carbohydrate Transgenomic CarboSep CHO682 column with mQ water as eluent, a flow of 0.4 mL/min, a column temperature of 80 °C and 10 μ L of injected volume.

The peak corresponding to lactose (Figure 4.1a) is well defined whereas the peak corresponding to LBA (Figure 4.1b) is widened. The tailing of the LBA peak is probably due to the occurrence of more than one mechanism for its retention. Indeed, in addition to nonspecific hydrophobic interactions with the stationary phase, there is obviously polar interactions between the stationary phase and the LBA due to the acid base equilibrium of this organic acid ^[102]. Moreover, even if the width of the LBA peak could be improved, the retention times of lactose (10.2 min) and LBA (10.6 min) are too close to obtain an acceptable peak separation in these conditions.

Therefore, a new column capable of separating sugars from acidic sugars was needed. Based on a publication by Pedruzzi *et al.*, it was decided to buy the strong hydrogen cation ion exchange resin column (ICSep ICE-ION-300 column, 300 mm $\times$ 7.8 mm, particle diameter 7 μ m) from Transgenomic (San Jose, CA, USA) ^[103]. Indeed, this publication underlines the ability of this column to separate lactose from LBA using 0.45 mM H₂SO₄ as eluent at a flow rate of 0.5 mL/min and a column temperature of 75 °C (see annexe A.4c) ^[103]. These parameters were applied to our system and an injection of 10 μ L of a 50:50 (v:v) mixture of lactose (3000 ppm) and LBA (3000 ppm) solutions was performed using this new column (Figure 4.2).

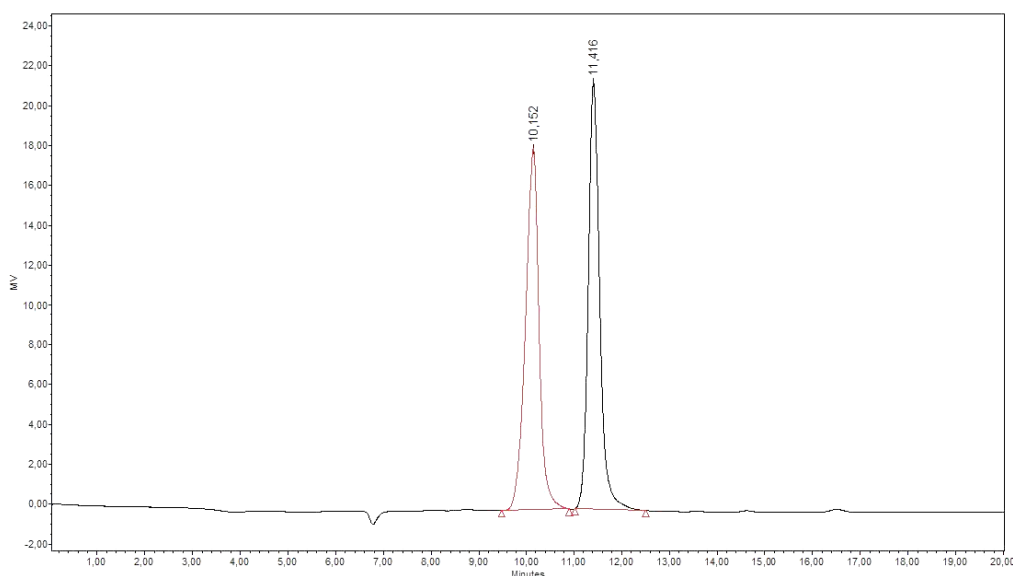


Figure 4.2 Chromatogram of a 50:50 (v:v) mixture of lactose (10.152 min) and LBA (11.416 min) solutions, both at 3000 ppm on the Transgenomic ICSep ICE-ION-300 column with 10 μ L of injected volume, 0.45 mM H_2SO_4 as eluent, a flux of 0.5 mL/min and a column temperature of 75 $^\circ\text{C}$.

Figure 4.2 shows a good separation between the two compounds. Indeed, retention times of 10.2 min for lactose and 11.4 min for LBA were obtained, and a LBA peak far less widened than with the previous column improved their separation. Based on these results, calibration curves of these two compounds were built on one injection of 5 different concentrations (see annexe A.3a and A.3b). For both the lactose and LBA curves, the R^2 factor is very high (> 0.999), which means that the converted lactose and the LBA produced can be accurately quantified based on those calibration lines. In the next sections, all the HPLC analyses will be performed by using these parameters developed by Pedruzzi *et al.*, except the injected volume (10 instead of 20 μ L) ^[103].

4.1.2 Attribution of the HPLC Peaks for a Representative Catalytic Reaction Filtrate

The analysis by HPLC of an aliquot of a batch reaction performed at 70 °C with 100 mg of NaW SiO₂ as catalyst is shown in Figure 4.3.

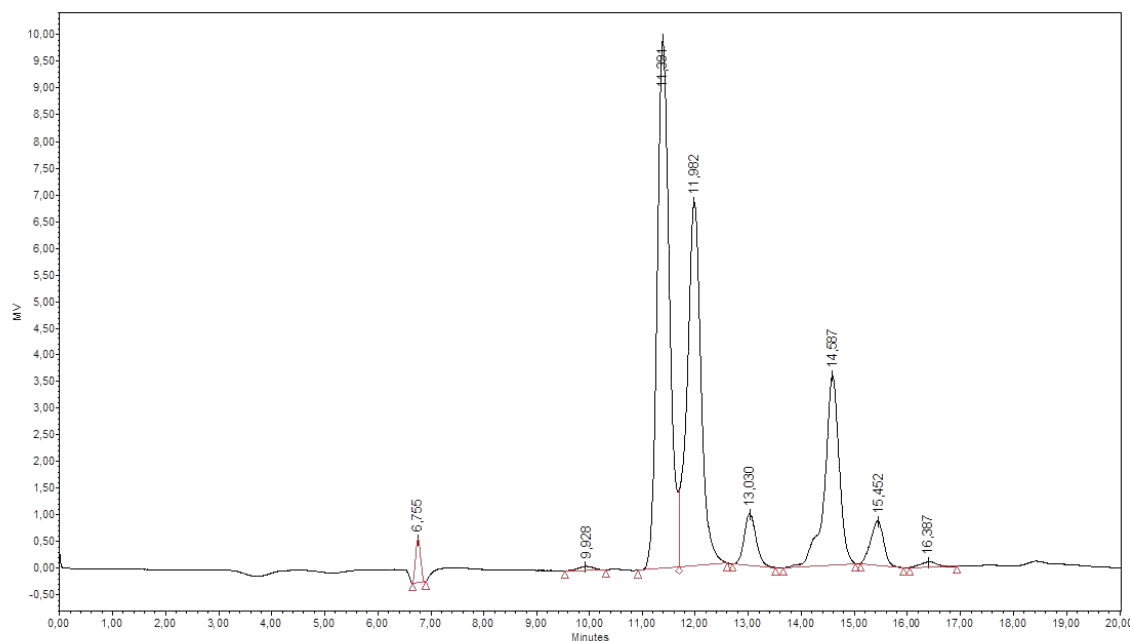


Figure 4.3 Chromatogram of a catalytic test carried out with 100 mg of NaW SiO₂ at 65 °C.

As one can see, eight different peaks are obtained in a typical chromatogram such as the one showed in Figure 4.3. The peak at 6.8 min can be attributed to the lactone intermediate according to the publication on which this HPLC method has been based ^[103]. As mentioned in section 1.2, the lactobionolactone is formed from lactose during the oxidation process and further hydrolysed to LBA ^[32, 37, 103]. The peaks at 9.9 and 11.4 min are respectively attributed to LBA and lactose from their chromatograms (see Figure 4.2). Concerning the peaks at 12.0, 13.0, 14.6, 15.5 and 16.4 min, their possible nature will be discussed in the paragraph below.

As described in section 1.1.3, the heterogeneous oxidation of lactose leads to LBA salt, which can undergo further oxidation to produce 2-keto-LBA salt. In addition, the alkaline conditions used for this reaction can lead to isomerisation of lactose into lactulose and epimerisation to epilactose as by-products ^[104]. Moreover, either from lactulose or epilactose, hydrolytic clivage can occur to form the isosaccharinate (ISA) salt and galactose ^[105]. Finally, given the high temperatures tested, some well-known lactose degradation products such as tagatose, fructose and formic acid can be formed ^[106]. Figure 4.4 summarises some of the products that can be

obtained from lactose when oxidation is carried out in an alkaline medium (with NaOH as a base).

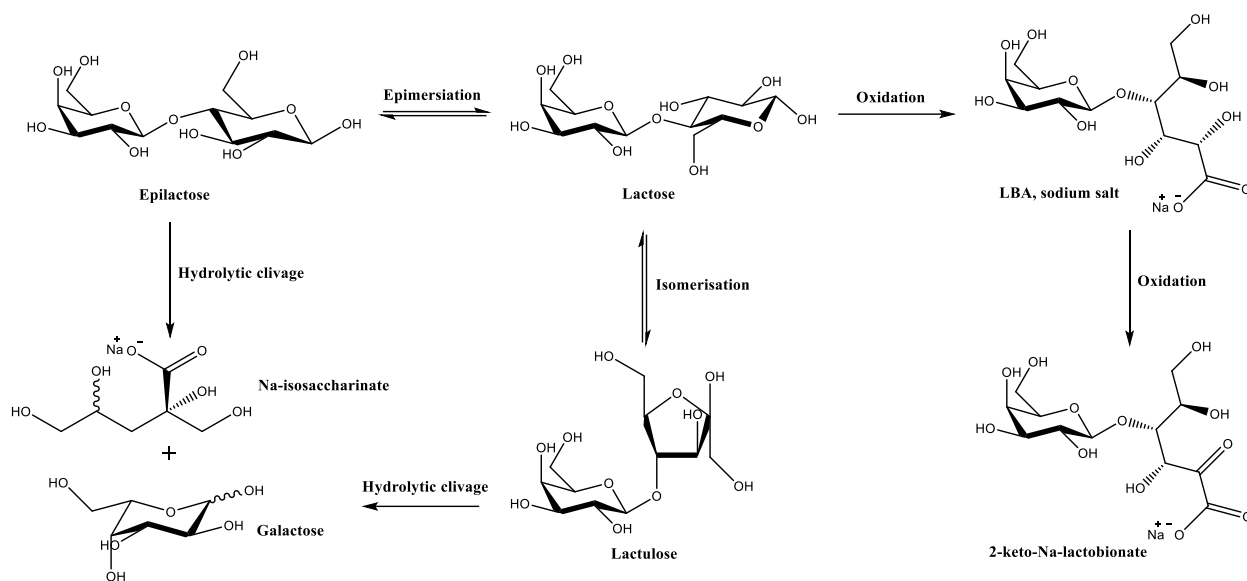


Figure 4.4 Schematic pathway through which lactose may get transformed under alkaline conditions in the presence of oxygen flow.

Since several peaks obtained by HPLC remained unidentified at this stage, some of the products represented in Figure 4.4 were analysed by HPLC and their retention times were compared with the ones obtained in Figure 4.3 (Table 4.1) (see annexes A.4a and A.4b for lactulose and galactose HPLC chromatograms).

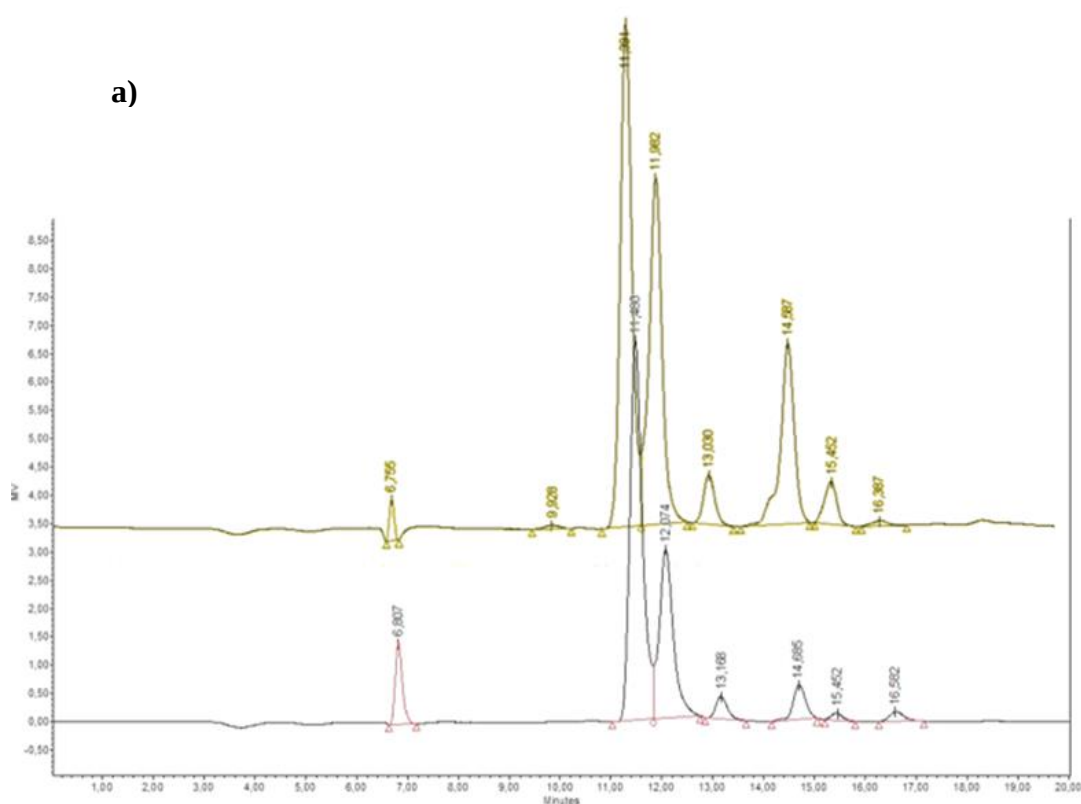
Table 4.1 List of lactose derivatives and their retention times.

Standard	Retention time (min)
LBA	10.0
Lactose	11.5
Lactulose	12.1
Tagatose	14.5
Galactose	14.7
Fructose	14.9

From the analysis of these standards, the peak at 12.0 min (Figure 4.3) could be attributed to lactulose (12.1 min) and the peak at 14.6 min (Figure 4.3) corresponds either to tagatose (14.5

min) or galactose (14.7 min). For the first one, based on a lactulose calibration curve (see annexe A.3c), it will be possible to determine the lactulose yield for our reactions. Regarding the peak at 14.6 min, it should be underlined that a retention time of 14.7 min in average was obtained, taking into account all the catalytic tests made subsequently. Therefore, this peak likely corresponds to galactose. Once more, thanks to the galactose calibration line (see annexe A.3d), it was possible to quantify the galactose yield. From this outcome, one of the remaining peaks (12.0, 13.0, 15.5 and 16.4 min) could be attributed to the ISA since it is produced in an equimolar ratio with galactose according to Figure 4.4 ^[105]. Concerning the quantification of the lactone (6.8 min), it was evaluated by means of the calibration curve of lactose and LBA since their slope are similar. This approximation allowed to calculate an approximative yield of lactone.

Another important factor to be considered is the pH of the solution. Indeed, since LBA has a pK_a value of 3.8 ^[11], both the acidic and basic forms of this compound co-exist at pH 9 (pH of the solution during the catalytic test) or pH 4 (pH of LBA in solution). Therefore, the ability of the column to separate these two forms of LBA was evaluated at pH 4 and pH 9 (Figure 4.5).



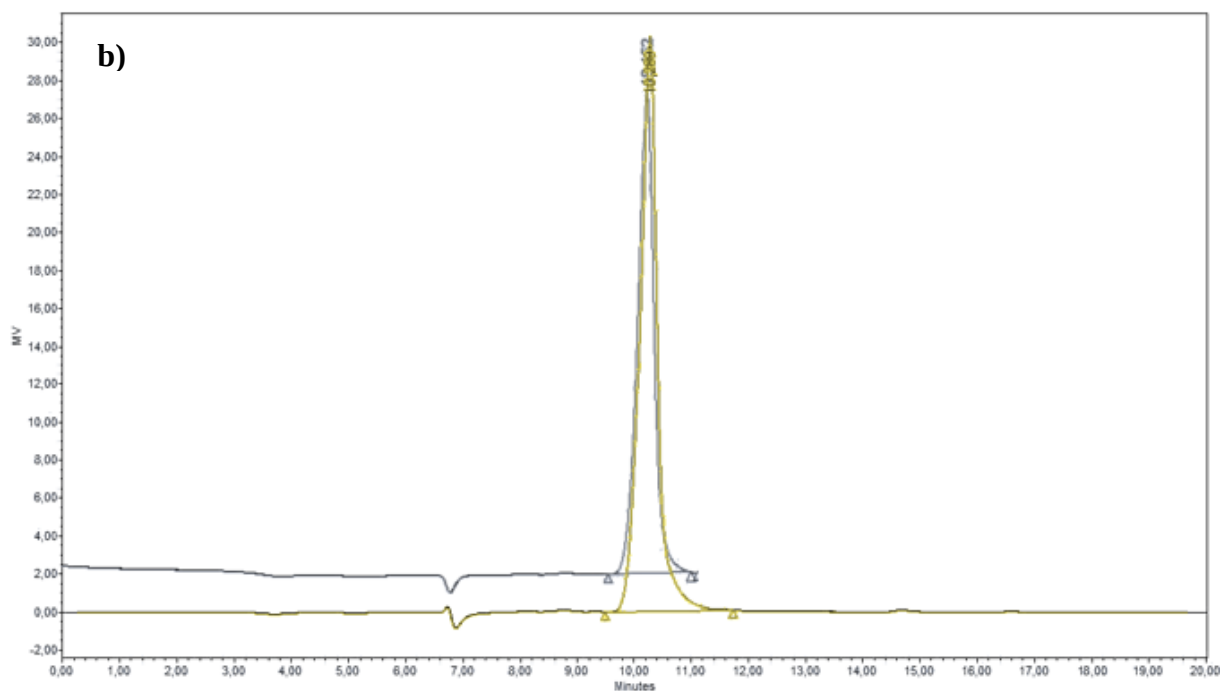


Figure 4.5 Chromatograms obtained for (a) a catalytic test set at pH 4 (black) and at pH 9 (yellow) after its ending and (b) a LBA solution at pH 4 (black) and set at pH 9 (yellow) after dilution.

As shown in Figure 4.5a, the peaks with a retention time of 12.0, 13.0, 15.4 and 16.6 min at pH 9 does not shift substantially when the sample is set at pH 4. The same kind of consideration takes place when the LBA solution is set at pH 9 instead of pH 4, with no significant shift observed for the peak at 10.0 min (10.2 vs 10.0 min, respectively). Hence, the pH value does not lead to a splitting of the peak related to LBA.

4.1.3 Conclusions

Based on a publication by Pedruzzi *et al.*, it was decided to use the ICSep ICE-ION-300 column with 0.45 mM H₂SO₄ as eluent at a flow rate of 0.5 mL/min and a column temperature of 75 °C to separate lactose from LBA. The new HPLC method enabled to obtain an adequate separation of lactose and LBA and therefore to quantify them by the use of calibration curves. However, multiple other HPLC peaks were detected in the catalytic filtrates. Based on the potential lactose derivatives produced under the reaction conditions, several products were investigated. From these, it turns out that we obtained galactose (14.7 min) and lactulose (12.1

min). Based on the publication by Pedruzzi *et al.*, it was also possible to identify the formation of lactone (6.8 min).

4.2 Catalytic Tests Results

The results of the catalytic tests are discussed in this section. First, the blank experiments will be discussed, followed by an evaluation of the performances of the Au/h-BN catalysts. Finally, the influence of the synthesis methodology as well as the impact of the mass of catalyst and temperature parameters used in the reaction will be studied for the Au/SiO₂ catalysts.

4.2.1 Blank measurements

Blank experiments were carried out using 1.8 g of lactose and an oxygen flow of 0.5 L min⁻¹ at 40 or 65 °C. A first hint on the catalytic activity is given by the amount of base added during the catalytic test by the automatic titration device to keep the pH constant. Indeed, if an acidic compound is produced as expected, an equimolar amount of base should be added. As shown in the Figure 4.6, no acid is produced after 4 h of reaction at 40 °C whereas 16 mL of KOH (0.1 M) were added at 65 °C. This indicates that even without any catalyst present, some conversion of lactose is occurring. Indeed, 9.3 % and 43.8 % lactose conversion are respectively observed at 40 and 65 °C, based on the HPLC analysis. Concerning the lactone, lactulose and galactose, the amount produced increases with the temperature (Table 4.2).

The products obtained at 40 and 65 °C are not the same and assigned to the following HPLC peaks: 12.3 (lactulose) and 13.2 min at 40 °C, and 6.8 (lactone), 12.2 (lactulose), 14.8 (galactose) and 15.6 min at 65 °C (Table 4.2). In the following, we will refer to this set of peaks as “the blank peaks”. As expected, lactose is mainly converted into lactulose due to the alkaline conditions ^[107].

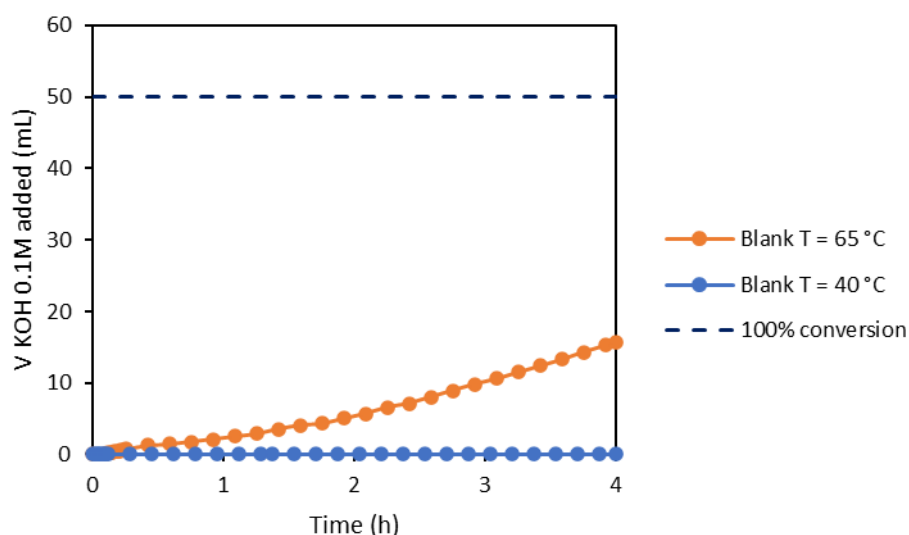


Figure 4.6 Evolution of the KOH volume added in function of the time for blanks at 40 (blue) and 65 °C (orange). The dark blue dashed line represents the volume that would be added for 100 % lactose conversion into a mono-acid product.

Table 4.2 Lactose conversion and yields in the known products during the blank catalytic tests at 40 and 65 °C after 4 h, with 0.5 L min⁻¹ oxygen flow and pH 9.

Temperature of the tests (°C)	Lactose conversion (%)	Yield in lactone (%)	Yield in LBA (%)	Yield in lactulose (%)	Yield in galactose (%)
40	9.3	0.0	0.0	8.8	0.0
65	43.8	1.0	0.0	29.8	12.0

4.2.2 Evaluation of the activity of the h-BN support

100 mg of h-BN were tested in a catalytic reaction with the parameters described in section 2.4. As expected, the h-BN alone does not lead to intense activity. Only 2.2 mL of KOH (0.1 M) were added after 2 h of reaction (Figure 4.7). The moderate activity of h-BN is also confirmed by HPLC analysis. Indeed, 23.9 % of lactose conversion is observed with 0.0 % yield into LBA. The products formed during this catalytic test correspond to 0.5 % yield of lactone (6.8 min), 22.5 % yield of lactulose (12.1 min), 2.9 % yield of galactose (14.7 min) and another unidentified product (detected at 16.6 min). Compared to the blank measurement at 65 °C

without any solid, both activities are of the same order, suggesting that the h-BN support alone does not change the kinetics of the reaction. Therefore, h-BN seems to be a relatively good support to avoid side-reactions promoted by the support surface, a phenomenon that is not so uncommon in heterogeneous catalysis.

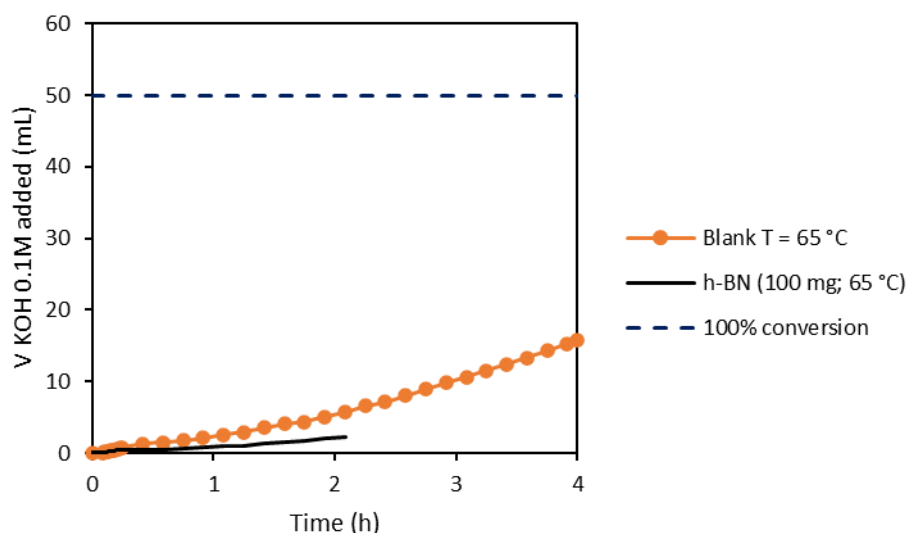


Figure 4.7 Evolution of the KOH volume added in function of time with 100 mg of h-BN and 1.8 g of lactose at 65 °C. The dark blue dashed line represents the volume needed to obtain 100 % lactose conversion into a mono-acid product.

4.2.3 Evaluation of the activity of the Au/h-BN catalysts

4.2.3.1 NM h-BN catalyst

As mentioned in section 3.2.3, the NM h-BN catalyst was prepared following exactly the procedure developed by N. Meyer in order to study the reproducibility of the process and the influence of the temperature. Therefore, 500 mg of this catalyst were tested at 40 and 65 °C (Figure 4.8). Interestingly, the best activity with optimal selectivity is found at 40 °C whereas it is reported at 65 °C in the literature with silica as support for this reaction ^[14]. Indeed, the lactose is converted at 100 % after 2 h for the test carried out at 40 °C while it requires 2.75 h at 65 °C. Both catalytic tests give rise to nearly 100 % yield in LBA with some trace amount of lactone, based on HPLC analysis (Table 4.4). N. Meyer obtained similar results with 100 % of conversion after only 2 h at 40 °C, confirming the reproducibility of the synthesis method, catalytic test and the device ^[2].

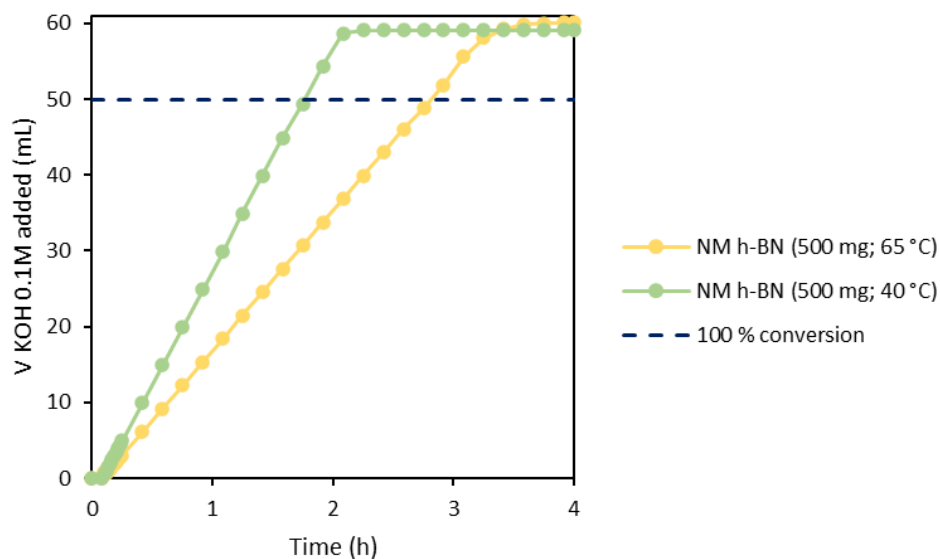


Figure 4.9 Evolution of the KOH volume added as function of time with 500 mg of NM h-BN catalyst and 1.8 g of lactose at 40 (green) and 65 °C (yellow). The dark blue dashed line represents the volume that would be added for 100 % lactose conversion into a mono-acid product.

Table 4.4 Lactose conversion and yields in the known products with NM h-BN as catalyst at 40 and 65 °C after 4 h, with 0.5 L min⁻¹ oxygen flow and pH 9.

Temperature of the tests (°C)	Lactose conversion (%)	Yield in LBA (%)	Yield in lactone (%)	Yield in lactulose (%)	Yield in galactose (%)
40	100	99.5	0.5	0.0	0.0
65	100	98.9	1.1	0.0	0.0

4.2.3.2 PVAW and NaA h-BN catalysts

Two different methodologies of gold deposition (section 3.2.3) using h-BN as support were tested in the reaction. Interestingly, the NaA and PVAW h-BN catalysts (from $t = 0$ to $t = 2$ h) follow the same curves and both develop a slightly better activity than the h-BN support alone (Figure 4.9). This means that both catalysts have similar activities. However, their performance are much lower than that obtained with the NM h-BN reference catalyst. By comparing via HPLC analysis the NaA h-BN catalyst to the h-BN support, it appears that the lactose

conversions are of the same order (29.0 vs 23.9 %). However, the NaA h-BN catalyst leads to 2.5 % of LBA whereas the h-BN leads to 0 % LBA and gives only one by-product: lactulose (12.1 min) (Table 4.5).

Using PVAW h-BN catalyst, a lactose conversion of 45 % with 5.6 % yield of LBA was obtained after 4 h. In addition, most of the peaks observed with PVAW h-BN catalyst are equivalent to the peaks obtained with h-BN support while they are not observed with NaA h-BN catalyst, suggesting that those peaks (12.1 and 14.7 min) appear between 2 and 4 h of reaction (Table 4.5). Hence, even if the PVAW and NaA h-BN catalysts present different gold particles sizes, they would probably show equivalent activities and equivalent selectivities after 4 h of reaction. N. Meyer demonstrated in her work that Au/h-BN catalyst does not suffer from diffusional limitation ^[30]. Therefore, one can expect to produce five times more LBA if 500 mg of PVAW and NaA h-BN catalysts were used instead of 100 mg. This would correspond to a yield of about 30 % in LBA, which is low compared to the 100 % achieved by the NM h-BN catalyst.

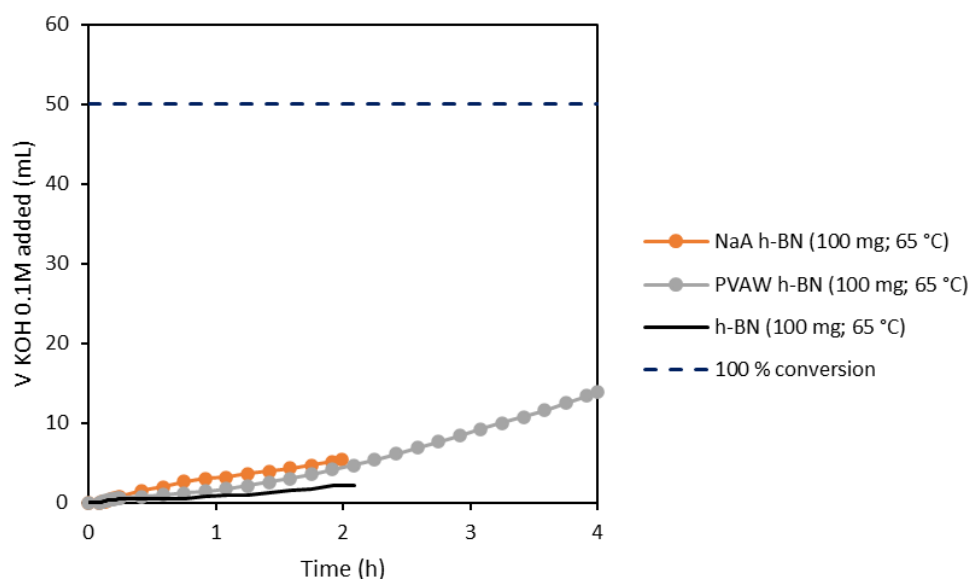


Figure 4.9 Evolution of the KOH volume added as function of time for 100 mg of NaA h-BN (orange), PVAW h-BN (grey) and h-BN (black) at 65 °C. The dark blue dashed line represents the volume that would be added for 100 % lactose conversion into a mono-acid product.

Table 4.5 Lactose conversion and yields in the known products with the h-BN catalysts after 2h (NaA h-BN and h-BN) and 4 h (PVAW h-BN), with 0.5 L min⁻¹ oxygen flow and pH 9.

Materials	Lactose conversion (%)	Yield in LBA (%)	Yield in lactone (%)	Yield in lactulose (%)	Yield in galactose (%)
h-BN	23.9	0	0.5	22.5	2.9
PVAW h-BN	45.2	5.6	0.8	28.9	9.7
NaA h-BN	29.0	2.5	0.8	25.2	0.0

4.2.4 Titration and evaluation of the activity of the SiO₂ support

In contrast to the h-BN support, silica has acidic properties due to the silanol groups present at its surface. Therefore, it is worthwhile to quantify the acidity of the silica full spheres used in this work to have an idea of the base consumption due to this acidity. The titration of 90 mg of the silica full spheres at pH 9 and a temperature of 65 °C by the KOH solution (0.1 M) results in 10 mL of KOH added after 95 min (Figure 4.10). This corresponds to an amount of titrated silanol groups of 11 mmol/g. This result is in agreement with a study carried out on 5 different types of silicas, with silanol group densities ranging from 3.6 to 7.0 mmol/g (determined by IR spectroscopy) ^[108].

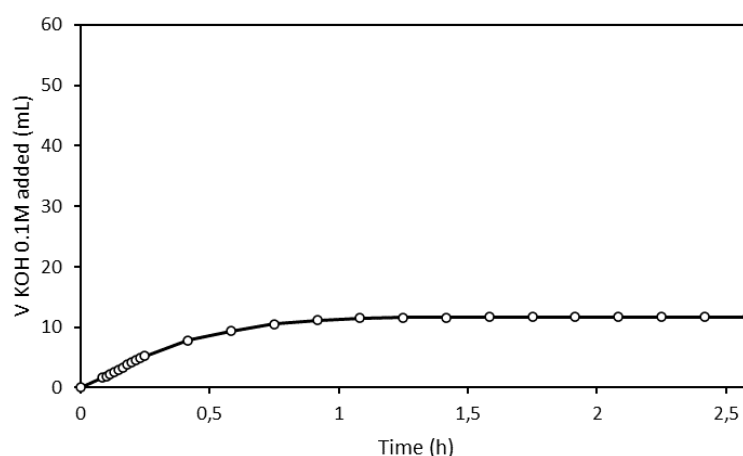


Figure 4.10 Titration curve of 90 mg of silica full-spheres at pH 9 and a temperature of 65 °C under 0.5 L/min oxygen flow.

Different masses of silica full-spheres (100 and 400 mg) were then tested in lactose oxidation at 40 and 65 °C respectively (Figure 4.11). From these tests, it turns out that at high mass loading and high temperature (400 mg and 65 °C), almost 50 mL of KOH (0.1 M) is added, corresponding to 100 % conversion into mono-acid. Based on HPLC analysis, the lactose conversion is 43.3 % (Table 4.6), suggesting that what was mainly titrated were the acid functions of the silica support. Indeed, based on the result shown in Figure 4.10, one would expect to add 11 mL of KOH solution for 100 mg of silica and 44 mL for 400 mg. The test carried out at 65 °C leads to the HPLC “blank peaks” set, while the test at 40 °C leads to 6 different peaks. Nevertheless, almost no LBA is produced for both tests (0.1 % for the test at 65 °C and 0 % for the other), which confirms that silica alone is not able to catalyse the selective oxidation of lactose into LBA (Table 4.6).

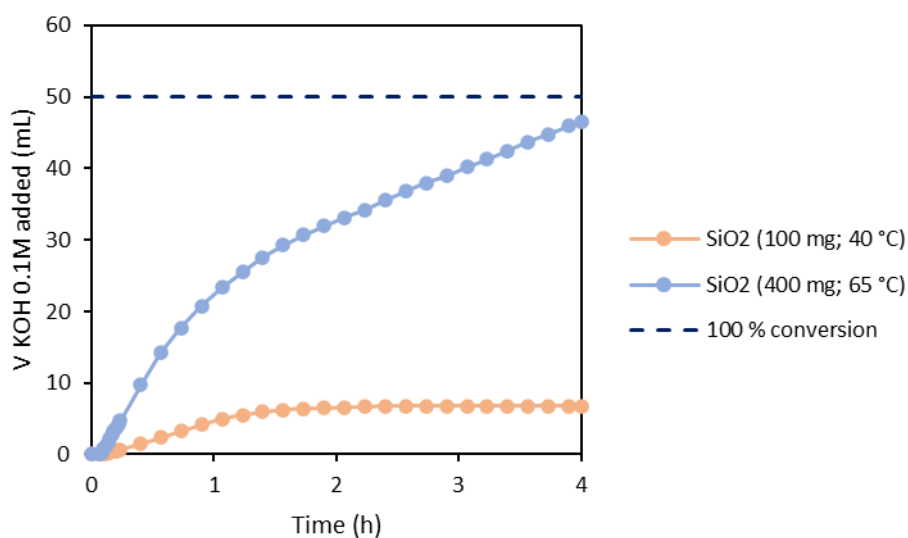


Figure 4.11 Evolution of the KOH volume added as function of time for 100 mg of SiO₂ at 40 °C (orange) and 400 mg of SiO₂ at 65 °C (blue). The dark blue dashed line represents the volume that would be added for 100 % lactose conversion into a mono-acid product.

Table 4.6 Lactose conversions and yields in the known products observed for the SiO₂ support at various mass loading and temperatures after 4 h, with 0.5 L min⁻¹ oxygen flow and pH 9.

Mass of silica and temperature of the test (mg; °C)	Lactose conversion (%)	Yield in LBA (%)	Yield in lactone (%)	Yield in lactulose (%)	Yield in galactose (%)
(400;65)	43.3	0	2.2	29.9	11.9
(100;40)	5.1	0.1	0.0	4.6	0.3

4.2.5 Evaluation of the activity of the Au/SiO₂ catalysts

4.2.5.1 Influence of solvent(s) and synthesis methodology

Five Au/SiO₂ catalysts prepared via a modification in the solvent used (NaA, NaW and NaW/A SiO₂) or a change in the gold deposition methodology (UFW SiO₂ and NH₃W SiO₂) were tested at 40 °C with a mass of 100 mg (Figure 4.12). The results comparison between the catalysts synthesised using several solvents (NaA and NaW/A SiO₂) to the NaW SiO₂ reference catalyst highlights the weak influence of the choice of solvent on the activity obtained. Those results were not surprising since only a slight difference in gold particles sizes is observed for these catalysts (section 3.2.2.1).

Regarding the results obtained using catalysts prepared with different gold deposition methods (NaW, UFW and NH₃W SiO₂), the activity of the UFW SiO₂ catalyst is the lowest while the activities of the NaW and NH₃ SiO₂ catalysts are comparable. Generally, all the catalysts give rise to similar activities, with the exception of the UFW SiO₂ catalyst that gives rise to half the activity compared to the others. Unfortunately, almost no LBA was produced through all these catalytic tests, except with the one using NaA SiO₂ as catalyst that gave a yield in LBA of 3.9 % (Table 4.7). The highest lactose conversion of 8.1 % is obtained using the NaA SiO₂ catalyst. All the catalytic tests yielded almost no galactose (0.0-0.3 %) and no lactone at all (Table 4.7). Similar amount of lactulose was produced from one test to another (4.1-5.3 %).

Surprisingly, all the catalytic tests carried out here give rise to a lower activity than that obtained with the SiO₂ support alone in these conditions. This would mean that either the mass loading

of the catalyst or the temperature parameter has to be changed to improve the activity of these catalysts. In the next section, we will discuss the optimisation of the catalytic conditions.

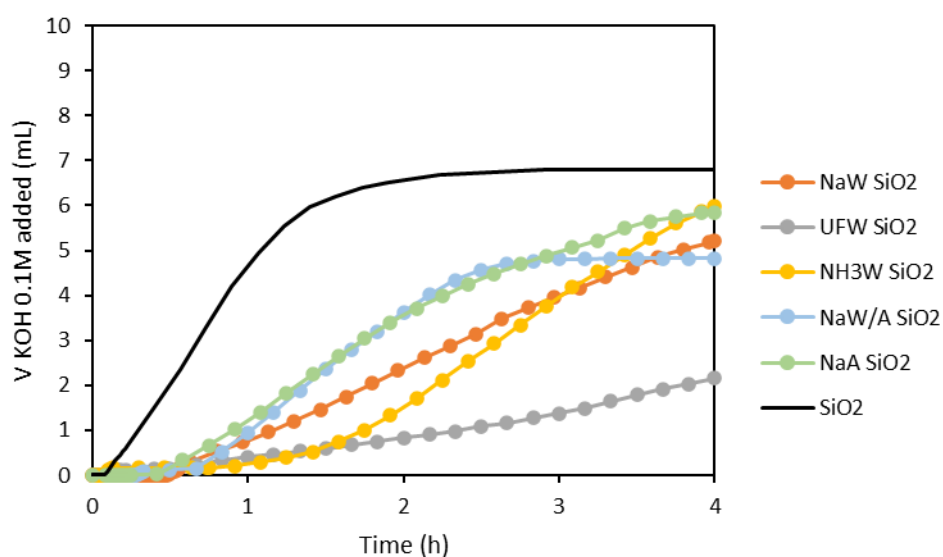


Figure 4.12 Evolution of the KOH volume added in function of time for 100 mg of Au/SiO₂ catalysts tested at 40 °C. The scale of the graph is different from the other figures presented in this section.

Table 4.7 Lactose conversions and yields in the known products with 100 mg Au/SiO₂ catalyst tested at 40 °C during 4 h, with 0.5 L min⁻¹ oxygen flow and pH 9.

Au/SiO ₂ catalyst	Lactose conversion (%)	Yield in LBA (%)	Yield in lactone (%)	Yield in lactulose (%)	Yield in galactose (%)
UFW SiO ₂	2.5	0	0.0	4.7	0.0
NH ₃ W SiO ₂	4.5	0.2	0.0	4.3	0.3
NaW SiO ₂	4.8	0.7	0.0	4.3	0.3
NaW/A SiO ₂	3.8	0.7	0.0	5.3	0.0
NaA SiO ₂	8.1	3.9	0.0	4.1	0.2

4.2.5.2 Influence of the mass of catalyst and temperature

The NaW SiO₂ reference catalyst has been chosen to test the effect of the mass of catalyst and the temperature on the catalytic performances.

From the literature, it appears that temperature has a very large influence on the activity of the catalyst as well as on the selectivity towards LBA (section 1.1.3). As a reminder, for an Au/SiO₂ type catalyst, the optimum temperature for maximising both activity and selectivity was found to be 65°C ^[14]. Figure 4.13 shows that the activity of our catalyst towards the production of acids increases with temperature. This result is confirmed by the HPLC analysis (see Table 4.8). The optimum LBA production is found to be at 65 °C with 1.1 % yield which is in accordance with the literature concerning the temperature ^[14]. However, the yield obtained is far from those reported in the literature for the oxidation of lactose (section 1.1.3).

Concerning the galactose, lactone and lactulose production, it appears that it increases with the temperature, indicating a temperature effect on the yield in those products (Table 4.8).

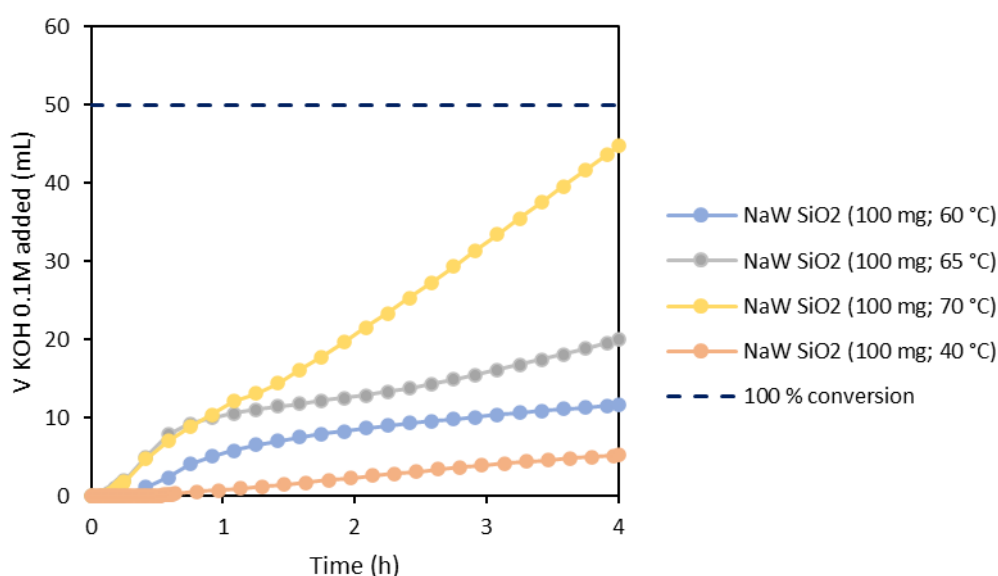


Figure 4.13 Evolution of the KOH volume added in function of time for 100 mg of NaW SiO₂ catalyst at 40 (orange), 60 (blue), 65 (grey) and 70 °C (yellow). The dark blue dashed line represents the volume that would be added for 100 % lactose conversion into a mono-acid product.

Table 4.8 Lactose conversion and yields in different products for 100 mg of NaW SiO₂ catalyst tested at 40, 60, 65 and 70 °C.

Temperature tested (°C)	Lactose conversion (%)	Yield in LBA (%)	Yield in lactone (%)	Yield in lactulose (%)	Yield in galactose (%)
40	4.8	0.7	0.0	4.3	0.3
60	23.9	0.6	0.5	19.8	3.5
65	38.2	1.1	0.6	26.9	10.1
70	63.5	0.3	1.2	30.0	30.5

The effect of temperature was also evaluated with the catalysts obtained via the different methods, as presented in section 3.2.2. Once more, the activity increases with the temperature, as expected (Figure 4.14). The highest yield to LBA of 3.9 % has been obtained using NaA SiO₂ catalyst at 65 °C (Table 4.9). Therefore, based on the temperature, it is not really possible to distinguish one synthesis method from another in terms of the resulting activity toward LBA. However, regarding lactose conversion, using NaA SiO₂ as catalyst at 65 °C gives rise to the best results with 49.9 %, while regarding selectivity to LBA, 48 % was obtained using the same catalyst at 40 °C.

Concerning galactose, lactone and lactulose production, the same trend as in Table 4.8 is observed here, with an increase in function of the temperature (Table 4.9).

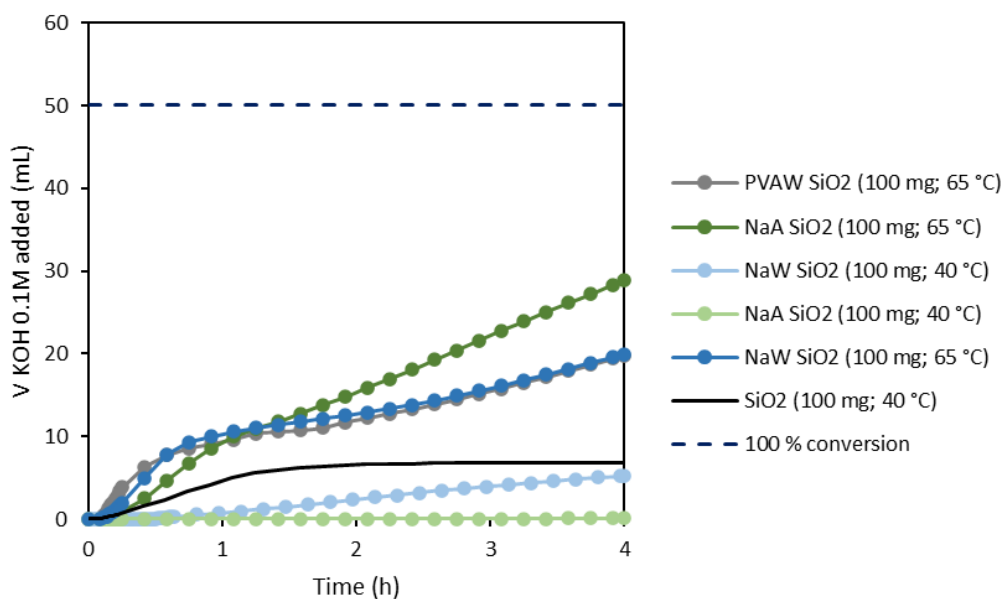


Figure 4.14 Evolution of the KOH volume added in function of time for 100 mg of Au/SiO₂ catalysts obtained via different methods at 40 and 65 °C. The dark blue dashed line represents the volume that would be added for 100 % lactose conversion into a mono-acid product.

Table 4.9 Lactose conversion and yields in different products with 100 mg of Au/SiO₂ catalyst tested at 40 and 65 °C.

Au/SiO ₂ catalysts	Lactose conversion (%)	Yield in LBA (%)	Yield in lactone (%)	Yield in lactulose (%)	Yield in galactose (%)
PVAW SiO ₂ (100 mg; 65 °C)	41.8	1.7	1.2	29.6	10.9
NaA SiO ₂ (100 mg; 65 °C)	49.9	1.3	0.8	30.0	17.5
NaA SiO ₂ (100 mg; 40 °C)	8.1	3.9	0.0	4.1	0.2
NaW SiO ₂ (100 mg; 65 °C)	38.2	1.1	0.6	26.9	10.1
NaW SiO ₂ (100 mg; 40 °C)	4.8	0.7	0.0	4.3	0.3

Regarding the improvement of the catalytic performances in this reaction, the catalyst mass factor will now be studied. To do so, 100 mg and 400 mg of the NaW SiO₂ reference catalyst were tested at various temperatures for the oxidation of lactose (Figure 4.15). From Figure 4.15, it can be seen that the activity increases with the mass of the catalyst. However, this increase of activity does not lead to substantial increase in the LBA yield (Table 4.10). Furthermore, the tests performed at 65 °C with 400 mg of silica support alone (without gold) or using Au/SiO₂ catalyst gave rise to identical activity, which is quite surprising (Figure 4.15).

Interestingly, at an identical temperature, the galactose production remains almost constant (Table 4.10). No particular trend can be connected to the lactone and lactulose production.

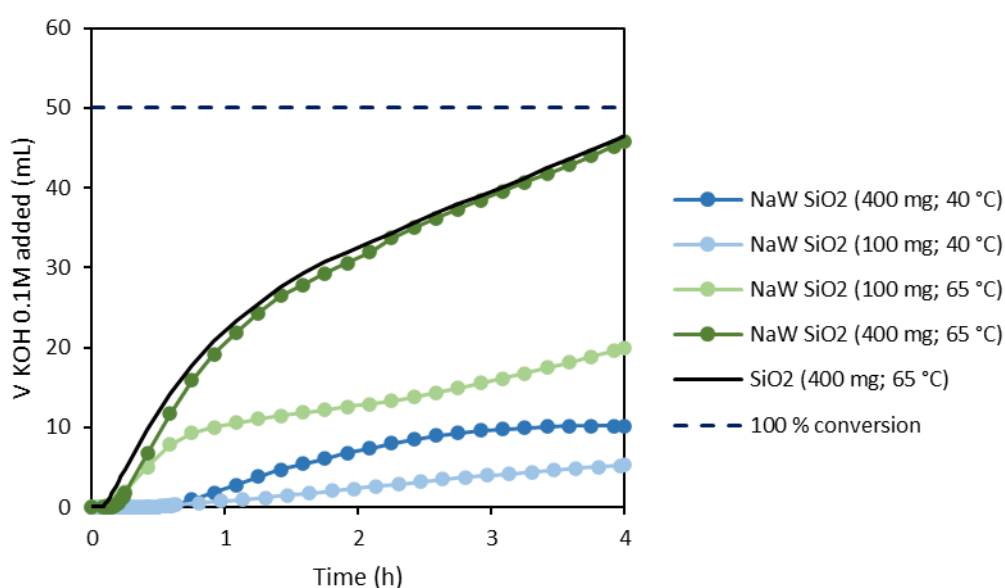


Figure 4.15 Evolution of the KOH volume added in function of time for 100/400 mg of Au/SiO₂ catalysts at 40 and 65 °C. The dark blue dashed line represents the volume that would be added for 100 % lactose conversion into a mono-acid product.

Table 4.10 Lactose conversion and yields in different products with various masses of catalyst (NaW SiO₂) and temperatures after 4 h, with 0.5 L min⁻¹ oxygen flow and pH 9.

Au/SiO₂ catalysts	Lactose conversion (%)	Yield in LBA (%)	Yield in lactone (%)	Yield in lactulose (%)	Yield in galactose (%)
NaW SiO ₂ (100 mg; 40 °C)	4.8	0.7	0.0	4.3	0.3
NaW SiO ₂ (100 mg; 65 °C)	38.2	1.1	0.6	26.9	10.1
NaW SiO ₂ (400 mg; 40 °C)	3.9	1.0	0.0	2.8	0.2
NaW SiO ₂ (400 mg; 65 °C)	49.8	2.0	2.3	30.6	13.1

4.3 Discussion of the Catalytic Tests Results

As seen above, a relatively large screening of gold particles sizes (between 8.9-12.0 nm and 34.2 nm) was carried out by changing the solvent used for gold deposition and the method of gold deposition on silica. Based on literature, one would expect a huge influence of the gold particles size on the resulting activity. Indeed, Gutierrez *et al.* obtained an initial rate (LBA g.min⁻¹.L⁻¹) of 0.12 for the smallest particles (7 nm) up to 0.02 for the largest (14 nm) [14]. However, this study did not reveal such an influence of size since similar LBA yield of 0.0-3.9 % were obtained using our series of Au/SiO₂ catalysts.

In addition, the influence of the mass of catalyst (100 and 400 mg) and temperature (40, 60, 65 and 75 °C) parameters was tested with the NaW SiO₂ catalyst. However, no matter the nature of the catalyst or the parameters set, there is no significant increase in LBA yield (from 0 % for the worst to 1.1 % for the best catalytic test). Even more surprisingly, the activity of the catalysts is comparable to that of silica alone which leads to the conclusion that gold is inactive in our case. This inactivity may have several reasons. Based on the TEM image of the NaW SiO₂ reference catalyst shown in section 3.2.1.2, gold NPs could be distributed in the inner part of the silica network. Therefore, the access to the active gold NPs would be hindered and the first step of the oxidation mechanism (adsorption of the lactose on the gold NPs surface) would be disfavoured. Indeed, it is well known that the location of the active sites in the inner part of the

catalyst leads to a limitation of the diffusion of reactants/products due to steric restrictions that affect the accessibility of large molecules ^[83]. However, based on the TEM image of PVAW SiO₂ catalyst (section 3.2.2.2), it was clear that the gold NPs were on the surface of the silica in that case. However, the catalytic performance of this material was still under the expected range. It could be proposed as an explanation that the PVA was not fully removed, limiting the access to the gold surface. Nevertheless, given the washing steps implemented and the clear image of the gold NPs obtained (no blurring around the particles), it seems unlikely that PVA is still present ^[109].

As seen in section 4.2.4, the silica support contains silanol groups (11 mmol/g) which are titrated by the KOH solution and therefore becomes negatively charged during the catalytic test. Therefore, due to the pH imposed during the reaction (pH 9), gold tends to be negatively charged (IEP = 2-3) as the silica support, resulting in unfavourable electrostatic interactions ^[110]. Hence, the leaching of gold should be taken into consideration due to these harsh conditions. However, no ICP or AAS analyses of the solutions after the catalytic tests were conducted yet, leaving this question open.

The main product obtained throughout the catalytic tests is lactulose. This compound has some applications as a drug, making it of interest ^[107]. The best yield (30.6 %) towards this compound was obtained at 65 °C using 400 mg of the NaW SiO₂ catalyst, giving slightly better results than the blank (29.8 %) and the silica alone (400 mg with 29.9 %) at 65 °C. Therefore, taking into account the experimental error, most of the gold catalysts tested tend to give the same lactulose yield compared to that obtained with silica alone or in the blank. However, given the disparity in lactulose selectivities between the different catalysts tested under the same conditions, there appears to be an influence of the catalysts on the selectivity obtained. In addition, some of the selectivities toward lactulose achieved by the Au/SiO₂ catalysts (≥ 80 %) outperforms that obtained with the silica alone (69 %) or the blank (69 %).

In contrast, the reactions carried out with the NM h-BN catalyst at 40 and 65 °C lead to 100 % lactose conversion and ~100 % in LBA. This discrepancy between the results seems to be due to a support effect. Indeed, the NaA and NaA h-BN catalysts gave the best results with yields approximately three times higher than their counterparts prepared on silica, indicating that the choice of support matters strongly for this reaction. Therefore, it appears that h-BN is the most appropriate choice of support for this reaction and that silica is not ideal for catalytic lactose oxidation maybe due to its acidity and low IEP.

CONCLUSIONS AND PERSPECTIVES

5.1 General conclusions

The main aim of this work was to produce materials made of gold particles supported on silica. For this purpose, we first prepared different morphologies of silica supports: full spheres, hollow spheres and hollow nanofibers. Concerning the full spheres, their preparation was a real success with a hydrodynamic diameter of about 40 nm as expected. In contrast, the hollow structures were more difficult to prepare. Indeed, we wanted to reduce the number of steps required to obtain the hollow structures by removing the steps of functionalization of the carbon template and of washing. However, the latter turned out to be essential to obtain a hollow structure. Interestingly, the removal of this step resulted in a silica material with a structure equivalent to CB when using it as a hard template. This similarity is observed both in terms of specific surface area developed and in terms of morphology. By opposition, the omission of the washing step when using CNF as a hard template gave a "stony" structure without real scientific interest. The addition of the washing step resulted as desired in hollow spheres with the correct morphology with the formation of an inner cavity within the material. By contrast, the material obtained with CNF as hard template presented a heterogeneous structure composed of both silica nanofibers with holes and "stony" materials. After XRD analysis of the sample, it was found that the pattern corresponds to that of α -cristobalite. However, this phase usually only forms at 1400°C, which would mean that the remaining Na present in the material catalyses the formation of this phase at lower temperature.

With regard to the deposition of gold on silica, and given the above-discussed results, we chose to focus on the use of full spheres as support. The primary goal was to obtain gold particles with a large size range. This goal was largely achieved by producing NPs with sizes ranging from 9-12 to 34 nm. We were able to prove via TEM and XRD measurements that metallic gold is present on the silica support. However, the TEM image obtained for the NaW SiO₂ catalyst suggests that the gold is present in the inner part of the silica support. Au/h-BN type catalysts were also prepared in order to deduce the effect of the support on the catalyst properties. Of

these catalysts, N. Meyer's catalyst was replicated as a reference for the catalytic reaction of lactose oxidation into LBA.

In the next step, a new HPLC method was developed to obtain an adequate separation of lactose and LBA and to be able to quantify them by the use of a calibration curve. Based on the potential lactose derivatives produced under the reaction conditions, several other compounds were investigated. From these, it turns out that we obtained galactose (14.7 min) and lactulose (12.1 min). Based on the publication by Pedruzzi *et al.*, it was also possible to identify the formation of lactone (6.8 min).

Finally, all the prepared catalysts were tested in the target reaction. The NM h-BN catalyst resulted in a lactose conversion of 100 % and an LBA yield of 100 %. Interestingly, the time required to achieve 100 % conversion with this catalyst is longer at 65 °C (2.75 h) than at 40 °C (2 h). This trend is the opposite than that observed in the literature for Au/SiO₂ type catalysts for the selective oxidation of lactose to LBA. Concerning the Au/SiO₂ catalysts, no significant influence of the gold particles size on the resulting activity could be highlighted, given the very low performance of all our new synthesized materials. In addition, the mass of catalyst and temperature parameters did not lead to any relevant increase in LBA yield. Therefore, the gold nanoparticles seem to be inactive in the catalysts prepared.

This inactivity might come from a hindrance of the gold particles due to their distribution in the inner part of the silica support or to the presence of the protecting agent (PVA) in the case of the PVAW SiO₂ catalyst. In addition, the basic conditions used for the catalytic tests might cause leaching of the gold particles and therefore deactivation of the catalysts. Another possible explanation for this inactivity would be that we did not succeed in obtaining gold particles small enough to be active for this reaction.

However, lactulose was found to be the main product, with a good selectivity toward this compound. The Au/SiO₂ type materials have therefore made it possible to promote a catalytic pathway, other than the one we hoped it would follow, but which leads to another product of interest. Indeed, lactulose is of interest for the pharmaceutical industry.

The Au/h-BN catalysts gave better LBA yield than their silica counterparts, suggesting that h-BN is a better support than silica for this reaction. This difference might be due to the acidity and low IEP of the silica compared to h-BN.

5.2 Perspectives

Several tasks remain to be completed if the work presented here was to be pursued. Firstly, with regard to the production of silica supports, hollow nanofibers with the right morphology still need to be obtained. To achieve this, we should test different conditions and especially a lower calcination temperature to avoid the appearance of the α -cristobalite phase. In addition, the removal of the APTES functionalisation step may have been deleterious to the efficiency of the material production. It might be appropriate to add it and see what influence it could have on the results obtained. We also obtained a special material by optimising the production method of the hollow structures. Indeed, the branched silica structure that exhibits the same specific surface area and morphology than CB deserves to be studied further. Due to its mechanical properties, which are probably different from those of CB, it might be an ideal candidate to replace it in applications where its robustness is insufficient, such as for the green-tires commercialised by Michelin.

Regarding the HPLC analyses, some peaks remain unassigned. In order to attribute them to a chemical species, it would be appropriate to use HPLC-MS rather than the "trial and error" method used in this work. This would not only be quicker but also allow us to be sure of the nature of the product behind each peak. Nonetheless, the majority of the converted lactose is explained by the peaks we were able to identify.

The low LBA yields obtained throughout this work are not in an expected range. A possible cause to this might be the low IEP of silica which makes it difficult to deposit gold on it due to bad electrostatic interactions between the gold particles and the silica support. One way to get around this difficulty would be to graft pre-formed gold NPs onto the silica via a covalent bond. One could then expect to get better anchoring of the gold particles and therefore higher yields in LBA if the covalent bond withstands the test conditions.

Finally, since we have succeeded in producing lactulose selectively and given that this product is of pharmaceutical interest, it would be interesting to optimise the Au/SiO₂ catalysts in order to obtain this product with maximum selectivity and yield.

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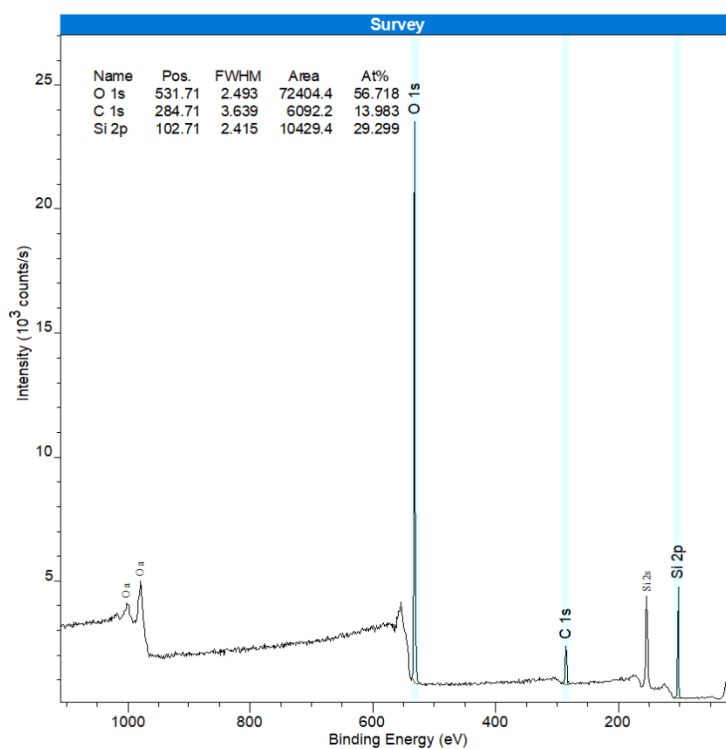
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ANNEXES

A.1 XPS analysis of the full spheres

The calculated ratio between oxygen and silica (based on the atomic percentages) is equal to 1.7. This ratio, close to a value of 2, is consistent with the formation of a silica network of SiO_2 type.



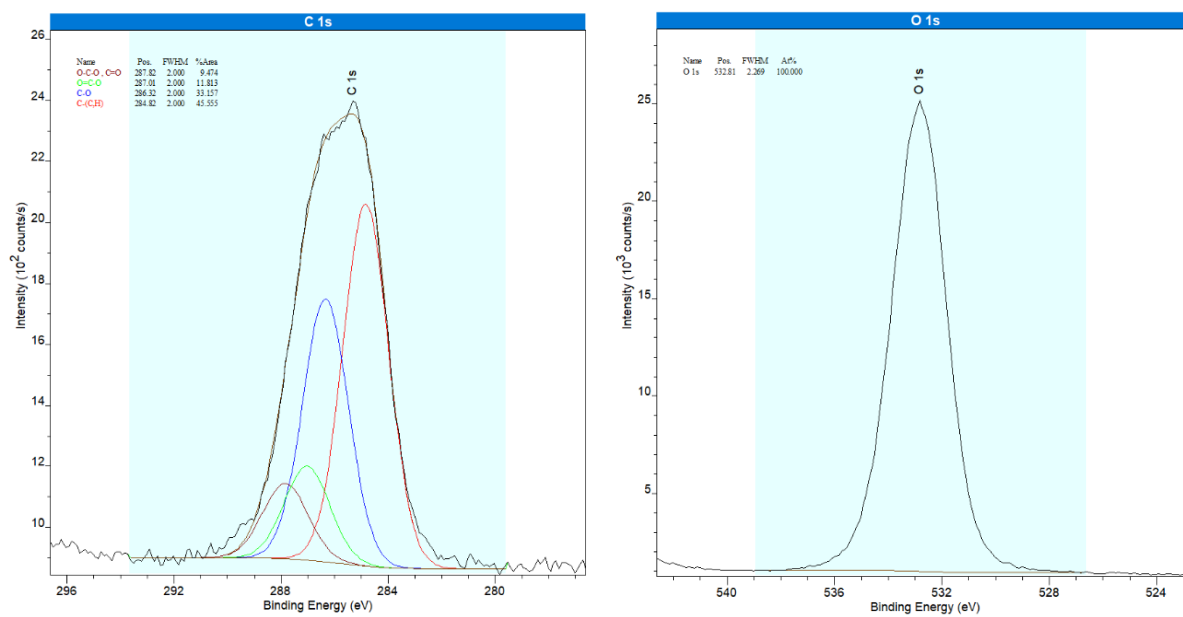


Figure A.1 XPS spectra of the silica full spheres.

A.2 Picture of the full spheres

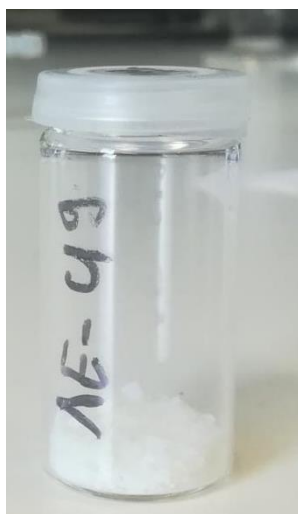


Figure A.2 Picture of the full spheres (white powder).

A.3 HPLC calibration curves

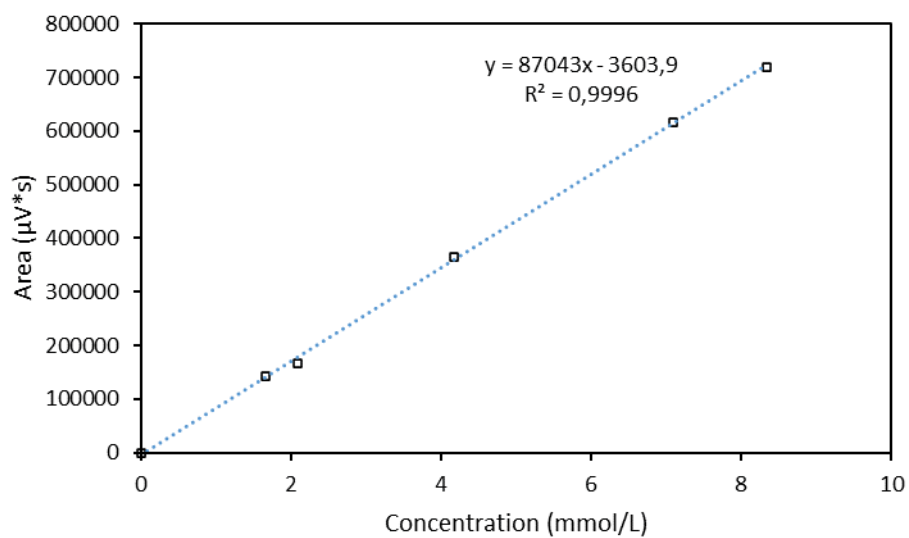


Figure A.3a Lactose calibration curve from 0 to 8.3 mmol/L.

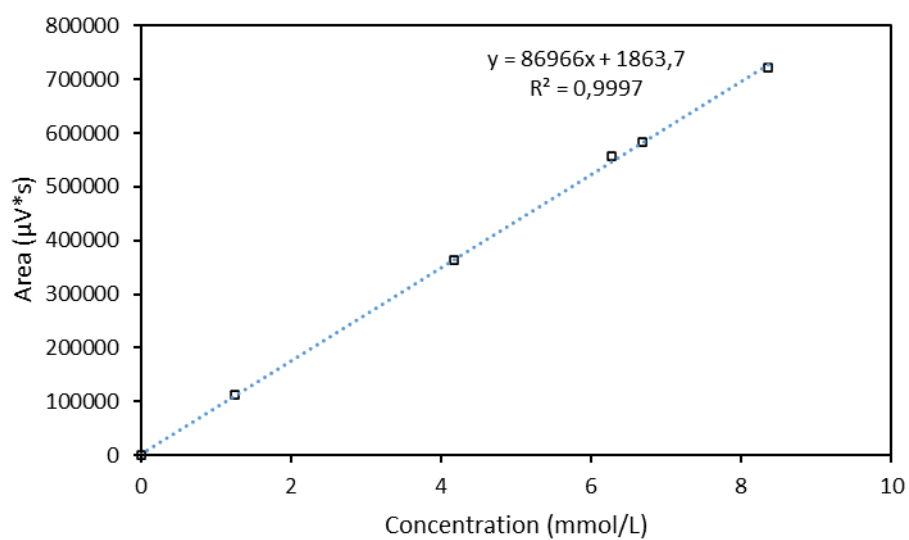


Figure A.3b LBA calibration curve from 0 to 8.4 mmol/L.

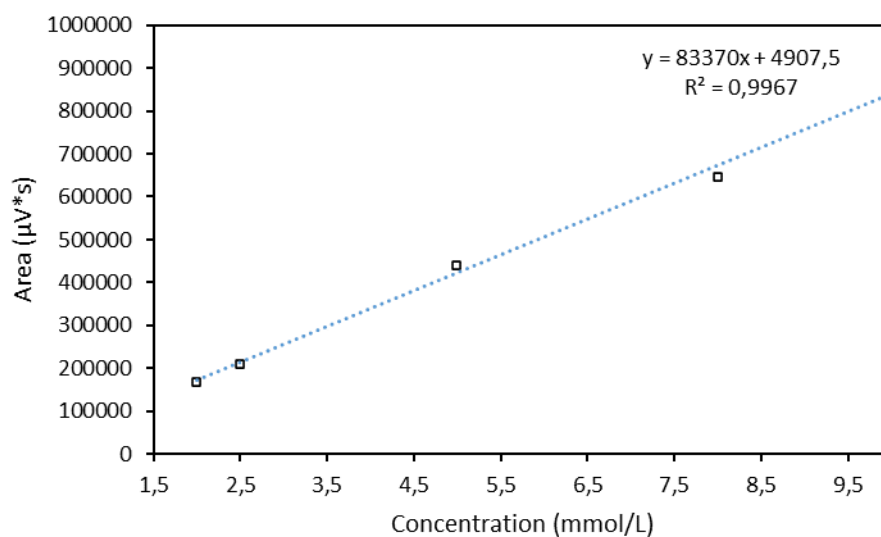


Figure A.3c Lactulose calibration curve from 2 to 10 mmol/L.

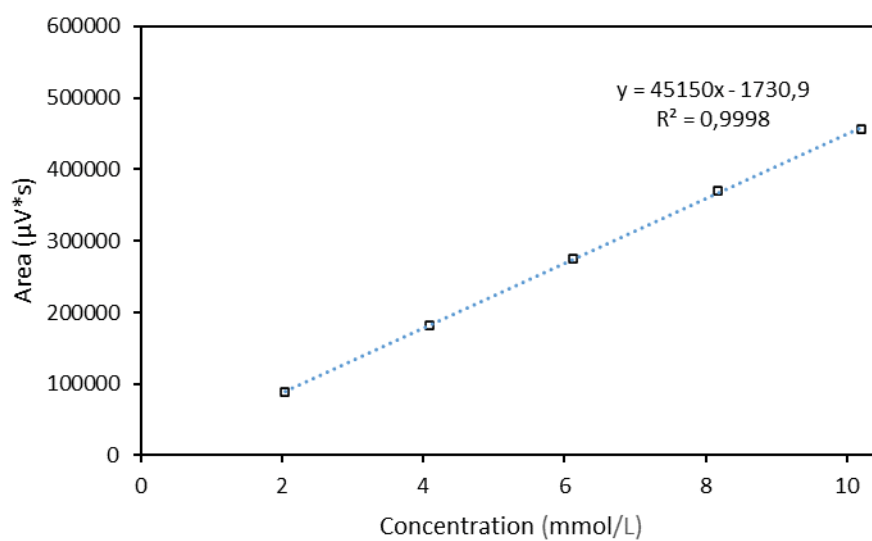


Figure A.3d Galactose calibration curve from 2 to 10 mmol/L.

A.4 HPLC chromatograms

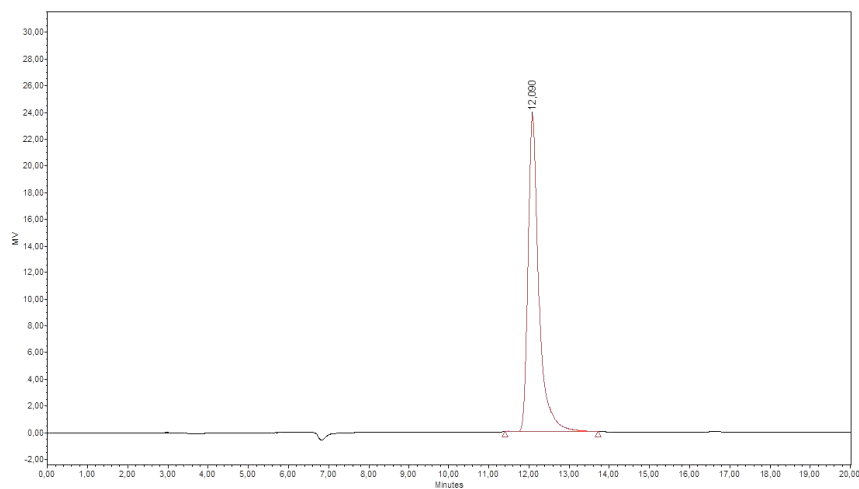


Figure A.4a Lactulose chromatogram.

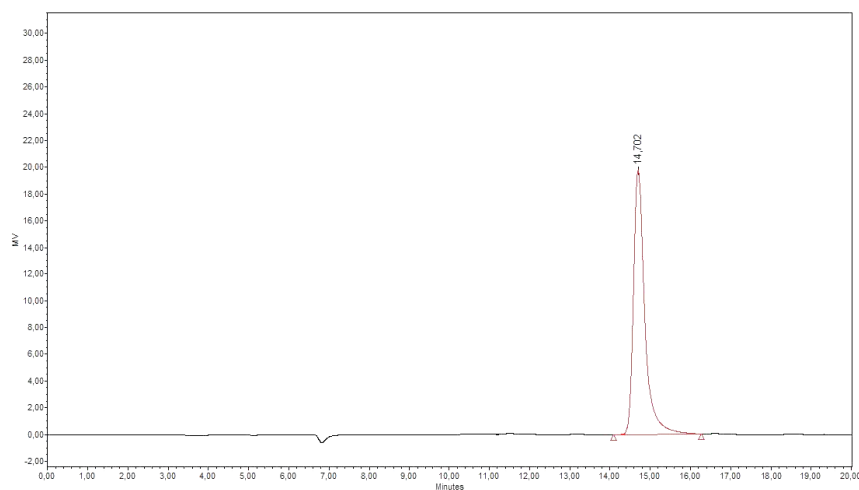


Figure A.4b Galactose chromatogram.

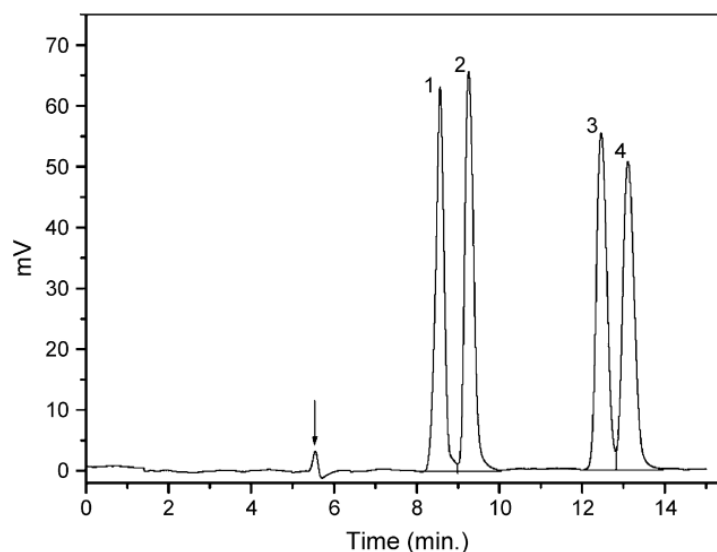


Figure A.4c Chromatogram of the reference solution prepared in $\text{Ca}(\text{OH})_2$ solution in equimolar ratio and a presence of pulse injection under arrow at 5.5 min retention time and symmetrical peak of lactobionic acid in sulfuric acid eluent (0.450 mM, pH 3.1). ICSep ICE-ION-300 column, 300mm $\times$ 7.8mm particle diameter, 7 μm at 75 $^\circ\text{C}$ and 0.5 mL.min $^{-1}$ (1 lactobionic acid, 2 lactose, 3 fructose and 4 sorbitol). From ^[103].

