# Nitrobenzene Hydrogenation on Au/TiO<sub>2</sub> and Au/SiO<sub>2</sub> Catalyst: Synthesis, Characterization and Catalytic Activity

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Received: 24 February 2013/Accepted: 31 May 2013/Published online: 13 June 2013 © Springer Science+Business Media New York 2013

**Abstract** Recently, gold has been proposed as an active phase for the hydrogenation of nitro-arenes. This metal has been rarely used in hydrogenation reactions because gold does not possess hydrogen chemisorption capacity. However, small gold particles behave differently and they may be able to chemisorb hydrogen to same extent, leading to possible activity in hydrogenation reactions. This may provide an advantage because the reactions catalyzed by highly dispersed gold particles may be better controlled. In this work, TiO<sub>2</sub> and SiO<sub>2</sub> supported Au catalysts were prepared by the deposition-precipitation method using urea and NaOH to precipitate the metallic component at different temperatures and hydrogen pressures. The metal loading for all the catalysts was 1 wt%. The catalysts were characterized by X-ray diffraction, high resolution transmission electron microscopy among others. The catalysts were then evaluated in the hydrogenation of nitrobenzene in a batch type reactor at 25 °C. All the catalysts were active in the hydrogenation reaction and the major obtained product was aniline.

**Keywords** Gold · Nitrobenzene · Hydrogenation · Heterogeneous

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## **1** Introduction

The preparation of compounds with potential biological activity has received considerable attention at both laboratory and industrial levels. For the production of fine chemicals to be economically viable, high selectivity and specificity is an important requirement. In addition, environmentally benign processes are fundamental in drug production. A process of particular interest that embodies these stringent requirements is the catalytic production of aromatic amines from aromatic nitro compounds [1, 2].

This process has been approached by three different procedures: (i) by stoichiometric reduction of the corresponding aromatic nitro compounds using iron, tin, zinc or a metal sulfide such as Na<sub>2</sub>S. However, this method displays low selectivity for nitro group, and large amounts of waste acids and residues are generated during the reaction. (ii) By catalytic hydrogenation of nitro compounds with H<sub>2</sub> over supported noble metal catalysts, e.g. Pd, Pt, Ru and Ni catalysts [3–7], etc. Nevertheless, the high hydrogenation ability of this metals usually procedures the hydrogenation of other groups existing in the arene substrates leading to undesirable byproducts. (iii) Another method is the chemioselective hydrogenation of aromatic nitro compounds catalysed by carbonyl or organic metals in the presence of CO and  $H_2O$  [8, 9]. It is therefore desirable to develop a more efficient and environmental process to achieve chemioselective hydrogenation to obtain valuable functionalized anilines.

The hydrogenation of nitrobenzene, which is used to produce aniline, has been carried out either in gas or liquid phase, using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions [10-13] and CO<sub>2</sub> under

supercritical conditions [14]. The use of these solvents has some drawbacks owing to their toxicity, flammability, or environmental hazards. In addition, the solvent may play a crucial role in the stabilization of reactive intermediates and have a decisive influence on chemical reactions. Though many studies have been carried out, the efficient hydrogenations with high selectivity, as well as with high activity, for nitro compounds have not so far been reported. The most frequently used nitro-group hydrogenation catalysts are palladium or platinum on carbon and Raney nickel [15–17]. The hydrogenation of aromatic nitro groups can be performed easily under mild conditions, while hydrogenation of aliphatic nitro groups is usually slower, requiring slightly elevated temperatures and pressures. In the hydrogenation of the former reactions, the nitroso and the hydroxylamine compounds have been observed as intermediates, while a series of side reactions might lead to the formation of hydrazo compounds, which can be sometimes isolated.

The activity and selectivity of this reaction depends on the catalysts as well as the reaction conditions [18]. Thus, one of the intermediates or side products may become the dominant product, for instance, azoxy, hydrazo and hydroxylamines can be in high yields [15, 17, 19]. The accumulation of hydroxylamines is [20] thermodynamically unstable. The accumulation may be diminished using iron or vanadium-modifies catalysts [21, 22]. Recently, the reaction was studied using gold as hydrogenation catalyst [23] that gave high selectivity to substituted anilines, but showing lower activity. Nevertheless a catalyst with the same selectivity as gold but with a higher activity would be desired for industrial application [24]. Thus, there is a scientific and technological challenge to transform active but not selective noble metals (Pt, Pd, Ru) and a non-noble metal (Ni) into highly active and chemioselective catalysts. Some recent studies have shown that the addition of cationic species or salts and presence of partially reduced species may contribute to enhance the selectivity in these systems. Additionally, in principle the behavior of gold catalysts, mainly in terms of activity may also be improved with appropriate preparation conditions.

In most of the researches published before 2000, the used support for these kind of reactions was activated carbon and in minor extent alumina, silica, and MCM-41. It has been pointed out that activated carbons seems to be the most appropriate support for this type of reactions because it can provide more sites to produce a high dispersion of the metal component. Water produced in the hydrogenation reaction may also affects the activity of the catalysts supported on oxides [14, 15]. Only few studies have been devoted to other oxides such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> [17, 18], ZrO<sub>2</sub> [25] which have shown interesting behavior.



Scheme 1 Hydrogenation mechanism of nitrobenzene proposed by Haber in 1898

As was mentioned previously, the experimental conditions affect significantly, the catalytic behavior. If the reaction is performed in liquid phase batch type reactors, usually the reaction temperature for this kind of reactions are in the range 80–120 °C, using mainly THF or ethanol as solvent and 10 bar of hydrogen pressure [8, 9], whereas in gas phase the reactions are studied at temperature close to 250 °C and 1 bar of hydrogen [26–30].

Gold has been proposed as an active phase for heterogeneous catalyst [31, 32]; it displays a lower hydrogenating ability in contrast to other noble metals such as Pt, Rh or Pd, leading to particular advantages as direct selectivity towards the functional group of interest.

More recently, it has been established that Au [20] catalysts exhibit high selectivity in hydrogenation reactions of nitro compounds, especially when Au metal particles are smaller than 5 nm.

In general these reactions proceed via intermediaries such as the azoxy, hydrazo, and hydroxylamines (Scheme 1) [22, 33]. The hydrogenation of these compounds is considered high risk due to the production of intermediaries such as hydroxylamines which are highly unstable and can reach disproportionation with an increase of temperature, consequently leading to an explosion [34]. The accumulation of these compounds is diminished by using catalysts modified by Fe or V, or by using additives based on vanadium, or by optimizing the reaction conditions [35]. Due to the large amount of secondary product it is of great importance to find the most direct possible route in order to avoid the formation of these compounds.

In this work we studied the hydrogenation of nitrobenzene on Au catalysts supported on  $TiO_2$  and  $SiO_2$  and determined how the catalytic activity is affected by the type of support. All catalysts were synthesized with a metal loading of 1 wt% using different preparation methods for active phase deposition, in order to obtain catalysts with metal particle size below 15 nm where Au is capable of chemisorbing H<sub>2</sub>.

#### 2 Experimental

#### 2.1 Reagents

Nitrobenzene (Fluka), absolute ethanol (Merck),  $TiO_2$ ( $S_{BET} = 168 \text{ m}^2 \text{ g}^{-1}$ , 99.7 % anatase, Alfa Aesar),  $SiO_2$ ( $S_{BET} = 298 \text{ m}^2 \text{ g}^{-1}$ ), gold(III) chloride trihydrate Sigma-Aldrich (99.9 %) and H<sub>2</sub> by AGA, Chile.

#### 2.2 Catalyst Preparation

#### 2.2.1 Deposition–Precipitation with NaOH at 100 °C

The appropriate amount of support (TiO<sub>2</sub> or SiO<sub>2</sub>) is placed in a round bottom flask together with 50 mL of water. The solution containing the required amount of the precursor, gold(III) chloride trihydrate, needed to obtain the desired metal loading is also added to the support suspension. An stoichiometric amount of an aqueous solution of NaOH is added and a flow of H<sub>2</sub> at atmospheric pressure is fed to the round bottom flask containing the mixture; the system is then heated to reflux with stirring at 100 °C until the color changes from yellow to violet. The obtained solid was filtered and washed with deionized water until constant conductivity. These are denoted Au/Support-T.

# 2.2.2 Deposition–Precipitation with NaOH at High H<sub>2</sub> Pressure

The required amount of support, 50 mL of water and the metal precursor was placed in an autoclave. Stoichiometric amount of NaOH was then used to neutralize the acidic environment generated by the precursor; finally, the autoclave was closed and it was flashed with hydrogen and then pressurized up to 40 bar of hydrogen [36], and kept under constant stirring for 2 h at room temperature. The obtained solid was filtered and washed with deionized water until constant conductivity. These samples are denoted Au/Support-H<sub>2</sub>.

## 2.2.3 Deposition-Precipitation with Urea

The procedure is similar to that proposed by Zanella [37]. An aqueous solution of the precursor,  $HAuCl_4$ , is added to urea in a 1:100 mol ratio and heated to 80 °C for 2 h under vigorous stirring. Urea decomposition causes the increase of pH due to the formation of hydroxyl ions. This preparation must be performed in an amber flask to avoid decomposition caused by light. The solid was filtrated and dried under vacuum for 2 h at 100 °C. The final solid was calcined with synthetic air from room temperature to 300 °C for 2 h and kept for 4 h. These are labeled Au/Support-U.

#### 2.3 Characterization

The characterization of the catalytic systems was conducted using the several techniques. X-ray diffraction (XRD) was performed on a Rigaku X-ray Geigerflex using a Ni filter and Cu K  $\alpha$  radiation within 2–80° 2 $\theta$  range. N<sub>2</sub> adsorption-desorption isotherms were carried out in an ASAP 2010 Micromettics apparatus. HR-TEM was performed using a Philips CM200 model high resolution electron microscope with energy dispersive analyzer and digital camera coupled to a high speed TVIPS FastScan F-114 model of  $1,024 \times 1,024$  pixels and 12 bits. UV-Vis spectra of diffuse reflectance of solid state was studied in the range of 200-900 nm on a Varian Cary 3 UV-Vis spectrophotometer equipped with an area of 150 mm in diameter covered with poly integration tetra-fluoroethylene (PTFE). The dust samples were mounted in a quartz cell, which provided a sample thickness greater than 3 mm and thus guaranteed "infinite" sample thickness. Chemical analysis was performed by inductively coupled plasmamass spectrometry on an ICP-MS Spectrometer Perkin Elmer Elas 6000. X-ray photoelectron spectroscopy (XPS) were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer, operated in a constant pass energy mode and Mg Ka X-ray radiation (hv1,253.6 eV) operated at 10 mA and 12 kV.

## 2.4 Hydrogenation Reaction

Catalytic evaluation was carried out in liquid phase in a Parr stainless steel batch reactor at 298 K using 100 mg of catalyst and 0.02 mol  $L^{-1}$  of nitrobenzene, under 40 bar hydrogen pressure. All the components (catalyst, solvent and substrate) were fed to the reactor and stirring at 800 rpm. Liquid samples were taken periodically from the reactor and analyzed in a GC–MS Shimadzu GCMS-QP5050 with a capillary column  $\beta$ -Dex 225 (Supelco).

Table 1 Chemical analysis, ICP-MS for Au/support

Catalyst	Au (wt%)	Ti (wt%)	Si (wt%)
Au/TiO <sub>2</sub> –T	0.81	58.9	-
Au/TiO <sub>2</sub> –H <sub>2</sub>	0.80	58.4	_
Au/TiO <sub>2</sub> –U	0.88	60.2	-
Au/SiO <sub>2</sub> –C–T	0.46	-	43.7
Au/SiO <sub>2</sub> –C–H <sub>2</sub>	0.72	-	43.1
Au/SiO <sub>2</sub> –U	0.77	-	48.2





Fig. 2 UV–Vis spectra of diffuse reflectance of  $TiO_2$ - and  $SiO_2$ -supported catalysts

## **3** Results and Discussion

#### 3.1 Characterization of Supports and Catalyst

The metal loading of the catalysts was determined using ICP-MS and summarized in Table 1. It can be observed that the experimental loadings were generally lower compared to the nominal ones, especially for the silica-supported catalysts. For silica supported catalysts, this can be attributed to the similarity of the isoelectric point between the metal precursor solution and the silica support, minimizing the metal/support interaction which leads to metal loss [13]. In the case of the TiO<sub>2</sub>-supported catalyst, the obtained Au loading only differed slightly from the theoretical loading which can be related to the higher metal/

 Table 2 Specific surface area, metal particle size and metal dispersion of Au catalysts

Catalyst	$S_{B.E.T.} (m^2 g^{-1})$	d <sub>HR-TEM</sub> (nm)	D (%)
Au/TiO <sub>2</sub> –T	159	5	22
Au/TiO <sub>2</sub> -H <sub>2</sub>	172	6	18
Au/TiO <sub>2</sub> –U	143	7	16
Au/SiO <sub>2</sub> -C-T	293	5	22
Au/SiO <sub>2</sub> -C-H <sub>2</sub>	287	5	22
Au/SiO <sub>2</sub> –U	284	10	11

support interaction generated during deposition of Au which occurs due to the precipitation of the metallic phase.

It is observed that for the three used methods, the one that favors the deposition of colloidal gold is the method using urea. For those supported on  $TiO_2$  no significant difference in the amount deposited was found despite the different methods of preparation.

Figure 1 shows the X-ray patterns of the prepared catalysts. It can be clearly observed that in the Au/TiO<sub>2</sub> catalyst series various diffraction lines appear which are assigned to the anatase phase. The most significant peak of Au corresponding to the (111) hkl plane overlaps with one of the titania approximately at 38° 20; however, at 45° 20 a broad and less intense peak corresponding to the plane (200) of gold can be observed. This is characteristics of species with low crystallinity. The XRD pattern of SiO<sub>2</sub>supported catalysts shows all the diffraction lines of Au due to the amorphous nature of support. For the Au/SiO<sub>2</sub>-T catalyst, no diffraction lines were detected which suggests that Au particles were below the instrument detection limit of 5 nm; furthermore, this catalyst was the one with the least amount of Au deposited.



Fig. 3 HR-TEM for a Au/TiO2-U, b Au/SiO2-T



Fig. 4 XPS spectra of Au catalysts supported on a TiO<sub>2</sub> and b SiO<sub>2</sub>

Figure 2 shows the UV–Vis diffuse reflectance spectra of the supports and catalysts. The bands displayed between 200 and 400 nm are ascribed to  $TiO_2$  while the peak centered at 550 nm belongs to the gold species present in the catalysts. The silica-supported catalysts also displayed the same type of peak indicating that the gold species were similar regardless of the type of support. The position in the spectra attributed to the Au species suggests the presence of spherical gold particles [38]. This shape of gold nanoparticles show a strong surface plasmon absorption band in the visible region [39, 40]. Additionally, peaks centered at 250 nm were observed for the silica-supported catalysts which are attributed to silica species. The plasmon absorption band also depends on the size of the particles [41–44]. Generally, formation of metal nanoparticles involves two processes: the nucleation and growth of nuclei. There is a competition between the nucleation and growth. In the general field of colloid chemistry, it is known that fast nucleation relative to the growth results in small particle size [44]. In the case of silica series the three catalysts showed significant differences in intensity due to the preparation method. Au/SiO<sub>2</sub>-U shows the highest intensity indicating that this catalyst contains the largest metal crystallites: which may be attributed to partial agglomeration. This can be explaining by the lower interaction of the support with the metallic phase due to the repulsive interaction between them, which leads to agglomeration of Au NPs in the precipitation stage. Au/ SiO<sub>2</sub>-T and Au/SiO<sub>2</sub>-H<sub>2</sub> shown same intensities indicating similar particles size which is verified by HR-TEM (see Table 2).

Specific surface area of the Au catalyst shows values slightly smaller than the corresponding supports which are explained in term of the partial blockage of the porous of the support.

High resolution transmission electron micrograph was used to determine the average metal particle size of the catalysts and the results are summarized in Table 2 and representative micrographs showed in Fig. 3. Metal dispersion was estimated from HR-TEM values assuming that the crystals possess spherical shapes.

For Au/TiO<sub>2</sub> catalyst the analysis of Au  $4f_{7/2}$  core level spectra reveals the presence of two types of gold, metallic Au at 83.8 eV and partially oxidizing species at 85.5 eV (See Fig. 4). Conversely, Au/SiO<sub>2</sub> catalyst only exhibits the presence of Au<sup>0</sup>, in line with the differences in interaction between gold and the support.

Table 3 Binding energies [eV] of inner core electrons and atomic surface ratio of supported gold catalysts

Catalizador	Binding energies, eV				Au/Ti at	Au/Si at
	Ti2p <sub>3/2</sub>	Si2p	O1 s	Au4f <sub>7/2</sub>		
Au/TiO <sub>2</sub> –T	458.6	_	530.0 (87)	83.8 (70)	0.0107	_
			531.5 (13)	85.6 (30)		
Au/TiO <sub>2</sub> -H <sub>2</sub>	458.6	-	529.9 (90)	83.9 (80)	0.0030	_
			531.4 (10)	85.5 (20)		
Au/TiO <sub>2</sub> –U	458.6	-	530.0 (88)	83.9 (81)	0.0033	_
			531.4 (12)	85.6 (19)		
Au/SiO <sub>2</sub> -T	_	103.4	532.8	84.1	-	0.0013
Au/SiO <sub>2</sub> -H <sub>2</sub>	_	103.4	532.8	84.0	-	0.0011
Au/SiO <sub>2</sub> –U	_	103.4	532.8	84.1	_	0.0033



Fig. 5 Reaction scheme of the hydrogenation of nitrobenzene



**Fig. 6** Nitrobenzene hydrogenation over **a** 1 % Au/TiO<sub>2</sub> y **b** 1 % Au/SiO<sub>2</sub>. Reaction conditions: NB concentration: 0.02 mol  $L^{-1}$ , PH2: 40 bar, stirring speed: 700 rpm

In addition, the O 1 s core level spectra of  $Au/TiO_2$  catalyst indicate the presence of two types of oxygen species, assigned to Ti–O–Ti and surface oxygen groups

Table 4 Catalytic data for NB hydrogenation at 25  $^{\circ}\rm C$  on TiO\_2-supported catalyst at a reaction time of 7 h

Catalyst	$k_g \; (h^{-1} \; g^{-1})^a$	Conversion (%)	Yield An15 % (%)
Au/TiO <sub>2</sub> –T	1.52	70.8	93.3
Au/TiO <sub>2</sub> -H <sub>2</sub>	1.20	59.9	100.0
Au/TiO2-U	1.05	58.5	88.7
Au/SiO <sub>2</sub> -T	1.46	67.4	93.2
Au/SiO <sub>2</sub> -H <sub>2</sub>	1.19	59.8	98.8
Au/SiO <sub>2</sub> –U	0.50	31.4	98.8

<sup>a</sup>  $k_g = k_1 + k_2 + k_3$  (see Fig. 5)

interacting with Au species on the support. A summary of the obtained results by XPS are compiled in Table 3.

#### 3.2 Catalytic Activity

A scheme of the hydrogenation of nitrobenzene is shown in Fig. 5. It is highly desirable that the first step be reaction limiting step, to avoid undesirable intermediates products.

Figure 6 shows the evolution of conversion on time during the hydrogenation of NB over the Au/TiO<sub>2</sub> catalysts: all the catalysts were active showing a pseudo first order dependence to NB. The Au/TiO<sub>2</sub>–T showed a behavior like an induction time during approximately 3 h, despite that it showed the most active behavior of all the catalysts reaching a conversion of 70 % after 7 h. (see Table 4). Au/TiO<sub>2</sub>–H<sub>2</sub> and Au/TiO<sub>2</sub>–U also showed a similar trends by this induction period is less marked than that displayed by Au/TiO<sub>2</sub>–T.

The highest activity displayed by the Au/TiO<sub>2</sub>–T catalyst can be related to the smaller metal particle size as revealed by XRD, UV–Vis and HR-TEM characterizations. The Au/Ti surface atomic ratio shows that this catalyst was the most highly dispersed of the TiO<sub>2</sub> series.

For all studied catalysts, the main observed products were aniline and hydroxylamine (NBNH-OH); however, for the Au/TiO<sub>2</sub>–U catalyst nitrosobenzene (NB-NO) was



Fig. 7 Evolution of products as a function of the time for Au/TiO<sub>2</sub>–U catalyst



Fig. 8 Product conversion versus total conversion for Au/SiO\_2–U catalyst

**Fig. 9** Schematic deactivation for Au/SiO<sub>2</sub>–U catalyst

also detected as an intermediate product. This indicates that the rate of the second step is very high.

X-ray photoelectron spectroscopy results for all the catalysts indicated the presence of  $Au^{\delta+}$  species which explain the induction time observed in Fig. 6. We attribute the induction time of all the series to the restructuration of the active phase, due to the reduction of the  $Au^{\delta+}$  to  $Au^0$  and the competition between  $Au^0$  and  $Au^{\delta+}$  for adsorbing the NB. Also this effect retards the dissociation of H<sub>2</sub> which delayed the start of the reduction of -NO2 group . The larger Au particle of Au/TiO2-H2 and Au/TiO2-U catalysts leads to a low catalytic activity due to the lower hydrogen chemisorption ability. In spite of Au/TiO2-U catalyst contains smaller average Au particles compared to the Au/TiO<sub>2</sub>-H<sub>2</sub> catalyst determined by HR-TEM, the higher intensity of the Au UV-Vis spectrum suggests a higher contribution of species of crystallite sizes greater than 10 nm. This explains why the former catalyst exhibited lower catalytic performance and the production of small amounts of intermediate products such as NB-NO and NB-OH (see Fig. 7 and Table 4).

SiO<sub>2</sub> supported catalysts also show pseudo first order kinetic behavior, similar to the TiO<sub>2</sub> supported catalysts; however, the SiO<sub>2</sub> series did not show any induction time. In line with XPS results which indicate the presence of only Au<sup>0</sup> species in the SiO<sub>2</sub>-supported catalysts. On the other hand, HR-TEM results displayed comparable metal particle sizes (5 and 6 nm for the Au/SiO<sub>2</sub>–T catalyst and Au/SiO<sub>2</sub>– H<sub>2</sub> catalyst, respectively). Notwithstanding, these catalysts presented different activities: this can be explained by differences in metal loading as a consequence of the amount of Au deposited during catalyst preparation, derived from ICP-MS results. The Au/SiO<sub>2</sub>–T catalyst contained lower amount of Au in the catalyst in spite of it showed higher



catalytic performance; this is due to the better distribution of the active phase on the support which indicate that even though the different size particle the Au NPs behave in similar way. The lower catalytic performance of the Au/ SiO<sub>2</sub>–H<sub>2</sub> catalyst is attributed to the possible loss of active sites due to particle size agglomeration as determined by XRD and DRS UV–Vis results. Au/SiO<sub>2</sub>–U was the less active one, this can explain due to the higher metal particle size determined by HR-TEM. Table 4 compiled the reaction rate constants determined for all the studied catalysts.

The Au/SiO<sub>2</sub>–U catalyst contains the largest metal particles as demonstrated by HR-TEM and DRS UV-Vis which revealed an intense plasmon at 550 nm, suggesting that most of the nanocrystals are larger than 10 nm. This explains why this catalyst showed a higher concentration of intermediates within the studied time interval, leading to the direct loss of yield to the product of interest (see Fig. 8). It was detected a change in the conversion attributed to the catalyst deactivation for hydroxylamine irreversible adsorption. The products show the same tendency up to 18 % conversion, and at higher conversion levels the production of aniline and hidroxilamine and increment nitrosobenzene (in this case kg-k1) take place. We attributed this behavior to the presence of hydroxyl groups (Si-OH) remaining after metal deposition-reduction on the  $SiO_2$  surface [45, 46]. Despite the calcination, the silanol groups can be interacting with the intermediate products from catalytic performance as shown in Fig. 9.

## 4 Conclusions

All the catalytic systems were active in the hydrogenation of nitrobenzene being the most active catalyst those prepared by deposition–precipitation with NaOH at 100 °C, due to these catalysts contain the smallest metallic crystals. The  $TiO_2$  supported catalysts performed better than the  $SiO_2$ -supported counterpart. It is has been clearly shown that the Au deposition on a support during preparation is controlled by the metal/support interaction, which in turn influences the stability of the catalyst. Characterization results suggested a stronger metal/support interaction for the  $TiO_2$ -supported catalyst. No preparation method used favored a complete Au deposition on  $SiO_2$  catalysts despite displaying reactivity in the NB hydrogenation.

Reaction intermediates were found as products for all the catalytic systems but it is important to mention that the second step (formation of nitrosobenzene) is very fast and in some cases this product was not detected.

Acknowledgments The authors thank the Project FONDECYT 1100259 for funding this research. C. Torres and C. Campos are

grateful to CONICYT for their doctoral Fellowship. We also thanks to REDOC.CTA Universidad de Concepción.

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