Proyecto Fin de Carrera

Hidrogenación Selectiva de Nitroestireno catalizada por Platino: Optimización del catalizador y de la reacción

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Anexos

NOTA:

Estos anexos se han obtenido llevando a cabo una selección de información de la memoria completa (más extensa) realizada como informe final del trabajo desarrollado en el GGRC-EPFL.

Anexo I-Concepts

1. Concepts of Heterogeneous Catalysis

Catalysis is a technology of modifying the rate at which a desired chemical reaction takes place. By using the catalyst, the yield to a specific product can be improved; the selectivity to the target product can be modified, and the generation of undesired compounds reduced or suppressed[1]. Catalytic materials are required to decrease the activation energies of the reactions without altering the thermodynamic equilibrium of the process[2]. Although theoretically they are not consumed during the reaction, their properties can change significantly with use[3]. Therefore, they must be active, selective, stable and/or easy to regenerate.

Heterogeneous catalysis refers to the type of catalysis where the catalyst phase differs from that of the reactants. This technology represents a promising solution for the production of chemicals, petrochemicals and fine chemicals[4] where new challenges and unceasing improvement in the area of the preparation of catalysts tailored for specific reaction and/or processes appear continuously[3]. Some examples of new type of heterogeneous catalysts include catalytic fibers, membranes, catalyst operating in supercritical conditions and heterogeneous enantioselective catalysts[3].

In Heterogeneous catalysis, the reaction takes place on the active sites of the catalyst suface where molecules are adsorbed and activated. In general, during a reaction over a solid porous catalyst, the following steps take place (Figure-appendix 1):

Firstly, there is a mass transfer of the reactants from the bulk phase to the external surface of the catalyst (external diffusion) and after, to the catalyst pores surface (Internal diffusion). The chemical reaction only takes place if the reactants are adsorbed and located and orientated correctly. Finally when the products are formed, they desorb and diffuse to the external catalyst surface (internal diffusion) and then to the bulk (external diffusion).

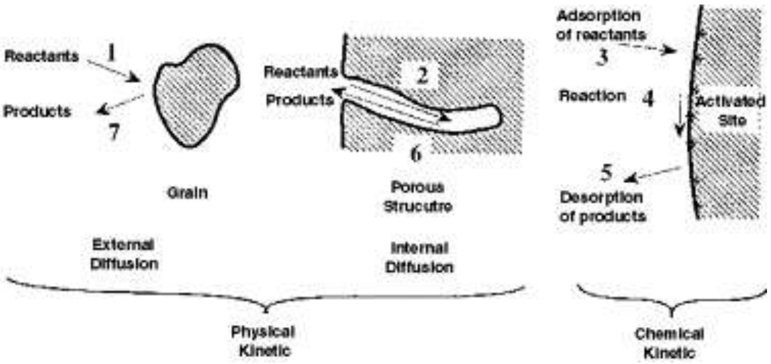


Figure-appendix 1.The catalytic cycle.

2. Selective Hydrogenation of Nitroarenes

2.1. Applications and Conventional (Non-Catalytic) Synthesis

Concerning the hydrogenation of nitroarenes, the production of aminoaromatics is the main application. The reason is that functionalized anilines are essential intermediates in the production of agrochemicals, dyes, pharmaceuticals, polymers and pigments[5] and therefore, nowadays they are of a great importance in the chemical industry.

Nevertheless, apart from the target product (aminoarenes), by-products are also formed. Therefore, the main challenges in the reduction of functionalized nitroarenes are the reduction of only the specific functional group, keeping untouched the other reducible groups presents in the corresponding Nitroarenes[6] (Figure-appendix 2) and the avoidance of decomposition of the molecule, which can lose its functional groups (Figure-appendix 3).

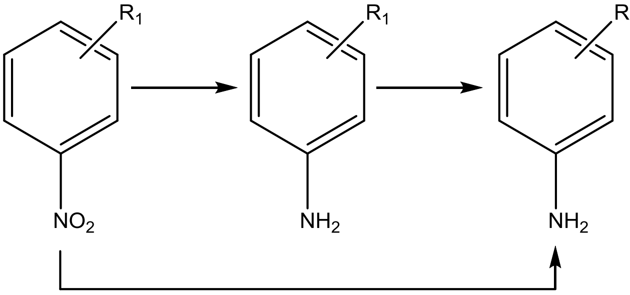


Figure-appendix 2. Hydrogenation of functional groups in nitroarenes

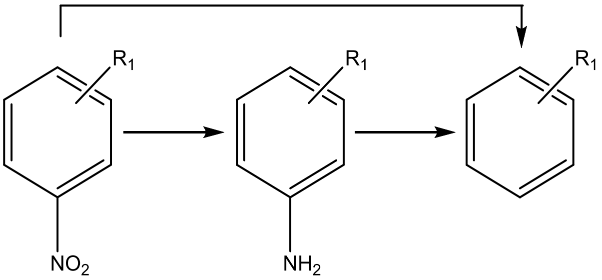


Figure-appendix 3. Decomposition of Nitroamines

To overcome these troubles non-catalytic processes are carry out industrially like Béchamp process with Fe/HCl or sulfide reduction with H_2S or NaSH as reducing agent[7]. On the one hand, the Béchamp process uses stoichiometric amounts of Fe-HCl as reducing system and includes the following steps[8]:

$$Fe + 2HCl + 2H_2O \rightarrow FeCl_2 + 2H_3O + 2H_3O^+$$

$$FeCl_2 + 2HCl + 2H_2O \rightarrow FeCl_4^{2-} + 2H_3O^+$$

$$RNO_2 + 3Fe + 5H_2O \rightarrow RNH_2 + Fe(OH)_2 + Fe(OH)_3 + FeO + H_3O^+$$

$$Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O$$

However, the large amount of Fe-FeO sludge produced as by-product together with the difficulties in the separation of the desired product and the use of corrosive acids make this process inconvenient for the environment.

On the other hand, the reduction of nitroarenes by negative divalent sulphur (sulfide, sulfhydrate and polysulfides) is called Zinin reduction[9]. The overall reaction is as follows:

$$4ArNO_2 + 6S^{2-} + 7H_2O \rightarrow 4ArNH_2 + 3S_2O_3^{2-} + 6OH^-$$

The mechanism of reduction nitro-aromatics in the Liquid-Liquid interphase is described in the following figure:

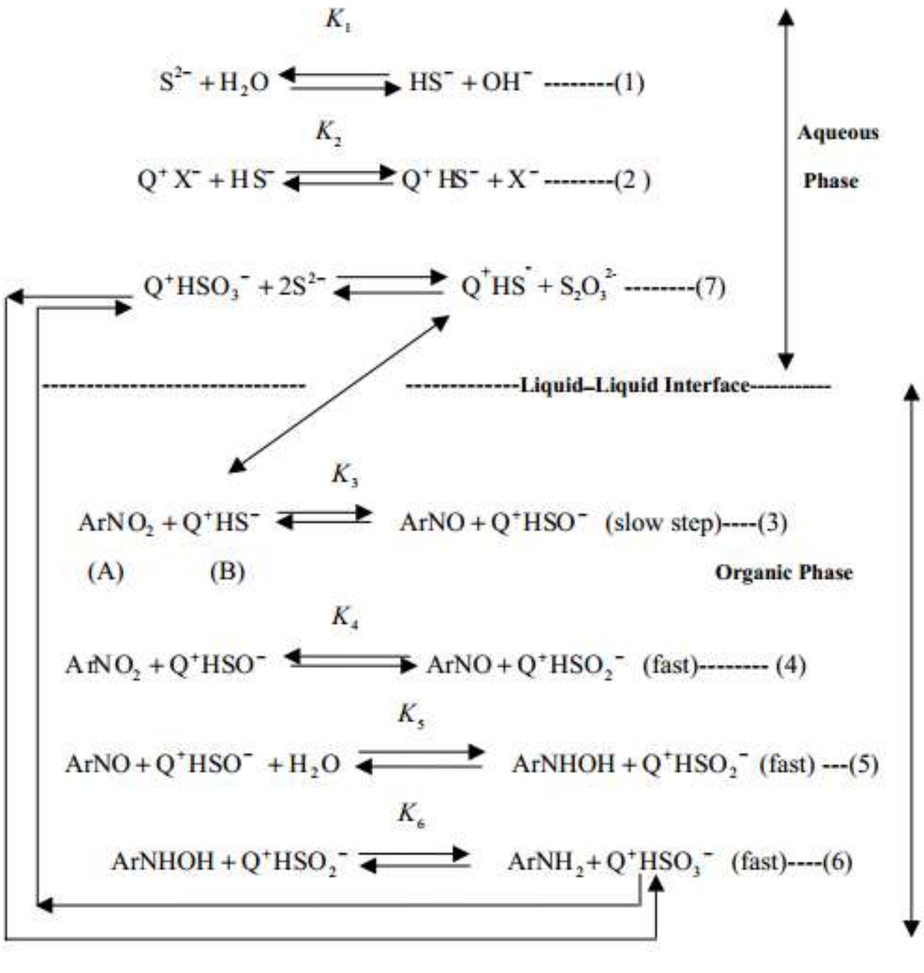


Figure-appendix 4. Mechanism of Sulfide reduction for Nitroaromatics compounds[9]

Both methods have as a main disadvantage the production of large amounts of waste and therefore it is important to develop economically feasible alternatives to non-catalytic processes[7].

2.2. Alternative Nitroarene Hydrogenation

It has been discovered that solid catalysts combined with H_2 as reducing agent are very efficient in nitroarene hydrogenation[10] and as a consequence, research is focused on finding new and better catalysts tailored for specific reactions and/or processes or improving the performance of the existing catalysts.

The generally accepted reaction pathway for the catalytic reduction of aromatic nitro compounds is based in the model presented by Haber[11] . There are two different routes in the proposed mechanism: direct and condensation route, which are shown in the Figure-appendix 5[12].

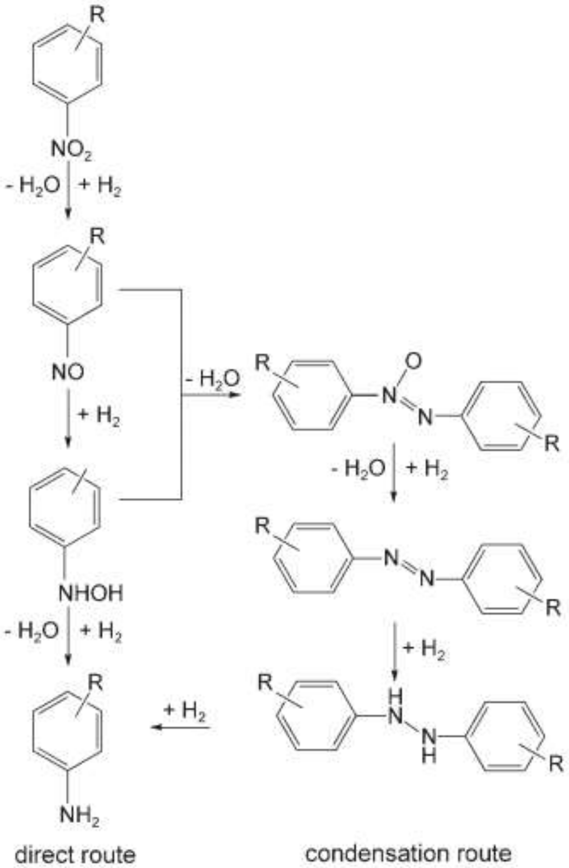


Figure-appendix 5. Possible reaction paths for functional Nitroarenes hydrogenation[12]

The nitro compound is reduced into a nitroso intermediate followed by its hydrogenation which produces the corresponding hydroxylamine specie (HA). These steps take place very fast and generate an intermediate, capable to react by two different ways; either direct or condensation route[12]. In the direct route the HA is directly hydrogenated into the desired amine while in condensation route, HA together with the nitroso compound are condensate into an azoxy group which is reduced rapidly into the corresponding azo, hydrazo (condensation products) and finally aniline compounds.

In spite of this general mechanism, there is no a global consensus[12] and as a consequence there are many proposals for the reduction of aromatic nitro-compounds to anilines, depending mostly on the catalyst used. On the one hand Siegris et al.[13]reported that the reduction occurs through both routes using Pt/$CaCO_3$ or Pt/C-H_3PO_4 as catalysts (*Figure-appendix 5*). On the other hand, other authors state the reaction takes place though the direct route; for example, Visentin et al.[14]established the direct hydrogenation route as mechanism, using Pd/C catalyst (*Figure-appendix 6*). Gender et al.[15]concluded there is only a direct route in the reaction scheme without formation of nitroso compounds with nickel catalyst (*Figure-appendix 7*). Makaryan and Savchenko[16] exposed the formation of amine products is a result of disproportionation of the corresponding HA on the catalyst when Ir, Pt, and Pd are supported on carbon (*Figure-appendix 8*) and Corma et al.[12]discovered that using Au as a catalyst, HA, formed though nitroso compounds or directly from the original nitro compounds, does not desorb from the catalyst, hydrogenating directly into aniline and avoiding the condensation pathway (*Figure-appendix 9*).

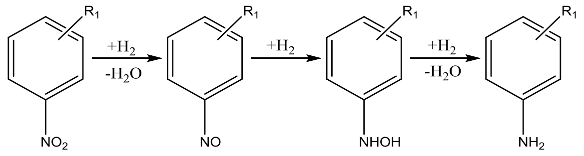


Figure-appendix 6. Alternative reaction mechanism I

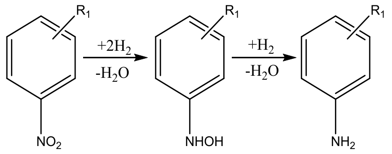


Figure-appendix 7. Alternative reaction mechanism II

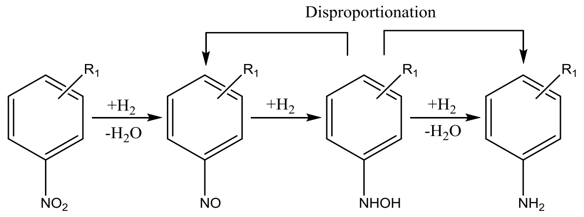


Figure-appendix 8. Alternative reaction mechanism III

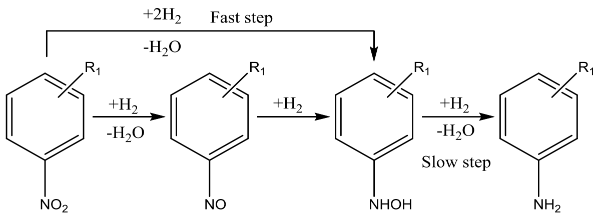


Figure-appendix 9. Alternative reaction mechanism IV

It is important to point that many studies[17,18] have concluded the possibility of accumulation of HA intermediate during the hydrogenation of nitroarenes. This is especially relevant when batch reactors are used, being even possible, in some special cases, that the hydrogenation could be supressed [17]. HA are compounds that can lead the formation of by-products. By the use of vanadium modifiers, the accumulation of the HA is reduced, the mechanism can be changed[18]; the HA is not anymore hydrogenated to the corresponding aniline with an slow reaction rate but disportionates rapidly, re-entering the nitroso intermediate into the catalytic cycle.

In order to design good catalysts of nitroarenes hydrogenation, it must be taken into consideration that they have to be both selective to the aminoarene and still very active for the fast nitroarene reduction. According to the literature the most efficient catalysts for the functionalized nitroarenes hydrogenation are summarized in table-appendix 1[7]:

Table-appendix 1. Industrial catalysts for nitroarenes hydrogenation [7]

Substituent	**Catalyst**	**Y (%)**
Cl	RaNi-N modifiers	99
	Fe, Cu-Ir/C, 1% Pt/C	99.3
Br, I	Pt/C-H_3PO_2-V, Pb-Pt/$CaCO_3$-$FeCl_2$	90
C=O	Pt/C-H_3PO_2-V	93
C≡N	Pb-Pt/$CaCO_3$-$FeCl_2$	50-88
C=C	Pt/C-H_3PO_2-V	95-98
C≡C	Pt/C- H_3PO_2-V	99
	Ru/Al_2O_3	100

Y: Yield

In most cases, commercially available catalysts have been used, either tailored by catalyst manufacturer such as promoted Ir and Pb-Pt/$CaCO_3$, or classical catalysts (Pt/C) were modified with amidines, H_3PO_2 or vanadium complexes.[7]

3. Selective production of vinylaniline

Heterocyclic compounds are very beneficial compounds for human life, since they are components of natural products, including the human body, and exhibit a variety of notable pharmaceutical applications[19]. In particular, vinylanilines (VA) are the key compound in the synthesis of quinolones, which exhibit a broad spectrum of pharmacological activity, including antibiotics, anticancer, antiviral, antihypertensive, etc[20].

They are also used for preparation of polymers with excellent pyroelectric properties with electro-optic, electro-mechanical and biomedical applications such as the copolymer (polypentafluorostyrene)-rac-poly(vinylaniline) (PPFS-r-PVA)[21]. Polybenzoexazines such as P-4VA are synthesized from VA and have many applications in construction, household facilities and electrical appliances due to their good heat resistance, flame retardancy and low dielectric properties[22].

VA is mainly obtained by the selective hydrogenation of Nitrostyrene (NS), which its most relevant physical properties are[23]:

- Melting point: -10°C
- Boiling point: 120°C
- Flash point: 107°C
- Density: 1.1552 g/ml
- Refraction Index: 1.5836
- Insoluble in water, soluble in EtOH, diethyl eter, bezene, choroform, ligroin, acetic acid.

However, the VA production is very challenging; it is a complex process which involves different intermediates and by-products. In this way, apart from VA, other compounds can be also formed, such as Ethylnitrobenzene (ENB) when only functional group reduced is the double bond or Ethylaniline (EA) when both nitro and double bond groups are reduced.

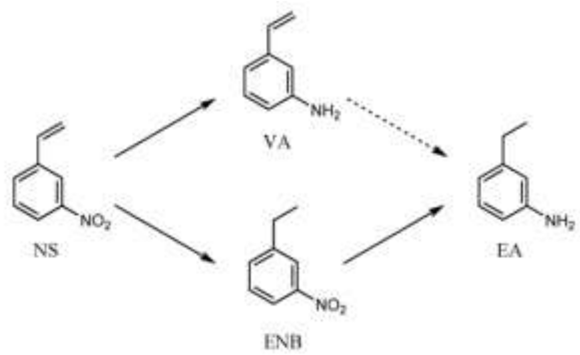


Figure-appendix 10. Reactant, target product and by-products involved in the reaction

For this reason, good selectivity to VA, while keeping considerable high the activity of the catalyst, is the main problem that must be solved. The selective hydrogenation of the NS has been carried out in many studies using different supported catalysts with the aim of improving activity and selectivity to the target product. Table-appendix 2 summarizes the best results found in the literature, where the conversions and selectivities were higher than 89%.

Table-appendix 2 .Compilation of literature results on liquid-phase hydrogenation of NS

Reactant/ Solvent	Metal	Support	T(°C)/P(bar)	$S_{VA,X=93-100\%}$(%)	$r_{X=100\%}$ $\left(\frac{Mol_{NS}}{Mol_M \times h}\right)$	$r_{X=40\%}$ $\left(\frac{Mol_{NS}}{Mol_M \times h}\right)$	Ref
3-NS/ Toluene	Pt	TiO_2	40/2	93	60		24
	Au	TiO_2	120/8	96	173		24
			120/9	99	82*		5
		Fe_2O_3	130/12	95	-		25
	Ni	TiO_2	120/15	90	15*		26
	Ru	TiO_2	120/15	96	53*		26
4-NS/ THF	Au	TiO_2	160/3	95		499	27
		Al_2O_3	160/3	89		3013	27
	Ag	Al_2O_3	160/3	96		183	28
		TiO_2	160/3	92		65	
		Sepiolite	160/3	89		19	

X: Conversion, S_{VA}: Selectivity to 3-Vinilaniline

**Reaction rate calculated considering the time required for achieving full conversion and the ratio between the amount of reactant used and the active metal of the catalyst.*

The literature shows that Pt, Au and Ag have achieved the best results where titania and alumina were the most employed supportsand toluene and tetrahydrofuran (THF) were used as solvents for the 3-NS and 4-NS hydrogenation respectively.

In the hydrogenation of 3-NS, Au shows the highest selectivity (96- 99%) but low activity (82-173mol $mol^{-1}h^{-1}$) while Pt , being the most active metal, gives a reasonable selectivity (93%). The fact is that, Serna et al [24] reported that using Pt/TiO_2 as a catalyst at 40°C and 2 bar,a total reaction rate of 60 mol_{NS} mol_{Metal}^{-1} h^{-1} is obtained while using Au/ TiO_2 the achieved total reaction rate was 173 at much harsher conditions (120°C, 8 bar). This confirms that Pt is much more active than Au but it is able to obtain proximate selective.

In the hydrogenation of 4-NS, both gold and silver catalysts show high selectivity, being the Au-supported catalyst much more active than the silver one, when the same reaction conditions are employed (160 °C, 3bar).

However, in order to overcome the problem of selectivity and activity, different modifiers can be introduced in the system or different support can be employed since both can have a final positive effect in the reaction.

4. Role of the Modifiers

Modifiers are used to increase the activity or selectivity of a catalyst. They can be classified as reaction modifiers or catalyst modifiers; depending if they are added to the reaction mixture or to the catalyst formulation.

4.1. Reaction Modifiers

Reaction modifiers are inorganic or organic compounds which are added in small amounts to the reaction mixture. They ideally interact strongly with active sites of the solid catalyst and induce favorable changes in the outcome of the reaction by interacting either with the catalyst or with the substrate[29]. In this way, commercially available catalysts can be tuned to achieve higher selectivity. However, complication may arise due to necessity of separation and product purification as well as low reaction rates.[30]

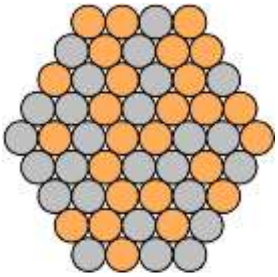
Taking into account the interaction with the catalyst, only a fraction of the modifier is absorbed on the active sites and equilibrium between the adsorbed and dissolved species is established. There is not a general agreement regarding the nature of the modifying effect due to its complexity and limited characterization methods. Regarding noble metal catalysts promoted by metal ions, they can be absorbed on the surface as ions or as reduced metal atoms[31]; blocking the active sites, producing electronic effects on the catalyst surface or forming bimetallic catalysts.

In nitroarenes hydrogenation, some metal salts have been demonstrated to be useful for improving selectivity to aminoaromatics. Indeed, one of the current used catalysts is Pt/C modified by -H_3PO_2 with soluble vanadium compounds as additives[10]. Low valent phosphorous compounds are known to decompose on the surface of hydrogenation catalysts thereby modifying the electronic structure of the surface and/or isolating active surface atoms[32] while the addition of vanadium allows to modulate the accumulation of hydroxylamine. In particular, Studer et al[17] reported that vanadium promoters can reduce the accumulation of hydroxylamine up to 70% with Raney Nickel as catalyst while Baumeister et al[18] achieved similar results with reduction of hydroxylamine up to 40% for the hydrogenation of Benzenesulfonamide-N-cyclohexyl-N-methyl-2-nitro, using Pd/C as catalyst.

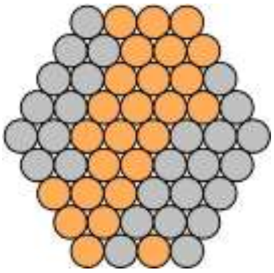
4.2. Catalyst Modifiers

Catalyst modifiers are components which are added to the catalyst during its synthesis in order to improve the catalyst properties with respect to a specific reaction. Among the different types of catalyst modifiers the introduction of a second metal in the catalyst with formation of bimetallic nanoparticles (NPs) is broadly study.

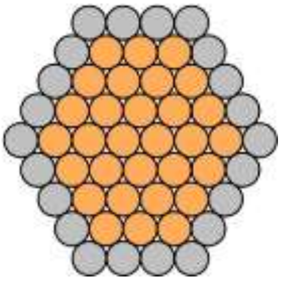
Bimetallic NPs are the combination of two different metals that interact in a certain way. Concerning the structure, there are different possible arrangements for bimetallic NPs, depending on their mixing enthalpy change[33] and the preparative conditions[34]:



Monophasic alloys



Cluster in cluster (Biphasic)



Core-Shell (Surface alloy)

- Alloy structure. This take place when the mixing enthalpy is negative. In addition, the less negative mixing enthalpy (closer to zero), the better is the mixing. In this way, alloys can be from completely random structures (mixing enthalpy small and negative) to ordered solutions (mixing enthalpy large and negative)[33].In particular, precious metals and light transition metals have been found to have such alloy structures. This could be the case of Cu-Pd and Ni-Pd[34].

- Cluster in cluster structure. It is characterized by the formation of particular segregations of metals. In particular, the elements form nanoclusters, aggrupation of atoms of the same metal, which are distributed thought the structure. This takes place when the enthalpy of mixing is small and positive. Some examples could be Au-Pd or supported Pd-Pt NPs[34].

- Core-shell structure, where one metal element forms an inner core and the other element surrounds the core to form a shell. This case occurs when mixing enthalpy is large and positive and it is characteristic of Poly (vinyl pyrrolidone) (PVP)-stabilized bimetallic NPs of precious metals, such as Pd-Pt[34].

The main advantage of bimetallic systems is that the catalytic properties of the original single-metal catalysts might be improved or even new properties might be created, which may not be achieved by monometallic catalyst[34]. These changes in the properties can be explained by the fact that the addition of a second metal can carry electronic or geometric effects on the catalyst.

On the one hand, the driving force of adsorption is the reduction of metal surface energy. This means catalytic particles with higher free surface energy will tend to attract more intensively. They are normally located on the corners or edges due to the fact they are coordinated by less atoms. As a consequence, when another metal is introduced in the catalyst they block the most attractive atoms and the activity of the catalyst is reduced. However this can be convenient for the selectivity of some catalysts since the activity and selectivity of metal nanocrystals strongly depend on their surface morphology[35]. On the other hand, when another type of metal is added to the catalyst, an electronic shift takes place thanks to the interactions of atoms with different electronegativities[36], which induces changes in the catalytic properties. In addition, in some cases, depending on the relative position of the active sites, the catalytic response could be different; this could be the case of the addition of a second metal which might change the relative position of the active sites.

Regarding the hydrogenation of 3-NS with bimetallic catalysts, Pt is the most active metal reported in the literature, which gives close selectivity to the ones given by gold, the most selective metal. For this reason, it is logic to believe that designing a catalyst of Pt modified by a second metal; the selectivity could be improved, keeping relatively high activity.

In a first attempting of using bimetallic catalyst, Corma et al[25] studied Au-Pd and Au-Pt catalyst over TiO_2 without finding good results in terms of selectivity to 3-VA. However, Cárdenas-Lizana et al.[37] studied the hydrogenation of other nitroaromatics like p-Choronitrobenzene over Pd/ZnO, and concluded that Pd/ZnO promote the reduction of the nitro group due to the formation of Pd-Zn alloy, achieving 100 % selectivity to p-choroaniline. Crespo-Quesada et al.[38] studied the catalyst Pd/ZnO, where Pd-Zn alloy is also formed, focus on the selective hydrogenation of the 2-methyl-3-butyn-2-ol to 2-methyl-3-buten-2-ol and showing an excellent catalytic performance for the reduction of the triple bond with a complete hindrance of the over-hydrogenation reaction. , In addition, in platinum-based bimetallic catalysts, some electropositive metals, such as Fe, Sn, Zn, Ni and Co have prominent promotion effects[39], for instance, Silvestre-Albero et al[40] suggested that PtZn alloy formation can change the electronic structure of Pt, which may hinder the adsorption of olefinic bond (C=C) during the hydrogenation of crotonaldehyde.

Therefore, as the combination of Pd-Zn promotes the selective reduction of nitro compounds and both Pd-Zn and Pt-Zn block the hydrogenation of the double bond, it is reasonable to expect that the combination of Pt-Zn could show promising results in the hydrogenation of 3-NS to 3-VA.

5. Role of the Support

The catalysts support is a material where active sites are fixed.Usually, the most suitable supports for the preparation of heterogeneous catalysts are those which have high porosity and specific surface area, since more amount of active area can be dispersed. There are different types of support but the most common ones are oxides of transition metals (alumina, silica, zirconia, titania) and activated carbon[41].

Supports play very important role in the catalytic properties. Throught modification of the surface area and pore distribution of the catalyst, the internal mass transfer can be controlled. Supports also affect the metal distribution, structure and morphology of metal particles and their acid/base properties might influence the catalyst performance[42]. In addition, by the metal-support interactions not only the metal particles are stabilized, reducing sintering, but also the activity and selectivity of the catalyst can be tuned[43].

There are different types of supports; metallic supports such as carbon nanofibers, zeolites, SiO_2, polymers or metal oxide supports, which can be divided in turn in reducible and non-reducible. Examples like ZnO, TiO_2, CeO_2, Fe_2O_3, and $SnO_2$are reducible while others such as MgO or Al_2O_3 are not.

The redox characteristics of the oxide support are crucial where partial reduction of carrier can result in partial/total blockage of the active site via migration of suboxide species and encapsulation of the metal particles, and/or the formation of new bimetallic phase with modified electronic and geometric properties affecting catalytic performance[41]. In this way, reducible supports permit control the activity and selectivity through these metal-support interactions. For example, chemical interactions between noble metal and the support, TiO_2, are referred as strong metal support interaction (SMSI)[44] and they are associated with the formation of new chemical bonds and drastic changes in the chemisorption properties of the noble metal[45]. Reducible supports, such as TiO_2, CeO_2 and SnO_2 were used to promote the hydrogenation of carbonyl bond by creating sites at the interface between the metal particle and suboxide species from the support, which decorate the particle surface[46,47]. Alloy formation was observed in Pt-ZnO and Pt-SnO_2 systems[48].

Conventionally, supported catalysts are used in the form of powders (ZnO, TiO_2, Fe_2O_3, MgO, CNFs), but they present some disadvantages like mass transfer limitations, difficulties to scale-up due to separation costs. To overcome these drawbacks structured support are gaining importance. They have regular structures free of randomness at a reactor level [49] . In spite of all their advantages, structured supports possess a much lower surface area, which can limit the dispersion of the active phase and therefore, low active metal loadings are normally used. To resolve this problem, either higher quantities of structured catalyst are required or non-structured supports are coated by a porous metal oxide layer with the aim of increasing the specific surface area.

Three types of structured catalysts can be distinguished[50]:

3. Monolithic catalysts: Continuous unitary structures containing many narrow parallel straight or zigzag passages which are made of ceramics or metals. The active material is dispersed uniformly over the whole porous monolithic structure. Using this supports, the pressure drop is low, the flow distribution is uniform, and the catalyst has high specific surface[49]. Nevertheless this kind of supports is expensive and shortly robust, requiring laminar flow profile and adiabatic conditions.

4. Membrane catalysts: Monoliths with communication between passages because the walls are permeable. Their main advantage is that they can combine catalytic reaction with reactant/product separation.

5. Arranged catalysts: Catalyst arranged in arrays or any other non-particulate catalyst such as packings covered with catalytically active material. In general lines, all of them allow a relatively fast mass transport over reaction zone in the direction perpendicular to the flow.For example, filamentous supports have easy recuperation of the catalyst, no catalyst agglomeration, low pressure drop and low resistance to external and internal mass transfer[49]. In particular, sintered metal fibers (SMF) are mechanically and chemically stable 3D thin structure of metal microfilament, so they are a kind of filamentous support. They can be made of different special alloys such as stainless steel, Inconel or Fecralloy. For being metal wires, they possess high mechanical strength and a high thermal conductivity which allows isothermal conditions in the reactor, an especially useful feature for highly exo/endothermic reactions. However, to achieve better performance, non-porous supports should be coated by a layer with high surface area, such as ZnO[51].

Concerning the hydrogenation of NS, it was found high activities and selectivities to VA using TiO_2[24,27] , Al_2O_3[27,28] as supports for the following catalysts: Pt/TiO_2, Au/TiO_2, Au/ Al_2O_3, Ag/ Al_2O_3.In addition, Beier et al.[52]reported the effect of the support on the catalytic response of the hydrogenation of 3-NS, using Pt as active metal. Considerable differences in terms of selectivity were not found (12 % of maximum difference) by using supports such as SiO_2, Al_2O_3, TiO_2, carbon nanotubes (CNTs) or unsupported Pt, being TiO_2 the most selective. In addition CNTs showed the highest activity (~250 mol mol^{-1} h^{-1}) while TiO_2 provided the lowest one (~70 mol mol^{-1} h^{-1}). The reason could be that the catalyst Pt/TiO_2 is generally expected to have strong interaction between the support and the metal[52] and TiO_x species can be generated by partial reduction of TiO_2 which could block the active surface of Platinum.

Boronat et al.[53]also studied the influence of the support on the hydrogenation of 3-NS, but using gold as active metal.

Table-appendix 3. Effect of the support in 3-NS hydrogenation over Au catalyst[53]

Support	S_{VA} (X(%)) (%)	r (mol mol_M^{-1} h^{-1})*
TiO_2[a]	96 (99)	173
Fe_2O_3[b]	95(23)	23
SiO_2[c]	30(10)	10
C[b]	41(6)	6

X: NS conversion, S_{VA}: Selectivity to 3-Vinilaniline, r: total reaction rate

Reaction conditions: 1ml feeding; 5.8mol% 3-NS, 90.5 mol% toluene, 1 mol% o-xylene (internal standar), 120°C, 9 bar of H_2. [a]1.5 wt%Au loading, [b] 4.5 wt% Au loading, [c]1.6 wt% Au loading

The authors have concluded that reducible supports such as TiO_2 and Fe_2O_3 lead to selective processes, whereas non-reducible ones such as SiO_2 or C produce both reduction of the double bond and the nitro functions[53], being the TiO_2 the one which shows highest activity.

The study of different supports was also carried out by Shimizu et al.[27,28] using 4-NS and Au and Ag as active metals:

Table-appendix 4. Effect of the support in 4-NS hydrogenation over Au catalyst27

Support	S_{VA} (X(%)) (%)	r (mol molM^{-1} h^{-1})*
Al_2O_3[a]	89(100)	3014
SiO_2[b]	76(79)	134
MgO[c]	59(90)	414
C[c]	6(28)	20
TiO_2[d]	95(100)	500

X: Conversion, S_{VA}: Selectivity to 3-Vinilaniline, r: total reaction rate. Reaction conditions: 160°C, 3 bar of H2,THF(15ml),2mmol of 4-NS, 0.04mol% catalyst, Au loading ([a] 1wt%, [b] 2.5wt%, [c] 0.2wt%, [d] 3wt%) *Initial reaction rate (X up to 40%)

It can be seen that SiO_2, MgO and C show lower selectivity to 4-VA than Al_2O_3 and TiO_2. The intrinsic activity of the gold NPs having similar mean size in all the catalysts(1.9-3.6 nm) depends strongly on the acid-base features of the support material[27]. The fact is that the catalyst with a strong basic character support (MgO) and the one with an acidic character support (SiO_2) give low initial reaction rate. This, in conjunction with the fact that the Au supported on carbon (neutral) shows the lowest activity, suggests that both acidic and basic surface sites are necessary. That could be why the Au supported on alumina, being the acid-based bifunctional support, shows the highest activity, almost 10 times more than in the other cases.

For the study with Ag, Shimizu et al, stated the following results:

Table-appendix 5. Effect of the support in 4-NS hydrogenation over Ag catalyst[25]

Catalyst	S_{VA} (X(%)) (%)	r (mol $molM^{-1}$ h^{-1})[b]
Al_2O_3[a]	96 (100)	183
TiO2 [a]	92(100)	65
Sepiolite [a]	89(100)	19
WO_3	98(11)	13
ZrO_2[a]	76(61)	19
CeO_2	74(59)	19
SnO2	79(3)	2
MgO	21(3)	0.32

X: Conversion, S_{VA}: Selectivity to 3-Vinilaniline, r: total reaction rate

Reaction conditions: 160°C, 3 bar of H2,THF(15ml),2mmol of 4-NS, 2mol% catalyst, Au loading 5wt). [a] *0.04 mol % catalalyst,* [b] *Initial reaction rate (X up to 40%)*

The selectivity did not markedly depend on the support material except for MgO[28]. The result shows that the support with strong basic character (CeO_2 and MgO) and that with acidic character (SnO_2 and WO_3) result in low activity, being the acid-based bifunctional support (Al_2O_3) the one which gives the highest activity and also selectivity.

6. Role of the Solvent

Solvents play an important role in heterogeneous catalysis to dissolve or dilute reactants and products, to control high reaction rates, to dissipate any reaction exothermicity; indeed, the solvent may have to be considered as a potential participant in the overall reaction.[54]

In the production of fine chemicals over heterogeneous catalysts, the choice of the solvent has a crucial impact since they could strongly influence the selectivity and activity of the catalyst. On the one hand, solvents can interact with the reactant and products positively: helping the mass transfer processes and freeing the catalyst surface of active site blockers. On the other hand, they can be adsorbed on the catalyst surface, generating competitive adsorption of the solvent and the reactant molecules on the active sites, and modifying catalytic properties. Therefore, the choice of a solvent and the understanding of solvent effects require a careful investigation[55].

For these reasons, solvent properties such as polarity, dielectric constant, acidity and factors like solvation of reactants and products, gas solubility and other mass transfer effects are needed to be considered[54].

Fujita et al.[56]studied the influence of the solvent in the hydrogenation of 3-NS to 3-VA. During all the study the catalyst employed was Pt/TiO_2 and using the same reaction conditions.

Table-appendix 6. Effect of the solvent in 3-NS hydrogenation over Pt/TiO_2[56]

Solvent	X(%)	S_{VA} (%)
Neat*	41	70
$scCO_2$**	64	75
tol [b]	43	55
EtOH [a]	99	48

*X: Conversion, S_{VA}: Selectivity to 3-VA. Reaction conditions: 3.6mmol of NS, 20mg of 0.5wt% Pt/TiO_2, 40 bar of H_2, 10 cm^3 of organic solvent, 100 bar of CO_2, 50°C, 1h of reaction. *No solvent.**Supercritical carbon dioxide ($scCO_2$).*

On the one hand, it can be deduced from the data that the highest activity was achieved by using ethanol (EtOH) as a solvent, although the selectivity to 3-VA kept low. On the other hand, the best selectivity to 3-VA was achieved by employing supercritical carbon dioxide, being its activity a middle point between the best and the worst activity. Therefore, the solvent affects both activity and selectivity.

7. Catalyst Preparation

Transition metals, especially precious metals NPs are more and more employed in catalysis; they possess a high surface-area-to-volume ratio compared to bulk materials, being able to improve catalytic performances with respect conventional catalystsfor many organic reactions[34].In particular, they play a decisive role in the 3-NS to 3-VA hydrogenation.

NPs are defined as a small object, sized between 1 and 100 nanometers that behave as a whole unit in terms of its properties. Their main advantage is that they may or may not exhibit properties that differ significantly from those observed in fine particles or bulk materials[57], for instance, Gold NPs melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C)[58]. NPs can be amorphous or crystalline; formed by several shapes and forms, composed of single or multi-chemical elements and they can exist individually or incorporated in a matrix[59].

The catalytic performance of NPs depends highly on their surface morphology.The number of planes, corners, and edges and the ratio between them depends ultimately on the NP size[48]. For these reasons, achieving controlled nanocatalyst morphology is the key to improve activity and selectivity[60]. However the main problem is that NPs are not thermodynamically stable due to their small size and high surface area. They possess a huge driving force to interact quickly with the surrounding atoms, trying to minimize their surface energy and increasing in this way their particle sizes. Small NPs tend to get dissolved while the larger particles grow up, generating a broad size distribution. Therefore, the main challenge is the generation of stable monodispersed NPs of different sizes.

7.1. Size-Controlled Preparation

Colloidal methods

In order to have good crystallographic control, colloidal methods have been widely implemented. They are advantageous because no specialized equipment is required, solution-based processing and assembly is easily implemented and large amounts of NPs can be obtained[48]. In most cases, a metal salt precursor is reduced in solution in the presence of a stabilizing and a reducing agent. Stabilizer adsorbs on the surface of the colloidal particles, thus guarding them against coagulation or improving their chemical stability, but at the same time modifying their catalytic properties[61].

These methods are based on two steps: nucleation and growth.

Nucleation

During nucleation, seed particles (nuclei) are formed. They act as nucleation sites for subsequent metal reduction, allowing the growth. Therefore, the seed particles formation is the key step because they determine the crystallographic growth[48]. The nucleation can be homogeneous or heterogeneous:

In homogeneous nucleation the seed particles are formed in situ and according to the LaMer model. Nucleation only takes place when the metal concentration achieves a saturation point[48] and all subsequent growth occurs on the pre-existing nuclei by atom addition. When concentration drops below the critical level, nucleation stops and the particles continue to grow until the equilibrium concentration of the precipitated species is reached[62]. In order to achieve highly monodisperse nanocrystals, nucleation must occur instantaneously, which is obtained by fast reduction of the metal precursor above the critical concentration.

In heterogeneous nucleation the seed particles are pre-formed ex-situ. They are later added to a growth medium to facilitate the reduction of the metal ions[48]. In this way, size control can be considered as overgrowth process and it allows wider range of growth conditions: milder reducing agents, lower temperatures or aqueous solutions[48]. In addition, it allows the introduction of seed particles of one metal into the growth medium of another metal.

Growth

The growth of the particles can be carried out through atom addition where reduced metal species are deposited on the solid surface of the nuclei or by aggregation between particles (secondary addition).

In order to stabilize NPs, either some surface protecting reagents such as organic ligands or inorganic capping materials must be added to the reaction mixture or NPs must be placed into an inert environment such as inorganic or polymers[62]. PVP is a linear polymer widely used as stabilizer due to its versatility and good results in size control of many metals[42]. For example monodisperse Pt particles of 1.7-3.6 nm were synthesized with alcohol as a reducing agent, PVP as stabilizer and methanol (MeOH), EtOH and ethylene glycol as solvents[63].

In general colloidal methods allow obtaining well size-controlled NPs with sharp size distribution. However, the main problem arrives when the formed NPs must be deposited on the support followed by stabilizer removal. Normally high temperature treatments are required and during these processes NPs agglomerations can take place resulting in broader size distributions.

Non-colloidal methods

Using supports is an alternative way to stabilize metal NPs. The principle of NPs formation is the same; reduction of metal precursors, but in this case, the reduction takes place on the support, allowing the formation of NPs directly on the surface of the support where they are more or less firmly anchored and effectively separated from each other. In this way they can be prepared quite easily, guaranteeing a high level of stability[43]. Indeed, this type of immobilization to prepare heterogeneous catalysts has been well investigated[34].

The average distance between particles will depend on the metal content, the particle size and the surface area of the support. To achieve adequate separation, metal loadings usually lie between 0.3-3 wt% and surface areas for supports are typically in the range from 50 to 500 $m^2 g^{-1}$ [43]. In addition, the metal-support preparation systems possess useful features: the location of the metal NPs within the support is in principle controllable, the particle size can be tuned by metal loading or temperature, further components like modifiers can be incorporated and two or more metal can be used to make supported alloys or bimetallic clusters[43].

Conventionally, oxides and zeolites are the dominant catalyst supports, because many of them are inexpensive and can be prepared with wide ranges of pore structures[64]. There are three main methods of supported NPs preparation:

- Impregnation method: The support is microporous, it soaks up by capillary action a solution of a metal salt. In this way, the metal solution is deposited in the pore, without exceed their volume. Then, the system is dried and finally reduced to generate small particle metal[43] (normally by heating treatment with hydrogen).Corma et al[26] achieved good results in terms of selectivity in 3-NS→3-VA hydrogenation by preparation of 0.2 wt% Pt/ TiO_2, 1.5wt% Ni/TiO_2, 5wt% Ru/TiO_2using incipient wetness technique and the following precursors: $H_2PtCl_6 \cdot 6H_2O$, $Ni(NO_3)_2$ and $RuCl_3$.

- Deposition-precipitation method mainly consists of a controlled precipitation of a hydroxide or other insoluble compound of the metal onto the support suspended in a liquid medium, followed by filtration, washing, drying and reduction. It is effective in generating well-dispersed metal NPs. Serna et al[10] designed 1wt% Au/TiO_2 catalyst by deposition-precipitation, using $HAuCl_4$ as precursor and obtained a particle of a 3.5nm size when the solution pH of 7 was employed, which gave good selectivity to 3-VA in the hydrogenation of 3-NS.

- Ion exchange method: the metal precursor reacts with the functional groups on a support (e.g., OH groups and oxygen atoms on oxides and zeolites), bonding chemically to the support[64]. This ion exchange process is followed by washing, drying and reduction and it also gives small NPs of metal. Hydroxyl groups at the surface of oxide supports may undergo either anion or cation exchange with a suitable metal ion complex, depending on the point of zero charge (PZC) of the support[43]:

$$S^+ + OH^- \leftrightarrows S - OH \leftrightarrows S\text{-}O^- + H^+$$

An important characteristic of ion exchange methods is that as the precursor ions are chemically linked to the support before reduction, the possibility of movement of the formed metal particles is reduced and as a consequence, the aggregation is diminished with respect to the impregnation and deposition-precipitation methods, where there is not such as initial chemical interaction.

Another type of supports that is becoming more and more popular are the polymers where metal precursor is introduced into the highly porous polymer framework and reduced to formed metal NPs, which remain stable by confinement in the small pores of the matrix. The main disadvantage is that since the NPs size corresponds to the polymer pores sizes, changing the NPs size implies designing a new polymeric matrix with the desired pores size. This approach has been successfully employed with complexes of several metals such as ruthenium [65] or palladium[66] resulting in increasing activity/selectivity/stability as compared to conventional supported metal catalysts. While applications to date have been mainly directed at selective oxidation[65,67,68 69], recent use in hydrogenations shows promise[66 70].

7.2. Synthesis of Bimetallic Catalysts

From the different existing methods of synthesis, the reduction of the metal precursors is broadly used. As occurs with monometallic catalyst, the bimetallic NPs can be formed in colloidal solution or by reduction of metal precursors on a support. However, controlling the size of the NPs is challenging since it depends on the metal composition[34].

Among the existing colloidal and non-colloidal methods, there are two mainly used techniques[34]:

- Co-reduction where the two metal precursors are chemically reduced together and in presence of stabilizers.
- Successive reduction metal precursors, where one metal is deposited on pre-formed monometallic NPs of the other metal. This is especially efficient for the formation of core-shell bimetallic structures.

7.3. Catalyst Activation

In order to finish the catalyst preparation, the catalyst must be activated prior to use. This step is crucial since it normally requires temperature treatments which can lead to many transformations on the surface of the catalyst; NPs can sinter, increasing their particle size and broaden the size distribution; while applying reducible support, they can interact with the active phase, generating alloy or decorating the metal NPs with suboxide species; or when bimetallic NPs are used different phases can appear. In this way, selectivity and activity to a certain reaction is strongly influenced by this temperature treatment. Some authors have investigated the effect of the catalyst reduction temperature on the 3-NS→3-VA hydrogenation, using different catalysts reduction temperatures.

Fujita et al.[56]reported the influence of the catalyst reduction temperature on the catalytic performance of Pt/TiO_2.

Table-appendix 7. Effect of the catalyst reduction temperature in 3-NS hydrogenation over Pt/TiO_2 [56]

$T_{reduction}$(°C)	X(%)	S_{VA} (%)
200	64	75
300	59	82
450	30	94

X: Conversion, S_{VA}: Selectivity to 3-Vinilaniline. Reaction conditions: 3.6mmol of NS, 20mg of 0.5wt% Pt/TiO_2, 40 bar of H_2, 100 bar of CO_2, 50°C, 1h

The activity shows an increase when the reduction temperature decreases. This could be attributed to the fact that at higher reduction temperature, the interactions between Pt and the support increase, reducing the exposed Pt active sites and that the metal particles are easily agglomerated, producing bigger nanoparticle size and reducing in this way the surface-area-to-volume ratio of the catalyst. In contrast, the selectivity to 3-VA enhances with the increase of the catalyst reduction temperature. This can be associated to the higher possibility of formation of SMSI at higher catalyst reduction temperatures.

The effect of the catalyst reduction temperature on the hydrogenation of 3-NS was also studied by Corma et al.[26] who studied three different active metals (Pt, Ni, Ru) on titania:

Table-appendix 8. Effect of the catalyst reduction temperature in 3-NS hydrogenation over Pt-Ni-Ru based catalysts[26]

$T_{reduction}$(°C)	S_{VA} (X(%))^a	S_{VA} (X(%))^b	S_{VA} (X(%))^c
200	42 (89)	55 (1)	71 (85)
450	93 (95)	90 (93)	96 (95)

X: Conversion, S_{VA}: Selectivity to 3-Vinilaniline. Reaction conditions: solvent: toluene, 1ml mixture of reactant and solvent. ^{a}0.2% Pt/TiO_2, 0.31 mol Pt/mol NS, 40°C, 3 bar. ^{b}5% Ni/TiO_2, 2.06 mol Pt/mol NS, 120°C, 15 bar. ^{c}1%Ru/TiO_2, 1.19 mol Ru/mol NS, 120°C, 15 bar

The catalytic performance is improved in terms of selectivity with the increase of the reduction temperature when TiO_2 is supporting the active metal, in all the studied cases. This can be explained by the fact that, at higher reduction temperatures, the exposed metal is reduced and number of M-Ti sites increased. It is assumed that SMSI occurs between the metals and the support, decorating the metal surface. This decreases the assemblies of accessible metal atoms, with a strong effect on the adsorption of the substituted nitroaromatics, in such a way that a preferential adsorption through the nitro groups occurs[26].

8. Catalyst Characterization

Catalysts can be characterized though different techniques. Among all the existing technologies, the following methods are widely used nowadays:

8.1. Atomic Absorption Spectroscopy (AAS)

This technique is mainly used for quantification of chemical elements in a substance.

The catalyst must be dissolved and diluted by distilled water to prepare a sample. Metal standard solutions with different concentration are required for calibration of the equipment. Once the sample is introduced, it is evaporated and atomized. Commonly, this takes place is an flame atomizer which can achieve temperatures around 2300°C using Air-Acetylene or around 2700°C using nitrous oxide. Once the sample is dissociated into free atoms, it is bombed by a radiation of a specific wavelength and since, in general, each wavelength corresponds to only one element, the excited state of the studied element can be achieved. Finally, the radiation flux without a sample and with a sample is measured by a detector and amplified. Thanks to a signal processor the ratio between the two values (the absorbance) is converted into analyte concentration applying the Beer-Lambert Law. This law states that the transmissivity of light though a substance (Trans) is equal to the ratio between the intensity of the incident light and the transmitted light, which corresponds to: $Trans = \frac{I}{I_0} = e^{-\sigma \times l \times N}$, being σ cross section of light absorption by a single particle, l the distance the light travel though the material and N the number per unit volume of absorbing molecules.

8.2. Transmission Electron Microscopy (TEM)

It is a very powerful microscopy technique where a beam of electrons is transmitted through the ultra-thin specimen. The interaction between the electrons and the sample is visualized by a fluorescent screen, and after recorded in images by a camera. In this way the morphology of the sample can be analyzed, being able to achieve sensitivity of the atom level.

8.3. Temperature-Programmed Reduction (TPR)

This technique is used to determine the redox properties of a catalyst and normally the most efficient reduction conditions.

A sample of the catalyst is introduced into a U-tube, placed in a furnace with temperature controller system. In order to control the sample temperature, a thermocouple is required. In addition, a flow system permits to create an reducing atmosphere, using inert gas like N_2 or Ar as a carrier and H_2 as a reducing agent. Finally, a detector, such as TCD, MS, IR, etc., is employed to detect the amount of gas flowing out of the furnace and be able to determine the gas reacted with the catalyst.

8.4. CO-Chemisorption

This technique is used to determine the metal dispersion in the catalyst, the metal surface area per gram of catalyst or per gram of supported metal and the mean particle diameter of the active metal.

Metal dispersion is evaluated by measuring chemisorption of CO on the surface of the catalyst. There are three different chemisorption conformations: Linear, Bridge or twin type, when one, two or half CO molecules are absorbed on one metal surface respectively (Stoichiometric factors: 1, 2, and 0.5). The adsorption conformation of CO on supported metal particle can be determined by infrared spectroscopy (IR). After pretreatment of the catalyst (oxidation or reduction at high temperatures) CO is introduced by pulse-dosing and the amount adsorbed in quantified.

9. Mass Transfer Limitations

In order to get kinetic rate expressions and the correct activity and selectivity values, the reaction should be carried out without any kind of transfer limitations. However it is often to find mass or heat transfer influence in the mechanism when very active catalyst are used. As a consequence it is required to verify if the reaction kinetics is free of the influence of transport phenomena as well as the absence of other type of effects like poisoning, channeling and by-passing[71].

9.1. Internal Mass transfer

Limitations in the internal mass transfer result in concentration gradients inside the catalyst particles, decreasing the surface concentration of reactants.

The Thiele modulus Φ is a good parameter to study the influence of the internal mass transfer in the reaction, and it represents reactivity on the external catalyst surface over diffusivity of the reacting species inside the porous[73]. In particular, Thiele modulus relates the intrinsic reaction rate at external surface conditions to the maximum effective rate of internal diffusion. The generalized equation is:

$$\phi = \frac{V_P}{A_P}\sqrt{\frac{\frac{n+1}{2}\times k_n \times C^{n-1}}{D_{eff}}}$$

Where n is the reaction order, D_{eff} the effective diffusion coefficient in the porous catalyst, k_n the intrinsic reaction rate, C the concentration on the surface and V_p and A_p the volume and area of the particle respectively.

For low values of Φ the internal diffusion rate is much higher than the reaction rate, which allows achieving uniform concentration across the pores. In this case, the surface reaction rate is the determining step in the process while for high values of Φ the surface reaction rate is faster than the diffusion, generation concentration profile inside the pores and therefore internal mass transfer limitations.

However, when the intrinsic reaction rate is not experimentally accessible, the Weisz Modulus, ψ, is employed since relate the observed reaction rate to the internal mass transfer rate:

$$\psi = \frac{V_p}{A_p}\times\frac{n+1}{2}\times\frac{-r_v(obs)}{D_{eff}\times C_{surf}}$$

Both modulus are connected by the following expression: $\varphi = \eta \times \phi^2$ being η the effectiveness factor.

D_{eff} value can be calculated as: $D_{eff} = \frac{\varepsilon_p \times D}{\tau_p}$ where ε_p and τ_p are the pore fraction and tortuosity factor respectively and diffusion coefficient, D, depends on the catalyst pore size, which determines the type of diffusion: molecular, Kundsen or surface diffusion. This diffusion coefficient can be estimated by Bosanquet equation: $\frac{1}{D} = \frac{1}{D_m} + \frac{1}{D_K}$

According to the literature, for Weisz modulus values lower than 0.1, $\varphi \leq 0.1$, the influence of the internal mass transfer is negligible[74].

Anexo II-Calibrations and Calculation Equations of the Reaction Parameters

1. Calibration of CG

In order to calculate the concentrations of the different compounds during the reaction, dodecane was used as an internal standard. A known amount of dodecane was added to the reaction mixture and since it kept inert during the reaction, its concentration was known and constant through the time. In this way, the concentration ratio of the reactant/products could be calculated according dodecane concentration and to the corresponding GC peak areas, which were calculated with a processing program called TotalChrom Navigator:

$$\frac{C_i}{C_{dod}} = K(i) \times \frac{A_i}{A_{dod}} \rightarrow C_i = K(i) \times \frac{A_i}{A_{dod}} \times C_{dod}$$

Being A_i =peak area of the compound i

However, implementing this method required the determination of the analytes calibration constantsk(i). For this, a series of solutions with different concentration ratios between the analytes and the internal standard had to be prepared; solutions were prepared by taking different volumes from an analytes containing mother solution and adding dodecane proportionally to keep equal internal standard concentration in all of them. Then, the solutions were injected in the GC and the peak areas measured. In this way, plotting the peaks area ratios versus the concentration ratios for each compound with respect dodecane, K factor was calculated:

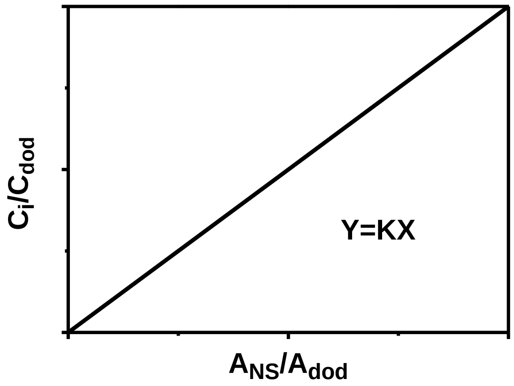


Figure-appendix 11. Calibration GC with an internal standard

This procedure was applied for each reactant/product:

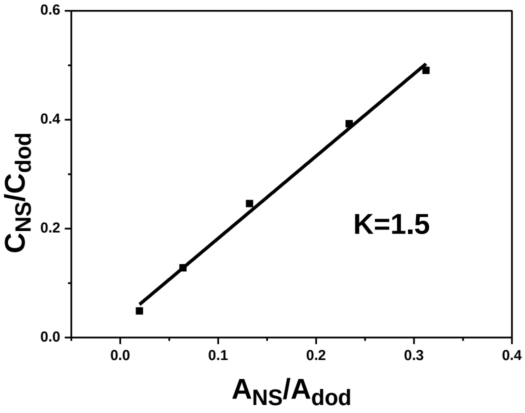


Figure-appendix 12. Calibration of NS with an internal standard

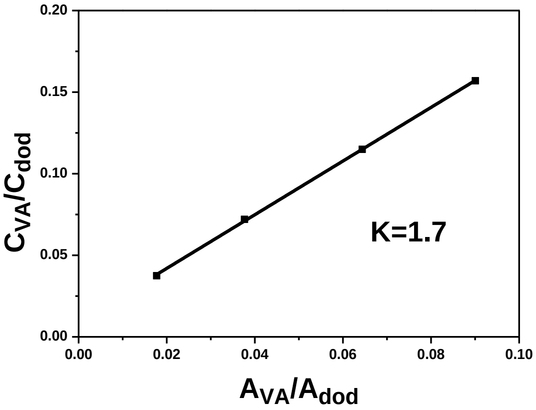


Figure-appendix 13. Calibration of VA with an internal standard

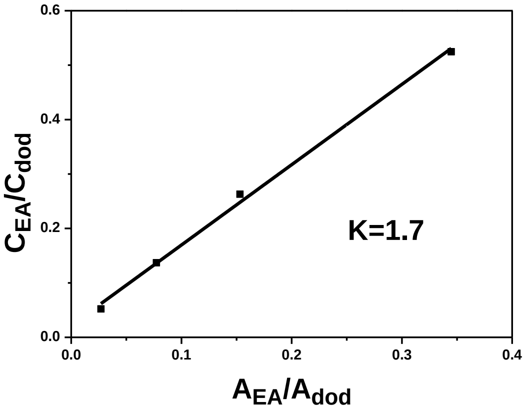


Figure-appendix 14. Calibration of EA with an internal standard

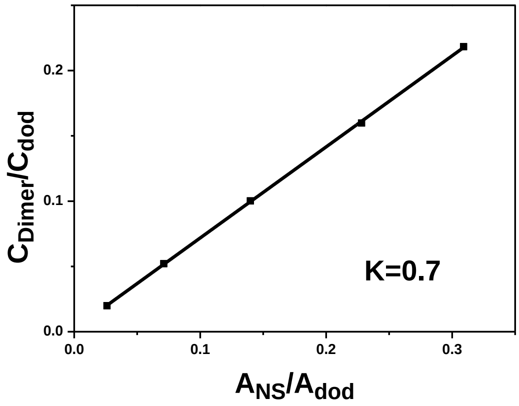


Figure-appendix 15. Calibration of Condensate products with an internal standard

2. Calculation Equations of the Reaction Parameters

It was already mention that the reactant molar concentration is calculated as:

$$C_i = K(i) \times \frac{A_i}{A_{dod}} \times C_{dod}$$

The conversion of 3-NSwas calculated from the difference between the reaction inlet and outlet concentrations:

$$X_{C_2H_2} = \frac{C_{NS,in} - C_{NS,out}}{C_{NS,in}}$$

The selectivity to a certain compound (i) was given by:

$$S_i = \frac{C_{i,out}}{C_{NS,\text{int}} - C_{i,out}}$$

For example,

For 3-VA, $$S_{VA} = \frac{C_{VA,out}}{C_{NS,\text{int}} - C_{VA,out}}$$

For 3-ENB, $$S_{ENB} = \frac{C_{ENB,out}}{C_{NS,\text{int}} - C_{ENB,out}}$$

For 3-EA, $$S_{EA} = \frac{C_{EA,out}}{C_{NS,\text{int}} - C_{EA,out}}$$

The yield to a certain compound (i) was defined as:

$$Y_i = \frac{X \times S_i}{100}$$

In order to estimate the activity of the catalyst, the initial reaction rate was measured. This one was defined as a number of consumed moles of reactant at maximum conversion of 20% per time and number of moles of active metal of catalyst:

$$r_0 = \frac{\mathrm{n}_{\mathrm{NS}}}{n_{Pt} \times t}$$

Anexo III-Catalyst Characterization

1. Atomic Absorption Spectroscopy (AAS)

Table-appendix 9. AAS analysis for the three designed catalysts

Catalysts	Theoretical Pt loading (wt%)	AAS analysis (wt%)
Pt/ZnO	0.4	0.4
Pt-Zn/HPS	2	1.6
Pt/ZnO	2	1.2

2. Temperature-Programmed Reduction (TPR)

The TPR activation profile is showed in figure-appendix 16 for Pt/ZnO catalyst. In this technique the Pt precursor, after being linked to the ZnO support is reduced.

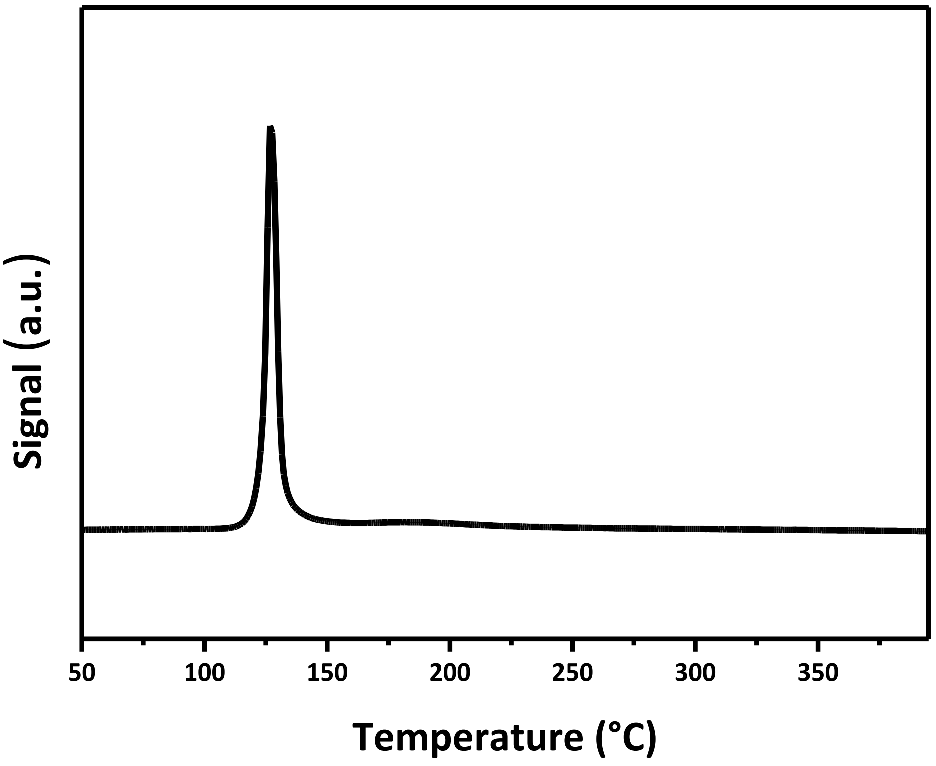


Figure-appendix-16. TPR profiles generated for reduction of Pt/ZnO at the heating rates of 5 K min^{-1}.

3. Transmission Electron Microscopy (TEM)

Pt-Zn/HPS: In this case, the Pt and Zn NPs are formed directly in the support by treatment in H_2 of the corresponding precursors.

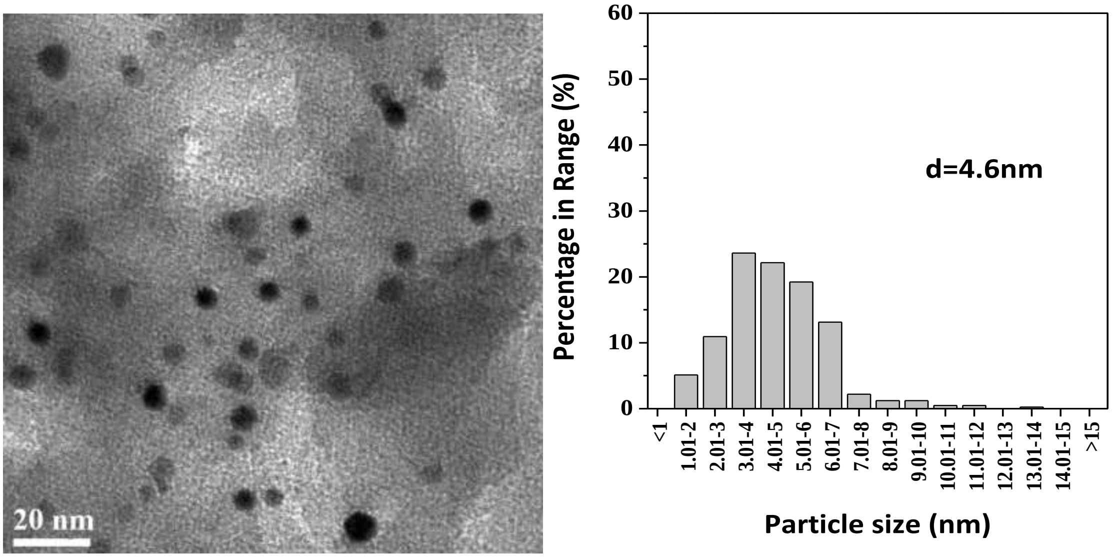


Figure-appendix 17. TEM image of Pt-Zn/HPS and metal particle size distribution

Pt/ZnO: In this case, Pt NPs are also formed directly on the support by reduction of the precursor after being linked chemically to the surface of the support.

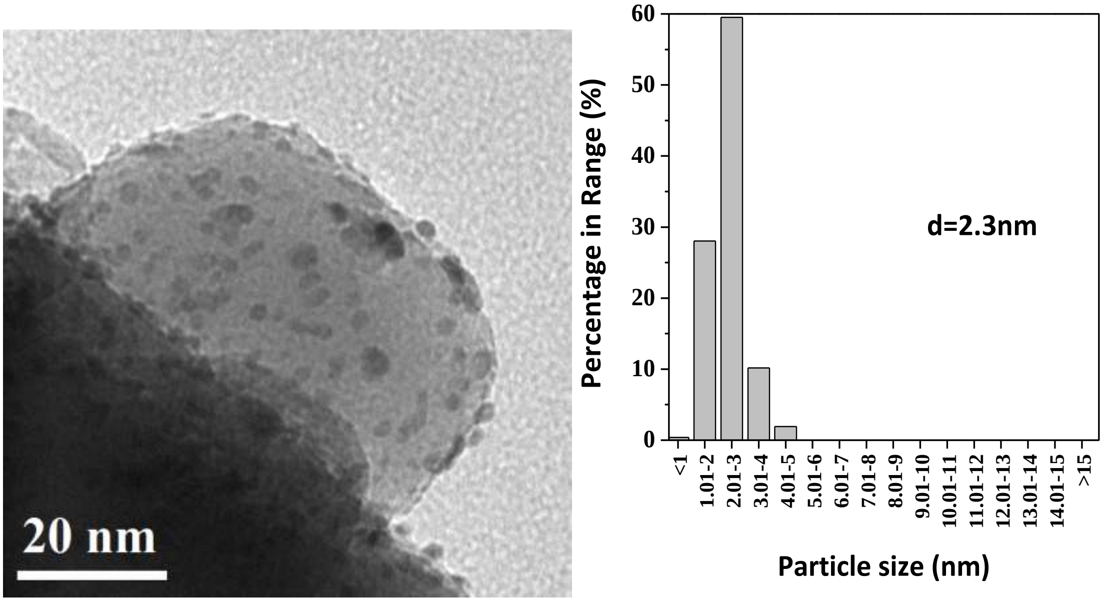


Figure-appendix 18. TEM image of Pt/ZnO and metal particle size distribution.

Anexo IV- Calculation of Mass Transfer Limitations

To evaluate the influence of internal mass transfer on the observed reaction rate, the Weisz modulus ψ for the Pt/ZnO catalyst was calculated according to the equation:

$$\psi = \frac{V_p}{A_p} \times \frac{n+1}{2} \times \frac{-r_v(obs)}{D_{eff} \times C_{surf}}$$

To implement the calculation, the active phase is supported on ZnO powder (>99%, Aldrich) with a particle diameter of 60 µm. In this way, $\frac{V_p}{A_p} = \frac{4/3 \times \pi \times \left(\frac{d_p}{2}\right)^3}{4 \times \pi \times \left(\frac{d_p}{2}\right)^2} = \frac{d_p}{6}$

Concerning the diffusion of NS, the effective diffusion coefficient, D_{eff}, in the catalyst layer was estimated based on a molecular diffusion coefficient of liquid in liquid at 75°C of 10^{-9} m^2/s. Assuming middle values of porosity and tortuosity ($\varepsilon_p \approx 0.5$, $\tau_p = 4$)[80], D_{eff} was calculates as $1.25 \times 10^{-10} m^2/s$. The reaction order n was assumed as that of nitrostyerene as 1, calculated in appendix number IX. In order to ensure the absence of mass transfer limitation during all the experiment, the observed reaction rate must be obtained at harsh reaction conditions (110°C, 10 bar). The value was $1.5366 \frac{mol}{mol_{Pt} \times s}$ which correspond to $2.63 \times 10^{-4} \frac{mol}{l \times s}$ with a surface concentration of $0.0223 \frac{mol}{l}$.

Based on these data the value for ψ is calculated as 0.009 and since it is lower than 0.1, it indicates an absence of internal mass transfer limitations in the catalytic surface layer. The molecular diffusion coefficient (D_m) is much smaller in liquid-liquid diffusion than in gas-liquid diffusion, since the gas molecules are generally much smaller and move easier. For this reason it is logic to think that since there is not internal mass transfer limitations for NS, H_2 will neither has such as limitations.

Anexo V- Mass Balance - Accumulation of Hydroxylamines

The figure-appendix 19 shows the evolution of the concentrations and mass disbalance with time for the hydrogenation of 3-NS using 0.4wt% Pt/ZnO.

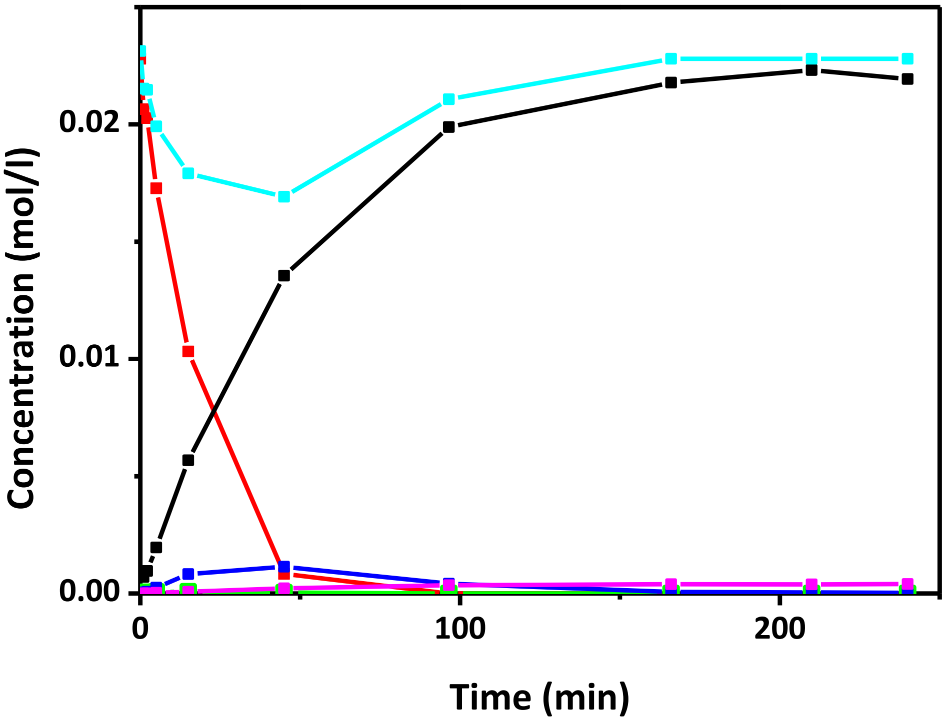


Figure-appendix 19. Evolution of the concentrations and disbalance (cyan blue line) with time for the hydrogenation of 3-NS using 0.4wt%Pt/ZnO. Reaction conditions: 75°C, 10 bar, EtOH, 2000 r.p.m., n_{NS} : n_{Pt} = 135 : 1.

In this figure a disbalance (up to 20%)in the middle of the reactions was observed. The mass balance was calculated as the sum of moles of all the measured compounds at the time the sample was taken and compared with the initial amount of 3-NS. This disbalance is attributed to the accumulation of hydroxylamines (HA), which cannot be quantified by GC due to their degradations at high temperature during the injection. Many authors have study this phenomenom[17,18]; Studer et al[17] reported that the accumulation of HA during the hydrogenation of nitroaromatic compounds can be very significant, for example, high accumulation of 70-80% was observed with unmodified Raney nickel catalyst for the hydrogenation of aromatic nitro compounds, or even worse, the hydrogenation could stop in some special cases. Since there was not disbalance at the end of the reaction over the investigated Pt-Zn catalysts, one can assume that the HA was converted into the final product, 3-VA, resulting in a high selectivity towards desired product. Figure-appendix 20 shows the evolution of selectivity to the desired product versus conversion of 3-NS.

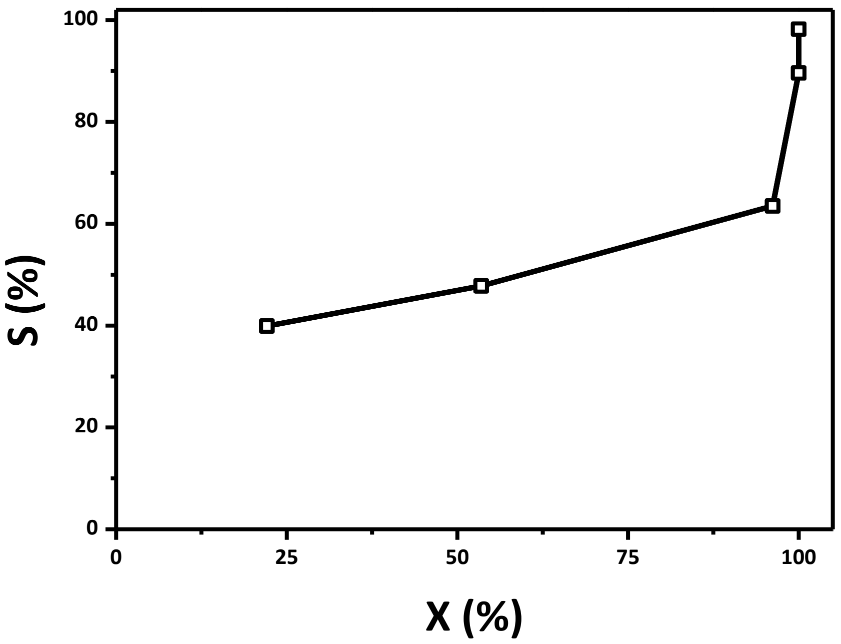


Figure-appendix 20. Evolution of selectivity (☐ 3-VA) over conversion of 3-NS for the hydrogenation of 3-NS using 0.4wt%Pt/ZnO. Reaction conditions: 75°C, 10 bar, EtOH, 2000 r.p.m., 135 mol NS mol Pt^{-1}

The selectivity is reduced in the middle of the reactions, caused by the accumulation of HA, which slowly transform into VA. Then, it is observed that the selectivity increases drastically after full conversion thanks to the transformation of these HA into the final product.

Anexo VI- Calculations and Tables of Activities

1. Reaction Rate at Different Temperatures

In order to be able to compare the results in terms of activity, the initial reaction rates over Pt/TiO_2 and Au/TiO_2 were recalculated for our experimental conditions (75°C). It was found in the literature that the activation energy for hydrogenation of different disubstituted nitroarenes[82], over Pt catalysts is in the range of 24-40 KJ mol^{-1}. So, considering an activation energy of 35 KJ mol^{-1}, the initial reaction rate of 3-NS hydrogenation using Pt/TiO_2 would be: 232 mol mol_{Pt}^{-1} h^{-1} at 75°C and 2 bar and using Au/TiO_2 the maximum initial rate would be 43 mol mol_{Au}^{-1} h^{-1} at 75°C and 8 bar. The required calculations were:

Arrhenius' law: $k = k_0 \times e^{-\frac{E_a}{R \times T}}$, Initial reaction rate equation: $r_0 = k_0 \times C_{NS,0}^{a} \times P_{H_2,0}^{b} \times e^{-\frac{E_a}{R \times T}}$

Considering two different temperatures: $\ln \frac{r_{0,1}}{r_{0,2}} = -\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

2. TOF (Turnover Frecuency)

Calculation of the activity per surface atom (TOF, turnover frequency) cannot be implemented rigorously since the amount of formed Pt-Zn alloyed is not known and as a consequence, the surface area of Pt covered by Zn cannot be measured. However, a roughly approximation of the activity per active site can be done, considering spherical Pt NPs free of Zn. Van Hardeveld et al[71] have calculated the dispersion of the atoms of spherical NPs for different sizes, hence the percentage of atoms on the surface of the NPs (active sites) can be calculated and TOF estimated (dividing the reaction rate value by the dispersion). Applied to this study and working at 75°C, 10 bar, Pt/ZnO (PVP) with an average diameter of 6.8nm, possess a dispersion of 15%, with a TOF of 2186 h^{-1}, Pt-Zn/HPS is characterized with a NPs size of 4.6nm which lead to a dispersion of 22% and an TOF value of 5609 h^{-1} and finally, Pt/ZnO with a particle size of 2.3nm in average, gives a dispersion of 41% which is translated into 3804 h^{-1} of TOF. Calculating as well, activity per active site for the literature results, it can be observed that Pt/TiO_2 with a NPs size of 5.5 nm achieved a TOF value of 1450 h^{-1} at 75°C, 2 bar while Au/TiO_2 characterized with a NPs size of 4 nm has a maximum TOF value of 215 h^{-1} at 75°C, 8 bar.

Table-appendix 10. Summary of activities in the hydrogenation of 3-NS for the catalysts

Catalyst	Particle size (nm)	Dispersion (%)	r_0 (mol mol_M^{-1} h^{-1})	TOF (h^{-1})
Pt/ZnO (PVP)	6.8	15%	328	2186
Pt-Zn/HPS	4.6	22%	1206	5609
Pt/ZnO	2.3	41%	1560	3804
Pt/TiO_2	5.5	17%	232	1450
Au/TiO_2	4	20	43	215

Anexo VII- Effect of the Solvent

In the production of fine chemicals over heterogeneous catalysts, the choice of the solvent has a crucial impact; since it can strongly influence the selectivity and activity of the catalyst[55]. In particular, some solvent properties such as polarity, dielectric constant and acidity and factors like solvation of reactants and products, gas solubility, competitive adsorption on the catalyst surface and other mass transfer effects may be responsible of this effect[54].

For these reasons, the influence of the solvent on the catalyst performance has been studied. In order to classify the solvents, the polarity was chosen as parameter. Polarity in organic chemistry refers to a separation of charge in a bond or an entire molecule and depends on the difference in electronegativity of atoms and the asymmetry of the molecular structure. Polarity underlies a number of physical properties such as solubility of the reactants in the solvent. Dielectric constant is the most common measure of solvent polarity and characterizes the capability of the solvent to solvate and stabilize charges[81]. Table-appendix 11 shows the dielectric constants of the solvents used in this study:

Table-appendix 11. Dielectric constants of the different solvents

Solvent	Dielectric constant
Toluene	2.4
THF	7.5
IPrOH	18
EtOH	24
MeOH	33
Acetonitrile	37

Anexo VIII- Calculations of the Apparent Activation Energy

In order to calculate the apparent activation energy, the reaction rate constant is defined according to Arrhenius's law as:

$$k = k_0 \times e^{-\frac{E_a}{R \times T}}$$

Being, E_a the apparent activation energy of the reaction, k_0 the pre-exponential factor, R the gas constant and T the reaction temperature in K

Applying the Arrhenius's law to the initial reaction rate,

$$r_0 = k_0 \times C_{NS,0}^{a} \times P_{H_2,0}^{b} \times e^{-\frac{E_a}{R \times T}}$$

Taking log in this expression,

$$\ln(r_0) = \ln(k_0) + a \times \ln(C_{NS,0}) + b \times \ln(P_{H_2,0}) - \frac{E_a}{R \times T}$$

While keeping constant the initial concentration of NS, reactions at different temperatures provide the information to calculate the apparent activation energy, by representing $\ln r_0$ versus 1/T .

$$\ln(r_0) = \ln(k^{'}) - \frac{E_a}{R \times T} \rightarrow slope = \frac{E_a}{R}$$

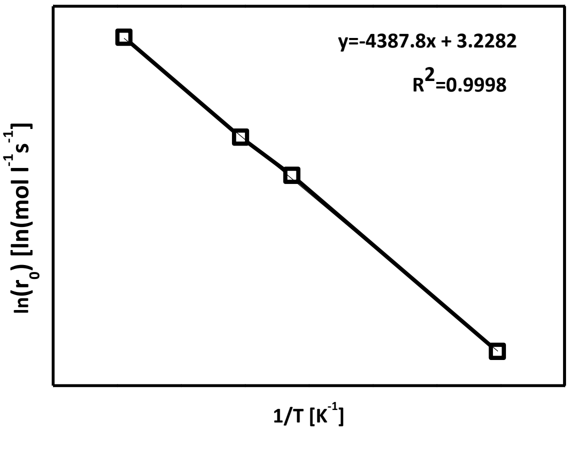


Figure-appendix 21. $\ln r_0$ versus 1/T for the calculation of the apparent activation energy to 3-NS in the hydrogenation of 3-NS, using Pt/ZnO as catalyst. Reaction conditions: Temperatures (40°C-110°C), 10 bar, EtOH, 2000 r.p.m., $n_{NS} : n_{Pt} = 135 : 1$.

The slope of the straight line is -4387.8 and knowing that gases constant (R) has a value of $8.3144 Jmol^{-1}K^{-1}$, the apparent activation energy acquires a value of $36.5 KJmol^{-1}$.

Anexo IX- Calculations of the Reaction Order to 3-NS

The kinetic model is based on Power Rate Law for the transformation rate of NS:

$$r = -\frac{dC_{NS}}{dt} = k \times C_{NS}^{a} \times P_{H_2}^{b}$$

Experiments carried out in excess of H_2 allow calculating the reaction order to NS, since the concentration of hydrogen keeps constant during the course of the reaction. In this way,

$$r = -\frac{dC_{NS}}{dt} = \left(k \times P_{H_2}^{b}\right) \times C_{NS}^{a} = k_1 \times C_{NS}^{a}, \quad \text{being } k_1 = k \times P_{H_2}^{b}$$

Considering,

$$r = -\frac{dC_{NS}}{dt} \approx -\frac{\Delta C_{NS}}{\Delta t} = k_{\cdot 1} \times C_{NS}^{a}$$

and taking lo $$r = \ln\left(-\frac{\Delta C_{NS}}{\Delta t}\right) = \ln(k_1) + a \times \ln(C_{NS})$$

Representing, $$\ln\left(\frac{\Delta C_{NS}}{\Delta t}\right) \text{ vs } \ln(C_{NS})$$

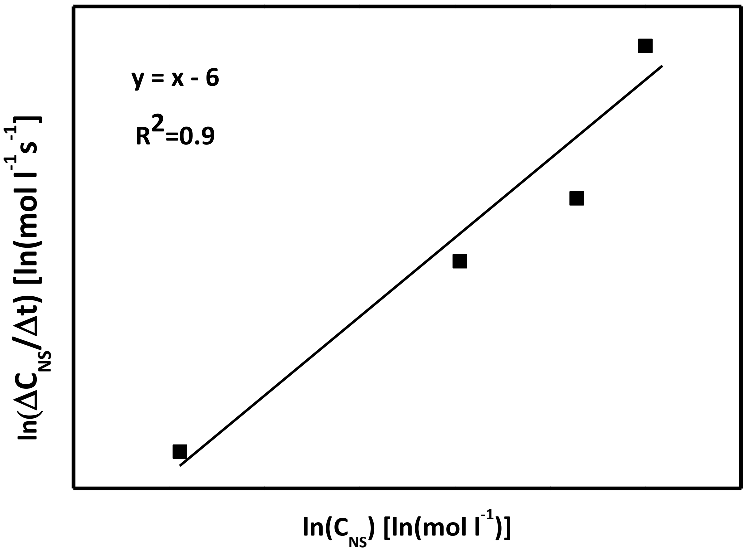


Figure-appendix 22. lnΔC_{NS}/Δt vs ln C_{NS} for the calculation of the reaction order to 3-NS in the hydrogenation of 3-NS, using Pt/ZnO as catalyst. Reaction conditions: 75°C, 10 bar, EtOH, 2000 r.p.m., $n_{NS} : n_{Pt} = 135 : 1$.

Therefore, the reaction order to NS is approximately 1 (a= 1).

Anexo X- Calculations of the Reaction Order to H_2

The kinetics expression for the reaction can be expressed as:

$$r = k \times C_{NS}^{a} \times P_{H_2}^{b}$$

Considering initial reaction rate, $r_0 = k \times C_{NS,0}^{a} \times P_{H_2}^{b}$

Experiments were carried out at different pressures while keeping constant the initial NS concentration. Therefore,

$$r_0 = k_2 \times C_{H_2,0}^{b} \text{,being } k_2 = k \times C_{NS,0}^{a}$$

Taking logarithms, $\ln(r_0) = \ln(k_2) + b \times \ln(P_{H_2,0})$

Representing $\ln(r_0)$ vs $\ln(C_{H_2,0})$

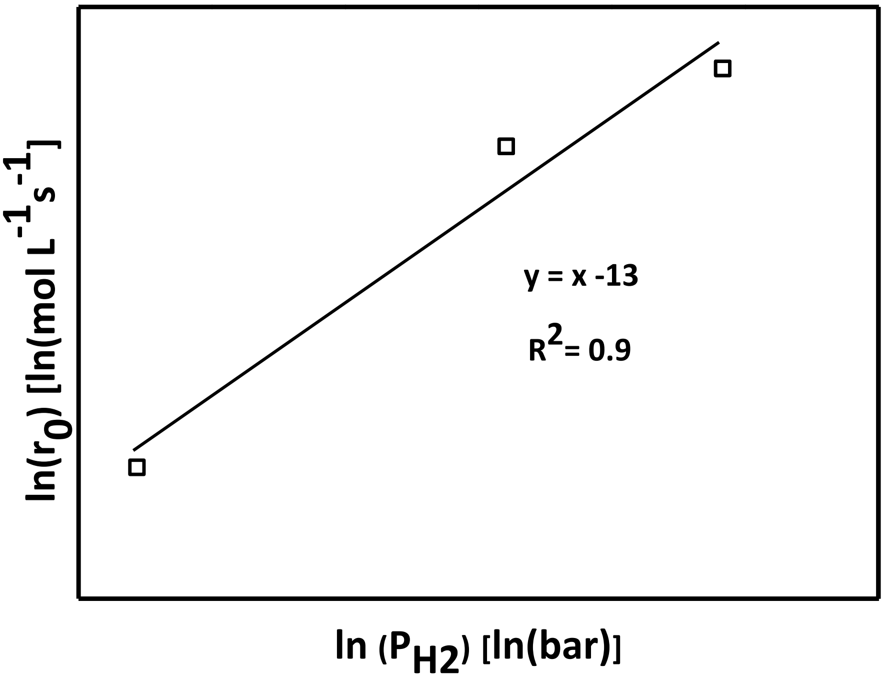


Figure-appendix 23. lnr_0 versus lnP_{H2} for the calculation reaction order to H_2in the hydrogenation of 3-NS, using Pt/ZnO as catalyst. Reaction conditions: Pressures (5-15 bars) ,75°C, EtOH, 2000 r.p.m., $n_{NS} : n_{Pt} = 135 : 1$.

Therefore, the reaction order to H_2 is approximately 1 (b= 1).

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