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THE HYDROGENATION OF NITROARENES MEDIATED BY PLATINUM NANOPARTICLES: AN OVERVIEW

P. Lara[a]* and K. Philippot[b,c]*

[a] *Instituto de Investigaciones Químicas (IIQ) and Departamento de Química Inorgánica, Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla*
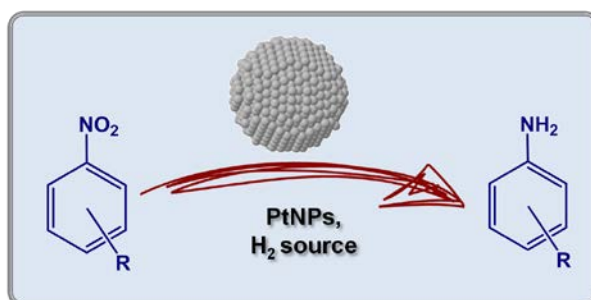*Avda. Américo Vespucio, 49, 41092 Sevilla (Spain)*
Fax: + 34 954 46 01 65
E-mail: patricia@iiq.csic.es

[b] *Laboratoire de Chimie de Coordination; CNRS; LCC; 205 Route de Narbonne, F-31077Toulouse, France*
[b] *Université de Toulouse; UPS, INPT; LCC; F-31077 Toulouse (France)*
E-mail: karine.philippot@lcc-toulouse.fr

Graphical Abstract (Table of Contents)

This review reports the most recent advances in the synthesis and application of platinum nanoparticles as catalysts in the hydrogenation reaction of nitroaromatics.

Abstract

Hydrogenation of nitroarenes is a catalytic reaction of high interest owing to the importance of the resulting anilines for the chemical industry. For this transformation, a huge number of catalysts based on different metals have been reported so far. However, the chemoselective reduction of the nitro group when other reducible functionalities are present in the nitroaromatic substrates remains a challenging goal, and a significant effort has been devoted to the development of more selective catalysts. In this context, metal nanoparticles (MNPs) have emerged as a good alternative to molecular complexes, and much attention is currently paid to their synthesis in order to achieve efficient and selective nanocatalysts. Non-supported and

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supported nanoparticles have been applied to this catalytic reaction, and among them, platinum nanoparticles (PtNPs) appear as promising catalysts, due to the fact that they combine a good activity in nitro reduction while keeping a certain degree of selectivity. Herein, the most recent advances related to the preparation and application of PtNPs as catalysts in the hydrogenation of nitroaromatics are reviewed.

Key-words

platinum; nanoparticle; nitroarene; hydrogenation; catalysis

1. Introduction

The reduction of nitroarenes is a reaction of remarkable interest as the resulting anilines are important organic intermediates in the industrial production of polymers, agrochemicals, dyestuffs and pharmaceuticals.[1] Conventional methods for the reduction of nitroarenes usually involve the use of reductants such as iron (Béchamp process), tin and zinc in acid media, and sulfides (H_2S or $NaSH$).[2] However, the use of H_2 as reducing agent makes this process environmentally preferable. Consequently, the development of new metal catalysts for this transformation is a subject of high interest nowadays. Nevertheless, the chemoselective reduction of the nitro group when other reducible functionalities, such as carbonyl, cyano and alkenyl or halide groups, are present in the nitroaromatic substrates is challenging. A number of catalysts, both homogeneous[3] (based on $Mo,$[3a] $Au,$[3b] of Fe[3c] complexes) and heterogeneous[4] (based on various metals) have shown significant levels of chemoselectivity, although in many cases this is accompanied by an intrinsically low catalytic activity. Among these catalysts, metal nanoparticles (MNPs) appear as promising systems.[5] It is expected that a complex but selective chemistry could arise from the use of nanoparticles with well-controlled shape, size and composition.[6]

Nanoparticles present an efficient combination of heterogeneous and homogeneous catalyst advantages such as a high specific surface area resulting in a high number of potential catalytic sites.[7] Owing to this, there has been in the past two decades an increase in the use of metal nanoparticles in catalysis.[8, 9] As MNPs properties depend on their characteristics, a large number of studies have been focused on the development of efficient synthesis methods able to give well-defined nanoparticles in order to study precisely the influence of their size, shape, surface properties, or crystalline structure on their catalytic performance. However, aggregation of nanoparticles after the catalytic process is a frequent problem which often turns out in a decrease of the catalytic activity and selectivity. To avoid this problem and gain in the stability of the catalysts, researchers are directing their efforts towards the immobilization of nanoparticles in different supports like carbon derivatives (carbon powder, carbon nanotubes,

nanofibers, etc.), polymers (polyvinylpyrrolidone, gum acacia ...) or metal oxides (titania, zirconia, etc.). Indeed, in those cases it is possible to recycle the catalysts, making these systems more efficient and interesting from the economic point of view.

The general mechanism accepted by the scientific community for the hydrogenation of nitrobenzene was proposed by Haber[10] and as depicted in Scheme 1.
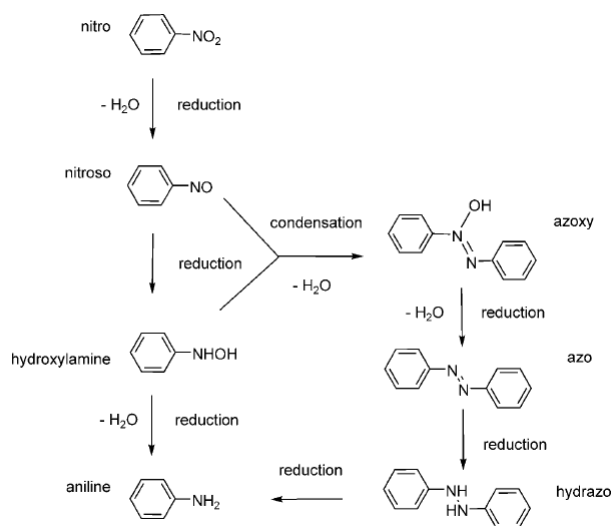
Scheme 1. Accepted mechanism for the hydrogenation of nitroarenes. Copyright *ChemCatChem* 2009, 1, 210-221.

In this process, the accumulation of the reaction intermediates such as hydroxylamines, azo and azoxy derivatives shown in Scheme 1, proceeding the last two of them from the condensation of hydroxylamines and nitroso species, represents a difficulty. Another difficulty to be faced concerns the dehalogenation reaction in the case of halonitroarenes, to afford a mixture of haloaniline and dehalogenation products.[11] Taking these key-points into account, it is desirable to synthesize new and efficient catalysts for the selective hydrogenation of nitrobenzene to aniline, especially able to operate under mild conditions (room temperature, atmospheric pressure or 1 bar H_2).

In this context, significant efforts have been made in the last years in the development of catalysts for the chemoselective hydrogenation of nitroarenes. It is interesting to point out the publication of recent works involving Pd catalysts[12] and Au catalysts.[13]. Within transition metals, platinum has been selected as one of the most promising elements for this catalytic transformation, since it combines a good activity in nitro reduction with a moderate degree of selectivity. According to Corma *et al*., the main drawback of Pt catalysts is that they are not selective for the reduction of the –NO_2 group when other functional groups are present in the nitroarene molecules. Because of this, improving the selectivity in the case of Pt catalysts is an issue of study nowadays. Thus, in this review, we analyze the efforts performed by the scientific

community in the field of the selective hydrogenation of nitroaromatics catalyzed by platinum nanoparticles (Pt NPs), both supported and non-supported. This review is not comprehensive but provides a short overview of the prepared platinum nanoparticles for the selected catalytic application herein disclosed.

2. PtNP-mediated hydrogenation of nitroaromatics.

2.1 PtNPs supported on carbon materials

Carbon-based supports are commonly used for the heterogeneization of metal nanoparticles dedicated to hydrogenation of nitroarenes. Examples of catalysts prepared with activated carbon, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are hereafter presented.

In 1998, Bönnemann and coworkers reported the synthesis of Pt hydrosols (d_{mean} = 2-3 nm) stabilized by surfactants (sulfobetaine SB12 and carboxybetaine CB12), using $PtCl_2$ as platinum source and charcoal as support.[14] The so-prepared catalysts were employed in the bachwise reduction of 3,4-dichloronitrobenzene in liquid phase (100-170 ºC, 100 bar H_2, 1 % Pt), finding that the sulfur-containing catalyst, Pt/SB12, is the most active. In general, very good results of selectivity (higher than 97 % in the first run) and low dehalogenation rates (lower than 0.60 %) were observed. Furthermore, the catalysts Pt/SB12 and commercial Pt/C were also tested in the continue hydrogenation of 3,4-dichloronitrobenzene during 100 h showing almost complete conversion of the substrate in both cases, and lower dehalogenation in the case of Pt/SB12. The authors concluded that the prepared catalysts represent a good alternative to traditional Pt/C ones for an industrial approach and showed the influence of the stabilizing agent on the surface of the particles, and as a consequence, on the catalytic activity.

In 2004, Ikushima *et al.* reported the hydrogenation of nitrobenzene in supercritical CO_2 ($scCO_2$) mediated by carbon-supported platinum nanoparticles.[15] The catalysts were prepared by H_2 reduction of commercial Pt/C at different temperatures (300-750 ºC) leading to Pt NPs with mean sizes in the range 7.2-19.6 nm, the larger particles being obtained at high temperatures. Figure 1 shows a transmission electron microscopy (TEM) image of 5% Pt/C catalyst prepared at 200 ºC. The use of $scCO_2$ as solvent instead of traditional organic ones was envisaged as an approximation to green chemistry.
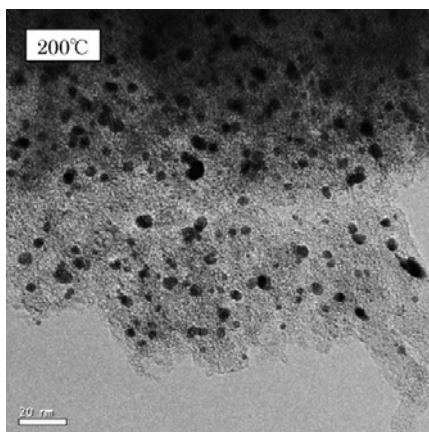
Figure 1. TEM image of Pt/C catalyst prepared by reduction at 200 ºC. (Copyright *J. Catal.*, ref. 15)

The influence of CO_2 pressure, particle size and solvent in nitrobenzene reduction (35ºC, 40 bar of H_2) was studied. Using $scCO_2$ as solvent, no influence of the particle size in the selectivity was observed, while the activity decreased from 78 to 22 % when the size of the particles changes from 7.2 to 19.6 nm. In contrast, using ethanol, the total conversion and the selectivity towards aniline decreased while the particle size increased. Indeed, TOF values were not dependent of Pt dispersion when the reaction was performed in $scCO_2$, while when using ethanol as solvent, the TOF values decreased with larger particle size. When particles of 8.3 and 19.6 nm were employed, the authors observed an increase of the conversion. But the conversion dropped at 140 bar, probably due to the presence of CO_2 molecules in the gas phase, so H_2 and nitrobenzene are more diluted in this phase.

In 2005, Yao and coworkers described the synthesis of carbon nanotubes (CNTs) supported Pt nanoparticles for the hydrogenation of nitrobenzene under mild conditions.[16] Two different catalysts containing 1% Pt (1% Pt/CNT, d_{mean} = 5-10 nm) and 3% Pt (3% Pt/CNT, d_{mean} = 3 nm) were prepared using H_2PtCl_6 as platinum source and an impregnation-calcination and reduction-calcination method, respectively, showing the influence of the preparation way in the mean size of the particles. A TEM image of the 3 % Pt/CNT particle is given in Figure 2. For comparative purpose, a Pt catalyst containing 3% metal supported in activated carbon (AC) was prepared (d_{mean} = 8 -10 nm). All the prepared catalysts were employed in the hydrogenation of nitrobenzene (RT, 1 bar H_2). The platinum particles prepared on AC were not active. The 3 % Pt/CNT catalyst showed an activity 3 times higher than 1% Pt/CNT. Mechanistic insights indicated that nitrobenzene was mainly converted directly to aniline, but a second process of condensation of nitrobenzene with aniline to yield azoxybenzene which finally converted into aniline could also take place.
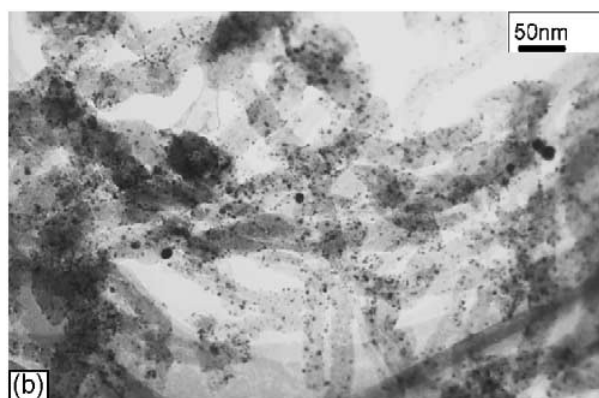
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Figure 2. TEM image of 3 % Pt/CNT particles (Copyright, *J. Mol. Catal. A: Chem.*, ref. 16)

Motoyama et al. reported in 2008 the use of PtNPs supported in three different types of carbon nanofibers, CNF-P (platelet), CNF-T (tubular) and CNF-H (herringbone) for the chemoselective hydrogenation of nitroaromatics. [17] Three different Pt catalysts, which differed in the type of nanofiber, were prepared using $Pt(dba)_2$ as metal precursor and mixing it with the CNF, to yield PtNPs of mean sizes between 1-3 nm in all cases. The catalytic activity of the so-obtained nanoparticles was evaluated in the hydrogenation of different nitroarenes. Table 1 shows the results obtained in the case of *p*-chloronitrobenzene (RT, 10 bar H_2, $R_{S/C}$=710-1630). In general, good results in terms of catalytic activity were observed.
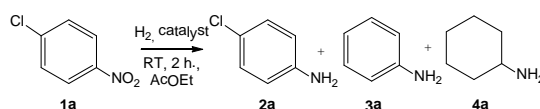
Catalyst	Solvent	2a (%)[a]	3a (%)[a]	4a (%)[a]	TOF (h⁻¹)
Pt/CNF-T	AcOEt	86	5	9	750
Pt/CNF-H	AcOEt	96	3	ND[b]	815
Pt/CNF-P	AcOEt	96.3[c]	3.7[c]	ND[b]	610
Pt/CNF-P	hexane	93	6	ND[b]	610
Pt/CNF-P	EtOH	86	7	7	610
Pt/CNF-P	AcOEt	97.0[c]	1.5c	ND[b]	610
Pt/CNF-H	AcOEt	97.1[c]	1.3c	ND[b]	815
Pt/CNF-P[d]	AcOEt	>99.9[c]	ND[b]	ND[b]	610

[a] Determined by ^1H NMR analysis, [b] ND = not detected, [c] Determined by GLC analysis, [d] 20μL of n-octylamine was added

Table 1. Hydrogenation of *p*-chloronitrobenzene mediated by Pt catalysts. Adapted from ref. 17.

An important dependence of the catalytic activity with the support was observed for Pt/CNFs. The best results were obtained in the case of Pt/CNF-H and Pt/CNF-P (96 %

selectivity, TOF = 815 and 610 h^{-1}, respectively). Pt/CNF-T gave a catalytic performance comparable to that of commercial Pt/C, and lower than Pt/CNF-H and Pt/CNF-P. The effect of the solvent was studied, finding better results of chemoselectivity in ethyl acetate than in hexane or EtOH. Indeed, full conversion to chloroaniline (without subproducts of dehalogenation) was achieved adding *n*-octylamine to the reaction media. When *o*- and *m*-chloronitrobenzene were employed as substrates, Pt/CNF-P provided almost quantitative yields, and in the case of the bromo derivative a 94 % yield was reached without any co-additive, while 99 % of conversion with 99.8 % selectivity is attained when *n*-octylamine was added, showing the influence of the amine to limit side reactions. In the case of the iodo substituted derivative, 97 % selectivity was reached with the Pt/CNF-P-amine system at 50 ºC. This catalyst also tolerated the presence of other functional groups such as alcohol, amide, ester, ketone, benzyl alcohol, benzyl ethers. The hydrogenation of *p*-nitrostyrene yielded *p*-ethylamine. Indeed, the catalyst can be recycled up to five times with any loss in the catalytic activity. The interactions between the PtNPs and the support, in terms of their steric and electronic effects, were pointed out by the authors as the main reason for the excellent chemoselectivity observed, rather than the size of the particles.

In 2009, Liu *et al.* reported the synthesis of cubic platinum nanoparticles supported on carbon black for their application as catalyst in the hydrogenation of *o*-chloronitrobenzene.[18] The catalyst was prepared by impregnation of the carbon support with a colloidal solution of Pt acetylacetonate in a mixture methanol-toluene to yield nanoparticles displaying 20 nm of mean size. This way of preparation was considered as the key point to have isolated Pt particles in the support. Figure 3 shows a HRTEM image of the cubic PtNPs on the carbon support.
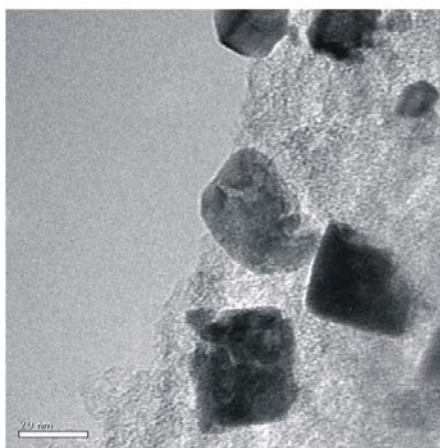
Figure 3. HRTEM image of the cubic PtNPs/C catalyst. (Copyright *Synlett*, ref. 18).

The catalytic activity of this catalyst was compared to that of two others incorporating 5 % Pt: a commercial Pt/C containing Bi as promoter and an amorphous Pt/C structure having aggregates of 13-20 nm. Bi, as Cr, Mn, Fe..., is used as doping metal in Pt particles to increase

the selectivity or decrease the presence of intermediates in the hydrogenation of halonitroarenes. The selected reaction was the hydrogenation of *o*-chloronitrobenzene (25 ºC, 10 bar H$_2$), finding that the cubic Pt/C catalyst was the slowest one, but with lower dehalogenation side reaction (0.28 % in 10 h). Byproducts as aniline and *o*-hydroxylamine-chlorobenzene were detected in these reaction conditions. This selectivity was explained in terms of the location of the particles in the boundary areas, more electron deficient and predisposed to absorb hydrogen atoms.

Yan *et al.* reported the synthesis of Pt nanoparticles supported on CNTs, γ-Al$_2$O$_3$ and silica for the hydrogenation of *o*-chloronitrobenzene (*o*-CNB).[19] The catalysts were prepared by laser vaporization deposition of bulk metal onto the corresponding support, finding better results of dispersion in the case of the CNTs. This can be explained in terms of the more ordered structure of this support, which is based on a graphitic structure with basal planes exposed, in comparison with γ-Al$_2$O$_3$ and silica. PtNPs mean size and Pt loading are summarized in Table 2.
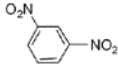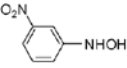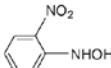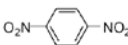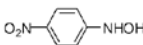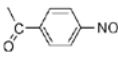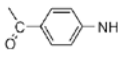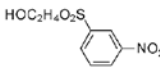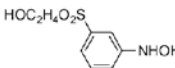
Catalyst	Mean size (nm)	Metal loading (*wt%.*)
Pt/CNTs	3-12	0.50
Pt/γ-Al$_2$O$_3$	4-15	0.47
Pt/SiO$_2$	6-20	0.51

Table 2. Metal content and mean size of the supported PtNPs.

The catalytic activity was evaluated in the hydrogenation of *o*-CNB (60 ºC, 10 bar H$_2$), finding the best results in the case of the CNTs-supported nanoparticles (full conversion). Both the support and the mean size have an influence on the catalytic activity. The contact between the catalytic sizes and the substrate (o-CNB) is favored in the case of smaller nanoparticles. However, the selectivity was comparable in all the cases (~ 99.5 % towards *o*-chloroaniline), with no influence of the support, which was not the case in the work reported by Coq and coworkers (*vide infra*). This fact was explained by the very weak interaction between the metal and the support, and also in terms of its properties and texture.

In 2010, Lu and coworkers reported the synthesis of supported PtNPs and their use as catalyst in the partial hydrogenation of nitroarenes to arylhydroxylamines.[20] The particles were prepared by reduction of H$_2$PtCl$_6$ with NaBH$_4$ in the presence of the carbon support (d$_{mean}$ = 3 nm). The hydrogenation of several substituted nitroarenes was performed in soft conditions (10.15 ºC, 1 bar H$_2$) to favor the formation of hydroxylamines, showing excellent activities and selectivities in this transformation. For example, in the case of *m*-dinitrobenzene, a catalyst containing 2 wt% Pt/C yielded the corresponding hydroxylamine in 92.3 % yield after 190 min. of reaction in THF. The authors used this transformation as model to investigate the mechanism, in which the formation of nitroso compounds and trace amounts of dimer can be present. The experiments demonstrated that the formation of hydroxylamine is favored in mild conditions

and using THF as solvent. Other commercial catalysts such as Pt/C and Pt/Al$_2$O$_3$ showed lower yield than the prepared catalyst. Pt colloid on carbon was a very active catalyst for this process in very mild conditions, which favored the accumulation of hydroxylamine in the reaction medium avoiding the further transformation in aniline. Indeed, when substrates bearing electron-withdrawing substituents (for example, -CHO or –Cl, which was the case of this work) were employed, the π interaction provided by these groups favors the stabilization of the hydroxylamine and its further conversion was retarded. Table 3 contains some examples of the substrates tested in this work.

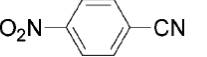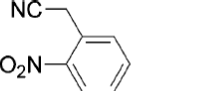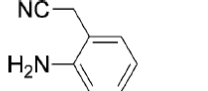| Entry	Substrate	Product	t/ min	Conv./ %	Sel./ %
1^a	O$_2$N—〈 〉—NO$_2$	O$_2$N—〈 〉—NHOH	190	100	92.3
2^b	〈 〉(NO$_2$)—NO$_2$	〈 〉(NO$_2$)—NHOH	170	100	91.9
3^b	O$_2$N—〈 〉—NO$_2$	O$_2$N—〈 〉—NHOH	115	100	86.3
4^b	\C(=O)—〈 〉—NO$_2$	\C(=O)—〈 〉—NHOH	65	100	86.3
5^c	HOC$_2$H$_4$O$_2$S—〈 〉—NO$_2$	HOC$_2$H$_4$O$_2$S—〈 〉—NHOH	210	100	93.4
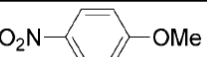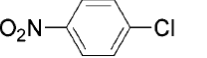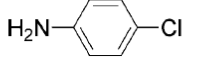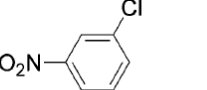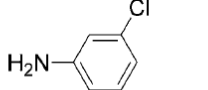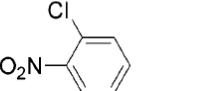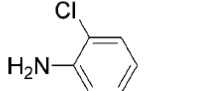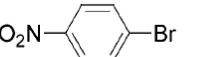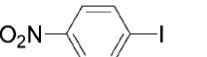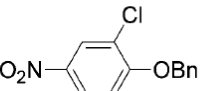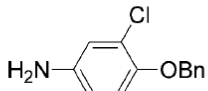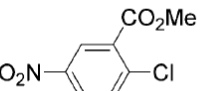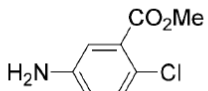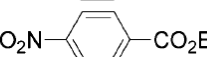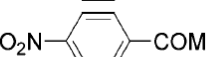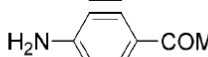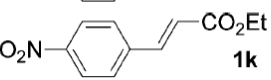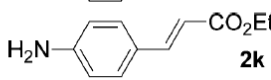
Reaction conditions: 10.15 ºC, 1 bar. ^{a}10 mmol substrate, 30 ml THF, 50 mg, 2 % wt Pt/C, ^{b}2 mmol substrate, 10 ml THF, 10 mg, 2 % wt Pt/C, ^{c}10 mmol substrate, 30 ml THF, 100 mg, 2 % wt Pt/C. The conversions and selectivities were determined by HPLC.

Table 3. Hydrogenations performed using Pt/C as catalysts. (Copyright *Chem. Commun.*, ref. 20).

Liu and coworkers reported in 2010 the synthesis of Pt nanoparticles supported on multi-walled carbon nanotubes (MWCNTs) for the hydrogenation of nitrobenzene.[21] Different catalysts with Pt content from 10 to 72.1% wt, and with mean sizes of nanoparticles between 1.9 and 3.5 nm were prepared by a tip sonication method using H$_2$PtCl$_6$·6H$_2$O as platinum precursor. No extra stabilizers neither a pre-treatment of the CNTs were employed in this preparation, and in all the cases narrow distribution of particles were observed by TEM. The particles were uniformly deposited on the CNTs at Pt content lower than 50 %, while all the exterior surface of the CNT was covered by particles in the case of the highest Pt content. HRTEM experiments showed the high crystallinity of the NPs, and XPS revealed that Pt was present in the zero oxidation state. The so-prepared catalysts were tested in the solvent-free hydrogenation of nitrobenzene. The catalysts having a 5 % Pt reached 100 % conversion and yielded aniline with 100 % selectivity in a reaction performed at 60 ºC and 40 bar of H$_2$. The

TOF value of 66900 h^{-1} was the highest one reported at that moment. When the reactions were performed at higher Pt content (from 5 to 27.4 and 50 % wt) and at lower temperatures and pressures, the TOF value decreased probably due to an increase of the Pt particle size. Mechanistic insights revealed that the mechanism mainly consisted in the fast hydrogenation of nitrobenzene to aniline, while a small proportion followed the transformation of nitrobenzene into nitrosobenzene, azoxybenzene and finally aniline. As it has been already pointed out in other works, the authors justify the excellent activity of the catalysts in terms of the interaction between the Pt particles and the support.

The synthesis of PtNPs supported on N-doped carbon nanofibers (CNFs) for the hydrogenation of nitroarenes to yield anilines or hydroxylamines was described by Motoyama *et al.* in 2011.[22] Two catalysts with Pt loading of 1 (Pt(1%)/N-CNF-H) and 3 % (Pt(3%)/N-CNF-H) were prepared by impregnation of the support with [Pt(dba)$_2$] (d_{mean} = 1.8 nm). For comparative purpose, catalysts Pt/CNF-H (without N$_2$ doping) and Pt/CNF-H-OctNH$_2$ (with addition of octylamine) were prepared. Hydrogenation of *p*-nitroanisole in mild conditions (25ºC, 1 bar H$_2$) revealed that the reaction is nine times slower in the case of Pt(1%)/N-CNF-H compared to Pt(1%)/CNF-H, showing the poisoning effect of the N atoms placed in the support on the catalytic activity. Very good results in terms of selectivity were obtained (see Table 4) in the reduction of nitroarenes bearing different functional groups with the catalysts Pt(3%)/N-CNF-H (RT and 10 bar of H$_2$). No dehalogenation was observed in the case of chloro-, bromo- and iodo- derivatives. No C-O bond cleavage was noticed in substrates bearing carbonyl and benzoloxy groups. Hydrogenation of substrates with CN groups was also accomplished with 99 % yield, even if it was required to increase the temperature to 100 ºC in the case of 2-(cyanomethyl)nitrobenzene. Catalyst Pt(1%)/N-CNF-H hydrogenated 4-nitrocinnamate with 97 % towards 4-amino-cinammate at 50ºC. Catalysts Pt(3%)/N-CNF-Hs could be reused five times in the reduction of 4-chloronitrobenzene without any loss of activity. It was possible to control the selectivity towards the formation of hydroxylamine using the catalysts Pt(1%)/N-CNF-H and ester, keto and cyano substituted nitroarenes, which was the opposite selectivity found with Pt(3%)/N-CNF-H.

Entry	Substrate		Product		Yield
1	O₂N—⟨⟩—OMe	**1a**	H₂N—⟨⟩—OMe	**2a**	99
2	O₂N—⟨⟩—Cl	**1b**	H₂N—⟨⟩—Cl	**2b**	98
3	O₂N—⟨⟩ (Cl)	**1c**	H₂N—⟨⟩ (Cl)	**2c**	99
4[b]	O₂N—⟨⟩ (Cl)	**1d**	H₂N—⟨⟩ (Cl)	**2d**	98
5	O₂N—⟨⟩—Br	**1e**	H₂N—⟨⟩—Br	**2e**	98
6[c]	O₂N—⟨⟩—I	**1f**	H₂N—⟨⟩—I	**2f**	99
7[b,c]	O₂N—⟨⟩ (Cl)—OBn	**1g**	H₂N—⟨⟩ (Cl)—OBn	**2g**	98
8[b,c]	O₂N—⟨⟩ (CO₂Me)—Cl	**1h**	H₂N—⟨⟩ (CO₂Me)—Cl	**2h**	98
9	O₂N—⟨⟩—CO₂Et	**1i**	H₂N—⟨⟩—CO₂Et	**2i**	99
10	O₂N—⟨⟩—COMe	**1j**	H₂N—⟨⟩—COMe	**2j**	99
11[b,c,d]	O₂N—⟨⟩—CH=CH—CO₂Et	**1k**	H₂N—⟨⟩—CH=CH—CO₂Et	**2k**	97[e]
12[f]	O₂N—⟨⟩—CN	**1l**	H₂N—⟨⟩—CN	**2l**	99
13[g]	NC—CH₂ / O₂N—⟨⟩	**1m**	NC—CH₂ / H₂N—⟨⟩	**2m**	99

[a] Unless stated otherwise, all reactions were performed usin(g)
(1 mmol) and the Pt(3 %)/N-CNF-H catalyst (5 mg) in ethyl acetate (3
at room temperature under H₂ (initial pressure = 10 atm) for 6 h. [b]
4 h. [c] At 50 °C. [d] Pt(1 %)/N-CNF-H catalyst (5 mg) was used inst(ead)
[e] 3 % ethyl (4-hydroxylamino)cinnamate was obtained. [f] At 70 °C un(der)
H₂ (initial pressure = 7 atm) for 8 h. [g] At 100 °C for 6 h.

Table 4. Hydrogenation of various nitroarenes to the corresponding anilines using Pt/N-CNF-H as catalyst. (Copyright *ChemCatChem*, ref. 22).

Yan *et al.* described the synthesis of Pt nanoparticles supported on Fe-modified active carbon for the hydrogenation of *o*-chloronitrobenzene.[23] The catalysts were prepared by adsorbing PtNPs (2.4 nm) in the Fe-modified support (Figure 4), yielding several samples which differed in the Fe content (2, 3 or 4 %). The presence of Fe enhanced the adsorption of the Pt particles on the support (and as a consequence the number of active sites) which may be

explained by the presence of iron seeds on the carbon supports. For comparative purpose, a commercial Pt/C(JM) catalyst was also employed.
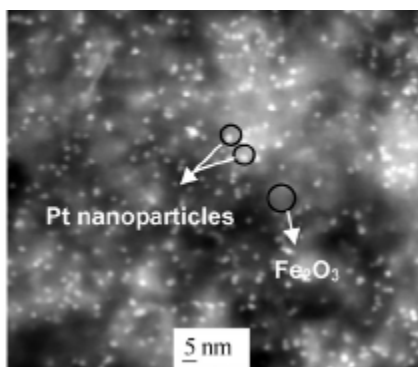

Figure 4. SEM image of Pt/C(Fe^2) catalyst (2 % Fe content). (Copyright *Appl. Catal., A*, ref. 23).

These two catalysts were investigated in the hydrogenation of *o*-chloronitrobenzene (60 ºC, 10 bar H$_2$). Good activities and selectivities were observed with an increase in the TOF values for the Fe-modified supports. The best TOF value observed (TOF = 78 mol$_{o-CNB}$/mol$_{Pt-s}$ and 99.5 % selectivity) appeared as the best combination of activity and selectivity reported at that time. Little dehalogenation reaction was observed, attributed to the electron-deficient state of the Pt on the support, as it was also suggested by Wang and co-workers in the case of γ-Fe$_2$O$_3$ supported Pt nanoparticles (*vide infra*). Pt/C(Fe^2) catalyst could be reused up to five times without any significant loss of activity or selectivity.

Hou *et al.* reported the synthesis of PtNPs supported on reduced graphene oxide (RGO) and their use as catalyst in the hydrogenation of nitroarenes.[24] Graphene oxide, a precursor of graphene, is described in this article as a good alternative to active carbon or carbon nanotubes, owing to its larger surface area. Indeed, its partial oxidation generates vacancies, defects, holes, etc. thus offering chemical active sites favoring the catalytic reaction as well as anchoring sites for PtNPs. The catalyst was prepared by a reduction reaction of H$_2$PtCl$_6$·6H$_2$O and yielded Pt/RGO particles of 3.1 (0.4) nm mean size (see Figure 5) when ethylene glycol (EG) was used as reducing agent, or aggregated structures of 100 nm when the reducing agent was hydrazine hydrate (HH). Pt nanoparticles deposited on MWCNTs and active carbons (AC) were prepared using the same approach for comparison purposes. In the case of Pt/MWCNTs, the size of the particles was comprised between 1.1 and 9.1, (d$_{mean}$ = 2.9 nm). When AC was employed as support, agglomerated particles were observed with a size in the range 1.4-6.7 nm (d$_{mean}$ = 3.5 nm).
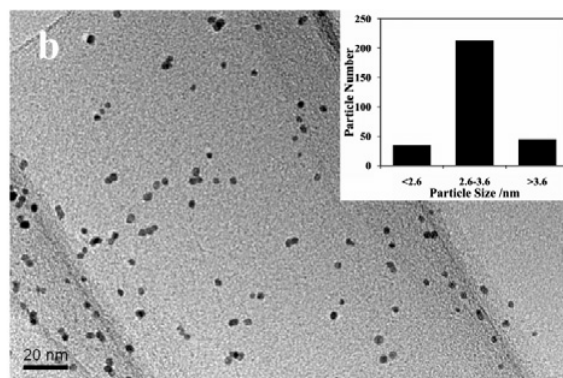
Figure 5. TEM image of Pt/RGO nanoparticles prepared using ethylene glycol as reducing agent. (Copyright *Carbon*, ref. 24).

The catalytic activity of these nanomaterials was evaluated in the hydrogenation of nitroaromatics to amines (0-20 ºC, 10 bar H_2). At 0ºC using the catalyst Pt/RGO$_{-EG}$ (prepared with EG as reducing agent) in the transformation of nitrobenzene, 94.3% of aniline was formed with 70.2 mol$_{-AN}$/mol$_{-Pt}$min. With the other supports, conversions into anilines were much lower with values of 48% (MWCNTs) and 30.6% (AC). When the catalysis was performed at 20 ºC, the yield increased to 99.1% in the case of GO. The course of the hydrogenation reaction of nitrobenzene was followed with time for the Pt/RGO catalysts. The presence of nitrosobenzene and N-phenylhydroxylamine as intermediates was observed. This catalyst could be recycled 5 times, observing still good activities towards the formation of aniline (72.2%). In the opinion of the authors, these good results were due to the good dispersion of the particles at the surface of the GO support, the good dispersion of the catalysts in the reaction mixture and the availability of both sides of graphene for the catalytic reaction. Finally, the hydrogenation of halonitrobenzenes was also tested leading to a conversion of 87.3 % (towards the formation of chloroaniline) in the case of *o*-chloronitrobenzene. Nitroarenes bearing electron-donating groups were easier to hydrogenate with very good yields (>98 %) under similar reaction conditions.

Vogt *et al.* have recently reported the preparation of Pt nanoparticles supported on activated carbon and promoted by a molybdenum salt $[(NH_4)_6Mo_7O_{24}]$.[25] The catalyst was prepared by a reduction-deposition method using H_2PtCl_6 as platinum source (d_{mean} = 2.3 (0.3) nm), followed by addition of the promoter for the nitroarene hydrogenation media. The catalytic activity was evaluated in the hydrogenation of 2-chloronitrobenzene (30 ºC, 4 bar H_2). The non-promoted catalyst conducted to a slow final hydrogenation of hydroxylamine, which was not the case for the promoted catalyst. Formation of azo or azoxy species was not observed. Both promoted and unpromoted catalysts showed high selectivity towards the formation of the aniline. Table 5 summarizes the results obtained using other substituted nitroarenes as substrates.

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Entry	Substrate	Product	Selectivity[b] [%]	TTFC[b] [min]
1	NO₂ (benzene)	NH₂ (benzene)	>99	50
2	NO₂, Cl, Cl (benzene)	NH₂, Cl, Cl (benzene)	98	70
3	NO₂, Br (benzene)	NH₂, Br (benzene)	93	–
4	NO₂, Br (benzene)	NH₂, Br (benzene)	93	50
5	NO₂, CN (benzene)	NH₂, CN (benzene)	99	400
6	NO₂, vinyl (benzene)	NH₂, ethyl (benzene)	99	1000
7	NO₂, acetyl (benzene)	NH₂, acetyl (benzene)	93	170

[a] Reaction conditions: (0.8 %Pt + 0.3 %Mo)/C (61 % H₂O) (70 mg), substrate (S/C = 20 000, 22.3 mmol), EtOH (80 mL), H₂ (4 bar, total pressure), 30 °C. [b] Selectivity and activity were determined by GC when the uptake of hydrogen ceased. TTFC = time to full conversion.

Table 5. Chemoselective hydrogenation of substituted nitroarenes. (Copyright *ChemCatChem.* ref. 25)

Br- and CN-substituted nitrobenzenes were hydrogenated chemioselectively. However, 3-nitrostyrene was fully hydrogenated. A premodification with H_3PO_4 on the catalysts was performed, to afford the formation of 3-aminonitrostyrene.

Very recently, Ma and coworkers reported the successful immobilization of platinum nanoparticles onto carbon coated magnetic microparticles for the hydrogenation of nitroaromatics.[26] The preparation of the particles (denoted as $Fe_3O_4@C@Pt$, $d_{mean-micro}$ = 500 nm, $d_{mean-PtNP}$ = 5 nm) is depicted in Scheme 2.
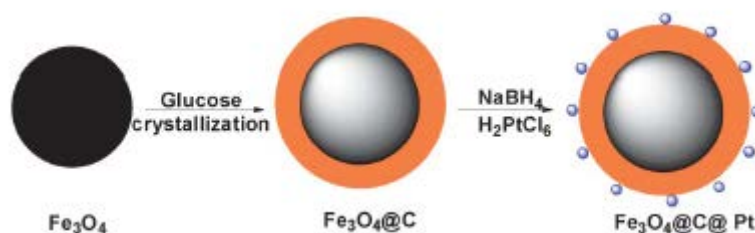
Scheme 2. Preparation of the particles. Reproduced from ref. 26.

Hydrogenation of nitroarenes bearing one or two nitro groups was performed (RT, 1 bar H_2), showing very good results in terms of activity and selectivity. For example, bromonitrobenzene was hydrogenated into the corresponding haloaniline with more than 99 % yield in 60 min. The catalyst tolerated the presence of electron donating or withdrawing

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substituents such as halogen atoms (little dehalogenation was observed), carbonyl, alcohol, etc; affording yields of over 95 %. Indeed, this catalyst could be recycled 10 times by magnetic separation without any significant loss of activity or selectivity.

The synthesis of bimetallic PtPd nanoparticles supported onto multi-walled carbon nanotubes (MWCNTs) for the chemoselective reduction of nitro compounds was reported by Kiam and coworkers.[27] The catalyst was prepared by reduction under hydrazine hydrate of K_2PdCl_4, followed by reduction under H_2 of K_2PtCl_4 in the presence of the carbon nanotubes (see Figure 6, d_{mean} = 9-10 nm, Pt content: 5.46 wt%, Pd content: 3.44 wt%).
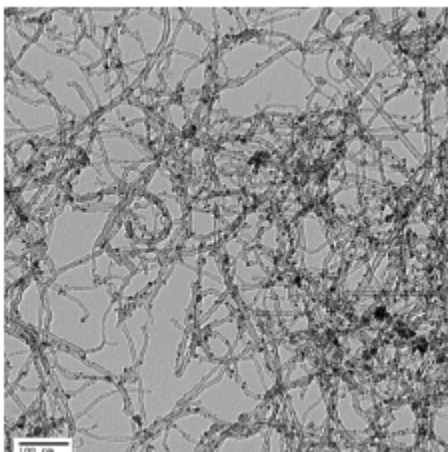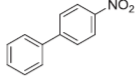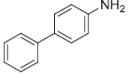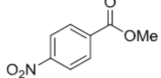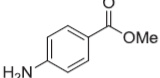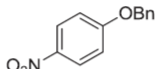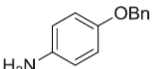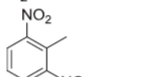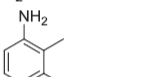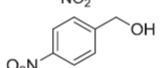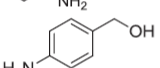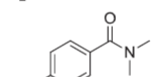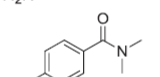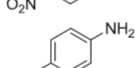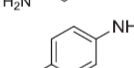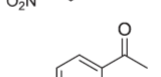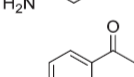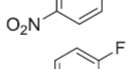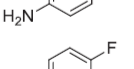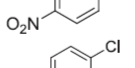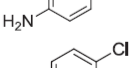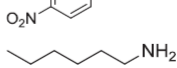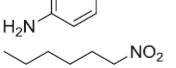
Figure 6. TEM images of the PtPd/CNTs. (Copyright, *Catal. Commun.*, ref. 27)

Reduction of nitrobenzene was carried out (RT, 1 bar H_2) with the PtPd catalysts, as well as monometallic Pt/CNT and Pd/CNT catalysts for a comparative purpose (see Table 6). The best results were obtained with the bimetallic systems (full conversion achieved in only 20 min, *versus* 1 h and 2 h for the Pd/CNT and Pt/CNT, respectively) in ethanol. This data highlighted the synergic effect of both metals in the catalytic reaction. The bimetallic catalysts could be recycled 10 times without significant loss of activity nor aggregation of the particles. However, a slight leaching of metals was observed. The catalytic activity in the reduction of nitroarenes with other functional groups such as benzyl, ester, halogen and ketones was also studied, giving rise to good reactivities (higher than 87 %). In particular, very good results were obtained in the case of nitroarenes containing olefin groups.

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Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	O₂N—⟨⟩—OMe	H₂N—⟨⟩—OMe	0.5	95
2	⟨⟩—⟨⟩—NO₂	⟨⟩—⟨⟩—NH₂	1	99
3	O₂N—⟨⟩—OH	H₂N—⟨⟩—OH	0.5	98
4	O₂N—⟨⟩—C(O)OMe	H₂N—⟨⟩—C(O)OMe	0.5	97
5	O₂N—⟨⟩—OBn	H₂N—⟨⟩—OBn	1	99
6	NO₂/NO₂ substituted toluene	NH₂/NH₂ substituted toluene	1	99
7	O₂N—⟨⟩—CH₂OH	H₂N—⟨⟩—CH₂OH	1	93
8	O₂N—⟨⟩—C(O)N(CH₃)	H₂N—⟨⟩—C(O)N(CH₃)	0.5	94
9	O₂N—⟨⟩—NH₂	H₂N—⟨⟩—NH₂	0.5	87
10	O₂N—⟨⟩—C(O)CH₃	H₂N—⟨⟩—C(O)CH₃	0.5	97
11	O₂N—⟨⟩—F	H₂N—⟨⟩—F	1	99[c]
12	O₂N—⟨⟩—Cl	H₂N—⟨⟩—Cl	1	99[c]
13	~~~NH₂	~~~NO₂	3	98[c]

[a] Reaction conditions: 0.5 mmol of nitro compound, hydrogen gas(1 atm), 4.0 mL of ethanol with 1 mol% of metal-CNT catalyst at ambient temperature.
[b] Yields of isolated products.
[c] Yields were determined by GC analysis using anisole as an internal standard.

Table 6. Substrate scope of Pt-Pt CNT catalyzed nitro groups reductions. (Copyright, *Catal. Commun.*, ref. 27).

2.2 PtNPs supported on inorganic oxides

Platinum nanoparticles deposited on various inorganic oxide supports play an important role in the hydrogenation of nitroaromatics. The efforts deployed by the scientific community using alumina, ferrite, silica, zirconia and metal organic frameworks (MOF) supported nanoparticles as catalysts for this reaction are hereafter disclosed.

Pioneer work describing the use of PtNPs/alumina for the hydrogenation of nitroarenes was reported at the early 90s by Coq and coworkers. [28] In this study, the authors showed the influence of the size of the nanoparticles on the selectivity of the hydrogenation of *p*-chloronitrobenzene. Different catalysts based on alumina supported platinum nanoparticles

which differed in the Pt content and in the size of the particles (with a range of sizes going from 1.2 to 12.3 nm) were prepared by an impregnation of $Pt(acac)_2$ followed by a reduction step. The catalytic tests (30 ºC, 1 bar H_2), showed that the TON value decreases with the decrease in the dispersion of the particles and that the dehalogenation reaction is favored with Pt particles of smaller size. *P*-chloronitrosobenzene and *p*-chlorophenylhydroxilamine as intermediates, and nitrobenzene, aniline and chlorobenzene as byproducts were detected. In a later work,[29] the same group studied the influence of both the support and the Pt precursor on the catalytic transformation. TiO_2, Al_2O_3, magnesia and graphite were evaluated as supports and $Pt(acac)_2$, H_2PtCl_6 and $Pt(NH_3)_4Cl_2$ as platinum precursors. The results in the hydrogenation of *p*-chloronitrobenzene (30 ºC, 1 bar H_2) showed no influence of the platinum precursor on the catalytic activity, while the support did have one. The best results in terms of activity and selectivity were found with titania as support: the value of TON was ten times higher using Pt/TiO_2 (for 98 % conversion, 99.3 % towards the formation of *p*-chloroaniline) in comparison with Pt/Al_2O_3.

In 1997, Vitulli *et al.* compared the catalytic activity of Pt nanoparticles deposited on a γ-Al_2O_3 membrane or on γ-Al_2O_3 powders on the selective hydrogenation of *p*-chloronitrobenzene. [30] The preparation of the catalysts was performed by deposition of mesitylene solvated Pt atoms on the γ-Al_2O_3, leading to catalysts with a Pt particle mean size of *ca.* 1-1.5 nm. Figure 7 shows a TEM image of the Pt NPs supported on γ-Al_2O_3 powder.
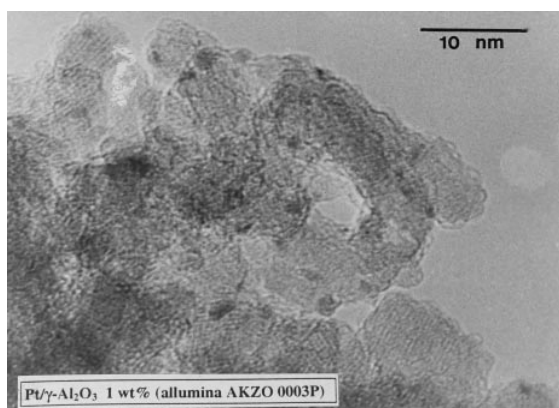

Figure 7. TEM image of Pt nanoparticles supported on alumina SCT (Copyright *Catal. Lett.*, ref. 30).

The catalytic results of the reaction (25 ºC, 1 bar H_2) revealed that the selectivity towards the formation of *p*-chloroaniline using Pt NPs supported on the γ-Al_2O_3 membrane (values found for this transformation of 95-100%) was higher than in the case of the Pt nanoparticles supported on γ-Al_2O_3 powders. Indeed, in the case of Pt/γ-Al_2O_3 powders, dehalogenation reaction was observed and further ring hydrogenation to yield cyclohexylamine

also took place. This result of selectivity can be related to the different H_2 availability in the supports: the catalytic membrane could supply more H_2 in comparison with the powders.

Wang and coworkers reported the synthesis of $Pt/\gamma\text{-}Fe_2O_3$ catalysts for the hydrogenation of *o*-chloronitrobenzene (CNB). [31] Well-dispersed $Pt/\gamma\text{-}Fe_2O_3$ nanoparticles (d_{mean} = 2.6 nm) were prepared by heating a mixture of preformed PtPVP nanoclusters and a ferric hydroxide colloid. For comparative purpose, a classical Pt/Fe_2O_3 was prepared employing an incipient wetness impregnation using H_2PtCl_6 as platinum precursor and a prepared iron oxide support (d_{mean} = 12.3 nm). The catalytic studies performed in the hydrogenation of *o*-CNB (60 ºC, 1 bar H_2) revealed that the unsupported PtPVP particles presented the highest activity but a low selectivity (45 % selectivity at full conversion). However, for $Pt/\gamma\text{-}Fe_2O_3$ catalyst, despite the rate of the reaction was 67 % the one observed for PtPVP, the selectivity was higher than 99.9 % and no dehalogenation was observed. Analogous selectivity was observed in the case of Pt/Fe_2O_3. The catalyst $Pt/\gamma\text{-}Fe_2O_3$ also worked at high pressures (40 bar H_2). Finally, the catalyst could be easily recovered, by applying a magnetic field, and reused up to 5 times without any loss in the activity.

In a later work, the same authors employed $Pt/\gamma\text{-}Fe_2O_3$ catalyst for the hydrogenation of bromonitrobenzenes (*o*-, *m*- and *p*-).[32] In the hydrogenation of *o*-bromonitrobenzene (30 ºC, 1 bar H_2), the catalyst $Pt/\gamma\text{-}Fe_2O_3$, gave excellent values of activity (two times the one observed for the Pt/C, which gave poor results) and 99.7 % of selectivity for the *o*-bromoaniline. At higher pressure of H_2, an increase of the hydrogenation rate was observed with a 99.9 % selectivity. In the case of *m*- and *p*- bromonitrobenzene, $Pt/\gamma\text{-}Fe_2O_3$ yielded the corresponding bromoanilines with selectivities of about 99.8 %; in contrast, low selectivity towards the formation of bromoaniline was obtained using the Pt/C catalyst. As it was observed for the *o*-derivative, an increase in the H_2 pressure of the reaction yielded to higher reaction rates while the selectivity was maintained. The authors also performed an interesting mechanistic study for the hydrogenation reaction and proposed a new hydrodebromination pathway over the $Pt/\gamma\text{-}Fe_2O_3$ catalyst.

In 2008, Corma *et al.* studied the influence of structure modification of different catalysts (Pt, Ru and Ni) with the aim of improving their selectivity in the hydrogenation of substituted nitroarenes.[33] Different platinum catalysts were prepared, like Pt/Al_2O_3, Pt/C and Pt/TiO_2 using an incipient wetness technique employing H_2PtCl_6 as metal precursor. In this work, the authors modified the size of the particles to have more Pt atoms located on edges and apexes than in faces. This situation would favor the hydrogenation of the nitro group *versus* the hydrogenation of double bonds, CO or other functional groups that could be present in the molecule, and, as a consequence, it would improve the selectivity. Several Pt/Al_2O_3 catalysts

(which vary in the % of metal content) were prepared, noticing that the smallest particle sizes were present in the catalysts having lowest Pt content. IR studies performed after CO adsorption showed that in the catalyst containing 0.2 % wt Pt, most of the atoms were located on edges and apexes, while for the catalyst with highest Pt content, CO also adsorbed in Pt(111) and Pt(100) extended faces. The catalytic activity of the so-prepared catalysts was evaluated in the reduction of 3-nitrostyrene to 3-aminostyrene (40 ℃, 3 bar H_2), finding that the chemoselectivity increased while the size of the particles decreased (60 % for 0.2 % wt Pt catalysts was the highest value). In order to improve these data, smaller particles were prepared by using activated carbon as support (d_{mean} = 0.5-1.7 nm), obtaining 90 % selectivity towards 3-aminostyrene at 95 % conversion with the 0.2 % wt Pt/C catalyst. However, the corresponding phenylhydroxylamine intermediate was detected in an important percentage. The influence of the support was also studied, finding that catalyst Pt/TiO_2 contained larger particles than Pt/C and a higher amount of Pt atoms on faces. The value found for the selectivity at the same conversion was lower than for Pt/C, but no phenylhydroxylamine was detected in this case. Finally, a Pt/TiO_2 catalyst was prepared, using a reduction step at high temperature which incorporated decoration of TiO_2 on the Pt faces. This catalyst showed 93 % selectivity in the reaction at 95 % conversion and no phenylhydroxylamine was detected. The optimized Pt/TiO_2 catalyst was employed in the reduction of nitroarenes bearing different functional groups, giving very good results to the amino derivatives (see Table 7). The authors evidenced that an improvement made in a Pt catalyst, by modifying their structural characteristics, can change its performance from non-selective to selective in the hydrogenation of nitroarenes.

substrate	solvent	Pt/nitro (mol, × 10^2)	T (K)	P (bar)	time (h)	conversion (%)	selectivity (%)
3-nitrostyrene	toluene	0.31	313	3	6.50	95.1	93.1
4-nitrobenzaldehyde[a]	THF	0.92	313	3	3.00	99.2	98.2
4-nitrobenzonitrile	THF	0.40	323	6	2.20	99.5	98.6
4-iodonitrobenzene	THF	1.02	333	6	0.35	99.5	99.5
4-nitrophenylacetylene	toluene	0.24	313	3	5.60	98.9	90.1
3-chloronitrobenzene	THF	0.75	318	4	1.00	99.0	99.6

[a] Mass balance ~85% because of an unavoidable polymerization of 4-aminobenzaldehyde

Table 7. Pt/TiO_2 mediated hydrogenation of substituted nitroarenes using 0.2 wt % Pt/TiO2 reduced at 450 ℃. Reprinted with permission from A. Corma, P. Serna, P. Concepción, J. J. Calvino, *J. Am. Chem. Soc*. 2008, **130**, 8748-8753. Copyright 2008 American Chemical Society.

Lu and coworkers reported in 2010 the synthesis of platinum nanoparticles supported on mesoporous materials for their application as catalysts in the hydrogenation of nitrobenzene.[34] For the preparation of the catalysts, the authors employed a "one-step methodology" using orthosilicate (TEOS) as silica source and cetyltrimethylammonium bromide (CTAB) as a template, in acid media and using H_2PtCl_6 as platinum source. Three different catalysts were

prepared, namely Pt-MCM-41, Pt-Al-MCM-41 and Pt-La-MCM-41, the last two of them incorporating Al^{3+} and La^{3+} ions in the meso material, respectively. TEM analysis showed that the three catalysts were spherical-like and the mean size was around 3μm. In particular, the Pt-MCM-41 was composed of spherical-like particles with different nano-sizes. Figure 8 shows a SEM image of the Pt-MCM-41 catalyst.
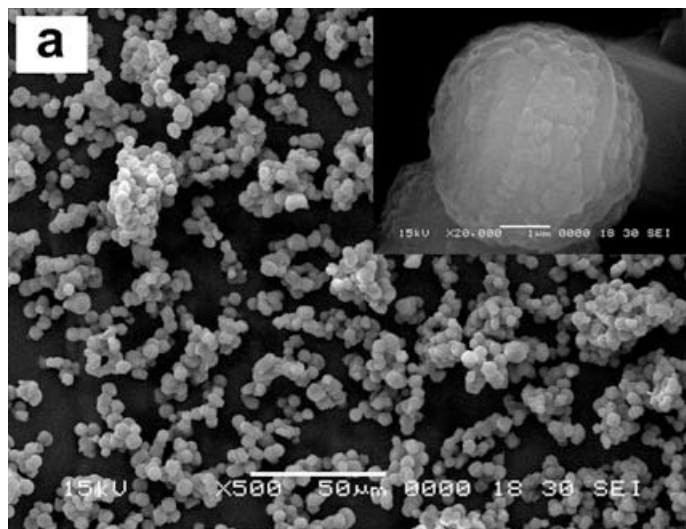

Figure 8. SEM image of Pt-MCM-41 catalyst. (Copyright *J Colloid Interface Sci*, ref. 34).

For comparative purposes, another catalyst (Pt/MCM-41) was prepared by the incipient wetness method. While the incorporation of Al^{3+} or La^{3+} to the meso material is very small, due to the high stability of these anions in the strong acid solutions employed in the synthesis method, the incorporation of Pt takes place in almost 100 %. XPS measurements showed that the surface contains Pt atoms in different oxidation states and confirmed that Al or La were present in very low amount. The catalytic performance of these new materials was evaluated in the hydrogenation of nitrobenzene (30 ºC, 5 bar H_2), finding an excellent catalytic activity giving rise to nitrosobenzene as the unique detected intermediate. The best performance was observed with the Pt-MCM-41 catalysts (91 % of conversion in 20 min of reaction) *versus* 64 % and 50 % found in the cases of Pt-Al-MCM-41 and Pt-La-MCM-41 catalysts, respectively. These results evidenced a negative effect of the presence of Al^{3+} and La^{3+} in the catalytic activity. In contrast, the catalyst Pt/MCM-41 was found inactive in this catalytic process.

Corma *et al.* worked on the improvement in the chemoselectivity of Pt catalysts.[35] Such a study was based on the consideration that the interaction between Pt and any functional group is generally very strong and that this renders difficult the control of the selectivity in chemical reactions. Thus, the authors studied the activity of distinct Pt/Al_2O_3 nanoparticles of different sizes (prepared by the wetness impregnation technique using H_2PtCl_6 as precursor) in the hydrogenation of styrene, nitrobenzene, a mixture of both of them and nitrostyrene. The results showed that in non-competitive experiments with styrene and nitrobenzene,

hydrogenation of styrene was faster in comparison with nitrobenzene, with an increase in the TOF value with the particle size. In competitive experiments, both molecules reacted from the very beginning, but while the TOF for hydrogenation of nitrobenzene is not dependent on the size of the particles, there is a dependence of the TOF value in the hydrogenation of styrene with the particle size (65 % selectivity to 2-vinylaniline with 0.2 % Pt catalysts, while less than 25 % selectivity for 1 % Pt catalysts). This means that smaller particles could give better results of selectivity. In addition, the authors prepared Pt/TiO_2 samples, and studied their selectivity in the reaction with nitrostyrene. The temperature used for the catalyst activation strongly influenced the selectivity, while the influence of the metal content and particles size is less important than in the case of the prepared Pt/Al_2O_3. This work showed that it is possible to transform the behavior of a catalyst from non-selective to selective by controlling the surface chemistry of the metallic atoms. The importance of the interaction between the particles and the support as a reason for the improvement of the selectivity is also highlighted.

Beland, Pagliaro *et al.* described the synthesis of silica-encapsulated PtNPs for the hydrogenation of nitrocompounds.[36] Different catalysts (denoted as SiliaCat Pt^0-1, 2 or 3) were prepared by a reduction of K_2PtCl_6 to yield encapsulated Pt nanoparticles in the range 1.7-3.15 nm and with different Pt content (from 0.05 to 0.2 (mmol g)$^{-1}$ Pt). The authors studied the effect of the solvent in the hydrogenation of 4-chloronitrobenzene to 4-chloroaniline (RT, 1 bar H_2), finding that the best results in terms of yield and time were obtained in MeOH. The catalysts denoted as SiliaCatPt^0-**2** (0.1 (mmol g)$^{-1}$ Pt) is the most active among all the prepared ones, and better than commercial ones as Pt/C, Pt/SiO_2 or Pt^0EnCat40.[37] Indeed, different nitroaromatics of diverse sizes and bearing distinct functional groups such as carbonyl, amide, and esters were selectively hydrogenated to the corresponding anilines. The CN group was the only one not tolerated by the catalysts, with the concomitant cleavage of the C–CN bond to yield mainly aniline. Hydrogenation of polynitroarenes took place in a regioselective way by controlling the reaction time. In the case of the hydrogenation of halonitroaromatics, selectivities higher than 99 % were obtained in the case of chloro-substituted compounds, between 85 and 98 %, and only 50 % in the case of the iodo- substituted. The catalysts could be reused up to 7 cycles in the reduction of 4-chloronitrobenzene without any change in the size of the particles nor any loss of the activity. The authors claimed the following advantages of using this catalyst: 1) the encapsulation ensures the stabilization of the Pt particles, 2) the nature of the support guarantee the absence of water, 3) the hydrophobic nature of the matrix ensures the preferential access of the most reactive –NO_2 groups to the hydride adsorbed on the Pt NPs.

Kantama *et al.* reported the preparation of Pt nanoparticles supported on zirconia for their application in the synthesis of N-acylamides from nitroarenes, by means of a first reduction of the nitro group followed by a reaction with an anhydride.[38] The catalysts

Pt(0)/ZrO$_2$ (2 % Pt wt, see Figure 9) was prepared by an impregnation method followed by a reduction step using H$_2$PtCl$_6$ as Pt source.
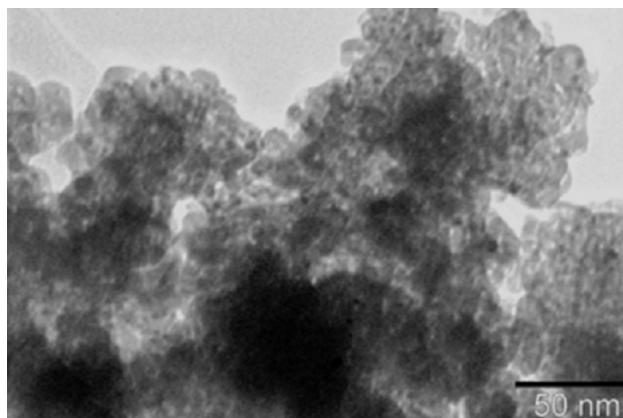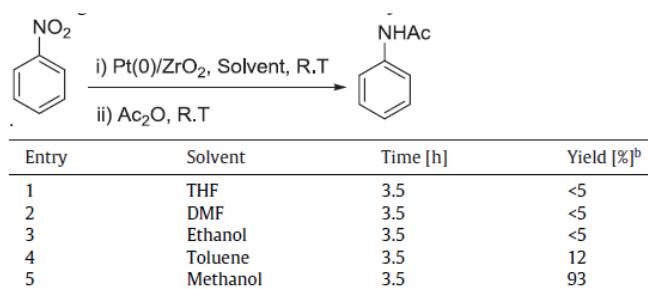

Figure 9. TEM image of Pt(0)/ZrO$_2$ catalyst. (Copyright *J. Mol. Catal. A: Chem.*, ref. 38).

For comparative purpose, Pt(0)/TiO$_2$ (prepared by the authors using the already described methodology) and commercial 1% Pt/C and 1% Pt/Al$_2$O$_3$ were also tested. The activity of those catalysts was evaluated in the reductive acylation of nitrobenzene in methanol (RT, 1 bar H$_2$, 0.15 % Pt) finding the best result, 93 % yield, with Pt(0)/ZrO$_2$. The study of the solvent effect in the reaction mediated by this catalyst showed that methanol was the best one, while the poorest yields were obtained using solvents with Lewis basic character (see Table 8). Further experiments performed with nitrobenzenes bearing other functionalities (such as halogen, acid, phenolic, keto, ester, etc…) showed that all these functional groups were well tolerated by the catalyst and any side reaction was observed. Indeed, it was possible to recycle the catalyst until the fourth cycle without any loss of the activity.

Entry	Solvent	Time [h]	Yield [%][b]
1	THF	3.5	<5
2	DMF	3.5	<5
3	Ethanol	3.5	<5
4	Toluene	3.5	12
5	Methanol	3.5	93

[b] Conversion determined by GC.

Table 8. Screening of solvents in the reductive acylation of nitrobenzene. (Copyright *J. Mol. Catal. A: Chem.*, ref. 38).

The same research group reported the synthesis of Pt nanoparticles homogeneously dispersed in the MOF ML-101 and their application as catalyst in the hydrogenation of nitrobenzene. [39] The catalyst (0.994 % Pt wt content) was prepared by a colloidal method using H$_2$PtCl$_6$ to yield MOF particles of 150-350 mean size containing Pt NPs of small size that could

not be observed by TEM in the fresh catalyst, probably due to their very small size (See Figure 10).
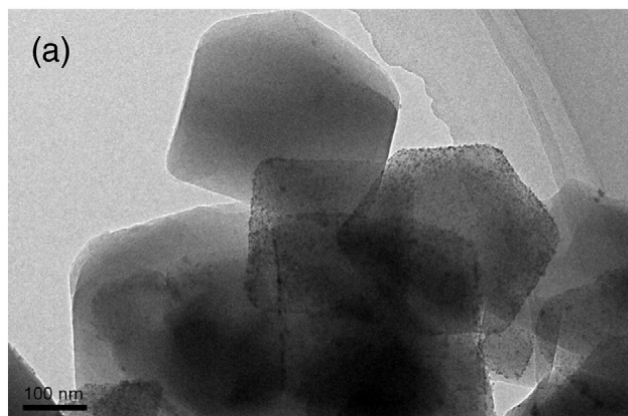
Figure 10. TEM image of the Pt@ML-101 nanoparticles. (Copyright *Catal. Commun.*, ref. 39).

The so-obtained catalyst (Pt@ML-101) was tested in the hydrogenation of nitrobenzene (20-30 °C, 10 bar H_2) at different metal/substrate ratios. Excellent conversions were observed (for example, 100 % at ratio metal/substrate 36000:1), even at very high ratio substrate/Pt atom (72000:1, 78.6 % conversion, TOF = 943.2 min^{-1} for each Pt atom). However, the selectivity towards the formation of aniline was not excellent and the presence of nitrosobenzene and azoxybenzene was detected in the reaction media. Recycling the catalysts was possible until the 5th cycle with any loss in the activity. The high activity of the catalyst was justified in terms of the dispersion of the Pt adatoms in the MOF and the good distribution of Pt@MIL-101 in the reaction mixture.

Evangelisti *et al.* prepared platinum nanoparticles supported in γ-Fe_2O_3 and γ-Al_2O_3 to study the role of the support in the chemoselective hydrogenation of nitroaromatics.[40] The catalysts were synthesized by adsorption of mesitylene Pt atoms on the support γ-Fe_2O_3 (d_{mean} = 2.0 (1.2) nm, 1 %Pt wt) or γ-Al_2O_3 (d_{mean} =1.9 (1.2) nm, 1 %Pt wt). In the case of Pt@γ-Al_2O_3, the particles were well separated but very close to each other, which was not the case in Pt@γ-Fe_2O_3. The so-obtained particles were used as catalysts in the hydrogenation of halonitrobenzenes under mild conditions (25 °C, 1 bar H_2). For comparative purpose, a commercial Pt@γ-Al_2O_3 (d_{mean} = 4.8(3.0) nm) was also tested. The prepared catalysts exhibited higher activity than the commercial one, with Pt@γ-Fe_2O_3 catalyst showing the best result in the reduction of *o*- and *p*-chloronitrobenzene (99.9 % selectivity in the case of *p*-chloronitroaniline, for example, versus 96.2 % for the Pt@γ-Al_2O_3 catalyst). The catalyst Pt@γ-Fe_2O_3 could be magnetically recovered up to 5 cycles without any decrease in the activity or selectivity. This catalyst, which gave the best performance, was employed in the hydrogenation of *m*-chloro, bromo-and iodo-derivatives. The rates of the bromo-substituted nitroarenes were

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higher than those of the chloro-analogous, while for the iodo derivatives, the opposite trend was observed.

Very recently, Corma, Llabrés i Xamena *et al*. reported the synthesis of MOF catalysts containing Pt or Pd atoms, with Cr^{+3}. [41] These catalysts were employed in different tandem processes, implying the first reduction of the nitroaromatic ring and a second process with the aim of transforming the nitroarenes in more valuable molecules. As this is not the scope of this review, we will not describe the results with further details.

Finally, we will include in this part, despite it is not an oxide-based support, the use of layered materials for the preparation of Pt catalysts to be used in the hydrogenation of *p*-chloronitrobenzene, reported by Xu *et al*.[42] For the preparation of the catalysts, the authors mixed preformed PVP-stabilized Pt nanoparticles with the γ-ZrP support to yield homogeneous nanoparticles of 3 nm size. The authors justified the good dispersion in terms of the strong interaction between the surface groups of the support and the metal atoms. In the catalytic hydrogenation of *p*-chloronitrobenzene (40 ºC, 20-40 bar H_2), 100 % conversion was reached increasing the H_2 pressure from 20 to 40 bar H_2, without a change in the selectivity towards the formation of the corresponding chloroaniline. When higher amount of catalyst was employed, dehalogenation took place in the reaction, which was not the case when a lower amount of catalyst was used. The presence of the intermediates *p*-chloronitrosobenzene and *p*-dichloroazoxybenzene was checked by GC, but when longer reaction times were used for the reactions, they converted into the desired *p*-chloroaniline. Further experiments performed at higher temperature showed that dehalogenation was favored in these conditions. It is interesting to mention that the catalysts can be reused but with a slightly decrease in the activity. Indeed, the analysis performed by TEM revealed that the particles agglomerate after the catalysis, and the size increased to 7 nm.

2.3 Other Pt NPs systems

In 1997, Liu *et al.* reported the influence of introducing metal ions in the catalytic hydrogenation of *o*-chloronitrobenzene performed over platinum colloidal clusters.[43] For the preparation of the catalysts, the authors used a reported methodology,[44] to obtain nanoparticles of 1.55 nm mean size. The catalytic activity of these particles was evaluated in the hydrogenation of *o*-chloronitrobenzene (30 °C, 1 bar H_2), finding *o*-chloroaniline, aniline, *o*-chloronitrosobenzene, nitrobenzene, azobenzene and azoxybenzene as products of the reaction. The tests performed revealed that promoting the reaction by addition of ions such as Na^+, K^+, Ba^{2+}, Al^{3+}, Cr^{3+} and Mn^{2+} had little effect on the activity or selectivity observed in comparison with the unpromoted reaction. In contrast, Li^+ had an effect of increasing both activity and selectivity, despite this effect was very little. Sn^{2+} and Zn^{2+} poisoned the catalysts and

Co^{2+} produced the lost of all the catalytic effect. Fe^{2+}, Co^{2+} and Ni^{2+} presented a positive effect both in the catalytic activity and selectivity. However, the most remarkable effect was found with Ni^{2+}, which increased the selectivity towards aniline from 46 % (unpromoted reaction) to 66.3 % and almost doubled the hydrogenation rate (to 0.64 mol H_2/mol Pt). TEM analysis after the catalysis revealed that little aggregation took place, excepting in the case of PVP-Pt-Ni^{2+}, probably due to the coordination between the amino groups of the products and the Ni^{2+}.

In 2011, Lu, Gu and coworkers described the synthesis of platinum nanowires (NWs) for the hydrogenation of nitroaromatics and "one-pot" amidation with carboxylic acids.[45] Pt nanowires were prepared by a reported procedure by Sun and coworkers consisting of the acidic etching of FePt nanowire in methanol.[46] Nanowires of 200 nm length and 1-2 nm in diameter were obtained. The catalytic activity of the Pt nanoparticles was evaluated in the hydrogenation of nitroaromatics (40-100 °C, 1 bar). In general, Pt nanowires showed good values for the formation of aniline both in polar and non polar solvents, being methanol the solvent in which the process require lower temperature (40 ºC) and shorter reaction time (99 % yield after 1 h of reaction). When acetic acid was employed as solvent, a "one-pot" amidation process took place with N-phenylacetamide as the main product of the reaction. Mechanistic insights revealed that the amidation occurred through the first reduction of nitrobenzene to aniline without its isolation. The influence of the temperature in the amidation of nitrobenzene was studied, showing an increase of selectivity with the temperature, that is, higher temperatures favored the formation of *N*-phenylacetamide (99 % at 100 ºC). On the other hand, the scope of the hydrogenation process was also studied, finding that both electron-withdrawing and electron-donating nitroarenes were reduced with selectivities higher than 97 %. In the case of the amidation process, good regioselectivities (higher than 92 %) were also observed. For comparative purposes, two other Pt catalysts were prepared, Pt nanoparticles (2 nm) and Pt nanorods (20 nm length, 2 nm diameter). The experiments performed revealed that lower yields for the corresponding amides were obtained in these cases (72 % for Pt NP and 87 % for Pt nanorod). The catalyst could be reused up to 6 times in the one-pot amidation reaction without significant loss in the activity.

The same year, Sreedhar *et al.* prepared gum acacia (GA)-supported Pt nanoparticles and tested their catalytic activity in the hydrogenation of nitroarenes in water.[47] The preparation of the catalyst was done employing gum acacia in water, both as stabilizing and reducing agent, to yield nanoparticles which presented a mean size of 2-3 nm (See Figure 11). The chemical bonding of the –OH and –COOH functional groups of the gum acacia with the surface of the platinum nanoparticles was marked as the reason for the good stabilization of the particles in this support.

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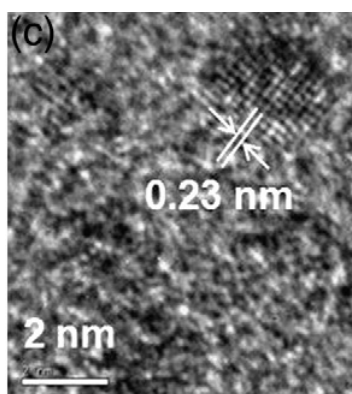
Figure 11. HRTEM image of the prepared GA-Pt NPs (Copyright *Catal. Commun.*, ref. 47).

The catalytic activity of the supported nanoparticles was studied in the hydrogenation of nitroarenes bearing different functional groups (-OH, -CH$_3$, -OCH$_3$) in water and mild conditions (1 bar H$_2$, RT, 0.24 % mol Pt, 1 mmol nitroarene) finding good conversions in all cases (from 82 % to 95 %, depending on the substrate). It is remarkable to mention the efforts made by the authors to work in more environmental friendly conditions, using water as solvent and a non toxic stabilizing agent. Also good results were observed for fluoro-, chloro-, and bromo- derivatives, and lower conversion in the case of the iodo-derivative. Finally, nitroarenes bearing keto- and aldehyde groups were also employed with good results, while the catalyst didn't work in the case of aliphatic nitroaromatics. Indeed, it was possible to recycle the catalyst with just a small loss in the activity from the first to the fifth cycle (from 91 % to 84%).

In 2011, Huang *et al.* reported the synthesis of PtNPs supported on a porous ionic copolymer (PICP) for the hydrogenation of nitroaromatics.[48] This polymer had been efficiently used as support for CuO nanoparticles.[49] The catalyst was prepared by reduction with NaBH$_4$ of H$_2$PtCl$_6$ in the presence of PICP in water, to yield particles of 2-4 nm mean size and a Pt content of 5% wt. The hydrogenation of nitrobenzene in mild conditions (RT, 1 bar H$_2$, 0.5 % Pt) was attempted. The study of the influence of the solvent in the catalytic reaction showed excellent results in THF, diethyl ether, ethyl acetate or without solvent (100 % of conversion, 99 % yield towards the formation of aniline). Other solvents such as ethanol, toluene and hexane gave very good results. No intermediates were detected even at low conversion in this reaction, which indicated that the nitrobenzene was hydrogenated directly to amine. The results obtained were better than those obtained when commercial Pt/C and Pd/C were employed. The catalyst could be reused with any loss of efficiency. The size of the particles slightly increased after the catalytic reaction (3-6 nm) but the particles were still active. Hydrogenation of functionalized nitroarenes was also performed, providing excellent results in the hydrogenation of halonitroarenes, with yields from 98 % in the case of the fluoro- derivative to 96% for bromo- and chloro-. A conversion of 92 % was obtained for the iodo-substituted aniline, with a higher amount of catalyst (2 % Pt) and higher temperature (50ºC). Other functional groups such as

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amine, hydroxy, ketone or nitrile remained untouched during the catalytic hydrogenation. However, the catalyst was not selective in the hydrogenation of 3-nitrostyrene, and the final product 3-ethylaniline was obtained after 3 h of reaction.

Liu, Yu *et al.* described the synthesis of bimetallic PVP-Pt/Ru nanoparticles for their application as catalysts in the hydrogenation of *o*-chloronitrobenzene.[50] The catalysts were prepared by co-reduction of $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3 \cdot nH_2O$ using ethanol as reducing agent. In this reaction, the Pt precursor was initially reduced, acting the Pt particles as seeds which catalyzed the decomposition of the ruthenium salt. Seven Pt/Ru ratios were employed, obtaining in all cases monodispersed nanoparticles of average size comprised between 2.1 – 3.1 nm. Analysis performed by XPS and HRTEM revealed the zero oxidation state for both elements, and a quasi core-shell structure in the particles, with more Pt atoms in the core and Ru in the shell. Figure 12 shows an image corresponding to the 1:1 PVP-Pt/Ru catalyst.
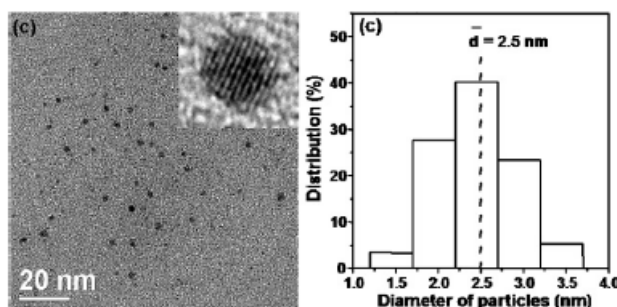
Figure 12. TEM image of PVP- 1Pt/1Ru nanoparticles (Copyright *J. Catal.*, ref. 50).

The catalytic activity of the nanoparticles was evaluated in the hydrogenation of *o*-chloronitrobenzene (25 ºC, 1 bar H_2). All the colloids showed activity very close to 100 %, with selectivities from 83 % to 99 % towards the formation of *o*-chloroaniline, depending on the system. Higher selectivities were observed for samples richer in Ru, while the activity was higher in the case of samples containing more platinum. For example, PVP-4Pt/1Ru showed a hydrogenation rate of 0.059 $(mol_{H2})/(mol_M)s$ and PVP-1Pt/4Ru a selectivity of 99 % towards the formation of *o*-chloroaniline.

$Co(OH)_2$ coated Pt nanoparticles as catalysts for the hydrogenation of halonitrobenzenes were recently prepared by Zhao and coworkers.[51] The nanoparticles were synthesized by microwave irradiation using $H_2PtCl_6 \cdot 6H_2O$ as metal precursor, ethylenglycol as reducing agent and $Co(OH)_2$ as support. The particles obtained in these conditions presented a mean size of 1.8 nm and flowerlike morphology (See Figure 13), and contained 2.3 % Pt.
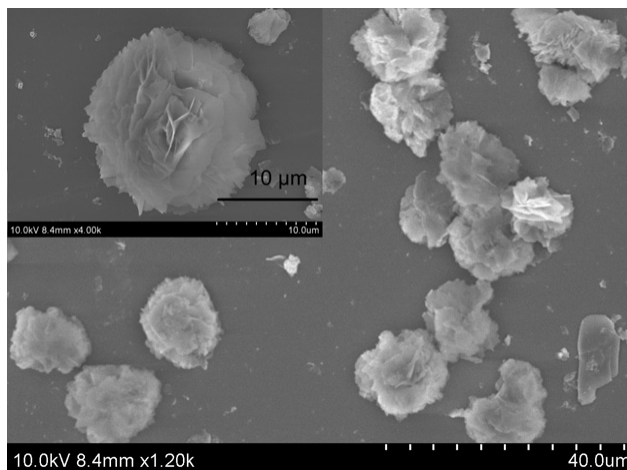
Figure 13. SEM image corresponding to the Pt/Co(OH)$_2$ catalyst (Copyright , *J. Colloid Interface Sci*, ref. 51).

These so-obtained particles were deposited in carbon black, yielding a catalyst (Pt/C) containing 1 % Pt. The performance of all the catalysts was evaluated in the hydrogenation of *o-*, *m-* and *p*-chloronitrobenzene and *p-* and *m*-bromonitrobenzene (60 ℃, 20 bar H$_2$, S/C ratio:1000/1). Pt/Co(OH)$_2$ gave in all the cases 100 % conversion and selectivities higher than 97% towards the formation of the haloaniline, with negligible formation of dehalogenation byproducts. In contrast, experiments performed using 1 % Pt/C catalyst produced dehalogenation products in the case of iodonitrobenzene (∼ 8%), which indicated that the support played a key role in the control of this process. Experiments performed employing Pt/C 1 % + Co(OH)$_2$ evidenced a decreasing in the dehalogenation reaction. The prepared Pt/Co(OH)$_2$ catalyst can be recycled up to five times in the hydrogenation of *o*-chloroaniline with a small loss of activity and selectivity (see Figure 14).
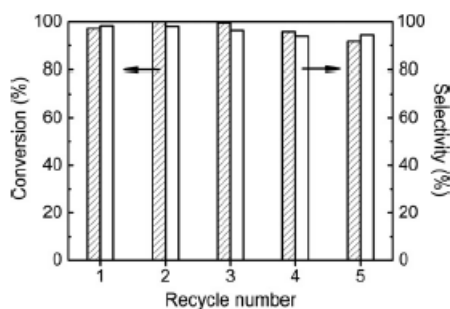
Figure 14. Recycling results of Pt/Co(OH)$_2$ catalyst. (Copyright , *J. Colloid Interface Sci*, ref. 51).

Beier, Baiker and coworkers reported in 2012 the synthesis of ionic liquid (IL) - supported platinum nanoparticles and their application as catalysts in the hydrogenation of 3-nitrostyrene.[52] The Pt nanoparticles (Pt@IL, d$_{mean}$ = 3.4 (1.2) nm, see Figure 15) were stabilized with the ionic liquid 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([BMIM][FEP]). IL-stabilized particles with additional stabilizers (quinoline, 1,10-

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phenantroline and 2,2'-bipyridine) were also synthesized, obtaining smaller nanoparticles in these conditions (mean sizes between 2 and 2.4 nm, depending on the co-stabilizer employed).
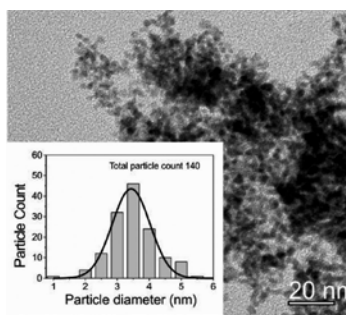
Figure 15. TEM image of Pt@IL nanoparticles. Reprinted with permission from M. J. Beier, J.-M. Andanson, A. Baiker, *ACS Catalysis* 2012, **2**, 2587-2595. (Copyright 2012 American Chemical Society).

The catalytic studies performed using Pt@IL (1 bar H_2, 30 ºC, ratio S/C=250) showed preferential activity for the hydrogenation of the C=C versus the NO_2 function, affording 90 % conversion and selectivity of 61 % after 4 h of reaction towards the formation of ethylnitrobenzene. These results were improved using the smaller PtNPs prepared with an additional stabilizer, showing the best results in the case of 2,2'-bipyridine Pt-B@IL (83 % selectivity at 90 % conversion). The influence of acidic or basic conditions in the catalytic reactions was studied, showing that this was a key parameter to control the selectivity. Acidic conditions favored the hydrogenation of the C=C bond, while reduction of NO_2 was higher in basic conditions (yielding a mixture of NO_2 hydrogenation products), with selectivities higher than 90 % in both cases. Furthermore, the authors prepared Pt nanoparticles adsorbed in different solid supports: SiO_2, Al_2O_3, TiO_2 and CNTs. The particles supported in SiO_2 gave the best result of selectivity towards the formation of ethylnitrobenzene, while the others showed higher reduction of the NO_2 and the subsequent formation of the amine. In the case of the Pt supported nanoparticles, the catalyst could be reused up to five times in acidic conditions and SiO_2 as support, while in basic conditions and employing CNTs as support the selectivity towards the formation of 3-aminostyrene could be increased from 40 to 90 %. The obtained results evidenced than in this system, the catalytic reaction could be controlled by the acidic or basic conditions, the support, the additional stabilizer and the use of an IL.

Pt nanoparticles confined within a hyper cross-linked polystyrene (HPS) polymeric matrix have been prepared by Kiwi-Minsher *et al.* by impregnating $H_2PtCl_6 \cdot 6H_2O$, in the HPS, followed by a final activation step with H_2 before its use in the catalytic reaction.[53] The characterization performed by CO chemisorption and microscopy analyses revealed a size of the particles (Pt/HPS) in the range 1-6 nm, with 65 % of particles in the range 2-5 nm. Other catalysts, namely Pt/C-I (3.0 nm), Pt/C-II (1.6 nm) and Pt/Al$_2$O$_3$ (1.7 nm) were prepared for

comparative purposes. The four catalysts were employed in the hydrogenation of *p*-chloronitrobenzene as model reaction (30 ºC, 1-20 bar H_2). The catalyst Pt/HDS employed in a molar ratio substrate:Pt of 1500, yielded *p*-chloroaniline as the main product (> 93%). Studies performed at different partial H_2 pressures showed that activity and selectivities increased with hydrogen pressure (for example, at 20 bar H_2, 100 % selectivity, TOF value 11.5 s^{-1}). Comparative analysis of the results obtained with the four catalysts showed that for the same degree of metal dispersion, the reaction pathway was independent of the support and that it did not have a significant impact in the catalytic response. The Pt/HDS catalysts could be recycled up to four times without loss of activity or selectivity. Other *p*-substituted nitroaromatics (-OH, -OCH_3, -CH_3, -H, -Br, -Cl, COOH, -NO_2) were tested, showing in all cases the exclusive formation of the substituted aniline.

Xu and coworkers have recently reported the synthesis of platinum nanoparticles generated in viologen (1,1'-dioctadecyl-4,4'-bipyridinium bromide, $C_{18}V^{2+}$) micelles for the reduction of 4-nitrophenol by $NaBH_4$.[54] The particles were prepared by reducing the platinum precursor $H_2PtCl_6 \cdot 6H_2O$ with DMF in water and in the presence of the $C_{18}V^{2+}$. TEM and HRTEM analysis showed the formation of nanospheres of 80 nm, with Pt NPs of 2 nm immobilized in the viologen spheres. Several samples which differed in the ratio surfactant:Pt were prepared, showing better results of dispersion in the samples with higher $C_{18}V^{2+}$ contain. The authors highlighted the double role of the $C_{18}V^{2+}$ in the reaction, not only as nucleation site for Pt but also as a controlling agent to avoid the aggregation of the metal. These nanoparticles efficiently hydrogenated the 4-aminophenol to the corresponding aniline at room temperature using $NaBH_4$ as reducing agent. In addition, it was possible to recycle the catalyst up to five times without any loss of activity, probably due, in the opinion of the authors, to the good dispersion of the particles in the micelles and their stability. The analogous hydrogenation performed with unprotected Pt nanoparticles showed a rapid decrease of the catalytic activity, which manifested the importance of the viologen micelles as stabilizing agent for the catalytic Pt nanoparticles.

Very recently, we have reported the organometallic synthesis of PtNPs stabilized by N-heterocyclic carbenes and their use as catalyst for the hydrogenation of nitroaromatics.[55] Platinum nanoparticles were synthesized by decomposition of [Pt(dba)$_2$] in THF at room temperature under 3 bar of H_2 and in the presence of variable amounts (0.2 or 0.5 equiv.) of the carbene ligands 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene ($I^iPr_2Me_2$). Figure 16 corresponds to a TEM image and the size histogram of the Pt nanoparticles prepared using 0.2 equiv. of the IPr carbene.
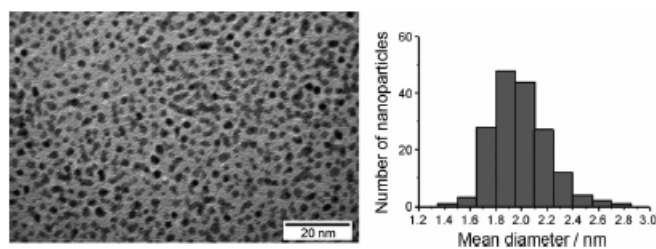
Figure 16. TEM image and histogram of the PrIPr$^{0.2}$ NPs. (Copyright *ChemCatChem*, ref. 55).

The catalytic activity of these carbene-stabilized nanoparticles was evaluated in the hydrogenation of different nitroaromatics in mild conditions (30 ºC, 1 bar H$_2$). The results showed that by a proper choice of the NHC stabilizer, and the adjustment of the NHC/metal ratio, these NHC-capped PtNPs exhibited high levels of activity and selectivity in the hydrogenation reactions. In particular, PtNPs stabilized with 0.2 equiv. of IPr carbene catalyzed the chemoselective reduction of diverse functionalized nitroarenes in the absence of additives or promoters. This catalyst tolerated the presence of a range of functional groups including hydroxyl, benzyloxy, carbonyl and olefinic moeities as well as halogens. Table 9 reports the results obtained in the case of the substituted nitroarenes employing PtIPr$^{0.2}$ as catalyst.

Entry	Substrate	Product	Conversion [%] (t [h])	Yield [%]
1	HO—C$_6$H$_4$—NO$_2$	HO—C$_6$H$_4$—NH$_2$	>99 (3.9)	>99
2	BnO—C$_6$H$_4$—NO$_2$	BnO—C$_6$H$_4$—NH$_2$	>99 (2.8)	>99
3	H$_2$NOC—C$_6$H$_4$—NO$_2$	H$_2$NOC—C$_6$H$_4$—NH$_2$	>99 (1.0)	>99
4	EtO$_2$C—C$_6$H$_4$—NO$_2$	EtO$_2$C—C$_6$H$_4$—NH$_2$	>99 (1.5)	>99
5	MeOC—C$_6$H$_4$—NO$_2$	MeOC—C$_6$H$_4$—NH$_2$	>99 (1.3)	>99
6	OHC—C$_6$H$_4$—NO$_2$	OHC—C$_6$H$_4$—NH$_2$	>99 (3.0)	94[b]
7	NC—C$_6$H$_4$—NO$_2$	NC—C$_6$H$_4$—NH$_2$	>99 (6.9)	>99
8	EtO$_2$C—CH=CH—C$_6$H$_4$—NO$_2$	EtO$_2$C—CH=CH—C$_6$H$_4$—NH$_2$	>99 (1.3)	79[c]
9	Cl—C$_6$H$_4$—NO$_2$	Cl—C$_6$H$_4$—NH$_2$	99 (1.5)	95[d]
10[e]	pyridine—NO$_2$	pyridine—NH$_2$	>99 (5.0)	>99

[a] Reaction conditions: 1 bar of H$_2$, 30 °C, THF, 0.2 mol% Pt, [substrate]= 0.75 M; conversion and yield were determined by GC–MS. [b] 6% of 4-aminobenzyl alcohol was observed. [c] 21% of ethyl 3-(p-aminofenil)pro-panoate was obtained. [d] 4% of aniline was obtained. [e] 4 bar of H$_2$, 60 °C.

Table 9. Hydrogenation of nitroarenes to functionalized anilines mediated by PtIPr$^{0.2}$.

(Copyright *Chem.Cat.Chem*, ref. 55).

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3. Current and future developments.

In this review, the most recent advances performed in the development of nanocatalysts consisting of carbon and oxide supported and non-supported platinum nanoparticles as well as an overview of their application in the catalytic hydrogenation of nitroarenes are given. The selected works here presented point out the strong efforts made by the scientific community in preparing new, stable and efficient catalysts for this catalytic reaction so important in industry. A large variety of supports and metal precursors as well as of synthetic methods have been employed to prepare the PtNPs. The interesting results obtained with various substrates evidence the high interest of using Pt-based nanocatalysts for the target catalytic reaction. High conversions and selectivities are obtained, for both supported and non-supported PtNPs. The strength of the interaction between the support and the particles is stated by some authors as the reason for the good conversion and selectivities observed; the use of supports avoids in some cases the formation of undesired intermediates. Others authors justify the good results of activity and selectivity obtained in terms of the location and/or dispersion of the metallic atoms on the supports. However, further research is needed in order to reach a better understanding of these effects. Another aspect of interest deals with the addition of promoters in the catalytic reaction. Both promotion and poisoning effects have been found by the researchers but more work is also required to clarify the promotion effects. The use of new supports such as reduced graphite oxide or γ-ZrP must also be stressed. The recovery of the catalyst is an issue of extreme importance, taking into account the economical aspects of this process. Magnetic supports, for example, present an advantage over others due to their easy separation by simply applying a magnetic field. Nevertheless, the recovery of the catalysts needs to be studied more deeply to get better recyclable nanocatalysts that present constant catalytic activities with time. Concerning non-supported systems, promising results are also observed, in particular with polymers, ionic liquids or ligands. In the later case, a great advantage is that ligands can be introduced at the metal surface to orientate the selectivity of the catalysis.

In conclusion, numerous efforts have been devoted to the preparation of platinum-based nanocatalysts for their application in hydrogenation of nitroaromatics. The high number of results obtained highlights the interest of this family of catalysts for this catalytic transformation, both in terms of reactivity and selectivity. Nevertheless, in our opinion, the huge variety of supports, stabilizers and reaction conditions used do not allow to propose a guideline for predicting reaction conditions within the aim to orientate the reaction towards the hydrogenation of the nitro group or the dehalogenation. We believe that deep studies are necessary to better understand which parameters are influencing the reaction and how as well as to improve the scope of the substrates.

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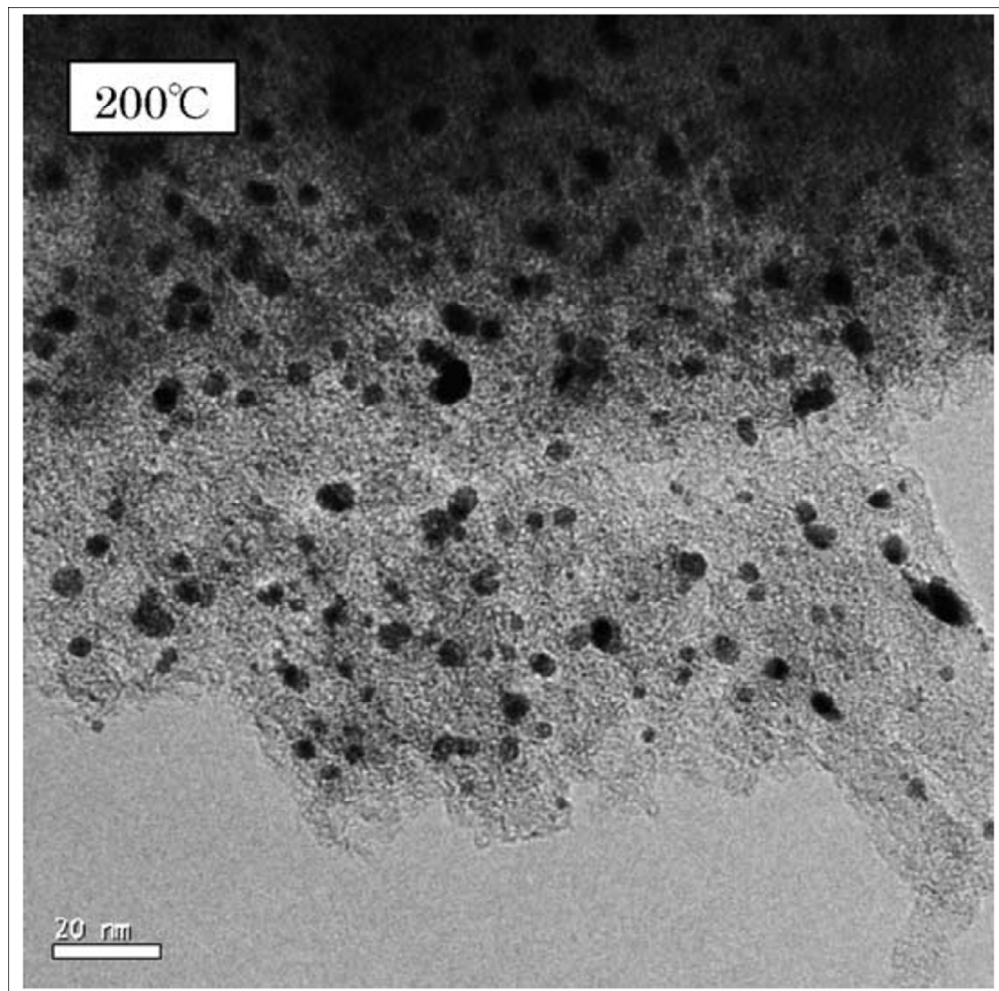
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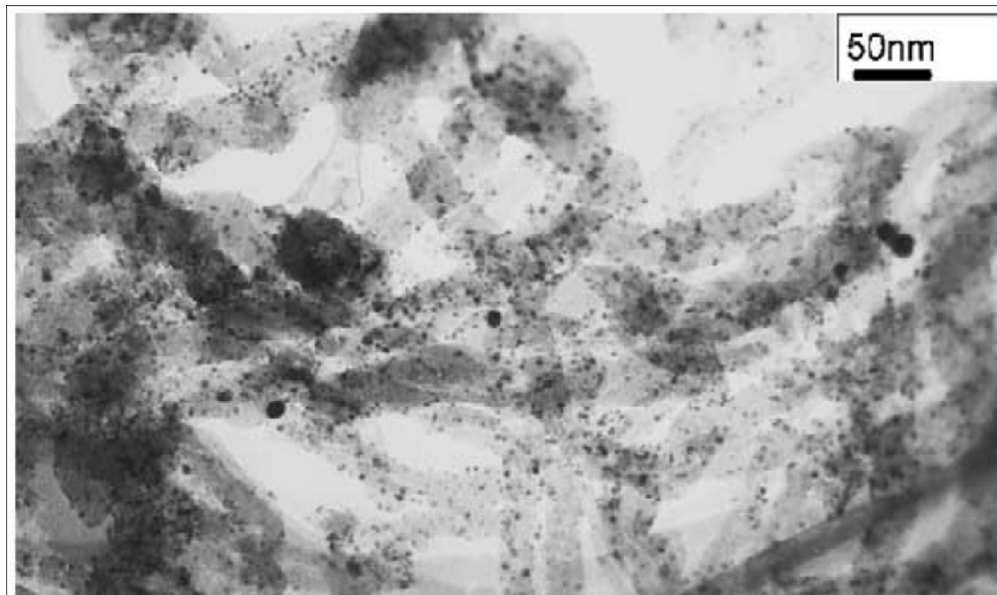
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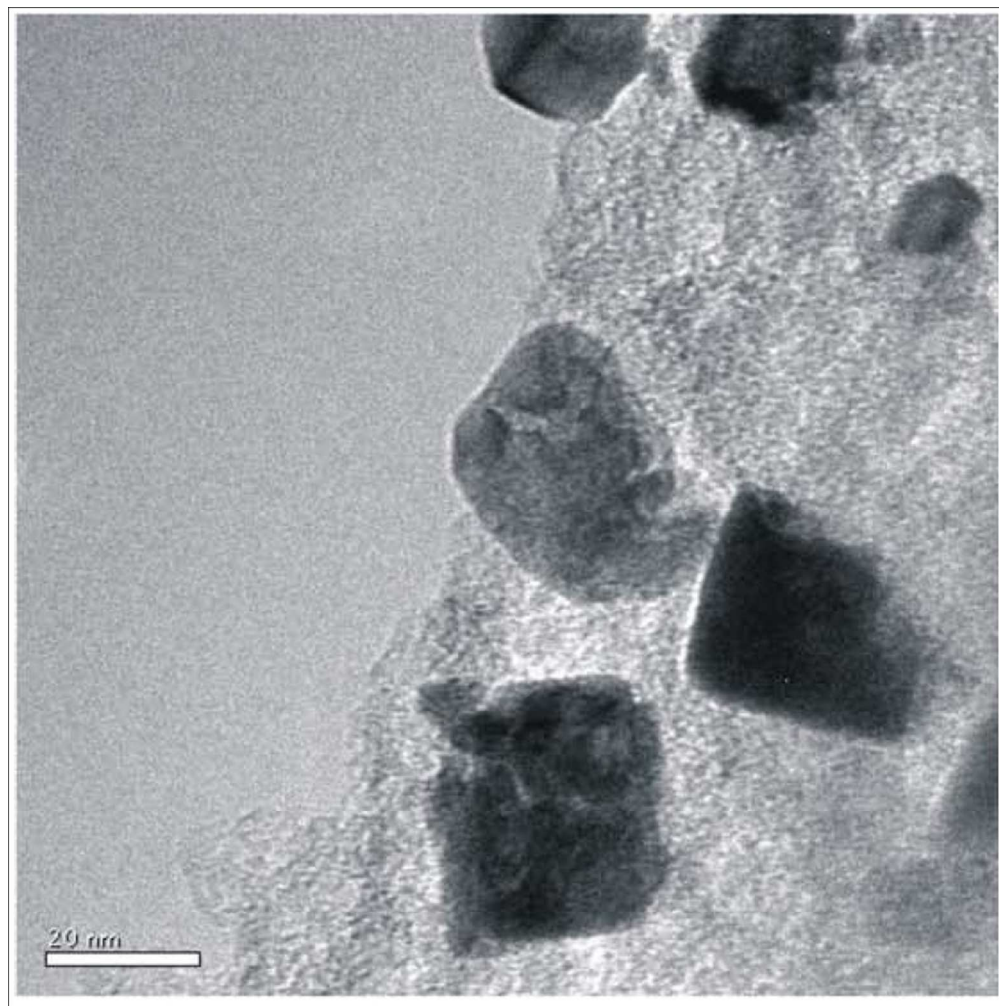
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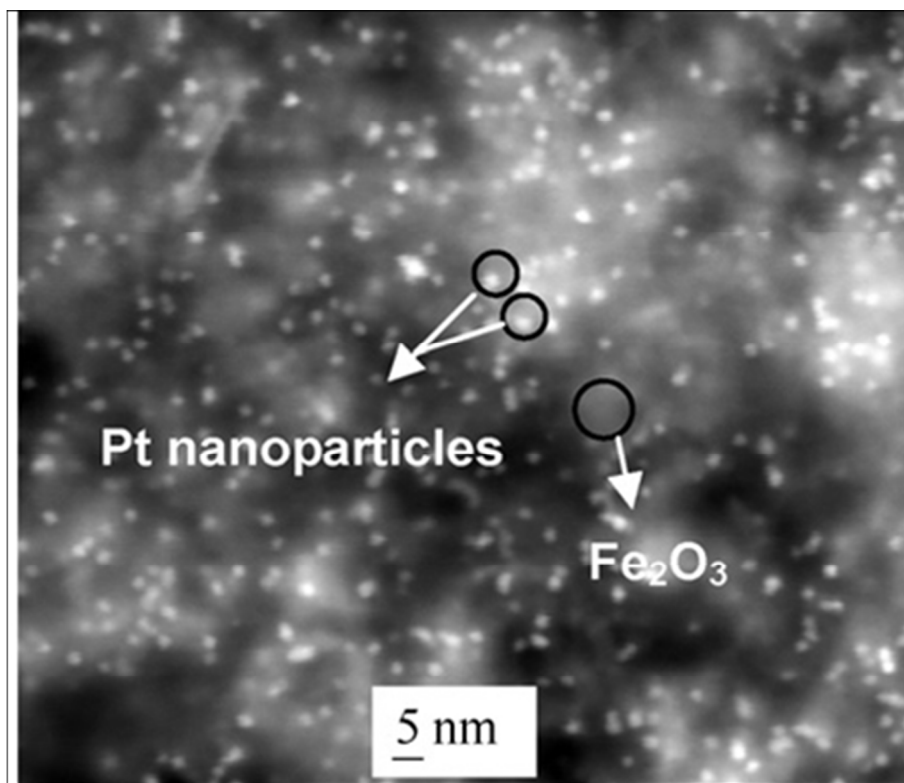
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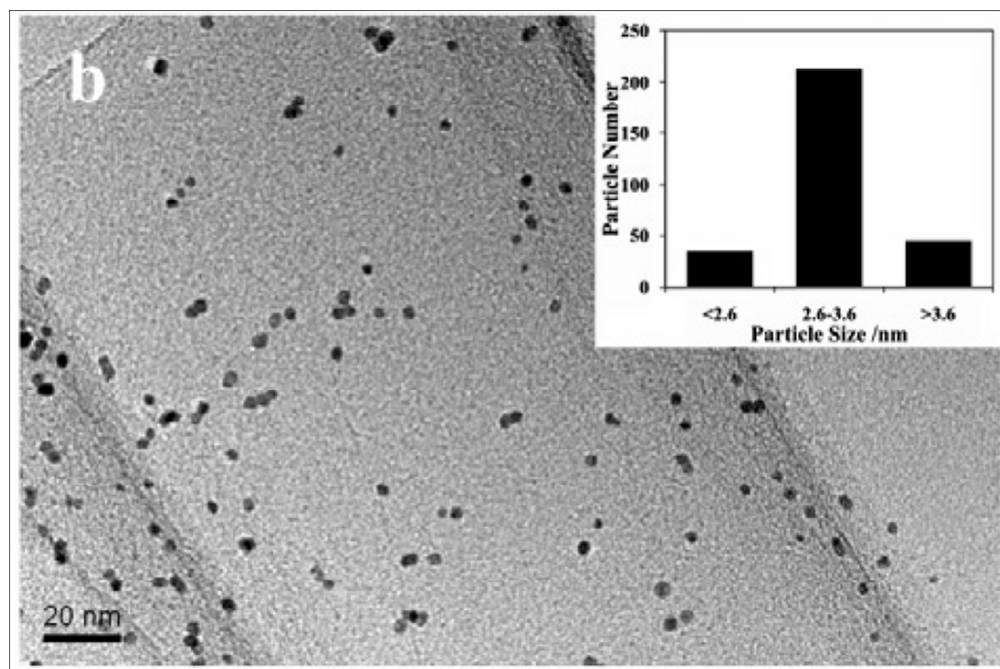
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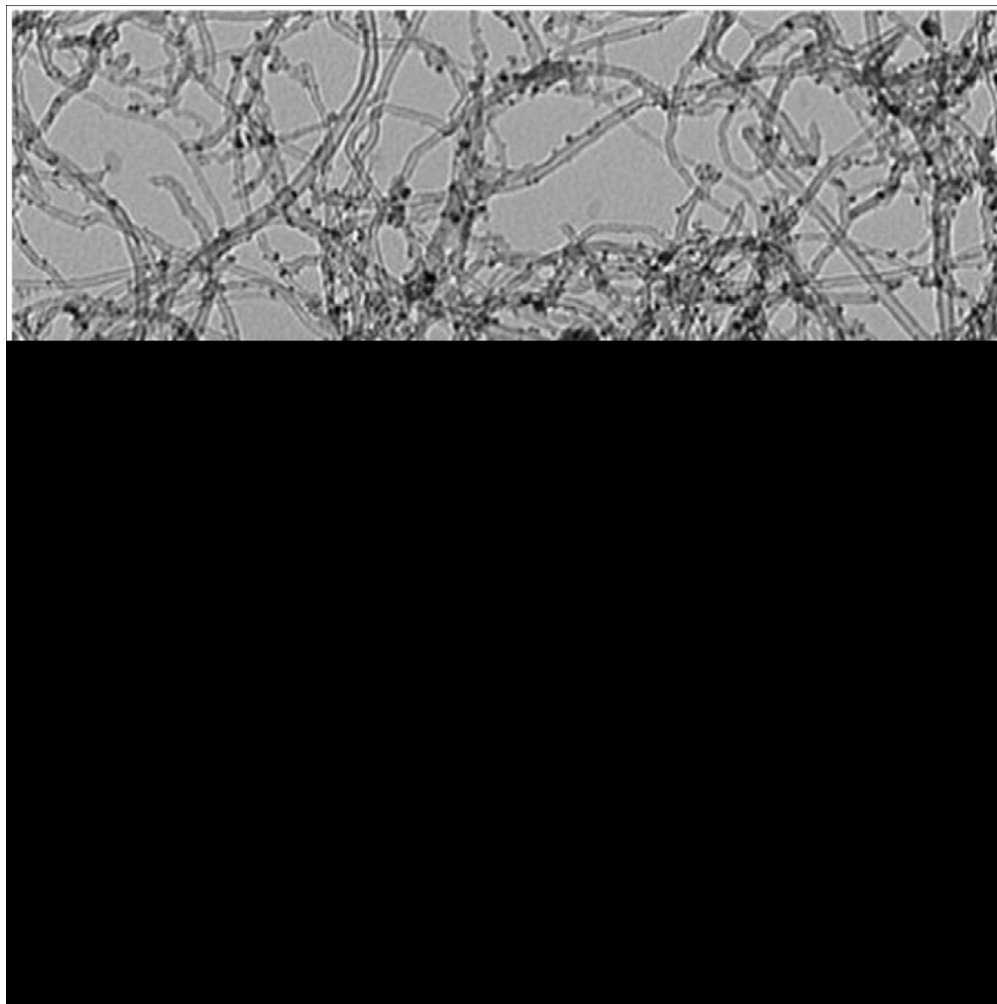
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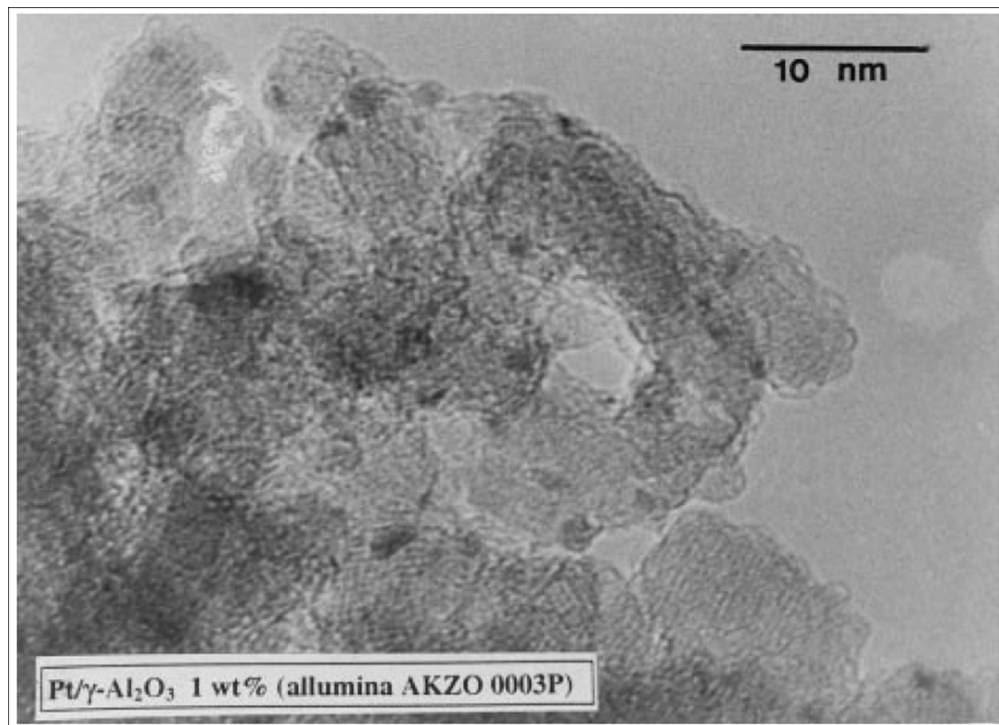
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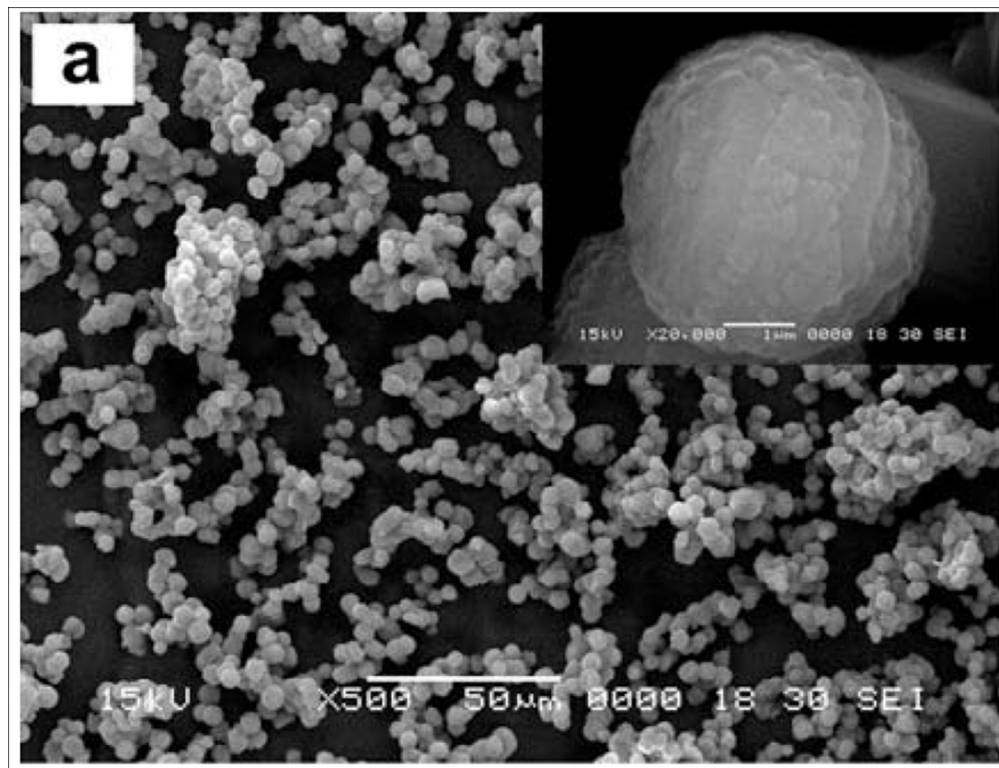
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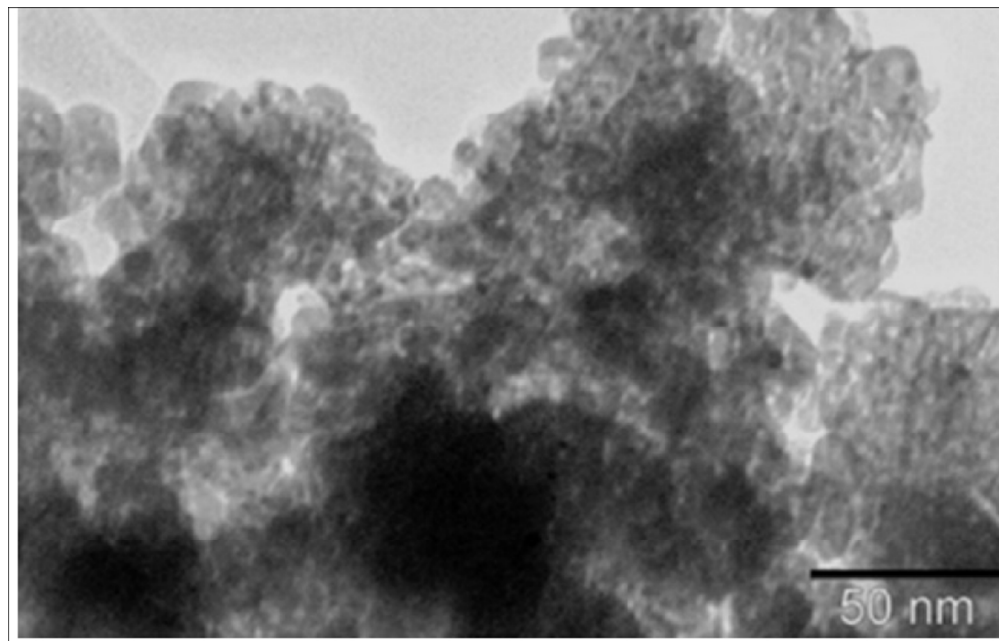
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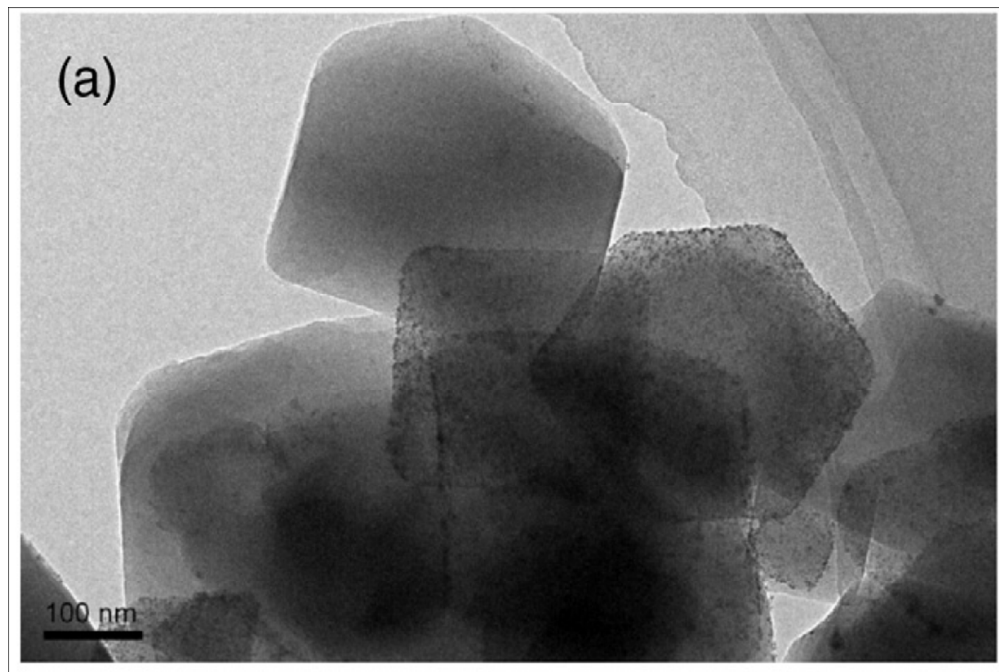
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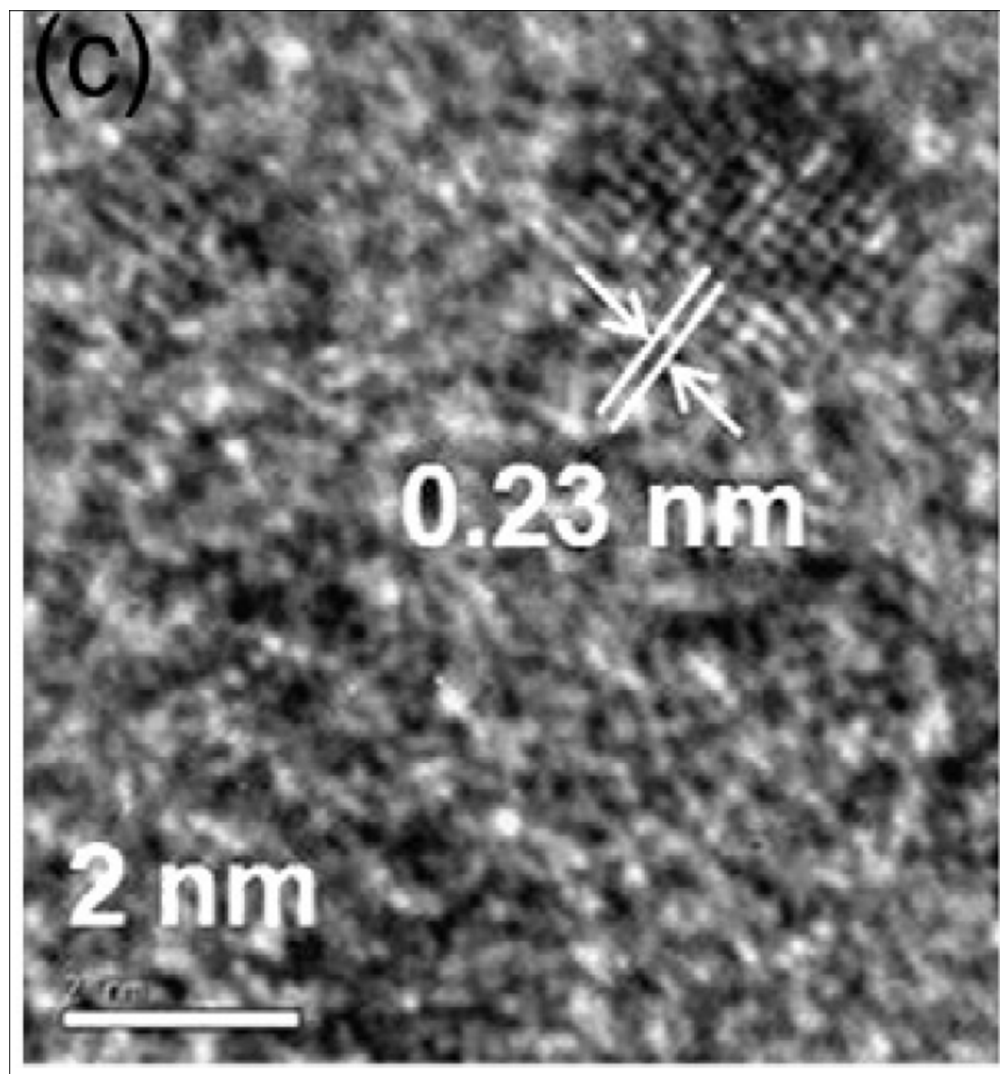
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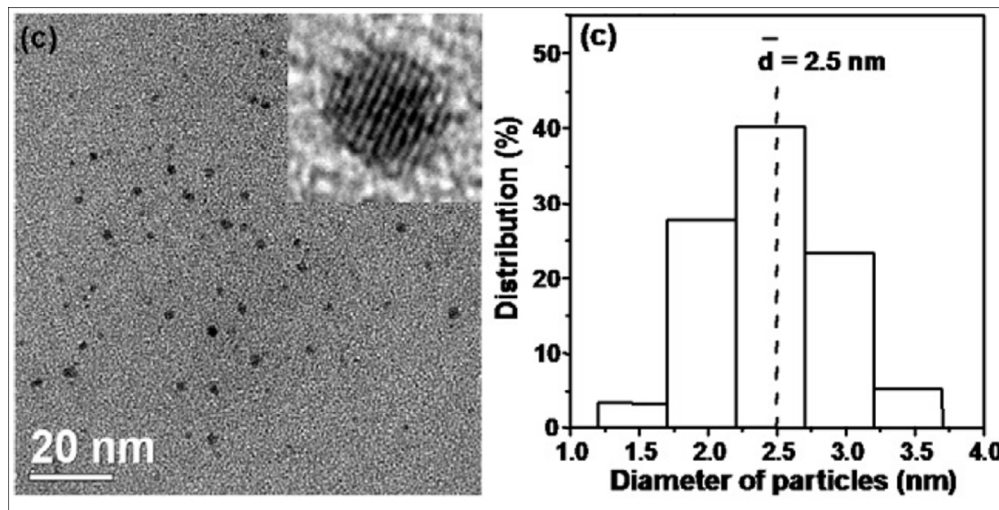
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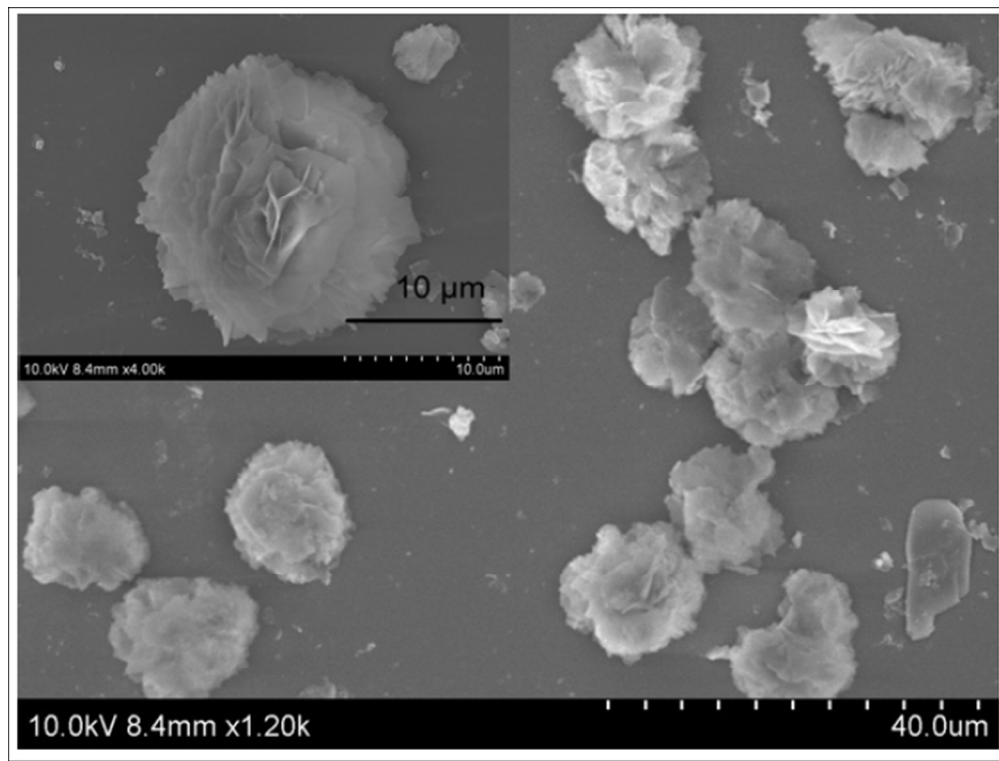
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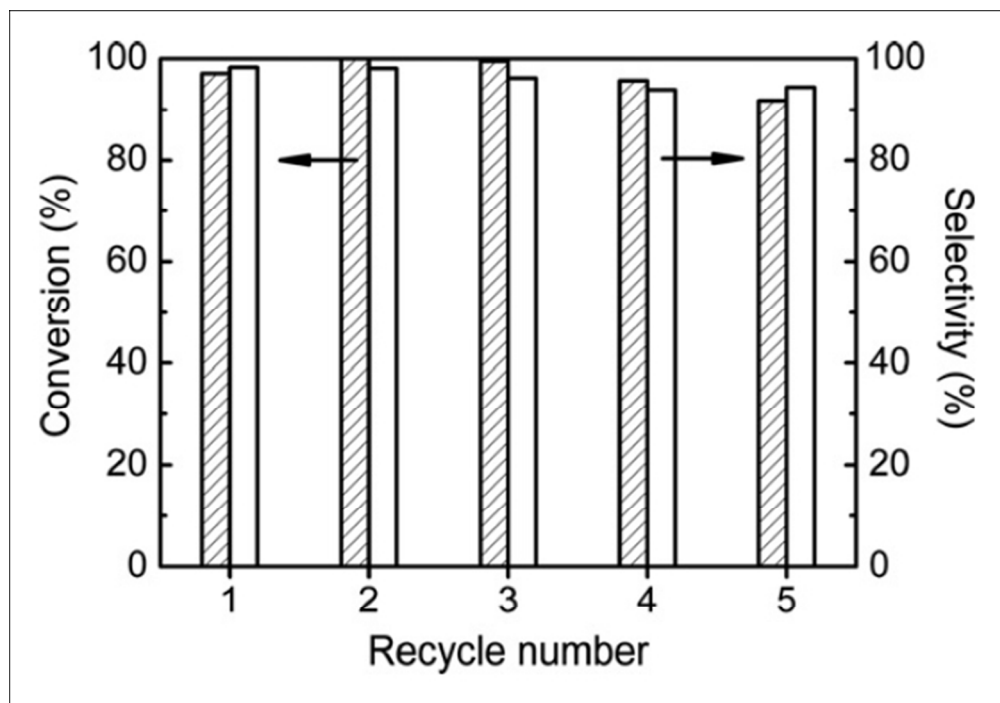
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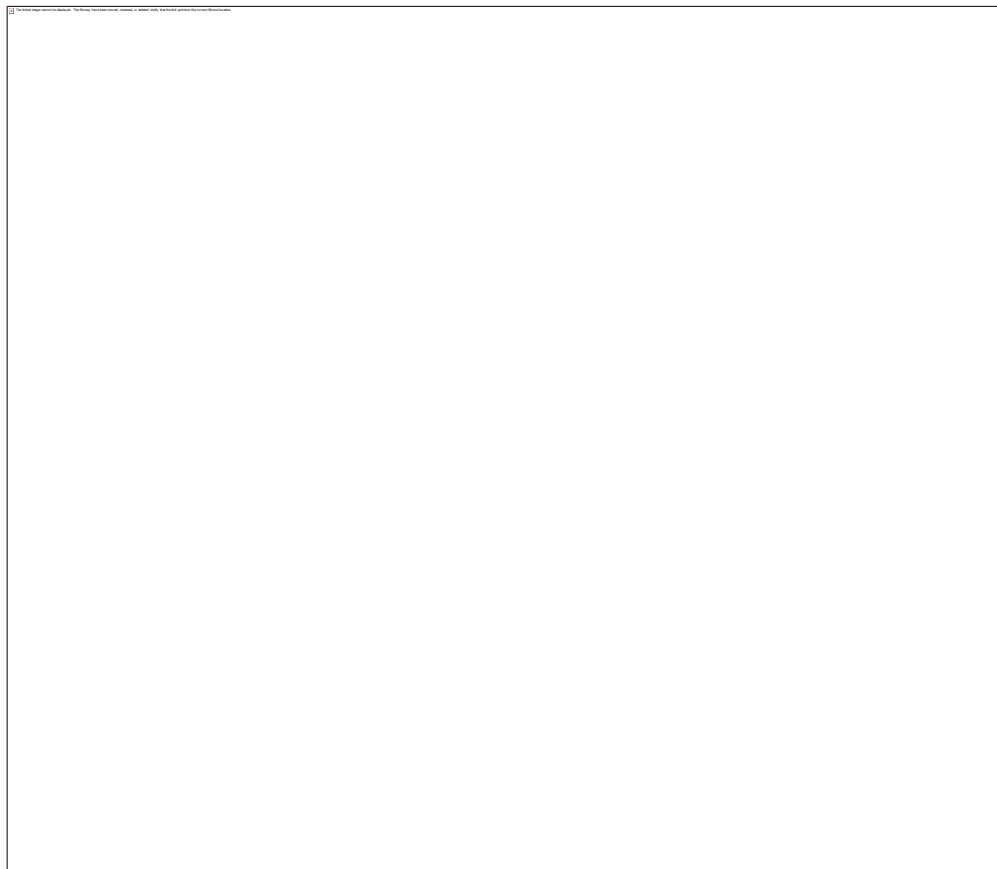
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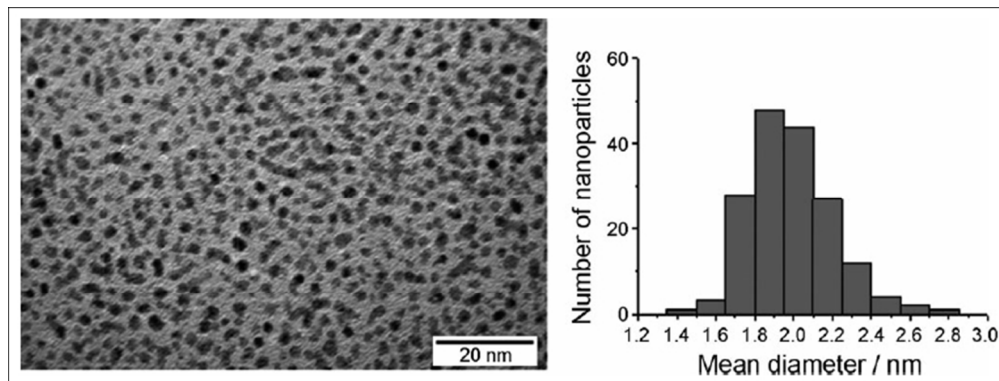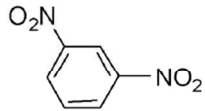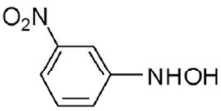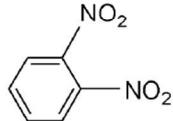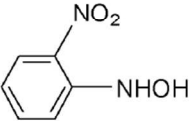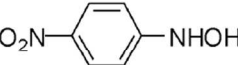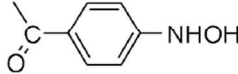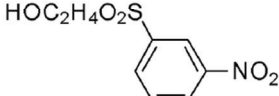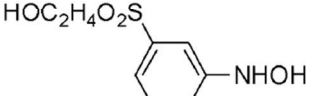
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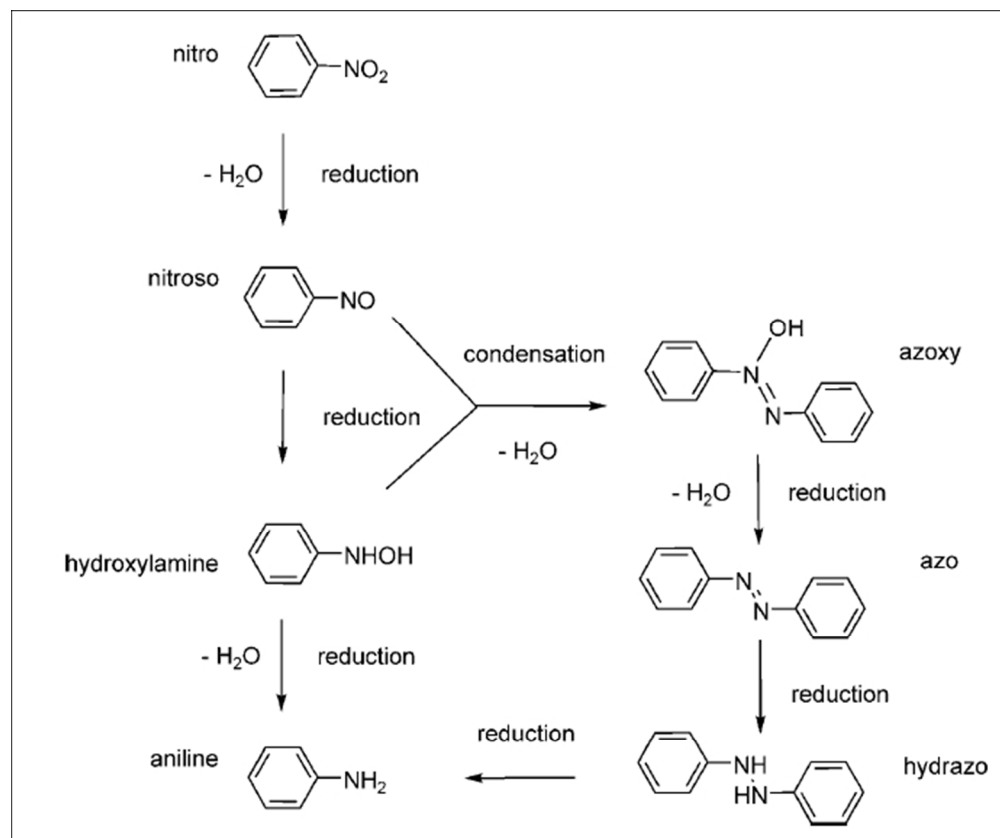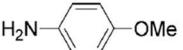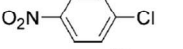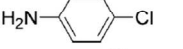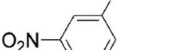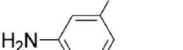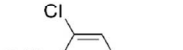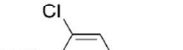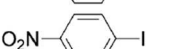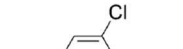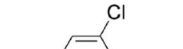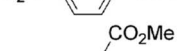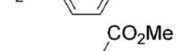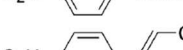
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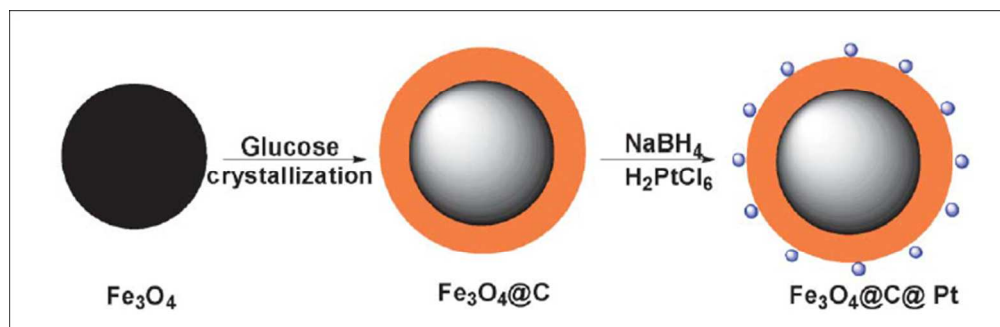
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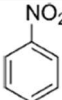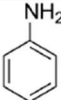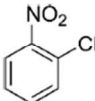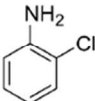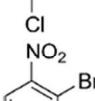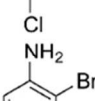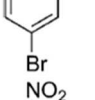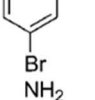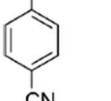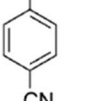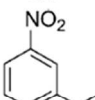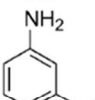
Entry	Substrate	Product	$t/$ min	Conv./ %	Sel./ %
1[a]			190	100	92.3
2[b]			170	100	91.9
3[b]			115	100	86.3
4[b]			65	100	86.3
5[c]			210	100	93.4

383x295mm (72 x 72 DPI)

Entry	Substrate		Product		Yield [%]
1	O$_2$N—⟨⟩—OMe	1a	H$_2$N—⟨⟩—OMe	2a	99
2	O$_2$N—⟨⟩—Cl	1b	H$_2$N—⟨⟩—Cl	2b	98
3	O$_2$N—⟨⟩ (Cl meta)	1c	H$_2$N—⟨⟩ (Cl meta)	2c	99
4[b]	O$_2$N—⟨⟩ (Cl ortho)	1d	H$_2$N—⟨⟩ (Cl ortho)	2d	98
5	O$_2$N—⟨⟩—Br	1e	H$_2$N—⟨⟩—Br	2e	98
6[c]	O$_2$N—⟨⟩—I	1f	H$_2$N—⟨⟩—I	2f	99
7[b,c]	O$_2$N—⟨⟩(Cl)—OBn	1g	H$_2$N—⟨⟩(Cl)—OBn	2g	98
8[b,c]	O$_2$N—⟨⟩(CO$_2$Me)—Cl	1h	H$_2$N—⟨⟩(CO$_2$Me)—Cl	2h	98
9	O$_2$N—⟨⟩—CO$_2$Et	1i	H$_2$N—⟨⟩—CO$_2$Et	2i	99
10	O$_2$N—⟨⟩—COMe	1j	H$_2$N—⟨⟩—COMe	2j	99
11[b,c,d]	O$_2$N—⟨⟩—CH=CH—CO$_2$Et	1k	H$_2$N—⟨⟩—CH=CH—CO$_2$Et	2k	97[e]
12[f]	O$_2$N—⟨⟩—CN	1l	H$_2$N—⟨⟩—CN	2l	99
13[g]	NC—CH$_2$—⟨⟩—NO$_2$	1m	NC—CH$_2$—⟨⟩—NH$_2$	2m	99
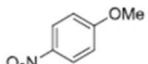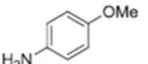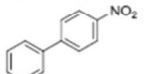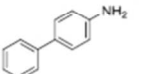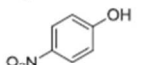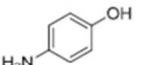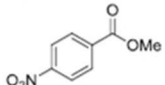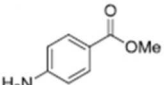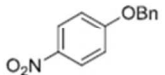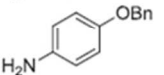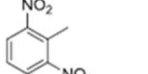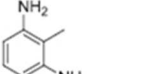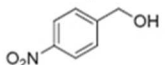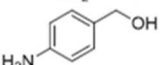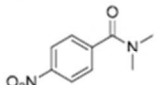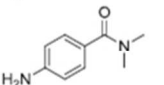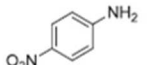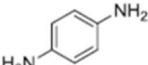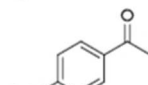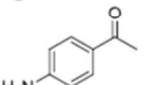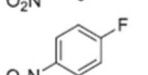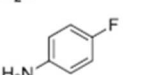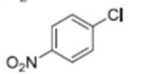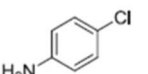
[a] Unless stated otherwise, all reactions were performed using **1** (1 mmol) and the Pt(3%)/N-CNF-H catalyst (5 mg) in ethyl acetate (3 mL) at room temperature under H$_2$ (initial pressure = 10 atm) for 6 h. [b] For 4 h. [c] At 50 °C. [d] Pt(1%)/N-CNF-H catalyst (5 mg) was used instead. [e] 3% ethyl (4-hydroxylamino)cinnamate was obtained. [f] At 70 °C under H$_2$ (initial pressure = 7 atm) for 8 h. [g] At 100 °C for 6 h.

268x405mm (104 x 104 DPI)

Entry	Substrate	Product	Selectivity[b] [%]	TTFC[b] [min]
1			>99	50
2			98	70
3			93	–
4			93	50
5			99	400
6			99	1000
7			93	170

[a] Reaction conditions: (0.8%Pt+0.3%Mo)/C (61% H_2O) (70 mg), substrate (S/C=20000, 22.3 mmol), EtOH (80 mL), H_2 (4 bar, total pressure), 30°C. [b] Selectivity and activity were determined by GC when the uptake of hydrogen ceased. TTFC=time to full conversion.

196x289mm (96 x 96 DPI)

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			0.5	95
2			1	99
3			0.5	98
4			0.5	97
5			1	99
6			1	99
7			1	93
8			0.5	94
9			0.5	87
10			0.5	97
11			1	99[c]
12			1	99[c]
13			3	98[c]
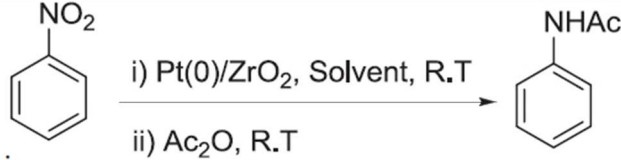
[a] Reaction conditions: 0.5 mmol of nitro compound, hydrogen gas(1 atm), 4.0 mL of ethanol with 1 mol% of metal-CNT catalyst at ambient temperature.
[b] Yields of isolated products.
[c] Yields were determined by GC analysis using anisole as an internal standard.

155x232mm (96 x 96 DPI)

substrate	solvent	Pt/nitro (mol, × 10^2)	T (K)	P (bar)	time (h)	conversion (%)	selectivity (%)
3-nitrostyrene	toluene	0.31	313	3	6.50	95.1	93.1
4-nitrobenzaldehyde[a]	THF	0.92	313	3	3.00	99.2	98.2
4-nitrobenzonitrile	THF	0.40	323	6	2.20	99.5	98.6
4-iodonitrobenzene	THF	1.02	333	6	0.35	99.5	99.5
4-nitrophenylacetylene	toluene	0.24	313	3	5.60	98.9	90.1
3-chloronitrobenzene	THF	0.75	318	4	1.00	99.0	99.6
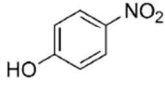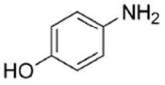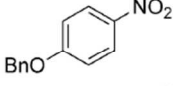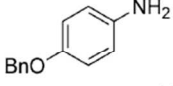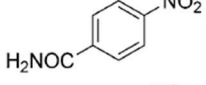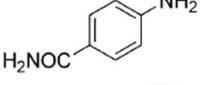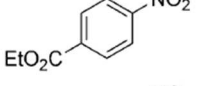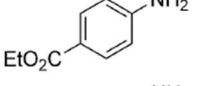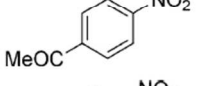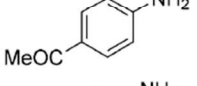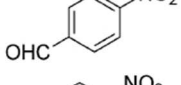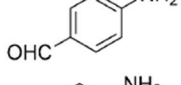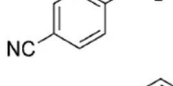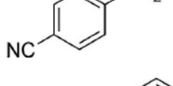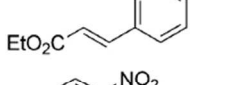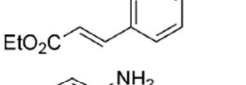
[a] Mass balance ~85% because of an unavoidable polymerization of 4-aminobenzaldehyde

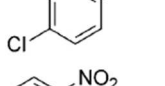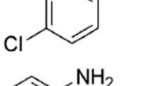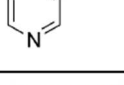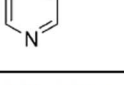205x92mm (96 x 96 DPI)

Entry	Solvent	Time [h]	Yield [%][b]
1	THF	3.5	<5
2	DMF	3.5	<5
3	Ethanol	3.5	<5
4	Toluene	3.5	12
5	Methanol	3.5	93

214x90mm (96 x 96 DPI)

Entry	Substrate	Product	Conversion [%] (*t* [h])	Yield [%]
1	HO–C6H4–NO2	HO–C6H4–NH2	>99 (3.9)	>99
2	BnO–C6H4–NO2	BnO–C6H4–NH2	>99 (2.8)	>99
3	H2NOC–C6H4–NO2	H2NOC–C6H4–NH2	>99 (1.0)	>99
4	EtO2C–C6H4–NO2	EtO2C–C6H4–NH2	>99 (1.5)	>99
5	MeOC–C6H4–NO2	MeOC–C6H4–NH2	>99 (1.3)	>99
6	OHC–C6H4–NO2	OHC–C6H4–NH2	>99 (3.0)	94[b]
7	NC–C6H4–NO2	NC–C6H4–NH2	>99 (6.9)	>99
8	EtO2C–CH=CH–C6H4–NO2	EtO2C–CH=CH–C6H4–NH2	>99 (1.3)	79[c]
9	Cl–C6H4–NO2	Cl–C6H4–NH2	99 (1.5)	95[d]
10[e]	pyridine-NO2	pyridine-NH2	>99 (5.0)	>99

[a] Reaction conditions: 1 bar of H_2, 30 °C, THF, 0.2 mol % Pt, [substrate] = 0.75 M; conversion and yield were determined by GC–MS. [b] 6 % of 4-aminobenzyl alcohol was observed. [c] 21 % of ethyl 3-(*p*-aminofenil)pro-panoate was obtained. [d] 4 % of aniline was obtained. [e] 4 bar of H_2, 60 °C.

195x280mm (96 x 96 DPI)