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Efficient reduction of aromatic nitro compounds catalyzed by nickel chloride supported on natural phosphate

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Abstract: Natural phosphates are an important natural resource in Morocco, which need to be valorized; they can be used not only as primary raw material to produce the fertilizers but also as catalysts. In this work, we have prepared natural phosphate-supported nickel chloride ($NiCl_2$/NP). This material was effectively used as a heterogeneous catalyst in the presence of sodium borohydride as a reducing agent. The reaction was carried out at room temperature in an aqueous medium. The catalyst showed an excellent activity for the reduction of aromatic nitro compounds under simple conditions along with good usability.

Keywords: Natural phosphate, Supported catalysts, Nickel chloride, Aromatic nitro compounds, Reduction.

Introduction

Hydrogenation of aromatic nitro compounds to corresponding anilines is among the most important reactions in synthetic organic chemistry. Aromatic amines are used as intermediates to prepare an important industrial chemical such as dyes and pharmaceutical and agricultural chemicals [1,2]. They can be obtained by the reduction of aromatic nitro compounds using catalytic hydrogenation. Many catalysts were used recently to perform this transformation [3-10]. However, despite the availability of the numerous process, it still strong need to develop new green catalysts that should be efficient, safe, involve an easy work-up and obtain higher yields in shorter reaction times.

In an effort to develop a new heterogeneous system, we have used the natural phosphate (NP) alone or doped for several reactions such as Claisen-Schmidt condensation [11], Bijinelli reaction [12], hydration of nitriles [13,14], photocatalytic process [15], cycloalkanones oxidation [16], crotonaldehyde hydrogenation [17], Suzuki and Suzuki–Miyaura coupling reaction [18,19] and reforming of methane [20]. NP has also been used as an adsorbent for metals and organic matter [21,22].

On the other hand, elimination of toxic organic solvents remains a scientific challenge of economic and environmental relevance. The use of these solvents is broadly accepted to be one of the major sources of waste in fine chemical industries and poses serious health as well as environmental risk. Hence, the need for alternative reaction media is widely recognized and has become a major focus of research in industry and academia. Using water as a reaction medium is highly effective in overcoming some of these problems.

In this work, we have prepared nickel chloride supported on natural phosphate and used it as an efficient heterogeneous catalyst for the rapid reduction of aromatic nitro compounds to the corresponding amino compounds in the presence of sodium borohydride ($NaBH_4$) as a mild reducing agent and using water as a solvent.

Experimental Section

Catalysts preparation

Preparation of NP catalyst

Natural phosphate came from an extracted ore in the region of Khouribga (Morocco). The fraction of 100 - 400 µm grain size was washed with water, calcined at 850-900 °C for 2 h and washed and calcined again at 850-900 °C for 0.5 h and crushed below 63 µm.

Preparation of $NiCl_2$/NP

The $NiCl_2$/NP (15%wt of $NiCl_2$) was prepared by aqueous slurry impregnation using a nickel chloride solution $NiCl_2$ $6H_2O$. The mixture was stirred at room temperature for 1 h, then the slurry was isolated and dried during 12 h at 120 °C before use.

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General procedure for the Reduction of Aromatic Nitro Compounds

All reactions were carried out under atmosphere air. Solvents and starting materials (Aldrich) were used without further purification. GC-MS analyses were performed on a Shimadzu GC 2010 Plus Gas Chromatograph equipped with cyclodex B (Agilent) capillary column (30 m x 0.32 mm I.D x 0.25 mm film thickness). In a typical procedure, a mixture of nitro benzene (1 mmol), $NaBH_4$ (4 mmol) and $NiCl_2$/NP (0.1 g) in water (3 mL) was placed in round bottom flask. The suspension was stirred at room temperature. The reaction was monitored by Thin Layer Chromatography (TLC). The catalyst was removed from the reaction mixture by filtration, and the obtained product was extracted from the aqueous medium using ether as the organic phase. Then, ether was removed from the product by evaporation. Pure product was obtained by column chromatography over silica gel using hexane/ethyl acetate as eluent. The product was identified with ^1H NMR, ^{13}C NMR and FT-IR spectroscopy techniques. The conversion was performed by GC-MS analyses.

Results and discussion

Catalysts characterization

X-ray diffraction analysis of the catalysts

The XRD patterns of $NiCl_2$/NP are similar to that of NP. The main peaks of natural phosphate appear at 2θ = 34.0° and 37.4° corresponding to (211) and (300) reflections, respectively as shown in Figure 1. The impregnation of the NP by $NiCl_2$ does not change the crystalline system of the solid material indicating that $NiCl_2$ were highly dispersed in the solid NP.

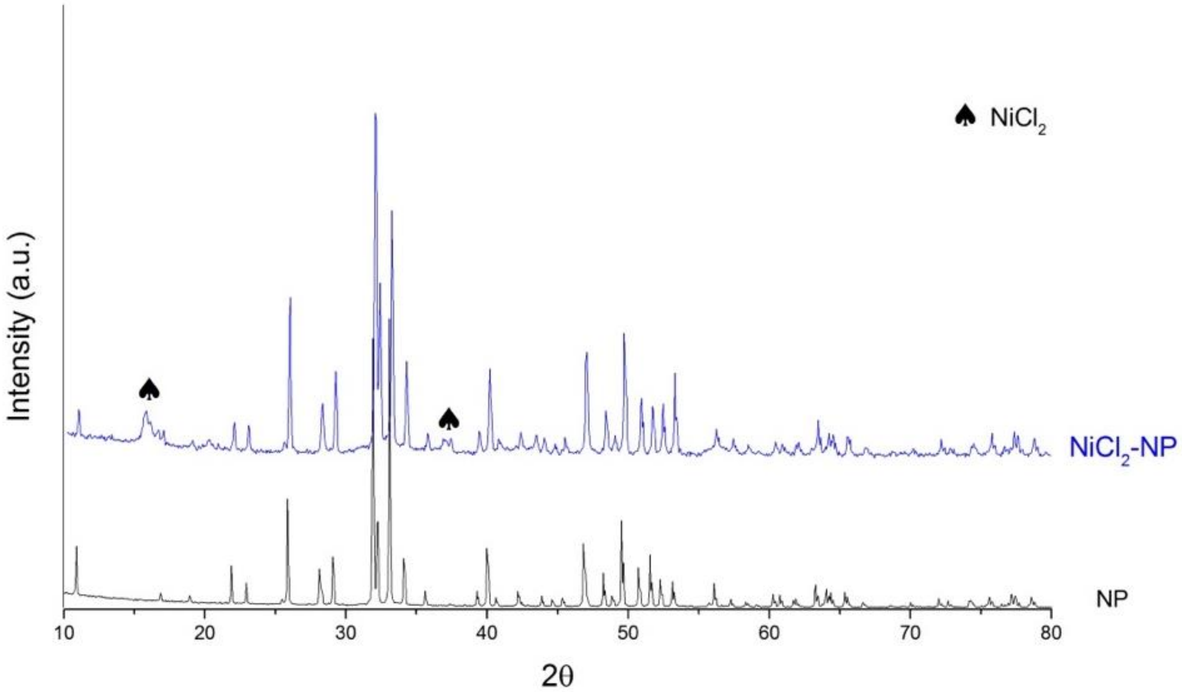


Figure 1. XRD diffraction patterns of NP and $NiCl_2$/NP.

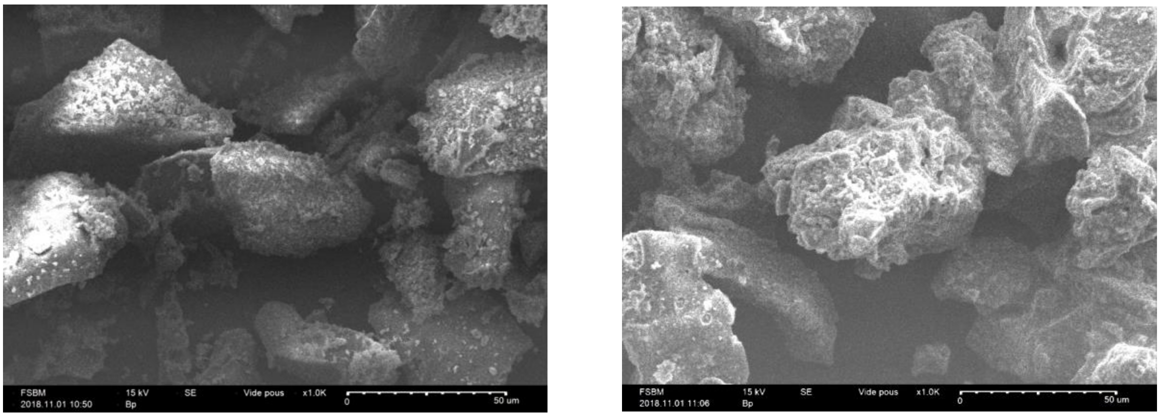
SEM images of the catalysts

The SEM images obtained for NP, $NiCl_2$/NP and $NiCl_2$/NP recovered after five reaction cycle, are shown in figure 2. The surface morphology of the NP (Fig 2 (a)) appears smooth while we can observe for $NiCl_2$/NP (Fig 2 (b)) the formation of a granular and quasi-homogeneous surface layer on the NP. This layer corresponds to the deposition of $NiCl_2$, and the surface became less smooth.

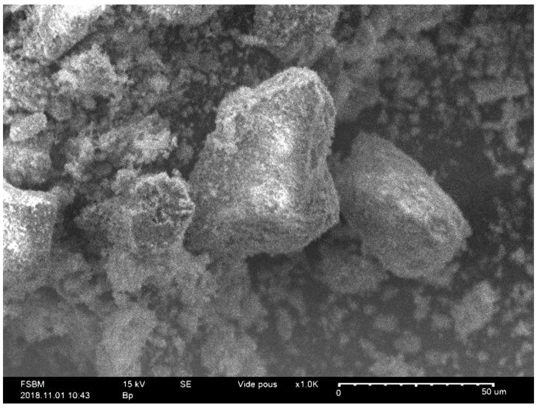
On the other hand, we note that the surface layer of recovered $NiCl_2$/NP catalyst (Fig. 2 (c)) has become less dense which suggests the degrease of the amount of $NiCl_2$ on the surface of NP, probably due to the leaching habitually observed in the doped catalysts.

EDX analysis

The surface composition of $NiCl_2$/NP and recovered $NiCl_2$/NP was evaluated by EDX. The measured weight atom ratios of Ni are 15.59, and 16.35 for $NiCl_2$/NP and $NiCl_2$/NP recovered, respectively (Fig. 3 and Table 1). These values are similar within the experimental limits of the method.

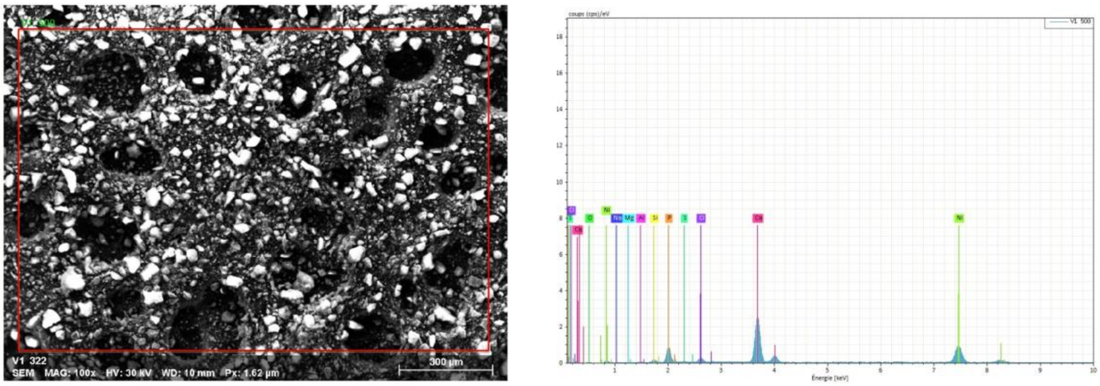


(a) NP (b) $NiCl_2$/NP

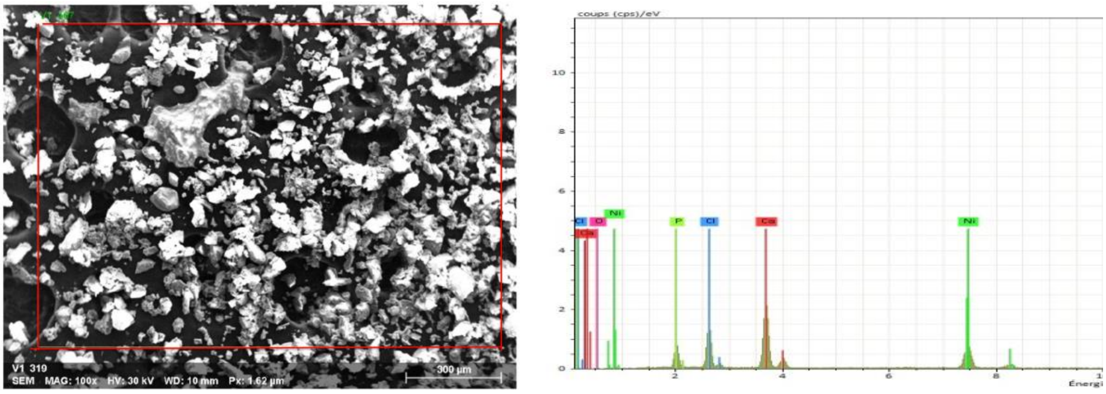


(c) $NiCl_2$/NP recovered

Figure 2. SEM images of: (a) NP, (b) $NiCl_2$/NP and (c) recovered $NiCl_2$/NP.



(a) $NiCl_2$/NP



(b) $NiCl_2$/NP recovered

Figure 3. EDX analysis of (a) $NiCl_2$/NP and (b) recovered $NiCl_2$/NP.

Table 1. EDX analysis.

Element	$NiCl_2$/NP	Recovered $NiCl_2$/NP
Ca	27.68	30.96
P	9.30	6.98
Ni	15.59	16.35
Cl	2.43	13.24

Activity of the catalyst in the reduction of aromatic nitro compounds

The reduction of nitrobenzene has been selected as a model reaction to investigate the catalytic activity of the $NiCl_2$/NP for the reduction of aromatic nitro compounds. This reduction reaction was produced in water as a solvent and at room temperature.

Synergic effect of catalyst

To carry out any study, it is necessary to appreciate the role of each element involved in the process. For this, we carried out the hydrogenation of nitrobenzene to test the role of the reducing agent, the metal and the support. Thus, we have noticed that the reaction is not carried out in the presence of $NaBH_4$ alone or NP alone and gives traces of the amino product in the presence of $NiCl_2$ (Table 2). Finally, the catalyst $NiCl_2$/NP allows this transformation with a 75% yield. It is therefore obvious to conclude that there is a very strong synergistic effect between $NiCl_2$ and NP and that it is decisive in the hydrogenation of the nitro group.

Table 2. *Synergic effect of a catalyst* on nitrobenzene reduction.

Substrate	Reducing agent	Catalyst [a]	Yield (%) [b]
Nitrobenzene	$NaBH_4$	-	-
	$NaBH_4$	NP	-
	$NaBH_4$	$NiCl_2$	Trace
	$NaBH_4$	$NiCl_2$/NP	75

[a] Reaction conditions: nitrobenzene (1 mmol), $NiCl_2$/NP (0.1 g), $NaBH_4$ (4 mmol), H_2O (3 mL), r.t.

[b] Isolated yield.

Influence of catalyst amounts

The effect of catalyst amount in the reduction of nitrobenzene to aniline was studied. It can be seen in Figure 4 that an ascending trend of aniline yield by raising catalyst amounts was observed until 0.1 g of $NiCl_2$/NP. After that, the excessive amount of the catalyst does not have any effect on this reaction.

The solvent effect

In order to study the solvent effect on the catalytic activity of $NiCl_2$/NP, methanol, ethanol and water were tested on the nitrobenzene reduction (Table 3). The reaction does not proceed in ethanol, and in contrary, the yields obtained in methanol and water were 65 and 75%, respectively after 15 min of reaction time. The great difference observed between the reaction in ethanol and methanol is very surprising, especially since in ethanol only traces of the product were observed.

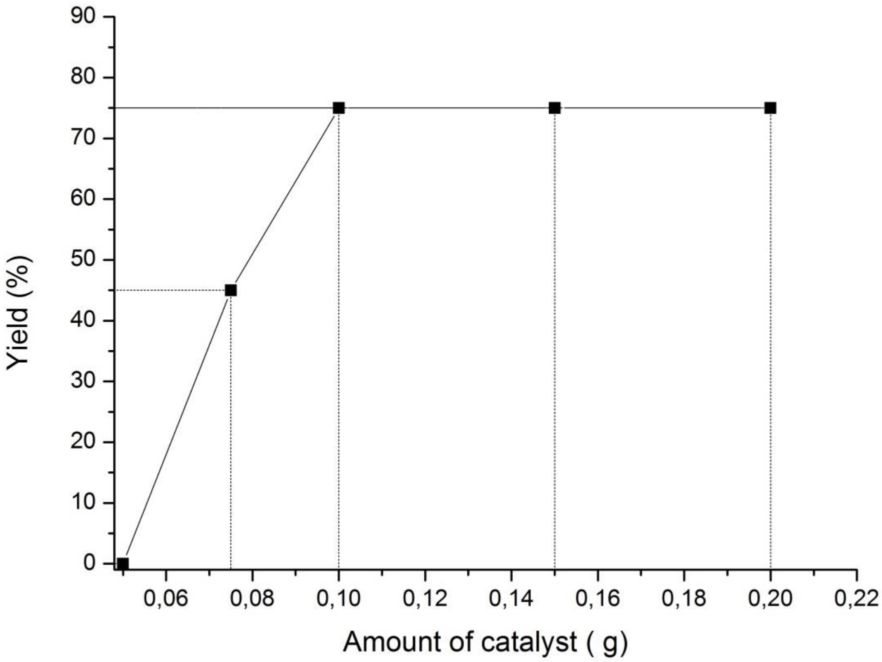


Figure 4. Effect of catalyst amount on the nitrobenzene reduction.

Table 3. Solvent effect on the nitrobenzene reduction.

Solvent	Reaction time (min) [a]	Yield (%)[b]
Ethanol	15	-
Methanol	15	65
Water	15	75

[a] Reaction conditions: nitrobenzene (1 mmol), $NiCl_2$/NP (0.1 g), $NaBH_4$ (4 mmol), solvent (3 mL), rt.
[b] Isolated yield.

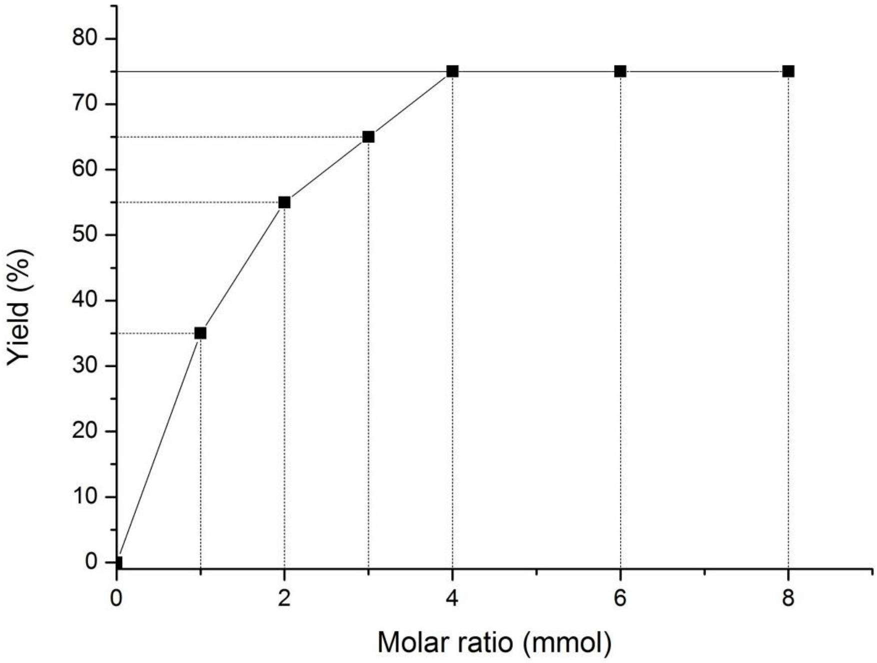


Figure 5. Effect of reducing agent $NaBH_4$ on the nitrobenzene reduction.

The effects of reducing agent $NaBH_4$

The effect of the $NaBH_4$ amount on the reaction reduction was investigated using 0.1 g of the catalyst and 1 mmol of nitrobenzene. The results showed that by increasing the amount of $NaBH_4$, the yield increased (Fig. 5). The best value of $NaBH_4$ was 4 mmol because fewer values were not enough for the reduction of the amount of aromatic nitro compounds and the excess values did not have any effect on the reaction.

Time-dependent UV–vis absorption spectra.

It can be seen in Figure 6 that aniline (bands at 233 and 283 nm) appears from 3 min of reaction while nitrobenzene (259 nm) has completely disappeared. This shows that the hydrogenation of the nitro group is easier than that of the reaction intermediates. After 1 min of reaction, some of the nitrobenzenes are probably converted to an unobserved intermediate in the UV spectrum. After 2 min of reaction, the band of the azoxybenzene intermediate (328 nm) is observed which disappears after 3 min. It can be concluded that the reaction is carried out in several stages and that the hydrogenation of the azoxybenzene intermediate takes place after the total hydrogenation of the nitrobenzene (Scheme 1). The aniline was confirmed by ^1H and ^{13}C NMR of the isolated product while azoxybenzene was identified by GC-MS in the reaction mixture.C

The mechanism of aromatic nitro compounds reduction is complex. The generally identified intermediates are nitroso compound (Ar-NO) azoxy compound (Ar-N(O)=N-Ar) and azo compound (Ar-N=N-Ar)[23,24].

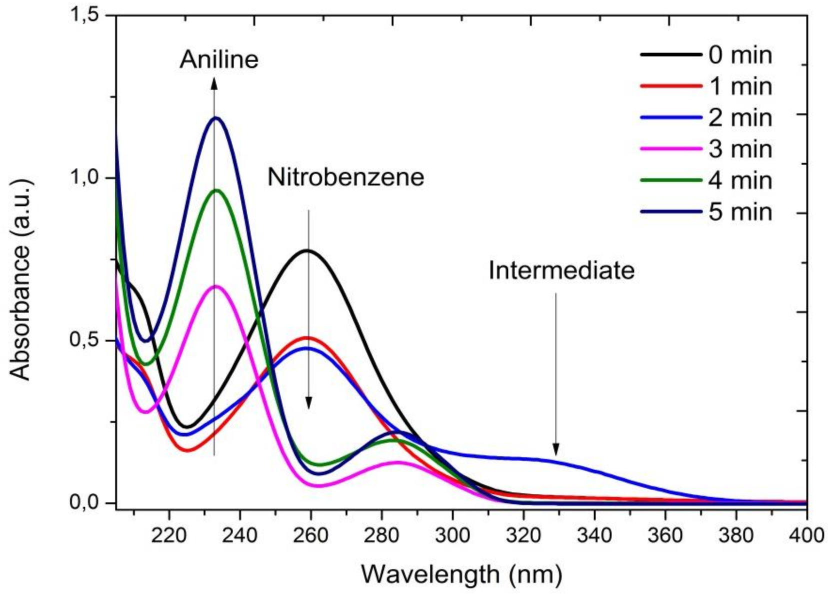
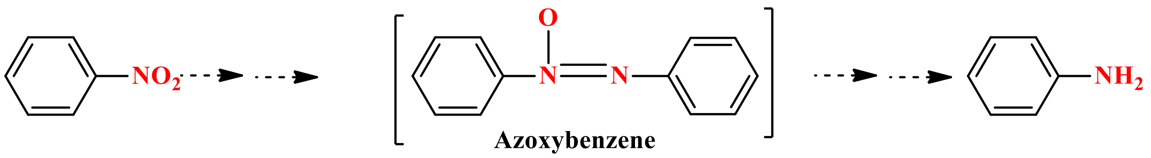


Figure 6. UV-visible spectra for the nitrobenzene reduction measured up to 5 min.



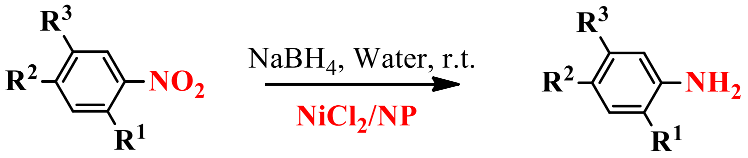
Scheme 1. Hydrogenation of nitrobenzene catalyzed by $NiCl_2$/NP.

Results of Reduction of various nitro aromatic compounds using $NiCl_2$/NP.

The optimum experimental conditions obtained with nitrobenzene as a model for the reduction reaction, catalyzed with $NiCl_2$/NP, was applied to the hydrogenation of various nitro aromatic compounds (Schemes 2 and 3). The results obtained are summarized in Table 4.

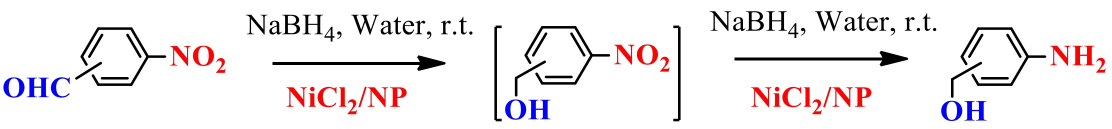
In the series of aromatic nitro compounds tested, they were all reduced to the respective primary amines with good to excellent yields within 5-10 min at room temperature. Electron with drawing/donating groups does not have a significant influence on the reaction times and yields.

The $NiCl_2$/NP catalyst showed high chemoselectivity in the reduction of the -NO_2 group without affecting chlorine (Table 4, entry 4) and the -CN group (Table 4, entry 5). In contrast, both nitro and carbonyl groups were reduced to the amino and alcohol groups, respectively (Table 4, entries 6, 7).



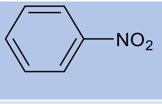
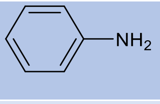
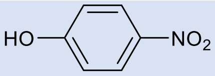
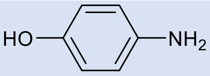
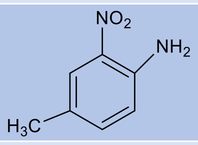
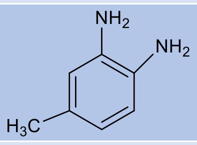
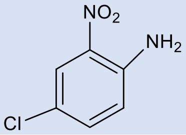
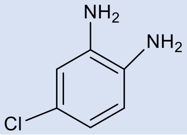
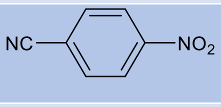
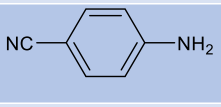
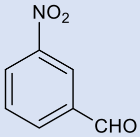
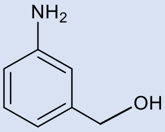
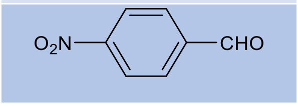
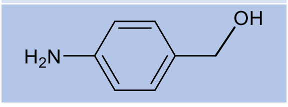
R1 = H R2 = H R3 = H
R1 = H R2 = OH R3 = H
R1 = H R2 = CN R3 = H
R1 = NH2 R2 = H R3 = CH3
R1 = NH2 R2 = H R3 = Cl

Scheme 2. Chemoselective reduction of nitro group catalyzed by $NiCl_2$/NP.



Scheme 3. Reduction of both nitro and carbonyl groups catalyzed by $NiCl_2$/NP.

Table 4. Reduction of various nitro aromatic compounds catalyzed by $NiCl_2$/NP.

Entry	Substrate	Product	Time [a] (min)	Conversion [b] (%)	Isolated yield [c] (%)
1			5	86	75
2			10	86	82
3			5	94	74
4			5	99	95
5			10	86	86
6			5	98	90
7			5	98	95

[a] Reaction conditions: nitrobenzene (1 mmol), $NiCl_2$/NP (0.1 g), $NaBH_4$ (4 mmol), H_2O (3 mL) at rt.
[b] Conversion was performed by GC-MS analyses.
[c] Pure product was obtained by column chromatography.

Determination of the hydrogenation order of the NO2 and CHO groups.

To found the order of nitro and aldehyde groups hydrogenation of the 3-nitrobenzaldehyde and 4-nitrobenzaldehyde substrates, we performed UV analysis at reaction times of 1 to 5 min. In both cases, it is found that the reduction of CHO is very fast and easier than the reduction of NO_2. Thus, after 1 min of the reaction, only the reduction of the aldehyde group is observed, the UV spectra show the presence of the 3-nitrobenzyl alcohol (269 nm, Fig.7) and 4-nitrobenzyl alcohol (276 nm, Fig.8). Analysis by GC-MC confirms this result and shows that only one product is obtained: 3-nitrobenzyl alcohol and 4-nitrobenzyl alcohol, respectively.

From 3 min of reaction, only the bands of the products corresponding to both hydrogenation of nitro and aldehyde groups are observed in the UV spectra. The 3-aminobenzyl alcohol (231 nm and 280 nm, Fig.7) and the 4-aminobenzyl alcohol (232 nm and 281 nm, Fig.8) are identified, respectively. This result is confirmed by GC-MS of the reaction mixture and by ^{1}H and ^{13}C NMR of the isolated products.

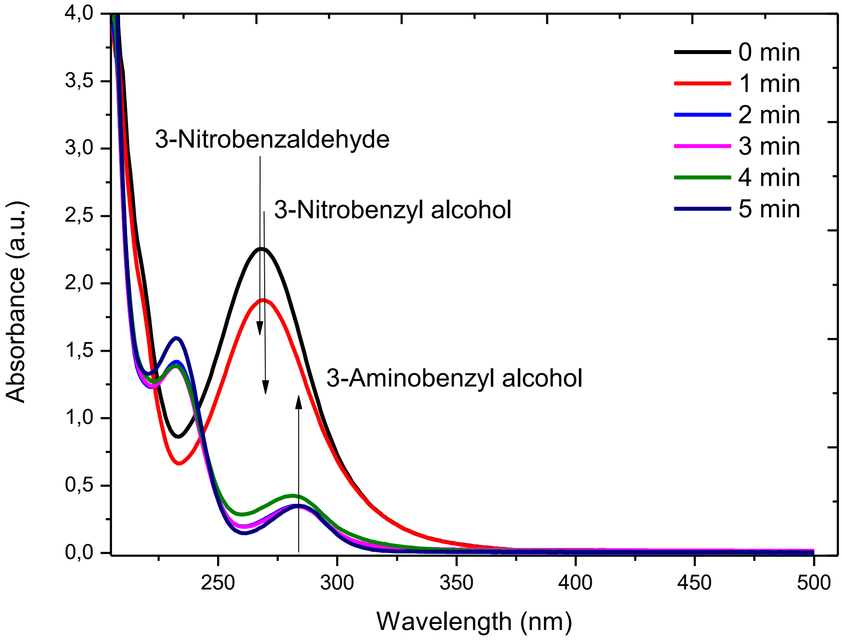


Figure 7. UV-visible spectra for the reduction of 3-nitrophenol measured at 5 min

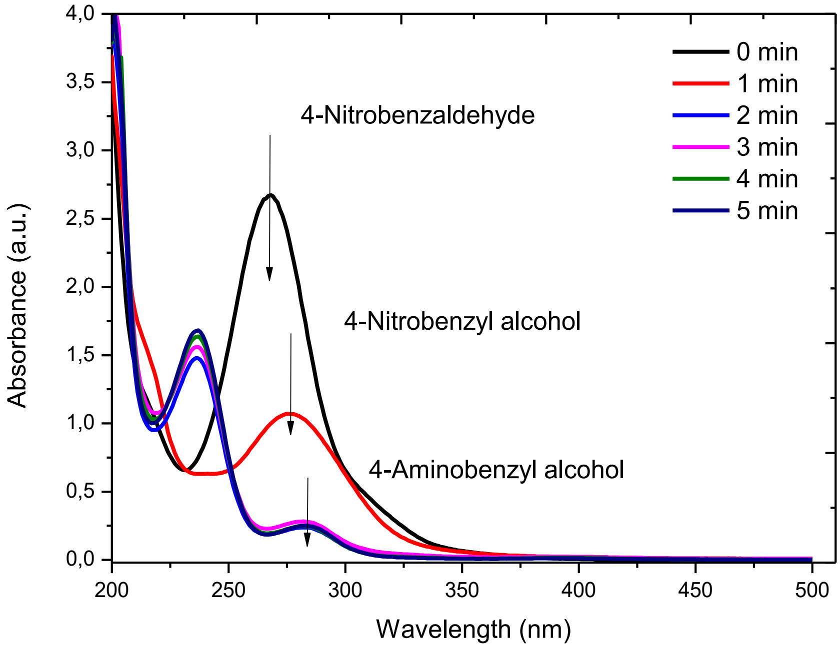


Figure 8. UV-visible spectra for the reduction of 4-nitrophenol measured at 5 min.

Recyclability studies of $NiCl_2$/NP.

The catalyst recycling is very important in the heterogeneous catalytic reactions. Thus, we have carried out the catalyst recycling experiments using 4-chloro-2-nitroaniline as a model substrate (Fig. 9). The $NiCl_2$/NP was recovered by simple filtration and washed with water and ethanol to remove any absorbed products then dried before use. Up to four passages, no loss of catalytic activity was observed, and the reaction yield remained 95%, and after that, a very few decreases of yield was observed. The few loss of catalytic activity was probably due to leaching of Ni from the support. Indeed, when this reaction is carried out using a catalyst containing only 10% by weight of Ni instead of 15%, a yield of 69% is obtained in the reduction of the nitro compound. This clearly shows that the catalytic activity of $NiCl_2$/NP is related to the percentage of Ni.

It is important to point out that after the first use a color of the $NiCl_2$/NP catalyst change from yellowish to dark black indicating the reduction of nickel (II) to nickel (0). This result is in full agreement with the results observed by Alonso et al.[25]

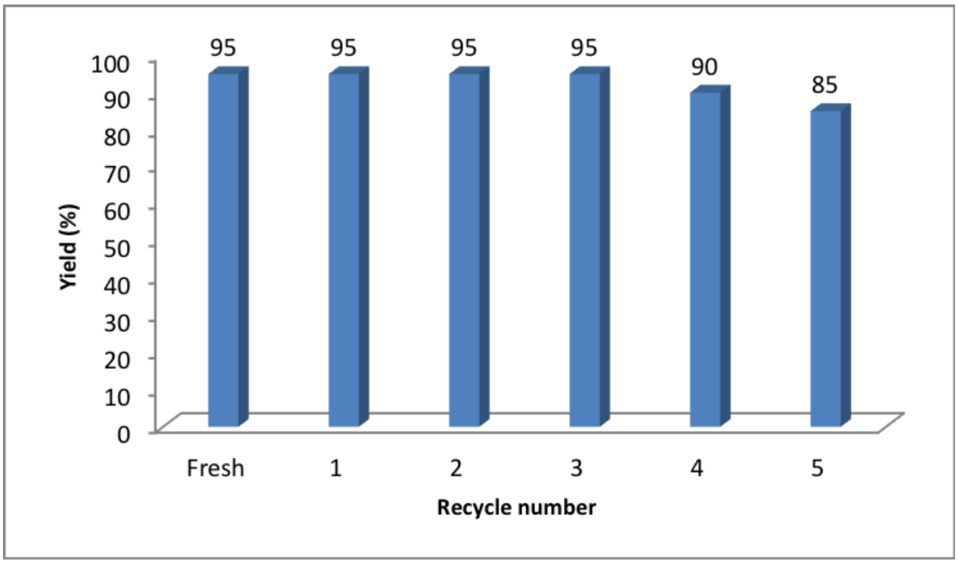


Figure 9. Catalyst reusability for the reduction of 4-chloro-2-nitroaniline.

Table 5. Comparisons of catalytic activity of $NiCl_2$/NP with some recently published catalytic systems.

Entry	Catalytic system	Reaction conditions	Yield (Time) % (min)			Ref
			Nitrobenzene	4-Nitrophenol	4-Nitrobenzonitrile	
1	$NiCl_2$/NP (This work)	H_2O, $NaBH_4$, r.t.	75 (5)	82 (10)	86 (10)	
2	Cu–Acac@Am–Si–Fe_3O_4	H_2O, $NaBH_4$, r.t.	98 (5)	100 (12)	94 (40)	26
3	Resin-AuNPs.	MeOH/H_2O, $NaBH_4$, 40 °C	85 (20)	82 (20)		27
4	Cu·Am-Sil@SiO_2	H_2O, $NaBH_4$, r.t.	94 (11)	100 (6)	92 (23)	28
5	PdNP@PPh2-PEGPIILP	H_2O, $NaBH_4$, 25 °C	99 (120)	90 (120)	86 (120)	29
6	SBA@Pincer@Au NPs	H_2O, $NaBH_4$, r.t.	98 % de conversion (7)	87 (3)		30
7	AgNC	H_2O, $NaBH_4$, 25°C	82 (210)	94 (120)		31
8	Au/TiO_2	EtOH, $NaBH_4$, r.t.	95 (180)	90 (180)		32
9	PdCu/graphene	H_2O–EtOH, $NaBH_4$, 50°C	95 (90)	98 (90)	80 (90)	33
10	RHPrNH2@Ag	H_2O, $NaBH_4$,	100 (50)	98 (68)		34

		reflux				

Comparison of natural phosphate-supported nickel chloride with some recent literature catalytic systems.

The catalytic activity of the $NiCl_2$/NP in the reduction of nitro aromatic compounds was compared with some recently published catalytic systems. It was seen that some cases require heating of the reaction medium (entries 3, 9 and 10, Table 5) and costly and scarce metals were used as catalysts as gold (entries 3, 6 and 8, Table 5), silver (entries 7 et 10, Table 5) and palladium (entries 5 and 9, Table 5). In contrast, despite that the yields obtained with our catalyst are slightly lower than others catalysts shown in Table 5, there are many advantages to the use of $NiCl_2$/NP. Thus, the substrates used are available and cheap materials such as natural phosphate. We have used a mild and efficient media: the reactions are carried out at room temperature in water as green solvent, the reaction times are very short and the catalyst is reusable.

Conclusion

We have prepared and use natural phosphate supported nickel chloride as catalyst under mild conditions. The $NiCl_2$/NP was found to be a highly efficient and reusable catalyst in the reduction of various nitro aromatic compounds by $NaBH_4$ in short reaction times and high yields. This organic transformation occurred in an environmentally friendly medium with room temperature and water as a “green” solvent. Additionally, upon completion of the reactions, the catalyst can be simply recovered from the medium easily and reused without any significant loss of its catalytic activity. Furthermore, $NiCl_2$/NP is an economical catalyst because all precursors are available and cheap.

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