

Colloid and Nanosized Catalysts in Organic Synthesis: XXI¹. Reduction of Nitroarenes Catalyzed by Immobilized Nickel Nanoparticles

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Abstract—It has been found that nickel nanoparticles on NaX zeolite, γ -alumina, activated carbon, or magnesium oxide support catalyze the reduction of nitrobenzene and its homologs affording aniline and its derivatives in high yield. The effect of the substrate on the process in a continuous reactor at atmospheric hydrogen pressure has been investigated. The use of activated carbon or magnesium oxide as a carrier allows proceeding of the reaction at 80–100°C.

Keywords: catalysis, nanoparticles, nickel, reduction, nitroarenes, aniline

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Aniline and its C-substituted homologs, which are widely used in the production of dyes, polyurethanes, and pharmaceuticals [2–6], are synthesized via hydrogenation of nitrobenzene in a liquid or gas phase. Most of the related industrial processes are performed under harsh conditions: high pressure or temperature.

Selective reduction of nitroarenes into aniline derivatives has been accomplished under catalysis with a series of metal catalysts such as Au/TiO₂ [7] Pd/C or Pt/C [8–10], PtO₂ [11], Raney nickel [12], or Ni/TiO₂ [13]. Nickel sulfide has been used as catalyst of hydrogenation at 250–350°C as well [14].

Nitrobenzene reduction has been catalyzed by nickel nanoparticles applied onto ZrO₂ or TiO₂ surface via reduction of the adsorbed salts with hydrazine hydrate. Nickel content in the catalyst was of 5%, nickel nanoparticles size being of 2–8 nm. The Ni/TiO₂ has revealed high activity (conversion up to 99% at high selectivity) [15], whereas the Ni/ZrO₂ has lost activity upon prolonged use at 250°C. Other catalysts which have been tested in gas-phase hydrogenation of nitrobenzene involve Ru/SBA15 (275°C, conversion 94%, selectivity 100%) [16], Pd on hydrotalcite (225°C, conversion 99%, selectivity 100%) [17], Ni/SBA-15 (250°C, conversion 97%, selectivity

100%) [18], and Cu/MgO (280°C, conversion 94%, selectivity 100%) [19].

The use of colloidal solution of nickel nanoparticles as a catalyst of the nitro group reduction in nitroarenes has been reported. For example, nitrobenzene and its homologs have been reduced into the corresponding substituted anilines under conditions of catalysis with nickel nanoparticles obtained via reduction of Ni(II) salts with hydrazine hydrate [20]. Hydrogenation of 4-nitrophenol with hydrogen in the presence of colloid nickel nanoparticles in an autoclave (100°C, 8 atm) has been performed as well [21]. The catalyst activity has been affected by the size of nickel nanoparticles, determined by the nature of the solvent. For example, the decrease in the particles size from 300 to 60 nm has led to the increase in the reaction yield after 2 h from 14 to 80%. It has been shown that the conversion of nitrobenzene in the presence of nickel nanoparticles is 8 times higher in comparison with Raney nickel, other conditions being the same. Nickel nanoparticles with size of 4 nm applied on silica gel have catalyzed the reduction of nitrobenzene at 90°C and 10 atm of hydrogen, with conversion 100% and selectivity with respect to aniline 99% [22].

Reduction of nitroarenes catalyzed by ferromagnetic nanoparticles have been widely studied [23]. For example, the use of palladium nanoparticles (3 nm) applied on

¹ For communication XX, see [1].

Fe_3O_4 (11 nm) for the reduction of nitrobenzene with hydrogen at 1 atm and room temperature has been reported [24]. The catalyst has been used repeatedly without a loss in activity.

We have previously shown that nickel nanoparticles applied on a support are catalytically active in a series of hydrogenation reactions at atmospheric pressure of hydrogen [25, 26]. This study aimed to investigate the reduction of nitroarenes at atmospheric pressure of hydrogen in a continuous reactor in the presence of nickel submicro- and nanoparticles immobilized on various supports: NaX zeolite, γ -alumina, activated carbon, and magnesium oxide.

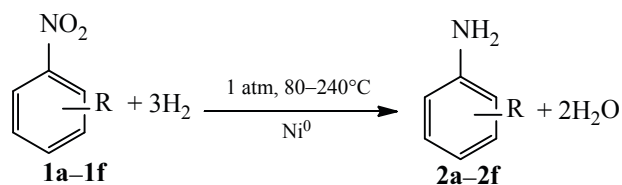
The catalysts were prepared via impregnation of the supports (the 1–1.5 mm fraction) with an aqueous solution of nickel(II) chloride hexahydrate during a day, filtration, and treatment with an aqueous solution of sodium borohydride at room temperature. The reactor was charged with moist catalyst which was dried in a hydrogen stream immediately prior to the reaction. The size of supported nickel nanoparticles was of 40–120 nm [27].

Nitroarenes **1a–1f** were reduced at 160–240°C in the presence of nickel nanoparticles applied on NaX zeolite at the substrate supply 0.6 or 0.9 L/(kg_{cat} h) depending on the amount of the catalyst and specific hydrogen supply 300–1700 L/(kg_{cat} h) (Scheme 1) Yield of the products was 91–100%, starting nitroarenes being the major admixtures.

The effects of temperature on the conversion of nitroarenes and the yield of anilines was investigated for the case of 2-nitrotoluene **1b** conversion into 2-methylaniline **2b**. The yield of compound **2b** was decreased from 99.9 to 97.2% with the increase in temperature in the 160–240°C range, due to side reaction occurring at temperature above 180°C. The decrease in temperature from 140 to 100°C led to the decrease in conversion of the starting nitroarene **1b** and yield of 2-methylaniline **2b** from 82.2 to 29.5%, the selectivity being 100%. In the case of 3-nitrotoluene **1c**, the yield of compound **2c** was decreased from 99.3 to 98.4% when the process temperature was decreased from 240 to 200°C.

The effect of the carrier nature was demonstrated using reduction of nitrobenzene as example. It was found that the studied catalysts exhibited high catalytic activity at specific supply of nitrobenzene 0.6 L/(kg_{cat} h), specific supply of hydrogen 1330 L/(kg_{cat} h), hydrogen : nitrobenzene molar ratio (10–15) : 1, and temperature 140–200°C; the conversion of nitrobenzene under those conditions

Scheme 1.



R = H (**a**), 2- CH_3 (**b**), 3- CH_3 (**c**), 4- CH_3 (**d**), 2- OCH_3 (**e**), 4- OCH_3 (**f**).

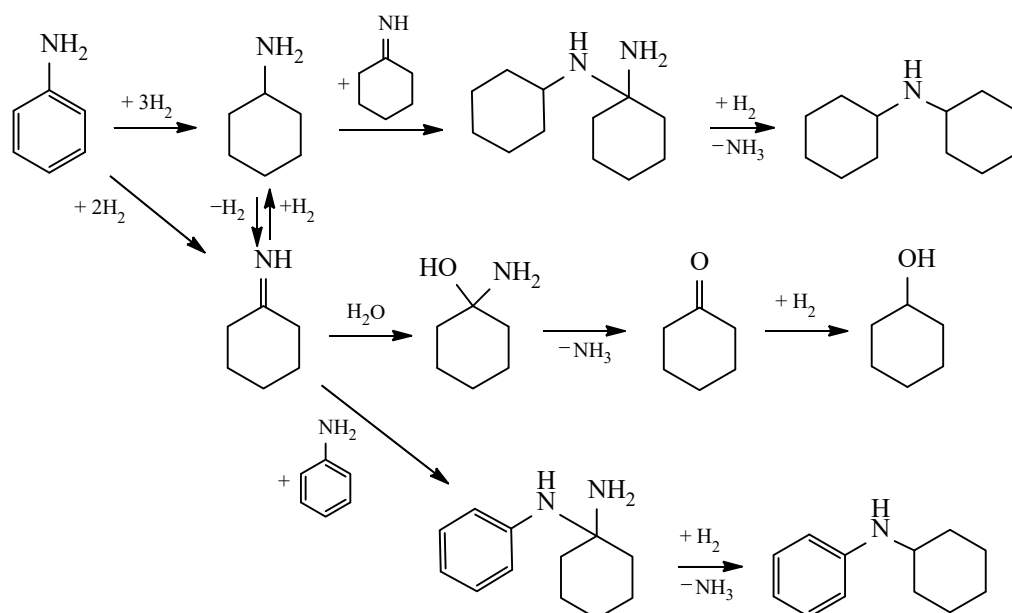
equaled 100%. However, the decrease in the activity of nickel particles on NaX zeolite and fast deactivation of the catalyst were observed at temperature below 180°C. When the substrate supply was stopped and the reactor was purged with hydrogen at 240°C during 30 min, the catalyst activity was fully restored.

In the cases of weakly acidic or basic carriers, the catalyst activity was retained with the decrease in temperature. For example, nickel nanoparticles applied on compressed magnesium oxide powder reduced nitroarene **1a** at 100–120°C. However, the catalytic activity was also decreased after 1 h operation in that temperature range, likely due to strong adsorption of nitrobenzene hampering its reduction with hydrogen. The catalyst activity was retained upon the increase in temperature to 180–200°C and purging with hydrogen (deblocking of active sites), that process was accompanied by desorption of up to 2.5 g of a mixture of compounds **1a** and **2a** from 3 g of the catalyst.

To prolong the catalyst activity at 100–120°C, nitroarene **1a** was diluted with an inert component (toluene), which allowed uniform distribution of the nitroarene and toluene molecules at the catalyst surface. Being more fugitive, toluene was easier desorbed from the catalyst surface, liberating the active sites for hydrogen adsorption and thus facilitating the reduction of nitroarene **1a**. The dilution at the nitrobenzene : toluene ratio 1 : 5 afforded aniline in quantitative yield at 120–180°C, the catalyst remaining active during 10 h of continuous operation. The catalyst was also active at temperature 80–100°C, allowing reduction of nitrobenzene with conversion of 94–96%.

As in the case of magnesium oxide, nickel nanoparticles applied on activated carbon (Norit RX 3 EXTRA) were active over wide temperature range (80–240°C), conversion of nitrobenzene being complete. In contrast to magnesium oxide, neither diffusion nor adsorption processes hindered the catalyst activity at 80–140°C, and the dilution of nitrobenzene was not needed. However, the catalyst on carbon exhibited lower selectivity with respect

Scheme 2.



to the target product. For example, gas-liquid chromatography (GLC) and mass spectrometry analyses of the reaction mixture obtained at 200°C revealed the presence of aniline (91.3 wt %), cyclohexylamine (1 wt %), cyclohexanone (1.6 wt %), cyclohexanol (0.4 wt %), phenylcyclohexylamine (2 wt %), and dicyclohexylamine (3.7 wt %). When the reaction temperature was increased to 300°C, the fraction of high-boiling side products was up to 20 wt %. The low selectivity could not be avoided even at 80–100°C: the content of aniline was as high as 93 wt %, but derivatives of cyclohexane were present as well.

The formation of side products (1–9 wt % in total) was also revealed when NaX zeolite or γ -Al₂O₃ were used as the catalyst carriers. On the other hand, aniline was formed with selectivity up to 100% using magnesium oxide as the carrier.

Hence, partial hydrogenation of the aromatic ring occurred under the probed conditions. The formation of cyclohexanone could be explained by hydrolysis of the imine intermediate (Scheme 2), and the presence of dicyclohexylamine could be due to the disproportionation of cyclohexylamine and cross-coupling with aniline, as had been observed earlier in the presence of nickel nanoparticles on a carrier [28].

It should be noted that the industrial catalysts such as NTK-4 and LOK exhibit the productiveness of 0.24 kg_{nb}/(kg_{cat} h) (nb = nitrobenzene) which is lower than that of the catalysts used in this study

[1.08 kg_{nb}/(kg_{cat} h) when using non-diluted nitrobenzene], thus evidencing the prospects of further studies and optimization of such catalysts.

In summary, we found that nickel nanoparticles immobilized on magnesium oxide, activated carbon, γ -alumina, or NaX zeolite exhibited catalytic activity towards reduction of nitroarenes. The experimental data revealed that the use of magnesium oxide as the carrier allowed aniline with selectivity up to 100%, whereas up to 20% of side products of aromatic ring hydrogenation were formed when using other carriers (NaX zeolite, γ -Al₂O₃, or activated carbon)

EXPERIMENTAL

Chromato–mass spectroscopy analysis was performed using a Saturn 2100 T/GC3900 instrument (EI, 70 eV). Quantitative GLC analysis of the reaction mixtures was performed using a Kristallyuks-4000M chromatograph ($t = 100$ – 210°C , $t_{\text{evap}} = 250^\circ\text{C}$, polar column HP-5, $l = 50$ m, $d = 0.32$ mm, carrier gas—nitrogen, flame ionization detector, $t_{\text{det}} = 250^\circ\text{C}$, solvent—acetonitrile). Scanning electron microscopy studies were performed using a FEI Versa 3D DualBeam instrument (working distance 10 mm, secondary electrons detector ETD, backscattered electrons detector CBS, elemental analysis method—EDS).

Catalyst preparation. The catalysts were prepared via impregnation of a carrier (fraction 1–1.5 mm) with an aqueous solution of nickel(II) chloride hexahydrate

during a day (0.7 g of nickel chloride per 2 g of NaX zeolite, 1 g of nickel chloride per 3 g of γ -Al₂O₃ or C_{act}, or 3 g of nickel chloride per 3 g of MgO) The saturated carrier was filtered off, washed with distilled water, and treated with an aqueous solution of sodium borohydride (3×0.1 g) at room temperature. Reduction with each portion was performed during 2 min. The reduced moist catalyst was loaded in a reactor and dried in a hydrogen stream at 300°C just prior to the reaction.

General procedure of the reaction. The reaction was performed in a continuous reactor plug-flow reactor at atmospheric pressure and temperature 80–240°C. At that temperature range, the reaction could occur either in the gas phase or in the gas–liquid–solid catalyst system, depending on the boiling point of the starting nitroarene. The laboratory reactor was made of a 12X18H10T steel tube (inner diameter 9 mm, heating zone height 50 mm) in an electric oven. Specific supply rate of the liquid mixture was of 0.6 or 0.9 L/(kg_{cat} h) depending on the catalyst amount. Hydrogen supply rate was of 300–1700 L/(kg_{cat} h) (10–15-fold molar excess)

Aniline (2a) a. Hydrogen [1330 L/(kg_{cat} h)] and nitrobenzene **1a** [0.6 L/(kg_{cat} h), uniflow with respect to hydrogen] were supplied on the Ni/NaX catalyst (3 g) at 200°C. Conversion 100%, selectivity and yield 90.7%. Mass spectrum, *m/e* (*I*_{rel}, %): 93.9 (13) [*M* + 1]⁺, 93.0 (100) [*M*]⁺, 92.0 (9), 66.0 (35), 65.0 (20), 63.0 (5)

b. Hydrogen [1330 L/(kg_{cat} h)] and nitrobenzene **1a** [0.6 L/(kg_{cat} h), uniflow with respect to hydrogen] were supplied on the Ni/C_{act} catalyst (3 g) at 200°C. Conversion 100%, selectivity and yield 91.3%.

c. The reaction was performed similarly using the Ni/ γ -Al₂O₃ catalyst (3 g) Conversion 100%, selectivity and yield 80.0%.

d. The reaction was performed similarly using the Ni/MgO catalyst (3 g) at 140°C. Conversion 100%, selectivity and yield 99.4%.

2-Methylaniline (2b) Hydrogen [1700 L/(kg_{cat} h)] and 2-nitrotoluene **1b** [0.9 L/(kg_{cat} h), uniflow with respect to hydrogen] were supplied on the Ni/NaX catalyst (2 g) at 200°C. Conversion 99.9%, selectivity 99.5%, yield 99.4%. Mass spectrum, *m/e* (*I*_{rel}, %): 108.0 (6) [*M* + 2]⁺, 107.0 (78) [*M* + 1]⁺, 106.0 (100) [*M*]⁺, 89.0 (7), 79.0 (12), 78.0 (6), 77.1 (16), 52.0 (7), 51.0 (7)

3-Methylaniline (2c) Hydrogen [1130 L/(kg_{cat} h)] and 3-nitrotoluene **1c** [0.6 L/(kg_{cat} h), uniflow with respect to hydrogen] were supplied on the Ni/NaX catalyst (3 g) at

240°C. Conversion 100%, selectivity and yield 99.3%. Mass spectrum, *m/e* (*I*_{rel}, %): 107.9 (7) [*M* + 2]⁺, 107.0 (69) [*M* + 1]⁺, 106.0 (100) [*M*]⁺, 79.0 (17), 77.0 (17), 51.0 (8)

4-Methylaniline (2d) Hydrogen [300 L/(kg_{cat} h)] and a mixture of 4-nitrotoluene **1d** {0.6 L/(kg_{cat} h) [molar ratio **1d** : toluene = 1 : 3]} 0.6 L/(kg_{cat} h) uniflow with respect to hydrogen] were supplied on the Ni/NaX catalyst (3 g) at 200°C. Conversion 96.9%, selectivity 97.5%, yield 94.5%. Mass spectrum, *m/e* (*I*_{OTH}, %): 108.0 (6) [*M* + 2]⁺, 107.0 (83) [*M* + 1]⁺, 106.0 (100) [*M*]⁺, 79.0 (11), 78.1 (7), 77.0 (13)

2-Methoxyaniline (2e) Hydrogen [1100 L/(kg_{cat} h)] and 2-nitroanisole **1e** [0.6 L/(kg_{cat} h), uniflow with respect to hydrogen] were supplied on the Ni/NaX catalyst (3 g) at 200°C. Conversion 100%, selectivity and yield 99.3%. Mass spectrum, *m/e* (*I*_{rel}, %): 123.9 (15) [*M* + 1]⁺, 123.0 (76) [*M*]⁺, 108.0 (88), 80.1 (100), 53.0 (26), 52.1 (13), 51.1 (8)

4-Methoxyaniline (2f) Hydrogen [1100 L/(kg_{cat} h)] and a mixture of 4-nitroanisole **1f** {0.6 L/(kg_{cat} h) [molar ratio **1d** : toluene = 1 : 3]} 0.6 L/(kg_{cat} h) uniflow with respect to hydrogen] were supplied on the Ni/NaX catalyst (3 g) at 200°C. Conversion 99.8%, selectivity 97.4%, yield 97.2%. Mass spectrum, *m/e* (*I*_{rel}, %): 123.9 (51) [*M* + 1]⁺, 123.0 (100) [*M*]⁺, 108.0 (63), 80.1 (66), 53.0 (14)

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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