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Colloid and Nanosized Catalysts in Organic Synthesis: IV.[1] Reduction of Nitroarenes with Hydrazine Hydrate Catalyzed with Metal Nanoparticles

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Abstract—Reduction of a series of nitroarenes with hydrazine hydrate catalyzed with colloid iron, cobalt, nickel, and copper particles has been studied. High catalytic activity of nickel and iron nanoparticles has been demonstrated. Special features of nitrobenzene reduction in the presence of cobalt particles have been revealed.

Keywords: catalyst, nanoparticles, nitroarenes, aniline

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Reduction of nitrobenzene and its homologs is a well studied industrial process. However, gas-phase reduction with heterogeneous catalysts is often too complicated and unreasonably expensive in view of its preparative application. The obsolete method of anilines preparation via reduction of nitrocompounds with iron filings in highly acidic medium is not universal.

The nitro group of aromatic compounds is known to be reduced with hydrazine hydrate under mild conditions at the Raney nickel [2]. This method suffers from the drawback of complicated Ni–Al alloy preparation, not suitable for laboratory practice. Hydrogenation processes utilizing nanodispersed catalysts have been recently studied in a number of works. For example, hydrogenation of aromatic compounds, dienes, and olefins with hydrogen in the presence of binary noble metal nanoparticles immobilized at the support has been reported in [3]. Almost quantitative hydrogenation of arenes in the presence of iridium and rhodium nanoparticles has been demonstrated in [4]. Reduction of chloronitrobenzene with hydrogen at 1 bar using platinum, palladium, and ruthenium nanoparticles or their mixtures has been described in [5]. Nitrobenzene has been reduced with hydrogen (1 bar) at nickel nanoparticles coated with palladium [6]. Reduction of 2-, 3-, 4-nitrophenols and 4-nitroaniline with sodium borohydride at gold or copper nanoparticles has been studied in [7, 8]. Gold nanoparticles have been used for nitroarenes hydrogenation with the amine–borane complex [9]. Application of platinum nanoparticles has allowed conversion of nitrobenzene to aniline at 25ºC and hydrogen pressure of 1 bar [10].

However, possibility of aromatic nitrocompounds reduction using metal nanoparticles as catalyst has not been systematically studied so far. We successfully reduced nitrobenzene and its homologs with hydrazine hydrate in the presence of nickel nanoparticles. The nickel nanoparticles were prepared as described elsewhere [11, 12], their average size being of 4–16 nm. The so obtained black suspensions were used as catalysts without isolation of nanoparticles or their stabilization in suspension. Both the nitrocompound and the metal precursor were reduced with hydrazine hydrate; hence, the whole synthesis was carried out as one-pot process starting from the nitrocompound, the nickel salt, and hydrazine hydrate.

The reduction was carried out via portionwise addition of nitrobenzene **Ia** or its homolog to the suspension of nickel nanoparticles in a mixture of hydrazine hydrate and 2-propanol at 20–80ºC. Reduction was almost immediate at 60–80ºC, accompanied with the mixture boiling up. The side alkylation of aniline with the formed 2-propanol was not observed. Yield of aniline **IIa** was close to quantitative, the

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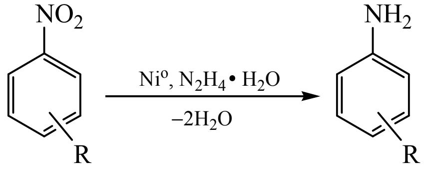
[1] For communication III, see [1].

product losses taking place during its isolation. Aniline content in the distilled product was of 100% (GLPC).



Ia–Ie **IIa–IIe**

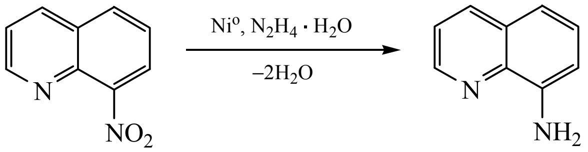
R = H (**a**), *o*-CH_3 (**b**), *n*-OC_2H_5 (**c**), *o*-NH_2 (**d**), *n*-NH_2 (**e**).

Reduction of 2-nitrotoluene, 4-ethoxynitrobenzene, 2-nitroaniline, and 4-nitroaniline proceeded similarly, but the heat evolution was somewhat lower. The yields of the reduction products were of 78–83%, and their properties were in agreement with the reference data [13].

The mass ratio of nitrobenzene and the catalyst used in this work was of 100 : 1 compared to 10 : 1 in the typical procedure involving the Raney nickel. Reduction of nitrobenzene in the presence of nickel nanoparticles was successfully carried out in the aqueous heterogeneous system upon vigorous stirring as well.

The nanoparticles dispersion was unstable towards coagulation and precipitation; therefore, the catalyst could be separated off the reaction mixture via careful filtration. Isolated from air, the catalyst could be used repeatedly without significant loss of activity. In contrast to the Raney nickel, the nanoparticles were not pyrophoric and were rapidly oxidized into the oxide without ignition in contact with air.

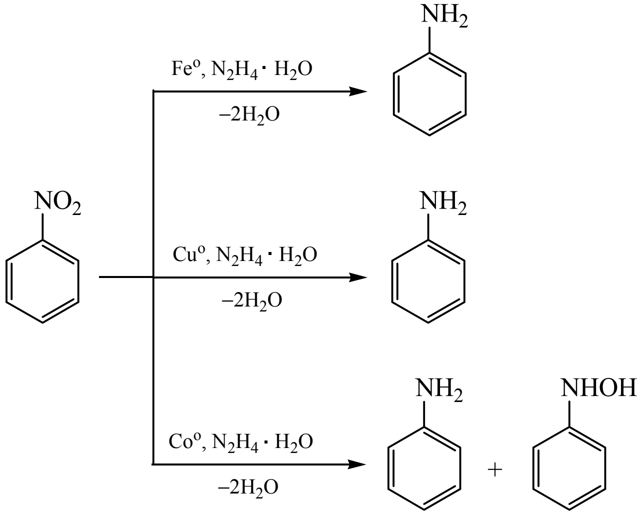
Colloid dispersion of the nickel nanoparticles was successfully used for reduction of 8-nitroquinoline **III** to 8-aminoquinoline **IV** with yield of 72%.



III **IV**

Creation of ferromagnetic colloid catalysts that can be easily removed and recycled has been among topical issues in the field of catalysis [14]. Keeping this in mind, we attempted reduction of nitrobenzene into aniline in the presence of iron nanoparticles prepared similarly to the nickel ones. The reduction was accompanied with significant heat evolution, being complete within several minutes at 40–80ºC. Yield of aniline was of 94%.

In contrast to Ni and Fe particles, reduction of nitrobenzene in the presence of cobalt nanoparticles led to formation of the side product, *N*-phenylhydroxylamine, along with aniline. Due to the low solubility in aqueous 2-propanol, it could be easily isolated in the form of white crystalline solid quickly becoming yellow in air. Its physical properties were in agreement with the reference data [15].



Selective reduction of nitroarenes to arylhydroxylamines catalyzed with platinum nanoparticles applied on carbon at 20ºC and hydrogen pressure of 1 bar was reported [16].

Apparently, colloid dispersions of all nanoparticles of the VIIIB group elements can act as catalysts of nitroarenes reduction. However, elements of other groups can catalyze such reduction reactions as well. For example, we carried out reduction of nitrobenzene with hydrazine hydrate in the presence of copper colloid dispersion, resulting in formation of aniline with 92% yield.

To summarize, the results reported in this work reveals promising potential of developing the nitroarenes reduction methods involving metal nanoparticles.

EXPERIMENTAL

GLPC analysis was carried out with the Crystallolux 4000M chromatograph (helium as carrier gas, HP-5 column, flame ionization detector, hexane as solvent, evaporator temperature 250ºC, programmed heating of the column at 12 deg/min from 100 to 210ºC).

Aniline Ia. *a.* A mixture of 0.6 g of NaOH, 1 mL of water, 50 mL of 2-propanol, and 61 g (1.22 mol) of hydrazine hydrate was heated to 60–80ºC. Then, a solution of 1 g (0.0054 mol) of $NiCl_2·6H_2O$ or 1.55 g (0.0054 mol) of $Ni(NO_3)_2·6H_2O$ in aqueous 2-propanol was added portionwise upon vigorous stirring. The so obtained black solution was refluxed during 30 min, and then 30 g (0.244 mol) of nitrobenzene was added dropwise avoiding violent boiling and foaming of the mixture. After addition of nitrobenzene, reaction mixture was refluxed during 10–15 min and filtered; 2-propanol was then distilled off. Water layer was separated off, and the organic layer was distilled to give 22.2 g on aniline (0.24 mol, 98%), bp 183–184ºC, n_D^{20} 1.5860 (bp 184ºC, n_D^{20} 1.5863 [13, p. 425]).

b. Iron nanoparticles prepared similarly from 0.5 g of NaOH, 1 mL of water, 50 mL of 2-propanol, 41 g (0.81 mol) of hydrazine hydrate, and 2.7 g (0.01 mol) of $FeCl_3·6H_2O$. Reduction of 20 g (0.163 mol) of nitrobenzene was performed similarly to yield 14.5 g (0.155 mol, 94%) of aniline, bp 182–184ºC, n_D^{20} 1.5862.

c. Cobalt nanoparticles were prepared similarly from 0.5 g of NaOH, 1 mL of water, 40 mL of 2-propanol, 25 g of hydrazine hydrate, and 2.4 g (0.01 mol) of $CoCl_2·6H_2O$. Reduction of 12.3 g (0.1 mol) of nitrobenzene was performed similarly to yield 6.1 g of aniline in the filtrate (0.065 mol, 65%), bp 183–185ºC, n_D^{20} 1.5865. The precipitate was twice extracted with boiling 2-propanol, and 3 g (0.028 mol) of *N*-phenylhydroxylamine precipitated from the filtrate upon cooling. Colorless crystals, mp 81–83ºC (mp 81ºC [15]).

d. Similarly, 27 g of hydrazine hydrate, 0.5 g of copper nanoparticles in 30 mL of 2-propanol, and 12.3 g (0.1 mol) of nitrobenzene gave 8.6 g (0.092 mol, 92%) of aniline was obtained, bp 182–184ºC, n_D^{20} 1.5862.

***o*-Toluidine (IIb).** Prepared similarly from 0.5 g of NaOH, 1 mL of water, 30 mL of 2-propanol, 18.3 g (0.365 mol) of hydrazine hydrate, 2.4 g (0.01 mol) of $NiCl_2·6H_2O$, and 10 g (0.073 mol) of 2-nitrotoluene. Yield 6.5 g (0.061 mol, 83%), bp 197–200ºC, n_D^{20} 1.5717 (bp 199–200ºC, n_D^{20} 1.5720 [13, p. 991]).

***o*-Phenylenediamine (IIc)**. Prepared similarly from 0.5 g of NaOH, 1 mL of water, 30 mL of 2-propanol, 25 g of hydrazine hydrate, 0.8 g (0.0028 mol) of $Ni(NO_3)_2·6H_2O$, and 13.8 g (0.1 mol) of 2-nitroaniline. Yield 8.4 g (0.078 mol, 77.5%), mp 99–100ºC (mp 100–102ºC [13, p. 1039]).

***p*-Phenylenediamine (IId)**. Prepared similarly from 0.5 g of NaOH, 1 mL of water, 30 mL of 2-propanol, 25 g of hydrazine hydrate, 0.8 g (0.0028 mol) of $Ni(NO_3)_2·6H_2O$, and 13.8 g (0.1 mol) of 4-nitroaniline. Yield 8.8 g (0.082 mol, 82%), mp 138–140ºC (mp 139–141ºC [13, p. 1041]).

4-Ethoxyaniline (IIe). Prepared similarly from 0.5 g of NaOH, 1 mL of water, 30 mL of 2-propanol, 25 g of hydrazine hydrate, 0.8 g (0.0028 mol) of $Ni(NO_3)_2·6H_2O$, and 16.7 g (0.1 mol) of 4-nitrophenetol. Yield 10.3 g (0.075 mol, 75%), bp 248–249ºC (bp 248.6ºC [13, p. 1037]).

8-Aminoquinoline (IV). Prepared similarly from 0.25 g of NaOH, 1 mL of water, 15 mL of 2-propanol, 15 g of hydrazine hydrate, 0.4 g (0.0014 mol) of $Ni(NO_3)_2·6H_2O$, and 8.7 g (0.05 mol) of 8-nitroquinoline. Yield 5.2 g (0.036 mol, 72%), mp 63–66ºC (mp 64–65ºC [17]).

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