ISSN 1070-3632, Russian Journal of General Chemistry, 2018, Vol. 88, No. 3, pp. 410–417. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © Zh.V. Ignatovich, A.L. Ermolinskaya, Ya.M. Katok, E.V. Koroleva, A.N. Eremin, V.E. Agabekov, 2018, published in Zhurnal Obshchei Khimii, 2018, Vol. 88, No. 3, pp. 382–389.

Catalytic Activity of Nickel Nanoparticles in the Reaction of Reduction of Nitroarenes

**Zh. V. Ignatovich[a], A. L. Ermolinskaya[a], Ya. M. Katok[b],
E. V. Koroleva[a]*, A. N. Eremin[a†], and V. E. Agabekov[a]**

[a] *Institute of Chemistry of New Materials, National Academy of Sciences of Belarus,
ul. F. Skoriny 36, Minsk, 220141 Belarus
e-mail: evk@ichnm.basnet.by

[b] *Belarusian State Technological University, Minsk, Belarus*

Received October 5, 2017

Abstract—Techniques for the production of nickel and nickel-cobalt nanoparticles and of their composites with polyvinylpyrrolidone were developed. The catalytic activity of the resulting compounds towards reduction of substituted nitroarenes was examined.

Keywords: catalyst, nickel nanoparticles, cobalt nanoparticles, composites, nitroarene reduction

DOI: 10.1134/S1070363218030064

The principal synthesis route to amines, which are key intermediates in synthesis of important chemical products, including dyes, pesticides, oil additives, and drugs, is catalytic reduction (in particular, hydrogenation) of nitro derivatives under high temperature and pressure in the presence of noble metals (Pt, Pd, and Au).

Reduction of nitroarenes often stops in an intermediate stage, yielding hydroxylamines, hydrazines, and azoarenes as byproducts. High chemoselectivity of the reaction is also required in the case of complex polyfunctional nitro derivatives containing carboxyl, ester, nitrile, aldehyde, and other groups. Despite high activity and selectivity exhibited by Pt, Pd, and Au catalysts, search for effective catalysts based on Ni, Co, Fe, and Cu or on their oxides is a priority task [1–3].

For the synthesis of aromatic amino derivatives, reduction with hydrazine hydrate in the presence of Raney nickel was proposed [4]. This method afforded a means of preparing m-phenylenediamine derivatives in a 75–80% yield from appropriate nitroaniline derivatives. Hydrazine hydrate, used as hydrogen donor in catalytic reduction of nitro compounds, is converted into harmless nitrogen gas and water, which makes it an environmentally preferable reagent. However, in the case of *N*-(3-nitrobenzylidene) derivatives of aromatic amines, hydrazine hydrate in the presence of Raney nickel reduced the C=N bond simultaneously with the nitro group in the molecule and, in some cases, the aromatic heterocycle as well.

Nanocatalysts possessing unique physical and chemical properties due to a large specific surface area represent a new generation of catalytic systems. Their catalytic activity and selectivity can be significantly enhanced by controlling the size, morphology, shape, composition, and electronic structure of such particles [5, 6].

Herein, we synthesized nickel and nickel-cobalt nanoparticles, as well as their composites with polyvinylpyrrolidone, and used the resulting compounds as catalysts in reduction of substituted nitroarenes with hydrazine hydrate.

Nanocatalysts based on Ni and Co nanoparticles were prepared by reduction of Ni and Co nitrates in a DMSO–H_2O medium with sodium tetrahydroborate dissolved in DMSO. The resulting sol of the particles was sonicated for 2 h, whereupon the nanoparticles were separated by centrifugation and washed twice with distilled water and/or with distilled water and ethanol (methanol).

[†] Deceased.

Nickel nanoparticles prepared by reduction of nickel nitrate with sodium tetrahydroborate are able to catalyze hydrolysis of $NaBH_4$, so the synthesis procedure requires its 2–5-fold excess [7]. Efficient formation of nickel nanoparticles also depends on the presence in the synthesis medium of DMSO which accelerates the formation of particles, prevents their agglomeration, and protects them against oxidation. The optimum DMSO concentration is 50 vol % [8].

$$\begin{gathered}Ni(NO_3)_2 + 2NaBH_4 + 6H_2O \\ \rightarrow Ni^{0\downarrow} + 7H_2 + 2NaNO_3 + 2H_3BO_3.\end{gathered}$$

The $Ni(NO_3)_2 \cdot 6H_2O$ reduction proceeds rapidly and is accompanied by gas evolution and blackening of the reaction medium. With increasing initial concentration of $Ni(NO_3)_2 \cdot 6H_2O$ the black color increases in intensity. The absorption intensity at 250 nm for the nickel nanoparticles in the synthesis medium and after purification has no clearly pronounced maximum and tends to decrease with wavelength increasing within 250–900 nm.

The nickel nanoparticles formed in a 5.0 mM $Ni(NO_3)_2 \cdot 6H_2O$ medium are known to be easily oxidized, and this is accompanied by a change in the sol color to gray, due obviously to the formation of oxide NiO [or $Ni(OH)_2$] which coats the particle surface with a dense film [9]. The nickel particles sol obtained in a 10–20 mM $Ni(NO_3)_2 \cdot 6H_2O$ medium preserved its black color, which indicates its resistance to oxidation. The presence of van der Waals forces between the nanoparticles and the strive of the system towards minimum total surface energy lead to formation of nickel nanoparticle agglomerates whose size varies from 300 to 1100 nm with increasing $Ni(NO_3)_2 \cdot 6H_2O$ concentration in the synthesis medium (Fig. 1). The optimal $Ni(NO_3)_2 \cdot 6H_2O$ concentration for the formation of stable nickel nanoparticles with an average size of 600 nm is 15 mM.

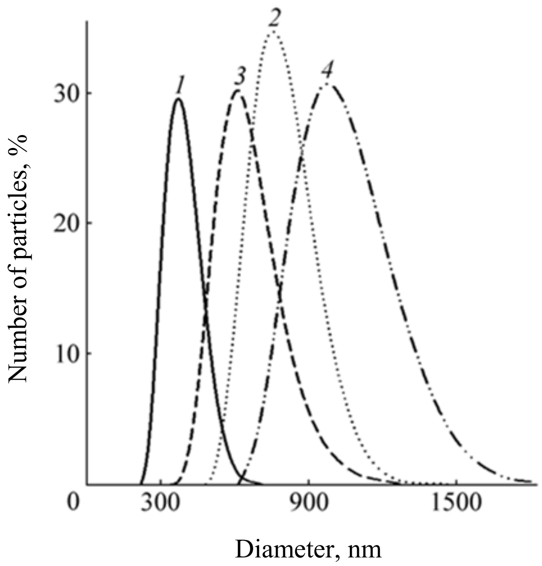


Fig. 1. Hydrodynamic diameter distribution for the nickel nanoparticle sols obtained in the medium with (*1*) 5, (*2*) 10, (*3*) 15, and (*4*) 20 mM $Ni(NO_3)_2 \cdot 6H_2O$.

To prevent agglomeration, the nickel nanoparticles were modified with polyvinylpyrrolidone (PVP). The Ni/PVP and (Ni/Co)/PVP composites were prepared by mixing an aqueous solution of PVP K-90 with nickel nitrate or with a mixture of nickel and cobalt nitrates, followed by addition of a sodium tetrahydroborate solution in dimethyl sulfoxide. The resulting sol was sonicated, whereupon the precipitate of the composite nanoparticles was separated by centrifugation, washed with distilled water, and stored at ~6°C.

As shown by IR and X-ray electron spectroscopic examinations [5], the carbonyl groups in PVP get strongly bound to the nickel nanoparticle surface, thereby preventing magnetic coupling between the particles [5]. Modification with polyvinylpyrrolidone enhances the aggregation stability of particles without significantly altering their electronic and magnetic properties [10]. In 1 mL of the reaction medium, ~43 mg of the PVP/Ni composite is formed.

By contrast to polyvinylpyrrolidone, the PVP/Ni composite did not show IR absorption at 2923, 1423 and 1387, 933 and 845 cm^{-1}, though exhibited shared absorption bands with nickel nanoparticles at 1462, 1035–1060, and 636–664 cm^{-1}. After purification of the PVP/Ni composite the absorption spectrum of the particles remained unchanged, with a maximum absorption intensity observed at 230–250 nm.

The size of the nickel and nickel-cobalt nanoparticles and composites was estimated by dynamic light scattering (Table 1) and transmission electron microscopy. The revealed significant differences in the particle size are apparently due to agglomeration of the nanoparticles and composites in an aqueous medium. For example, the average size of the nickel nanoparticles is 35–40 nm, with hydrodynamic diameter of the nickel nanoparticles agglomerates remaining practically unchanged upon sol dilution, 650–680 nm (Table 1). The ζ-potential of the nickel nanoparticles in distilled water is 20.1–24.9 mV irrespective of the initial $Ni(NO_3)_2 \cdot 6H_2O$ concentration. When the sol is diluted with distilled water, the potential-determining

Table 1. Hydrodynamic characteristics of the nickel and nickel-cobalt nanoparticles and their composites dispersed in distilled water

Sample	Degree of sol dilution	Average particle diameter, nm	PdI	ζ-Potential, mV	Conductivity, mS/cm
Ni Nanoparticles	0	690	0.28		
	20	680	0.18		
	40	650	0.19	20.1	0.012
	100	680	0.36	24.9	0.006
Ni/Co	0	165	0.942		
	2			5.20	1.65
	10	520	0.752	12.8	0.508
	100	870	0.827		
PVP/Ni	20	2500	0.12		
	40	1800	0.29	6.9	0.042
	100	1900	0.40	6.0	0.033

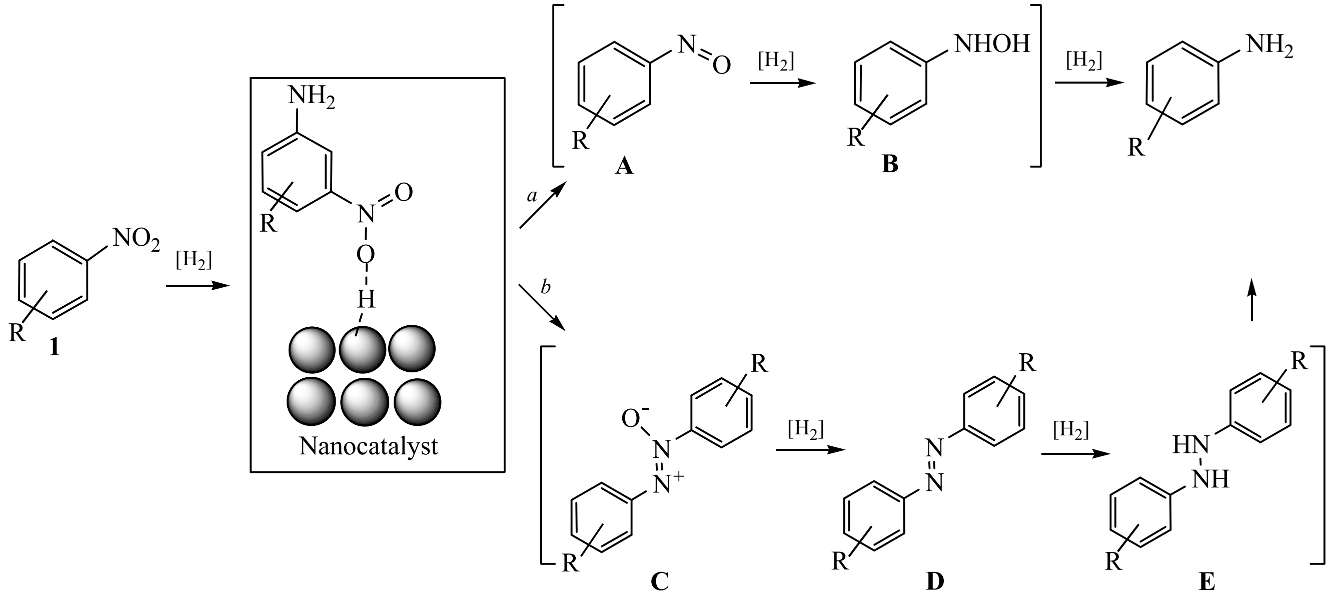
ions are concentrated on the nickel nanoparticles surface, thereby increasing the ζ-potential.

For the Ni/Co composite the average particle size is 45–50 nm; the hydrodynamic diameter of the agglomerates in a concentrated sol is 165 nm, and 10- and 100-fold dilution of the sol caused it to increase to 520 and 870 nm, respectively (Table 1).

The PVP/Ni nanoparticles also tend to agglomerate in an aqueous medium. The average hydrodynamic diameter of the PVP/Ni agglomerates significantly exceeds that of the nickel nanoparticles; also different are their ζ-potentials (Table 1), which agrees with the data from [11, 12].

The catalytic activity of the nanocatalysts was examined with the reaction of reduction of substituted nitroanilines. The reduction of the nitro group can be carried out both along the path of direct reduction (*a*) and along the condensation path (*b*) through the formation of intermediates **A**–**E** [13] (Scheme 1).

Scheme 1.



The reduction reactions catalyzed by platinum group metals (Pd, Ru, Pt) follow the direct reduction pathway *a* to form nitroso (**A**) and hydroxylamine derivatives (**B**) [14]. In the reaction using the nickel nanocatalyst, alongside the target 1,3-phenylenediamine, azobenzene **D** (*m/z* 212 $[M]^+$) was isolated as a byproduct, indicating the condensation pathway *b*.

The use of a 5–8-fold excess of hydrazine hydrate led to formation of 1,3-phenylenediamine from 3-nitroaniline **1** in water within 4 h in a 5–20% yield both at room temperature and at 35–40°C. When the temperature was increased to 75–80°C, the target product was obtained in a preparative yield of 80–90%, with fivefold excess of hydrazine hydrate being optimal.

The catalytic activity of the PVP/Ni composite depends on the molecular weight of polyvinylpyrrolidone bound to the nickel nanoparticles. The conversion of 3-nitroaniline and the yield of 1,3-phenylenediamine were maximal in the reactions catalyzed by composites **2** and **5** containing polyvinylpyrrolidone with molecular weight of 10 and 360 kDa, respectively (Fig. 2). In the case of composite **5** the reaction time was shortened from 4 to 2 h.

Increase in the catalyst amount from 1.0 to 2.5 mg/mL enabled complete conversion of nitroaniline to 1,3-phenylenediamine (90% yield). In the reaction catalyzed by the PVP/Ni composite that was not washed to remove the synthesis medium components the yield of the target 1,3-phenylenediamine was 45%, and the return of the initial 3-nitroaniline, 50%. Thus, obtaining a catalytically active PVP/Ni composite requires washing its surface to remove the sodium nitrate and boric acid formed in the synthesis, which hinder the chemisorption of 3-nitroaniline on the particles surface.

The PVP/Ni composites based on polyvinylpyrrolidone having molecular weight of 24 and 40 kDa exhibited low catalytic activity, with conversion and yield of 1,3-phenylenediamine not exceeding 50% (Fig. 2). These data highlight the importance of the structural organization of the PVP/Ni composite as determined by the molecular weight of polyvinylpyrrolidone. Nickel nanoparticles are most accessible for the substrate when sorbed on a high-molecular-weight polyvinylpyrrolidone. The use of polyvinylpyrrolidone with the molecular weight of 24 and 40 kDa in an aqueous medium leads to formation of agglomerates with the nickel nanoparticles evidently located inside [11, 12].

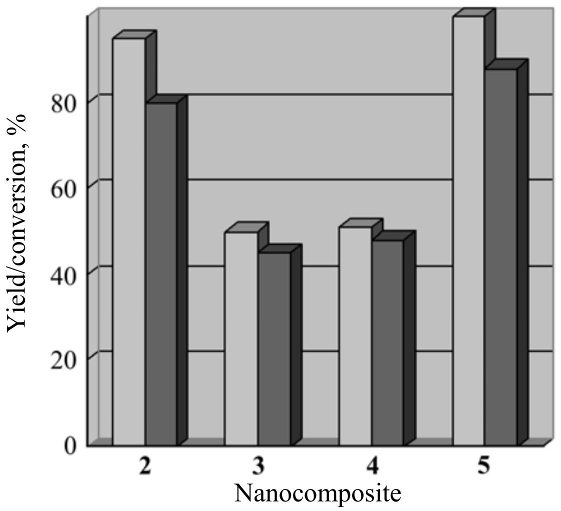


Fig. 2. Nitroaniline conversion and yield of 1,3-phenylidenediamine, achieved with PVP/Ni nanocomposites **2**–**5** based on polyvinylpyrrolidone with the molecular weight of (**2**) 10, (**3**) 24, (**4**) 40, and (**5**) 360 kDa.

The nickel nanoparticles and their composites synthesized were employed in reduction of more complex aromatic systems, nitropyrimidines **6**–**8** containing pyridine and substituted aniline moieties (Scheme 2). Under the conditions of reduction of 3-nitroaniline **1**, target amines **12**–**14** and **16** were formed in trace amounts, probably because of solubility of the substrate, so the solvent used in the reaction was methanol or ethanol.

Reduction of **1**–**10** in the alcohol, catalyzed by Ni/Co and PVP/(Ni/Co) composites, gave the target amines in 74–82% yields (Table 2). The Ni/Co nanoparticles composite proved to be the most effective catalyst. When used in ethanol, it afforded target amines in 75–85% yields; the reaction times were shorter, and 100% conversion of the substrate was achieved within 45 min for nitroarenes **1**, **7**, **9**, and **10** and within 20 min, for nitropyrimidines **6** and **8**.

A known route to improve the catalytic activity of nanoparticles is their heat treatment modifying the particles structure and morphology [16]. However, calcination of the Ni/Co composite at 400°C for 4 h did not significantly increase its catalytic activity in the conversion of nitroarene **7**. The calcined Ni/Co in methanol caused no substantial changes in the reaction time and in the yield of the target product, and in ethanol it proved to be a less effective catalyst, with complete conversion of the substrate achieved within 120 min (Table 2).

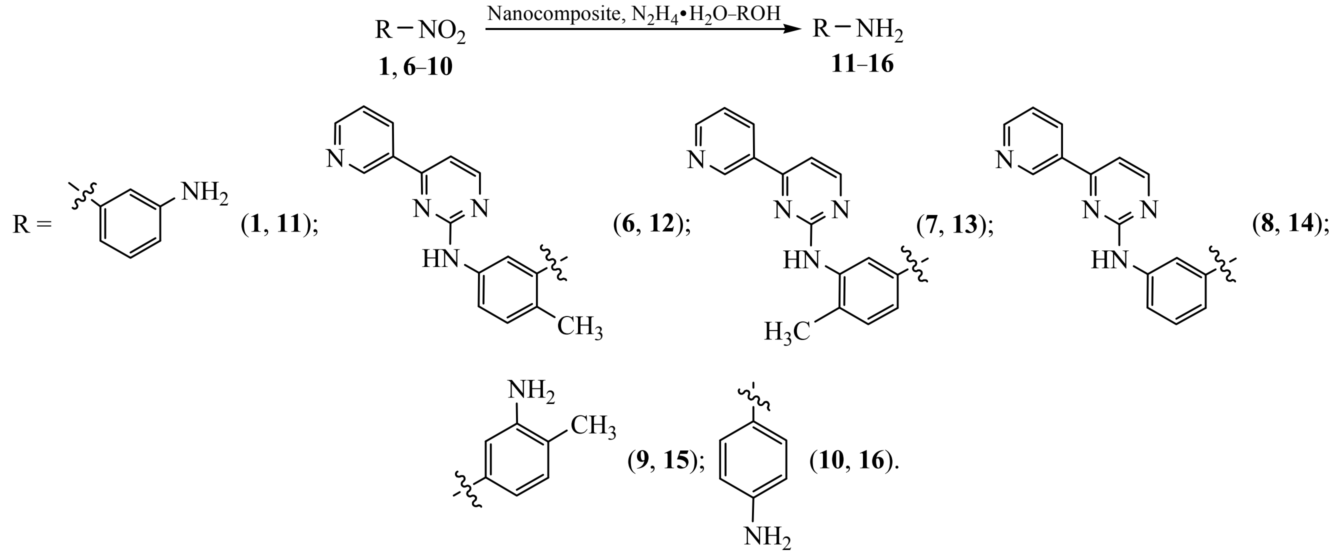
Table 2. Conditions and results of the catalytic reduction of nitroarenes **1, 6–10** to substituted anilines **11–16**

Substrate	Catalyst	$N_2H_4{\cdot}H_2O$, equiv.	Solvent	*T*, °C	Reaction time, min	Conversion, %	Yield of amine, %
1	Ni	5–8	H_2O	75–80	240	100	83
	PVP/Ni	5	H_2O	75–80	120	100	90
	Ni/Co	5	EtOH	75–78	45	100	81
6	PVP /Ni	8	MeOH	55–60	60	100	80
	PVP/(Ni/Co)	5	MeOH	55–60	120	100	74
	Ni/Co	5	EtOH	75–78	20	100	74
7	PVP/Ni	8	MeOH	55–60	180	60	46
	Ni/Co	5	MeOH	55–60	90	100	69
	Ni/Co[a]	5	MeOH	55–60	60	100	76
	Ni/Co[a]	5	EtOH	75–78	120	100	70
	Ni/Co	5	EtOH	75–78	45	100	77
8	PVP/Ni	5	MeOH	55–60	240	40	28
	PVP/Ni	8	MeOH	55–60	180	50	39
	PVP/(Ni/Co)	5	MeOH	55–60	120	66	48
	PVP/(Ni/Co)	5	MeOH	55–60	120	100	75
	Ni/Co	5	EtOH	75–78	20	100	77
9	Ni/Co	5	EtOH	75–78	45	100	82
10	Ni/Co	5	EtOH	75–78	45	100	82

[a] Nanocomposite was calcined at 400°C for 4 h.

Essential for catalytic efficiency of the Ni/Co composite is the ratio of the initial concentrations of nickel and cobalt nitrates. For the composite obtained at $[Ni(NO_3)_2{\cdot}6H_2O] : [Co(NO_3)_2{\cdot}6H_2O]$ ratio of 5 : 1 the yield of the target amine exceeded that in the case of the 2 : 1 ratio: 74% against 48%.

Scheme 2.



Thus, in reactions of reduction of nitroarenes with hydrazine hydrate the nanocatalysts based on nickel and nickel-cobalt nanoparticles are comparable in efficiency with Raney nickel skeletal catalyst, and their use satisfies the “green” chemistry principles [17].

EXPERIMENTAL

Hydrazine hydrate (Vekton, Russia), 3-nitro-aniline, 4-nitroaniline, 4-methyl-3-nitroaniline (Sigma-Aldrich, the United States), 2-methyl-5-nitroaniline (Acros Organics, the United States), $Ni(NO_3)_2\cdot 6H_2O$ (Alfa Aesar, FRG), $Co(NO_3)_2\cdot 6H_2O$ (Merck, FRG), $NaBH_4$ (Carl Roth, FRG), and polyvinylpyrrolidone K 90 (Sigma-Aldrich, the United States) were used.

Absorption spectra were measured on a CM2203 spectrofluorimeter (SOLAR, Belarus). IR spectra were obtained for KBr pellets on a Bruker Tenzor 27 recorded Fourier spectrometer tablets. Hydrodynamic characteristics of the particles were determined by dynamic laser light scattering using a Zetasizer Nano ZS analyzer (Malvern, United Kingdom). Mass spectra were measured on a Thermo Scientific Trace GC Ultra/DSQ II quadrupole gas chromatograph-mass spectrometer in direct injection mode. Thin layer chromatography was carried out on Merck DC-Plastikfolien Kieselgel 60 F_{254} plates in chloroform–methanol (85 : 15) and butanol–ethanol–NH_4OH (8 : 1 : 1). Elemental analysis was performed using a VARIO Micro Cube CHNS analyzer. Melting points were determined on a Kofler block.

Synthesis of nickel nanoparticles. To a mixture of aliquots of distilled water, 200 mM $Ni(NO_3)_2\cdot 6H_2O$, and DMSO, 300 mM $NaBH_4$ dissolved in DMSO was added. The resulting sol was stirred for 5 min, then sonicated (Elmasonic S 30 H bath, Germany) for 2 h with temperature rising from 20 to 58°C. The components of the reaction medium were used in the following concentrations: 15 mM for $Ni(NO_3)_2\cdot 6H_2O$ and 45 mM for $NaBH_4$; the water:DMSO ratio was 1 : 1. The nickel nanoparticles were separated from the synthesis medium by centrifuging the resulting sol at 10000 rpm speed for 10 min; the precipitate was washed twice with distilled water, and the purified particles were dispersed in distilled water. Also used were precipitates of nickel nanoparticles, that were washed initially with distilled water and then with ethanol or methanol. The nickel nanoparticles sols and precipitates were stored at ~6°C.

Synthesis of PVP/Ni composite. To a mixture of 5.81 mL of an aqueous solution of PVP K 90 (M 360000 g/mol) containing 3.23 mg/mL polyvinipyrrolidone and 563 μL of 200 mM $Ni(NO_3)_2\cdot 6H_2O$, three 375-μL aliquots of 300 mM solution of $NaBH_4$ in DMSO were added at 1-min intervals, and the resulting sol was sonicated for 2 h. The components of the reaction medium were used in the following concentrations: 2.5 mg/mL PVP, 15 vol % DMSO, 15 mM $Ni(NO_3)_2\cdot 6H_2O$, and 45 mM $NaBH_4$. The resulting PVP/Ni sol was centrifuged at 10000 rpm speed for 10 min; the precipitate was washed thrice with distilled water and stored at ~6°C.

Synthesis of Ni/Co composite. To a mixture of aliquots of distilled water, 200 mM $Ni(NO_3)_2\cdot 6H_2O$, and 200 mM $Co(NO_3)_2\cdot 6H_2O$, three 458-μL aliquots of 300 mM solution of $NaBH_4$ in DMSO were added at 1-min intervals under stirring, and the resulting sol was sonicated for 2 h. The components of the reaction medium were used in the following concentrations: 15 vol % DMSO, 15 mM $Ni(NO_3)_2\cdot 6H_2O$, 3.0 mM $Co(NO_3)_2\cdot 6H_2O$, and 55 mM $NaBH_4$. The Ni/Co sol was centrifuged at 10000 rpm speed for 10 min. The particles precipitate was washed with distilled water and then with ethanol and either stored wet at ~6°C or calcined at 400°C for 4 h.

Synthesis of PVP/(Ni/Co) composite. Composite samples were prepared at different $Co(NO_3)_2\cdot 6H_2O$ concentrations (3.0 and 7.5 mM). To a mixture of aliquots of 3.39 mg/mL PVP K 90 (M 360000 g/mol), distilled water, 200 mM $Ni(NO_3)_2\cdot 6H_2O$, and 200 mM $Co(NO_3)_2\cdot 6H_2O$, 375-μL aliquots of 300 mM $NaBH_4$ were added at 1-min intervals under stirring. The resulting sol was sonicated for 2 h. The components of the reaction medium were used in the following concentrations: 2.5 mg/mL PVP, 2.5 vol % DMSO, 15 mM $Ni(NO_3)_2\cdot 6H_2O$, 3.0 or 7.5 mM $Co(NO_3)_2\cdot 6H_2O$, and 45–55 mM $NaBH_4$. The sol was centrifuged at 9000 rpm speed for 10 min; the resulting precipitate was washed twice with distilled water and once with methanol and used while wet.

Reduction of 3-nitroaniline1 in the presence of the nickel nanoparticles and PVP/Ni composite. To a suspension of 0.1 g (0.7 mmol) of 3-nitroaniline **1** in 0.5 mL of H_2O, 1.0 mL of the hydrous sol of the particles (0.07 mmol, 0.1 equiv.) was added at room temperature, and after 5 min 0.3 mL (5-fold excess) of hydrazine hydrate was poured into the resulting mass. After 15 min, the reaction mixture was foamed; it was stirred at 70–80°C for 4 h (TLC control), and upon completion of the reaction the catalyst was separated by filtration, and the precipitate was washed with ethanol. The filtrate was evaporated to reduce by 2/3 its original volume and acidified with 0.4 mL of concentrated HCl to pH 1, and the resulting 1,3-phenylenediamine dihydrochloride precipitate was washed with dilute HCl (1 : 1), dried, and recrystallized from a methanol–hexane mixture.

1,3-Phenylenediamine dihydrochloride (11). Yield 88–90%, white crystals, mp >205°C (decomp.). IR spectrum, ν, cm^{-1}: 3410, 2965 b (NH), 1608, 1584, 1600, 1490, 1200, 1185. Mass spectrum, *m/z* (I_{rel}, %): 108.05 (90) $[M - \text{H}]^+$. Found, %: C 39.79; H 5.59; N 15.46; Cl 39.17. $C_6H_{10}Cl_2N_2$. Calculated, %: C 39.80; H 5.57; N 15.47; Cl 39.16.

Reduction of nitroarylaminopyrimidines 6–8 and nitroanilines 1, 9, 10. *a*. To 0.177 g (0.5 mmol) of **1** or **6–10,** the nanocatalyst (0.05 mmol, 0.1 equiv.) dispersed in 2 mL of methanol was added at room temperature, after which 0.3 mL of hydrazine hydrate (3.5 mmol, 5 or 8 equiv.) was poured dropwise into the resulting mass. The reaction mixture was refluxed for 1–4 h; after ~15 min of heating it started to foam. Warm reaction mixture was filtered through Celite, washed with methanol, and the combined filtrate was evaporated. The residue was dissolved in 10 mL of ethyl acetate, washed with water, dried, and evaporated to reduce by 2/3 its original volume, and the product was precipitated by the addition of petroleum ether.

b. To a suspension of 0.5 mM of nitro derivative in 1 mL of ethanol, the Ni/Co or PVP(Ni/Co) sol (0.05 mmol in 1 mL of ethanol) was added under stirring and heating to 50°C. After 5–7 min, 0.18 mL of hydrazine hydrate (3.5 mmol, 5 equiv.) was added. The reaction mixture was refluxed for 0.3–0.75 h (TLC control). Upon completion of the reaction, warm reaction mixture was filtered through Celite, washed with ethanol, and the combined filtrate was evaporated. The residue was dissolved in 10 mL of ethyl acetate, washed with water, evaporated to reduce by 2/3 its original volume, and the product was precipitated by the addition of petroleum ether. To isolate the products of reduction of compounds **1, 9,** and **10,** the filtrate was acidified with 0.4 mL of concentrated HCl to pH 1. The dihydrochloride precipitated was washed with dilute HCl (1 : 1), dried, and recrystallized from a methanol–hexane mixture.

***N*-(4-Methyl-3-aminophenyl)-4-(pyrid-3-yl)pyrimidin-2-amine (12).** Yield 74–80%, yellow crystals, mp 160–162°C (mp 164–165°C [14]). IR spectrum, ν, cm^{-1}: 3440–3360, 1630, 1580, 1450. Mass spectrum, *m/z* (I_{rel}, %): 277 (100) $[M]^+$, 262 (78) $[M - \text{CH}_3]^+$, 121 (9), 77 (5.5).

***N*-(2-Methyl-5-aminophenyl)-4-(pyrid-3-yl)pyrimidin-2-amine (13).** Yield 69–77%, yellow crystals, mp 138–140°C (mp 134–136°C [15]). IR spectrum, ν, cm^{-1}: 3340, 3235, 3044, 1580, 1551, 1450. Mass spectrum, *m/z* (I_{rel}, %): 277 (100) $[M]^+$, 262 (90) $[M - \text{CH}_3]^+$, 121 (20), 77 (4.5).

***N*-(3-Aminophenyl)-4-(pyrid-3-yl)pyrimidin-2-amine (14).** Yield 75–77%, yellow crystals, mp 89–91°C (mp 89–92°C [14]). IR spectrum, ν, cm^{-1}: 3414, 3315, 1630, 1579, 1560, 1410. Mass spectrum, *m/z* (I_{rel}, %): 262 (100) $[M]^+$, 263 (80) $[M + 1]^+$, 247 (11) $[M - \text{NH}_2]^+$, 156 (6.3).

4-Methyl-1,3-phenylenediamine dihydrochloride (15). Yield 82%, white crystals, mp > 200°C (decomp.). IR spectrum, ν, cm^{-1}: 3300, 2980 (NH), 1612, 1580, 1475, 1200, 1190. Mass spectrum, *m/z* (I_{rel}, %): 122.05 (100) $[M]^+$, 108.02 (52) $[M - \text{CH}_3]^+$, 78.01 (26), 51 (15), Found, %: C 43.00; H 6.22; N 14.35; Cl 36.37. $C_7H_{12}Cl_2N_2$. Calculated, %: C 43.10; H 6.20; N 14.36; Cl 36.35.

1,4-Phenylenediamine dihydrochloride (16). Yield 82%, white crystals, mp > 220°C (decomp.). IR spectrum, ν, cm^{-1}: 3995, 2923 (NH), 1620, 1512, 1435, 1250, 1130. Mass spectrum, *m/z* (I_{rel}, %): 108.05 (100) $[M]^+$, 80.01 (44), 51 (17). Found, %: C 39.79; H 5.58; N 15.47; Cl 39.17. $C_6H_{10}Cl_2N_2$. Calculated, %: C 39.80; H 5.57; N 15.47; Cl 39.16.

REFERENCES

1. Saha, A. and Ranu, B., *J. Org. Chem*., 2008, vol. 73, no. 17, p. 6867. doi 10.1021/jo800863m
2. Cantillo, D., Moghaddam, M.M., and Kappe, C.O., *J. Org. Chem*., 2013, vol. 78, no. 9, p.4530. doi 10.1021/jo400556g
3. Blaser, H.U., Steiner, H., and Studer, M., *Chem. Cat. Chem.*, 2009, vol. 1, p. 210. doi 10.1002/cctc.200900129
4. Ignatovich, Zh.V., Kadutskii, A.P., Koroleva, E.V., Baranovskii, A.V., and Gusak, K.N., Russ. *J. Org. Chem*., 2009, vol. 45, no. 7, p. 1083. doi 10.1134/S1070428009070148
5. Mitsudome, T. and Kaneda, K., *Chem. Cat. Chem.*, 2013, vol. 5, no. 7, p. 1681. doi 10.1002/cctc.201200724

6. Chang, L.L., Erathodiyil, N., and Ying, J.Y., *Acc. Chem. Res.*, 2013, vol. 46, no. 8, p. 1825. doi 10.1021/ar300197s
7. Wade, R.C., Holan, D.G., Hughes, A.N., and Hui, B.C., *Catal. Rev. Sci. Eng.*, 1976, vol. 14, no. 2, p. 211.
8. Sinyutich, Yu.V., Ignatovich, Zh.V., Koroleva, E.V., Eremin, A.N., and Agabekov, V.E., *Izv. Nats. Akad. Nauk Belarusi, Ser. Khim. Nauk*, 2017, no. 1, p. 14.
9. Ershov, B.G., *Ross. Khim. Zh.*, 2001, vol. 45, no. 3, p. 20.
10. Wang, W., Xu, Y., Wang, D.I.C., and Li, Z., *J. Am. Chem. Soc.*, 2009, vol. 131, no. 36, p. 12892. doi 10.1021/ja905477j
11. Ely, T.O., Amiens, C., and Chaudret, B., *Chem. Mater.*, 1999, vol. 11, no. 3, p. 526. doi 10.1021/cm980675p
12. Couto, G.G., Klein, J.J., Schreiner, W.H., Mosca, D.H., Oliveira, A.J.A., and Zarbin, A.J.G., *J. Colloid Interface Sci.*, 2007, vol. 311, no. 2, p. 461. doi 10.1016/j.jcis.2007.03.045
13. Rai, R.K., Mahata, A., Mukhopadhyay, S., Gupta, S., Li, P.-Z., Nguyen, K.T., Zhao, Y., Pathak, B., and Singh, S.K., *Inorg. Chem.*, 2014, vol. 53, p. 2904. doi 10.1021/ic402674z
14. Koroleva, E.V., Ignatovich, Zh.V., Ermolinskaya, A.L., Sinyutich, Yu.V., Baranovskii, A.V., and Makhnach, S.A., *Izv. Nats. Akad. Nauk Belarusi, Ser. Khim. Nauk*, 2013, no. 3, p. 79.
15. Szakacs, Z., Beni, S., Vagra, Z., Orfi, L., Keri, G., and Noszal, B., *J. Med. Chem.*, 2005, vol. 48, p. 249. doi 10.1021/jm049546c
16. Vikarchuk, A.A., Gryzunova, N.N., and Romanov, A.E., in *Perspektivnye materialy i tekhnologii* (Advanced Materials and Technologies), Vitebsk: Vitebsk. Gos. Tekhnol. Univ., 2015, vol. 2, p. 253.
17. Polshettiwar, V. and Varma, R.S., *Green Chem.*, 2010, vol. 12, p. 743. doi 10.1039/B921171C