Nickel catalysis for hydrogenation of *p*-dinitrobenzene to *p*-phenylenediamine

E. V. Shuvalova,[a]★ O. A. Kirichenko,[a] and L. M. Kustov[a,b]

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation
Fax: +7 (499) 135 5328. E-mail: evshouvalova@yandex.ru
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Build. 3, 1 Leninskie Gory, 119992 Moscow, Russian Federation

The activity of supported nickel catalysts (5—20% Ni) in the hydrogenation of *p*-dinitrobenzene to *p*-phenylenediamine was investigated. The catalysts were obtained by urea-induced precipitation. Activated carbon, alumina, titania, and silica gel were evaluated as supports. The most active catalysts, 5%Ni/TiO_2 and 20%Ni/SiO_2, provided 50—54% yields of *p*-phenylenediamine at complete dinitrobenzene conversion.

Key words: hydrogenation, nickel catalysis, aromatic dinitro compounds.

Hydrogenation of nitro groups in aromatic dinitro compounds is the key method for the preparation of aromatic diamines both in the laboratory practice and in industry. This reaction is carried out by reduction of the nitro groups of a dinitro compound with iron in acid medium (Béchamp method) or by catalytic hydrogenation of the initial dinitroarene over heterogeneous catalysts.

As a rule, catalytic hydrogenation of 1,3-dinitrobenzene (1,3-DNB) and 1,4-dinitrobenzene (1,4-DNB) is carried out using catalysts containing noble metals, in particular, Pd, Pt, and lately also Au[1—5] or Raney Ni catalyst.[6,7] Although Raney Ni has a high catalytic activity, the role of this catalyst in the industrial practice is modest, because of its pyrophoricity, high content of nickel metal, and labor-consuming preparation.[6,7]

Supported nickel catalysts represent an alternative to the Raney Ni. Owing to their relatively low cost, high catalytic activity, and higher safety, they are rather widely used in industry.[8—10] Meanwhile, the details of application of these catalysts for hydrogenation of nitro groups in aromatic compounds are poorly covered in the literature. The catalysts containing 20% Ni supported on silica gel provide a high conversion and selectivity in the hydrogenation of nitro groups of 1,3-DNB dissolved in ethanol at 100 °C, a hydrogen pressure of 2.6 MPa, and the DNB : Ni ratio of 17. Under the same conditions, the diatomite-, TiO_2-, MgO-, or Al_2O_3-supported catalysts are less active and non-selective, which is attributable to the lower surface area of active nickel particles and strong interaction of the metal with the support, which gives rise to poorly reducible bimetallic oxide phases.

This communication describes an attempt to prepare supported nickel catalysts with a decreased Ni content that would possess high activity and selectivity in the hydrogenation of dinitrobenzenes at moderate temperatures and pressures.

Experimental

Preparation of supported Ni catalysts. Nickel was deposited on the support from the nickel precursor, which was then reduced to to Ni^0. Unlike impregnation of the support with a solution of nickel nitrate according to incipient wetness method,[11] this procedure gives rise to particles of nickel precursors on the support surface, so that these particles decompose in air or in hydrogen without interacting with the support. The following commercial materials were used as supports: silica gel KSKG, granulated TiO_2-based Aerolyst support, TiO_2 Aeroxide P-25, active alumina A-6, and activated carbon SKT-6A. Due to the markedly different nature of supports used for deposition of the nickel precursor of similar composition and high degree of dispersion, the procedure of urea-induced precipitation on heating of a support suspension in a nickel salt solution was used.[12]

The catalysts were prepared in the following way. A support in an amount needed to obtain the desired content of nickel was added to an aqueous solution containing $Ni(NO_3)_2$ (0.12—0.37 mol L^{-1}) and urea (2.4—3.3 mol L^{-1}). The suspension was heated to 96 °C and kept at this temperature up to complete precipitation of nickel. The completeness of precipitation was verified by the test reaction with a 1% solution of dimethylglyoxime. The precipitate was separated from the mother liquor, washed with distilled water, and dried at 110 °C. The samples were reduced in a hydrogen flow at 350—400 °C. The samples cooled down to ~20 °C were either passivated in an argon flow with a low content of oxygen (105 ppm), or covered with hexane and transferred into a glass vial. The samples, both annealed in air and dried were reduced. The annealing and reduction temperatures were chosen on the basis of published data[11—14] and analysis of the results of temperature-programmed reduction of annealed samples.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 0034—0038, January, 2017.

Determination of catalytic activity. *p*-Dinitrobenzene (*p*-DNB) (98%, Acros Organics) was used as the initial substrate. The reaction was carried out in a 100-cm^3 autoclave at a hydrogen pressure of 0.5—2 MPa and a reaction temperature of 60—170 °C. In all experiments, the amounts of the initial *p*-DNB and the catalyst were 0.4 and 0.2 g, respectively. Tetrahydrofuran (30 mL) was used as the solvent, as it was shown in preliminary experiments that hydrogenation to diaminobenzene takes place in THF in the presence of nickel-containing reference catalysts and the 5%Ni/P-25 catalyst. When ethanol was used as the solvent, no products of nitro group hydrogenation were formed even upon complete conversion of DNB, while in DMF, the products of DMF reactions with the substrate and nitroaniline were formed. The commercial Ni/kieselguhr catalyst (TU 38.101396-89E) and nickel chromium catalyst (OST 113-03-4001-90) were tested as the reference catalysts.

During the reaction, samples of the reaction mixture were taken at intervals through a special high-pressure sampling valve. The concentrations of the reactants and products in the samples were determined on a CrystaLux-4000-M chromatograph with a 30 m×0.25 mm Supelco capillary column with the OV-1 stationary phase and a flame ionization detector. Nitrogen was used as the carrier gas. The evaporator and detector temperatures were 240 °C. Analysis was carried out in the temperature programmed mode: the column was initially heated to 150 °C, held at this temperature for 6 min, heated from 150 °C to 240 °C at 20 °C min^{-1}, and held at 240 °C for 10 min.

Eicosane ($C_{20}H_{42}$) was used as the internal standard for quantitative calculations of *p*-DNB conversion and selectivity; the retention time of eicosane is close to the retention times of the reaction products, but the peaks are well resolved. Prior to the experiment, an exact portion of the internal standard (100 mg with a 0.1 mg accuracy) was added to the reaction mixture and the sample was analyzed before the reaction. The analyte to standard peak area ratio was used for determination of the concentrations of compounds detected in the reaction mixture.

The results of chemical analysis of the reaction mixture were used to calculate the DNB and internal standard peak area ratio, and the change in this ratio was used to calculate the selectivities to nitroaniline and diaminobenzene.

Results and Discussion

The *p*-DNB hydrogenation conditions were selected in the preliminary experiments carried out at a temperature of 60 °C and a hydrogen pressure of 1.3 MPa using the commercial Ni/kieselguhr catalyst. These experiments showed that the *p*-DNB conversion to *p*-phenylenediamine (PDA) was relatively slow under these conditions. Indeed, the *p*-DNB conversion within 60 min was <10% with a selectivity of 50%, while complete hydrogenation of the nitro groups took place in 150 min. When the reaction temperature was increased to 85—100 °C, the time required for complete reduction of the nitro groups decreased. It was found that under relatively mild conditions (85 °C, 1.3 MPa), complete conversion can also be attained in 60 min (Fig. 1). However, this requires a low DNB : Ni ratio (1.3), which is inapplicable for industrial processes. In order to search for a more active catalyst operating under high loads and to select the optimal support, we prepared catalysts with 5% nickel content on various supports and tested them in the hydrogenation of DNB with variation of temperature and hydrogen pressure. All catalysts were pre-reduced at 350 °C in a hydrogen flow and then passivated in argon containing an oxygen admixture. Table 1 and Figures 1—3 summarize the results of experiments on *p*-DNB transformation catalyzed by Ni/kieselguhr and by catalysts containing 5% nickel on various supports. It can be seen from these data that in the presence of a catalyst with a high nickel content, Ni/kieselguhr, complete conversion of *p*-DNB occurs over a short period of time, the selectivity to PDA being 54%; the reaction involves the intermediate formation of nitroaniline, which is then fully hydrogenated to PDA (see Fig. 1). Similarly, hydrogenation *via* nitroaniline was also observed on the NT-27-390H catalyst (see Fig. 2). However, in the case of catalysts synthesized on silica gel, no nitroaniline was detected. The absence of nitroaniline in the reaction products can be attributed to the fact that hydrogenation of the second nitro group is much faster than hydrogenation of the first one. A different hydrogenation mechanism without the intermediate formation of nitroaniline cannot be ruled out either.

The nature of the support has a substantial effect on the catalytic properties of the nickel catalysts. Alumina- and carbon-supported catalysts were shown to provide a nearly complete conversion of *p*-DNB only at 160—170 °C in 4—5 h; however, diaminobenzene was not formed in these cases and the selectivity to nitroaniline was relatively low (see Table 1). The catalyst supported on the TiO_2 Aerolyst was even less active than other catalysts. However, catalysts containing TiO_2 Aeroxide P-25 as the support provided complete conversion of *p*-DNB to nitroaniline and to PDA *via* successive hydrogenation; furthermore, this

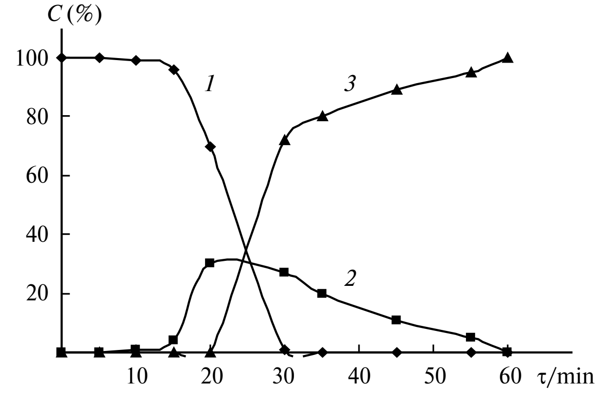


Fig. 1. Effect of the time (τ) of *p*-dinitrobenzene hydrogenation catalyzed by Ni/kieselguhr on the composition of the reaction mixture: *p*-dinitrobenzene (*1*), *p*-nitroaniline (2), *p*-phenylenediamine (*3*); 85 °C, hydrogen pressure 1.3 MPa.

Table 1. Results of *p*-dinitrobenzene conversion experiments on the synthesized nickel catalysts*

Catalyst	Support	[Ni] (%)	*T*/°C	τ/min	DNB conversion	Selectivity to NA	Selectivity to PDA
						%	
NA-1-350H	γ-Al_2O_3	5	145	60	45	7	0
			168	300	93	82	0
NC-1-350H	AU SKT 6A	5	145	60	9	98	0
			163	240	98	38	0
	Oxidized	5	138	30	2.3	0	0
	AU SKT 6A		160	300	95	64	0
NT-1-350H	TiO_2 Aerolyst	5	145	90	3.4	1	0
			165	240	59	43	0
	TiO_2 P-25	5	98	70	99.9	0	54
OANiS-239-380H	SiO_2 KSKG	5	95	180	0	0	0
	SiO_2 KSKG	10	106	180	77	0	0
	SiO_2 KSKG	20	90	80	99.9	0	52
Ni/K-400H	Kieselguhr	54	85	60	99.9	0	54

* Reaction conditions: hydrogen pressure 1.3 MPa, *p*-DNB weight 0.4 g, catalyst weight 0.2 g.

took place at a lower temperature and over shorter time periods (see Table 1).

In order to investigate the effect of nickel content in the catalyst on the catalytic properties, samples with nickel contents of 5, 10, and 20% were prepared, with silica gel being used as the support. The results of determination of the activity of these catalysts are also presented in Table 1. The catalysts containing 5 and 10% nickel were virtually inactive toward hydrogenation of the *p*-DNB nitro groups even at elevated temperature of 120 °C. However, increasing the nickel content in the catalyst to 20% resulted in complete reduction of nitro groups in 80 min at a temperature of 90 °C. The intermediate formation of nitroaniline was not detected in this case and the selectivity to PDA did not exceed 52% (see Fig. 3).

The nickel catalyst NT-27-390H, which we synthesized, has a higher productivity than the commercial Ni/kieselguhr catalyst in which the nickel content is an order of magnitude greater and, hence, the load on nickel is lower than in the NT-27-390H sample (Table 2).

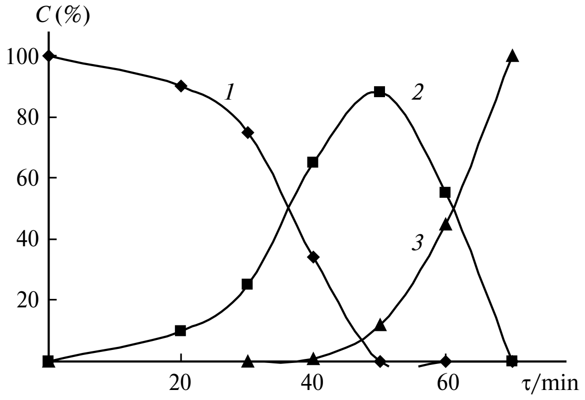


Fig. 2. Effect of the time (τ) of *p*-dinitrobenzene hydrogenation catalyzed by NT-27-390H on the composition of the reaction mixture: *p*-dinitrobenzene (*1*), *p*-nitroaniline (2), *p*-phenylenediamine (*3*); 98 °C, hydrogen pressure 1.3 MPa.

The low selectivities of the Ni/K-400H, OANiS-238-380H, and NT-27-390H nickel catalysts in the hydrogenation of nitro groups can be attributed to the contribution of side reactions of hydrogenation intermediates. Apparently, hydrogenation of nitro groups proceeds according to Scheme 1.

The reduction of nitro group to the amino group proceeds through the formation of all possible nitrogen derivatives, including nitroso groups and hydroxylamine derivatives (Scheme 2).[15]

These compounds can react both with one another and with the primary amine, which is the final reduction product. This gives azobenzenes, azoxybenzenes, and possibly hydrazobenzenes, which form resinous side products on further condensation. These compounds could not be reliably identified by GLC, as they are

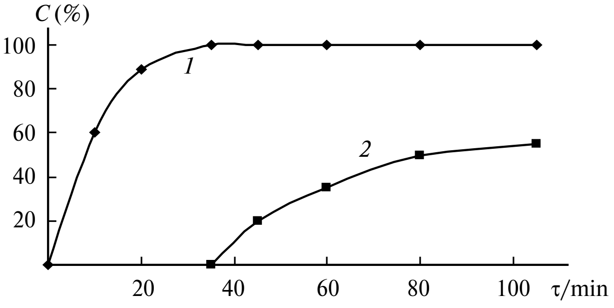


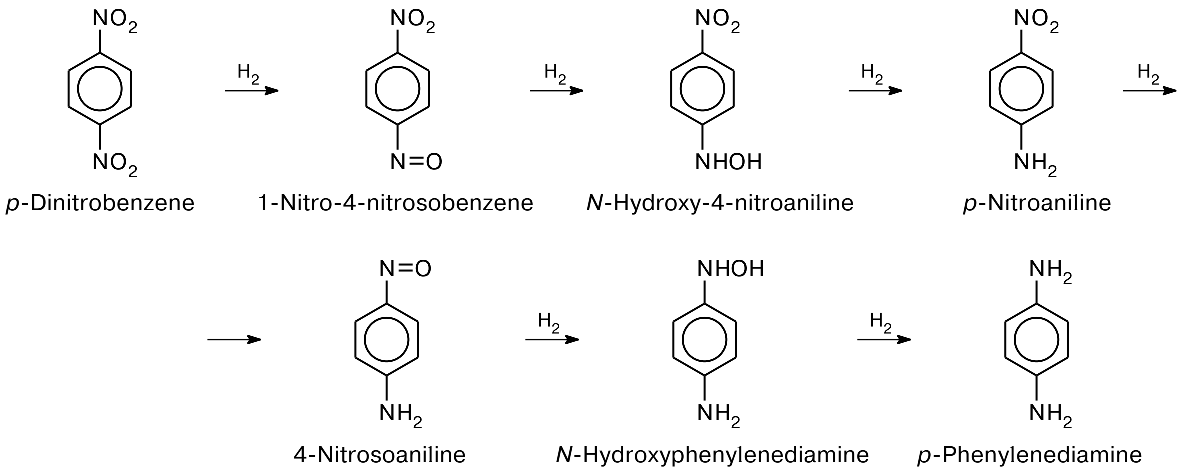
Fig. 3. Conversion (*1*) and selectivity to *p*-phenylenediamine (*2*) *vs.* time (τ) of *p*-dinitrobenzene of hydrogenation catalyzed by OANiS-238-380H; 90 °C, hydrogen pressure 1.3 MPa.

Table 2. Parameters of the *p*-DNB hydrogenation process

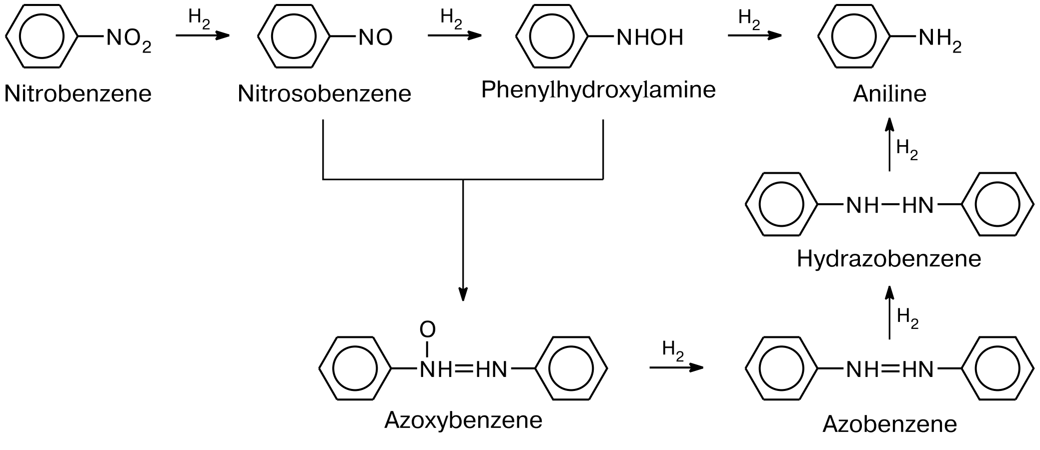
Catalyst	Load /mol of DNB (mol of Ni)$^{-1}$	T/°C	$\tau_1{}^a$	$\tau_2{}^b$	$S_{PDA}{}^c$ (%)	$\eta_{PDA}{}^d$ /mol of PDA (mol of Ni)$^{-1}$ h^{-1}
			min			
Ni/K-400H	1.3	85	30	60	54	0.7
OANiS-238-380H	4	90	20	80	52	1.6
NT-27-390H	14	98	50	70	54	6.5

[a] Time required for complete conversion of *p*-DNB.
[b] Time required for complete conversion of nitroaniline.
[c] Selectivity at complete conversion of nitroaniline.
[d] Catalyst productivity per unit time.

Scheme 1



Scheme 2



thermally unstable and have high molecular weights. The target product can be separated from the resinous impurities by crystallization with partial solvent evaporation.

Thus, the catalysts containing 20% nickel supported on silica and 5% nickel supported on titania showed high activity toward selective hydrogenation of *p*-DNB to PDA under mild conditions.

This work was financially supported by the Russian Science Foundation (No. 14-50-00126).

References

1. M. M. Telkar, J. M. Nadgeri, C. V. Rode, R. V. Chaudhari, *App. Catal. A: General*, 2005, **295**, 23.
2. H. Rojas, G. Borda, P. Reyes, M. Brijaldo, J. Valencia, *J. Chil. Chem. Soc.*, 2011, **56**, 793.
3. J. J. Martinez, H. Rojas, L. Vargas, C. Parra, M. H. Brijaldo, F. B. Passos, *J. Mol. Catal. A: Chem.*, 2014, **383—384**, 31.
4. F. Cádenas-Lizana, S. Gómez-Quero, N. Perret, M. A. Keane, *Catal. Sci. Technol.*, 2011, **1**, 652.
5. H. Rojas, G. Borda, M. Brijaldo, P. Reyes, *Reac. Kinet. Mech. Cat.*, 2012, **105**, 271
6. RF Pat. 2085554, 1997; http://www.freepatent.ru/patents/2085554.
7. E. F. Litvin, V. Z. Sharf, *Ross. Khim. Zh.* (*Zh. Ross. khim. o-va im. D. I. Mendeleeva*), 2000, **44**, No. 2, 90 [*Mendeleev Chem. J.* (*Engl. Transl.*), 2000, **44**, No. 2].
8. RF Pat. 2333796, 2009; http://www.freepatent.ru/patents/2333796.
9. E. Z. Golosman, V. N. Efremov, *Katal. v Prom-sti* [*Catalysis in Industry*], 2012, No. 5, 36 (in Russian).
10. RF Pat. 2330718, 2008; http://www.freepatent.ru/patents/2330718.
11. Y. Liu, J. Chen, J. Zang, *Chin. J. Chem. Eng.*, 2007, **15**, 63—67.
12. J. W. Geus, A. Jos van Dillen, *Preparation of Supported Catalysts by Deposition—Precipitation*, in *Handbook of Heterogeneous Catalysis*, 2nd ed., Vol **1**, Eds G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Wiley-VCH Verlag GmbH& Co. KGaA, Weinheim, Germany, p. 428—467.
13. L. A. M. Hermans, J. W. Geus, in *Preparation of Catalysts II*, *Studies in Surface Science and Catalysis*, Eds B. Delmon, P. Grange, P. Jacobs, G. Poncelet, Elsevier, Amsterdam, 1979, p. 113.
14. R. Burch, A. R. Flambard, in *Preparation of Catalysts III*, *Studies in Surface Science and Catalysis*, Eds G. Poncelet, P. Grange, P. A. Jacobs, Elsevier, Amsterdam, 1983, p. 311.
15. L. Zhao, J. Chen, J. Zhang, *J. Mol. Catal. A: Chem.*, 2006, **246**, 140.

Received June 14, 2016;
in revised form June 29, 2016