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# Hydrogenation of nitroarenes on silica-supported copper catalyst

**Elena V. Shuvalova* and Olga A. Kirichenko**

*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: evshouvalova@yandex.ru*

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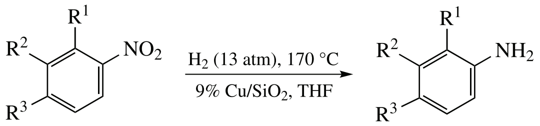
**A 9% $Cu/SiO_2$ catalyst prepared by the deposition–precipitation technique was active in the hydrogenation of substituted nitrobenzenes at 170 °C and 13 atm $H_2$ in a batch reactor. Nitro groups were selectively reduced to $NH_2$ groups except for the case of 5-bromo-1,3-dinitrobenzene. The selectivity of the overall process is somewhat suppressed by inevitable formation of azo compounds and traces of tars due to the reactions of the obtained amines with nitroso intermediates.**



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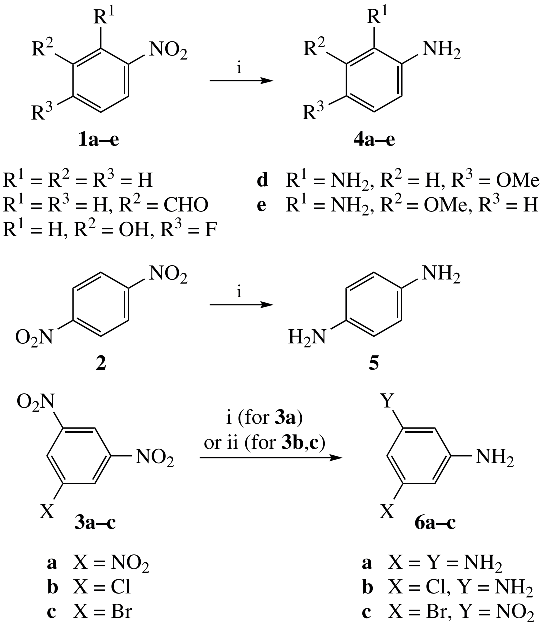
Aromatic amines are widely used as raw materials for various bulk and fine chemicals, drugs, dyes, polymers, additives, *etc*. The most important method for their synthesis is reduction of the corresponding nitroarenes. Although the classical Beauchamp method is still used for obtaining some of arylamines, the catalytic techniques are much more important since they are convenient, versatile and highly effective. Based on the nature of a reducing agent, the catalytic reduction of nitroarenes is classified as (*1*) the direct catalytic hydrogenation at high pressures and (*2*) the catalytic transfer hydrogenation using the reductants such as hydrazine, $NaBH_4$, alcohols, or formic acid.[1–3] The direct hydrogenation is preferable from standpoint of the process sustainability. Noble metals, including palladium,[4] platinum,[5] ruthenium,[6] gold,[7] silver[8] and iridium[9] were tested as the catalysts. Recently, they have been gradually displaced by less expensive 3d metals.[3] Nickel is the most studied and practically used non-noble metal for hydrogenation of nitroarenes, with the hydrogenation being performed over both monometallic Ni catalysts[10,11] and the Ni-based catalysts that contain other metals and different supports.[12] However, nickel is recognized to be highly hazardous, and its usage drops, especially in Europe. Iron-based catalysts were proposed to substitute the nickel-based ones,[3,13–15] however their catalytic activity is relatively low in direct hydrogenation,[3] and they are more suitable for transfer hydrogenation of nitroarenes.

Last decade, copper nanoparticles were successfully employed as the catalysts for the transfer reduction of nitroarenes,[3] yet the direct hydrogenation of nitroarenes with molecular hydrogen over Cu-based catalysts was documented scarcely.[16–18] In the presence of Cu-based catalysts ‘0.11 mol%/N-CNTs’, some nitroarenes were reduced to the corresponding amines within several hours under hydrogen atmosphere in acetic acid and ethanol at room temperature.[16] A copper-based intermetallic material $LaCu_{0.67}Si_{1.33}$ was active in selective hydrogenation of substituted nitrobenzenes into the corresponding anilines, the yields having exceeded 92% at 3.0–5.0 MPa $H_2$ and 120 °C.[17] However, the preparation of those catalysts was rather complicated.

In our previous publications,[18–20] we reported on the catalytic activity of the silica-supported copper nanoparticles and copper-based phyllosilicate prepared by a simple deposition–precipitation method using thermal hydrolysis of urea, with no preliminary calcination or reduction with hydrogen having been utilized.[18] Both types of catalysts were highly active and selective in hydrogenation of nitrobenzene into aniline as well as *p*-dinitrobenzene to *p*-nitroaniline or *p*-phenylenediamine, respectively, in THF at 13 bar $H_2$ and 110–170 °C. The catalytic behavior was shown to depend on the Cu content, support texture and temperature of thermal treatment of the Cu phyllosilicate phase. The highest activity and 99% selectivity to amines at complete conversion of nitrobenzene and *p*-dinitrobenzene were achieved over the catalysts with a 9 wt% Cu loading that was prepared on the $SiO_2$ support with the high specific surface area.[18] This value of the Cu content was optimal for reduction of *p*-dinitrobenzene in the case of the catalyst preparation on the commercial $SiO_2$ support with the low specific surface area.[19] Physicochemical studies of catalysts confirmed formation of chrysocolla-like structure in the samples prepared on both types of support.[18,19]

The goal of the present work was to reveal the possibility of selective reduction of nitroarenes into the corresponding aminoarenes bearing other functional groups using the direct catalytic hydrogenation with molecular hydrogen over the Cu hydrosilicate catalyst with the optimal Cu loading of 9 wt%. The catalyst was synthesized by the deposition–precipitation method using thermal hydrolysis of urea as described previously.[19,20] The prepared catalyst, which was only dried at 110 °C (catalyst **A**), was used in reaction tests (Scheme 1, Table 1). Catalyst **A** is active in hydrogenation of nitro group of several nitroarenes **1a**–**e**, **2** and **3a**–**c** under the conditions selected, and the activity and selectivity depends on the nature of a substituent and its position in the aromatic ring. The complete conversion of the substrate has been reached over the dried catalyst for nitrobenzene **1a**, *p*-dinitrobenzene **2** and 1,3,5-trinitrobenzene **3a**, the selectivity for **1a**, **3a** being higher than for **2** (see Table 1, entries 1, 6, 7). Replacement of one nitro group for a halogen atom in the trinitrobenzene molecule caused a decrease in the catalytic



**Scheme 1** *Reagents and conditions*: i, $H_2$ (initial pressure 13 atm, 30 atm at 170 °C), catalyst **A** ($Cu/SiO_2$ dried, 9 wt%), 170 °C, 2.5 h; ii, $H_2$ (initial pressure 13 atm, 30 atm at 170 °C), catalyst **B** ($Cu/SiO_2$ calcined, 9 wt%), 170 °C, 3–12 h.

**Table 1** Hydrogenation of nitroarenes over $Cu/SiO_2$ catalysts.[a]

| Entry | Substrate | Procedure[b] | Conversion (%) | Product | Selectivity (%) |
|---|---|---|---|---|---|
| 1 | **1a** | A | 100 | **4a** | 96 |
| 2 | **1b** | A | 100 | **4b** | 42 |
| 3 | **1c** | A | 80 | **4c** | 64 |
| 4 | **1d** | A | 68 | **4d** | 94 |
| 5 | **1e** | A | 100 | **4e** | 73 |
| 6 | **2** | A | 100 | **5** | 73 |
| 7 | **3a** | A | 100 | **6a** | 90 |
| 8 | **3b** | A | 12 | **7** | 82 |
| 9 | **3b** | B | 49[c] | **6b** | 31[c] |
| 10 | **3c** | A | 0 | mixture | – |
| 11 | **3c** | B | 29/60/80[d] | **6c** | 54/46/40[d] |

[a] Stainless-steel 100 ml autoclave, substrate loading 0.2 g (0.8–1.6 mmol), THF (15 ml), catalyst loading 0.1 g, 13 atm $H_2$ (30 atm upon heating), 170 °C, 2.5 h. [b] Procedure A with dried 9% $Cu/SiO_2$, procedure B with calcined 9% $Cu/SiO_2$. [c] Reaction time 6 h. Other products: 1-nitro-3-nitrosobenzene, (3-nitrophenyl)hydroxylamine; azoxybenzene, azobenzene; hydrazobenzene (not detected by GLC). [d] Reaction time 3, 6 and 12 h, respectively.

activity, namely, the conversion of 5-chloro-1,3-dinitrobenzene **3b** was only 12%, while the main product was 3-nitroaniline **7**, partially reduced and hydrodechlorinated substrate. No conversion of 5-bromo-1,3-dinitrobenzene **3c** occurred over dried catalyst **A**.

The catalyst became considerably more efficient after its calcination at 300 °C (catalyst **B**), however a noticeable substrate conversion and selectivity towards valuable products was observed after more than 2.5 h processing (see Table 1, entries 9 and 11). This can be accounted for by the removal of structural water molecules from copper hydrosilicate of chrysocolla-like structure,[20,21] which resulted in formation of the new centers for adsorption of nitro group, and allowed for decrease in the reduction temperature of Cu phase.[19,22,23] Reduction of both nitro groups has been reached in 5-chloro-1,3-dinitrobenzene **3b** with no chlorine elimination, yet the selectivity was only 31% at the substrate conversion of 49%. The catalyst exhibited the lower activity in reduction of 1-bromo-2,4-dinitrobenzene **3c**, namely, only one nitro group was reduced, and the selectivity towards 5-bromo-3-nitroaniline **6c** decreased from 54 to 40%, when the substrate conversion grew from 29 to 80%.

The high substrate conversion and selectivity of $NO_2 \rightarrow NH_2$ reduction were achieved for other four nitroarenes bearing additional functional groups (see Scheme 1 and Table 1). Under the conditions of hydrogenation that resulted in a complete selective reduction of nitroarenes over catalyst **A**, the conversion of 5-fluoro-2-nitrophenol **1c** was only 80% with the selectivity 64%. The difference in results for isomeric methoxy-substituted nitroarenes **1d**,**e** could be explained regarding inductive effects of the methoxy group into the different positions with respect to the nitro group. The low selectivity in the case of nitrobenzaldehyde **1b** is undoubtedly caused by the reaction of the carbonyl group with the newly obtained amino group.

In summary, the direct heterogeneous catalytic reduction of nitroarenes to the corresponding amino derivatives has been performed using molecular hydrogen and a Cu-based catalyst for a series of different chemotypes. The high values of conversion and selectivity have been achieved under relatively mild conditions of 13 atm $H_2$ and 170 °C within 2.5–12 h. The obtained results exhibit prospective implementation of the direct selective reduction of nitro groups in nitroarenes over the heterogeneous Cu-based catalyst that can be prepared by a simple environmentally safe procedure.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.036.

## References

1 J. Song, Z.-F. Huang, L. Pan, K. Li, X. Zhang, L. Wang and J.-J. Zou, *Appl. Catal., B*, 2018, **227**, 386.
2 H. K. Adam and S. G. Tilve, *RSC Adv.*, 2015, **5**, 83391.
3 D. Formenti, F. Ferretti, F. K. Scharnagl and M. Beller. *Chem. Rev.*, 2019, **119**, 2611.
4 C. Sá Couto, L. M. Madeira, C. P. Nunes and P. Araújo, *Chem. Eng. Technol.*, 2015, **38**, 1625.
5 N. J. Zainab, A. Mohammednoor, A. M. Hussein, H. A. Mansour, J. Zhong-Tao and B. Z. Dlugogorski, *ACS Omega*, 2018, **3**, 14380.
6 P. Tomkins, E. Gebauer-Henke, W. Leitner and T. E. Müller, *ACS Catal.*, 2015, **5**, 203.
7 G. A. Monti, N. M. Correa, R. D. Falcone, G. F. Silbestri and F. Moyano, *RSC Adv.*, 2020, **10**, 15065.
8 A. L. Nuzhdin, G. A. Bukhtiyarova, T. Lin, E. Yu. Gerasimov and V. I. Bukhtiyarov, *Mendeleev Commun.*, 2019, **29**, 553.
9 C. Campos, C. Torres, M. Oportus, M. A. Peña, J. L. G. Fierro and P. Reyes, *Catal. Today*, 2013, **213**, 93.
10 E. F. Litvin and V. Z. Sharf, *Ross. Khim. Zh.*, 2000, **44** (2), 90 (in Russian).
11 E. V. Shuvalova, O. A. Kirichenko and L. M. Kustov, *Russ. Chem. Bull., Int. Ed.*, 2017, **66**, 34 (*Izv. Akad. Nauk, Ser. Khim.*, 2017, 34).
12 M. Varkolu, V. Velpula, R. Pochamoni and A. R. Muppala, *Appl. Petrochem. Res.*, 2016, **6**, 15.
13 L. Huang, Y. Lv, S. Wu, P. Liu, W. Xiong, F. Hao and H. Luo, *Appl. Catal., A*, 2019, **577**, 76.
14 M. Tejeda-Serrano, J. R. Cabrero-Antonino, V. Mainar-Ruiz, M. López-Haro, J. C. Hernández-Garrido, J. J. Calvino, A. Leyva-Pérez and A. Corma, *ACS Catal.*, 2017, **7**, 3721.
15 W.-C. Cheong, W. Yang, J. Zhang, Y. Li, D. Zhao, S. Liu, K. Wu, Q. Liu, C. Zhang, D. Wang, Q. Peng, C. Chen and Y. Li, *ACS Appl. Mater. Interfaces*, 2019, **11**, 33819.
16 A. A. Shesterkina, A. A. Strekalova and L. M. Kustov, *Russ. J. Phys. Chem. A*, 2020, **94**, 1180 (*Zh. Fiz. Khim.*, 2020, **94**, 888).
17 G. Kour, M. Gupta, B. Vishwanathan and K. Thirunavukkarasu, *New J. Chem.*, 2016, **40**, 8535.
18 T.-N. Ye, Y. Lu, J. Li, T. Nakao, H. Yang, T. Tada, M. Kitano and H. Hosono, *J. Am. Chem. Soc.*, 2017, **139**, 17089.
19 E. V. Shuvalova, O. A. Kirichenko, G. I. Kapustin and L. M. Kustov, *Russ. Chem. Bull., Int. Ed.*, 2016, **65**, 2850 (*Izv. Akad. Nauk, Ser. Khim.*, 2016, 2850).

20 O. A. Kirichenko, E. V. Shuvalova, A. A. Strekalova, N. A. Davshan, G. I. Kapustin and V. D. Nissenbaum, *Russ. J. Phys. Chem. A*, 2018, **92**, 2417 (*Zh. Fiz. Khim*., 2018, **92**, 1894).
21 O. A. Kirichenko, E. V. Shuvalova and E. Redina, *Russ. Chem. Bull., Int. Ed*., 2019, **68**, 2048 (*Izv. Akad. Nauk, Ser. Khim*., 2019, 2048).
22 C. Xu, G. Chen, Y. Zhao, P. Liu, X. Duan, L. Gu, G. Fu, Y. Yuan and N. Zheng, *Nat. Commun*., 2018, **9**, 3367.
23 C. J. G. van der Grift, A. F. H. Wielers, A. Mulder and J. W. Geus, *Thermochim. Acta*, 1990, **171**, 95.
24 H. Zhang, H.-R. Tan, S. Jaenicke and G.-K. Chuah, *J. Catal*., 2020, **389**, 19.

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