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Hydrogenation of nitroarenes on silica-supported copper catalyst

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Preparation of catalyst. Cu/SiO_2 samples were synthesized by the method of deposition–precipitation using the thermal hydrolysis of urea (DPU). The industrial silica support KSKG with S_{BET} = 98 m^2 g^{-1} and V_{pore} =1.05 cm^3 g^{-1} (KhimMed), urea (Acros Organics) and $Cu(NO_3)_2 \cdot 3H_2O$ (Aldrich) were used. A silica suspension in a solution (40 g dm^{-3}) containing 0.076 mol dm^{-3} of copper(II) nitrate and 0.79 mol dm^{-3} of urea was heated for 50 min under vigorous stirring and kept at 92 °C for 8 h. The resulting precipitate was separated from the mother solution by centrifugation, washed three times with distilled water using intermediate centrifugation, and then dried consequently on a rotary evaporator at 40 °C at 40 mbar for 4 h, and then in an oven at 110 °C for 16 h. The expected Cu weight loading in the sample was 10%, and it was calculated with respect to the system CuO-SiO_2.

Nitrobenzene **1a**, aniline **4a**, *p*-dinitrobenzene **2**, *p*-phenylenediamine **5**, 1,3,5-trinitrobenzene **3a**, 1,3,5-triaminobenzene **6a**, 3-nitrobenzaldehyde **1b**, 3-aminobenzaldehyde **4b**, 1-chloro-3,5-dinitrobenzene **3b**, 1,3-diamino-5-chlorobenzene **6b**, 1-bromo-2,4-dinitrobenzene **3c**, 5-bromo-3-nitroaniline, 2-fluoro-5-nitrophenol **1c**, 5-amino-2-fluorophenol **4c**, 5-methoxy-2-nitroaniline **1d**, 3,4-diamino-1-methoxybenzene **4d**, 2-methoxy-6-nitroaniline **1e**, 2,3-diamino-1-methoxybenzene **4e** (Aldrich) were used as the starting compounds and GC references.

Hydrogenation experiments. Catalytic evaluation was carried out in a liquid phase in a 100 ml stainless-steel reactor equipped with a stirrer operating at 500 rpm. The substrate (0.2 g), the catalyst (0.1 g), THF (15 ml), and eicosane (GC standard, exact weight portion of 100 mg with a 0.1 mg accuracy) were loaded into the reactor. The reactor was preliminarily flushed with hydrogen three times up to 5 atm, and then the pressure was adjusted to 13 atm. The reactor was heated at 170 °C with stirring for 2.5 h (or other times specified in Table 1 of the main text), the pressure upon heating having risen to 30 atm. Liquid samples were taken every 30 minutes from the reactor through a special high-pressure sampling valve. The reaction parameters were chosen according our previous work [E. V. Shuvalova, O. A. Kirichenko, G. I. Kapustin and L. M. Kustov, *Russ. Chem. Bull., Int. Ed.,* 2016, **65**, 2850 (*Ivz. Akad. Nauk, Ser. Khim.,* 2016, 2850)].

GC analysis. The concentrations of the reactants and products in the samples were determined using a CrystaLux 4000M GC instrument equipped with a 30 m×0.25 mm capillary column Optima-1 (Macherey-Nagel). Nitrogen was used as a carrier gas. The injector and detector temperatures were 240 °C. Analysis was carried out in the temperature programmed mode: the column was initially heated to 150 °C, kept at this temperature for 6 min, heated from 150 to 240 °C at the rate of 20 deg min^{-1}, and kept at 240 °C for 10 min.

Eicosane ($C_{20}H_{42}$) was used as the internal standard for quantitative calculations of the nitroarene 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 nitro compounds and internal standard peak area ratio, and the change in this ratio was used to calculate the selectivityies to nitrobenzenes and aminobenzenes.

The identification of the compounds was performed by comparison of the retention times with those of the authentic samples.

Compound	Retention time, min	Column temperature, °C
Nitrobenzene **1a**	6.90	150
Aniline **4a**	5.09	150
p-Dinitrobenzene **2**	5.63	170
p-Phenylenediamine **5**	3.91	170
1,3,5-Trinitrobenzene **3a**	3.49	220
1,3,5-Triaminobenzene **6a**	3.45	220
3-Nitrobenzaldehyde **1b**	6.40	170
3-Aminobenzaldehyde **4b**	5.82	170
1-Chloro-3,5-dinitrobenzene **3b**	7.39	170
5-Chloro-1,3-diaminobenzene **6b**	4.23	170
1-Bromo-2,4-dinitrobenzene **3c**	7.60	170
5-Bromo-3-nitroaniline **6c**	8.99	170
2-Fluoro-5-nitrophenol **1c**	2.77	170
2-Amino-5-fluorophenol **4c**	3.41	170
5-Methoxy-2-nitroaniline **1d**	9.05	170
3,4-Diamino-1-methoxybenzene **4d**	6.64	170
2-Methoxy-6-nitroaniline **1e**	8.87	170
2,3-Diamino-1-methoxybenzene **4e**	6.65	170

Other products, such as 1-nitro-3-nitrosobenzene, (3-nitrophenyl)hydroxylamine, azoxybenzene, azobenzene, hydrazobenzene are not detected by GLC. We did not any further attempt of identification because intermediate products were not of interest for our investigation.