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Hydrogenation of dinitrobenzenes over titania-supported palladium nanoparticles

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Preparation of catalysts. The synthesis of supported Pd^0 NPs on the TiO_2 commercial nonporous carriers P-25 supplied by Evonic (S_{BET} = 57 m^2 g^{-1}) and Acros Organics (S_{BET} = 61 m^2 g^{-1}) was performed via deposition-precipitation of Pd-PHC precursor nanoparticles on the surface of the carrier followed by their reduction to metallic Pd^0 nanoparticles with molecular hydrogen in a slurry as described previously [S1]. The preparation procedure included (1) hydrolysis of H_2PdCl_4 in 0.004M solution at 4°C by dropwise addition of 1M Na_2CO_3 solution (the molar ratio Na_2CO_3/Pd was 2.10 or 4.34, depending on a support used further, for Evonic and Acros Organics respectively); (2) immersing the TiO_2 powder in the thus prepared solution at 4°C and deposition of Pd-PHC by keeping the slurry stirring consequently at 4°C and at 23°C for 1 hour, at 60°C for 4 h; (3) reduction of Pd-PHC with H_2 in the slurry at 23°C for 2 hours; (4) separation of the solid by centrifuging, triple washing followed by drying in a rotary evaporator under vacuum of 40 mbar at 40°C. The Pd loading in the samples was 1 wt.%. The samples were marked as "Pd/TA", where A means the TiO_2 supplier (1 - Evonic, 2 - Acros Organics).

Nitrobenzene, aniline, *m*-dinitrobenzene, *m*-phenylenediamine, *m*-nitroaniline, *p*-dinitrobenzene, *p*-phenylenediamine, *p*-nitroaniline (Aldrich) were used as the starting compounds and GC references.

Hydrogenation experiments. The catalytic behavior of the supported Pd nanoparticles was tested in the model reaction of the selective hydrogenation of dinitrobenzenes (*m*-DNB and *p*-DNB) to the corresponding phenylenediamines. For comparison with data published for other Pd catalysts, tests in NB hydrogenation to aniline were performed as well. The batch mode tests were performed in a Teflon-lined 100 mL autoclave at 25 °C or 50 °C and the initial H_2 pressure 0.5 MPa (5 atm) similar to the reaction conditions previously used for hydrogenation of nitroarenes over the 1%Pd/C catalyst prepared via Pd PHC in [S2]. The specified amounts of substrate 200 mg or 500 mg and solvent (THF for *p*-DNB or ethanol for *m*-DNB and NB, 20 mL) were introduced into the reactor, and the mixtures were vigorously stirred for 30 min to form solutions with a substrate (concentration 0.06 – 0.15 mol L^{-1}), then 0.100 g of internal standard (eicosane $C_{20}H_{42}$ for *p*-DNB or $C_{16}H_{34}$ for *m*-DNB and NB) was added into the solution. Before catalyst addition (0.025 or 0.050 g, molar ratio substrate/Pd = 240 - 860) the stirring was stopped, and the probe of the initial solution was taken for analysis. Then the reactor was closed and preliminarily

flushed with hydrogen three times up to 0.5 MPa, and finally the pressure was adjusted to 0.5 MPa at room temperature. Reaction was started by stirring at room temperature or after heating to the required temperature.

The time dependence curves of a substrate conversion and selectivity to the individual amines were constructed analyzing the liquid probes withdrawn from the reactor every 5-10 min using a special high-pressure sampling valve. The CrystaLux 4000M GC instrument equipped with a 30 m × 0.25 mm capillary S2 column Optima-1 (Macherey-Nagel) was used to carry out a probe analysis 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 a rate 20 K min^{-1}, and kept at 240 °C for 10 min. The analyte to standard peak area ratio was used to determine the concentrations of substrates and amines detected by GC in the reaction mixture. The substrate conversion and the selectivity to the individual amines were calculated based on the changes in the relative concentrations, which were corrected as to the area of a standard peak in an initial reaction mixture. We did not make any attempt to reveal and identify intermediate hydroxyamino, azoxy, hydrazo and azo products because they were not of interest for our investigation.

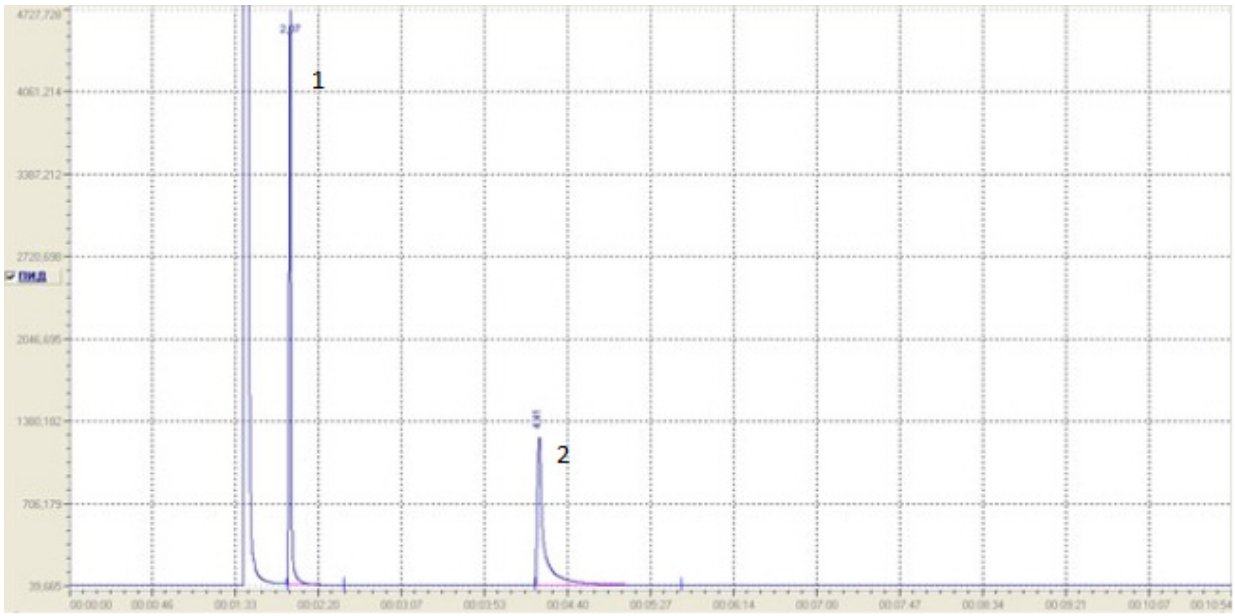

Figure S1 Chromatogram of initial mixture.

1 Standard $C_{16}H_{34}$ retention time 2.07 min
2 *m*-DNB retention time 4.41 min

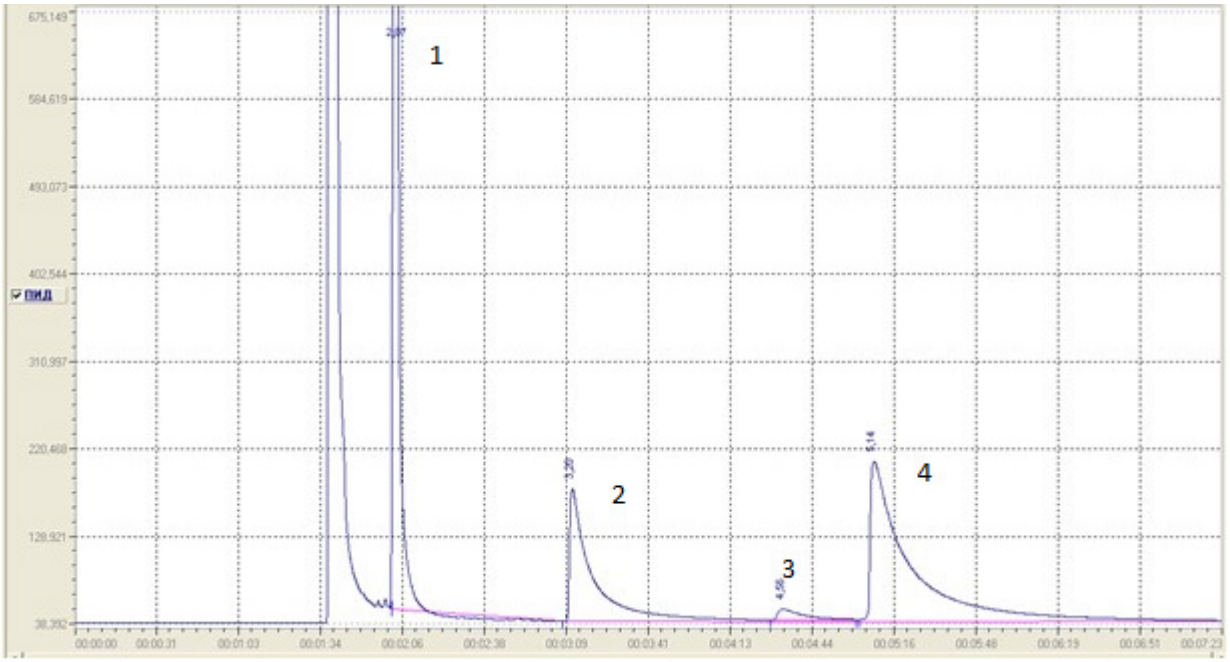

Figure S2 Chromatogram of reaction mixture.

1 Standard $C_{16}H_{34}$ retention time 2.07 min
2 *m*-DNB retention time 4.41 min
3 *m*-DAB retention time 3.20 min
4 NA retention time 5.14 min

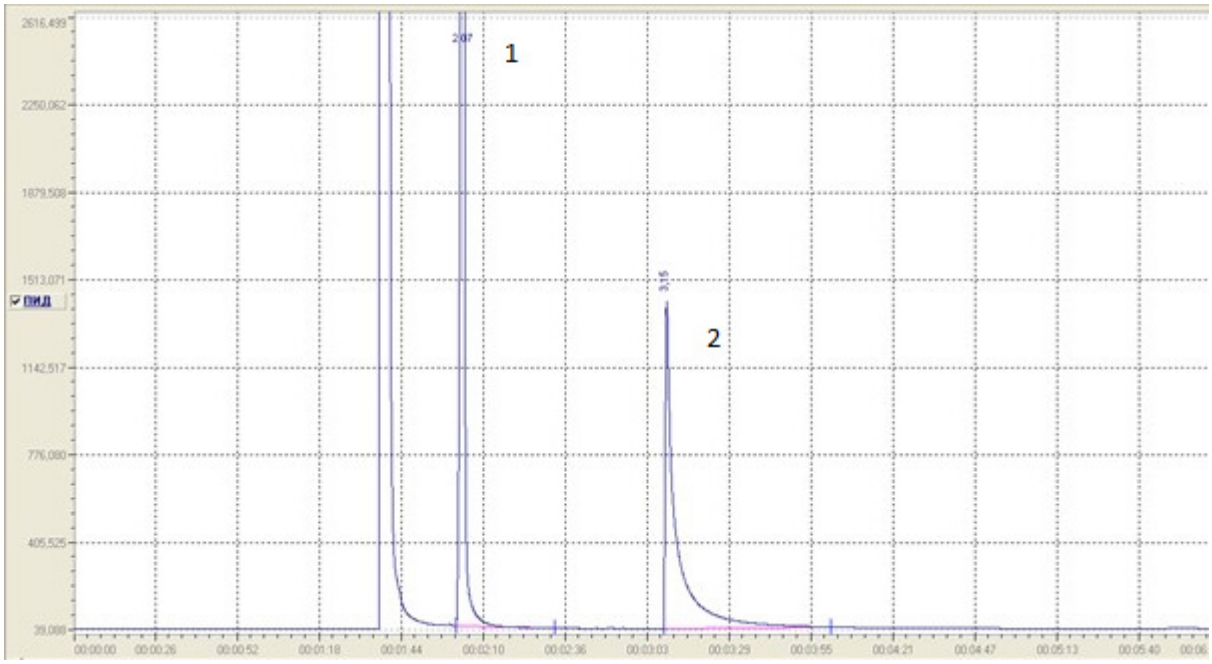

Figure S3 Chromatogram of the final reaction mixture.

1 Standard $C_{16}H_{34}$ retention time 2.07 min
2 *m*-DAB retention time 3.20 min

References

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