Chemoselective hydrogenation of 3-nitrostyrene over Ag/TiO₂-SiO₂ catalyst in a flow reactor

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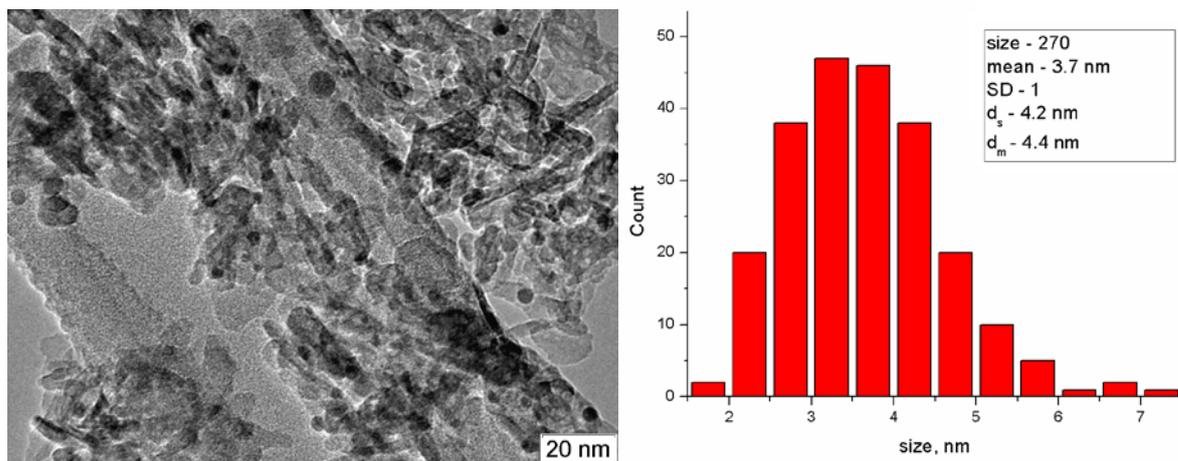
Chemicals

Silver nitrate (99.5%), 3-nitrostyrene (97%) and *n*-decane (99+%) from Acros Organics, as well as titanium (IV) ethoxide (approx. 80%) from Sigma, were used as supplied. Toluene (99.5%, ECOS, Russia), methanol (99.8%, J.T. Baker) and 2-propanol (≥99.7%, Sigma-Aldrich) were employed as solvents.

The γ-alumina support was prepared by extrusion of a paste obtained by mixing of aluminum oxide (Puralox TH 100/150, Sasol), aluminum oxyhydroxide (Disperal, Sasol) and aqueous solution of nitric acid as described [S1, S2]. The silica (KSKG) was supplied from KhromAnalit (Russia). In order to prepare the TiO₂-SiO₂ support, the preliminarily dried silica gel (2.0 g) was impregnated with a solution of titanium(IV) ethoxide (0.56 ml) in 2-propanol in a vacuum rotary evaporator at a pressure of 0.086 bar and a temperature of 40 °C. After the removal of the solvent, the sample was hydrolyzed in water at room temperature, dried at 120 °C for 2 h, and calcined at 400 °C for 3 h [S2].

Catalyst characterization

The silver content was analyzed by XRF technique on an ARL instrument (Thermo Scientific, USA). Textural characteristics were determined from nitrogen adsorption-desorption isotherms (–196 °C) obtained using Micromeritics ASAP 2400 instrument (Micromeritics, USA). The transmission electron microscopy (TEM) studies were carried out using a JEM-2010 (JEOL, Japan) electron microscope with a lattice resolution of 0.14 nm and a 200 kV accelerating voltage. The average diameters of silver particles for each sample were determined by counting of 250–350 particles in TEM images taken with a medium magnification.
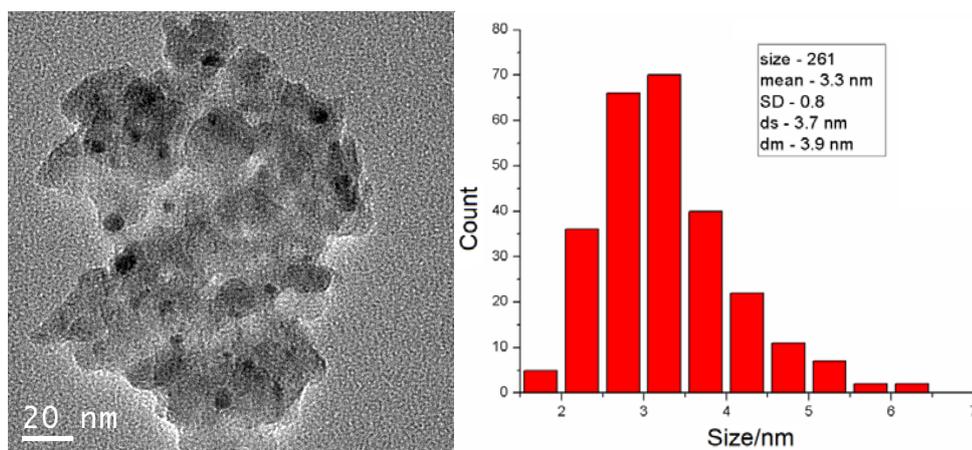
TEM data

Figure S1. TEM images of the Ag/Al$_2$O$_3$-A catalyst.
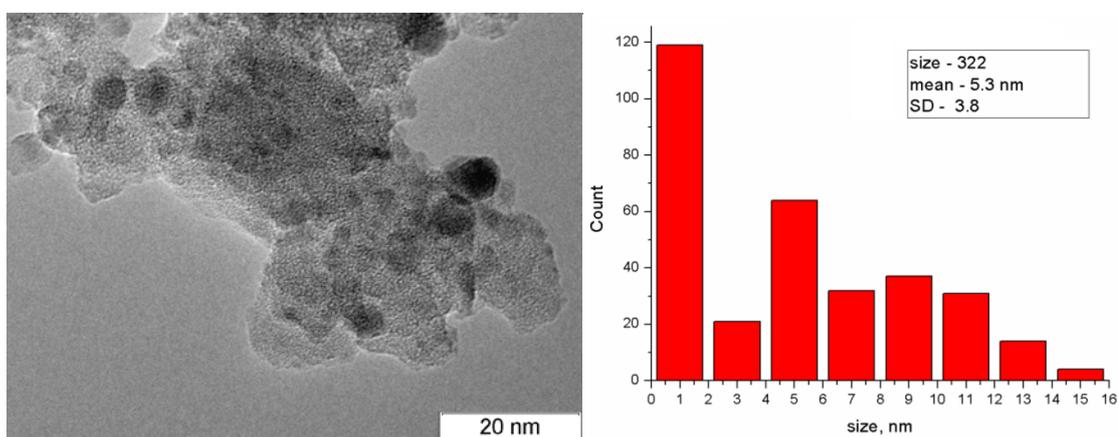
Figure S2. TEM images of the Ag/TiO$_2$-SiO$_2$-A catalyst.


Figure S3. TEM images of the regenerated Ag/TiO$_2$-SiO$_2$-H catalyst.

Table S1. Physico-chemical characteristics of the fresh and regenerated Ag/TiO$_2$-SiO$_2$-H catalysts

	Fresh	Regenerated
Content of Ag, wt.%	1.8±0.1	1.9±0.1
Content of TiO$_2$, wt.%	8.8	8.7
Mean diameter of Ag nanoparticles, nm	4.2	3.3

GC analysis was carried out using Agilent 6890N instrument equipped with 19091S-416 HP 5-MS capillary column (60.0 m × 320 μm × 0.25 μm) and the flame ionization detector.
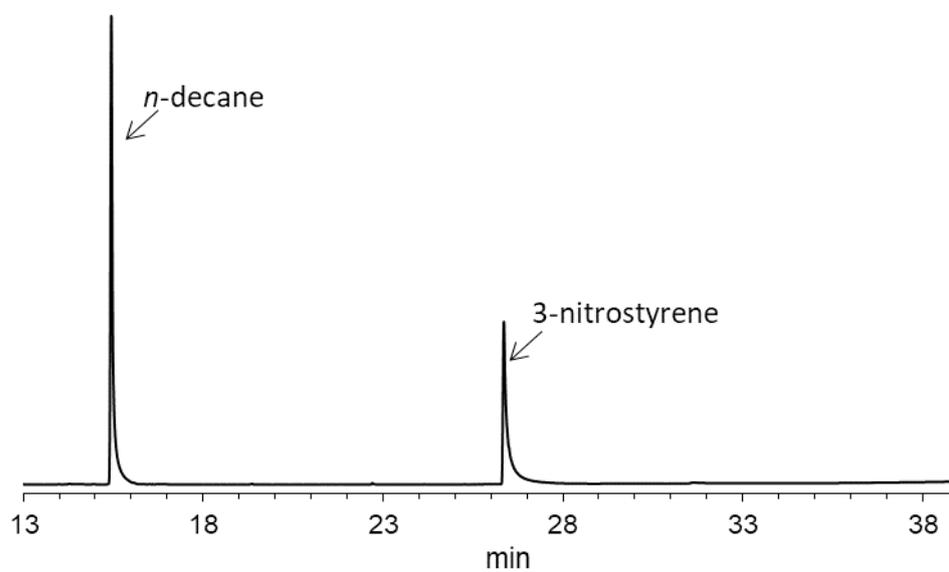
Figure S4. Chromatogram of the initial reaction mixture.
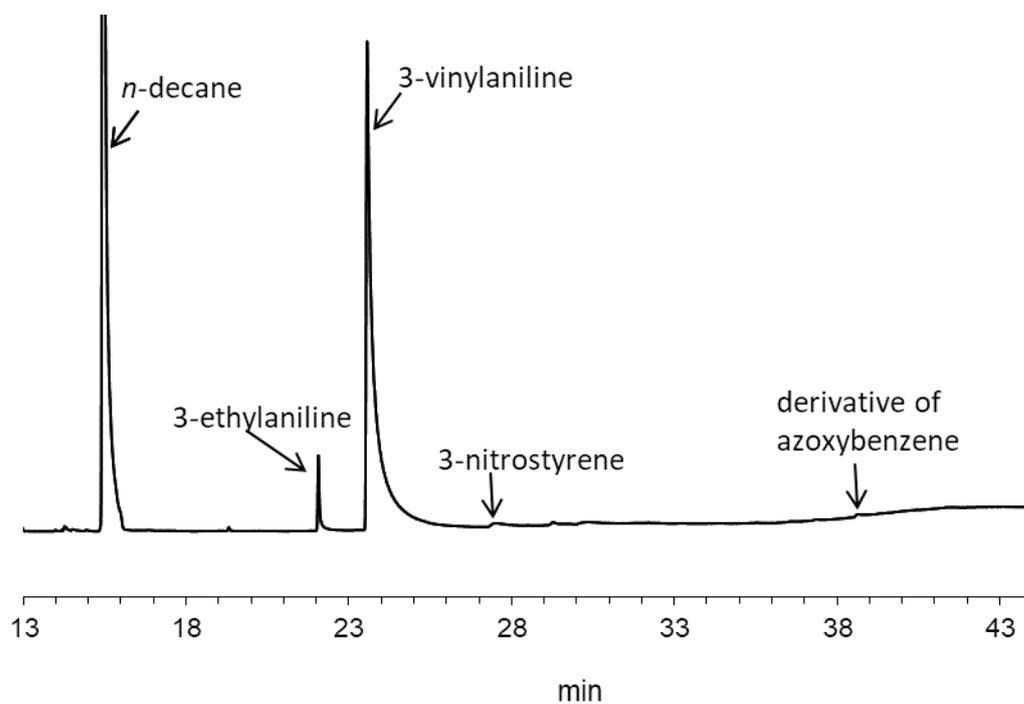
Figure S5. Chromatogram for Table 2 entry 8 (main text): after reaction.

References

[S1] A. L. Nuzhdin, B. L. Moroz, G. A. Bukhtiyarova, S. I. Reshetnikov, P. A. Pyrjaev, P. V. Aleksandrov and V. I. Bukhtiyarov, *ChemPlusChem*, 2015, **80**, 1741.

[S2] E. A. Artyukha, A. L. Nuzhdin, G. A. Bukhtiyarova, E. A. Derevyannikova, E. Yu. Gerasimov, A. Yu. Gladkii and V. I. Bukhtiyarov, *Kinet. Catal.,* 2018, **59**, 593 (*Kinet. Katal.*, 2018, **59**, 583).