

Electronic Supplementary Information for

Flow synthesis of secondary amines over Ag/Al₂O₃ catalyst by one-pot reductive amination of aldehydes with nitroarenes

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1. Catalyst characterization

The silver content in the samples was measured by using the X-ray Fluorescence (XRF) technique on an ARL instrument equipped with a Rh anode (X-ray tube voltage, 50 kV, tube current, 40 mA, exposure time, 10 s).

Transmission electron microscopy (TEM) studies were performed with a JEM-2010 (JEOL, Japan) electron microscope with a lattice resolution of 0.14 nm and a 200 kV accelerating voltage.

Textural characteristics were determined from adsorption–desorption isotherms of nitrogen measured at 77 K by using an automatic volumetric device ASAP 2400 (Micromeritics).

The phase composition was determined using powder X-ray diffraction (XRD) patterns, which were collected on a Bruker D8 diffractometer, Cu-K α radiation. Diffraction intensities were measured with the LynxEye position sensitive detector. XRD patterns were collected in 2 Θ range 15-90°, with 0.05° step size and 5 s collection time. Phase analysis was performed using ICDD PDF-2 data base. The XRD data were treated by EVA (Bruker).

The XPS experiments were performed on a SPECS spectrometer equipped with a PHOIBOS-150 hemispherical energy analyzer and the X-Ray source with double Al/Mg anode. In the present work the AlK α ($h\nu = 1486.6$ eV, 200 W) was used as a primary irradiation. The binding energy (BE) scale was pre-calibrated using positions of Au4f $_{7/2}$ (BE = 84.0 eV) and Cu2p $_{3/2}$ (BE = 932.7 eV) core level peaks. The samples in form of powder were supported onto the double-sided conducting copper scotch tape. The sample measured after reduction was supported from ampoule opened directly before loading into load lock chamber of the spectrometer, thus the contact of sample with air was minimized and did not exceed one minute. The binding energy was calibrated by position of the Al2p peak (BE = 74.5 eV) corresponding to Al $^{3+}$ from Al $_2$ O $_3$ [Moulder J.F., Stehle W.F., Sobol P.E., Bomben K.D. Handbook of X-Ray Photoelectron Spectroscopy. Perkin- Elmer, Eden Prairie. MN, 1992, p. 261].

2. BET results

Adsorption isotherms of the as-prepared, spent and regenerated Ag/Al $_2$ O $_3$ catalysts are a type IV that characterizes mesoporous adsorbents [ISO 9277:2010 (en), Determination of the

specific surface area of solid by gas adsorption–BET method]. Figure S1 shows the adsorption-desorption isotherm of N₂ on the as-prepared Ag/Al₂O₃ catalysts at 77 K.

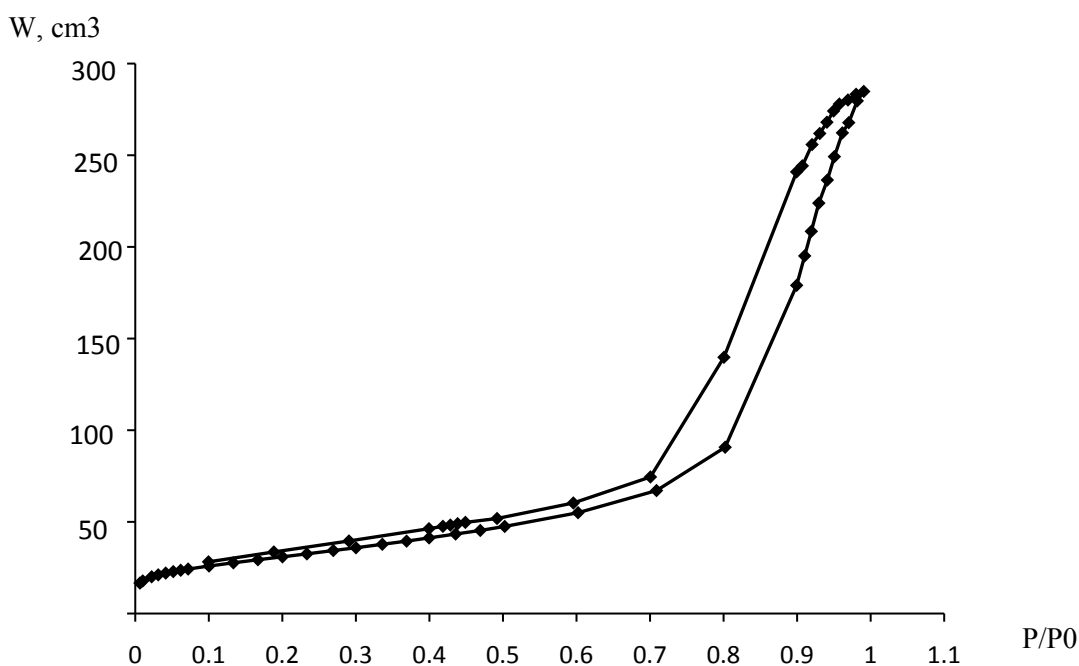


Figure S1. Adsorption-desorption isotherm of N₂ on the as-prepared Ag/Al₂O₃ catalysts at 77 K

3. X-ray photoelectron spectroscopy (XPS)

X-Ray photoelectron spectroscopy (XPS) was used to investigate two similar Ag/Al₂O₃ samples, one being a freshly prepared catalyst and the other, preliminary reduced by a mixture of hydrogen with toluene at 110 °C and 3.0 MPa for 1 hour (flow rates of toluene and H₂: 0.5 and 60 mL min⁻¹, respectively). Analysis of the survey photoelectron spectra shows that only aluminum, carbon, oxygen and silver are present on the surface of the catalyst. For analysis of surface chemical composition (chemical states and atomic concentrations of the elements) narrow regions (Al2p, C1s, Ag3d, O1s and Ag MVV) were measured.

It is quite difficult to use the Ag3d_{5/2} binding energy value to identify the Ag chemical state due to a slight shift of the Ag3d line position depending on the oxidation state of Ag, thus precluding one from making conclusions about the oxidation state of the Ag particles supported on the surface. Therefore, the Auger parameter ($\alpha_{Ag} = E_b(\text{Ag}3d_{5/2}) + E_{kin}(\text{Ag MVV})$) is used for that [1, 2]. The Ag3d XPS and Ag MVV Auger spectra for the as-prepared and pre-reduced Ag/Al₂O₃ catalysts are presented in Figure S2. For the as-prepared Ag/Al₂O₃ catalyst the α_{Ag} is equal to 724.2 eV, which corresponds to the silver in the oxidized state [3, 4]. For the reduced Ag/Al₂O₃ catalyst the slight shift of Ag3d_{5/2} together with a changing of the Ag MVV spectra

shape occurs in comparison with a fresh sample (Fig. S2). We would suppose the presence of two different Ag charging states of silver – the oxidized state ($\alpha_{\text{Ag}} - 724.2$ eV) and metallic silver ($\alpha_{\text{Ag}} - 726.0$ eV) [1-3]. These data suggest the oxidation of Ag nanoparticles supported on Al_2O_3 even with a short contact with air during the sample loading to the spectrometer chamber.

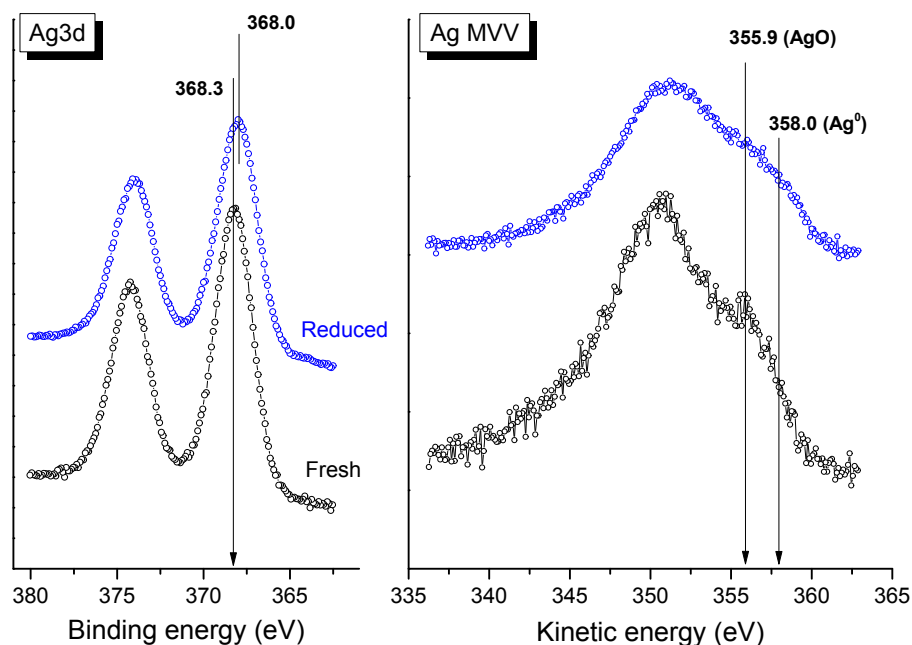


Figure S2. Ag3d and Ag MVV Auger spectra for the fresh and pre-reduced Ag/ Al_2O_3 catalyst

- [1] V. K. Kaushik, *J. Electron Spectr. Relat. Phenom.* 1991, 56, 273.
- [2] A.V. Bukhtiyarov, A.Yu. Stakheev, A.I. Mytareva, I.P. Prosvirin, V.I. Bukhtiyarov, *Russ. Chem. Bull.*, 2015, 64, 2780.
- [3] C.D. Wagner, L.H. Gale, R.H. Raymond, *Anal. Chem.*, 1979, 51, 466.
- [4] T.D. Thomas, *J. Electron Spectr. Relat. Phenom.*, 1980, 20, 117.

4. TG–DSC–MS data for the as-prepared, spent and regenerated Ag/Al₂O₃ catalyst

The simultaneous TG–DSC–MS measurement of the as-prepared, spent and regenerated catalysts was performed in an apparatus consisting of a STA 449 F1 Jupiter thermal analyzer and a QMS 403D Aëolos quadrupole mass spectrometer (NETZSCH, Germany). The measurements were made in a "synthetic air" flow (80 % vol. Ar and 20 % vol. O₂) in the temperature range of 30–800 °C using the heating rate of 10 °C min⁻¹, the gas flow rate of 25 mL min⁻¹ and open Al₂O₃ crucibles. The sample weight is 25 mg.

The DTG curve of the as-prepared catalyst exhibits a broad peak with a maximum at ~120 °C, which is related to removal of physically adsorbed water (the loss of the sample weight in the 30–200 °C temperature range is 1.4%) (Figure S3). Additionally, the weight loss of about 1.2% is observed in the 200–500 °C range, probably due to the gradual removal of hydroxyl groups from the γ -alumina surface or water removal from micropores.

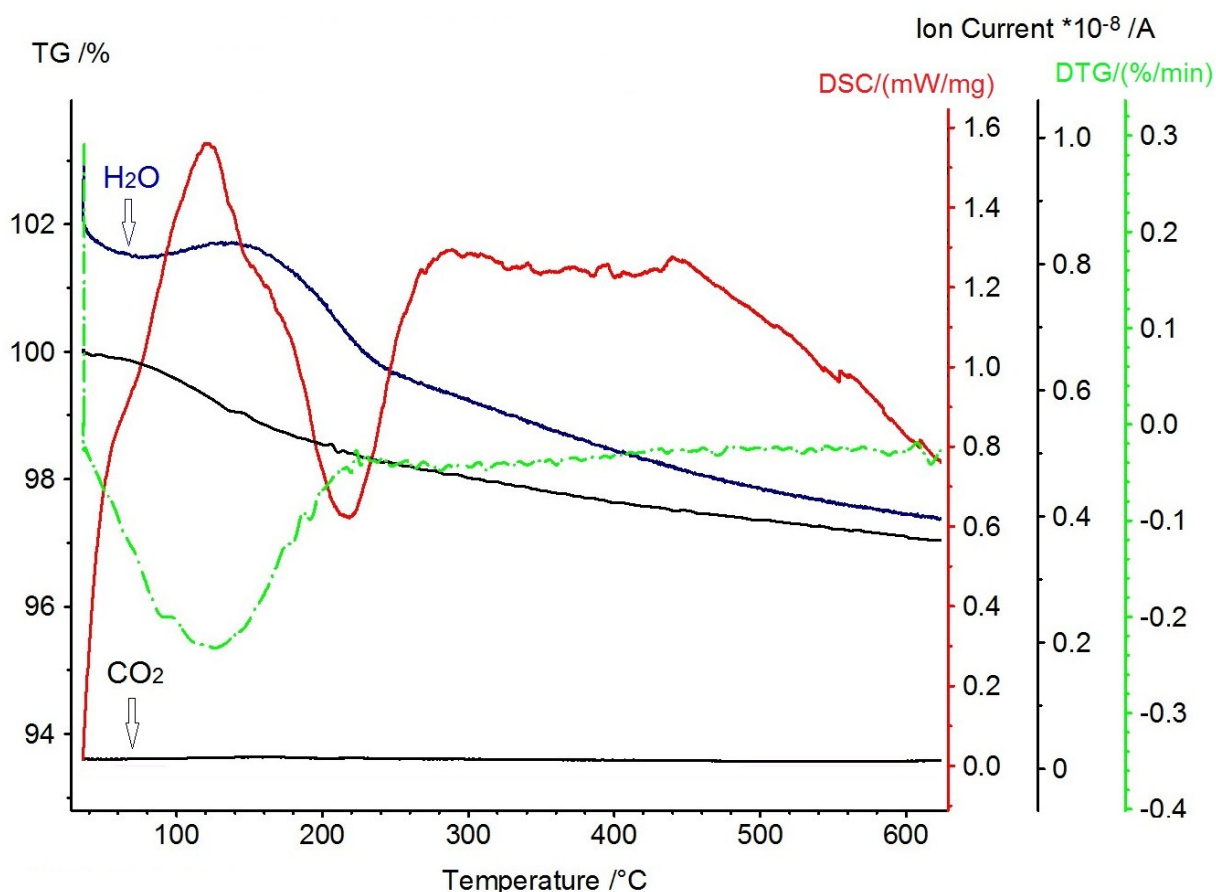


Figure S3. TG–DSC–MS data for the as-prepared Ag/Al₂O₃ catalyst

TG–DSC–MS results for the spent Ag/Al₂O₃ catalyst are presented in Figure S4. Prior to TG–DSC–MS analysis the sample was washed with toluene for 30 minutes (0.5 mL min⁻¹) and placed in the vacuum heat chamber at room temperature, evacuated to 5 mbar and then slowly

heated up to 80 °C with the subsequent drying at this temperature for 3 hours. The DTG curve of spent catalyst exhibits two weight loss regions: the first (30–200 °C) is caused by the removal of adsorbed water (the weight loss in this temperature range is 0.8%) and the second (200–500 °C) could be explained by combustion of hydrogen-enriched carbonaceous species on the catalyst surface, which was confirmed by the exothermic peak on DSC curve and carbon dioxide and water peaks on MS curves in this region. According to TG curve, the weight loss in the temperature region of 200–500 °C is 5.4 %. The amount of carbonaceous deposits in the sample was determined as follows: the corresponding weight loss of the as-prepared catalyst equal to 1.2% was subtracted from the amount of relative weight loss of the spent catalyst in the temperature range 200–500 °C (TG curves). Thus an estimated amount of carbonaceous deposits in the spent Ag/Al₂O₃ catalyst was approximately 4.2 wt%.

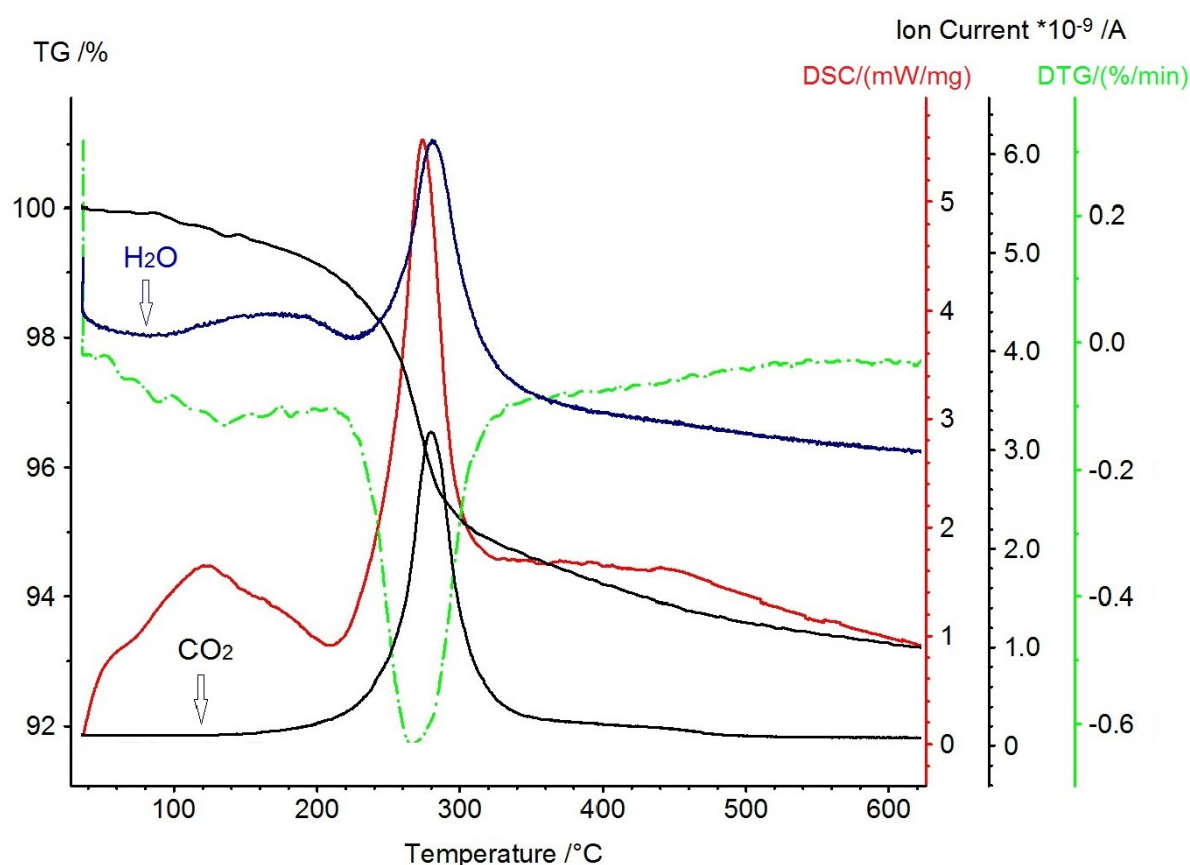


Figure S4. TG–DSC–MS data for the spent Ag/Al₂O₃ catalyst

TG–DSC–MS results for the regenerated Ag/Al₂O₃ catalyst are presented in Figure S5. According to TG curve, the weight loss in the temperature region 200–500 °C is 1.2 % and thus the regenerated catalyst contains almost no carbonaceous deposits.

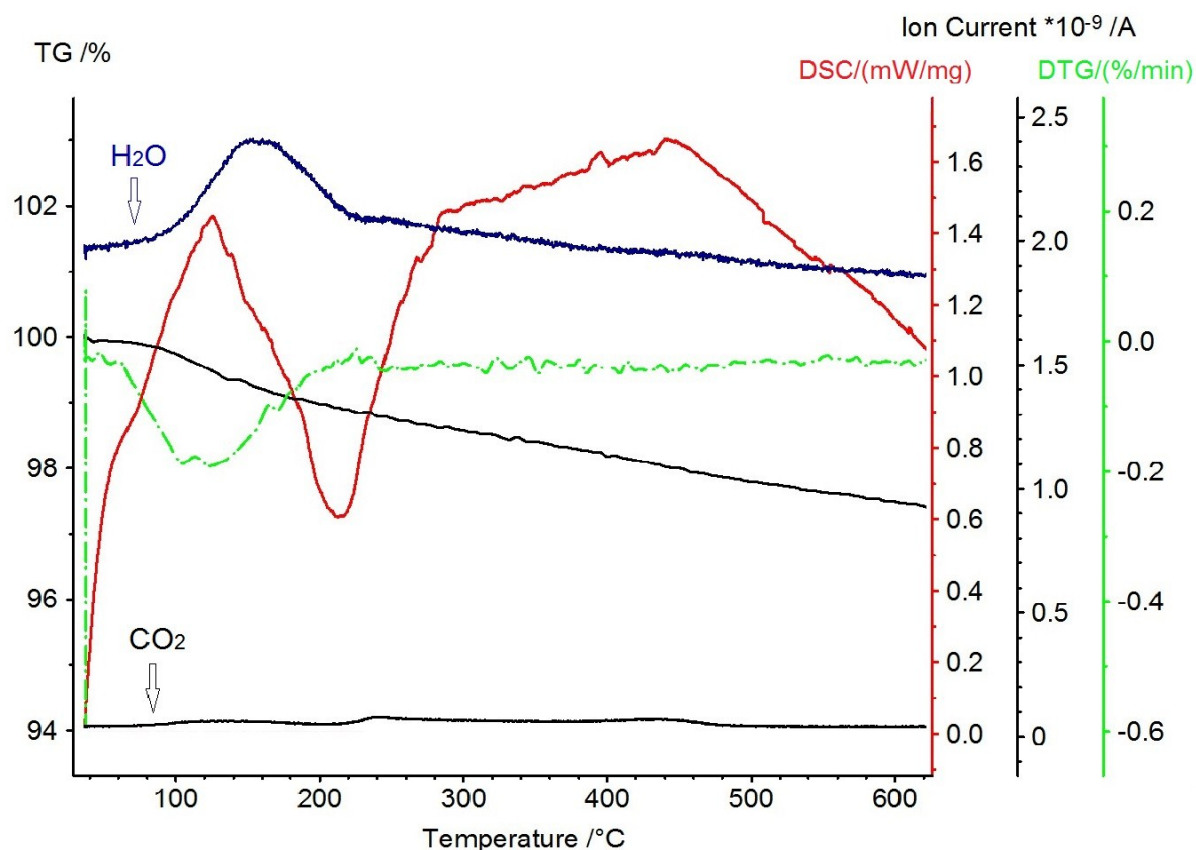


Figure S5. TG–DSC–MS data for the regenerated Ag/Al₂O₃ catalyst

5. Catalyst regeneration

After the reaction was finished, a flow of pure toluene (0.5 mL min⁻¹) was fed into the reactor instead of a reaction mixture, and the catalyst sample was washed for 30 min, and then completely dumped out from the reactor. To remove toluene the sample was placed in the vacuum heat chamber at room temperature, evacuated to 5 mbar, slowly heated up to 80 °C and dried at this temperature for 3 hours. Subsequently, the spent catalyst was heated in an air oven from room temperature to 330 °C at a heating rate of 1 °C min⁻¹ and then maintained at this temperature for 20 hours [A. L. Nuzhdin, E. A. Artiukha, G. A. Bukhtiyarova, S. Yu. Zaytsev, P. E. Plyusnin, Yu. V. Shubin, V. I. Bukhtiyarov, *RSC Advances*, 2016, 6, 88366].

6. TEM data of the regenerated Ag/Al₂O₃ catalyst

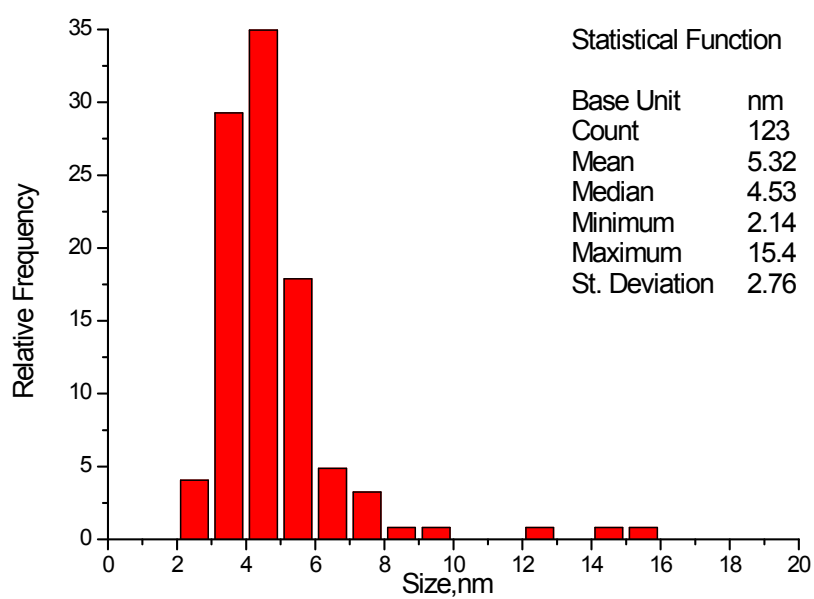
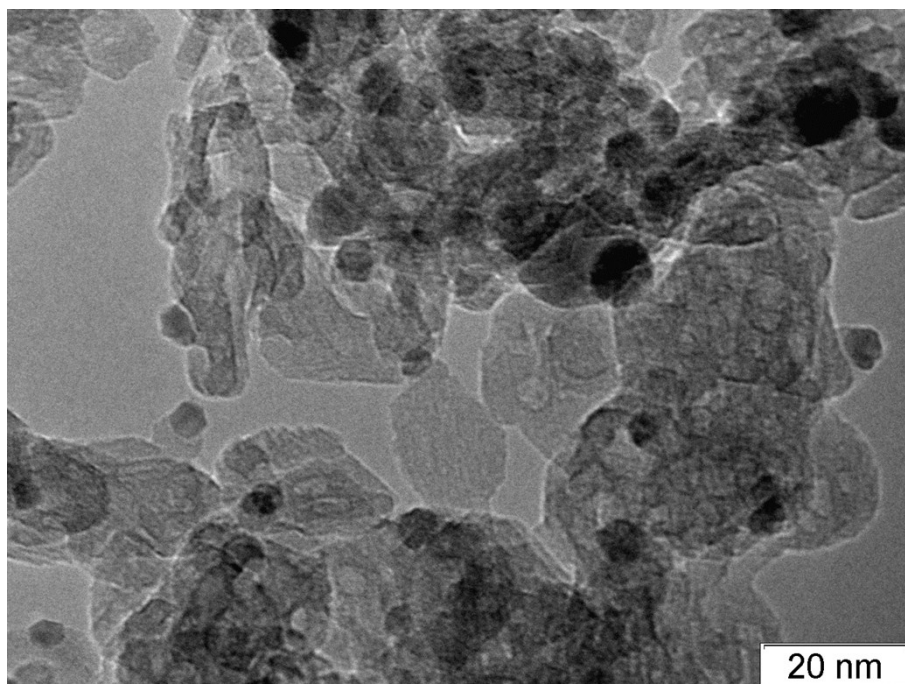


Figure S6. TEM images of the Ag/Al₂O₃ catalyst after the reductive amination of *n*-heptanal (0.0375 M) with nitrobenzene (0.025 M) at 100 °C (~2.5 hours on-stream) and the subsequent regeneration.

7. GC chromatograms

GC chromatograms for Table 2 Entry 16

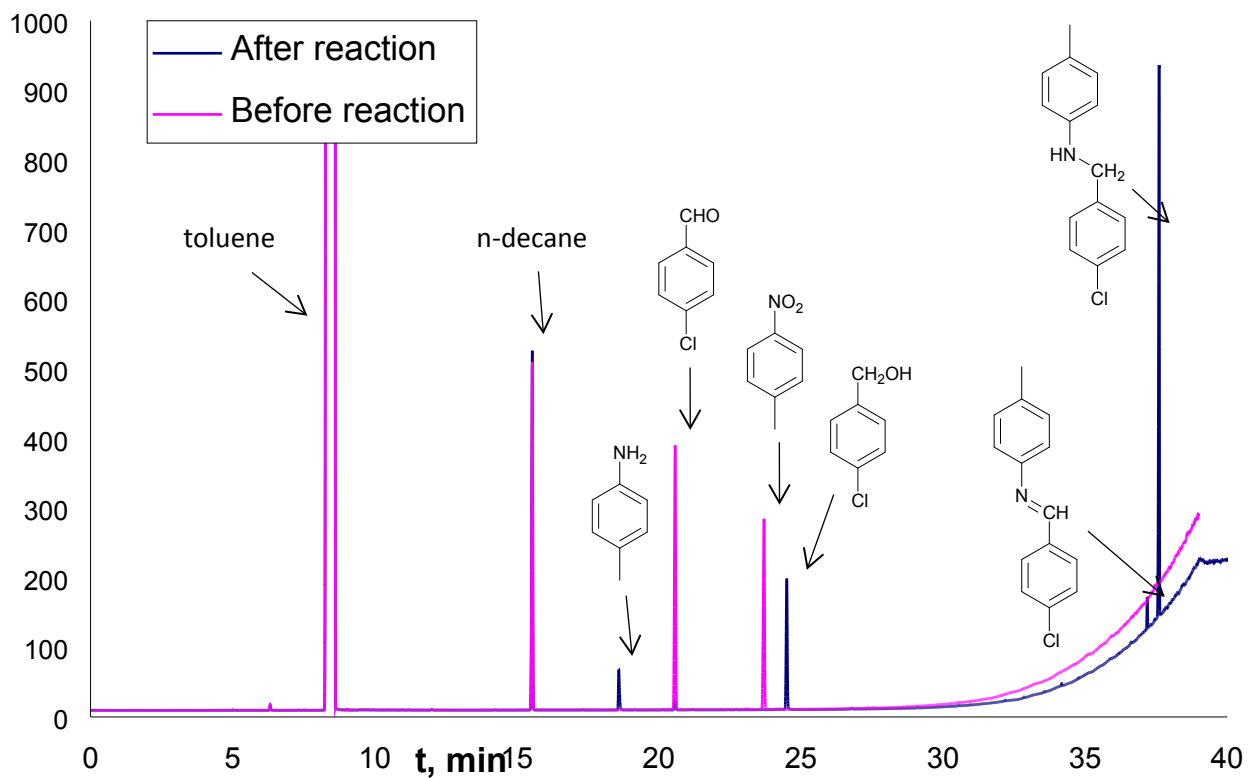


Figure S7. Chromatograms represent the formation of products in the course of the reductive amination of *p*-chlorobenzaldehyde (0.0375 M) with *p*-nitrotoluene (0.025 M) at 110 °C and $p(\text{H}_2)=3.0$ MPa.