Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Flow hydrogenation of *p*-nitrophenol with nano-Ag/Al_2O_3

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Experimental section

General: p-nitrophenol (≥ 99.5 %), p-aminophenol (≥ 98%) and $NaBH_4$ (≥ 99%) were purchased from Fluka and used without any further purification. Silver nitrate ($AgNO_3$, ≥ 99%) was purchased from Sigma-Aldrich. Aluminium oxide (Vanoxide, α-alumina, (≥ 250 μm) was purchased from Vantman manufacturing CO Fallbrook, California, USA.

Analytics: UV-vis spectroscopy: All the samples were analyzed with an UV-vis setup equipped with a deuterium tungsten halogen light source (DH-2000-BAL, Ocean Optics) and a Flame detector. Spectra were recorded in a standard quartz cuvette with an optical path of 10 mm, recorded between 200-800 nm (data presented between 200-500 nm). The Ocean Optics software suite was used for data storage.

Catalyst preparation: $AgNO_3$ (0.085 g) was dissolved in 50 ml of dry ethanol at room temperature under magnetic stirring. Subsequently 1 g of alumina was added, followed rapidly by a certain amount of NaOH (0.12 M). Upon stirring the solution turned brown and was left to stir for an additional hour. The solvent was removed in a rotary evaporator until there was obtained a grey powder.

Characterization:

X-ray diffraction (XRD) data of the samples were recorded on a Siemens D 5000 diffractometer in the 2θ range from 20° to 90° with Cu Kα radiation (λ = 1.5406 Å), with a scanning rate of 4°/min, step scan 0.02°, on a rotation sample stage.

Transmission electron microscopy (TEM) measurements were carried out by using the electron microscope Titan G2 60-300 kV FEI company[1], equipped with: field emission gun (FEG), monochromator, three condenser lenses system, the objective lens system, image correction (Cs-corrector), HAADF detector and EDS spectrometer

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[1] G.Słowik , M. Greluk, A. Machocki, *'Microscopic characterization of changes in the structure of KCo/CeO_2 catalyst used in the steam reforming of ethanol'* Mater. Chem. Phys. **2016**, 173, 219–237

(Energy Dispersive X-Ray Spectroscopy). Microscopic studies of the catalyst were carried out at an accelerating voltage of the electron beam equal to 300 kV. The mapping was carried out in the STEM mode by collecting point-by-point EDS spectrum of each of the corresponding pixels in the map. The collected maps were presented in the form of a matrix of pixels with the color mapped significant element and the intensity corresponding to the percentage of the element.

The averages sizes of particles were calculated from the equation:

$$d_{average} = \sum N_i D_i / \sum N_i \quad (1)$$

where: N_i – the numbers of metal crystallites in a specific size range, D_i – the average diameter in each diameter range.

X-ray Photoelectron Spectroscopy (XPS) was performed on a Physical electronics Quantum 2000 spectrometer, using monochromatic Al Kα radiation (hν = 1486.7 eV). Both survey and higher resolution spectra of selected spectral regions were attained using an analysis spot with a diameter of 200 µm. All measurements were performed under constant charge neutralisation from very low energy electrons and Ar^+ ions, ensuring stable measurement conditions.[1] Charge referencing was performed setting the binding energy C1s from of adventious carbon to 284.8 eV.

Typical procedure for catalytic reaction

A) Batch mode: 1.8 ml of PNP (0.057mM) in water was mixed with 1.2 ml of $NaBH_4$ (0.0156M) in water in a quartz cuvette equipped with a magnetic stirring bar. To this solution, approximately 5 mg of catalyst was introduced and the stirring was started at a speed of 380 rpm.

B) Continuous-flow mode: The so-called CatCart® (30 mm length) was filled with 150 mg of Ag/Al_2O_3 catalyst. A fresh solution of PNP in water (0.057mM) was passed through the catalyst with a flow of 2 ml/min, at room temperature and a pressure of 50 bar. Once the concentration of the PNP at the exit of the reactor was equal to the initial PNP solution (by UV-vis measurements), the reaction conditions were loaded, i.e. flow: 0.2 ml/min, 80 ^oC, 50 bar H_2. When the system reached stability (within 5 minutes) it was recorded as time zero. Fractions of the reaction mixture were collected at different time intervals and analyzed with UV-vis spectroscopy (NaOH was used to form the corresponding Na compounds derived from PNP and PAP). For PNP conversion we used a typical calibration curve.

For the blank reaction we used an empty CatCart® in identical conditions as for the catalyzed reaction.

Recycling: Immediately after the first reaction, the system was purged with water until no PNP or PAP were detected in the effluent solution. A fresh solution was passed through the catalyst in identical conditions/steps as the first reaction.

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[1] P.E. Larson, M.A. Kelly, J. Vac. Sci. Technol. A 16/6 (1998) 3483.