Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 718–720

Performance of PdAu/Al_2O_3 egg-shell catalyst with isolated Pd_1 sites for selective hydrogenation of acetylene

Igor S. Mashkovsky, Nadezhda S. Smirnova, Pavel V. Markov, Galina N. Baeva, Anastasia E. Vaulina, Dmitry P. Melnikov and Alexander Yu. Stakheev

Catalyst preparation

The egg-shell Pd/Al_2O_3 catalyst was obtained by incipient-wetness impregnation of commercial γ-Al_2O_3 spheres (d_{out} = 2.8 ± 0.2 mm, S_{BET} ~ 150 m^2/g, pore volume 0.51 cm^3/g, CJSC ‘Nizhegorodsky Sorbents’) by $PdCl_2$ solution in hydrochloric acid (pH ~ 1.5). After that the catalyst was dried at 120 °C overnight, calcined at 450 °C for 3 h, and wet-reduced with aqueous HCOONa at 75 °C for 1 h. The reduced catalyst was washed chlorine free with deionized water and dried out at 120°C overnight.

Bimetallic egg-shell PdAu/Al_2O_3 catalyst with molar Au/Pd ratio of 5 was prepared by incipient wetness impregnation of as prepared Pd/Al_2O_3 with aqueous $HAuCl_4$. The catalyst was dried-out at vacuum at 60 °C for 30 min, followed by wet reduction and washing procedure as described above. The nominal palladium and gold loading was 0.04 and 0.4 wt.%, respectively.

Catalyst characterization

Transmission electron microscopy (TEM). TEM micrographs were obtained on a JEM-2100 electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. To obtain the analytical material, the outer layer of spherical Al_2O_3 granules with a high content of active compounds was gently removed with a scalpel, crushed in a mortar and ultrasonically suspended in ethanol. The resulting suspension was then placed on Formvar grids (Ted Pella) and vacuum dried. The interplanar distances in the metal crystals were estimated from the TEM micrographs based on two-dimensional Fourier transform patterns using the ImageJ software.

Electron probe microanalysis (EPMA). The distribution of Pd and Au across the cross-section of the catalyst granules was assessed using a JEOL JXA-iSP100 electron probe microanalyser equipped with wavelength dispersive detectors. The measurements were carried out with an electron beam having an acceleration voltage of 25 kV. The granules were preliminarily coated with a carbon layer to ensure their conductivity. Measurements were made point-by-point (probe diameter 10 μm) over the entire cross-section of the granules with a constant spacing of 20 μm between measurements.

DRIFT spectroscopy of adsorbed CO (DRIFTS CO). DRIFTS CO spectra were acquired using Bruker Tensor 27 DRIFT Spectrometer (Leipzig, Germany) equipped with Harrick high temperature cell (Pleasantville, NY, USA) and MCT detector, cooled by liquid N_2. The high temperature cell's construction enables *in situ/operando* studies in various gaseous environments. The loading of spherical catalyst (4-5 granules) was placed on the steel plate in the sample compartment, purged with pure Ar flow and reduced *in situ* at 500 °C in a flow of 5 vol.%H_2/Ar (30 ml/min, 'Linde Gas Rus', purity 6.0) for 1 h. After that the sample was subjected to high-temperature (350°C) oxidative treatment in a flow of 20%O_2/N_2 ('Linde Gas Rus', 30 ml/min) for 1 h following *in situ* reduction under the conditions described above. The cell was cooled down from 500 to 150°C under the 5 vol.%H_2/Ar flow; then the flow was switched to argon. Before the introduction a flow of 0.5 vol.%CO/N_2 (30 ml/min, 'Linde Gas Rus', purity 6.0) the cell was cooled to 50°C. DRIFT spectra of adsorbed CO were collected under 0.5 vol.%CO/N_2 flow at 50°C after 10 min exposure in CO-containing atmosphere. The spectrum obtained under Ar prior the CO chemisorption was used as background. The resulting spectra were processed using Opus 7.2.139.1294 software.

Catalytic test

Samples were tested in the selective hydrogenation of acetylene in excess ethylene using a conventional flow reactor placed in tube electric furnace. Approximately 250 mg of spherical catalyst was placed in the quartz reactor (inner diameter of 6 mm) to obtain a bed height of 1.9 cm between two plugs of quartz wool. Prior to catalytic test, the catalysts were calcined in a flow of 20%O_2/N_2 (100 ml/min) for 0.5 h at 500°C and *in situ* reduced in 5%H_2/Ar (100 ml/min) for 1 h at 500°C. The catalytic measurements were typically performed at the atmospheric pressure using a mixture of 1.0 vol % acetylene, 94% ethylene, 5.0 vol % hydrogen (H_2: C_2H_2 ratio was 5) balanced in argon. The inlet gas mixture was introduced to the reactor by Brohkhorst mass-flow meter to obtain GHSV of 11500 h^{-1}. The reaction temperature was varied from 30 to 120°C with 4 h time on stream to obtain activity/selectivity data for tested samples. The on-line system for analysis of reaction products consisted of a gas chromatograph (Meta-Chrom, Crystallux-4000M) equipped with a flame ionization detector and an alumina capillary column (50 m×0.53 mm, 10 μm).

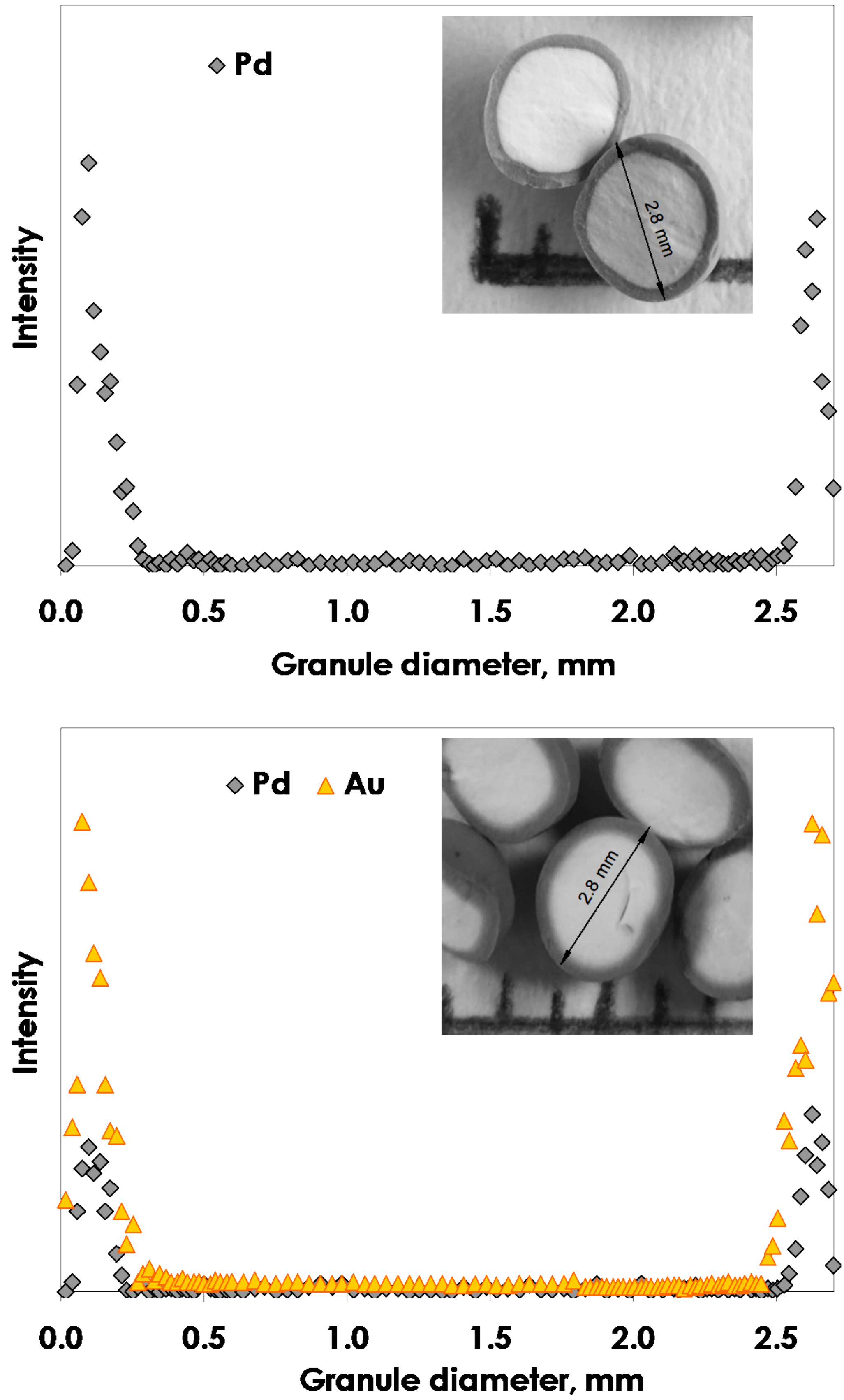

Figure S1. A distribution profile of palladium (Pd) and gold (Au) over the diameter of granules of egg-shell Pd/Al_2O_3 (top) and PdAu/Al_2O_3 (bottom) catalysts. Inlets represent a cross-sectional view of the corresponding catalysts.