Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 468-471

Intermetallic Pd_xIn_y/Al_2O_3 catalysts with isolated single-atom Pd sites for one-pot hydrogenation of diphenylacetylene into *trans*-stilbene

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Catalyst preparation

Parent α-Al_2O_3 support (S_{BET} = 8 m^2 g^{-1}, Alfa Aesar) was preliminarily calcined in air flow at 550°C for 4 h. The Pd-In/α-Al_2O_3 catalyst (2.5 wt. %Pd, 2.7 wt. % In; Pd:In = 1:1 molar ratio) was prepared by incipient wetness impregnation of α-Al_2O_3 with $Pd(\mu\text{-}O_2CMe)_4In(O_2CMe)$ heterobimetallic complex (aq. solution). For preparation of Pd_2-In_3/α-Al_2O_3 catalyst (2.5 wt. %Pd, 4.5 wt. % In; Pd:In = 2:3 molar ratio) aqueous $Pd(\mu\text{-}O_2CMe)_4In(O_2CMe)$ and $In(OAc)_3$ acetate were used. Both catalysts were dried at ~20°C overnight and reduced at 550°C (5% H_2/Ar, 3 h) immediately prior to catalytic tests. Monometallic catalyst Pd/α-Al_2O_3 (2 wt. % Pd) was prepared by impregnation of α-Al_2O_3 with $Pd(NO_3)_2$ solution followed by calcination in air flow at 550°C for 4 h and reduction in flow of 5% H_2/Ar for 3 h. The obtained catalysts were designated as follows: Pd/α-Al_2O_3 – Pd; PdIn/α-Al_2O_3 – Pd_1In_1; Pd_2In_3/α-Al_2O_3 – Pd_2In_3.

Catalyst characterization

Transmission Electron Microscopy (TEM) The micro-structure of the samples was studied by transmission electron microscopy on an HT7700 instrument (Hitachi, Japan). Images were acquired in bright-field TEM mode at 100 kV accelerating voltage. Before measurements the sample was deposited from 2-propanol suspension onto the 3 mm carbon-coated copper grids. Target-oriented approach was utilized for the optimization of the analytic measurements [V.V. Kachala, L.L. Khemchyan, A.S. Kashin, N.V. Orlov, A.A. Grachev, S.S. Zalesskiy and V.P. Ananikov, *Russ. Chem. Rev.*, 2013, **82**, 648]. The average diameter of metal particles and their size distribution were determined on the basis of measuring 160–180 particles in microscopic images of various sample regions.

X-ray diffraction (XRD) Powder XRD patterns were obtained on a D8 Advance diffractometer (Bruker, Karlsruhe, Germany; CuKα, Ni filter, LYNXEYE detector, reflection geometry). The peaks identification was performed using the Inorganic Crystal Structure Database (ICSD). The experimental details were reported elsewhere [A.V. Gavrikov, P.S. Koroteev, Z.V. Dobrokhotova, A.B. Ilyukhin, N.N. Efimov, D.I. Kirdyankin, M.A. Bykov, M.A. Ryumin and V.M. Novotortsev, *Polyhedron*, 2015, **102**, 48].

X-ray Photoelectron Spectroscopy (XPS) For studying surface transformation all catalysts were re-reduced at 450°C in 5%H_2/Ar flow for 1 h in the pretreatment chamber and after that transferred to the analytical chamber under vacuum without contact with air. The measurements were performed on a SPECS photoelectron spectrometer (Germany) using Al*K*α radiation ($h\nu =$ $= 1486.6$ eV, 150 W). The scale of binding energies (BE) was preliminarily calibrated based on the peak positions of the gold and copper core levels: Au $4f_{7/2}$ (BE = 84.0 eV) and Cu $2p_{3/2}$ (BE = = 932.67 eV). The residual gas pressure in the course of the measurements was no higher than 8×10^{-9} mbar. All powdered samples were fixed on conductive bilateral copper tape on a standard holder. For elevated pressure experiments with the SPECS photoelectron spectrometer cell, the sample of PdIn/Al_2O_3 calcined at 550°C was rubbed into stainless steel gauze spot welded to a standard holder. The Al2*p*, Pd3*d*, C1*s*, In3*d* and O1*s* regions were measured to determine the chemical (charge) states of the elements on the sample surfaces. For the calibration of the experimental spectra, the Al 2*p* line (BE= 74.5 eV) from alumina carrier as was used as an internal standard. The relative concentrations of the elements on the sample surface and ratios between their atomic concentrations were determined from the integrated intensities of photoelectron lines corrected for appropriate atomic sensitivity coefficients [J. H. Scofield, *J. Electron. Spectrosc. Relat. Phenom.*, 1976, **8**, 129].

Fourier-transform infrared spectroscopy of CO (FTIR-CO) DRIFT spectroscopy of adsorbed CO was performed with Tensor 27 spectrometer (Bruker, Germany) equipped with a liquid-nitrogen-cooled MCT detector and high temperature cell (Harrick, United Kingdom) for the *in situ* pretreatment of catalysts. The catalyst (20 mg) was placed in a cell with CaF_2 windows. The sample was reduced *in situ* at 500°C for 1 h with a 5% H_2/Ar mixture (30 cm^3 min^{-1}) and cooled from 500 to 200 °C in the H_2/Ar flow before measurements. The subsequent cooling to 50°C was carried in Ar flow. Recording of background spectrum was also carried at 50°C under Ar. DRIFT spectra of adsorbed CO were recorded under 0.5 % CO/He flow (30 cm^3 min^{-1}) at 50°C.

Catalytic tests

The liquid-phase hydrogenation of diphenylacetylene (98%, Aldrich) was carried out in a stainless steel autoclave-type reactor at 10 atm H_2, 25°C in *n*-hexane (98%, Merck). The reaction was monitored by periodically sampling the reaction mixture. Analysis of the reaction products was performed on a Crystal 5000 GC chromatograph (Chromatec, Russia) equipped with a capillary column HP5-MS (5% phenyl(dimethyl)siloxane, 30 m, 0.25 mm×0.25 µm, helium as the carrier gas) and flame ionization detector. On the basis of sampling time-dependences of components, yields were plotted and rates of components formation and consumption were calculated.

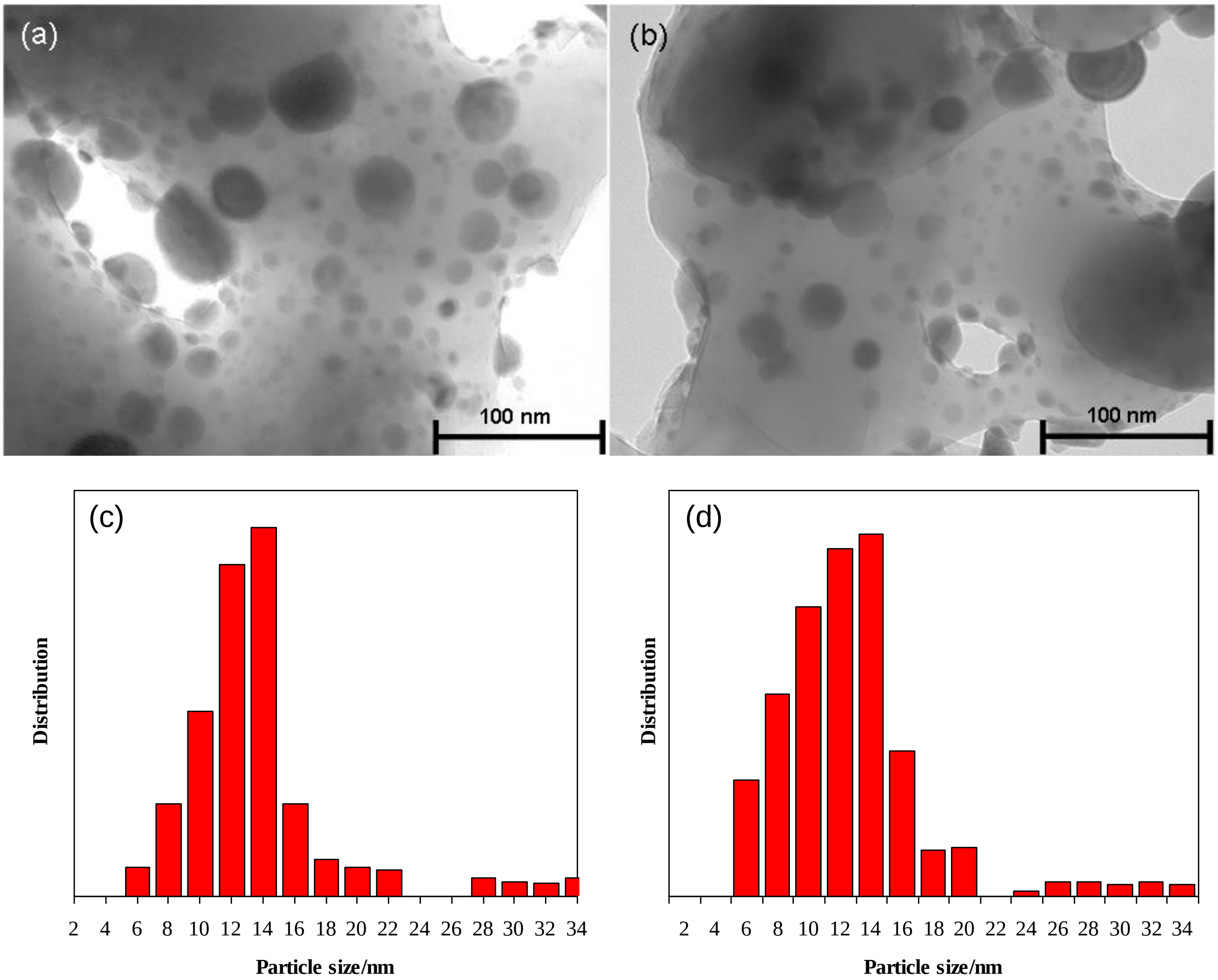

Figure S1 Representative TEM images and histograms of particle size distributions of Pd_1In_1 (*a*,*c*) and Pd_2In_3 (*b*,*d*) catalysts.

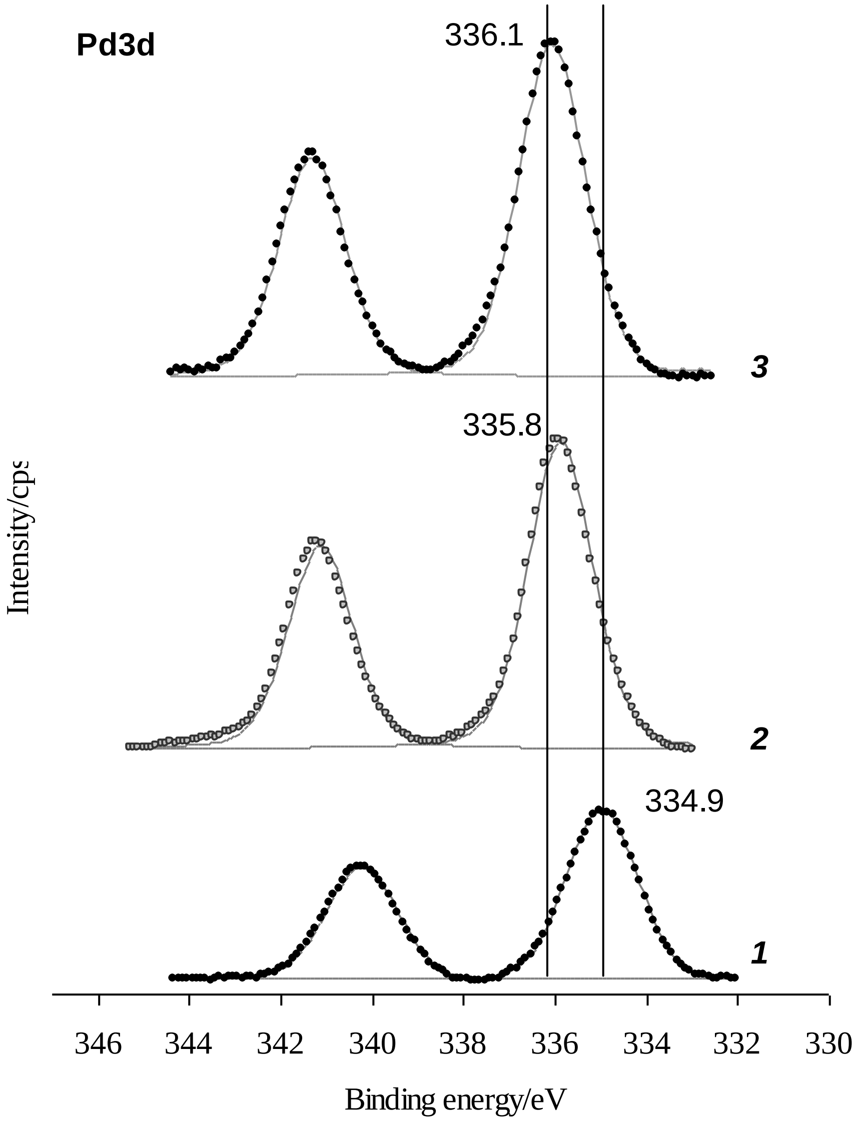

Figure S2 Pd3*d* XPS spectra for Pd (*1*), Pd_1In_1 (*2*) and Pd_2In_3 (*3*) catalysts.