Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 807–809

In situ FTIR study of surface sites transformations in $Pd_3In/\alpha\text{-}Al_2O_3$ and $Pd_3Ag/\alpha\text{-}Al_2O_3$ induced by CO adsorption

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Experimental

Catalyst preparation

Bimetallic Pd_3In (3% wt. Pd, 1.07 wt.%In) and Pd_3Ag (3wt.% Pd, 1 wt.%Ag) samples were obtained via incipient wetness co-impregnation of $\alpha\text{-}Al_2O_3$ (S_{BET} = 8 m^2/g, Alfa Aesar) by aqueous solutions of $Pd(NO_3)_2$ and $AgNO_3$ or $In(NO_3)_3$ (≥ 99.0 %, Sigma-Aldrich).

The reference 3 wt.%$Pd/\alpha\text{-}Al_2O_3$ sample was also prepared via incipient wetness impregnation by $Pd(NO_3)_2$ aqueous solution. The samples were dried in air and reduced in 5%H_2/Ar (Linde Gas Rus, Russia) flow at 550 °C for 3 h.

DRIFT-CO

DRIFT spectra of adsorbed CO were obtained from a Tensor 27 spectrometer (Bruker, Billerica, MA, USA) equipped with cooled by liquid nitrogen MCT detector and a high-temperature cell with CaF_2 windows (Harrick Scientific Products, Inc., Pleasantville, NY, USA). 20 mg of the powdered sample was placed into the cell and purged by an argon flow. The catalyst was reduced *in situ* at 500°C in a 5% H_2/Ar flow (30 cm^3/min) for 1h and then cooled down to 150°C; further cooling to 50°C with subsequent recording of background spectrum was carried under Ar flow. The difference spectra of adsorbed CO were recorded under 0.5 vol % CO/He flow (30 cm^3/min) at 50°C for 10 min (5 spectra, 250 scans, resolution of 4 cm^{-1}).

Adsorbate induced CO segregation was carried out by keeping the sample in a flow of 0.5 vol % CO/He at 200°C. The temperature was selected on the basis of literature data and our previous experimental results indicating that this temperature is sufficient to provide necessary mobility of Pd and Ag atoms and overcome the kinetic barrier of their inter-diffusion[S1-S5]. The spectra of adsorbed CO were collected for 4 h by recording the spectra each 2 min.

TEM

The morphology of the samples was studied by Hitachi HT7700 transmission electron microscope (Hitachi Ltd., Tokyo, Japan). TEM images were acquired at an accelerating voltage of 100 kV in the bright-field mode. Before the measurements powdered samples were dispersed from isopropanol suspension onto 3 mm carbon-coated copper grids. The distribution of particle size and their average diameter were calculated from measurements of 150-180 particles of various catalyst regions.

XRD

The diffraction patterns of the samples were obtained from a DRON-4 diffractometer (Russia) within the range 20°–90° 2θ with a step of 0.02° in the Bragg–Brentano geometry using CuK_α radiation (Ni filter). The exposure at each point was 1 s. Phase identification was carried out using PDF-4 2018 database. Rietan-FT computer program[S6] based on the Rietveld method was used for calculation of crystallographic parameters. The composition of bimetallic nanoparticles was calculated from the shift of Pd-Ag (111) peak using the Vegard's law[S5].

Results and discussion

TEM

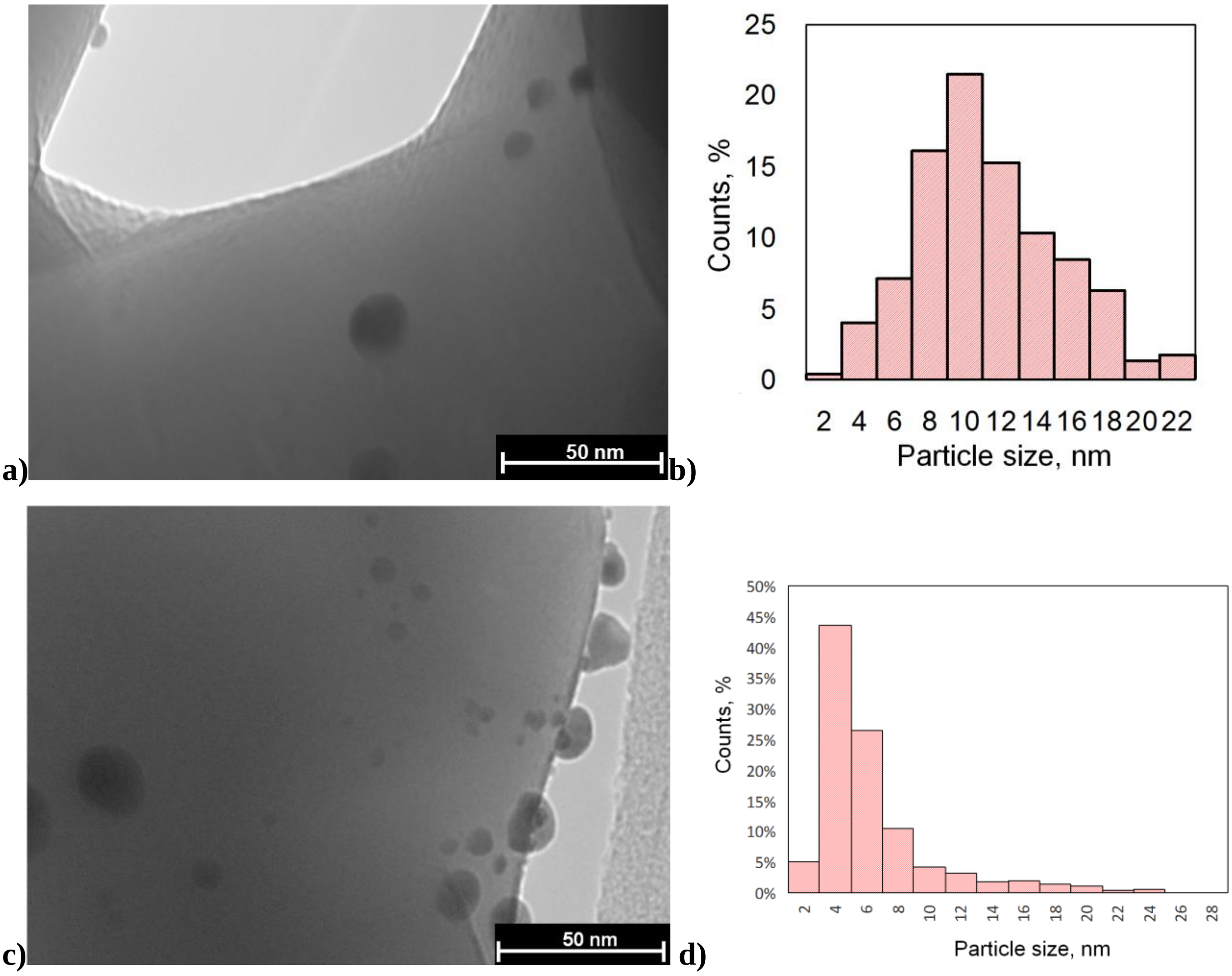

Figure S1. Representative TEM images for Pd_3Ag (a, b) and Pd_3In (c, d) samples

The representative TEM images for Pd-Ag (Fig. S1, a and b) and Pd-In samples (Fig. S1, c and d) revealed the presence of contrast near-spherical bimetallic nanoparticles. The average diameter for Pd_3Ag catalyst was 11.6 nm, whereas for Pd_3In sample this value was about 2 times smaller (5.4 nm). Both samples have a broad particle size distribution from 2 to 22-24 nm.

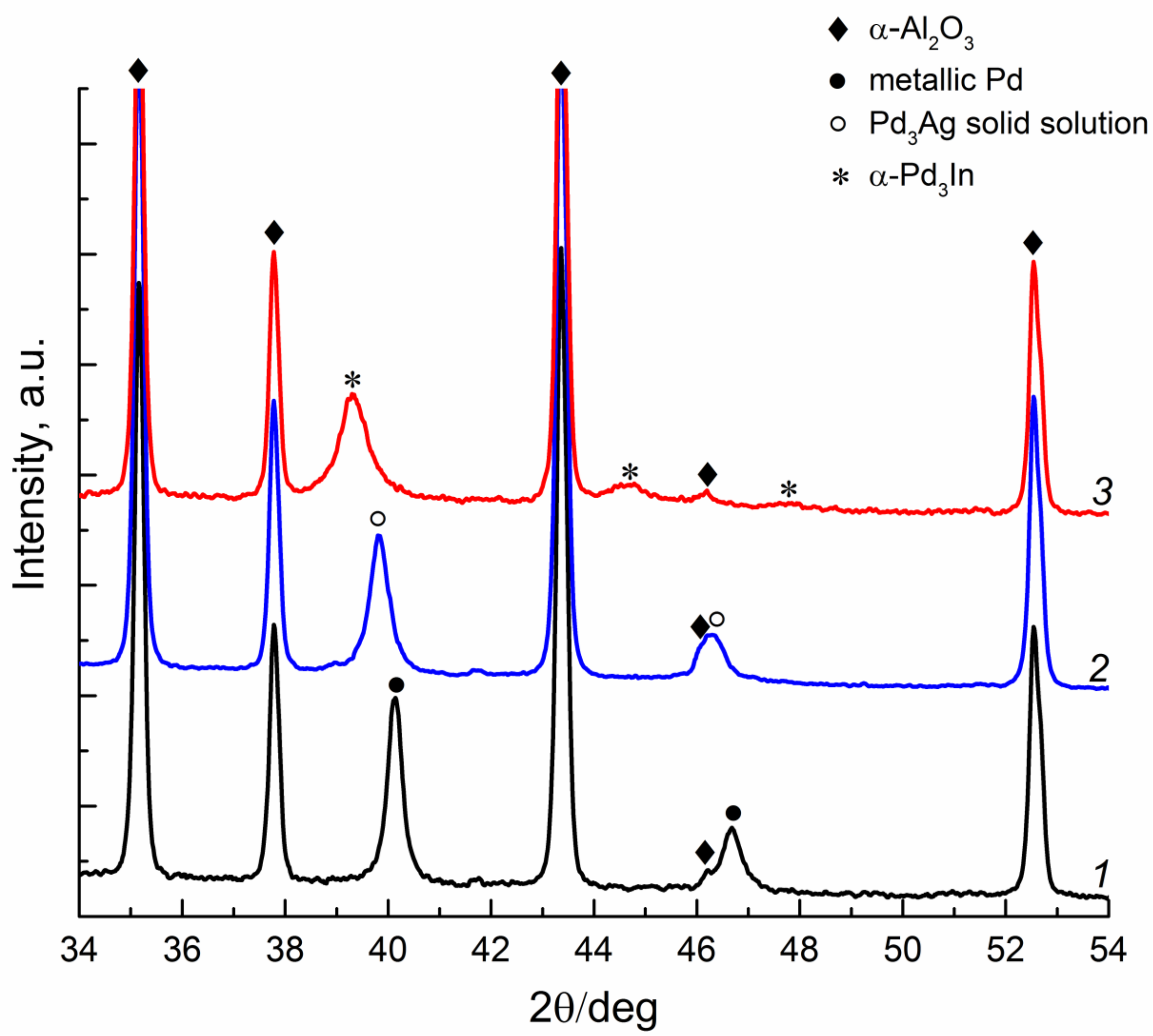

Figure S2. XRD patterns for monometallic Pd/α-Al_2O_3 (1), Pd_3Ag/α-Al_2O_3 (2) and Pd_3In/α-Al_2O_3 (3) samples

XRD patterns for Pd_3Ag/α-Al_2O_3, Pd_3In/α-Al_2O_3 and the reference monometallic Pd/α-Al_2O_3 catalysts within the range of 2θ = 34–54° are plotted in Fig. S2. The intensive narrow reflexes at 2θ of *ca*. 35.2, 37.8, 43.3, 46.3 and 52.4° are related to α-Al_2O_3 support. Small peaks at 40.1 and 46.7° attributed to Pd(111) and Pd(200), respectively, indicated the presence of palladium nanoparticles (Fig. 2, pattern 1). XRD pattern for Pd-Ag sample has two peaks at 39.8 and 46.3° which correspond to (111) and (200) reflections of fcc of solid palladium-silver solution with molar Pd:Ag ratio close to 3:1. XRD profile for Pd-In catalyst exhibits three peaks at 39.3, 44.7 and 47.8° assigned to a (114), (200) and (008) reflections from tetragonal α-Pd_3In intermetallide[S7, S8]. No reflections from other phases were found in these samples.

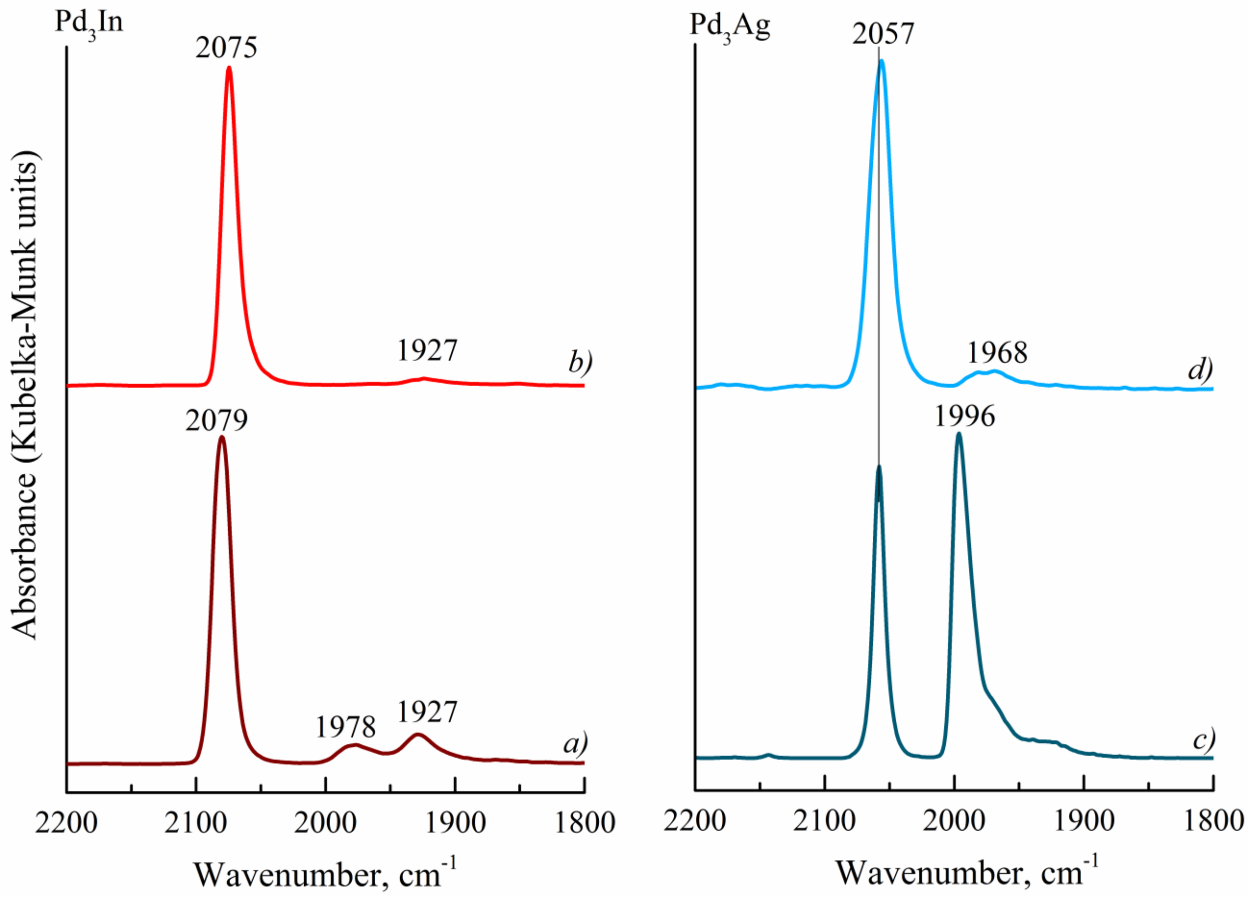

Figure S3. DRIFT spectra of adsorbed CO for Pd$_3$In and Pd$_3$Ag samples after 4h of CO segregation (a, c) and after subsequent reduction in 5%H$_2$/Ar (b, d)

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