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# Tuning the surface structure and catalytic performance of PdIn/$Al_2O_3$ in selective liquid-phase hydrogenation by mild oxidative-reductive treatments

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*Catalyst preparation*

As a catalyst support alumina oxide was used supplied by «Sasol» ($S_{BET}$ = 56 $m^2$/g). A bimetallic 2.5 wt.% Pd – 2.7 wt.% In/$Al_2O_3$ (In:Pd molar ratio is 1) catalyst was prepared by incipient wetness impregnation from heterobimetallic $PdIn(OAc)_5$ complex in accordance with a preparation procedure described elsewhere.[1] The sample was dried in air at room temperature and reduced in 5%$H_2$/Ar flow at 500 °C for 3 h. The final catalyst was grinded in a mortar to obtain a fine powder.

*Transmission electron microscopy*

Samples morphology was studied using Hitachi HT7700 transmission electron microscope. Images were acquired in bright-field TEM mode at 100 kV accelerating voltage. Before measurements the sample was deposited from isopropanol suspension on the 3 mm carbon-coated copper grids. Target-oriented approach was utilized for the optimization of the analytic measurements.[2]

*DRIFT spectroscopy of adsorbed CO*

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed with Tensor 27 spectrometer (Bruker, Germany) equipped with high-temperature cell (Harrick a Harrick Diffuse Reflectance Kit, UK) for *in situ* treatments. The sample compartment was filled with catalyst powder (20 mg). To study the surface transformation of the PdIn catalyst at

1 P. V. Markov, G. O. Bragina, G. N. Baeva, O. P. Tkachenko, I. S. Mashkovskii, I. A. Yakushev, M. N. Vargaftik and A. Yu. Stakheev, *Kinet. Catal.*, 2016, **57**, 617 (*Kinet. Katal.*, 2016, **57**, 621).

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different conditions the series of treatment oxidative/reductive was carried out *in situ* in a spectrometer cell according to the following scheme:

Step 1. The sample was reduced *in situ* in the 5 % v/v $H_2$/Ar flow at 500 °C during 1.5 h to obtain single-atom structure. After that the temperature was decreased to 50 °C under Ar flow and the background spectrum was recorded. Then CO (0.5% v/v CO/He, 30 ml/min) was adsorbed for 10 min and the difference spectra of adsorbed CO were collected (250 scans, 4 $cm^{-1}$ resolution).

Step 2. At this step the cell was cooled to 25 °C under Ar flow and then purged with 20 % v/v $O_2$/$N_2$ (synthetic air) at 25 °C for 30 min. Synthetic air was replaced by Ar followed by the subsequent heating to 50°C in Ar flow and recording adsorbed CO spectra by the method described above.

Step 3. At the third step the catalyst was subjected to oxidation by synthetic air at 150 °C for 30 min followed by cooling to 50°C and recording DRIFT spectra.

Step 4. The final step was the reductive treatment at 250°C with 5 % v/v $H_2$/Ar flow for 1.5 h. After cooling to 50 °C in Ar flow the DRIFT spectra were collected.

The catalyst loading of 2.5 mg was used to correlate the state of the surface after various treatments and its catalytic activity. In this case the sample after treatments was transferred under argon flow from the spectrometer cell to a catalytic reactor.

*Catalytic performance*

Hydrogenation of diphenylacetylene was carried out in a stainless-steel autoclave-type reactor at 5 atm of $H_2$ and 25°C. *n*-hexane (98%, Merck) was used as a solvent. Before the experiment an argon flow (~ 30 ml/min) was passed through the solvent for 3 hours to remove dissolved oxygen. The reaction products were analyzed on a Crystal 5000 chromatograph with a flame-ionization detector (Chromatek, Russia) equipped with HP5-MS column (5% Phenyldimethylsiloxane; 30 m length × 0.25 mm I.D. × 0.25 µm film thickness; A carrier gas is He).

The selectivity to desirable olefin formation ($S_=$) was calculated using the following equation:

$$S_= = n_=/(n_= + n_-),$$

where $n_=$ and $n_-$ are the mole fractions of the resulting olefin and alkane, respectively, determined via GC analysis. Note that selectivity to *cis-*/*trans*-isomer formation ($S_{cis}$, $S_{trans}$) was determined at DPA conversions of 95% ($X_{95\%}^{\equiv}$), and selectivity to diphenylethylene ($S_{=}$) was determined at DPA conversions of 50% ($X_{50\%}^{\equiv}$) and 95% ($X_{95\%}^{\equiv}$).

The reaction rate was determined from the rate of hydrogen uptake on the first (hydrogenation of triple bond to double bond) and the second (conversion of alkene to alkane) steps ($r_1$ and $r_2$, respectively). The specific activity (*TOF*) of the samples was calculated as the ratio of the number of molecules of the converted alkyne ($TOF_1$) or alkene ($TOF_2$) to the total number of palladium atoms in the catalyst per second. More details regarding catalytic tests and calculations can be found elsewhere.[3]

*X-ray Photoelectron Spectroscopy (XPS)*

For studying surface transformation of $PdIn/Al_2O_3$ induced by reductive and oxidative treatment the catalyst was re-reduced at 450°C in 5%$H_2$/Ar flow for 1 h in the pretreatment chamber and after that the sample was 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*ν = 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 $8 \times 10^{-9}$ 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 Pd–In/$Al_2O_3$ 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.[4]

For investigation the effect of partial oxidation treatment the catalyst was holded *in-situ* under conditions mimicking the ones of the catalyst oxidation in FTIR cell ($P_{O2}$ = 200 mbar, T = 150°C, 1 h).

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3 P. V. Markov, G. O. Bragina, A. V. Rassolov, G. N. Baeva, I. S. Mashkovsky, V. Yu. Murzin, Ya. V. Zubavichus and A. Yu. Stakheev, *Mendeleev Commun*., 2016, **26**, 502.

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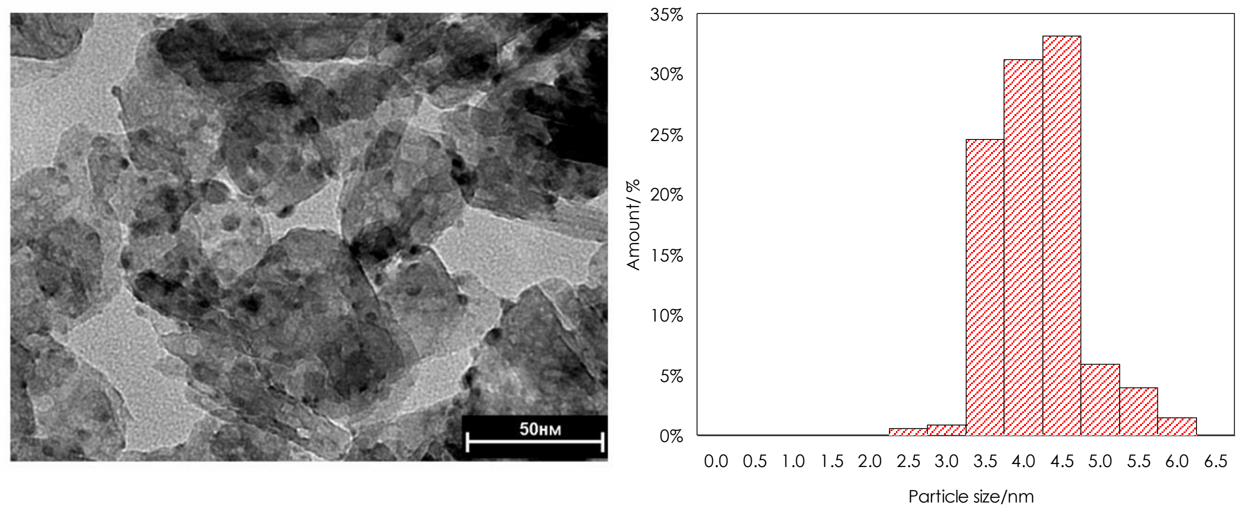


**Figure S1** Representative TEM micrograph and particle size distribution of 2.5 wt.% Pd – 2.7 wt.% In/$Al_2O_3$ catalyst.

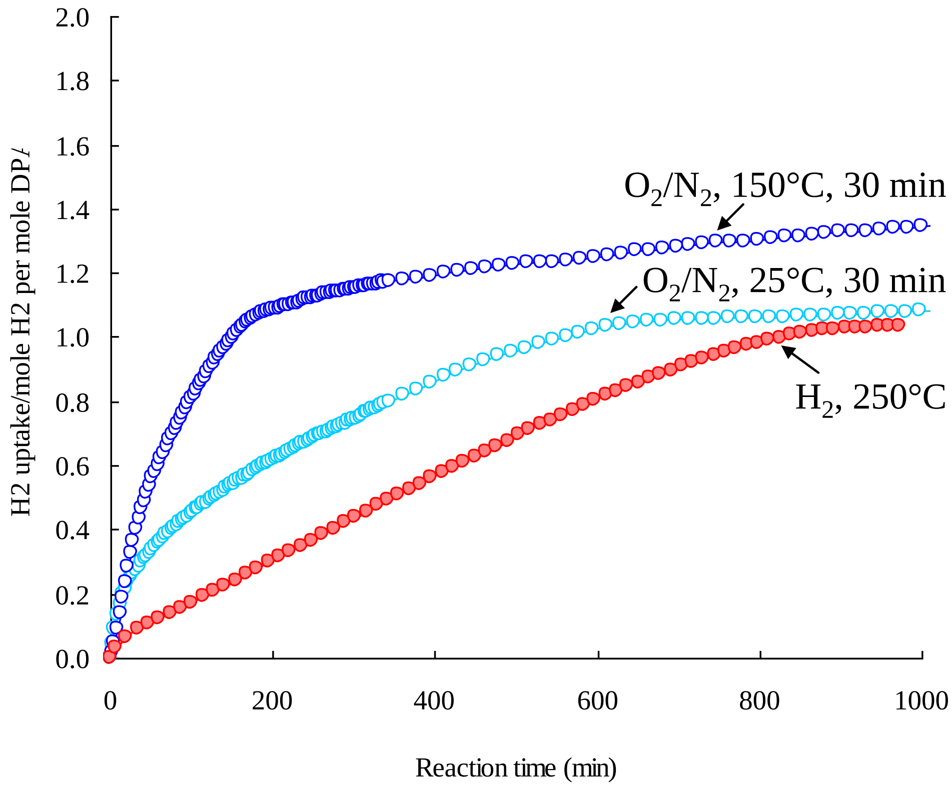


**Figure S2** Effect of oxidation/reduction treatments on the kinetic performance of Pd-In/$Al_2O_3$ catalyst.