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$PdZn/\alpha\text{-}Al_2O_3$ catalyst for liquid-phase alkyne hydrogenation: effect of the solid-state alloy transformation into intermetallics

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Catalysts preparation

For preparation of 3 wt.% Pd-1.8 wt.% $Zn/\alpha\text{-}Al_2O_3$ catalyst pre-calcined support ($\alpha\text{-}Al_2O_3$, S_{sp} = 8 m^2/g, «Alfa Aesar») was impregnated with an equimolar aqueous solutions of $Pd(NO_3)_2$ and $Zn(NO_3)_2$ to form an intermetallic compound with PdZn stoichiometry. After impregnation, the samples were dried at room temperature and then calcined in an air flow at 500°C for 4 h. To study the formation of intermetallic nanoparticles, the samples were reduced at 150, 200, 250, 300, 350 and 400°C (5% H_2/Ar, 2 h).

Monometallic $Pd/\alpha\text{-}Al_2O_3$ samples with 1 wt.% Pd (for TEM analysis) and 2 wt.% Pd (for XRD study) were also prepared by incipient wetness impregnation with an aqueous solution of $Pd(NO_3)_2$ nitrate. After air drying, the samples were reduced at 200°C (5%H_2/Ar, 2 h) without preliminary high-temperature calcination.

Selective alkyne hydrogenation

The liquid-phase hydrogenation of diphenylacetylene (98%, Aldrich) was carried out in an autoclave type reactor equipped with a magnetic stirrer, a gas supply system, and a sampling unit. The reaction was performed at 25°C and an initial hydrogen pressure of 10 bar in *n*-hexane (98%, Merck). The amount of absorbed hydrogen was estimated from the pressure drop using an electronic pressure sensor. The catalyst amount and the intensity of mixing were selected in such a way as to be sure that the process runs in the kinetic region.[1]

The reaction rate r ($mmol_{H2}$ mg_{Cat}^{-1} min^{-1}) was determined evaluating rate of hydrogen absorption from the graphic dependence of the amount of absorbed hydrogen on the reaction

[1] P. V. Markov, G. O. Bragina, G. N. Baeva, O. P. Tkachenko, I. S. Mashkovsky, I. A. Yakushev, N. Yu. Kozitsyna, M. N. Vargaftik and A. Yu. Stakheev, *Kinet. Catal.*, 2015, **56**, 599 (*Kinet. Katal.* 2015, **56**, 591).

time.[2] Because the hydrogenation of alkyne occurs in two stages, the reaction rate was calculated for both of them: in an range of 0.1-0.5 eq. H_2 absorption for the first stage (r_1) and 1.2-1.5 eq. H_2 absorption for the second stage (r_2).

The catalytic activity of the samples at each stage of the reaction was evaluated from the turnover frequency (TOF, s^{-1}). The amount of surface Pd atoms cannot be determined by electron microscopy for bimetallic catalysts because a part of the surface is occupied by the atoms of the second metal. Thus the value of TOF was calculated based on the total number of palladium atoms (N_{Pd}) in the catalyst as:

$$TOF = r/N_{Pd}$$

Selectivity to target olefin formation ($S_=$) was calculated based on the data of the GC analysis of the reaction mixture via the formula

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

where $n_=$ and n_- are the mole fractions of the resulting olefin and alkane, respectively.

The effectiveness of the kinetic process control was also evaluated by comparing the r_1/r_2 ratios between the rates of parent alkyne hydrogenation at the first and second stages in accordance with [3],[4].

The reaction mixture was analyzed on a Crystal 5000 chromatograph equipped with a flame-ionization detector and autosampler injector (Kchromatek, Russia). The components of the mixture were separated on an HP5-MS column (5% phenyldimethylsiloxane; 30 m × 0.25 mm ID with stationary phase film thickness 0.25 μm; and helium as carrier gas).

X-ray diffraction (XRD)

The diffractograms of the samples were measured on a D8 Advance diffractometer (Bruker, Germany; Cu*K*α, Ni filter, LYNXEYE detector, reflection geometry) at the Center of Collective Use of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences (IGIC RAS). The identification of peaks was performed using the PDF-2-2014 database. The experimental details were reported elsewhere[5].

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[2] I. S. Mashkovsky, P. V. Markov, G. O. Bragina, A. V. Rassolov, G. N. Baeva and A. Yu. Stakheev, *Kinet. Catal.*, 2017, **58**, 480 (*Kinet. Katal*., 2017, **58**, 508).

[3] J. Spee, J. Boersma, M. D. Meijer, M. Q. Slagt, G. van Koten and J. W. Geus, *J. Org. Chem.*, 2001, **66**, 1647.

[4] I. S. Mashkovsky, P. V. Markov, G. O. Bragina, O. P. Tkachenko, I. A. Yakushev, N. Yu. Kozitsyna, M. N. Vargaftik and A. Yu. Stakheev, *Russ. Chem. Bull., Int. Ed.*, 2016, **65**, 425.

[5] A. V. Gavrikov, P. S. Koroteev, Zh. V. Dobrokhotova, A. B. Ilyukhin, N. N. Efimov, D. I. Kirdyankin, M. A. Bykov, M. A. Ryumin and V. M. Novotortsev, *Polyhedron*, 2015, **102**, 4.

Transmission electron microscopy (TEM)

The microstructure of the samples was studied by TEM on a Hitachi HT7700 (Japan) instrument. The optimization of microscopic measurements was carried out within the framework of an approach described earlier.[6] Before the measurements, powdered samples were supported from a suspension in isopropanol onto copper gauzes 3 mm in diameter covered with a layer of carbon. The images were obtained in the transmitted electron detection mode (bright field imaging) at an accelerating voltage of 100 kV. The average size of metal particles was determined based on the measurement of 100–130 particles in the micrographs of different sections of the samples.

Hydrogen Temperature-Programmed Desorption (H_2-TPD)

Hydrogen temperature-programmed desorption were performed on a semiautomatic continuous flow setup consisting of a U-shaped quartz reactor, a water vapor trap, a thermal conductivity detector (TCD), and a data acquisition and processing unit. A trap cooled to –70°C (dry ice/ethanol bath) was placed between the reactor and the detector to remove water formed in the course of reduction from the gas phase. The sample (25 mg) was placed to the reactor and dryed in Ar flow (300°C, 1 h). Than the sample was saturated in a 5% H_2/Ar flow for 15 min and cooled down to -70°C. The H_2 saturation temperature corresponds to the catalyst reduction temperature at the preparation stage. H_2-TPD analysis was performed at temperature range from -70 to 300°C with 10°C/min ramp and the consumption of hydrogen was continuously measured by TCD.

X-ray Photoelectron Spectroscopy (XPS)

$PdZn/Al_2O_3$ catalyst was reduced *in-situ* at 200, 250, 300 and 400°C before experiment. 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 (E_b) was preliminarily calibrated based on the peak positions of the gold and copper core levels: Au $4f_{7/2}$ (E_b = 84.0 eV) and Cu $2p_{3/2}$ (E_b = 932.67 eV). The residual gas pressure in the course of the measurements was no higher than 8×10^{-9} mbar. The powdered samples were fixed on conductive bilateral copper tape on a standard holder. For high pressure experiments with the SPECS photoelectron spectrometer cell, the sample of $Pd–Zn/Al_2O_3$ calcined at 550°C was rubbed into stainless steel gauze spot welded to a standard holder. The Al 2*p*, Pd 3*d*, C 1*s*, Zn 2*p*, Zn LMM, O 1*s*, and Pd MNN regions were measured to determine the chemical (charge) states of the elements on the

[6] 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.

sample surfaces. For the calibration of the experimental spectra, the Al 2*p* line (E_b = 74.5 eV) from aluminum as a constituent of the α-Al_2O_3 support was used as an internal standard. The relative concentrations of the elements on the sample surface and ratios between their atomic concentrations were found from the integrated intensities of photoelectron lines corrected for appropriate atomic sensitivity coefficients.[7]

[7] J. H. Scofield, *J. Electron. Spectrosc. Relat. Phenom.*, 1976, **8**, 129.

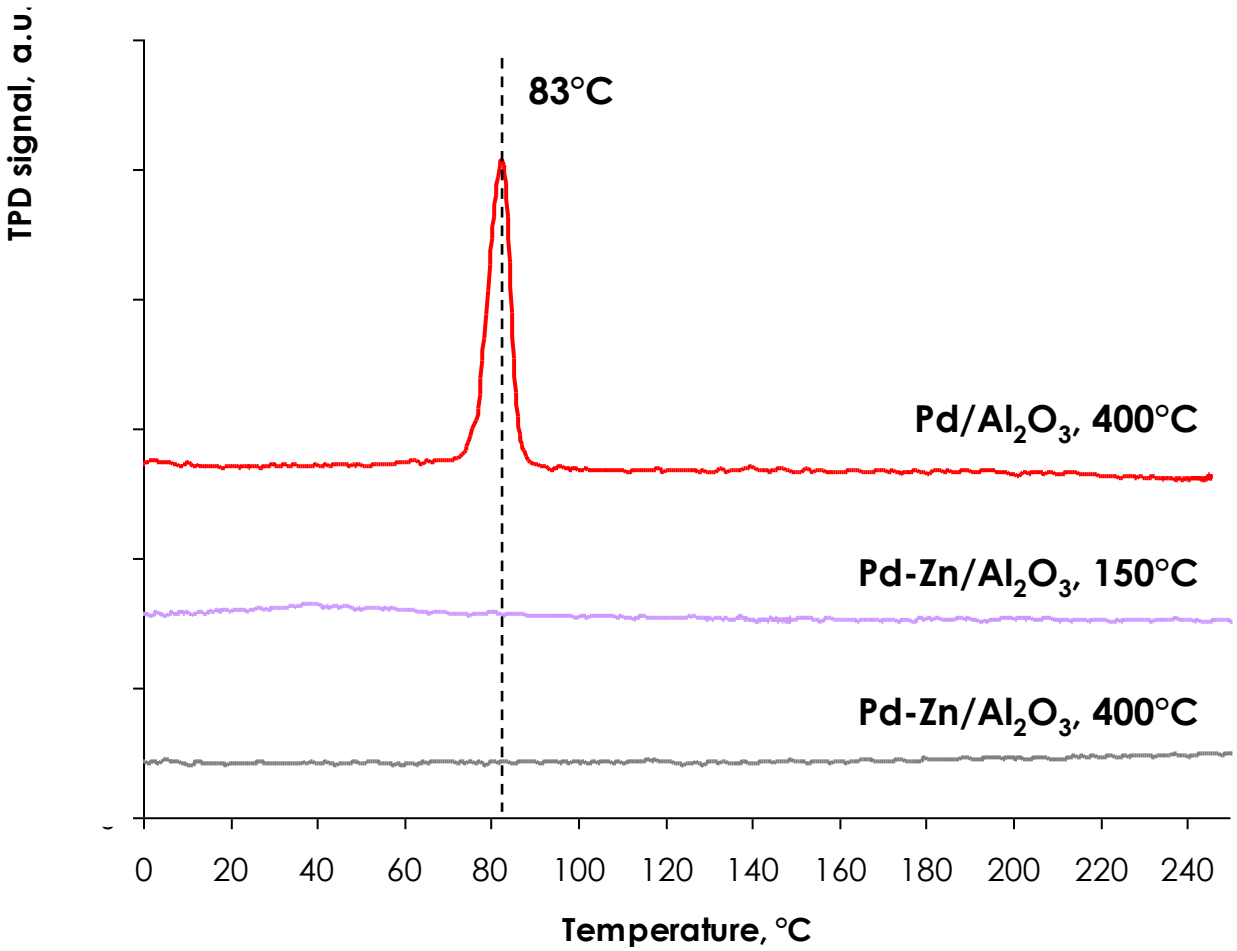

Figure S1 H_2 - TPD profiles of Pd- and PdZn- supported catalysts reduced *in-situ* (5%H_2/Ar, 1 h) at 150°C and 400°C.

Table S1 Kinetic parameters of synthesized catalysts in liquid-phase diphenylacetylene hydrogenation (P_{H2}, = 10 bar, 25 °C, m_{cat} = 5 mg, *n*-hexane as solvent).

Catalyst	T_{red}, °C	TOF_1, s^{-1}	TOF_2, s^{-1}	TOF_1/TOF_2	$S_{=}^{90\%}$, %
Pd/α-Al_2O_3	as received*	2.69	0.28	9.61	91
PdZn/α-Al_2O_3	200	0.631	0.0168	37.56	92
	250	0.534	0.0085	62.82	94
	300	0.578	0.0118	48.98	94
	350	0.526	0.0084	62.62	94
	400	0.354	0.0038	93.16	94

* see *Catalyst preparation* section for details