Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 547–549

CO-induced segregation as an efficient tool to control the surface composition and catalytic performance of $PdAg_3/Al_2O_3$ catalyst

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Catalyst preparation

Alumina oxide (purchased from Sasol, specific surface area of 56 $m^2\ g^{-1}$) was used as the catalyst support. A bimetallic Pd(2%)–Ag(6%)/Al_2O_3 (wt%, molar ratio Ag : Pd = 3 : 1) catalyst was prepared by incipient wetness impregnation with an aqueous solution of corresponding nitrates. The sample was dried in air and reduced in H_2(5%)/Ar flow at 550 °C for 3 h. This catalyst is signed as $PdAg_3/Al_2O_3$ throughout the manuscript.

DRIFT spectroscopy of adsorbed CO

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded using a Tensor 27 spectrometer (Bruker, Germany) equipped with a high-temperature cell for *in situ* treatments (Harrick DRIFT kit). The sample compartment was filled with catalyst powder (20 mg). The sample was initially reduced *in situ* under a H_2(5 vol%)/Ar flow at 500 °C for 1h to obtain PdAg bimetallic nanoparticles featuring the surface structure of Pd_1 single-atom. After that, the temperature was lowered down to 50 °C under Ar flow, and the background spectrum was recorded. Then CO (CO(0.5 vol%)/He, 30 ml min^{-1}) was adsorbed, and the difference spectra of adsorbed CO were collected (250 scans, resolution of 4 cm^{-1}).

The CO-induced segregation was carried out as follows: after heating to 250 °C, the cell was filled with CO(30%)/N_2 (30 ml min^{-1}) and kept for 1h. After cooling to 50 °C under Ar, the CO(0.5 vol%)/He mixture was introduced, and the difference spectra of adsorbed CO were recorded.

X-ray Photoelectron Spectroscopy (XPS)

X-ray measurements were performed using 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 basing on the peak positions of copper and gold core levels: Cu $2p_{3/2}$ (BE = 932.67 eV) and Au $4f_{7/2}$ (BE = 84.0 eV). The High-Pressure Cell (HPC) introduced in one of the chambers of the photoelectron spectrometer allows one to made pretreatments of the samples under different gases at the pressures up to 1 bar and temperatures ranging from 50 to 500 °C. After the pretreatment, the sample was cooled down to RT and the cell was pumped out to UHV conditions. Thus, the sample could be transferred to analyzer chamber after reduction without any contact with air, *i.e.* the additional oxidation of the catalyst surface by oxygen presented in air was excluded. The samples were supported on the stainless steel mesh spot welded on the standard sample holder. To investigate the $PdAg_3/Al_2O_3$ surface transformation, the sample was re-reduced at 450 °C under H_2 (100 mbar) for 1 h in the HPC and transferred without any contact with air to the analysis chamber for photoelectron spectra measuring. At the next step, the sample was treated with CO (300 mbar) at 20, 100 and 200 °C for 1h with the subsequent registration of spectra as described above. Integral intensities of the Auger lines of silver and palladium (Ag MNN and Pd MNN, respectively) were used for the estimation of redistribution of atoms on the surface of bimetallic particles.

Transmission electron microscopy

The microstructure of samples was investigated using a Hitachi HT7700 transmission electron microscope.[S1] The images were obtained in the bright-field mode at 100 kV accelerating voltage. The samples were deposited before imaging from isopropanol suspension on carbon-coated copper grids with the diameter of 3 mm.

Catalytic performance

Selective hydrogenation of acetylene into ethylene was performed in a continuous-flow quartz reactor under atmospheric pressure at the temperature ranging from 25 to 150 °C. The as-prepared catalyst was additionally diluted with Al_2O_3 to minimize the reaction heat effect. The components were thoroughly grounded in a mortar, pressed, crushed, and sieved in order to obtain an appropriate particle size for the catalytic evaluation (0.2–0.4 mm). For catalytic test, a granulated mixture (40 mg, wherein 2 mg of catalyst and 38 mg of Al_2O_3) was loaded into the reactor. The temperature of catalyst bed was monitored with a Cr–Al thermocouple and maintained using a Termodat (Perm', Russia) temperature controller within an accuracy of ±0.5 °C. A total gas flow of 64 ml min^{-1} consisting of commercial pre-mixed C_2H_2 (1.09 vol%) in C_2H_4 and H_2 (5 vol%) in Ar (H_2 : C_2H_2 molar ratio was 5 : 1) was used as the reactant feed. The gases were mixed using Bronkhorst's mass flow controllers. The reaction products were

analyzed by gas chromatography using a Crystallux-4000M instrument (Meta-Chrom, Yoshkar-Ola, Russia) equipped with a CP7518 column (CP-Al_2O_3/KCl, 50 m×0.53 mm, 10.00 μm) and flame ionization detector. Immediately before the catalytic measurements, the initial sample was calcined under air flow at 500 °C for 1 h with the consequent treatment with a high purity nitrogen flow at 500 °C for 30 min and reduction with H_2(5%)/Ar flow at 500 °C for 1 h. The treatment with CO flow was carried at 250 °C for 1 h followed by thorough nitrogen purging to remove any residual CO from the catalyst surface.

The acetylene conversion ($X_{C_2H_2}$) was calculated as the ratio of total amount of the reacted acetylene (ΔC_2H_2) to the initial amount of acetylene in the feed ($C_2H_{2(initial)}$):

$$X_{C_2H_2} = \Delta C_2H_2/C_2H_{2(initial)}$$

The selectivity towards the ethylene formation ($S_{C_2H_4}$) was estimated as follows:

$$S_{C_2H_4} = (\Delta C_2H_2)/(\Delta C_2H_2 + C_2H_6),$$

wherein ΔC_2H_2 is the total amount of reacted acetylene and C_2H_6 is the amount of resulting ethane.

Table S1 Characteristics of $PdAg_3/Al_2O_3$ catalysts obtained after various treatments in the hydrogenation of C_2H_2.

H_2 at 500 °C			**CO at 250 °C**		
***T*/°C**	***X* (%)**	***S* (%)**	***T*/°C**	***X* (%)**	***S* (%)**
37	0.0	0.0	36	0.1	0.0
45	1.2	94.4	44	2.9	94.3
51	2.1	93.8	55	10.1	95.5
61	6.2	92.9	69	26.5	95.2
69	11.5	93.5	74	33.3	95.3
77	17.7	93.8	80	46.1	95.0
84	24.6	94.1	86	57.5	94.1
91	35.8	94.1	92	69.5	92.3
99	48.9	94.0	97	78.4	90.0
106	63.3	93.1	102	84.9	87.9
111	73.4	91.8	108	90.7	85.2
117	81.5	89.7	113	94.9	82.2
122	86.5	88.3	118	96.6	80.6
126	90.7	86.5	123	97.9	77.9
132	93.6	84.9	133	100.0	70.3
143	97.1	81.8			
151	98.3	79.7			
156	100.0	75.2			

Table S2 Comparison of the experimental data with literature.

Catalyst	Preparation technique	Pd	M	Reaction mixture C_2H_2 : H_2 : C_2H_4 (vol%)	*T*/°C	$X_{C_2H_2}$	$S_{C_2H_4}$	Reference
		(wt%)				(%)		
$PdAg_3/Al_2O_3$	Incipient wet impregnation	2	6	0.5 : 2.6 : 46.4	108	90.7	85.2	This work
$AgPd/Al_2O_3$	Surface redox (SR)	1	0.3	1.01 : 2.02 : 96.97	60	> 90	< 0	S2
$Pd@Ag/TiO_2$	Photodeposition	0.95	0.97	0.73 : 1.46 : 52.6	60	82	79	S3
$PdIn/Al_2O_3$	Incipient wet impregnation	0.5	0.45	0.6 : 1.8 : -	60	90	70	S4
$AgPd/SiO_2$	Electroless deposition	1.85	2.05	1 : 5 : 20	65	~60	~60	S5
$AgPd/Al_2O_3$ industrial sample	N_2O pretreated	-	-	1.46 : 1.71 : 81.36	70	< 50	< 95	S6
$PdAg/Al_2O_3$	Incipient wet impregnation	3	6	0.58 : 30.45 : 57.33	85	95	80	S7
$AgPd/TiO_2$	Incipient wet co-impregnation	1	3	1.14 : 4.76 : 94.1	95	-	< 25	S8
$PdCu/Al_2O_3$	Incipient wet co-impregnation	1.67	10	0.6 : 1.8 :-	150	99	71	S9
$AgPd_{0.01}/SiO_2$	Incipient wet co-impregnation	0.046	4.87	1 : 20 : 20	160/320	> 90	> 80	S10
$AgPd_{0.01}/SiO_2$	Incipient wet co-impregnation	0.046	4.87	1 : 20 : 20	160	90	80	S11
$CuPd_{0.006}/SiO_2$	Incipient wet co-impregnation	0.046	4.96	1 : 20 : 20	160	100	85	S11
$AuPd_{0.025}/SiO_2$	Incipient wet co-impregnation	0.046	4.78	1 : 20 : 20	160	90	25	S11
$GaPd_n$ (n = 1,2) unsupported nanoparticles	two-step synthesis	-	-	0.5 : 5 : 50	200	> 90	65–80	S12

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