Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 836–838

An egg-shell PdAg/α-Al_2O_3 single-atom alloy catalyst for selective acetylene hydrogenation

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Catalyst preparation

Commercial spherical Al_2O_3 (1.4mm ±0.2mm) with S_{sp} ~ 8 m^2/g was used as the support. The XRD pattern of this alumina showed the presence of alfa-alumina phase only. The preliminary calcined at 500°C spherical support pellets were treated in acetic acid (pH=2.8) at room temperature for 1 hour to increase the concentration of adsorption sites, which is beneficial for the formation of egg-shell structure.[S1] Then the material was washed with distilled water until neutral pH and dried at 120°C.

Bimetallic PdAg/Al_2O_3 catalysts with 0.06 wt % Pd and 0.12 wt % Ag loadings (Pd:Ag molar ratio 1:2) was obtained by incipient-wetness impregnation of pretreated alumina spheres with a methanol solution of heterobimetallic complex $PdAg_2(OAc)_4(HOAc)_4$. An advantage of such precursor is that the Pd and Ag atoms in the structure of this complex are strongly bonded by acetate bridges and thus is favorable for the formation of bimetallic Pd-Ag particles on the catalyst surface. The absence of competing ions in the impregnating solution encourages the formation of egg-shell distribution of the adsorbate. The product was air-dried at room temperature overnight. The “impregnation-drying” procedure was repeated 5 times in all. The reference monometallic Pd/Al_2O_3 (0.06 wt % Pd) was prepared by incipient-wetness impregnation of pretreated alumina spheres with $Pd(CH_3COO)_2$ solution. The catalysts were subsequently dried overnight at 120°C and calcined in dry-air (300 mL/min) at 500°C. The egg-shell structure was revealed for both Pd and Pd_1Ag catalysts (Fig. S1).

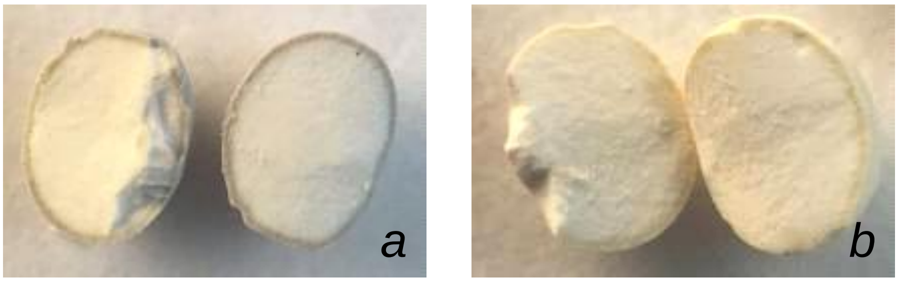

Figure S1 Photos of Pd_1Ag (a) and Pd (b) SAA egg-shell catalysts.

Catalyst characterization

DRIFT CO

DRIFT spectroscopy of adsorbed CO was performed using Bruker Tensor 27 spectrometer (Leipzig, Germany) with a Harrick high temperature cell (Pleasantville, NY, USA) and MCT detector, cooled by liquid nitrogen. About 25-30 spheres of egg-shell catalyst were placed in a sample compartment and *in situ* reduced with a 5% H_2/Ar flow (30 cm^3/min) supplied by «Linde Gas Rus» (purity 6.0) at 500°C for 60 h. Subsequent oxidative treatment was carried out at 350°C, 1 h under 20%O_2/N_2 flow. After each *in situ* treatment the cell was flushed with Ar for 10 min. After that the final reduction of sample at 500°C for 1.5 h with a flow of 5% H_2/Ar was performed. Then the sample compartment was cooled down in 5% H_2/Ar flow to 150°C. In case of monometallic palladium sample the cell was cooled in 5% H_2/Ar flow to 200°C to avoid the formation of palladium hydrides. Subsequent cooling to 50 °C and recording of background spectrum was carried under Ar flow («Linde Gas Rus», purity 6.0, 30 cm^3/min).

DRIFT spectra of adsorbed CO were collected in 0.5%CO/N_2 flow (30 cm^3/min) («Linde Gas Rus», purity 6.0) at 50°C during 10 min of exposure to CO-containing atmosphere (500 scans, 4 cm^{-1} resolution).

FESEM-EDS

Before measurements the pre-reduced (5 wt.%H_2/Ar flow, 500°C, 90 min) PdAg sample was mounted on a 25 mm aluminum specimen stub, fixed by conductive plasticine-like carbon adhesive and coated with a 15 nm film of carbon. The observations were carried out using Hitachi Regulus 8230 field-emission scanning electron microscope (FE-SEM). Images were acquired in backscattered electron mode (compositional contrast) at 20 kV accelerating voltage. EDS-SEM studies were carried out using Bruker Quantax 400 EDS system equipped with XFlash 6|60 detector at 20 kV accelerating voltage. Target-oriented approach was utilized for the optimization of the analytic measurements.[S2]

XPS

The XPS measurements were performed using a «PREVAC EA15» electron spectrometer. In the current work, AlKα (hν = 1486.74 eV, 150 W) was used as a primary radiation source. The pressure in analytical chamber did not exceed 5×10^{-9} mbar during spectra acquisition. The binding energy (BE) scale was pre-calibrated using the positions of $Cu2p_{3/2}$ (932.7 eV), $Ag3d_{5/2}$ (368.3 eV) and $Au4f_{7/2}$ (84.0 eV) from copper, silver and gold foils, respectively. A pre-reduced

(5 wt.%H_2/Ar flow, 500°C, 90 min) spherical egg-shell catalyst was placed on the sample holder of spectrometer and the spectra were recorded from outer surface of pellets. Along with survey photoelectron spectrum, the regions of the Pd3d, Al2p, O1s, and C1s were recorded. The survey spectra were obtained at pass energy of 200 eV and; the narrow-range spectra, at pass energy of 2 eV. To calibrate the recorded spectra, the C1*s* line (E_b = 284.5 eV) from carbon was used as an internal standard The XPSPeak software was used to fit the XPS spectra and Shirley background subtraction. The surface composition of egg-shell catalyst pellet was estimated from XPS integral intensities of Pd3d, Ag3d and Al2p photoelectron peaks corrected by atomic sensitivity factors.[S3]

Catalytic tests

The selective hydrogenation of acetylene in excess ethylene was performed at ambient pressure in quartz reactor (D_{in}=4mm) placed in tube electric furnace. Spherical catalyst diluted with silicone carbide SiC to have a bed height of 12 mm was retained in the reactor between two plugs of quartz wool. In order to get an accurate measurement of the catalyst temperature, thermocouple was positioned in the bottom of catalyst bed. The test gas mixture consists of 1.0 vol % acetylene, 94% ethylene, 5.0 vol % hydrogen balanced in argon was introduced through a Brohkhorst mass flow meter at 50 nml/min to obtain GHSV of 5000 h^{-1}. The reaction temperature was varied to study the selectivity-conversion behavior of the catalysts. To compare the catalysts performance in the same temperature range for PdAg and monometallic Pd catalysts, the used loads were adjusted according to the activity of the catalysts and were 150 mg and 300 mg for Pd and PdAg samples. Specific activity normalized by amount of Pd was calculated for better catalysts comparability. The reaction products were analyzed by a gas chromatograph (Meta-Chrom, Crystallux-4000M) equipped with alumina capillary column (50 m×0.53 mm, 10.00 μm) and a flame ionization detector (FID).

Acetylene conversion was calculated by estimating the changes in corresponding chromatographic peak area before and after reaction according to:

$$X_{C2H2}=(A(C_2H_2)_{feed}-A(C_2H_2))/A(C_2H_2)_{feed}$$

where $A(C_2H_2)_{feed}$ and $A(C_2H_2)$ are a chromatographic peak areas of acetylene before and after reaction.

The formation of ethylene could not be measured directly because of it extremely high concentration in the feed mixture and therefore acetylene and ethane are the only two components serve to reaction performance calculation. Therefore, ethylene selectivity S_{C2H4} was calculated according to:

$$S_{C2H4}=100\%-=(A(C_2H_2)_{feed}-A(C_2H_2))/((A(C_2H_2)_{feed}-A(C_2H_2))+A(C_2H_6))$$

where $A(C_2H_6)$ is a chromatographic peak area of formed ethane. The activity A ($mmol(C_2H_2)/mg(Pd)/min$) of the catalysts was calculated using the following equation:

$$A=X_{C2H2}*Flow_{feed}*C_{C2H2}/V_m/(m_{cat}*C_{Pd})$$

where $Flow_{feed}$ and C_{C2H2} are total gas flow through the reactor (nml/mon) and acetylene concentration in the feed (vol.%), m_{cat} and C_{Pd} are amount of catalyst loaded into the reactor (mg) and Pd concentration in the catalysts (wt.%), Vm – molar volume of gas at STP, 22.4 ml/mmol.

Table S1. Atomic ratios of elements for Pd and Pd_1Ag samples on the basis of XPS data from the external surface of catalyst pellet and according to bulk composition.

Catalyst	**XPS data**			**Bulk composition**		
	Ag/Pd	**Pd/Al**	**Ag/Al**	**Ag/Pd**	**Pd/Al**	**Ag/Al**
Pd	-	$2.83x10^{-2}$	-	-	$3.82x10^{-4}$	-
PdAg	3.8	$5.68x10^{-2}$	0.22	2.0	$3.83x10^{-4}$	$7.64x10^{-4}$

Table S2. Catalytic characteristics of Pd and Pd_1Ag egg-shell catalysts in acetylene hydrogenation.

Catalyst	**A, mmol(C_2H_2)/mg(Pd)/min**	**X, %**	**S,%**
Pd	0.071	90.1	57.1
Pd_1Ag	0.042	90.3	91.8

References

S1 F. Pinna, *Catal. Today*, 1998, **41**, 129.

S2 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.

S3 J. H. Scofield, *Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 129.