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Single-atom alloy Pd_1Ag_{10}/Al_2O_3 catalyst: effect of CO-induced Pd surface segregation on the structure and catalytic performance in the hydrogenation of C_2H_2

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Catalyst preparation procedure

The bimetallic $PdAg/Al_2O_3$ catalyst was obtained by incipient wetness coimpregnation of the preliminary calcined γ-Al_2O_3 (Sasol, Germany; S_{BET} = 56 m^2/g) at 550°C for 3 h. As an aqueous impregnation solution, a mixture of $Pd(NO_3)_2$ (99.9 %, Alfa Aesar, 14.86% Pd) and $AgNO_3$ ($\geq$ 99.0 %, Sigma Aldrich) was used in suitable amounts to obtain the Pd and Ag loads of 0.5 wt.% and 5 wt.%, respectively. The impregnated material was subsequently dried overnight at ambient temperature, calcined in a flow of dry-air (300 ml/min) at 550°C for 3 h and then treated in a 5%H_2/Ar flow (70 ml/min) at 500°C for 3 h. The temperature was ramped from room temperature to 500°C at 3°C/min. The selected reduction conditions provide a high degree of metals reduction maintaining their good dispersion.[S1] The Pd (0.47 wt. %) and Ag (5.1 wt. %) contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The catalyst is denoted as Pd_1Ag_{10}/Al_2O_3 throughout the text.

Experimental

High-resolution transmission electron microscopy (HRTEM). The HRTEM images were obtained with a ThemisZ electron microscope (Thermo Fisher Scientific, Waltham, MA, USA) operated at an accelerating voltage of 200 kV and equipped with a corrector of spherical aberrations, which provided a maximum lattice parameter resolution of 0.06 nm and an EDX SuperX spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a semiconductor Si detector providing an energy resolution of 128 eV. Images were obtained using a Ceta 16 CCD sensor (Thermo Fisher Scientific, Waltham, MA, USA). For HRTEM analysis samples were ultrasonically deposited on a holey carbon film mounted on an aluminum grid.

DRIFTS CO. DRIFT spectra of adsorbed CO were obtained via Tensor 27 IR spectrometer (Bruker Optics Inc, Billerica, MA, USA), equipped with a high temperature cell and an MCT detector cooled by liquid nitrogen. The Harrick Diffuse Reflectance Kit (Harrick Scientific Products Inc, Pleasantville, NY, USA) included the cell with CaF_2 windows designed for *in situ* experiments in a flow of different gaseous mixtures. The load of powdered

Pd_1Ag_{10}/Al_2O_3 catalyst (~ 10 mg) was placed into the cell, purged by an argon flow and was *in situ* reduced at 500°C by a flow of 5 vol.% H_2/Ar (30 ml/min) during 1 h. Then the sample was cooled from 500 to 150°C under blowing 5 vol.% H_2/Ar, a subsequent cooling to 50°C was carried under an Ar flow. Background spectrum was recorded at 50°C under blowing Ar, the difference spectra of adsorbed CO (250 scans, 4 cm^{-1} resolution) were collected under a flow of 0.5 vol.%CO/N_2 (30 ml/min) for 10 min.

CO-induced segregation procedure. The sample was heated to 200°C in an Ar flow and maintained for 1 h in the flow of 30 vol.% CO/N_2 (30 ml/min). The cooling to 50°C was carried in an Ar flow, the difference spectra of adsorbed CO was taken by the same procedure as described above using background from the previous run. The obtained spectra were processed using the Opus Software Version 7.2 (Bruker Optics Inc, Billerica, MA, USA) and Origin Pro 2021 Version 9.8.0.200 (OriginLab, Northampton, MA, USA) software codes.

X-ray Photoelectron Spectroscopy (XPS). The XPS experiments were performed with a SPECS photoelectron spectrometer (Germany) using AlK_α radiation (hν = 1486.6 eV, 150 W). The scale of binding energies (BE) was preliminarily calibrated using peak positions of $Cu2p_{3/2}$ (BE = 932.67 eV) and $Au4f_{7/2}$ (BE = 84.0 eV) measured for copper and gold foils. The High-Pressure Cell (HPC) introduced in one of the chambers of the spectrometer allows one to made pretreatments of the samples under different gases at the pressure up to 1 bar and temperature range 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 the analyzer chamber after reduction without the contact with air, i.e., avoiding probable oxidation of the catalyst surface by oxygen presented in air. The samples were supported on the stainless-steel mesh spot welded on the standard sample holder. The Pd_1Ag_{10}/Al_2O_3 samples freshly reduced (50 mbar H_2 at 500˚C) and treated in 300 mbar CO at 200°C were comparatively studied. The Al2p, C1s, O1s, Pd3d and Ag3d core-level spectra were measured after each treatment step. Spectral analysis and data processing were performed with an XPS Peak 4.1 software (R.W.M. Kwok, Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong).[S2] To take into account the effect of surface charging, the Al2p line at BE = 74.5 eV of the support (Al_2O_3) was used as an internal standard. Integrated line intensities were calculated from the area of peaks in the corresponding narrow regions (Al2p, C1s, O1s, Pd3d and Ag3d). The relative amount of the elements on the sample surface and the ratio of their atomic concentrations were determined from the integrated intensities of the lines corrected against their atomic sensitivity factors.[S3]

Selective acetylene hydrogenation. The hydrogenation of acetylene in an excess of ethylene was carried out in a quartz reactor (D_{in}=4mm) at ambient pressure. Prior to the catalytic tests the finely powdered catalyst was pressed into a pellet (preliminarily crushed and sieved to get a particle size of 0.2-0.4 mm) to ensure a proper flow in the reactor and prevent channeling of the gas. The typical catalyst loading was 0.030 g to form the catalyst bed of ~5 mm height that was held in place between two plugs of quartz wool in the middle of the reactor. A fresh catalyst load was applied for each test. A thermocouple placed just after the catalyst bed was used to accurately monitor the process temperature.

To study the effect of CO-induced segregation on the Pd_1Ag_{10}/Al_2O_3 catalytic performance the sample was pretreated *in situ* as follows: (1) Heating the catalyst under 50 ml/min air flow to 500°C during 1 hour ramp and holding for 30 min; (2) Flushing the catalyst with N_2 at 500°C and switching to a flow of 50 ml/min 5%H_2/Ar for 90 min at the same temperature. To perform CO-induced segregation the catalyst was cooled down to 200°C and exposed to 50 ml/min of 30% CO/N_2 during 1 h followed by cooling to room temperature in flow of 50 ml/min N_2 to remove any residual CO.

After the CO-induced segregation procedure, the gas mixture containing 0.5 vol. % C_2H_2, 45.1 vol. % C_2H_4, 2.65 vol.% H_2 balanced in Ar with a total flow of 64 ml/min was introduced into the reactor using Bronkhorst mass flow controllers (Bronkhorst Instruments GmbH, Leonhardsbuch, Germany). All catalysts were tested in acetylene hydrogenation from room temperature to 120°C. Reaction temperature was kept constant for 20 min and being increased to the next point after product sampling. The reaction products were analyzed by an on-line gas chromatograph Crystallux-4000M (Meta-Chrom, Yoshkar-Ola, Russia) equipped with an alumina capillary column (Agilent CP7518, CP-Al_2O_3/KCl, 50 m×0.53 mm, 10.00 μm) and a FID detector.

The acetylene conversion (X_{C2H2}) was calculated as the ratio of the total amount of reacted acetylene ($\Delta C_2H_2 = [C_2H_{2(initial)}]-[C_2H_{2X}]$) to the initial amount of acetylene in the feed $[C_2H_{2(initial)}]$:

$$X_{C2H2}= \Delta C_2H_2 /[C_2H_{2(initial)}]$$

The change in the ethylene amount cannot be accurately measured because of its extremely high concentration in the reaction mixture and therefore C_2H_2 and C_2H_6 are the only two components that were used for the calculation of reaction performance characteristics. Calculation of the ethylene selectivity (S_{C2H4}) assumes that the formation of higher hydrocarbons and carbon deposits are negligible and the ethane formation is the only undesirable side reaction that leads to a selectivity loss:

S_{C2H4}=100%-C_2H_6/ΔC_2H_2,

where C_2H_6 is the ethane amount in the product stream.

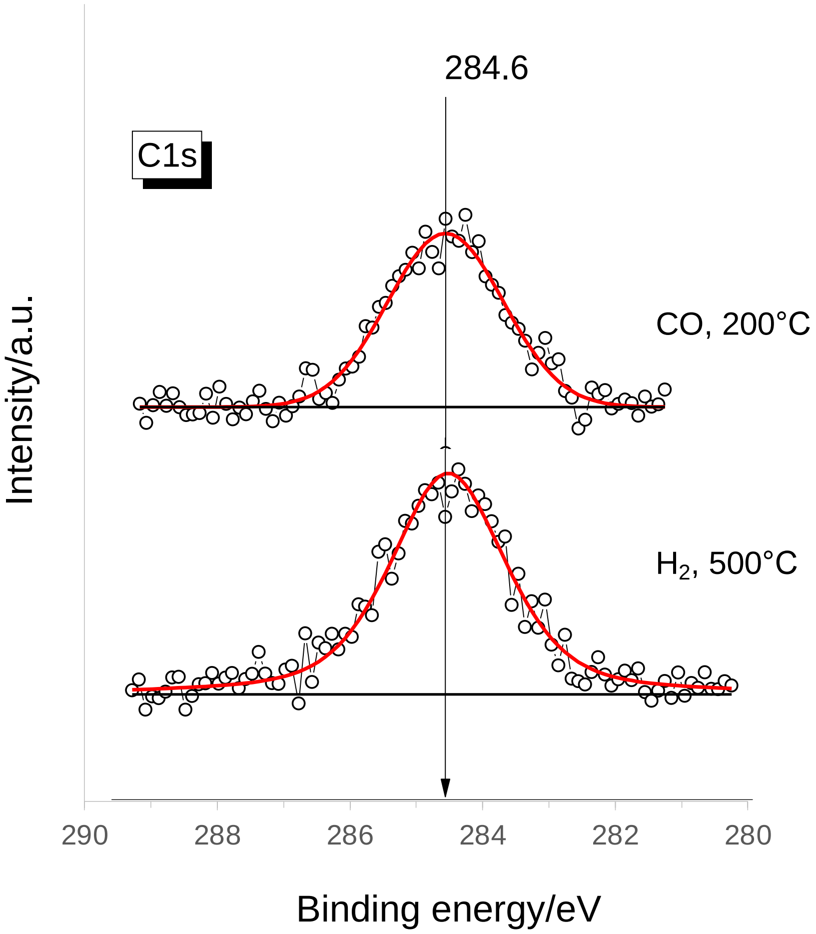

Figure S1 C1s core-level spectra for the Pd_1Ag_{10}/Al_2O_3 catalyst reduced at 500 °C and treated in CO at 200°C.

References

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