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Efficient performance of the Pd_1Cu_n/Al_2O_3 catalyst in front-end acetylene hydrogenation

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Catalyst preparation

The series of bimetallic Pd-Cu/Al_2O_3 with Cu:Pd molar ratios of 1, 5 and 10 was obtained. Gamma-Al_2O_3 («Sasol», S_{BET}=56 m^2/g) was used as a support. All catalysts were obtained via the incipient wetness impregnation of preliminarily calcined Al_2O_3 (air flow, 550°C, 5°C/min ramp, 3 h,) with a mixed solution of $Cu(NO_3)_2$ and $Pd(NO_3)_2$ followed by drying in air overnight at room temperature. Following the drying the samples were exposed to calcination at 550°C (5°C/min ramp) for 3 h in flowing air and reduction in 5%H_2/Ar flow at 550°C (5°C/min ramp) for 2h.

The metal content in the catalysts was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an OPTIMA 2000 instrument (Perkin Elmer Inc., USA). The instrument was equipped with a solid-state CCD detector and a double monochromator. The spectra were recorded in the range of 160–900 nm with a resolution of 0.007 nm at a wavelength of 193 nm. The measurements showed: 1 wt. % Pd and 0.6 wt. % Cu for Pd_1Cu_1/Al_2O_3, 1 wt. % Pd and 3 wt. % Cu for Pd_1Cu_5/Al_2O_3, and 1 wt. % Pd and 6 wt. % Cu for Pd_1Cu_{10}/Al_2O_3. Thus, catalysts with Cu/Pd ratios of 1, 5 and 10 were synthesized.

The monometallic 1 wt. % Pd/Al_2O_3 and 6 wt. % Cu/Al_2O_3 reference catalysts were also prepared according to the described procedure.

Catalyst characterization

A target-oriented approach was utilized for the optimization of the analytic measurements.[S1] To collect TEM micrographs a Hitachi HT 7700 electron microscope (Japan) was used at an accelerating voltage of 100 kV in the bright-field regime. Before measurements the samples were deposited on the 3 mm carbon coated copper grids from isopropanol suspension. More than 180 metal particles located in different parts of the samples were measured to estimate the particle size distribution. The average metal particle size (d_{av}) was calculated according to the following formula:

$$d_{av} = \frac{\Sigma n_i d_i}{n},$$

where n_i is the number of nanoparticles with a diameter d_i; n is the total number of nanoparticles.

DRIFT spectra of adsorbed CO were obtained using Bruker Tensor-27 FTIR Spectrometer (Bruker, Germany), equipped with Praying Mantis™ Diffuse Reflection Kit (Harrick Scientific Products Inc, USA), including a high-temperature reaction chamber with CaF_2 windows for sample treatment and *in situ* measurements. The powdered catalyst (~10-15 mg) was loaded into the sample holder and placed into the reaction chamber. The sample was *in situ* calcined in 20%O_2/N_2 flow at 350°C for 1 h, then cooled down to 90°C and flushed with Ar. After oxidation treatment the sample was *in situ* reduced in the flow of 5%H_2/Ar at 500°C for 1h, cooled down to 150°C in 5%H_2/Ar flow with subsequent cooling to 50°C in Ar. The background was recorded at 50°C under Ar; the flow was then switched to 0.5%CO/N_2 and the difference spectra of adsorbed CO were collected (250 scans, 4 cm^{-1} resolution). The processing of obtained spectra was performed with the use of OPUS 7.2.139.1294 software.

Selective acetylene hydrogenation

All catalysts were tested in a flow-type setup at ambient pressure. The catalysts were placed in a quartz reactor. Prior to testing, the catalysts were activated in a 5% H_2/Ar flow (Moscow Gas Refinery Plant, Russia) at 550°C for 1 h and were cooled to room temperature in a N_2 (99.999% pure, Moscow Gas Refinery Plant, Russia) flow. The reaction was temperature-controlled using a chromel–alumel thermocouple placed in the catalyst bed. The reaction products were analyzed using a Crystallux 4000M chromatograph (Meta-Chrom, Russia) equipped with a flame ionization detector. A 50 m×0.53 mm×10 μm CP-Al_2O_3/KCl capillary column was used to separate the reaction products.

The acetylene conversion, $X(C_2H_2)$, was derived from the corresponding chromatographic peak areas by internal normalization. Specifically, it was quantified as the ratio of the change in the acetylene concentration at the reactor outlet to the acetylene concentration at the inlet:

$$\boldsymbol{X(C_2H_2) = \frac{C(C_2H_2)_{in} - C(C_2H_2)_{out}}{C(C_2H_2)_{in}} \times 100},$$

where $C(C_2H_2)_{in}$ and $C(C_2H_2)_{out}$ are the acetylene concentrations at the inlet and outlet of the reactor, respectively.

The relative concentrations of acetylene, ethylene, and ethane were evaluated using relevant correction factors.[S2] A 1%C_2H_2/C_2H_4 gas mixture (Monitoring, Russia) was used to determine the absolute concentrations.

The ethylene selectivity, $S(C_2H_4)$, was calculated by the equation:

$$\boldsymbol{S(C_2H_4) = \frac{\Delta C_2H_2 - \Delta C_2H_6}{\Delta C_2H_2} \times 100},$$

where ΔC_2H_2 and ΔC_2H_6 are the amounts (in moles) of the reacted acetylene and the ethane product, respectively.

A front-end acetylene hydrogenation conditions were simulated as follows: the H_2/C_2H_2 ratio was equal to 60, meaning that the reaction mixture contained 0.5 vol. % C_2H_2, 50 vol. % C_2H_4, 30 vol. % H_2, 150 ppm CO, with the balance being N_2. All gases were of a high purity and were supplied by Moscow Gas Refinery Plant, Russia.

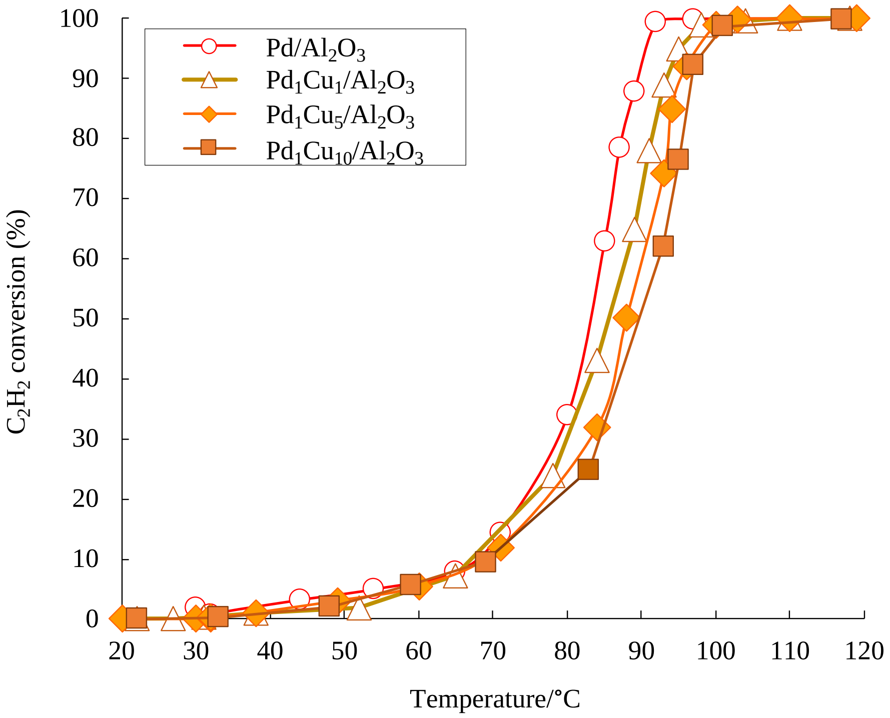

Figure S1 Acetylene conversion as a function of temperature for Pd/Al_2O_3 and Pd_1Cu_n/Al_2O_3 catalysts in acetylene hydrogenation under front-end conditions.

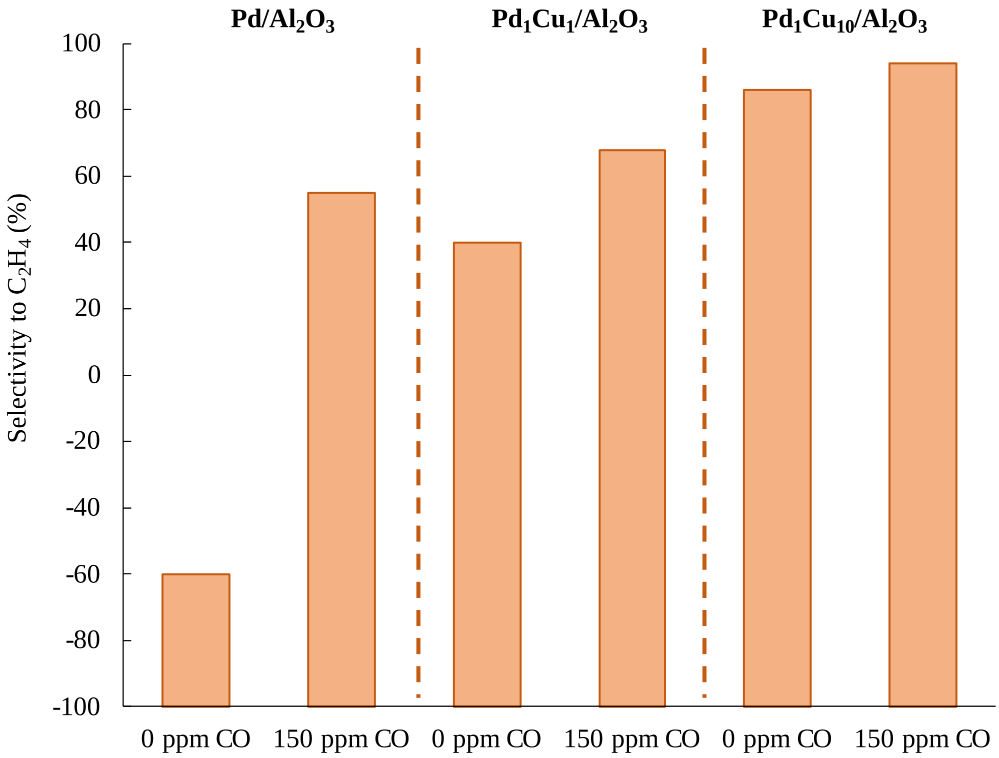

Figure S2 Effect of CO on the performance of Pd/Al_2O_3, Pd_1Cu_1/Al_2O_3, and Pd_1Cu_{10}/Al_2O_3 catalysts in acetylene hydrogenation under front-end conditions at C_2H_2 conversion of ~ 90%.

References

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S2 W. A. Dietz, *J. Chrom. Sci.*, 1967, **5**, 68; https://doi.org/10.1093/chromsci/5.2.68.