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The influence of the support on the efficiency of Pd_1Cu_3 catalysts in two-stage olefin synthesis

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Experimental

Catalyst preparation

The catalysts were prepared using a traditional method of incipient wetness impregnation of supports calcined in an air stream at 550°C with solutions of the corresponding metal nitrates. Commercially available oxides such as CeO_2 (S_{BET} = 6 m^2/g, ChemCraft, Russia), SiO_2 (S_{BET} = 101 m^2/g, Chrom-lab, Russia), Al_2O_3 (S_{BET} = 6 m^2/g, Sasol, Germany), and TiO_2 (Degussa P25, S_{BET} = 51 m^2/g, Sigma Aldrich, Germany) were used as supports. After impregnation, the resulting samples were dried at room temperature, calcined in an air stream for 4 hours, and reduced in a flow of 5 % H_2/Ar at 550°C for 3 hours. The temperature regime was chosen to ensure high mobility of the catalyst components on the support surface and the formation of more uniform bimetallic nanoparticles. The quantitative metal content of the finished catalysts corresponded to 3 wt. % Pd and 5.4 wt. % Cu, as confirmed by inductively coupled plasma mass spectroscopy (ICP-MS) and X-ray diffraction analysis. In addition, monometallic reference samples of Pd/TiO_2 and Cu/TiO_2, containing 3 wt. % Pd and 5.4 wt. % Cu, were synthesized using a similar procedure.

XRD

The phase composition of the synthesized catalysts was studied by X-ray phase analysis (XRD). Diffraction patterns of the starting supports, monometallic and bimetallic Pd_1Cu_3 catalysts were obtained on a DRON-4 diffractometer (NPP Burevestnik, Russia) using Cu-Kα radiation (Ni filter, wavelength λ = 1.54059 nm). The samples were studied in the angle range of 20 – 85° (2 Θ) with a step of 0.02° (2θ) and holding at a point for 3 seconds. Crystallographic data were calculated using the Rietan-FT software, which uses the Rietveld method.

Low temperature nitrogen adsorption

The textural characteristics of the samples were studied using the method of low-temperature nitrogen adsorption at 77 K on an Autosorb iQ gas sorption analyzer (Quantachrome inst., USA). Previously, the samples were subjected to degassing in a vacuum environment at 50 Torr for 3 hours at a temperature of 300°C. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The total pore volume was calculated from the amount of nitrogen gas adsorbed at a relative pressure close to unity. The average pore size was determined from the ratio of the pore volume and their surface area. The porous structure of the samples was assessed by the DeBoer method (t-plot). Pore size distribution was calculated using the BJH method (Barrett-Joyner-Halenda).

IR spectroscopy of adsorbed CO

IR spectra were recorded using a Tensor 27 IR spectrometer (Bruker, Germany) equipped with a Harrick Diffuse Reflectance Kit (Harrick, UK). Sample surface treatment and characterization were performed in situ in a thermostatted cell using the following procedure.

In the first step, a sample of crushed catalyst (0.01 g) was placed in a cell with CaF_2 glasses and heated in a flow of Ar (30 ml/min) (Linde Gas Rus, Balashikha, Russia) to 500°C. The sample was then subjected to reduction treatment with a 5% H_2/Ar mixture (30 ml/min) for 1 hour at 500°C. The cell was then cooled first in a flow of 5% H_2/Ar to 100°C and then in a flow of Ar (30 ml/min) to 50°C to record the background spectrum. After this, adsorption of 0.5% CO/He (Linde Gas Rus, Balashikha, Russia) was carried out at a temperature of 50°C for 10 min and spectra were recorded (250 scans, resolution 4 cm^{-1}).

Transmission electron microscopy

The morphological characteristics of monometallic Pd/TiO_2, Cu/TiO_2 and bimetallic Pd_1Cu_3 catalysts were studied by transmission electron microscopy (TEM) using a JEM-2100 electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. Before imaging, the powder sample was ground in a mortar and suspended in ethanol in an ultrasonic bath. A drop of the suspension was applied to Formvar grids (Ted Pella) and dried in vacuum. The average diameter of the metal nanoparticles was ascertained by graphical means, whereby approximately 250 particles were measured in TEM images of various samples.

Evaluation of catalytic performance

The catalytic properties of the obtained samples were studied using the example of sequential Sonogashira reactions and liquid-phase hydrogenation of the resulting product. For this purpose, the following reagents were placed into a vial equipped with a magnetic stirrer: phenylacetylene (0.45 mmol, 46 mg, 1.1 eq.), iodobenzene (0.45 mmol, 91.8 mg, 1 eq.), catalyst (1.1 mol % Pd), K_2CO_3 (0.6 mmol, 1.3 eq.), internal standard naphthalene (0.1 mmol, 12.8 mg), and dimethylacetamide (2 mL). The initial stage of the tandem process (cross-coupling) was conducted for a duration of 8 hours at a temperature of 80 °C, under atmospheric pressure, and with a stirrer speed of 350 rpm.

The hydrogenation of the product obtained in the Sonogashira reaction (diphenylacetylene) was carried out in a catalytic autoclave unit equipped with an electronic pressure sensor and a gas dosing and sampling system. Prior to the initiation of the hydrogenation reaction, a quantity of quartz (0.1 g) was incorporated into the reaction mixture with the objective of preventing catalyst adhesion to the vial walls. Thereafter, the vial was placed within the autoclave. In order to expel air from the autoclave and gas lines, the unit was purged with helium (6.0 purity). Subsequently, the reactor was pressurized with He to the designated operating pressure (5 bar), and the heating was initiated. Upon reaching 80°C, the pressure was released and the autoclave was filled with hydrogen to the operating pressure (5 bar). A pre-installed pressure sensor was utilized to monitor the constant pressure and the rate of hydrogen uptake. The second stage lasted 16 hours.

The reaction products were analyzed by gas chromatography using a Crystal 5000 chromatograph («Chromatec», Russia) equipped with a flame ionization detector and an HP5-MS capillary chromatographic column (5% phenyldimethylsiloxane) with a length of 30 m, an internal diameter of 0.25 mm, and a stationary phase film thickness of 0.25 μm. The composition of the reaction mixture was determined quantitatively, with naphthalene as the internal standard. In addition, the composition of carbon-containing products after each stage of the process was studied by GC-MS method using a Maestro-2 chromatograph.

The conversion of phenylacetylene in the first stage of the two-stage process was calculated according to formula

$$X_{PhA} = \frac{\left(m^0_{PhA} - m^6_{PhA}\right)}{m^0_{PhA}} \times 100\%$$, where

m_{PhA}^0 – mass of phenylacetylene before the cross-coupling reaction; m_{PhA}^6 – mass of phenylacetylene after the cross-coupling reaction;

The mass of phenylacetylene after the cross-coupling stage was calculated using formula

$$m_{PhA}^{8} = \frac{m_{PhA}^{0}}{m_{Nap}^{0}} \times \frac{S_{Nap}^{0}}{S_{PhA}^{0}} \times \frac{S_{PhA}^{8}}{S_{Nap}^{8}} \times m_{Nap}^{0}$$, where

m_{Nap}^{0} – mass of naphthalene before the cross-coupling reaction; S_{Nap}^{0} – peak area of naphthalene before the cross-coupling reaction; S_{PhA}^{0} – peak area of phenylacetylene before the cross-coupling reaction; S_{PhA}^{8} – peak area of phenylacetylene after the cross-coupling reaction; S_{Nap}^{8} – peak area of naphthalene after the cross-coupling reaction; m_{Nap}^{0} – mass of naphthalene before the cross-coupling reaction.

The selectivity for target olefins ($S_{\sum cis\text{-}+\ trans\text{-}}$) was calculated according to formula

$$S_{\sum cis\text{-}+\ trans\text{-}} = \frac{n_{cis\text{-}} + n_{trans\text{-}}}{\left(n_{cis\text{-}} + n_{trans\text{-}} + n_{alkane}\right)}$$, where

$n_{cis\text{-}}$, $n_{trans\text{-}}$ and n_{alkane} – the molar fractions of the resulting alkenes and alkane, respectively.

Results and discussion

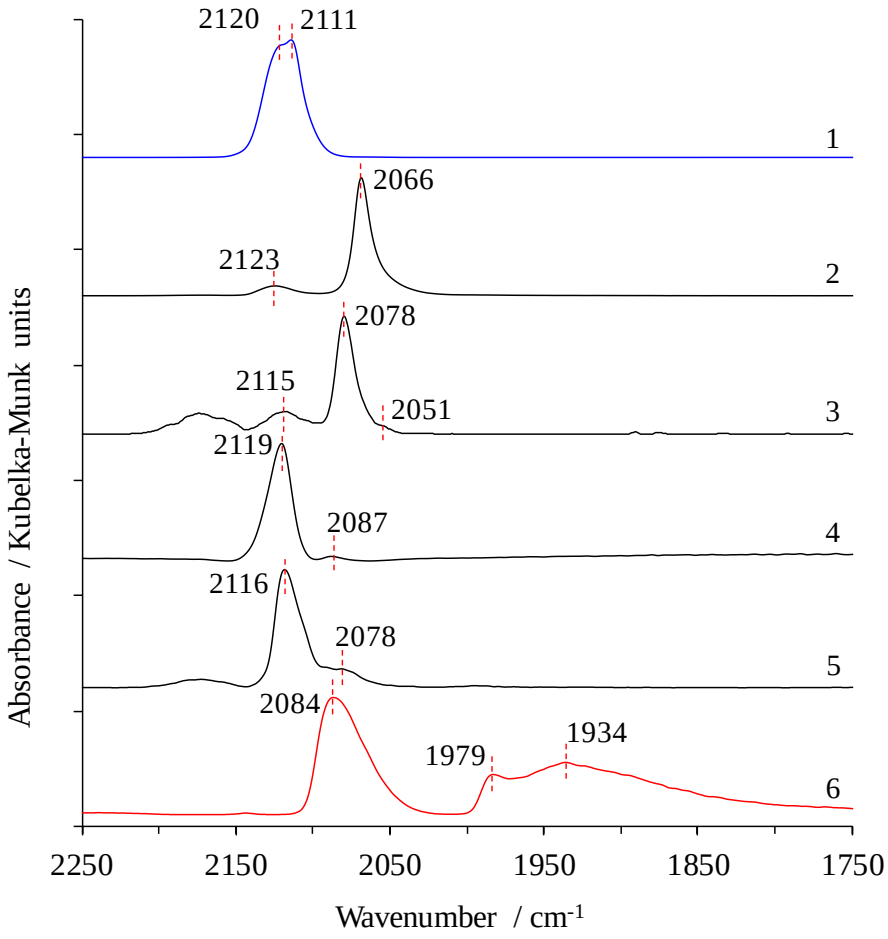


Figure S1 Normalized DRIFT-CO spectra for in situ reduced monometallic (1) Cu/TiO_2, (6) Pd/TiO_2 and bimetallic Pd_1Cu_3 catalysts supported on (2) Al_2O_3, (3) SiO_2, (4) TiO_2 and (5) CeO_2.

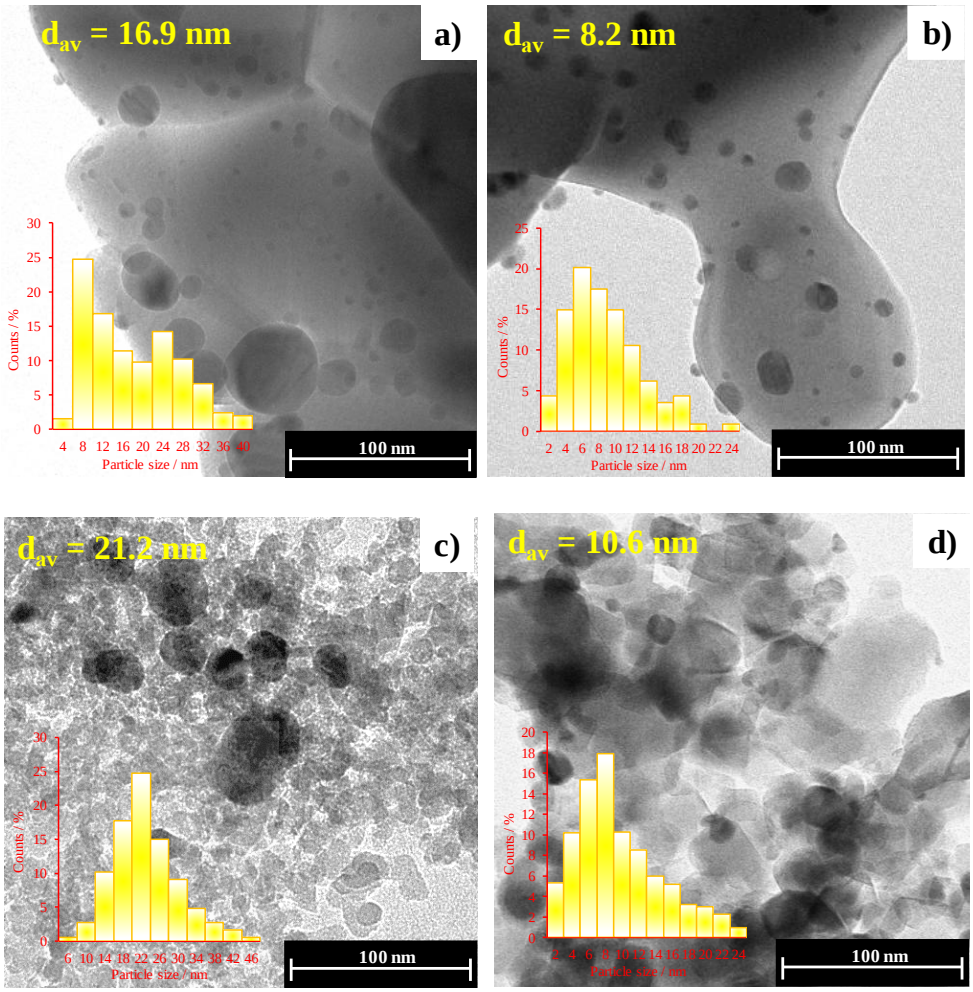


Figure S2 TEM images and histograms of nanoparticle size distribution for (a) Pd_1Cu_3/CeO_2, (b) Pd_1Cu_3/Al_2O_3, (c) Pd_1Cu_3/SiO_2 and (d) Pd_1Cu_3/TiO_2.

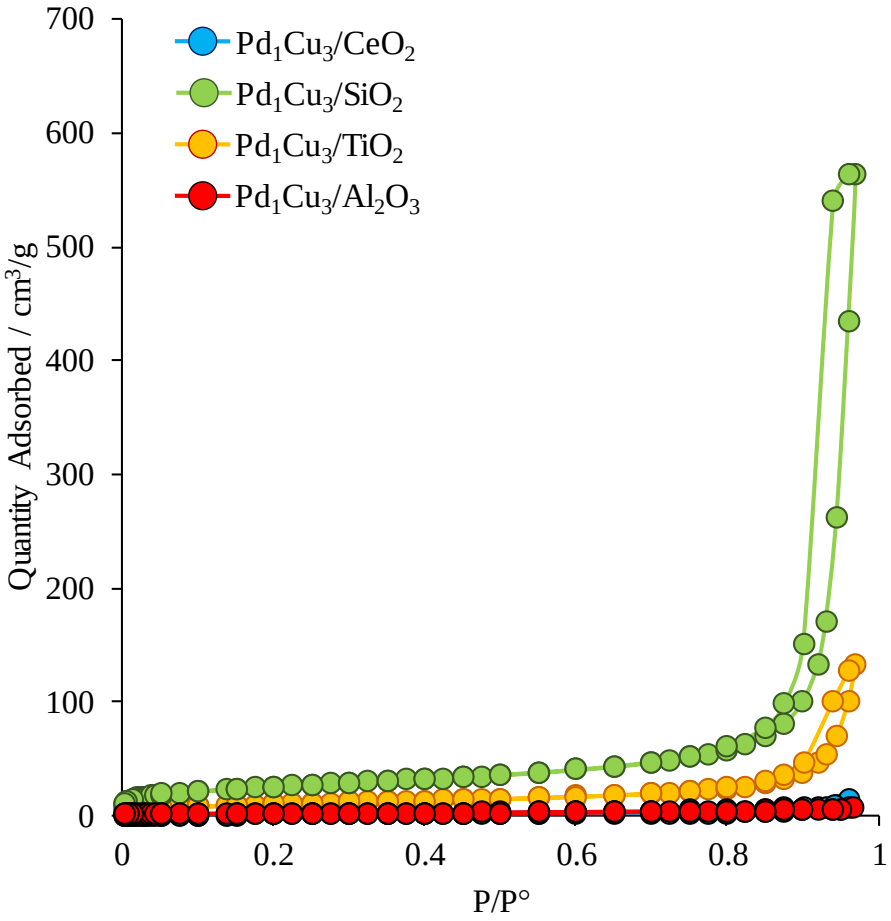


Figure S3 Adsorption–desorption isotherms for Pd_1Cu_3/CeO_2, Pd_1Cu_3/SiO_2, Pd_1Cu_3/TiO_2, Pd_1Cu_3/Al_2O_3 bimetallic catalysts.

Table S1. Composition and samples porous structure

Catalyst	S_{BET}, m^2/g	D^{Av}_{pore}, nm	V_{total}, cm^3/g
Pd_1Cu_3/CeO_2	3 (6)[a]	20.6 (30.1)	0.02 (0.03)
Pd_1Cu_3/TiO_2	36 (51)	22.6 (22.3)	0.21 (0.27)
Pd_1Cu_3/Al_2O_3	5 (6)	7.2 (6.2)	0.01 (0.08)
Pd_1Cu_3/SiO_2	89 (101)	39.4 (40.0)	0.87 (0.94)
Pd/TiO_2	43	16.9	0.18
Cu/TiO_2	37	22.3	0.22

[a] – values in brackets refer to individual supports