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Effect of TiO_2 textural characteristics on the performance of supported PdCu nanoparticles in two-stage olefin synthesis

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Experimental

Catalyst preparation

A series of supported bimetallic $PdCu_3/TiO_2$ catalysts containing 3 wt.% Pd and 5.4 wt.% Cu were prepared by incipient wetness co-impregnation of the support with aqueous solutions of $Pd(NO_3)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$. The atomic ratios of the metals were optimized for a ratio of 1:3. Commercially available TiO_2(50) (Degussa P25, S_{BET} = 51 m^2/g, «Sigma Aldrich», Germany), TiO_2(40) (Saint-Gobain 3·119 S_{BET} = 40 m^2/g, France) and TiO_2(85) (Umicore, S_{BET} = 85 m^2/g, Belgium) pre-calcined in a stream of N_2 at 550°C for 3 hours, were used as supports. Following the impregnation stage, the samples were subjected to a drying process at ambient temperature for 24 hours. Thereafter, the samples were calcined in air at a temperature of 550°C for 4 hours. The final step involved reducing the samples in a flow of 5% H_2 in Ar at a temperature of 550°C for 3 hours. Upon completion of the reduction process, the samples were cooled in two stages: firstly, to 220°C in a flow of 5% H_2 in Ar, and subsequently to room temperature in a flow of N_2.

Monometallic Pd/TiO_2(50) (3 wt.% Pd) and Cu/TiO_2(50) (5.4 wt.% Cu) catalysts were prepared using a similar procedure to that employed for the reference samples.

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).

XRD

The phase composition of the synthesized catalysts was studied by X-ray phase analysis (XRD). Diffraction patterns of the catalysts and starting supports 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.

Transmission electron microscopy

The morphological characteristics of monometallic Pd/TiO_2 and bimetallic $PdCu_3/TiO_2$ 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 300 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 6 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 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.

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

$$X_{\mathrm{PhC2H}} = \frac{\left(m^{0}_{\mathrm{PhC2H}} - m^{6}_{\mathrm{PhC2H}}\right)}{m^{0}_{\mathrm{PhC2H}}} \times 100\%$$, where

m_{PhC2H}^{0} – mass of phenylacetylene before the cross-coupling reaction; m_{PhC2H}^{6} – mass of phenylacetylene after the cross-coupling reaction;

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

$$m^{6}_{\mathrm{PhC2H}} = \frac{m^{0}_{\mathrm{PhC2H}}}{m^{0}_{Nap}} \times \frac{S^{0}_{Nap}}{S^{0}_{\mathrm{PhC2H}}} \times \frac{S^{6}_{\mathrm{PhC2H}}}{S^{6}_{Nap}} \times m^{0}_{Nap}$$, 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_{PhC2H}^{0} – peak area of phenylacetylene before the cross-coupling reaction; S_{PhC2H}^{6} – peak area of phenylacetylene after the cross-coupling reaction; S_{Nap}^{6} – 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

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

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

Results and discussion

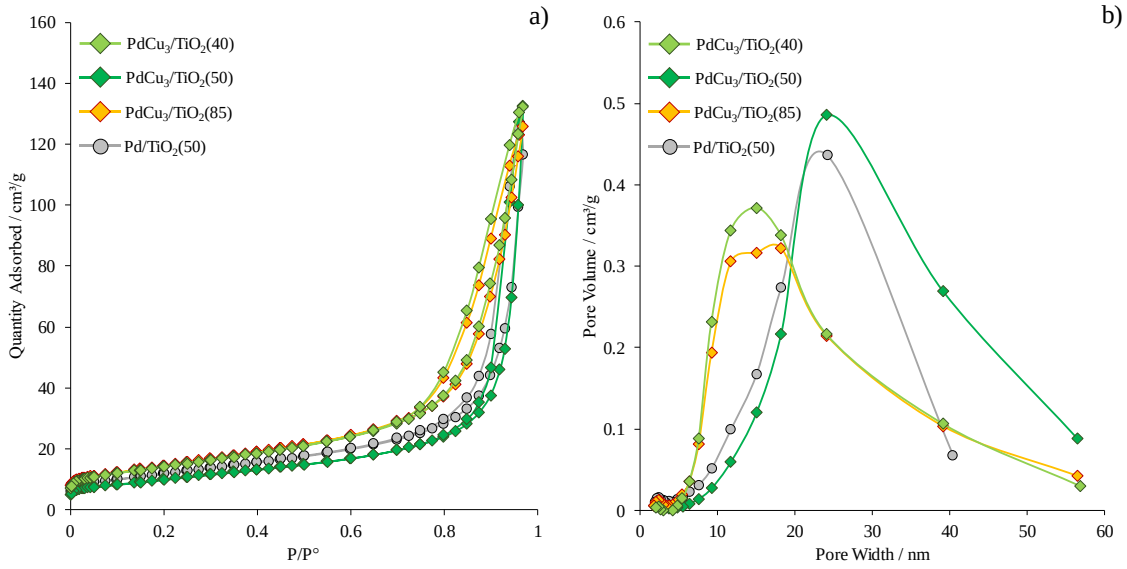


Figure S1 (a) Adsorption–desorption isotherms and (b) pore size distribution curves for $Pd/TiO_2(50)$ and $PdCu_3/TiO_2$ catalysts.

Table S1. Composition and samples porous structure

Catalyst	ω_{Pd}, wt. %	ω_{Cu}, wt. %[a]	S_{BET}, m^2/g	V_{total}, cm^2/g	D^{Av}_{pore}, nm
TiO_2 (40)			40	0.30	28
TiO_2 (50)			50	0.32	30
TiO_2 (85)			85	0.31	25
Pd/TiO_2(50)	3.0		43	0.18	16.9
Cu/TiO_2(50)		5.4	39	0.20	14.6
$PdCu_3/TiO_2$ (40)	3.0	5.4	31	0.21	16.0
$PdCu_3/TiO_2$ (50)	3.0	5.4	36	0.21	22.6
$PdCu_3/TiO_2$ (85)	3.0	5.4	52	0.19	14.9

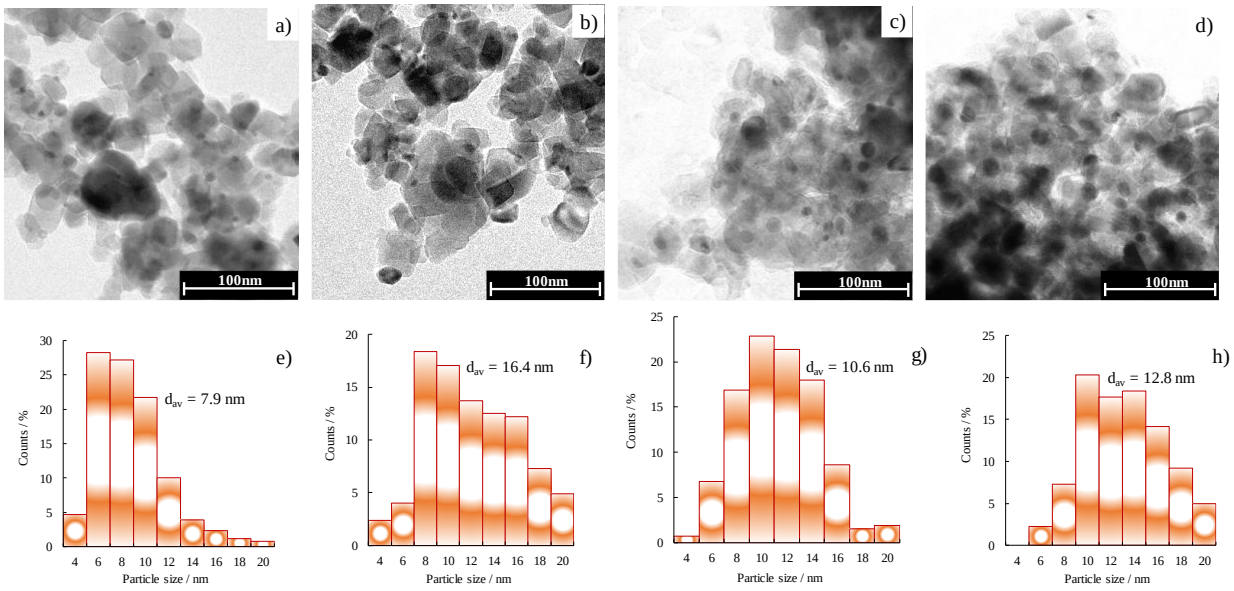


Figure S2 TEM images and histograms of nanoparticle size distribution for (a, e) $Pd/TiO_2(50)$ and bimetallic (b, f) $PdCu_3/TiO_2(50)$, (c, g) $PdCu_3/TiO_2(85)$, (d, h) $PdCu_3/TiO_2(40)$.

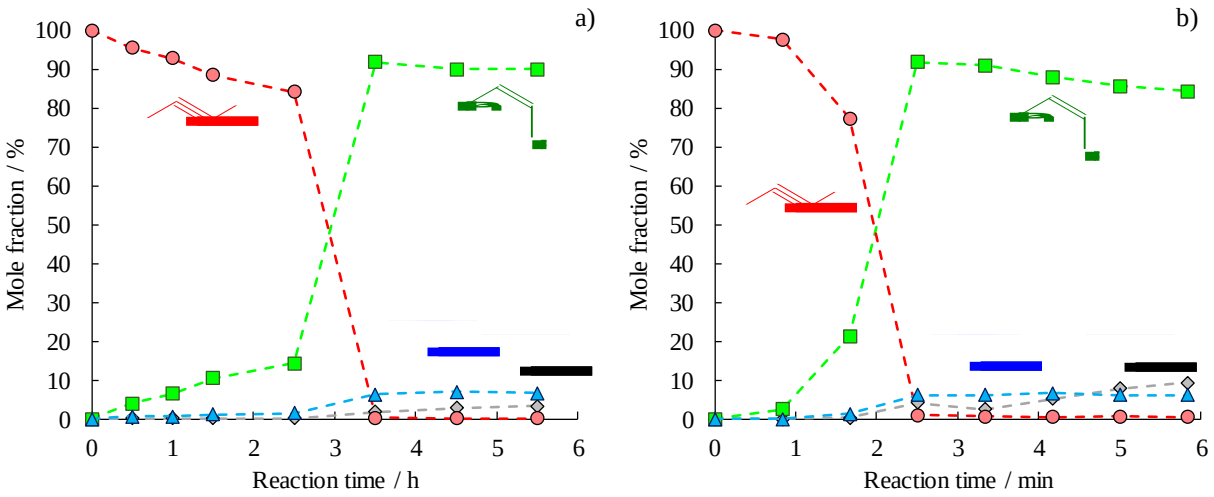


Figure S3 Variation of the reaction mixture composition during formed Ph_2C_2 hydrogenation in the presence of (a) $PdCu_3/TiO_2(50)$ and (b) $Pd/TiO_2(50)$.