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Nanosizing Pd-Au bimetallic phases on carbon nanotubes for selective phenylacetylene hydrogenation

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catalysts	Pd/wt%	Au/wt%
Pd/CNTs before reaction	3.02 (3.00)	-
Pd/CNTs after reaction	3.01	-
Pd-Au/CNTs before reaction	3.01 (3.00)	8.32 (8.36)
Pd-Au/CNTs after reaction	3.00	8.31
Au/CNTs before reaction	-	0.22 (8.36)
Au/CNTs after reaction	-	0.16

Table S1. The actual loadings of the catalysts from the ICP measure (the expected values are shown in brackets). To ensure that the reference catalyst of Au/CNTs possesses a relatively equal amount of Au in comparison to the Pd-Au/CNTs, a new Au/CNTs catalyst was prepared by the same liquid-phase reduction method, but without the filtration step (please see the main content for details).

1. Experimental

1.1 Catalyst preparation

Carbon nanotubes (CNTs) were purchased from Pyrograf Products Inc. (Ohio, USA). The CNTs were cleaned by immersion in concentrated nitric acid (analytical grade) in an ultrasonic bath for 30 min. Then they were refluxed at 120°C for 1 h under vigorous stirring conditions. After that, the mixture was cooled to room temperature, filtered and then washed twice with ultrapure water. Finally, the sample obtained was dried overnight in the fume cupboard and in the oven at 40 ℃ for 12 h. The Pd-Au supported on CNTs catalyst was prepared by the liquid phase reduction method with H_2 as a reductant in the following route: the obtained functionalized CNTs (250 mg) were dissolved in the 250 mL three necked flask with 125 mL ethanol (guaranteed reagent, Sinopharm) as solvent. The solution was subjected to sonication for 5-10 min to attain the state of uniform ink. 163.9 uL palladium nitrate solution (10 wt % $Pd(NO_3)_2$ in 10 wt % nitric acid, Sigma-Aldrich) and 47.15 mg gold (Ⅲ) chloride trihydrate (Sigma-Aldrich) were respectively dissolved in 10 mL ethanol and added dropwise into the above solution under stirring. The mixture was subjected to sonication for 5 min and transferred to the magnetic stirring apparatus for the following reduction. High-purity He in a flow of 100 mL/min was bubbled into the solution for 30 min to remove O_2 dissolved prior to the reduction. Then the hydrogen valve was opened, the reduction lasted for 1 h with 100 mL/min He and 50 mL/min H_2 at ambient temperature under the stirring condition. After that the solution was filtered and the sample was taken down from the filter paper. The resultant was subjected to the vacuum drying at 60°C for 12 h. The supported monometallic Pd catalysts were prepared with the same procedure without adding gold (Ⅲ) chloride trihydrate. The Au/CNTs catalyst was prepared by the same liquid-phase reduction method, but without the filtration step. The actual catalyst loadings of these three catalysts were measured by the ICP-OES.

1.2 Catalyst characterization

The metal content of each sample was measured with an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000). The samples were treated with aqua regia, and the solution was filtered and analyzed by ICP-OES. To determine the crystalline structures of the catalysts, X-ray diffraction (XRD) analysis of the samples was carried out using a Bruker D8 Advance X-ray diffractometer with a Cu Kα monochromatized radiation source (40 KV, 40 mA). The diffraction data were collected between 5 and 90° (2θ) with a resolution of 0.01°. Raman spectroscopy was acquired at 514.5 nm line of Ar^+ ion laser using Horiba Jobin Yvon LabRAM HR 800 Raman spectrometer with spectral resolution of 2 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 instrument using monochromatic Al Kα radiation with 1486.6 eV, operating at 150 W. The morphology and microstructure of the catalysts were characterized using scanning electron microscopy (SEM) with Hitachi S-4800 and transmission electron microscopy (TEM) with JEOL JEM-ARM 200F. For the TEM measurements, powder samples were suspended in ethanol and dispersed ultrasonically. Drops of suspensions were deposited on a copper grid covered with a porous carbon film. The H_2 temperature programmed desorption (H_2-TPD) were performed on Chemisorption Analyzer AutoChem II. The samples were purged and further heat-treated in purified Ar, when the reactor was cooled to 50°C in Ar, the samples were exposed to pure H_2 for 30 min, and purged with Ar for 2 h at the same tempertures in order to eliminate the physically adsorbed H_2. The TPD measurements were conducted in a Ar stream (50 mL/min) from room temperature to 800°C at a heating rate of 10 °C/min. The change of hydrogen signal was monitored by a TCD and quantitatively calibrated by H_2 pulses.

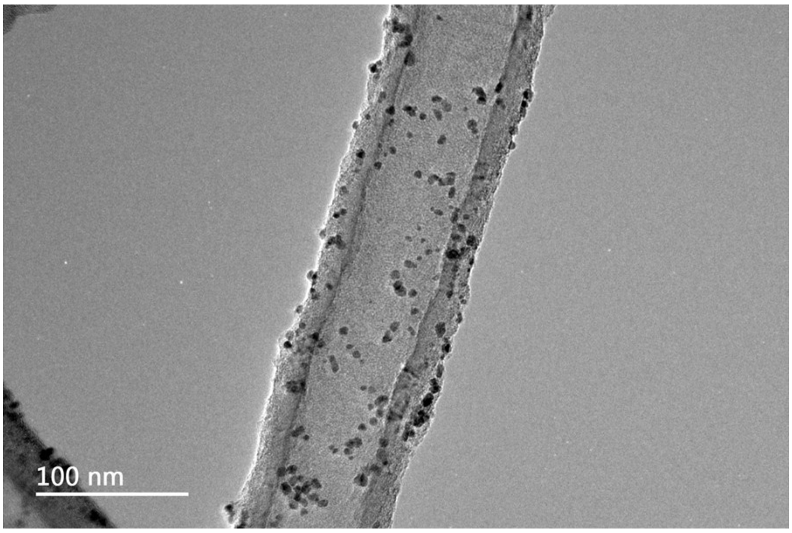

Fig. S1 TEM image of Pd/CNTs.

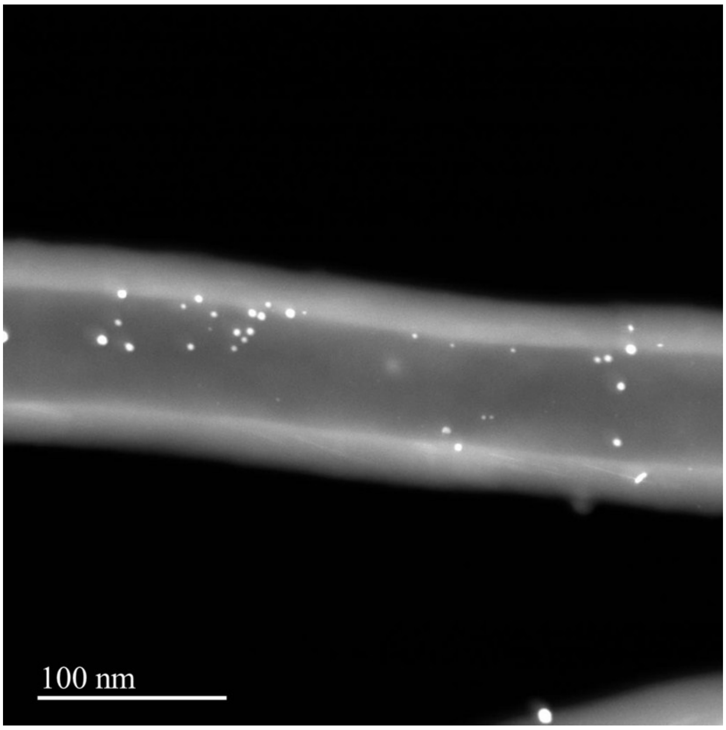

Fig. S2 STEM image of Au/CNTs.

1.3 Phenylacetylene hydrogenation

The catalyst Pd-Au/CNTs of 20 mg with 0.02 mol/L phenylacetylene reactant of 20 mL was added into a 100 mL three necked flask. The intermixture was subjected to the sonication for 2 min and transferred to the oil bath of 40 ℃. High-purity He in a flow of 85 mL/min was bubbled into the solution for 10 min to remove O_2 and then the selective hydrogenation reaction of phenylacetylene was carried out. The reaction lasted for 60 min with stirring under the condition of 85 mL/min He and 30 mL/min H_2. The sample was collected every 10 min, centrifuged, diluted and analyzed by a LC-20A high performance liquid chromatography (HPLC) using a SPD-20A detector with an InertSustain® C18 column. After 60 min reaction, the H_2 valve and He valve were turned off in sequence. The residual solution was centrifuged, the supernatant was removed and the obtained catalyst was recycled by vacuum drying.

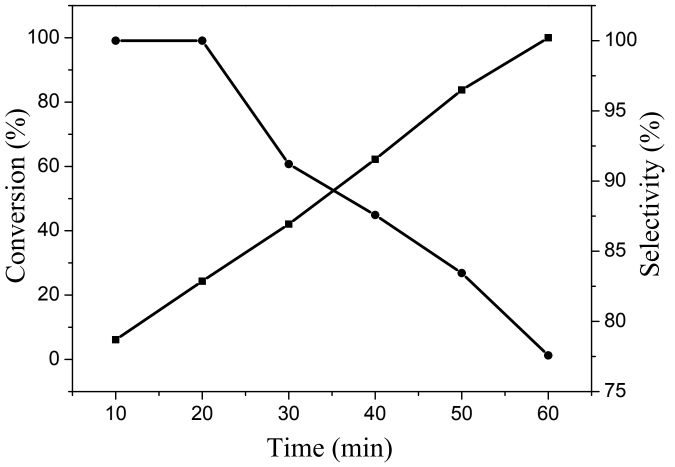

Fig. S3 (a)The catalytic performances of the Pd-Au/CNTs.■ Conversion of phenylacetylene. ●Selctivity to styrene.