Supporting Information

Nanosized palladium on phosphorusincorporated porous carbon frameworks for enhanced selective phenylacetylene hydrogenation

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EXPERIMENT

Preparation of PCFs

8g sodium hydroxide was mixed with 40 mL acetone under vigorous magnetic stirring for 1 h, and the mixture was placed at ambient air, temperature and pressure. After 120 h, the mixture was transformed into dark brown solid products. Then the products were calcined at 600°C for 2 h in He atmosphere, at a heating rate of 10 °C min⁻¹. Finally, the calcined products were washed with 1M HCl solution and deionized water several times and then dried at 100 °C under vacuum for 12 h. Then the porous carbon frameworks (PCFs) can be obtained.

Preparation of P-PCFs

200 mg PCFs and 5.3g sodium hypophosphite were mixed and put in the center of a quartz boat, then the mixture were calcined at 1000°C for 1 h in He atmosphere, at a heating rate of 10 °C min-1. After that, the calcined products were washed with deionized water several times and then dried at 60 °C under vacuum for 12 h. Then the phosphorus oxides incorporated porous carbon frameworks (P-PCFs) can be obtained.

Preparation of Pd/P-PCFs and Pd/PCFs

Pd/P-PCFs catalyst was synthesized by the wetness impregnation method. 50 mg PCFs were dissolved with 10 mL ethanol. A solution of palladium nitrate (10 wt% Pd(NO₃)₂ in 10 wt.% nitric acid, Sigma-Aldrich)was dissolved with 2 mL ethanol added dropwise into the PCFs solution under stirring, and then subjected to 1-minutes sonication. Finally, the mixture was dried under stirring. Collected powder was reduced in a flow of 25 vol.% H₂ (total flow of 25 sccm) mixed with He (total flow of 100 sccm) at 250°C for 2 h to give a 3 wt.% Pd loading catalyst. The preparation of Pd/PCFs follows the same procedure as that for the preparation of Pd/P-PCFs except for the use of PCFs as the precursor. 3 wt.% Pd/C catalysts and Lindlar catalyst with a 5wt.% Pd loading were sourced from Sigma-Aldrich.

Characterization

X-ray diffraction (XRD) patterns were conducted on a Bruker D8-Advanced Xray diffractometer with Cu- $K\alpha$ radiation (λ =1.5418 Å) operated at 40 kV. The morphologies and microstructures of the as-prepared carbon samples were analyzed by transmission electron microscopy (TEM) (JEOL JEM-2100F, operated at 200 kV). The surface elemental contents and chemical states were determined by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250 instrument under ultra-high vacuum (UHV) conditions with monochromatic Al $K\alpha$ radiation(1486.6 eV), operating at 150 W. The Pd content of the catalyst samples were measured with an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000).

Catalyst Tests of Phenylacetylene Hydrogenation

Hydrogenation was carried out in a fully-automatized continuous-flow floodedbed reactor (ThalesNano H-Cube ProTM)where the liquid phenylacetylene and gaseous hydrogen concurrently flowed upwards through a fixed bed of catalyst particles. The catalysts (10mg) were loaded into a capsule of approximately 30 mm length \times 3.5 mm internal diameter, except Lindlar catalyst was 6mg in order to test the catalyst with the same Pd content. A 0.02 M stock solution of phenylacetylene in ethanol was pumped into the capsule of flow reactor at a flow rate of 0.9 mL/min. The catalytic tests were performed at 20°C and 3bar, with the hydrogen flow rate equalling 6 mL/min. The reaction mixture was allowed to flow through the catalyst after reaching steady-state operation. The reaction products were collected every 10 min and each collection lasted 0.5 min. The reaction products were analyzed by high performance liquid chromatography (HPLC) using a SPD-20A detector with an InertSustain^R C18 column. The same procedures were repeated for other catalysts. The hydrogenation cycle was also lasted two hours for each catalyst in order to evaluate the catalytic stabilities of Pd/P-PCFs. The collected catalytic results are within 2% deviation.

The conversion of phenylacetylene was determined as the amount of reacted phenylacetylene divided by the amount of phenylacetylene at the reactor inlet, whereas the selectivity to a given styrene or ethylbenzene was quantified as the amount of the respective compound divided by the total amount of products.



Figure S1 Effect of H_2 flow rate (A) and pressure (B) on the conversion of phenylacetylene and styrene selectivity.



Figure S2 The catalytic performance of Pd/P-PCFs in selective phenylacetylene hydrogenation for 10 hours.



Figure S3 Typical TEM image of the Pd/PCFs with an inset showing the size distribution of the palladium nanoparticles.



Figure S4 XRD patterns of the Pd/PCFs, Pd/P-PCFs and reacted Pd/P-PCFs.



Figure S5 (A) XPS survey scan of the Pd/PCFs. (B) C 1s region of the spectra of the Pd/PCFs. (C) XPS spectra of the Pd 3d region of the Pd/PCFs. (D) XPS spectra of the Pd 3d region of the reacted Pd/P-PCFs.

Table S1

Surface atomic concentrations determined from XPS analysis

Sample	Pd 3d	P 2p	O 1s	C 1s
	(at%)	(at%)	(at%)	(at%)
Pd/P-PCFs	1.77	0.75	31.69	63.02
Pd/PCFs	1.75	0	14.72	81.00