

## Supporting Information

# Nanosizing Pd on 3D porous carbon frameworks as effective catalysts for selective phenylacetylene hydrogenation

*Weizhen Yu,<sup>a</sup> Hongshuai Hou,<sup>b</sup> Zhiling Xin,<sup>a</sup> Shuo Niu,<sup>a</sup> Yanan Xie,<sup>a</sup> Xiaobo Ji,<sup>b,\*</sup> and*

*Lidong Shao<sup>a,\*</sup>*

<sup>a</sup>Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, China

<sup>b</sup>College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China. E-mail: [xji@csu.edu.cn](mailto:xji@csu.edu.cn)

\*Correspondence to: [lidong.shao@shiep.edu.cn](mailto:lidong.shao@shiep.edu.cn) (L.D.S.)

\* Correspondence to: [xji@csu.edu.cn](mailto:xji@csu.edu.cn) (X.B.J.)

### EXPERIMENTAL

#### Preparation of PCFs

Sodium hydroxide (8g) was mixed with acetone(40 mL) under vigorous magnetic stirring for 1 h, and the mixture was placed at ambient air, temperature and pressure. After 120 h, the color of the mixture changed to dark brown and the liquid acetone was transformed into solid products. The products were calcined at 600°C for

2 h in He atmosphere, at a heating rate of 10 °C min<sup>-1</sup>. Finally, the calcined products were washed with 1M HCl solution and deionized water and separated by vacuum suction filtration and then dried at 100 °C under vacuum for 12 h. Then the porous carbon frameworks (PCFs) can be obtained.

### **Catalyst Synthesis**

Pd/PCFs catalysts were synthesized by the wetness impregnation method. PCFs were dissolved in ethanol at a concentration of 0.1 g/L. A solution of palladium nitrate (10 wt% Pd(NO<sub>3</sub>)<sub>2</sub> in 10 wt.% nitric acid, Sigma-Aldrich) was added into the PCFs ethanol solution under stirring, and the mixture was subjected to 1-minute sonication. Collected powder was reduced in a flow of 25 vol.% H<sub>2</sub> (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 catalysts. 3 wt.% Pd/C catalysts and Lindlar catalyst were sourced from Sigma-Aldrich.

### **Characterization**

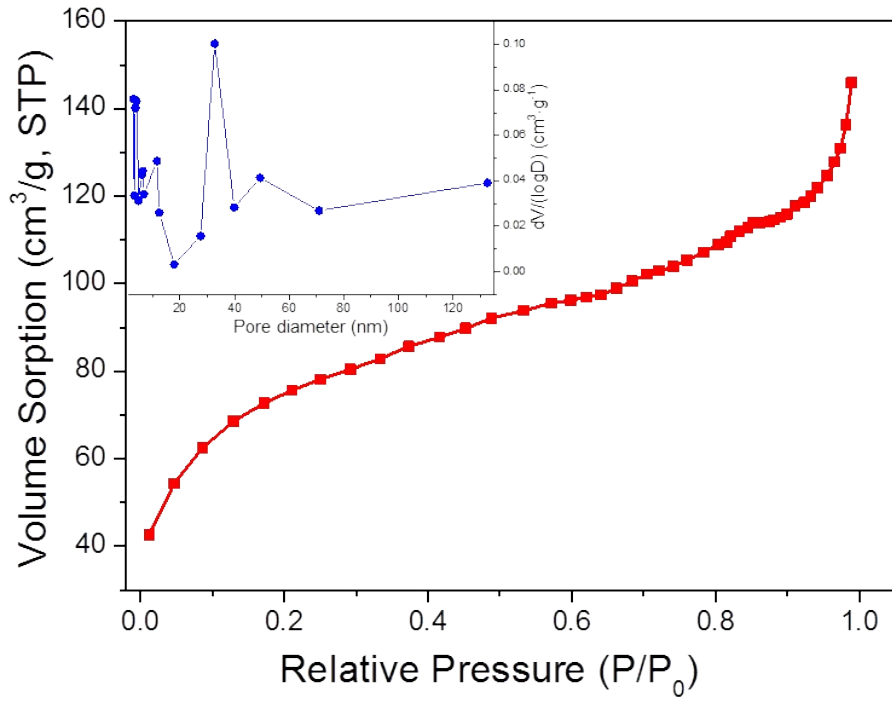
X-ray diffraction (XRD) patterns were conducted on a Bruker D8-Advanced X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda=1.5418$  Å) operated at 40 kV, for diffraction angles ( $2\theta$ ) of 10-90° at a rate of 2° min<sup>-1</sup> in steps of 0.02°. Raman spectra were recorded at ambient temperature on a Horiba Scientific LabRAM HR Evolution system with an Ar-ion laser at an excitation wavelength of 633 nm. 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 3 wt.% Pd/PCFs samples was measured with an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000). The H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) were performed on Chemisorption Analyzer 2920 AutoChem II. The dispersion of Pd particles was also measured by carrying out chemisorption of H<sub>2</sub> using the same instrument. The change of hydrogen signal was monitored by a TCD and quantitatively calibrated by H<sub>2</sub> pulses.

### **Catalyst Tests of Phenylacetylene Hydrogenation**

Hydrogenation was carried out in a fully-automatized continuous-flow flooded-bed reactor (ThalesNano H-Cube Pro<sup>TM</sup>) where the liquid phenylacetylene and gaseous hydrogen concurrently flowed upwards through a fixed bed of catalyst particles. For comparison, the catalytic properties of two kinds of catalysts were tested under the same hydrogenation conditions. Hydrogen was generated in situ by the electrolysis of Millipore-filtered water and supplied to the reaction chamber by a mass-flow controller. The catalysts (10mg) were loaded into a capsule of approximately 30 mm length  $\times$  3.5 mm internal diameter. A 0.02 M stock solution of phenylacetylene in ethanol was pumped into the capsule of flow reactor at a certain flow rate. The catalytic tests were performed at various temperatures (20–35 °C), pressures (0–10 bar), and liquid flow rates (0.3–0.9 mL/min) and H<sub>2</sub> flow rates (3–60 mL/min). Each capsule carried the same amount of catalysts, except the Lindlar catalysts were 6mg.

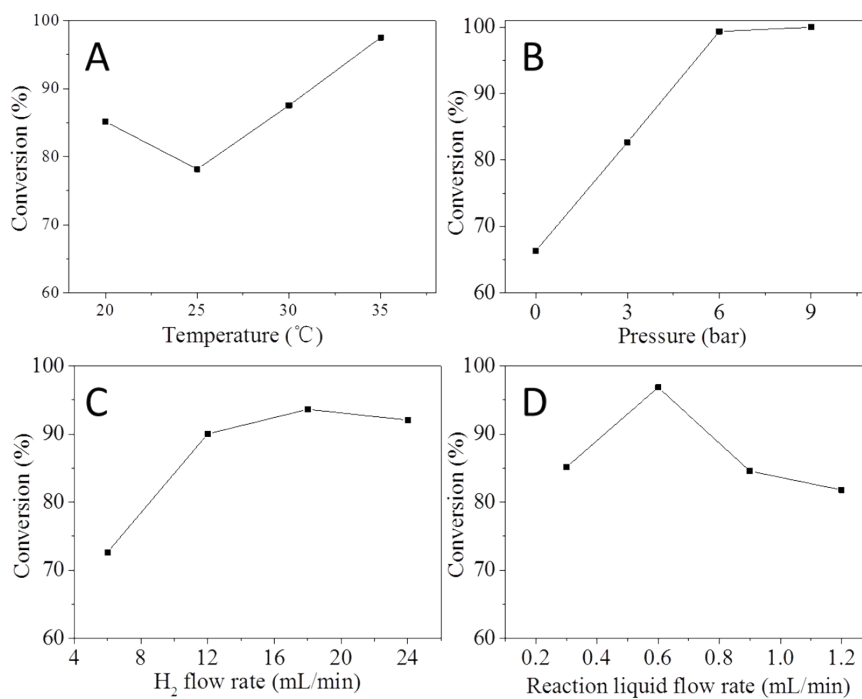
The reaction mixture was allowed to flow through the catalyst after reaching steady-state operation. The reaction products were collected every 5 min and each collection lasted 0.5 min. After collecting the effluent solution for three times, the reactor was washed by solvent. The reaction products were analyzed by high performance liquid chromatography (HPLC) using a SPD-20A detector with an InertSustain<sup>®</sup> 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. 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.



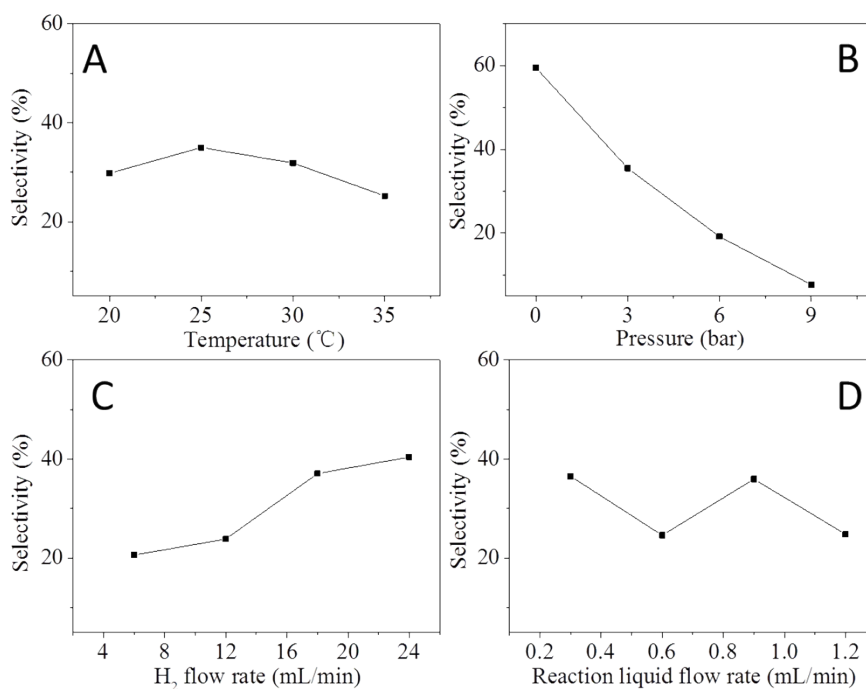
**Figure S1.** Nitrogen sorption isotherms of the PCFS and together with their corresponding pore size distribution (inset).

**Table S1.** Result and analysis of orthogonal test

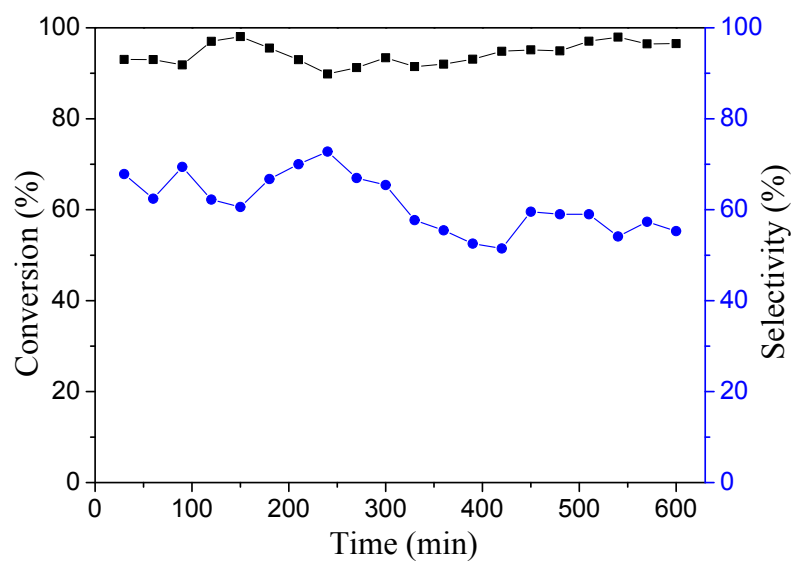
No.	Temperature (°C)	Pressure (bar)	H <sub>2</sub> flow rate (mL/min)	Reaction liquid flow rate ( mL/min)	Conversion (%)	Selectivity (%)
1	20	0	6	0.3	40.61	79.29
2	20	3	12	0.6	100.00	17.62
3	20	6	18	0.9	100.00	18.87
4	20	9	24	1.2	100.00	3.32
5	25	0	12	0.9	60.09	60.18
6	25	3	6	1.2	52.59	79.77
7	25	6	24	0.3	100.00	0
8	25	9	18	0.6	100.00	0
9	30	0	18	1.2	74.57	53.24
10	30	3	24	0.9	78.19	41.62
11	30	6	6	0.6	97.40	32.57
12	30	9	12	0.3	100.00	0
13	35	0	24	0.6	90.06	45.07
14	35	3	18	0.3	100.00	3.03
15	35	6	12	1.2	100.00	25.19
16	35	9	6	0.9	100.00	27.51



**Figure S2.** Effect of temperature (A), pressure (B), H<sub>2</sub> flow rate (C) and reaction liquid flow rate (D) on the conversion of phenylacetylene.



**Figure S3.** Effect of temperature (A), pressure (B), H<sub>2</sub> flow rate (C) and reaction liquid flow rate (D) on the selectivity to styrene.



**Figure S4.** The catalytic performance of Pd/PCFs in selective phenylacetylene hydrogenation for 10 hours. ■ Conversion of phenylacetylene. ● Selectivity to styrene.