

## Supporting information

# Pd-P nanoalloys supported on porous carbon frame as efficient catalyst for benzyl alcohol oxidation

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## **1. Material synthesis**

### **1.1 Preparation of support**

Preparation of PCF: 8 g NaOH was mixed with 40 mL acetone and stirred by a magnetic stirrer for 1 h. The liquid mixture was left in air for 120 h, which gradually afforded a dark brown solid. Subsequent calcining at 600 °C and then at 1000 °C under the He atmosphere obtained 3D PCF.

Preparation of CNT: 1 g pristine carbon nanotube was mixed with 300 mL concentrated nitric acid in a round-bottom flask and vibrated by ultrasound for 30 min, and then the round-bottom flask was left in a 120 °C oil-bath pan for 1 h with reflux condensation. Finally, the liquid mixture was filtered and washed with ultrapure Milli-Q water for three times, and the filter cake was placed in a fume hood to dry naturally overnight, subsequent vacuum-dried at 70 °C for 12 h and obtained the CNT.

## 1.2 Catalysts synthesis

Synthesis of Pd/PCF: The Pd/PCF catalyst was prepared through a classic method using NaBH<sub>4</sub> as the reducing agent. Specifically, 472.5 μL of 0.05 M PdCl<sub>2</sub> and 40 mL of H<sub>2</sub>O were put into the round-bottom flask. 67 mg of PCF was also added to form a projected 3 wt % metal loading. After being sonicated for 1 min and stirred for 0.5 h, the pH of the carbon slurry was adjusted to 8.5 by adding NaOH dropwise under vigorous stirring. Next, 10 mL of freshly prepared 0.08 M NaBH<sub>4</sub> was added dropwise through a peristaltic pump at a rate of 0.6 mL/min. The mixture was further stirred at room temperature overnight. Finally, the Pd/PCF was repeatedly filtered and rinsed with a copious amount of ultrapure Milli-Q water, and vacuum-dried at 70 °C for 12 h and obtained the Pd/PCF.

Synthesis of Pd/CNT: The preparation of Pd/CNT follows the same procedure as that for the preparation of Pd/PCF except for the use of CNT as the support.

## 2. Catalyst characterization

**ICP:** The Pd content of the sample was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000).

**TEM/STEM:** The morphologies and microstructures of the as-prepared carbon samples were analyzed by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) modes (JEOL JEM-2100F, operated at 200 kV), EDX spectrum elemental maps were acquired in the STEM mode.

**SEM:** The morphology of the catalysts was characterized using scanning electron microscopy (SEM, JSM 6701F).

**XRD:** X-ray diffraction (XRD) analysis of the samples were carried out to explore the crystalline

structures of the catalysts, using a Bruker D8 Advance, X-ray diffractometer with a Cu K $\alpha$  monochromatized radiation source (40 KV, 40 mA).

**Raman:** 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.

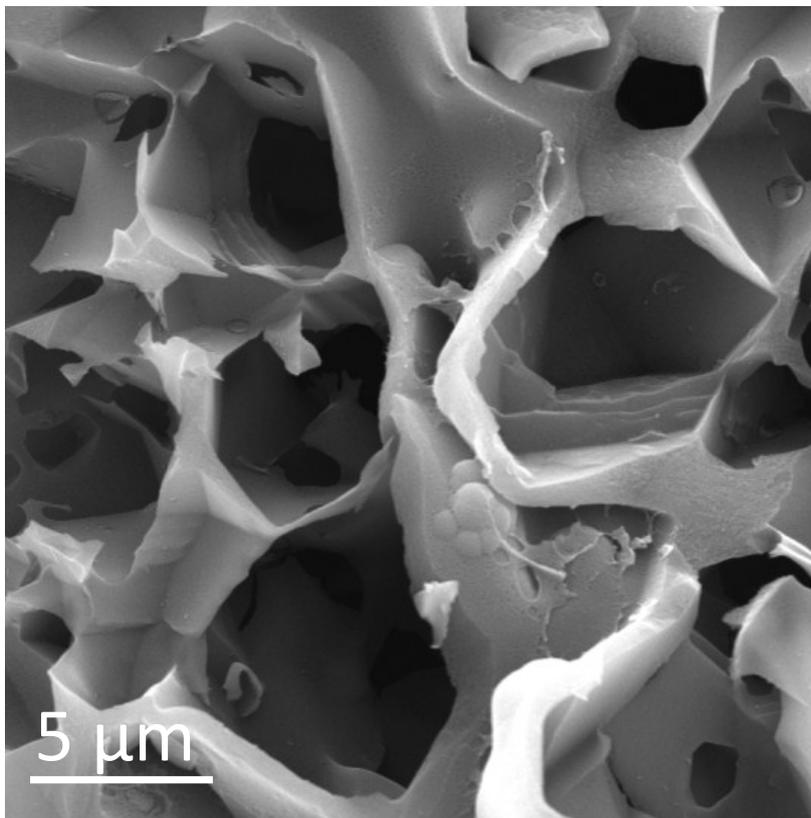
**XPS:** X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo ESCALAB 250 instrument, using monochromatic Al K $\alpha$  radiation with 1486.6 eV operating at 150 W.

**TPD:** The temperature programmed desorption (TPD) analysis was performed using Chemisorption Analyzer 2920 AutoChem II apparatus. The samples were purged and further heat-treated in purified Ar, and then samples were exposed to pure CO<sub>2</sub> or 20% NH<sub>3</sub>/Ar for 30 min, and purged with Ar for two hours at the same temperatures in order to eliminate the physically adsorbed CO<sub>2</sub>/NH<sub>3</sub>.

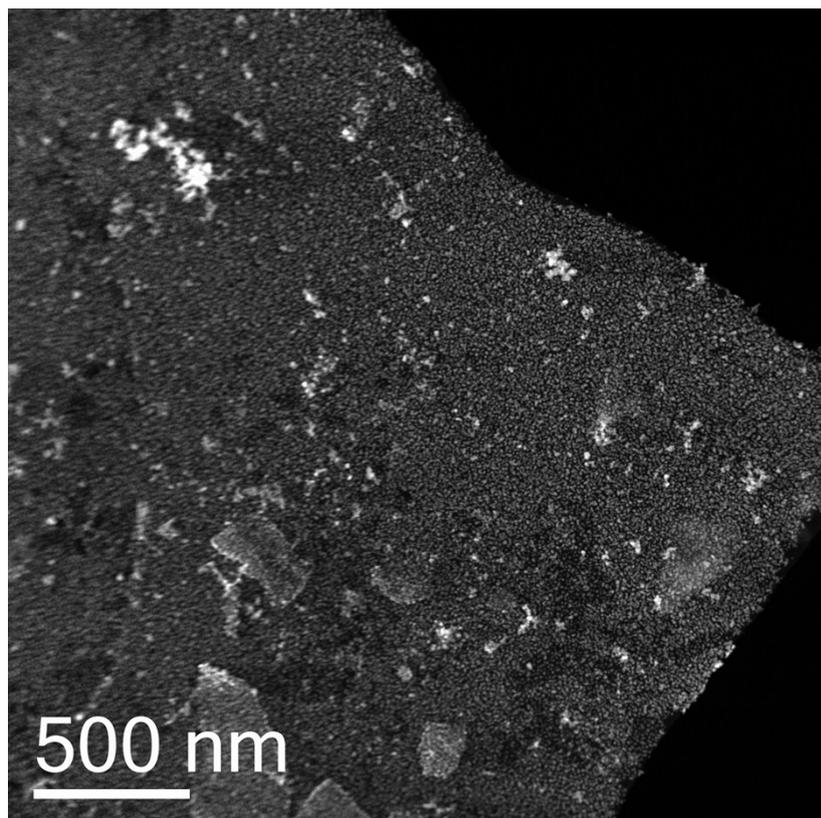
### 3. Catalyst test

The oxidation reaction was carried out in a continuous-flow system (Thales Nano Phoenix Reactor™) where the liquid benzyl alcohol and gaseous oxygen concurrently flowed upwards through a fixed bed of catalyst particles. The catalysts (10 mg) were loaded into a capsule of approximately 30 mm length  $\times$  3.5 mm internal diameter. A 0.05 M stock solution of benzyl alcohol in cyclohexane was pumped into the capsule at a flow rate of 0.05 mL/min. Experiments were performed at 70 °C and atmospheric pressure, with the oxygen flow rate equaling 5 mL/min. The reaction products were collected every 20 min for three times, and each collection lasted 0.5 min. The oxidation cycle was lasted 2 h for each catalyst in order to evaluate the catalytic stabilities.

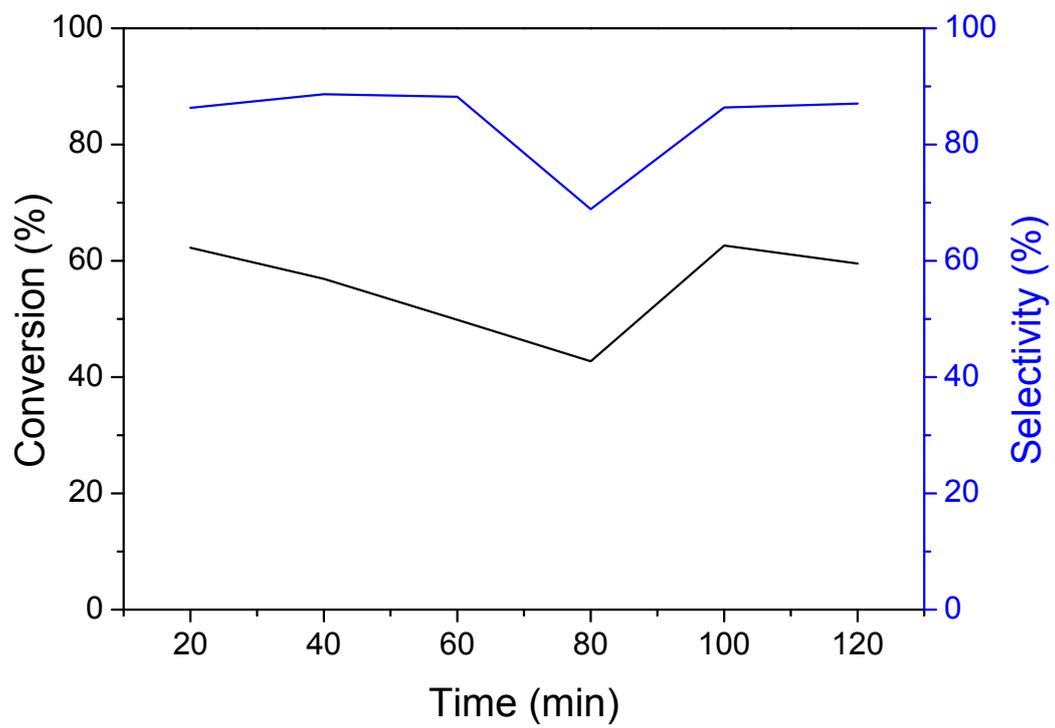
The products were analyzed by high performance liquid chromatography (HPLC) using a SPD-20A detector with an Inert Sustain<sup>®</sup> C18 column. The conversion of benzyl alcohol was determined as the amount of reacted benzyl alcohol divided by the amount of benzyl alcohol at the reactor inlet, whereas the selectivity to a given benzaldehyde or other by-products were quantified as the amount of the respective compound divided by the total amount of products.



*Fig. S1* SEM image of fresh PCF.



*Fig. S2* STEM image of fresh Pd-P/PCF



**Fig. S3** Catalytic performances of Pd/C catalyst for benzyl alcohol oxidation.

**Table S1** Orthogonal test result and analysis of Pd-P/PCF.

No.	Temperature(°C)	Reaction			Conversion of Benzyl Alcohol (%)	Selectivity of Benzaldehyde (%)	Yield (%)
		O <sub>2</sub> Flow Rate (mL/min)	Liquid Flow Rate (mL/min)	Solution Concentration* (%)			
1	60	3	0.05	0.1	69.00	60.73	41.90
2	60	10	0.1	5	21.30	71.59	15.25
3	60	15	0.2	0.5	48.33	75.09	36.29
4	60	5	0.3	2	36.50	74.93	27.35
5	70	5	0.05	0.5	76.84	84.85	65.20
6	70	15	0.1	2	37.23	79.10	29.45
7	70	10	0.2	0.1	54.17	76.49	41.43
8	70	3	0.3	5	25.03	31.86	7.97
9	80	10	0.05	2	11.82	27.31	3.23
10	80	3	0.1	0.5	48.23	63.03	30.40
11	80	5	0.2	5	31.07	51.87	16.12
12	80	15	0.3	0.1	19.86	48.01	9.53
13	90	15	0.05	5	11.05	54.28	6.00
14	90	5	0.1	0.1	61.45	66.00	40.56
15	90	3	0.2	2	67.58	61.76	41.74
16	90	10	0.3	0.5	58.29	52.42	30.56

\* using cyclohexane as the solvent.

**Table S2** Univariate (temperature) analysis results of Pd-P/PCF.

Temperature(°C)	Conversion of Benzyl Alcohol (%)	Selectivity of Benzaldehyde (%)	Yield (%)
60	43.96	100.00	43.96
70	76.84	84.85	65.20
80	77.81	63.39	49.32
90	81.74	56.74	46.38
100	84.01	42.92	36.06

**Selective oxidation conditions:** atmospheric pressure, an oxygen flow rate of 5 mL/min, and a reaction solution (0.05 M solution of benzyl alcohol using cyclohexane as the solvent) flow rate of 0.05 mL/min.