Supporting information

Pd@C core-shell nanoparticles on carbon nanotube as highly stable and selective catalysts for hydrogenation of acetylene to ethylene

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Experiment Section

1. Catalyst synthesis

The synthesis of oxidized Carbon nanotube (CNT) supported Pd catalyst. CNT supported Pd catalyst was prepared by a deposition-precipitation method. First, the pH values of Pd(NO$_3$)$_2$ solution were adjusted using 0.25 M Na$_2$CO$_3$ solution to about 7, and the pH values of CNT solutions were adjusted to about 10 using the 0.25 M Na$_2$CO$_3$ solution. Second, the Pd(NO$_3$)$_2$ solutions were added to the carbon supports solutions dropwise under stirring at 100 °C. After stirring for 1 h, the mixtures were cooled to room temperature, filtrated and washed. Afterwards, the solids were dried at 100 °C and reduced with H$_2$ at 200 °C for 2 h. This sample was labeled as Pd/CNT.

Preparation of core-shell Pd@C nanoparticle supported on CNT (Pd@C/CNT). First, Pd/CNT was modified with an nitrogen-containing ionic liquid (IL), 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]), by dispersing Pd/CNT into the IL phase and removing the excess IL with centrifugation. Then the IL modified Pd/CNT was annealed at 350
°C for 1h in vacuum, followed by being annealed at higher temperature in Ar atmosphere for 1h. The obtained sample was labeled as Pd@C/CNT.

2. Characterization

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were obtained by using an FEI Tecnai G² F20 microscope equipped with EDAX and HAADF detectors. X-ray diffraction (XRD) patterns of the catalysts were acquired using an X-ray diffractometer (D/MAX-2400) with Cu Kα source at a scan rate of 2° min⁻¹. X-ray photoelectron spectroscopy (XPS) spectra were carried out by ESCALAB 250 instrument with Al Kα X-rays (1489.6 eV, 150 W, 50.0 eV pass energy). The quasi in situ XPS analyses were performed on a PHI5000 Versaprobe-II Scanning XPS Microprobe system. This system also employed an Al Kα X-rays, and the pass energy was 46.95 eV. The binding energy (BE) was relative to the adventitious C1 s line at 284.6 eV.

3. Thermal treatment

In order to investigate the effect of in situ formed N-doped carbon layers, a control experiment was performed by annealing the as-prepared catalysts Pd/CNT in tubular furnace under flowing Ar gas conditions at 700 °C for 1h, which is same with the annealing condition of IL-modified Pd/CNT. To further study the thermal stability of Pd nanoparticles (NPs), Pd/CNT and Pd@C/CNT were annealed with an in situ heating TEM holder and a tubular furnace under flowing Ar gas conditions, respectively. The in situ heating experiments were carried out in vacuum condition by DENSsolutions heating TEM holder, from room temperature (RT) via 350 °C for 1h, 500 °C for 1h to 700 °C for 1h, respectively. Actual metal loadings of the as-prepared catalysts were quantified on a Leeman Laboratories Prodigy inductively coupled plasma mass spectrometry (ICP-MS).

4. Reaction test

The partial hydrogenation of acetylene in excess ethylene was conducted in a fixed-bed flow quartz reactor. The feed gas consisted of 2.99% H₂, 20.11% C₂H₄, 0.504% C₂H₂ with He as the balance gas from Dalian Special Gases Co., Ltd.. The total flow rate was kept at 20 ml/min, which was controlled by mass flow controller. The amount of uncoated Pd/CNT catalyst was 5 mg, while the amount of carbon layers coated Pd@C/CNT catalyst was 20 mg. The reaction was conducted in a temperature-programmed mode, ramping at 1 °C/min. The gas composition
from the microreactor outlet was analyzed by online gas chromatography (Agilent Technologies 7890A) equipped with a FID detector.

Acetylene conversion and selectivity to ethylene were calculated as follows:

\[
\text{Conversion} = \frac{C_2H_2(\text{feed}) - C_2H_2}{C_2H_2(\text{feed})} \times 100\%
\]

\[
\text{Selectivity} = (1 - \frac{C_2H_6 + 2 \times C_4}{C_2H_2(\text{feed}) - C_2H_2}) \times 100\%
\]

\(C_4\) represents butane and dibutene.

**Supporting Figures**

![Figure S1. TEM images of Pd/CNT.](image)

**Figure S2.** TEM images of Pd@C/CNT.

**Figure S3.** N 1s XPS core level spectrum of Pd@C/CNT.

**Figure S4.** TEM images of Pd/CNT-700, which was obtained by annealing Pd/CNT at 700 °C in Ar atmosphere.
Figure S5. TEM images of Pd/CNT (a) and Pd@C/CNT (b) annealed using an *in situ* heating TEM holder at RT, 350 °C for 1h, 500 °C for 1h, and 700 °C for 1h.

Figure S6. C₄ species selectivity as a function of reaction temperature over Pd/CNT and Pd@C/CNT.
Figure S7 (a) TEM image, (b) HAADF-STEM image, (c) HRTEM image, (d) N1s XPS spectrum of used Pd@C/CNT, the inset in (b) is the corresponding histogram of particle size distribution.

Figure S8 Deconvolution results of Pd 3d XPS core level spectra of (a) fresh Pd@C/CNT and (b) used Pd@C/CNT at 150 °C, obtained by quasi-in situ XPS technique.
Supporting Table

Table S1. Elemental analysis of Pd/CNT and Pd@C/CNT.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Carbon content [at. %] (^a)</th>
<th>Oxygen content [at. %] (^a)</th>
<th>Nitrogen content [at. %] (^a)</th>
<th>Palladium content [at. %] (^a)</th>
<th>Palladium weight loading [wt. %] (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/CNT</td>
<td>94.66</td>
<td>4.50</td>
<td>0.39</td>
<td>0.45</td>
<td>2.0</td>
</tr>
<tr>
<td>Pd@C/CNT</td>
<td>87.58</td>
<td>6.73</td>
<td>5.41</td>
<td>0.28</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\(^a\) Determined by XPS; \(^b\) Determined by ICP-MS.