

Electronic Supplementary Information

**TiO<sub>2</sub> supported Pd@Ag as highly selective catalysts for hydrogenation of acetylene in excess ethylene**

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## Experimental Section

### 1. Catalyst preparation

TiO<sub>2</sub> supported Pd@Ag bimetallic catalysts were prepared by sequential deposition of metallic Pd and Ag on TiO<sub>2</sub>. For the preparation of Pd/TiO<sub>2</sub>, 2.0 g of TiO<sub>2</sub> (P25, Degussa) was suspended in 480 ml of distilled water containing a required amount of Pd(NO<sub>3</sub>)<sub>2</sub>, and 10 ml of methanol. The suspension was purged by N<sub>2</sub> (60 ml min<sup>-1</sup>) under stirring for 1 h in the dark. Then, the suspension system was irradiated under a high pressure Hg lamp (500 W) for 4 h. The Pd/TiO<sub>2</sub> sample was recovered by filtration, followed by washing with distilled water, and drying at 110 °C for 4 h. The photodeposition of Ag on Pd/TiO<sub>2</sub> was carried out according to the above described procedure but with AgNO<sub>3</sub> as the metal precursor. The resulting bimetallic catalyst was denoted as *pd*-Pd(x)@Ag(y)/TiO<sub>2</sub>, where x was the Pd content (wt.%) and y was the Ag content (wt.%).

For comparison purpose, supported bimetallic catalyst was also prepared by the conventional impregnation method. The catalyst was denoted as *im*-Pd(x)-Ag(y)/TiO<sub>2</sub>, where x was the Pd content (wt.%) and y was the Ag content (wt.%).

### 2. Catalyst characterization

Brunauer-Emmett-Teller (BET) surface areas of the samples were determined using the nitrogen adsorption method on a Micromeritics ASAP 2020 (Micromeritics Instrument Co., Norcross, GA) at -196 °C (77K). The contents of Pd and Ag in the samples were measured by X-ray fluorescence (ARL-9800) (ARL Co., Switzerland). The UV-vis spectra were determined in a SHIMADZU UV-2450 UV/vis spectrophotometer (Shimadzu Co., Kyoto, Japan) using BaSO<sub>4</sub> as a reference. TEM

images of the samples were obtained on a JEM-200CX electron microscope (JEOL Co., Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was carried out on a Perkin-Elmer PHI-5000 (ULVAC-PHI Inc., Chigasaki, Japan) equipped with a monochromatized Al K $\alpha$  X-ray source ( $h\nu=1486.6$  eV) and a hemispherical electron analyzer. The C 1s peak (284.6 eV) was used for the calibration of binding energy values.

The exposed Pd sites of the catalysts were measured using the CO chemisorption method. Briefly, the sample was activated at 300 °C in H $_2$  (40 ml min $^{-1}$ ) for 1 h, followed by purging at 300 °C by He (40 ml min $^{-1}$ ) for 1 h. After cooling to room temperature, CO chemisorption was conducted using a pulse titration mode. CO contents in the pulses were determined by an online gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

CO adsorption was monitored in a vacuum IR system using a Nicolet 5700 FT-IR spectrometer (ThermoElectron, Madison, US) at 4 cm $^{-1}$  resolution. About 10 mg of sample was pressed into a self-supporting wafer, which was placed in an IR cell connected to the vacuum system. The sample was first activated in H $_2$  at 300 °C for 2 h. After cooling to room temperature, the sample was exposed to 15 mbar CO for 30 min. After evacuation ( $< 10^{-5}$  mbar) for 30 min, IR spectra were recorded.

### **3. Catalytic hydrogenation of acetylene**

The activity and ethylene selectivity of the catalyst for the catalytic hydrogenation of acetylene in excess ethylene was tested at 60 °C under atmospheric pressure. Briefly, 50 mg of catalyst was pressed into wafers, sieved to 20–40 mesh,

and loaded on a quartz reactor. The catalyst was first activated in H<sub>2</sub> (40 ml min<sup>-1</sup>) at 250 °C for 2 h. After cooling to 60 °C, the selective hydrogenation of acetylene in excess ethylene was conducted. The gas mixture (60 ml min<sup>-1</sup>) consisted of 0.73 vol.% C<sub>2</sub>H<sub>2</sub>, 1.46 vol.% H<sub>2</sub>, and 52.6 vol.% C<sub>2</sub>H<sub>4</sub> in He. The reaction products were analyzed using an online GC equipped with a capillary column (HP-AL/S) and a flame-ionization detector (FID).

Selectivity and conversion was calculated as follows:<sup>1</sup>

$$S_{C_2H_4} = \left[ 1 - \frac{(x_{C_2H_6} - x_{C_2H_6}^0) - 2(x_{C_4H_8} - x_{C_4H_8}^0)}{x_{C_2H_2}^0 - x_{C_2H_2}} \right] \times 100\% ;$$

$$S_{C_2H_6} = \left[ \frac{x_{C_2H_6} - x_{C_2H_6}^0}{x_{C_2H_2}^0 - x_{C_2H_2}} \right] \times 100\% .$$

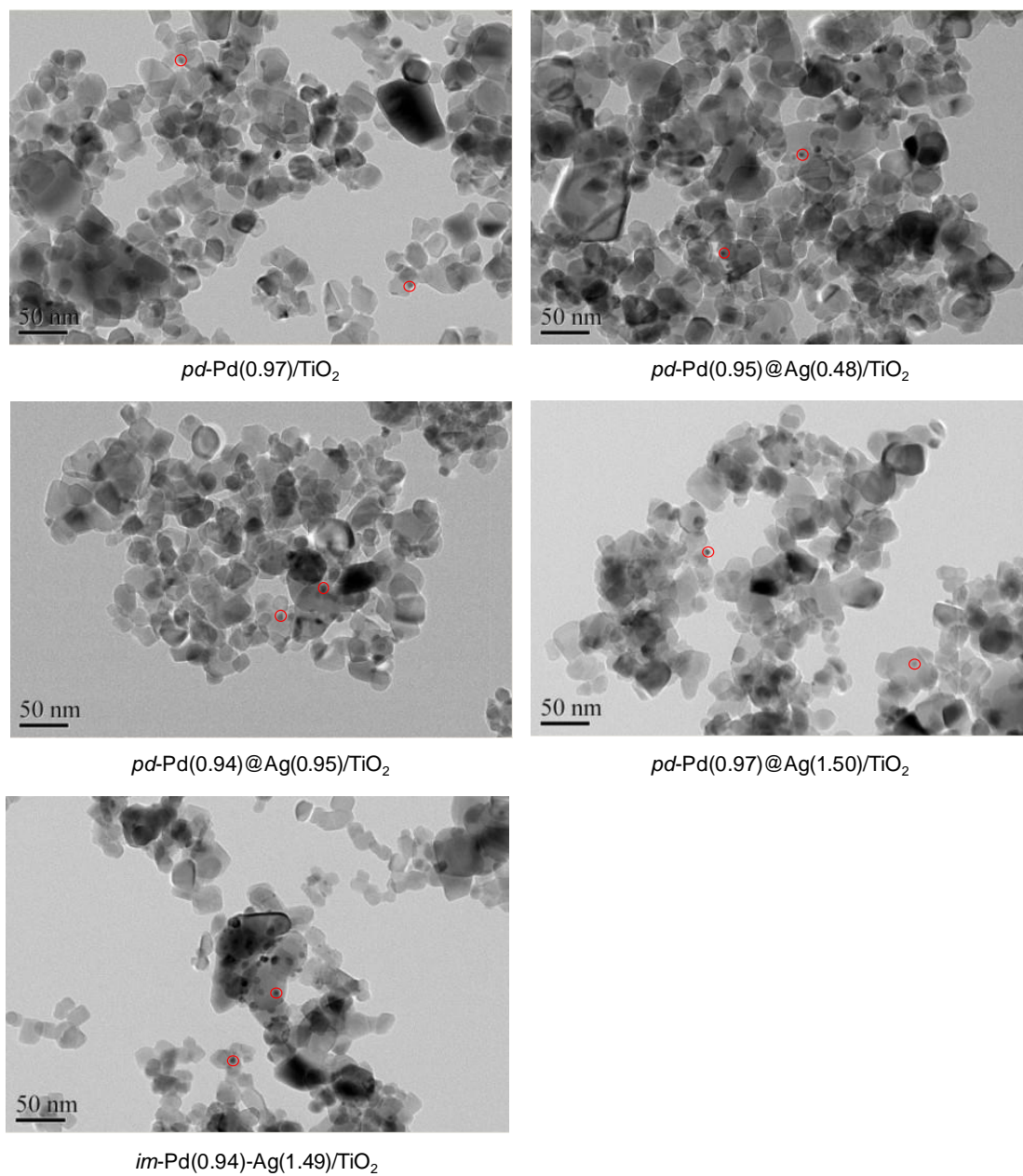
$$X_{C_2H_2} = \left[ 1 - \frac{x_{C_2H_2}}{x_{C_2H_2}^0} \right] \times 100\% .$$

$x_i$  : mole concentration of  $i$  ;

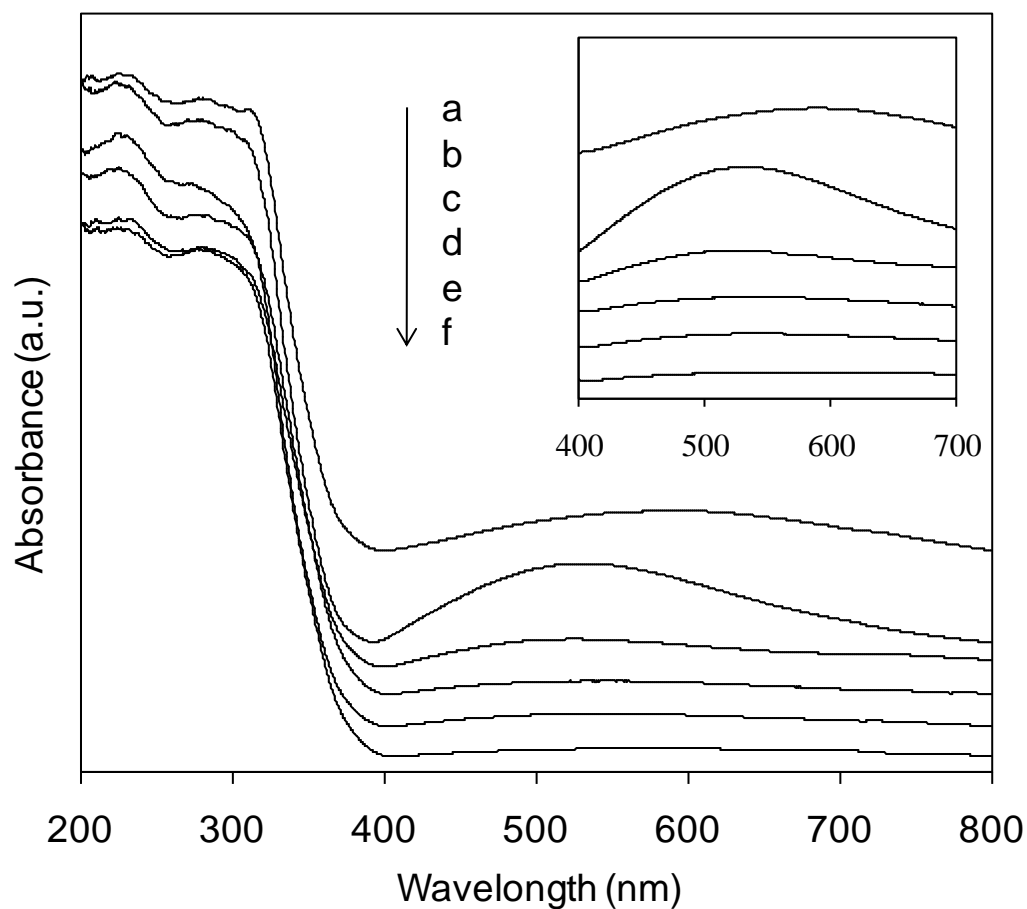
$x_i^0$  : initial mole concentration of  $i$  ;

$X_i$  : conversion of  $i$  ;

$S_i$  : selectivity to  $i$  .



**Fig. 1S** TEM images of the catalysts.



**Fig. 2S** UV-vis spectra of (a) *pd*-Ag(0.98)/TiO<sub>2</sub>; (b) *pd*-Pd(0.97)@Ag(1.50)/TiO<sub>2</sub>; (c) *pd*-Pd(0.95)@Ag(0.97)/TiO<sub>2</sub>; (d) *pd*-Pd(0.94)@Ag(0.48)/TiO<sub>2</sub>; (e) *im*-Pd(0.94)-Ag(0.96)/TiO<sub>2</sub>; (f) *pd*-Pd(0.97)/TiO<sub>2</sub>.

### References:

- 1 A. Pachulski, R. Schodel and P. Claus, *Appl. Catal. A.*, 2001, **400**, 14.