

## *Supplementary Information*

# **Highly Efficient and Selective Dicarbonylation of Acetylene Catalytic by Palladium Nanosheets Supported on Activated Carbon**

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## **Experimental Section**

### 1. Chemicals and Materials

Activated carbon (AC, 1.0–1.4 mm in diameter), Palladium chloride (PdCl<sub>2</sub>),  $\gamma$ -aluminum trioxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), Silica (SiO<sub>2</sub>), Cerium oxide (CeO<sub>2</sub>), Magnesium oxide (MgO), sodium hydroxide (NaOH) and hydrochloric acid (36~38%), Potassium iodide (KI), N,N-dimethylformamide (N,N-DMF), Methanol (CH<sub>3</sub>OH); Dimethyl maleate, Dimethyl fumarate were purchased from Shanghai Aladdin Co. Ltd. 1M HCl and 1M NaOH were freshly configured. High purity N<sub>2</sub>, O<sub>2</sub>, CO and CH $\equiv$ CH raw gas were purchased from Special Gas Research Co., Ltd. All the chemicals were of analytical grade and used as received without any further purification. Deionized water (18.25 M $\Omega$ ) was used throughout the experiment.

### 2. g-C<sub>3</sub>N<sub>4</sub> preparation

The g-C<sub>3</sub>N<sub>4</sub> support was prepared by polymerization of dicyandiamide molecules under high temperature in a tube furnace. In detail, dicyandiamide was heated at 823 K for 3h under air condition with a ramp rate of 2.5K/min for the heating process. Then the orange g-C<sub>3</sub>N<sub>4</sub> powder was obtained.

### 3. Pd nanosheets preparation

1 mol/L H<sub>2</sub>PdCl<sub>4</sub> aqueous solution was prepared by reacting PdCl<sub>2</sub> with concentrated HCl stoichiometrically at 70 °C under stirring for 1 hour, to give a red solution. Precursors [Pd<sub>2</sub>( $\mu$ -CO)<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> was synthesized as literature method.<sup>1</sup> 30  $\mu$ L of

1M  $\text{H}_2\text{PdCl}_4$  aqueous solution was added into a glass pressure vessel containing 5 mL  $\text{N,N}$ -DMF. Then 1 atm CO atmosphere was introduced at room temperature under stirring. The color changed from brown red to golden yellow in several minutes. After 15 min vigorous stirring, CO gas was removed, to give the target product  $[\text{Pd}_2(\mu\text{-CO})_2\text{Cl}_4]^{2-}$ . Adding DW (1 ml) to the solution dropwise under stirring, the color changed from golden to dark blue to give the Pd nanosheets.

#### 4. 3 % Pd/AC preparation

Commercial Pd/AC was synthesized by impregnation method according to the literature method.<sup>2</sup>  $\text{PdCl}_2$  (50 mg) was dissolved in a pear-shaped flask with methanol (5 ml) and activated carbon powder (1 g) with further vigorously stirred for 24 hours. Then remove the solvent under reduced pressure at  $30^\circ\text{C}$ . The obtained powder was washed with ethanol and deionized water for several times and calcined in a tube furnace at 675 K for 5 h with a heating rate of  $5 \text{ min}^{-1}$ , then cooled to room temperature and finally obtained 3 wt.% Pd/AC catalyst.

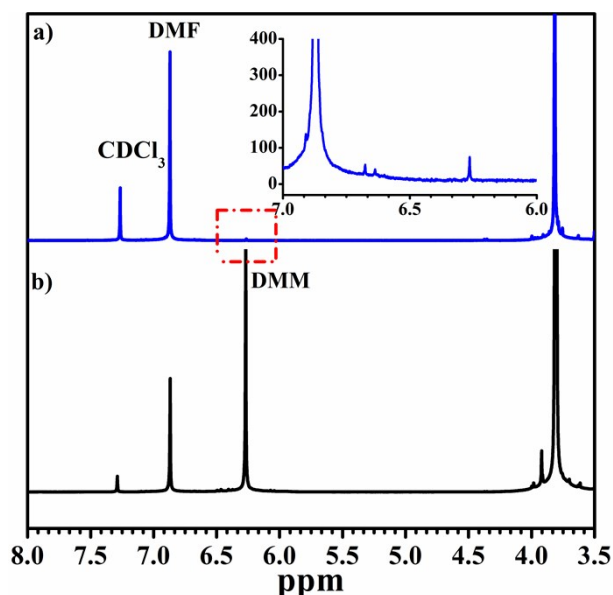


Fig. S1  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of dimethyl fumarate (DMF) and dimethyl maleate (DMM) products catalyzed by  $\text{Pd}_{\text{CO}}/\text{AC}$  (a) and Pd/AC (b).

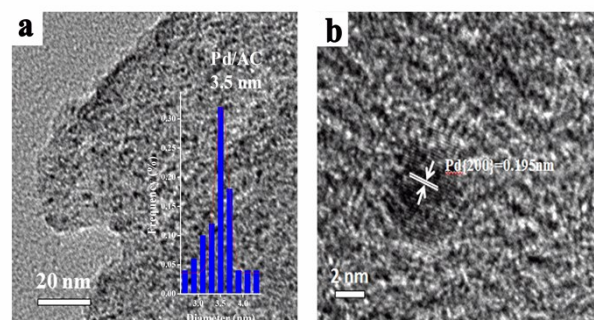


Fig. S2 Typical TEM (a) and STEM-HAADF (b) images of Pd/AC catalyst, and histogram of palladium particle size distribution (inset).

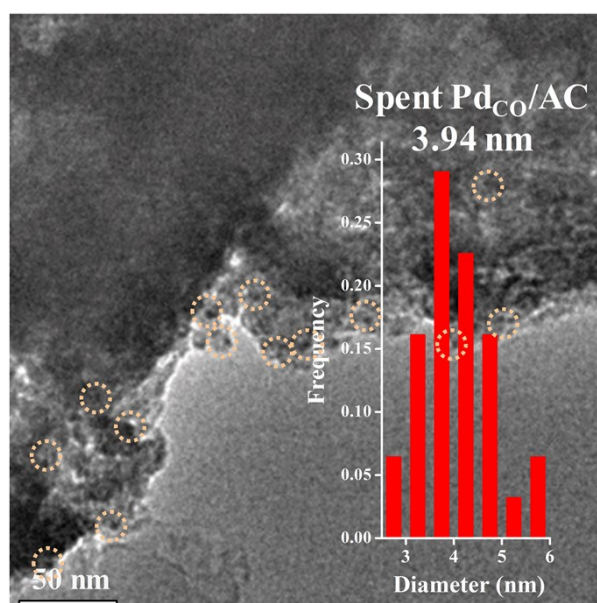


Fig. S3 TEM image of the spent Pd<sub>CO</sub>/AC catalyst and the histogram of Pd particle size distribution (inset).

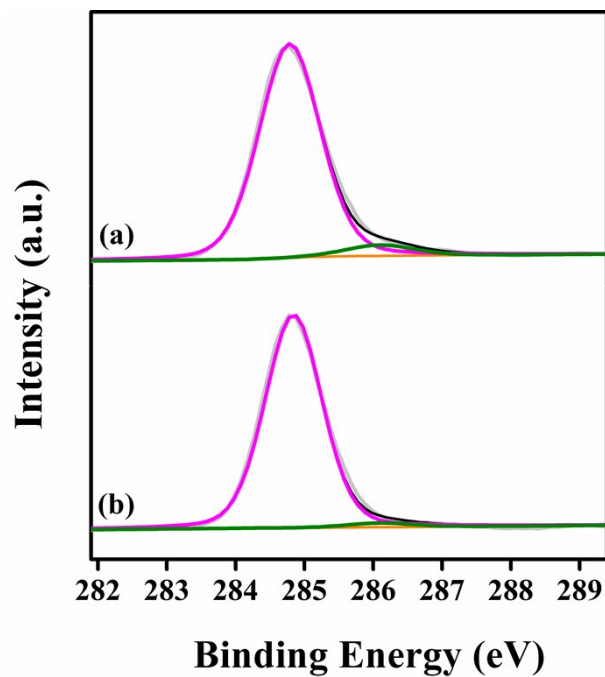


Fig. S4 High resolution XPS spectra of C 1s of the (a) Pd<sub>Co</sub>/AC and (b) Pd/AC catalysts.

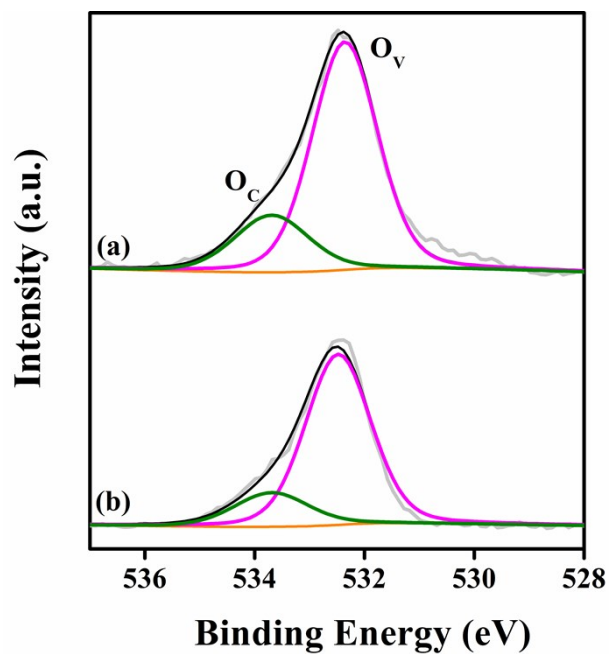


Fig. S5 High resolution XPS spectra of O 1s of the (a) Pd<sub>Co</sub>/AC and (b) Pd/AC catalysts.

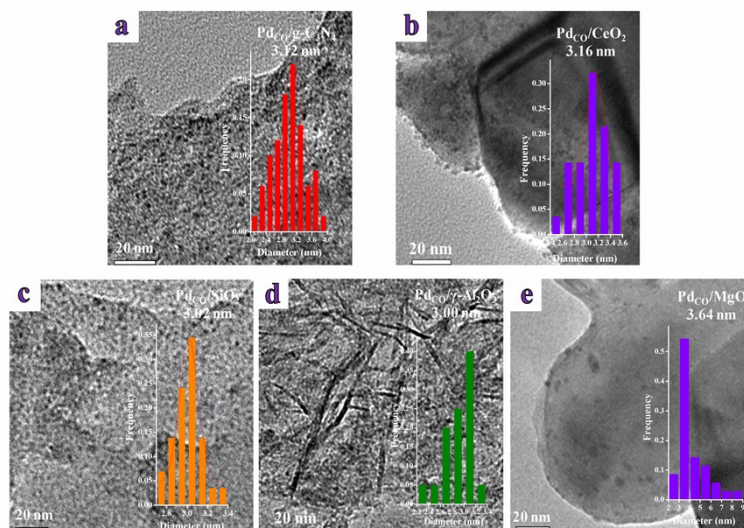


Fig. S6 Typical TEM images of Pd<sub>CO</sub>/g-C<sub>3</sub>N<sub>4</sub> (a), Pd<sub>CO</sub>/CeO<sub>2</sub> (b), Pd<sub>CO</sub>/SiO<sub>2</sub> (c), Pd<sub>CO</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (d) and Pd<sub>CO</sub>/MgO (e) catalysts and the corresponding histograms of palladium particle size distribution (*inset*).

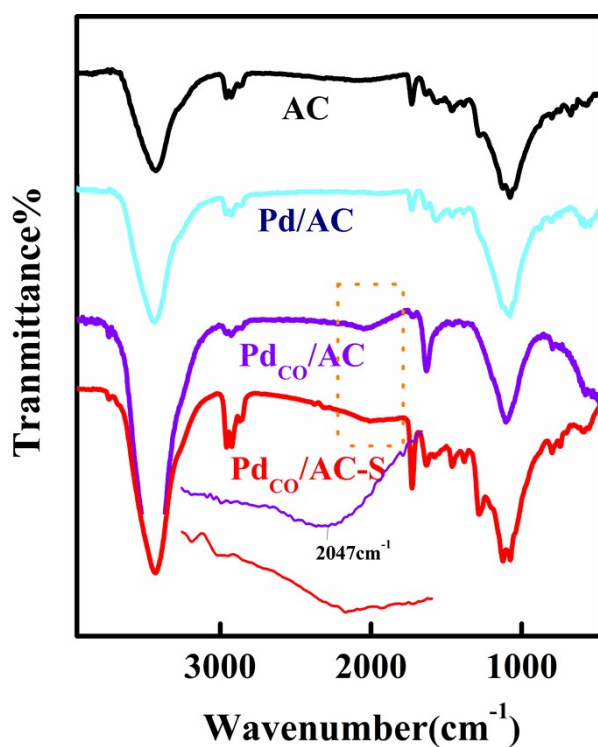
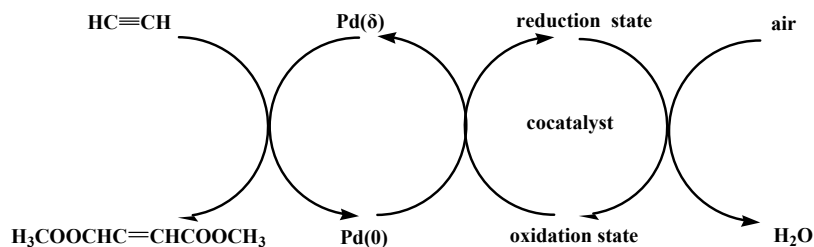


Fig. S7 FT-IR spectra of activate carbon (black), Pd/AC (blue), Pd<sub>CO</sub>/AC (purple), and the spend Pd<sub>CO</sub>/AC catalysts (red).

The wide band at about  $3420\text{ cm}^{-1}$  is assigned to O–H stretching of adsorbed water,  $2960\text{--}2850\text{ cm}^{-1}$  corresponding to the asymmetric C–H band. The characteristic peaks of activated carbon at  $1075$  and  $1689\text{ cm}^{-1}$ ,<sup>3,4</sup> can be observed on all the samples. The new broad band at  $2033\text{ cm}^{-1}$  (purple) could be indexed to the stretching vibration of terminal carbonyl C=O, indicated the remaining of terminal carbonyl adsorbed on the surface of palladium nanosheets. The stretching vibration peak of the carbonyl group still exists at  $1967\text{ cm}^{-1}$  in the spectrum of the catalyst after catalysis (red), which could be assigned to bridge carbonyl on the catalyst after catalytic. The peaks at  $1279\text{ cm}^{-1}$  and  $1727\text{ cm}^{-1}$  could be assigned to the anti-symmetric stretching vibration of C–O–C and the stretching vibration of C=O, respectively. These might associated with the adsorption of products on the catalyst. These results confirmed that the AC support is rich in surface functional groups, which may lead to more defects on the surface of the catalysts and provide strong cooperation with palladium.



Scheme S1. The specific  $\text{Pd}^{\delta+}\text{-Pd}^0\text{-Pd}^{\delta+}$  catalytic reaction process.

Table S1. Conversion of acetylene raw material with Pd-supported catalysts and corresponding selectivity for target products<sup>a</sup>

Catalyst	T (°C)	P (MPa)	Conv. (%)	Sel. <sub>product</sub> (%)		
				3	4	Others
Pd/AC	80	5	21.9	25.5	74.5	–
Pd <sub>CO</sub> /AC	80	5	43.8	99.0	1.0	–
Pd <sub>CO</sub> /SiO <sub>2</sub>	80	5	12.6	49.4	–	50.6
Pd <sub>CO</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	80	5	10.2	91.5	8.5	–
Pd <sub>CO</sub> /CeO <sub>2</sub>	80	5	8.0	82.0	18.0	–
Pd <sub>CO</sub> /g-C <sub>3</sub> N <sub>4</sub>	80	5	trace	–	–	–
Pd <sub>CO</sub> /MgO	80	5	trace	–	–	–

<sup>a</sup>Reaction conditions: T = 353 K; 0.05 g catalyst; P<sub>CO</sub> = 4.55 MPa; P<sub>O<sub>2</sub></sub> = 0.45 MPa; t = 10h.

Table S2 The relative amount of different components.

Sample	Pd <sup>0</sup> (%)	Pd <sup>2+</sup> (%)	Pd <sup>4+</sup> (%)	O <sub>v</sub> (%)	O <sub>c</sub> (%)
Pd <sub>CO</sub> /C	9.78	35.88	54.34	86.9	13.1
Pd/C	10.70	53.80	35.50	82.1	17.9

Table S3. Bands observed in the FTIR spectra of the series of catalysts as well as corresponding functional groups

Sample	Band (cm <sup>-1</sup> )				
	$\nu(\text{C-H})$	$\nu(\text{C=O})$	$\nu(\text{H-O})$	$\nu(\text{C=O})$	$\nu(\text{C-O-C})$
AC	3429	—	2962、2927、2857	1725	1279
Pd/AC	3431	—	2962、2927、2857	1725	—
Pd <sub>CO</sub> /AC	3431	2047	2962、2927、2857	1725	—
Pd <sub>CO</sub> /AC-S	3431	1969	2960、2925、2863	1727	1279

### Notes and references

- 1 Li, H.; Chen, G.; Yang, H.; Wang, X.; Liang, J.; Liu, P.; Chen, M.; Zheng, N., *Angew Chem Int Ed Engl* 2013, **52**, 8368-72.
- 2 Bhanage, B.; Gadge, S., *Synlett* 2013, **24**, 981-986.
- 3 Trotus, I. T.; Zimmermann, T.; Schuth, F., *Chem Rev* 2014, **114**, 1761-82.
- 4 Sun, X.; Li, Y., *Angew Chem Int Ed Engl* 2004, **43**, 597-601.