Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Single palladium site catalyst as a bridge for converting homogeneous to heterogeneous in dimerization of terminal aryl acetylenes

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1. Material Synthesis and Characterization:

Chemicals:

Analytical grade Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 2-methylimidazole, $NaBH_4$were obtained from Shanghai Chemical Reagents, China. $PdCl_2$ (99%), phenylacetylene were purchased from Alfa Aesar. All of the chemicals used in this experiment were analytical grade and used without further purification.

Methods

Experimental Section:

Synthesis of ZIF-67.

In a normal procedure, Co $(NO_3)_2 \cdot 6H_2O$ (0.546 g) and 2-methylimidazole (0.616 g) were dissolved in 15mL of methanol, respectively. Then the Co $(NO_3)_2 \cdot 6H_2O$inmethanol solution was rapidly injected into solution of 2-methylimidazoleunder ultrasound for 5 min at room temperature. The resulting suspension was transferred to 50mL Teflon-lined stainless-steel autoclaves and then heated at 120 ^oC for 4 h. Finally, the as-obtained precipitates were centrifuged and washed with methanol several times and dried in vacuum at 343 K for overnight.

Synthesis of Pd_1/H-ZIF catalyst.

Typically, as-prepared ZIF-67 was annealed at 180 ^oC for 2 h under Ar atmosphere. Then, 30 mg ZIF-67 was dispersed in 10mL methanol under vigorous stirred, and the corresponding amount Na_2PdCl_4 was added to the above suspension at room temperature for 4 h. After centrifugation of suspension to removed solvent and vacuum drying, the resulting $PdCl_2$/ZIF-67 was reduced at 200 ^oC for 2 h under flowing 10% H_2/Ar atmosphere and then cooled naturally to room temperature. Finally, the obtained powders were dispersed in 20mL of deionized water. The mixed solution was heated to 100 ^oC for 2 h, during which the ZIF-67 can be completely removed. The product was washed by ethanol for several times and dried at 80 ^oC overnight.

Synthesis of Pd cube@ZIF-67.

Typically, Co $(NO_3)_2 \cdot 6H_2O$ (0.546 g) and 2-methylimidazole (0.616 g) were dissolved in 15mL of methanol, respectively. The corresponding amount Pd cube was evenly dispersed in the methanol solution of Co $(NO_3)_2 \cdot 6H_2O$, then the mixture was rapidly injected into the solution of 2-methylimidazoleunder ultrasound for 10 min at room temperature. The resulting suspension was transferred to 50mL Teflon-lined stainless-steel autoclaves and then heated at 120 ^oC for 4 h. Finally, the as-obtained precipitates were centrifuged and washed with methanol several times and dried in vacuum at 80 ^oC for overnight.

Synthesis of Pd cube/ZIF-67.

The corresponding amount Pd cube was dispersed in 10mL methanol, then, 30 mg ZIF-67 was added to 10mL the above suspension, the mixture was stirred at room temperature for 4 h. After centrifugation of suspension to removed solvent, the as-prepared Pd cube/ZIF-67 was dried at 80 ^{o}C overnight.

Synthesis of Pd NPs/ZIF-67.

First, 30 mg ZIF-67 was dispersed in 10mL methanol under vigorous stirred, and the corresponding amount Na_2PdCl_4 was injected into the above suspension at room temperature. Then three times amount of $NaBH_4$ was added to the mixture for 4 h. After centrifugation of suspension to removed solvent and vacuum drying, the as-prepared Pd NPs/ZIF-67 was washed by ethanol for several times and dried at 80 ^{o}C overnight.

Characterizations:

Powder X-ray diffraction patterns of samples were recorded using a Rigaku Miniflex-600 with Cu Kα radiation (Cu Kα, λ=0.15406 nm, 40 kV and 15 mA). The morphologies are characterized by TEM (Hitachi-7700, 100KV). The high-resolution TEM, HAADF-STEM images the corresponding Energy dispersive x-ray spectroscopy were recorded by a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope working at 200 kV and on a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector working at 300 kV. The SEM was carried out by a JSM-6700F SEM. Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at 77 K. Photoemission spectroscopy experiments (XPS) were performed at the Catalysis and Surface Science End station at the BL11U beam line of National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. Thermo gravimetric analyses (TG) were carried out on aTASDTQ600 thermal analyzer heating from room temperature to 900 ^{o}C at the rate of 10 ^{o}C min^{-1}.Elemental analysis of Pd in the solid samples was detected by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). XAFS measurement and data analysis：XAFS spectra at the Pd K-edge were recorded at the XAS station (BL14W1) of the Shanghai Synchrotron Radiation Facility (SSRF), China. The Pd K-edge XANES data were recorded in a fluorescence mode. Pd foil and $PdCl_2$ were used as references. The storage ring was working at the energy of 3.5 GeV. The hard X-ray was monochromatized with Si (111) double-crystals. The acquired EXAFS data were extracted and processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k3-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k3-weighted χ(k) data in the k-space ranging from 2.5–11.2 Å^{-1} were Fourier transformed to real (R) space using a hanning windows (dK = 1.0 Å^{-1}) to separate the EXAFS contributions from different coordination shells.

2. Catalytic Measurements：

Catalytic dimerization of phenylacetylene.10 mg Pd_1/H-ZIF catalyst, 1mmol of reactant and 5mL of toluene were added into a 25mL Schlenkglass vessel tubes under 10% H_2/Ar atmosphere. The mixture was then charged with 1 bar 10% H_2/Ar and stirred at 120 ^{o}C in an oil bath. The 100μL reaction solution was extracted for GC-MS analysis and determination. The reaction conditions were kept the same with that forthe other catalysts (i.e, Pd/C, $PdCl_2$ and Pd cube/ZIF-67).

3. Supporting Figures and Tables:

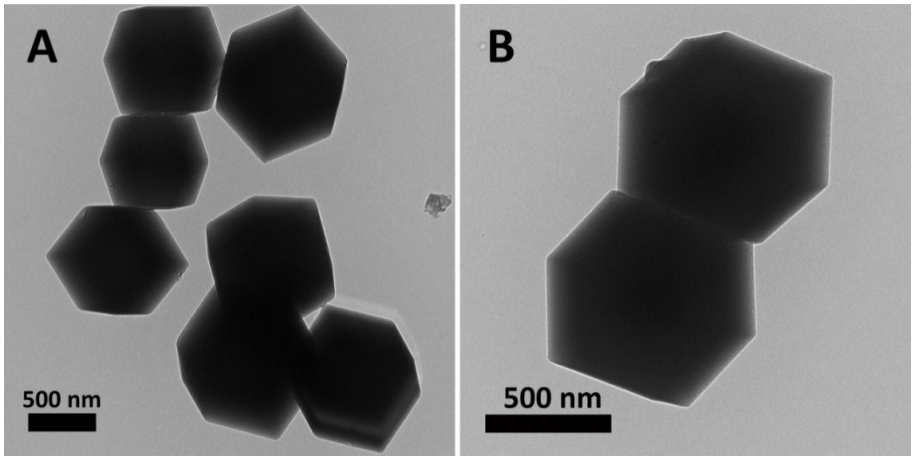


Figure S1. TEM images of ZIF-67 and $PdCl_2$/ZIF-67.

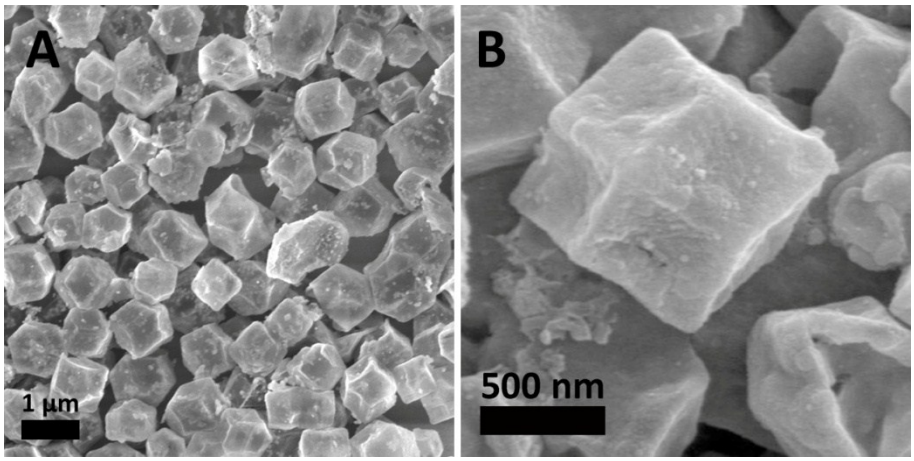


Figure S2. SEM images of Pd_1/H-ZIF.

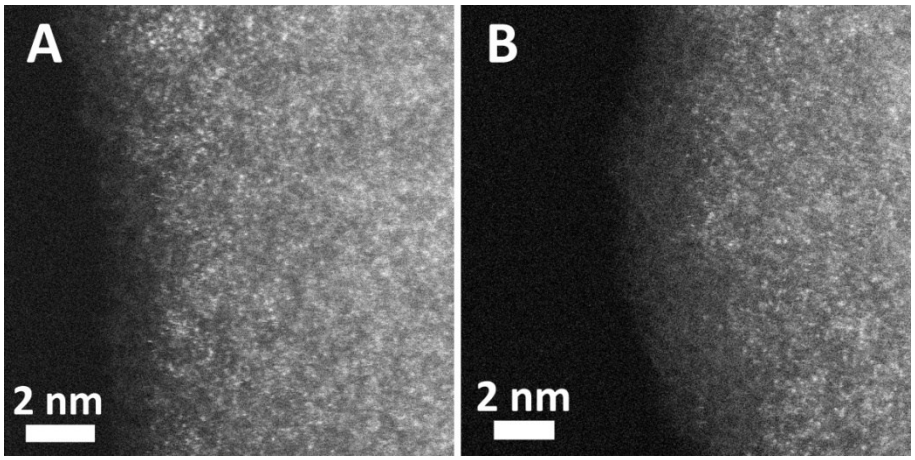


Figure S3. Aberration corrected HAADF-STEM images of Pd_1/H-ZIF.

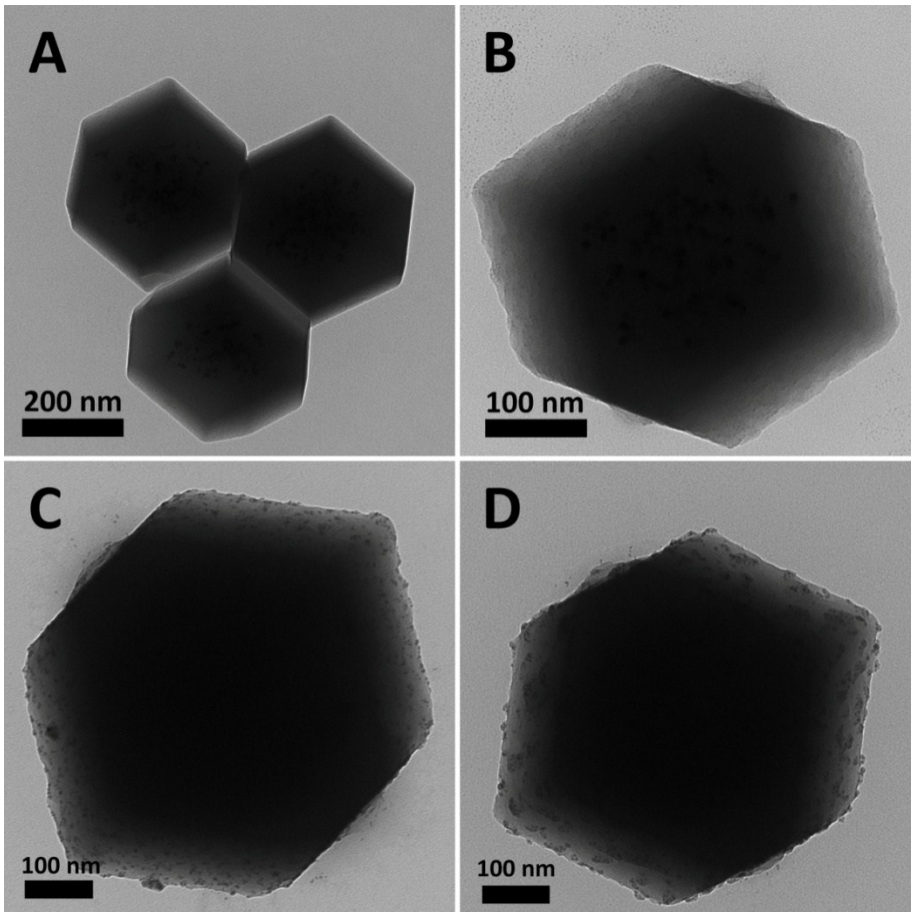


Figure S4. (A, B) TEM images of Pd cube@ZIF-67. (C, D) TEM images of Pd NPs/ZIF-67.

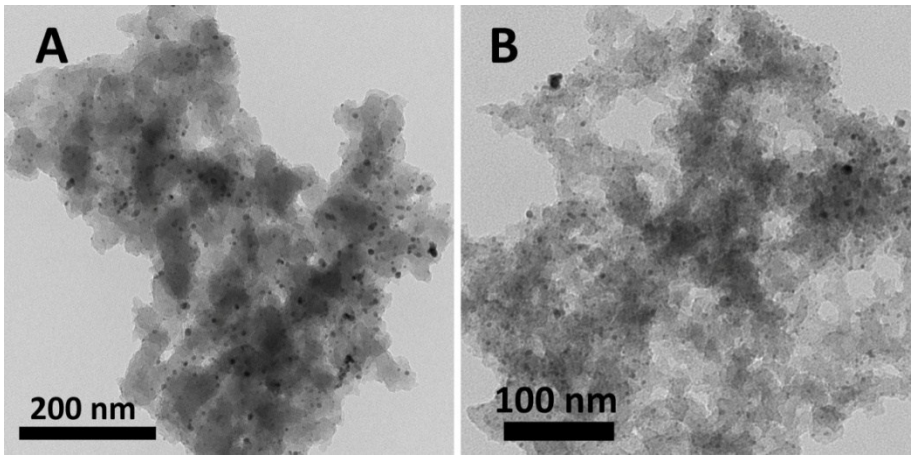


Figure S5. TEM images of the commercial Pd/C catalyst.

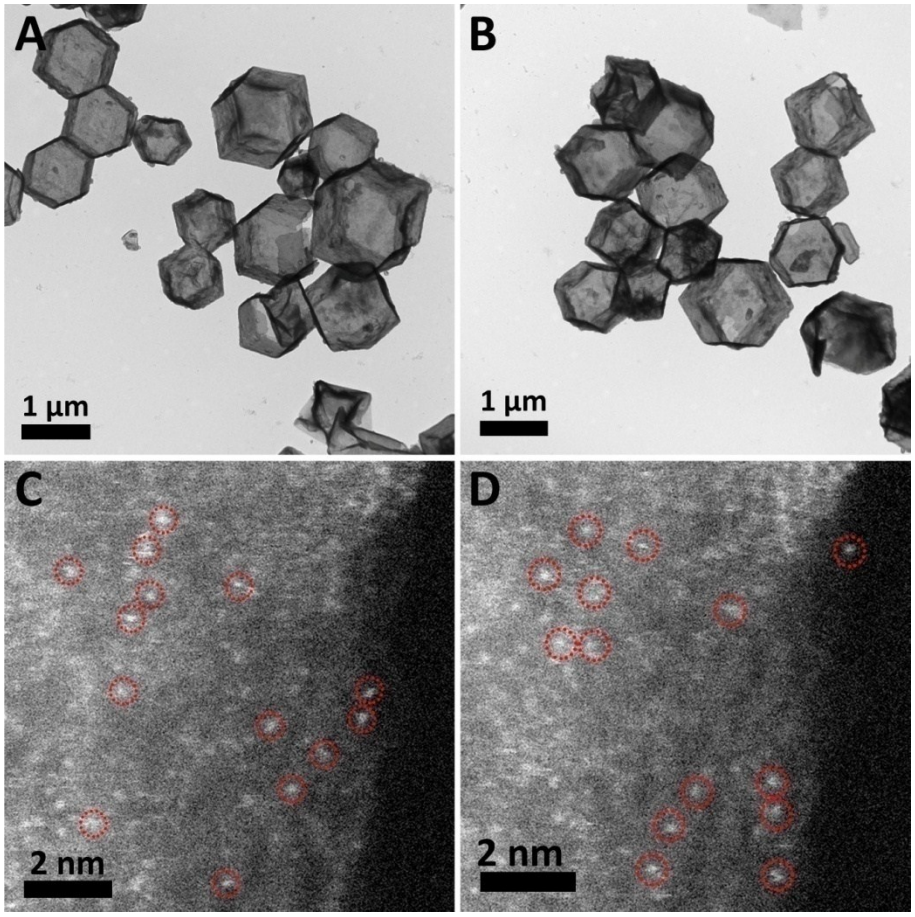


Figure S6. (A, B) TEM images, (C, D) Aberration corrected HAADF-STEM images of Pd_1/H-ZIF after catalysis reaction.

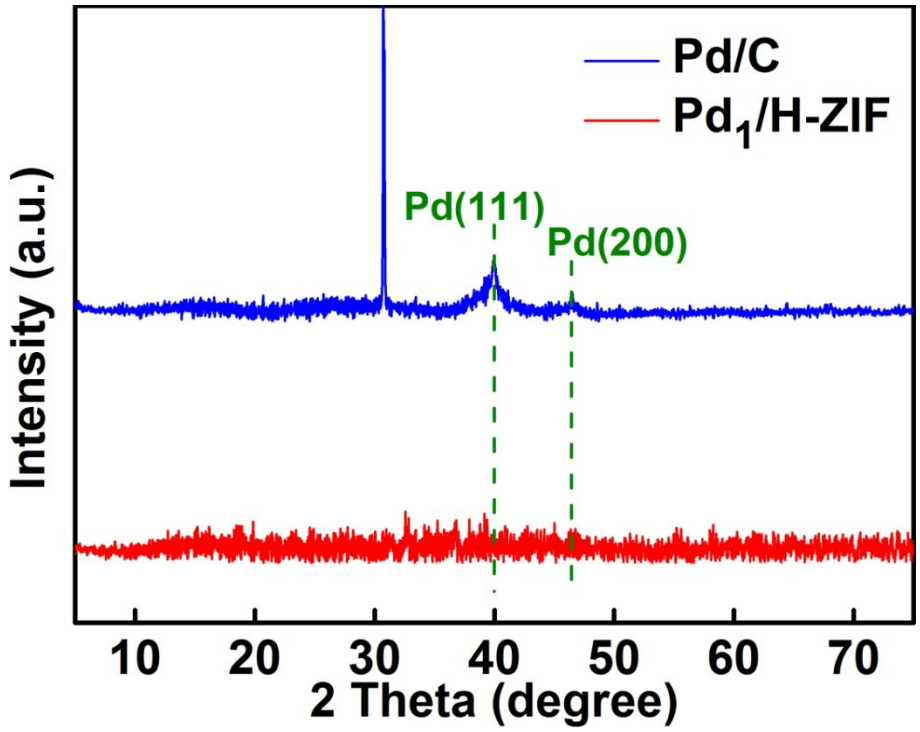


Figure S7. XRD patterns of the commercial Pd/C and Pd_1/H-ZIF catalyst.

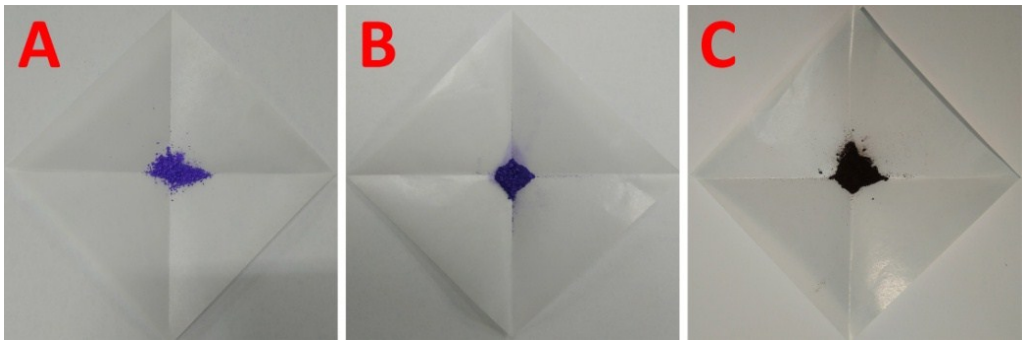


Figure S8: The color evolution during the preparation ofPd_1/H-ZIF catalyst. The photos of (A) ZIF-67, (B) Pd_1/ZIF-67, (C) Pd_1/H-ZIF catalyst.

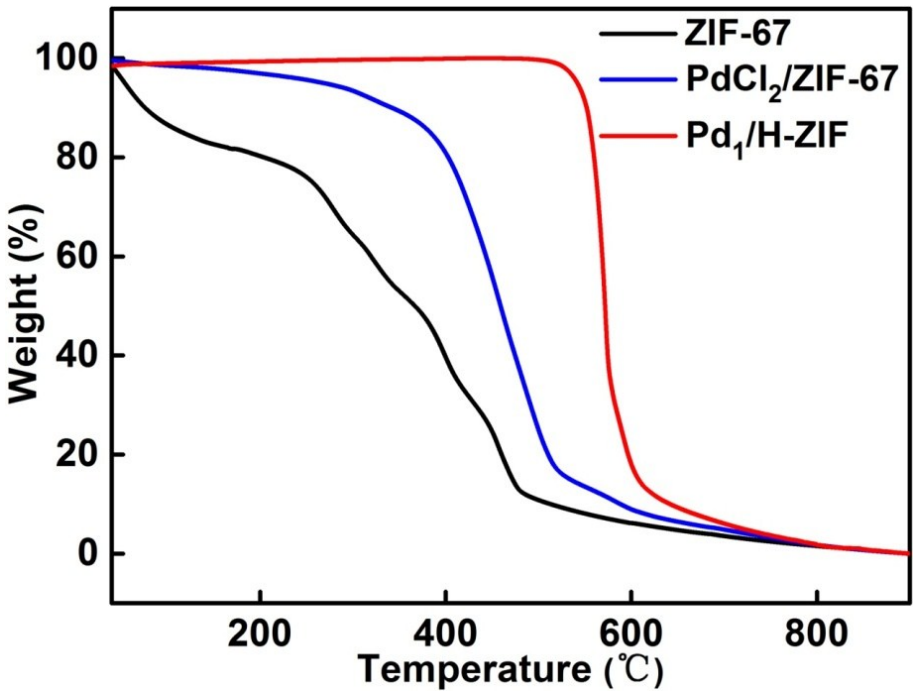


Figure S9: Thermo gravimetric analysis (TGA) of ZIF-67, $PdCl_2$/ZIF-67 and Pd_1/H-ZIF. The Pd species coordinate with the surface unsaturated dangling N bond of ZIF-67 obviously enhanced the thermo stability of Pd_1/H-ZIF catalyst.

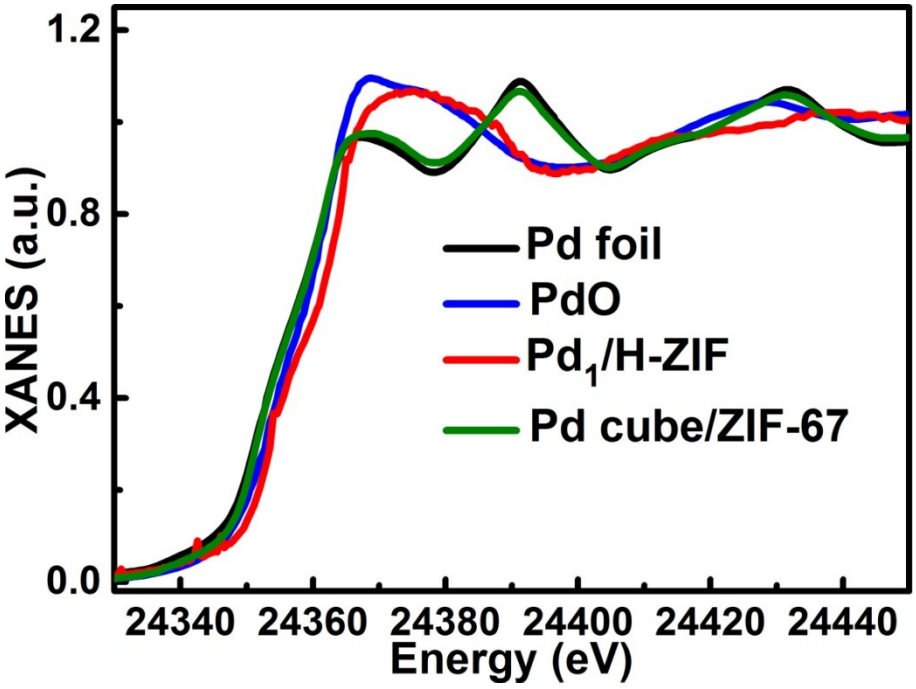


Figure S10: Pd K-edge XANES spectra.

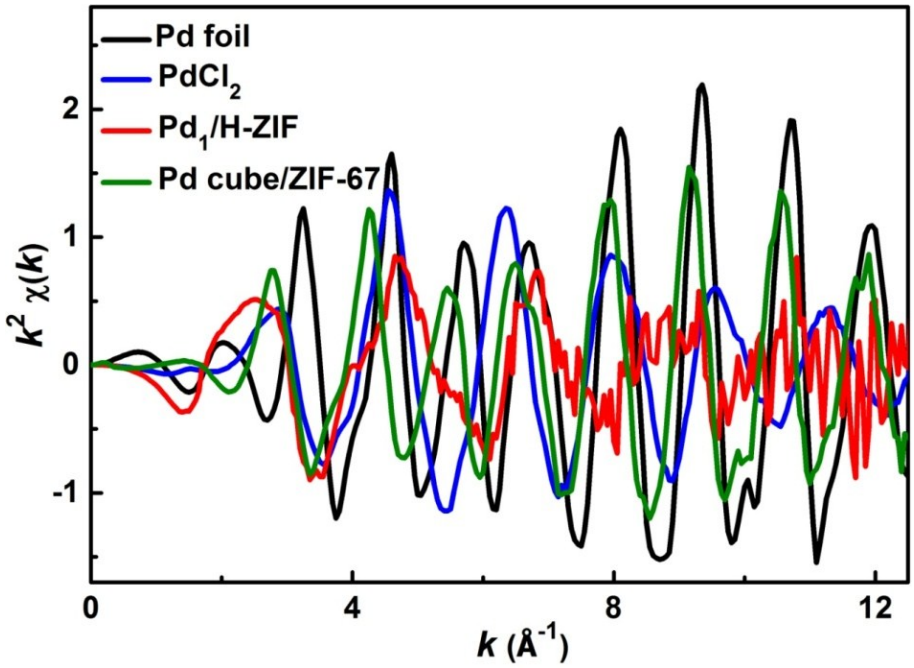


Figure S11: XAFS spectra of the Pd foil, $PdCl_2$, Pd_1/H-ZIF and Pd cube/ZIF-67 catalysts at the Pd K-edge.

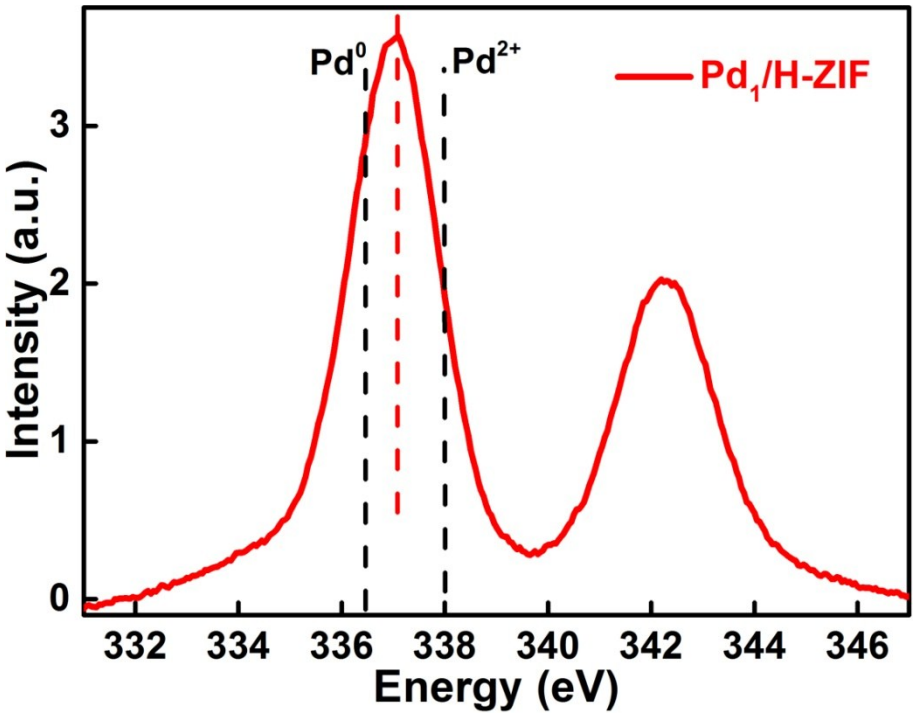


Figure S12: XPS spectra of the Pd_1/H-ZIF.

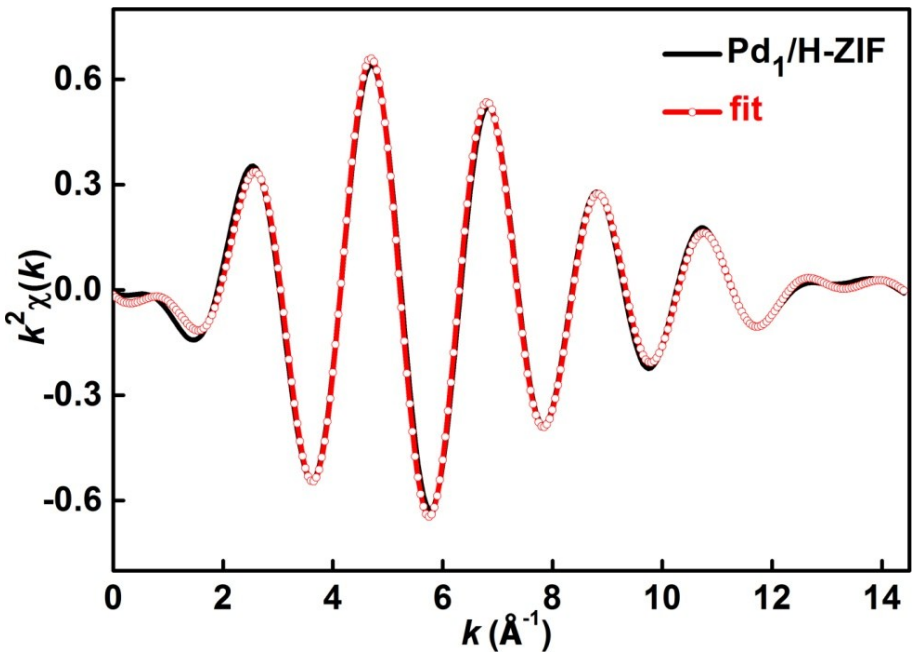


Figure S13. FT-EXAFS Fitting result of Pd_1/H-ZIF catalyst.

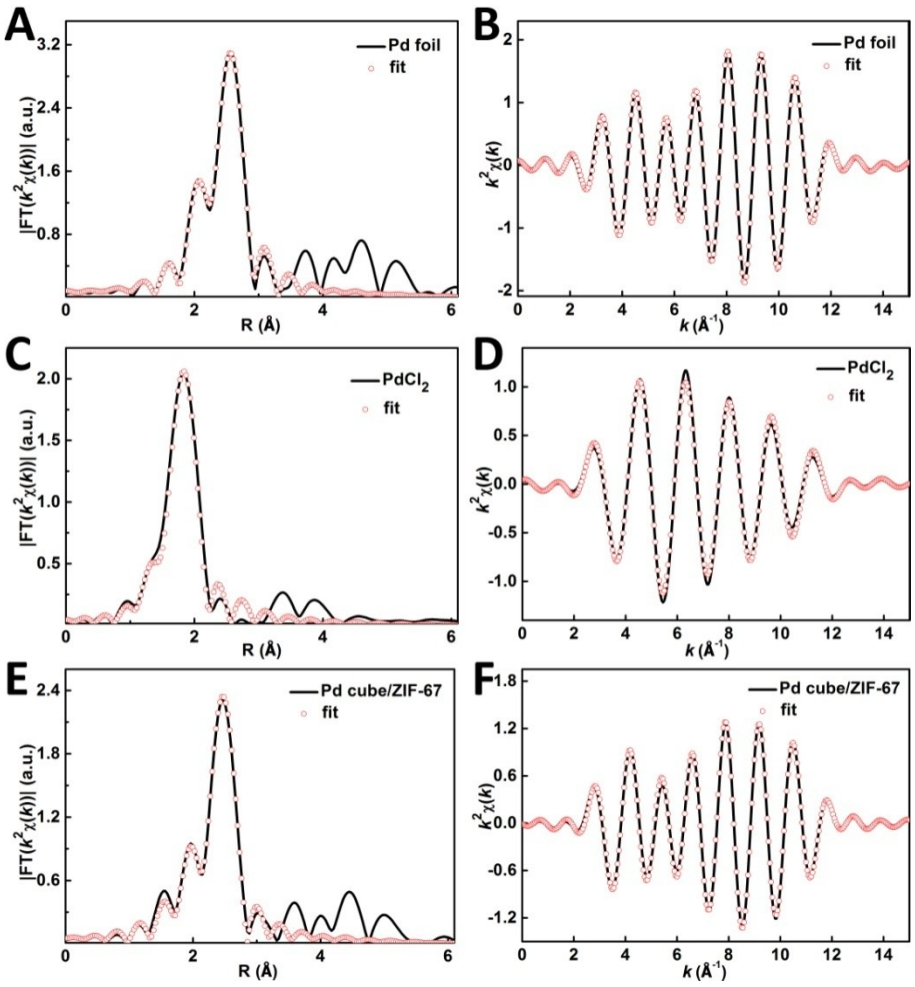


Figure S14. R space and inverse FT-EXAFS Fitting result of Pd K-edge. (A, B)Pd foil, (C, D) $PdCl_2$, (E, F) Pd cube/ZIF-67.

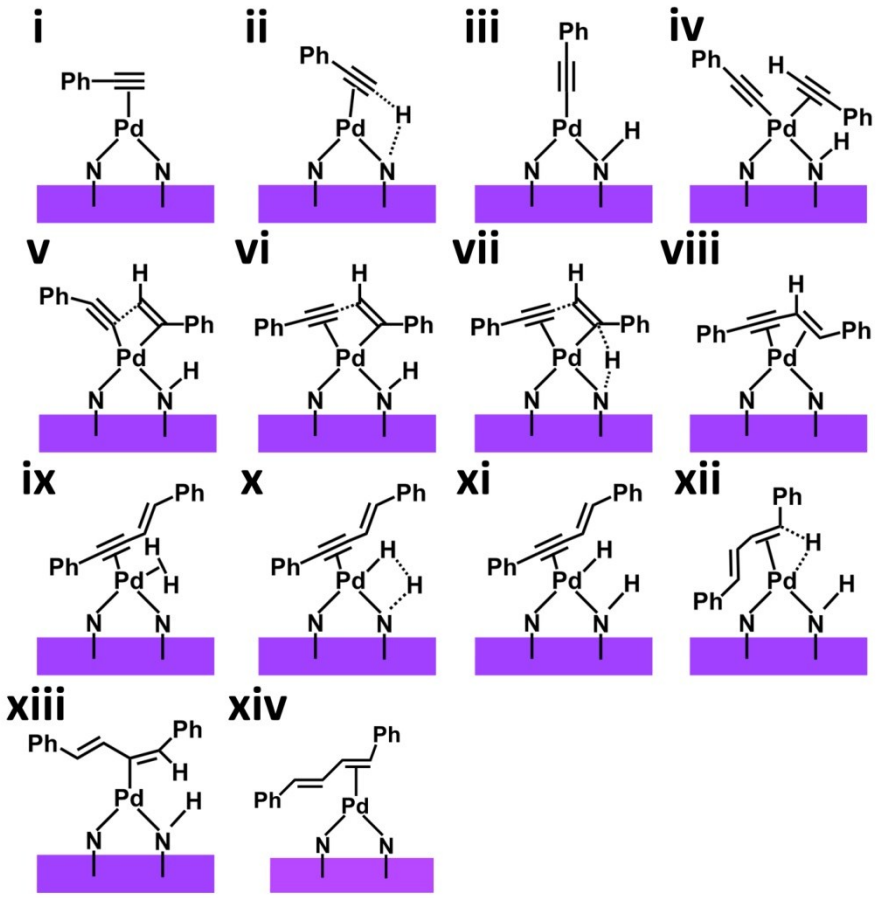


Figure S15. The optimized structures and transition state for catalytic dimerization reaction of phenylacetylene over Pd_1/H-ZIF.

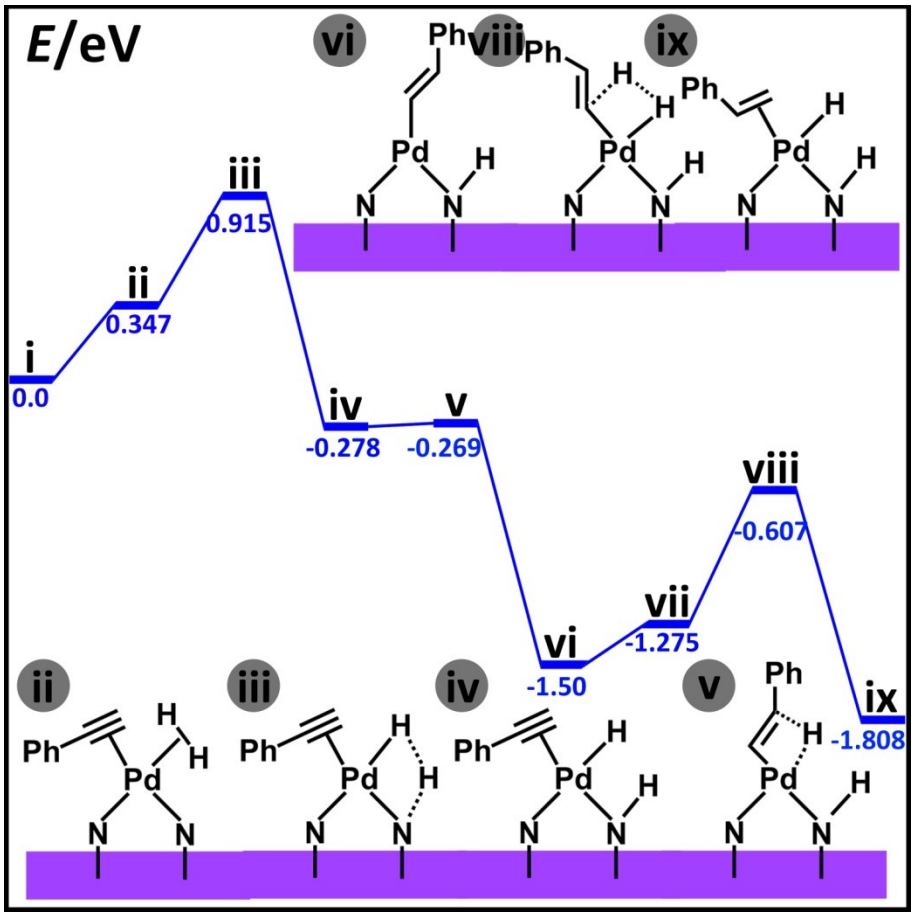


Figure S16. Calculated free energies for the phenylacetylene hydrogenation produce styrene.

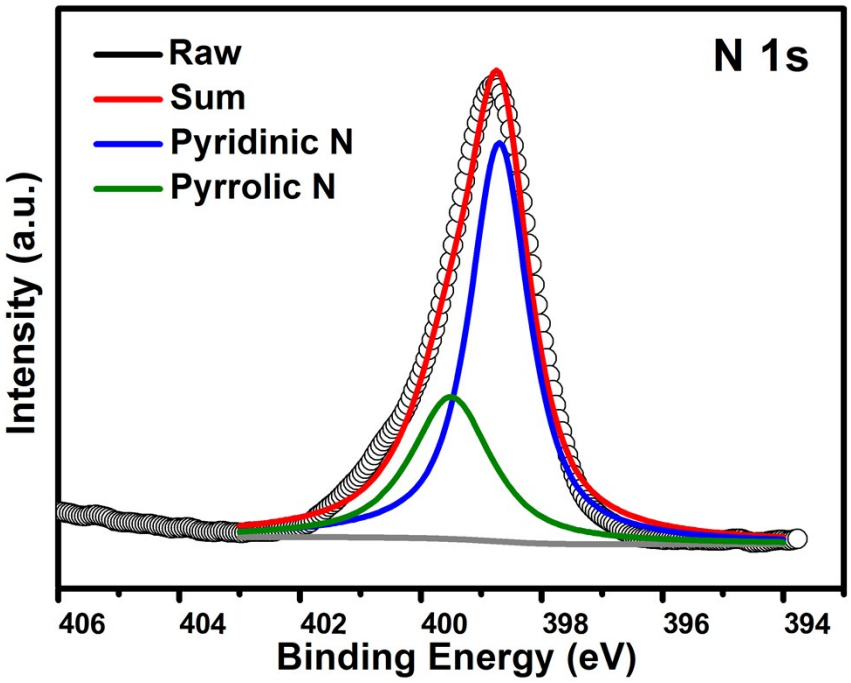


Figure S17. N 1s XPS spectra of the Pd_1/H-ZIF.

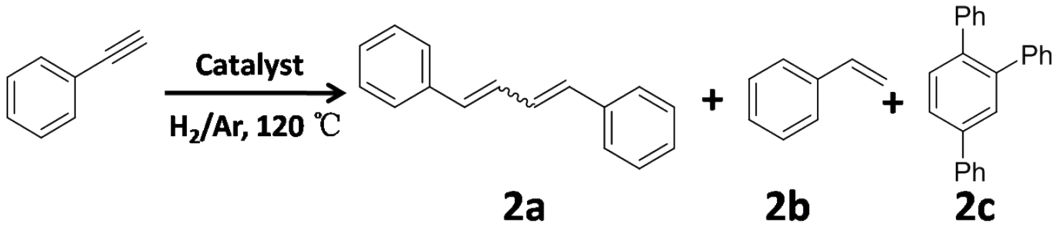
Table S1: EXAFS data fitting results of Pd foil, $PdCl_2$, Pd cube/ZIF-67, Pd_1/H-ZIF. (S_0^2=0.8)

Sample	Scatteringpair	CN	R(Å)	$\sigma^2(10^{-3}$ Å$^2)$	ΔE_0(eV)	R-factor
Pd foil	Pd-Pd	12	2.74	5±0.2	3.4±0.3	0.0002
$PdCl_2$	Pd-Cl	4	2.31	2±0.4	4.5±1	0.0014
Pd cube/ZIF-67	Pd-Pd	10.6	2.74	6±0.1	-7.5±0.4	0.0006

Pd_1/H-ZIF	Pd-N Pd-O	2 2	1.93 2.03	4±0.3 6±0.2	4.9±2 5.0±2	0.001

CN, coordination number; R, interatomic distance; σ^2, Debye–Waller factor; ΔE_0, edge-energy shift.

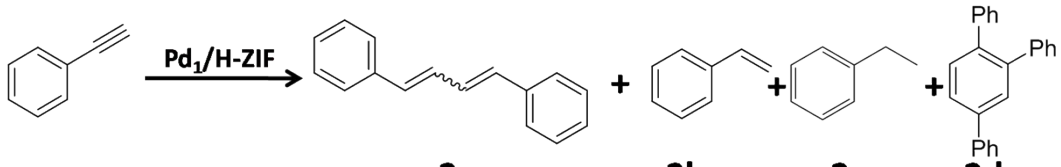
Table S2: Different Pd catalysts for dimerization of phenylacetylene.



Entry	Catalyst	Con.(%)	Yie.2a(%)	Yie.2b(%)	Yie.2c(%)	Others (%)
1	Pd_1/H-ZIF	>99	84.5	8.3	7.0	<1
2	Pd/C	>99	9.8	40.3	11.5	38.4
3	Pd cube/ZIF-67	>99	5.8	72.4	6.5	15.3
4	Pd NPs/ZIF-67	>99	3.6	81.5	3.9	11
5	Pd cube@ZIF-67	6.6	1.9	4.7	<1	<1
6	$PdCl_2$/ZIF-67	11.3	4.2	3.8	<1	3.3
7	None	<1	<1	<1	<1	<1
8	ZIF-67	<1	<1	<1	<1	<1
9	$PdCl_2$	>99	13.1	74.3	8.6	4
10	$Pd(acac)_2$	92.5	4.6	80	5	2.9
11	$Pd(OAc)_2$	>99	8.8	75.4	10.6	5.2
12	$[PdCl(C_3H_5)]_2$	>99	1.4	90.6	3.3	4.7
13	$Pd(PPh_3)_4$	>99	<1	84	5.3	10.7
14	Pd_2dba_3	>99	<1	78.5	13.6	7.9
15[29]	$CoCl_2$+PPh_3+$NaBH_4$	>99	65	<1	<1	<1
16[25]	NaH+$MgBr_2$+CuCl	>99	60	<1	<1	<1
17[30]	$(Ind)_3ZrH$	>99	68	<1	<1	<1
18[30]	$(Ind)_2Zr(CO)_2$	>99	77	<1	<1	<1

Reaction conditions: Pd, 0.002 mmol; phenylacetylene，1mmol ; toluene, 5mL; 1bar 10% H_2/Ar; 120 °C.

Table S3: The dimerization of phenylacetylene under different conditions.



2a 2b 2c 2d

Entry	Atmosphere	Temperature(℃)	Conversion(%)	$Yield_{2a}$(%)	$Yield_{2b}$(%)	$Yield_{2c}$(%)	$Yield_{2d}$(%)
1	Ar	120	19.87	<1	<1	<1	19.87
2	10%H_2/Ar	120	>99	80.7	8.0	1.0	11.3
3	20%H_2/Ar	120	>99	18.8	12.5	58.9	9.8
4	H_2	120	>99	9.6	90.3	<1	<1
5	H_2	30	>99	<1	96.6	3.4	<1
6	20%H_2/Ar	30	>99	<1	>99	<1	<1
7	H_2	50	>99	<1	97.8	2.2	<1
8	H_2	80	>99	<1	>99	<1	<1
9	20%H_2/Ar	80	>99	<1	>99	<1	<1
10	H_2	100	>99	3.8	89.6	6.6	<1

Reaction conditions: 0.5mmol of phenylacetylene, 10 mg of Pd_1/H-ZIF catalyst, 5mL of toluene, 1 bar of atmosphere.