Effect of acidic functional groups in Carbon Supported Pd Catalyst For Efficient Acetylene Dicarbonylation followed by Hydrogenation to Dimethyl Succinate

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Text S1. Catalysts Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were collected on a JEM-2010 TEM with an accelerating voltage of 200 KV. Powder X-ray diffraction (XRD) was collected on an Smartlab-SE equipped with Cu Kα radiation (λ =1.54050 Å) with an instrument scan speed of 0.5°/min and a scan angle range of 10° to 90° . X-ray photoelectron spectrometer (XPS) measurement was performed on a Thermo Scientific ESCALAB 250Xi system with an Al Kα radiation X-ray source, using the binding energy of adventitious carbon (C 1s) at 284.6 eV as standard. The Fourier transform infrared (FTIR) spectroscopy was performed on a NEXUS 670 FT-IR spectrometer, with samples prepared using the potassium bromide (KBr) pellet method, and infrared spectra were recorded in the wavelength range of 500 cm^{-1} - 4000 cm^{-1}. NH_3 programmed temperature desorption (NH_3-TPD) and C_2H_2 programmed temperature desorption (C_2H_2-TPD) profiles were performed on a chemical adsorption instrument TP-5080 with a thermal conductivity detector (TCD). Before the NH_3-TPD test, the samples (100 mg) were pretreated at 200°C under He atmosphere for 15 min, followed by adsorption under NH_3/He (1:9, 40ml) atmosphere for 60 min. Then heated from 30 °C to 900 °C at a rate of 10 °C /min. For the C_2H_2-TPD test, 100 mg of catalyst was

pretreated at 100°C for 15 minutes, followed by adsorption for 60 minutes in a mixed gas atmosphere of C_2H_2/He (1:9, 40 mL). Then, the temperature was ramped from 30°C to 600°C at a rate of 10°C/min.

Text S2. Computational methods

DFT calculations were conducted through the Vienna ab initio Simulation Package (VASP) with the projector augment wave method. Generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) functional was used as the exchange-correlation functional. The Brillouin zone was sampled with 2 × 2 × 1 K points for surface calculation. The cutoff energy was set as 500 eV, and structure relaxation was performed until the convergence criteria of energy and force reached 1 × 10^{-5} eV and 0.02 eV $Å^{-1}$, respectively. A vacuum layer of 15 Å was constructed to eliminate interactions between periodic structures of surface models. The van der Waals (vdW) interaction was amended by the zero damping DFT-D3 method of Grimme.

The adsorption energy (ΔE_{ads}) of adsorbate adsorption on surface is defined as

$$\Delta E_{ads} = E(*adsorbate) - E(*) - E(adsorbate)$$

where E(*adsorbate) and E(*) are the total energy of surface systems with and without adsorbate, respectively, E(adsorbate) is the energy of an isolated adsorbate. According to this definition, negative adsorption energy suggests that the adsorption process is exothermic and the adsorption system is thermodynamically stable. Contrarily, a positive value corresponds to an endothermic and unstable adsorption.

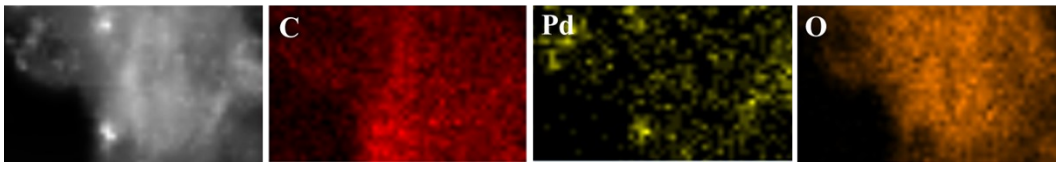

Fig. S1 Elemental mapping Pd/HAC-5 catalyst.

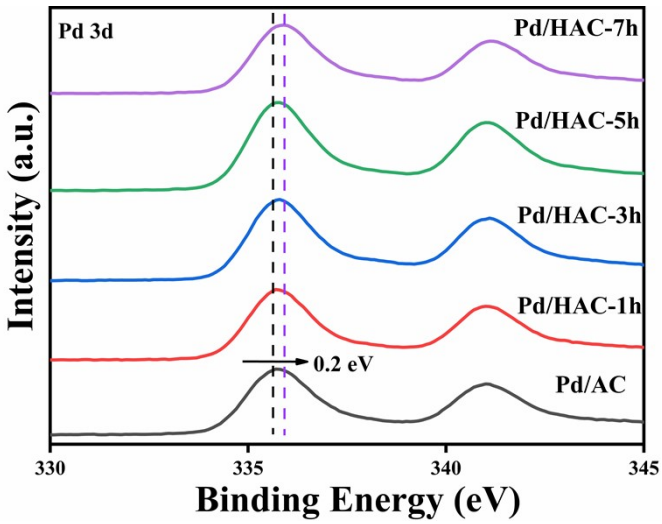

Fig. S2 high resolution spectrum of Pd 3d in Pd/AC and Pd/HAC catalyst.

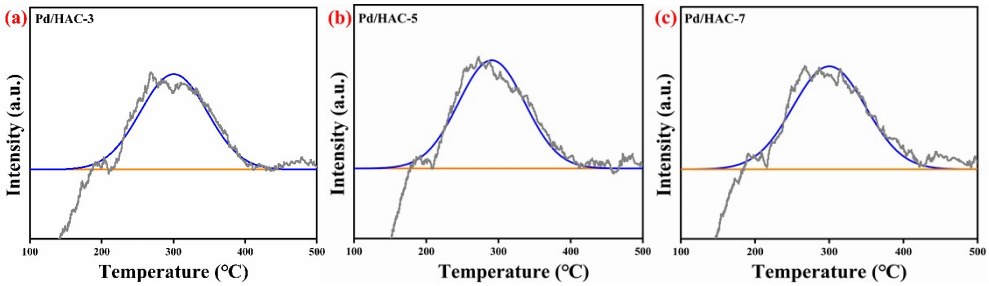

Fig. S3 Peak fitting results of NH_3-TPD in Pd/HAC catalyst.

Fig. S4 Deconvolution of the NH3-TPD profiles of Pd/HAC catalysts.

Simples	Peak Tem. (℃)	Peak area
	Peak I	S I
Pd/HAC-3	300.6	481.25
Pd/HAC-5	300.4	533.54
Pd/HAC-7	300.1	545.89

Fig. S5 The adsorption energy of acetylene adsorption on surface of (003) crystal plane of pure AC and AC modified with different oxygen groups (C=O, C-OH and C-OOH).

System	E(*)	E(C_2H_2)	E(*C_2H_2)	ΔEads
AC	-336.528	-22.9481	-359.554	-0.0779
HAC(C=O)	-338.658	-22.9481	-361.84	-0.2339
HAC(C-OH)	-343.014	-22.9481	-366.177	-0.2149
HAC(C-COOH)	-358.218	-22.9481	-382.24	-1.0739