

Supplementary Information

Semi-hydrogenation of Alkynes to Alkenes over Pd Nanoparticles Embedded in Mo₂C Prepared from High- Temperature Pulse

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EXPERIMENTAL SECTION

Catalyst preparation

$\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ (AR), $\beta\text{-Mo}_2\text{C}$ (99%), $\gamma\text{-Al}_2\text{O}_3$ (99%), commercial Pd/C catalyst (5.5 wt% Pd, designated as Pd/C-commercial), 3-butyn-1-ol (AR), 3-buten-1-ol (AR), 3-butyn-2-ol (AR), 3-buten-2-ol (AR), but-2-yne-1,4-diol (AR), but-2-ene-1,4-diol (AR), 2-methylbut-3-yn-2-ol (AR), 2-methylbut-3-en-2-ol (AR), phenylacetylene (AR), styrene (AR), 4-bromophenylacetylene (AR), and 4-bromostyrene (AR) were purchased from Aladdin chemical Co., Ltd. Activated carbon (AR) and ethanol (AR) were bought from Sinopharm Chemical Co., Ltd. Commercial Pd/ Al_2O_3 catalyst (5 wt% Pd, designated as Pd/ Al_2O_3 -commercial) was purchased from Bidepharm Co., Ltd.

Synthesis of Pd/ Mo_2C -HT and Pd/C-HT catalysts. The synthesis of Pd/C-HT and Pd/ Mo_2C -HT catalysts were treating the $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ -containing Mo_2C -HT or activated carbon through high-temperature pulse method. Typically, Mo_2C -HT or activated carbon was mixed with a desired amount of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ solution and aged at room temperature overnight. H_2O was evaporated by grinding the above mixture at 60 °C. The obtained solid was then treated at 1800 °C (0.4 S × 10 times) in N_2 atmosphere by high-temperature pulse to obtain the Pd/C-HT or Pd/ Mo_2C -HT catalyst. The Pd loading amount in the Pd/C-HT and Pd/ Mo_2C -HT catalysts were determined to be 0.10 wt% and 0.08 wt%.

Synthesis of Mo_2C -HT. Typically, 0.1 g of commercially available $\beta\text{-Mo}_2\text{C}$ powder (Aladdin chemical Co., Ltd, 99%) was put into a high temperature oven (Jilin Padike Precision Instruments Co., Ltd.), followed by purging with N_2 for 3 times to remove the air in the oven. Then, the Mo_2C -HT catalyst was obtained by treating the $\beta\text{-Mo}_2\text{C}$ powder at 1800 °C in N_2 atmosphere by high-temperature pulse (0.4 s/time × 10 times).

Synthesis of Pd/ Al_2O_3 -HT and Pt/ Mo_2C -HT catalysts. The synthesis method of Pd/ Al_2O_3 -HT and Pt/ Mo_2C -HT were the same as that of Pd/ Mo_2C -HT, expect that $\gamma\text{-Al}_2\text{O}_3$ was used as the carrier and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ was used as the precursor.

Catalytic hydrogenation of alkynes. The catalytic hydrogenations of 3-butyn-1-ol, 3-butyn-2-ol, but-2-yne-1,4-diol, 2-methylbut-3-yn-2-ol, phenylacetylene, and 4-

bromophenylacetylene were performed on an autoclave equipped with a magnetic stirrer and a heating jacket. Typically, the reaction substrate was mixed with ethanol and catalyst in the autoclave. The autoclave was purged with 3 MPa of H₂ for 5 times and charged with 1 MPa of H₂. Afterwards, the autoclave was heated in the heating jacket for desired reaction time. The detailed feeding amounts, reaction temperature, and time are as following: 1.75 g of 3-butyn-1-ol, 100 mg of catalyst, 30 g of ethanol, 40 °C, 1 MPa of H₂, and 60 min; 1.75 g of 3-butyn-2-ol, 100 mg of catalyst, 30 g of ethanol, 40 °C, 1 MPa of H₂, and 20 min; 2.00 g of but-2-yne-1,4-diol, 85 mg of catalyst, 30 g of ethanol, 50 °C, 1 MPa of H₂, and 90 min; 2.05 g of 2-methylbut-3-yn-2-ol, 85 mg of catalyst, 30 g of ethanol, 30 °C, 1 MPa of H₂, and 8 min; 10.00 g of phenylacetylene, 200 mg of catalyst, 30 g of ethanol, 50 °C, 3 MPa of H₂, and 22 min; 2.26 g of 4-bromophenylacetylene, 100 mg of catalyst, 30 g of ethanol, 50 °C, 1 MPa of H₂, and 72 min. After reaction, the catalyst was separated by centrifugation and the products were analyzed on a gas chromatography equipped a flame-ionization detector (FID). The alkyne conversion and alkene selectivity are calculated as following:

$$\text{alkyne conversion} = \frac{n_{\text{alkyne,converted}}}{n_{\text{alkyne},0}} \times 100\% \quad (1)$$

$$\text{alkene yield} = \frac{n_{\text{alkene,produced}}}{n_{\text{alkyne},0}} \times 100\% \quad (2)$$

$$\text{alkene selectivity} = \frac{n_{\text{alkene,produced}}}{n_{\text{alkyne,converted}}} \times 100\% \quad (3)$$

where $n_{\text{alkyne},0}$, $n_{\text{alkyne,converted}}$, and $n_{\text{alkene,produced}}$ stand for the feeding alkyne, the converted alkyne, and the produced alkene during the reaction. To test the activity of catalyst, we measured turnover frequency (TOF) values at low conversion (<10 %) based on the equation in the following:

$$\text{Turnover frequency (TOF}_i\text{)} = \frac{n_{\text{alkyne,converted}}}{n_{\text{Pd}} \times \text{reaction time}} \quad (4)$$

Catalytic hydrogenation of acetylene was performed on a fixed bed reactor with an inner diameter of 10 mm. Typically, 300 mg of catalyst (40-60 mesh) was diluted with the same volume of quartz. The catalysts were pretreated at 200 °C in flowing H₂ (30 mL/min) before tests and cooled to the reaction temperature. Then, the reaction gas with a composition of 1% C₂H₂ / 20% C₂H₄ / 20% H₂ / 59% N₂ (60 mL/min) was

introduced on the catalyst to start the reaction. The productive gas was on-line analyzed by the gas chromatography. The acetylene conversion and the ethylene selectivity were calculated as following:

$$\text{acetylene conversion} = \frac{[\text{C}_2\text{H}_2]_{\text{inlet}} - [\text{C}_2\text{H}_2]_{\text{outlet}}}{[\text{C}_2\text{H}_2]_{\text{inlet}}} \times 100\% \quad (5)$$

$$\text{ethylene selectivity} = \frac{[\text{C}_2\text{H}_2]_{\text{inlet}} - [\text{C}_2\text{H}_2]_{\text{outlet}} - [\text{C}_2\text{H}_6]_{\text{outlet}}}{[\text{C}_2\text{H}_2]_{\text{inlet}} - [\text{C}_2\text{H}_2]_{\text{outlet}}} \times 100\% \quad (6)$$

The hydrogenation of nitrobenzene and 1-nitronaphthalene were performed on an autoclave equipped with a magnetic stirrer and a heating jacket. Typically, 1.3 mmol of the reaction substrate was mixed with 7.5 g of ethanol and 13 mg of catalyst within the autoclave. The autoclave was purged with 3 MPa of H₂ for 5 times and charged with 1 MPa of H₂. Afterwards, the autoclave was heated to 50 °C and maintained at this temperature for desired reaction time. After the reaction, the catalyst was separated by centrifugation and the products were analyzed on a gas chromatography equipped a flame-ionization detector (FID). The average reaction rates values were calculated as follows:

$$\text{Average reaction rates} = \frac{n_{\text{reactant, converted}}}{n_{\text{pd}} \times \text{reaction time}} \quad (7)$$

Catalyst Characterization

X-Ray Diffraction (XRD) patterns were obtained using a Rigaku XRD-6000 diffractometer with Cu K_α radiation source ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV and 30 mA. Transmission electron microscopy (TEM) images, scanning transmission electron microscopy (STEM) images, and element energy-dispersive spectroscopy (EDS) mappings were acquired using a JEOL JEM-3100F electron microscope with an acceleration voltage of 300 kV. Raman spectra were collected on a HORIBA JobinYvon spectrometer from 500 to 2500 nm. CO chemisorption and temperature-programmed desorption of H₂, acetylene, or ethylene (H₂, C₂H₂, C₂H₄-TPD) experiments were measured with a Micromeritics Chemi-Sorb 2920 instrument equipped with a thermal conductivity detector (TCD). For CO chemisorption, 100 mg of catalyst (40-60 mesh) was placed in a quartz tube, pretreated in flowing He (25 mL min⁻¹) at 400 °C for 30

min. After cooled to 50 °C, 10% CO/Ar was pulse introduced on the catalysts until saturation adsorption. The Pd dispersion was calculated by CO adsorbed amount/Pd loading amount. Temperature programmed desorption (TPD) experiments were performed under the same pretreatment conditions, after cooled to 30 °C, H₂, C₂H₂, or C₂H₄ was introduced on the catalyst. After adsorbing for 1 h, the physisorbed H₂, C₂H₂, or C₂H₄ was swept by flowing Ar for 1 h. Then the catalyst was temperature-programmed-heated (10 °C/min) to 500 °C. X-ray photoelectron spectroscopy (XPS) was recorded by a Quantum 2000 Scanning ESCA Microprobe. Fourier transform-infrared spectroscopy (FT-IR) spectra were recorded on a VERTEX 70 BRUKER spectrometer equipped with a *in situ* cell and a MCT detector. Prior to testing, all samples were subjected to vacuum-treated at 200 °C for 1 h.

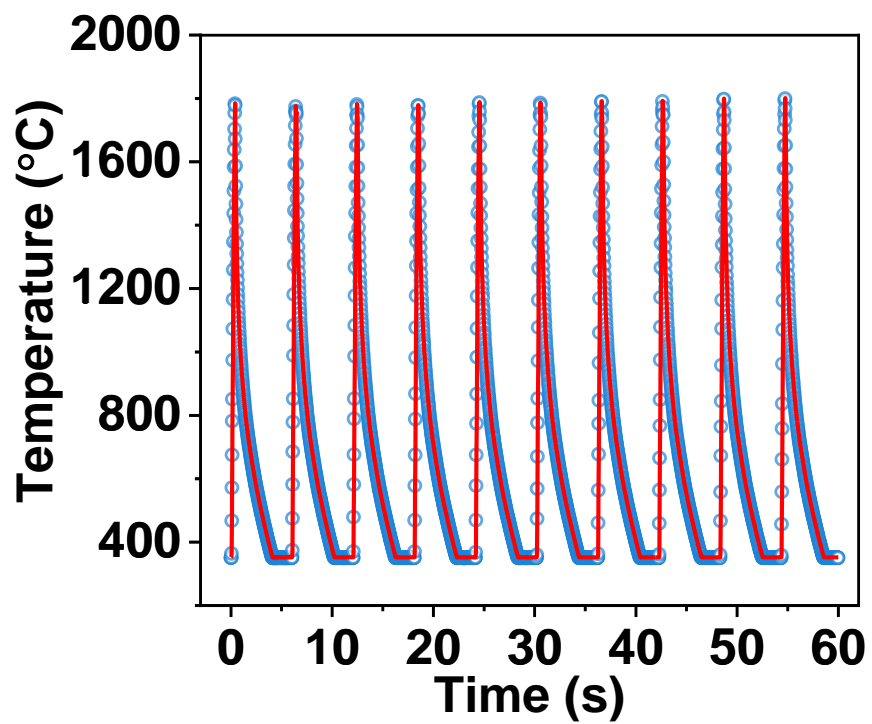


Fig. S1 Temperature as a function of time during the high-temperature pulse.

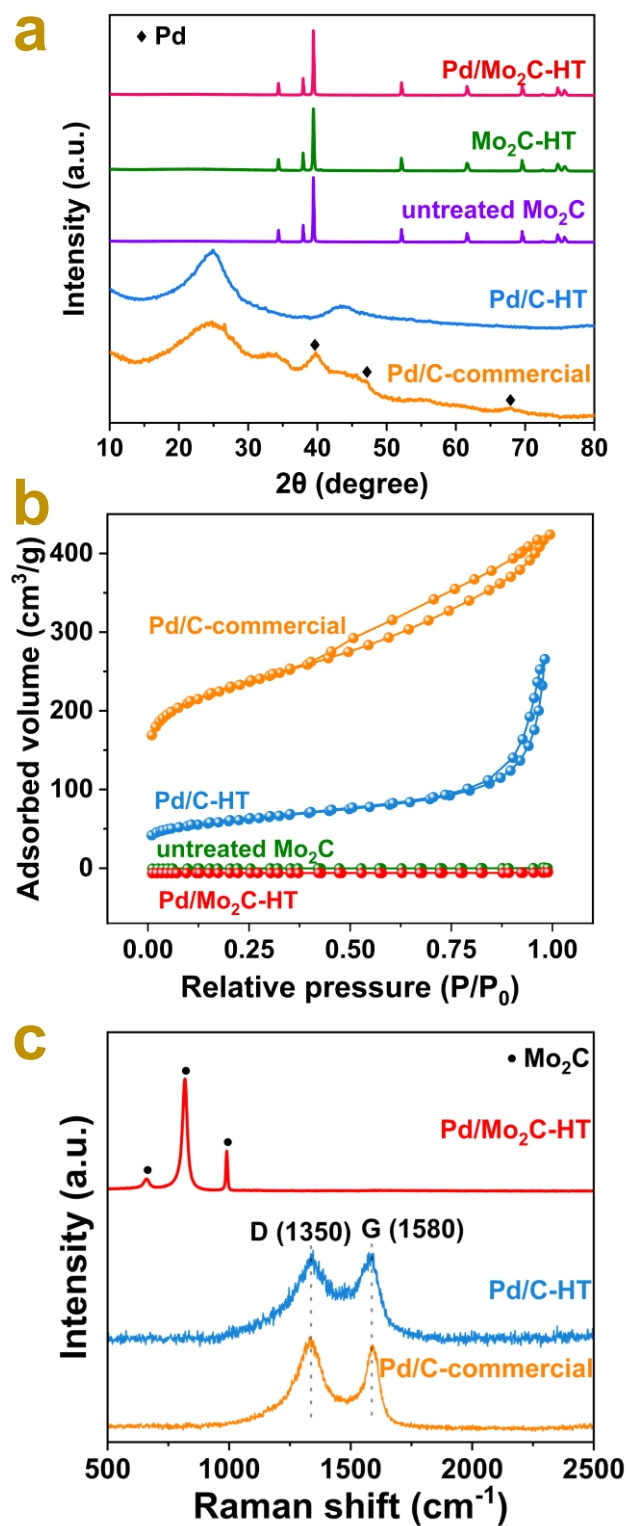


Fig. S2 (a) XRD patterns of the Pd/Mo₂C-HT, Mo₂C-HT, Pd/C-HT, and Pd/C-commercial samples; (b) N₂-sorption isotherms of the untreated Mo₂C, Pd/Mo₂C-HT, Pd/C-commercial, and Pd/C-HT samples; (c) Raman spectra of the Pd/Mo₂C-HT, Pd/C-HT, and Pd/C-commercial catalysts.

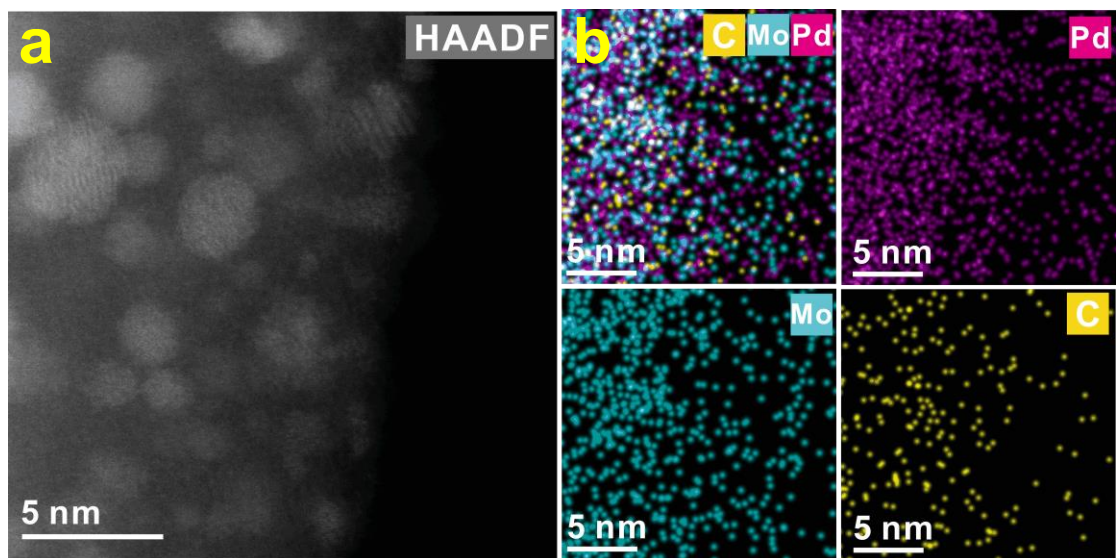


Fig. S3 (a) HAADF-STEM image and (b) corresponding elemental mapping of the Pd/Mo₂C-HT sample.

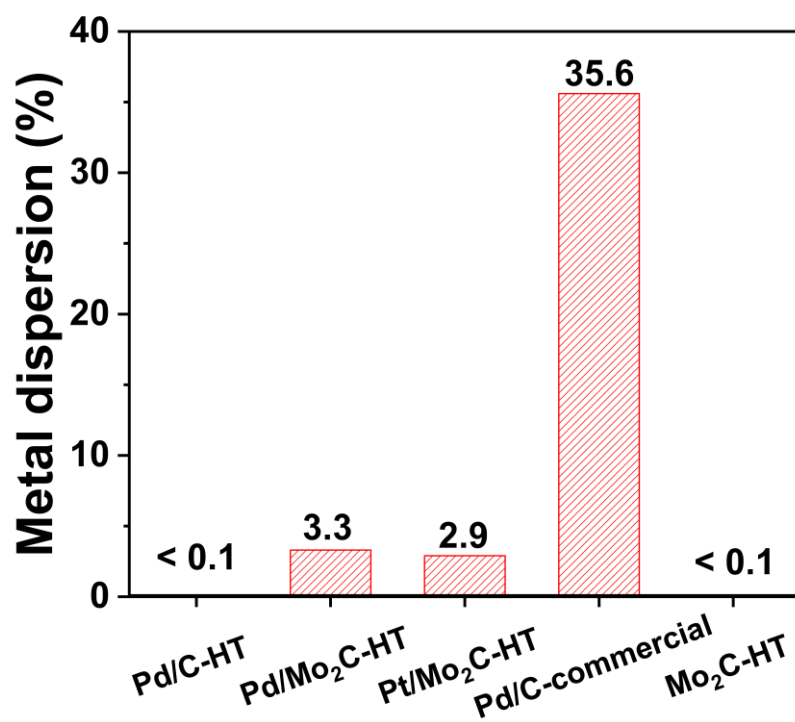


Fig. S4 Pd dispersion values of the Pd/C-HT, Pd/C-commercial, Pd/Mo₂C-HT, Pt/Mo₂C-HT, and Mo₂C-HT samples.

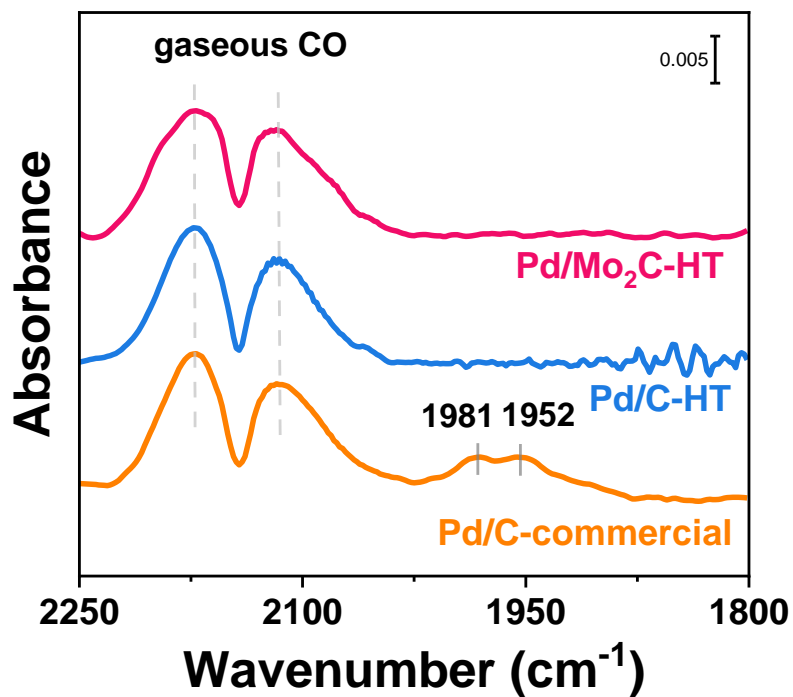


Fig. S5 In situ CO-adsorption FT-IR spectra of Pd/Mo₂C-HT, Pd/C-HT and Pd/C-commercial. Pretreatment conditions of catalysts: N₂, 200 mL/min, 200 °C, 1 h; CO adsorption conditions: 0.5% CO/N₂, 100 mL/min, 30 °C.

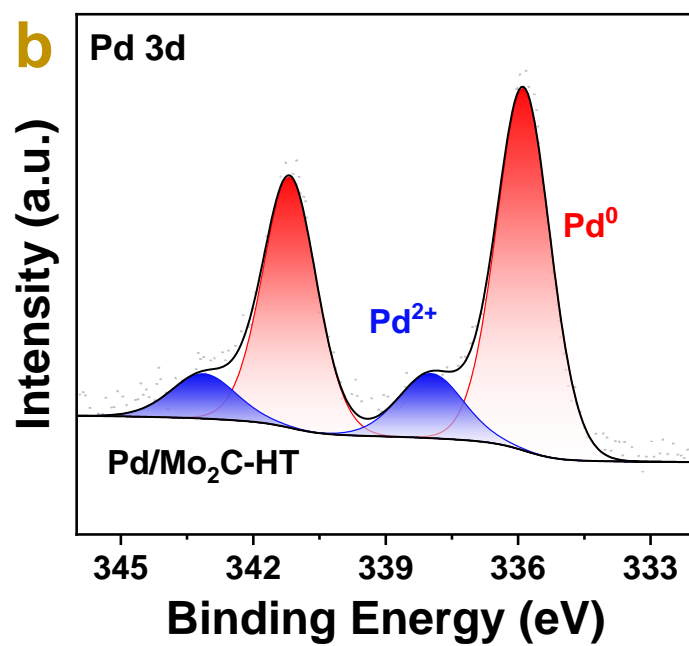
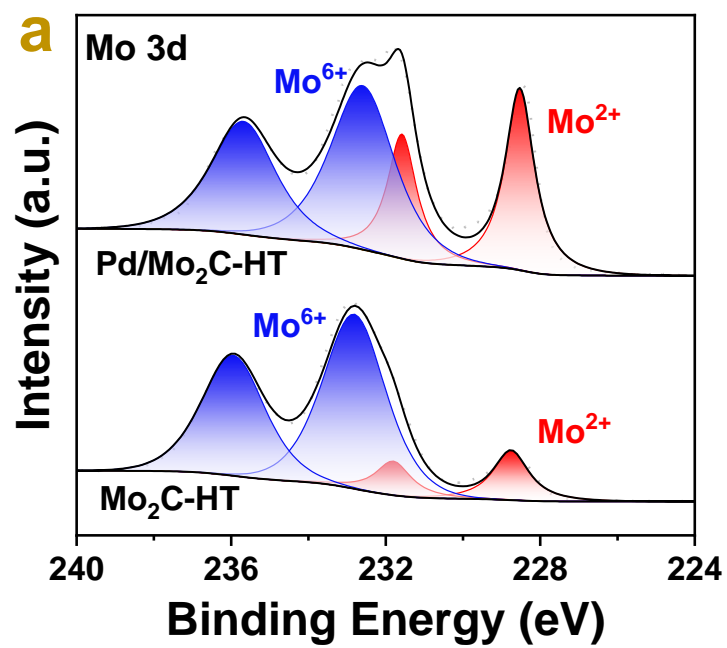


Fig. S6 (a) Mo3d XPS spectra of the Pd/Mo₂C-HT and Mo₂C-HT samples; (b) Pd3d XPS spectrum of the Pd/Mo₂C-HT samples.

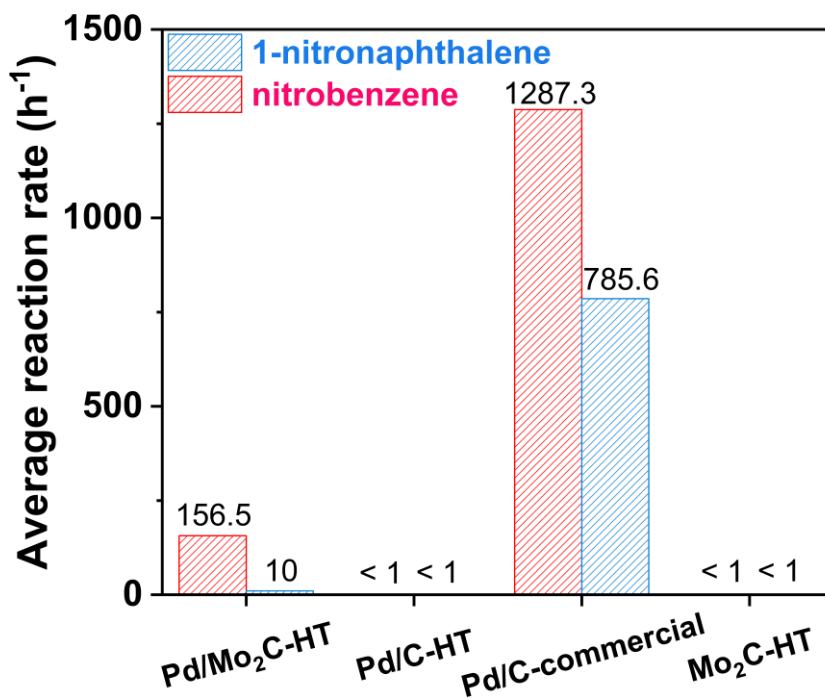
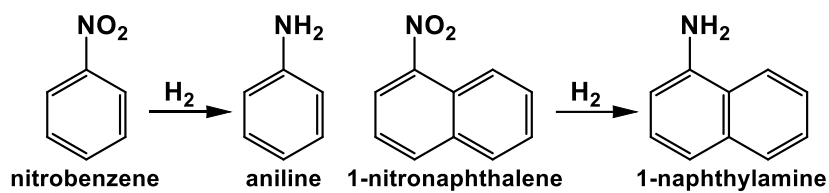


Fig. S7 Reaction rates in the hydrogenation of nitrobenzene and 1-nitronaphthalene over the Pd/C-HT, Pd/C-commercial, Pd/Mo₂C-HT, and Mo₂C-HT catalysts. Reaction conditions: 1.3 mmol of nitrobenzene or 1-nitronaphthalene, 13 mg of catalyst, 7.5 g of ethanol, 1 MPa of H₂, and 50 °C, 1 h.

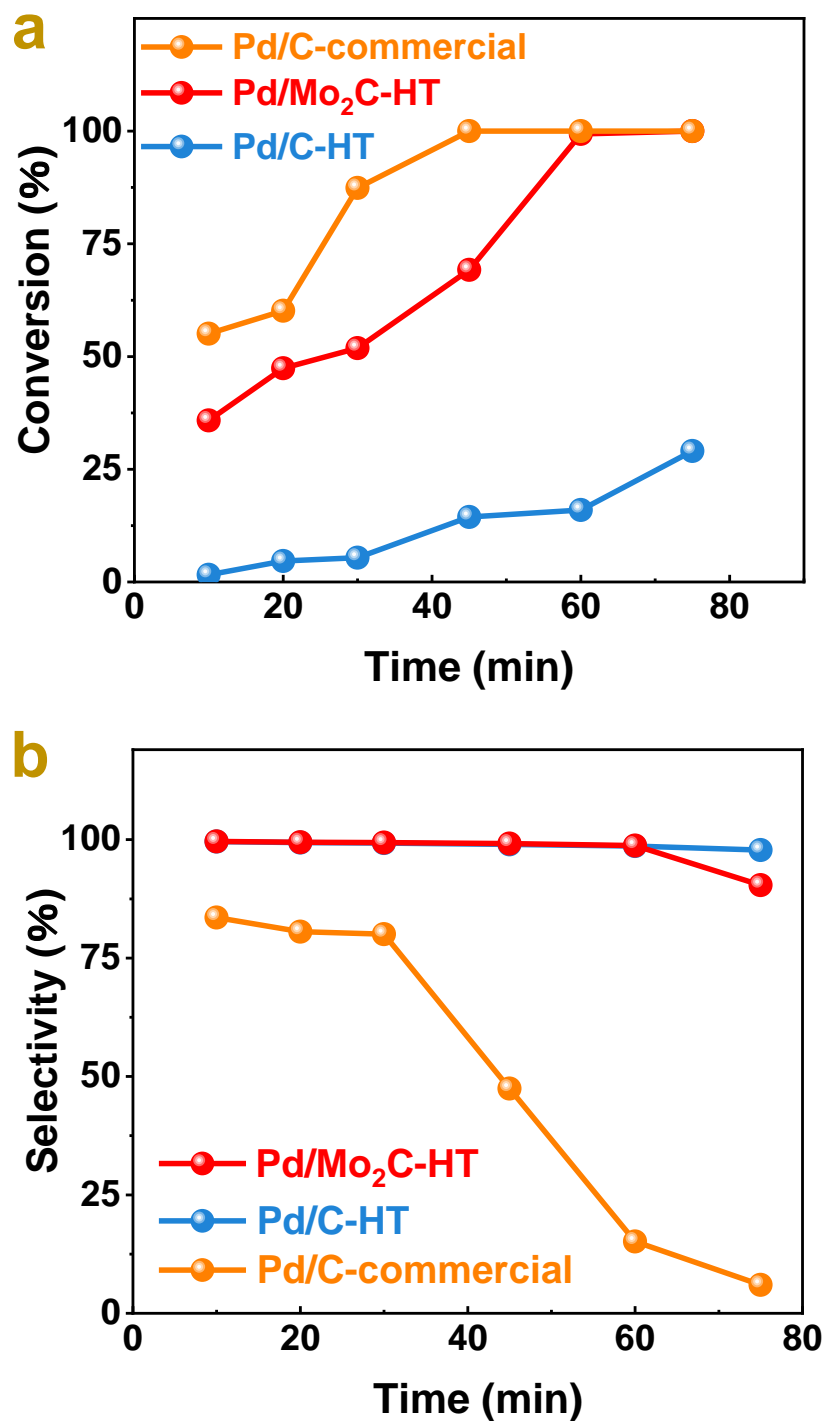


Fig. S8 (a) 3-Butyn-1-ol conversion and (b) selectivity to 3-buten-1-ol as a function of reaction time in the hydrogenation of 3-butyn-1-ol to 3-buten-1-ol over the Pd/C-HT, Pd/C-commercial, Pd/Mo₂C-HT catalysts. Reaction conditions: 1.75 g of 3-butyn-1-ol, 100 mg of catalyst, 30 g of ethanol, 40 °C, 1 MPa of H₂.

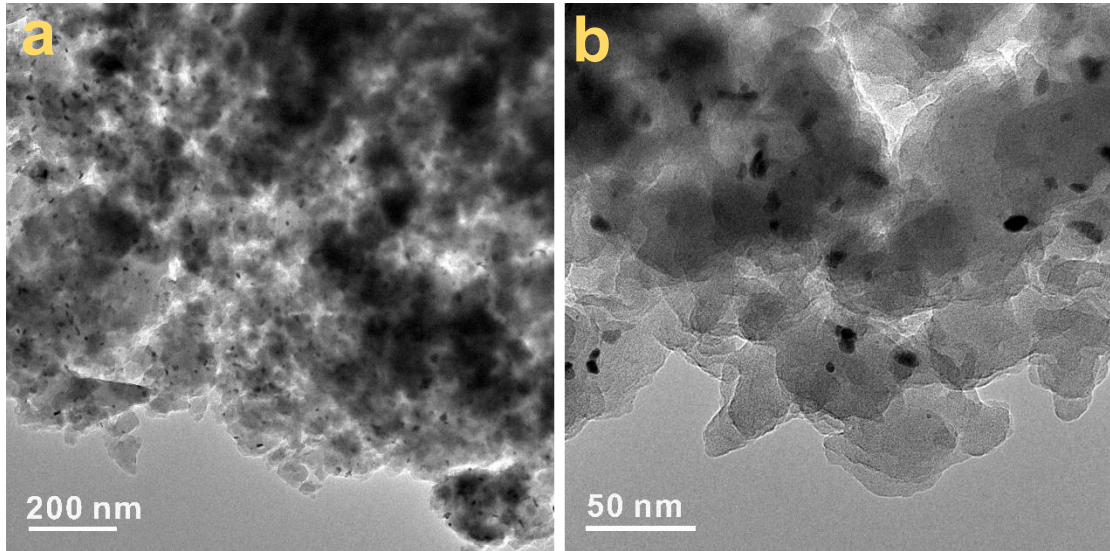


Fig. S9 (a and b) TEM images of the Pd/Al₂O₃-commercial sample.

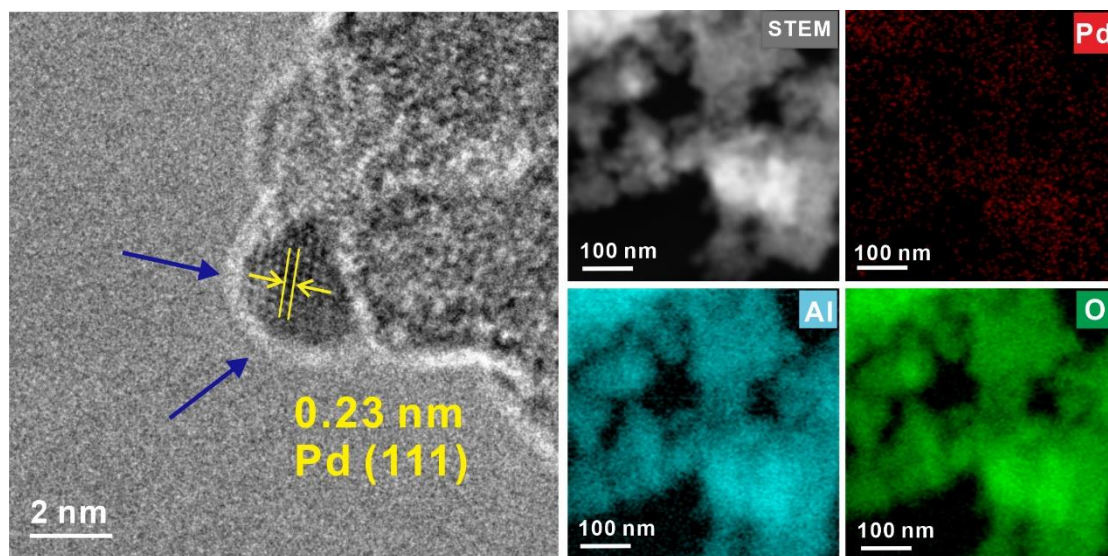


Fig. S10 (a) TEM image, (b) STEM image, and corresponding elemental mapping of the Pd/Al₂O₃-HT sample.

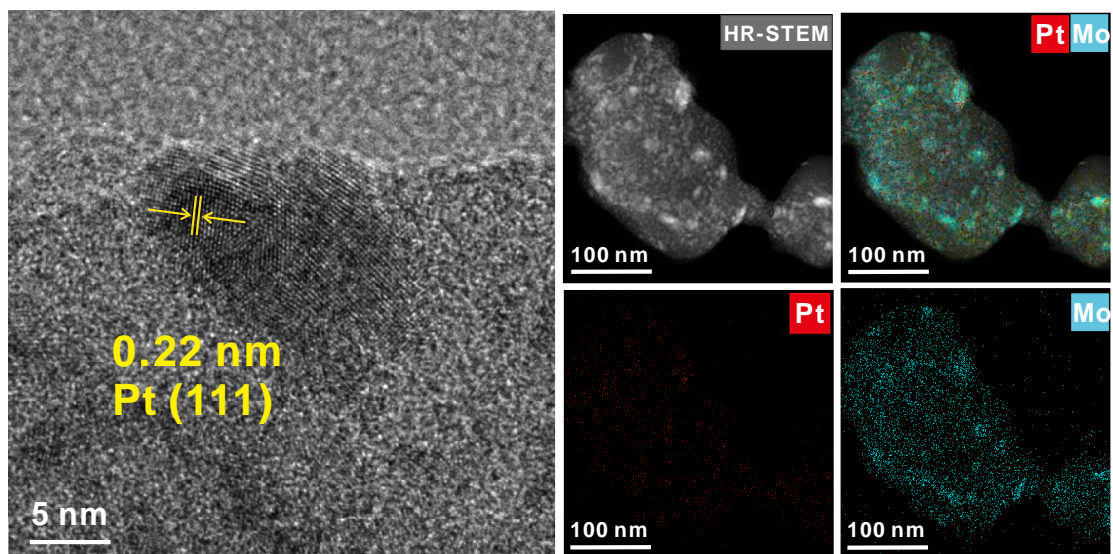


Fig. S11 (a) TEM image, (b) HR-STEM image and the corresponding elemental mapping of the Pt/Mo₂C-HT sample.

Note: We have also synthesized Mo₂C supported Pt catalyst (designated as Pt/Mo₂C-HT) through the high-temperature pulse method (Fig. S11), which also possessed comparable embedded Pt nanoparticle (Fig. S4) and charge transfer from Mo₂C to Pt as the Pd/Mo₂C-HT catalyst (Fig. S12).

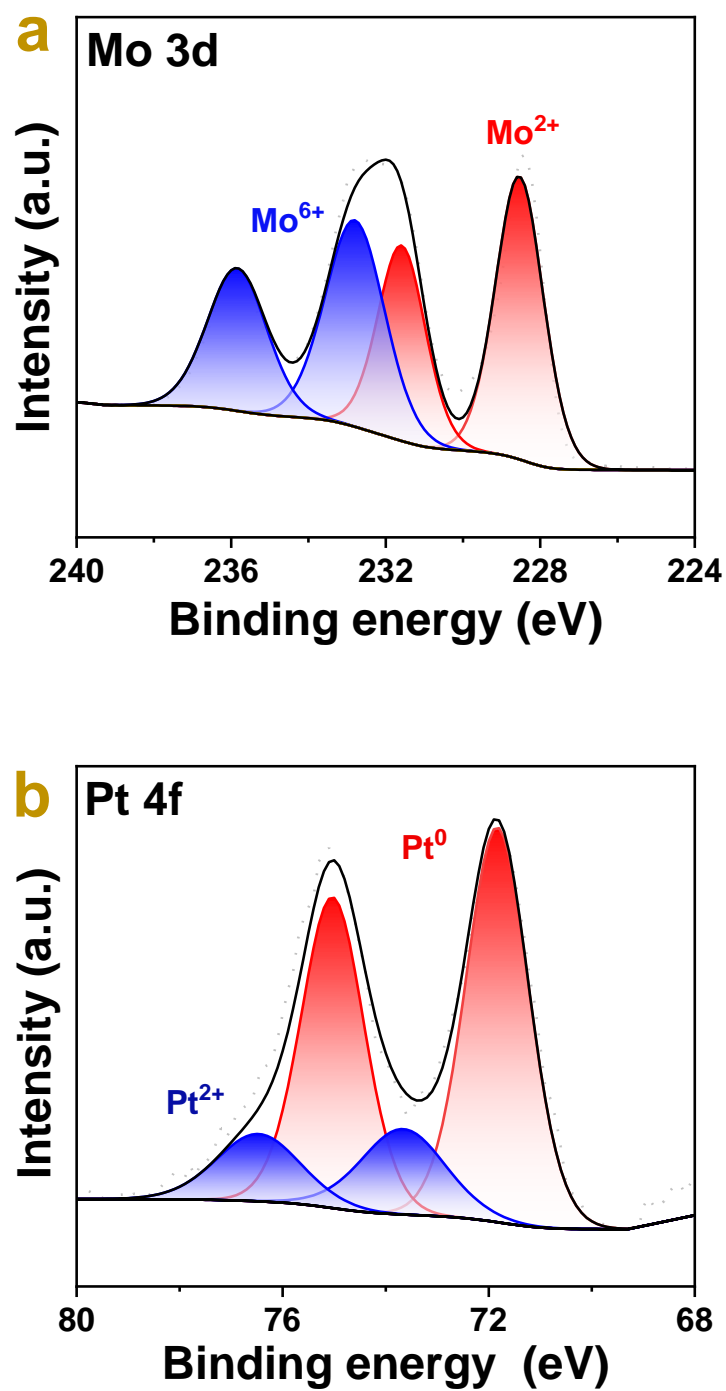


Fig. S12 (a) Mo3d and (b) Pt4f XPS spectrum of the Pt/Mo₂C-HT samples.

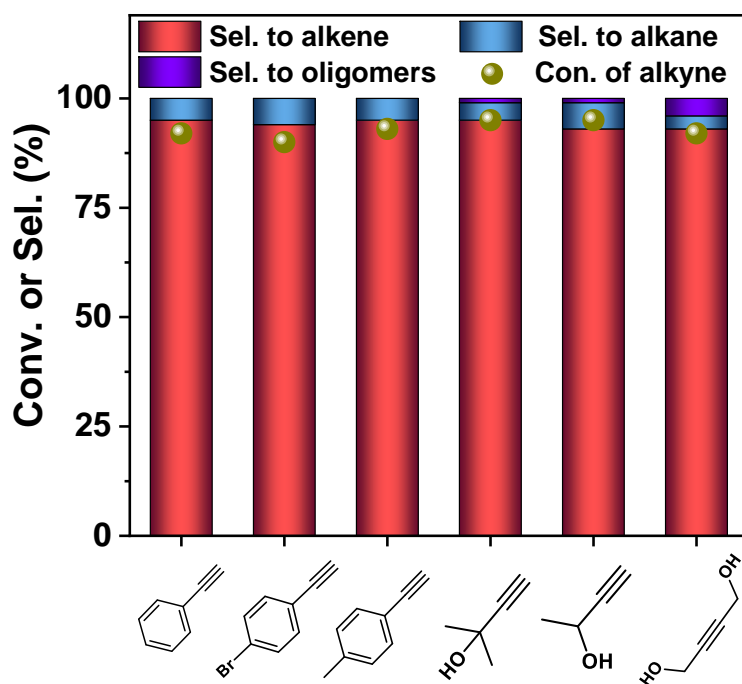


Fig. S13 Alkyne conversions and selectivities to the corresponding alkenes over the Pd/Al₂O₃-HT catalyst in the semi-hydrogenation of phenylacetylene, 4-bromophenylacetylene, 4-methylphenylacetylene, 2-methylbut-3-yn-2-ol, 3-butyn-2-ol, and but-2-yne-1,4-diol. Reaction conditions: 1.22 g of phenylacetylene, 24.8 mg of catalyst, 30 g of ethanol, 25 °C, 1 MPa of H₂, and 22 min; 1.03 g of 4-bromophenylacetylene, 51.3 mg of catalyst, 30 g of ethanol, 25 °C, 1 MPa of H₂, and 45 min; 1.41 g of 4-methylphenylacetylene, 27.1 mg of catalyst, 30 g of ethanol, 25 °C, 1 MPa of H₂, and 20 min; 0.86 g of 2-methyl-3-butyn-2-ol, 25.2 mg of catalyst, 30 g of ethanol, 25 °C, 1 MPa of H₂, and 46 min; 0.85 g of 3-butyn-2-ol, 25.0 mg of catalyst, 30 g of ethanol, 25 °C, 1 MPa of H₂, and 36 min, 1.04 g of but-2-yne-1,4-diol, 26.4 mg of catalyst, 30 g of ethanol, 25 °C, 1 MPa H₂, and 59 min.

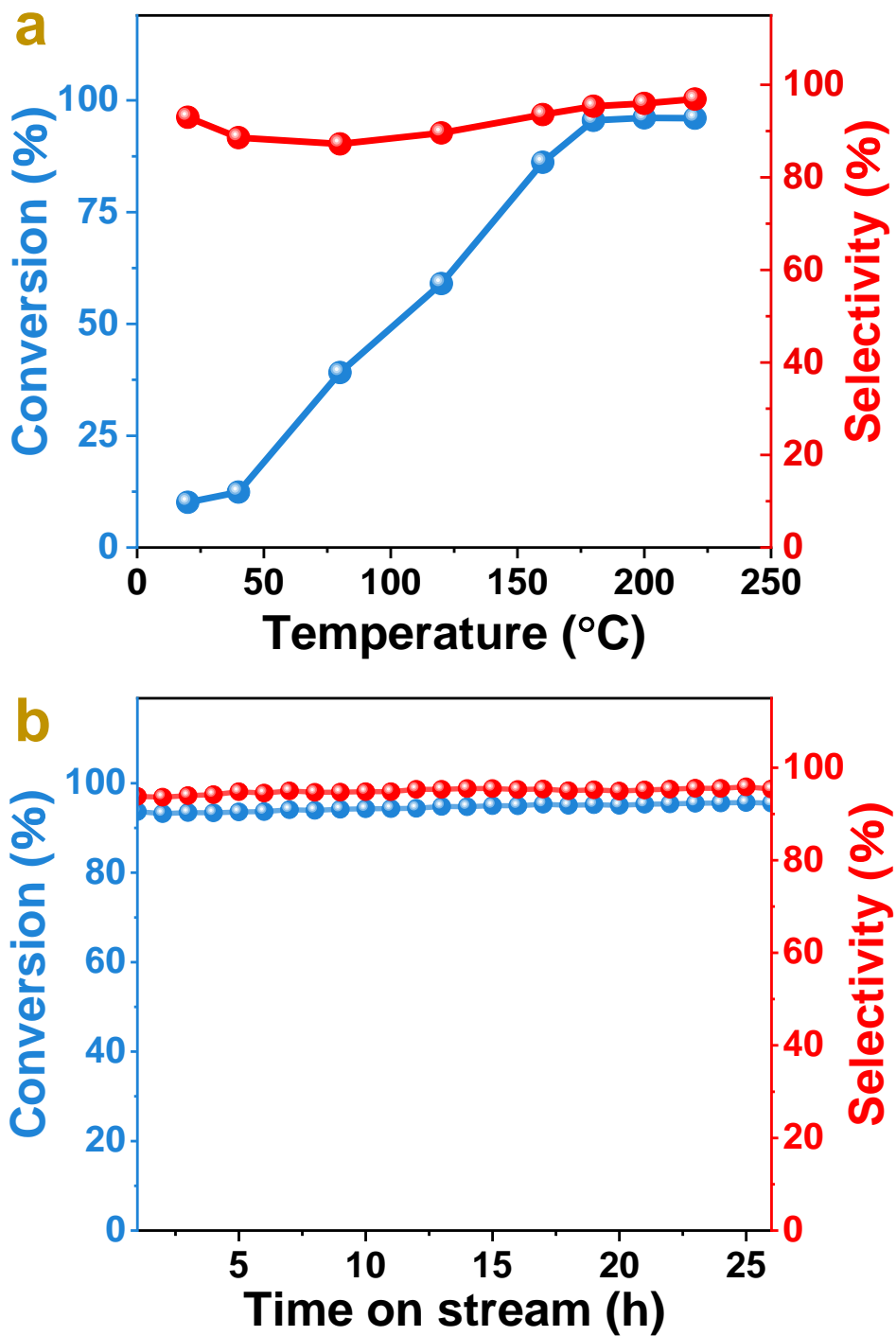


Fig. S14 Acetylene conversion and ethene selectivity as a function of reaction (a) temperature and (b) time in the hydrogenation of acetylene to ethene over the Pd/Mo₂C-HT catalyst. Reaction conditions: 1% C₂H₂ / 20% C₂H₄ / 20% H₂ / 59%N₂, 60 mL/min, 300 mg of catalyst.

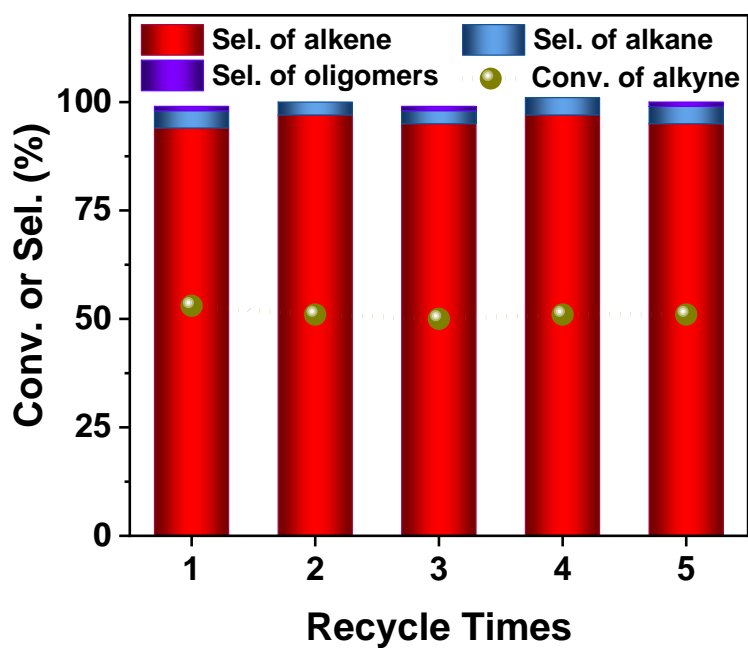


Fig. S15 Catalytic stability of Pd/Al₂O₃-HT in the semi-hydrogenation of 2-methylbut-3-yn-2-ol. Reaction conditions: 5.0 mg of Pd/Al₂O₃-HT, 0.3000 g of MBY, 5 mL of ethanol, 25 °C, 1 MPa of H₂, 10 min.

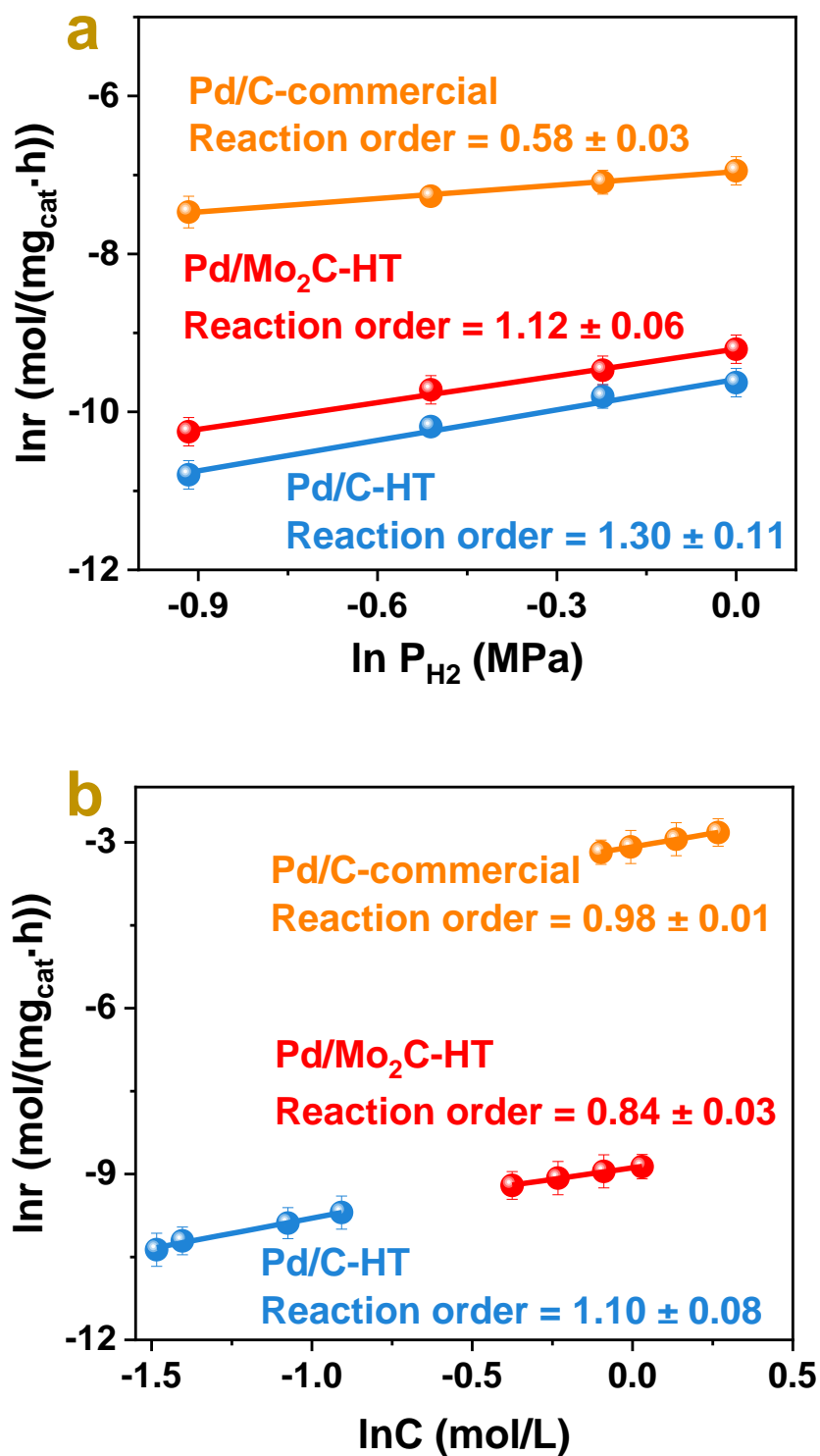


Fig. S16 Data characterizing the reaction order of (a) H₂ and (b) 3-butyne-1-ol in the hydrogenation of 3-butyne-1-ol to 3-buten-1-ol over the Pd/Mo₂C-HT, Pd/C-HT, and Pd/C-commercial catalysts.

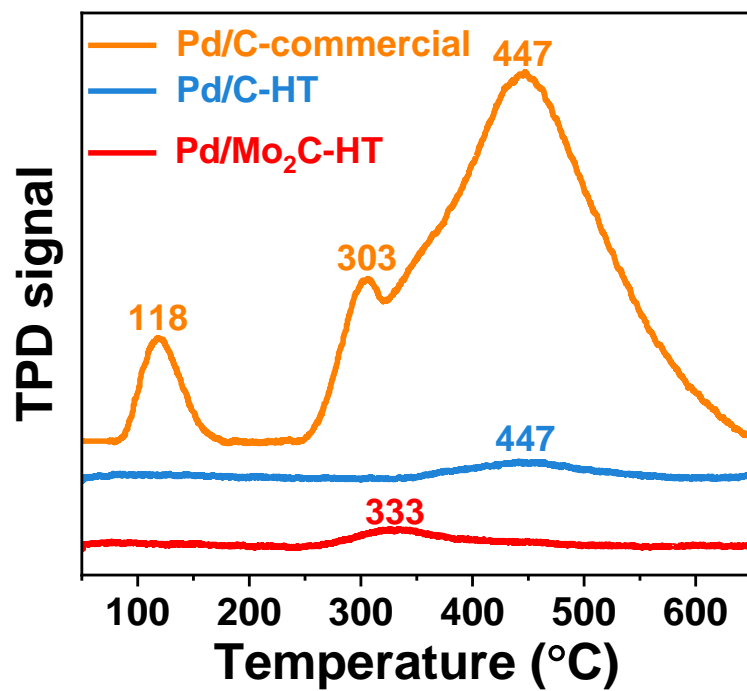


Fig. S17 H₂-TPD profiles of the Pd/Mo₂C-HT, Pd/C-HT, and Pd/C-commercial catalysts.

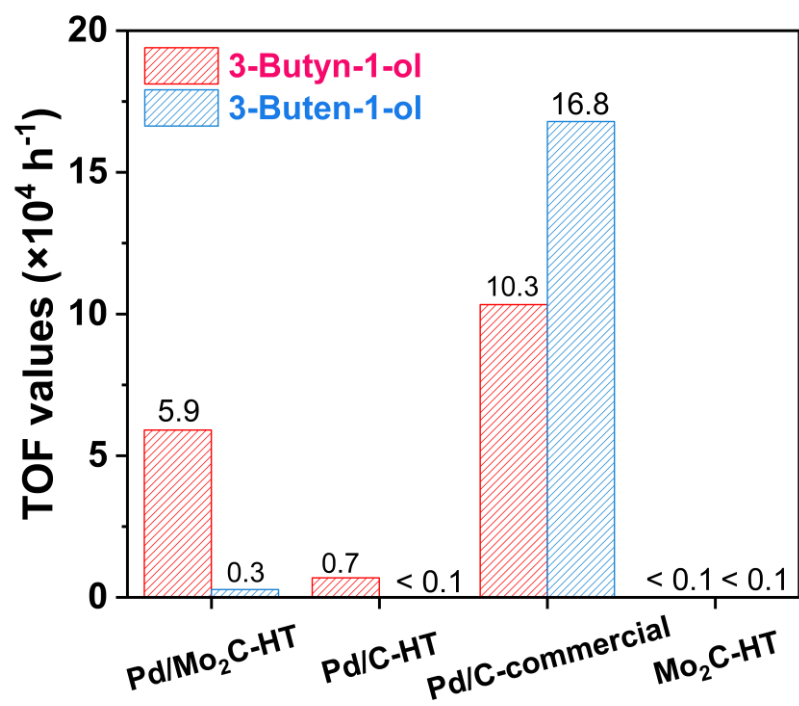


Fig. S18 TOF values in the hydrogenation of 3-butyn-1-ol and 3-buten-1-ol over the Pd/C-HT, Pd/C-commercial, Mo₂C-HT, and Pd/Mo₂C-HT catalysts.

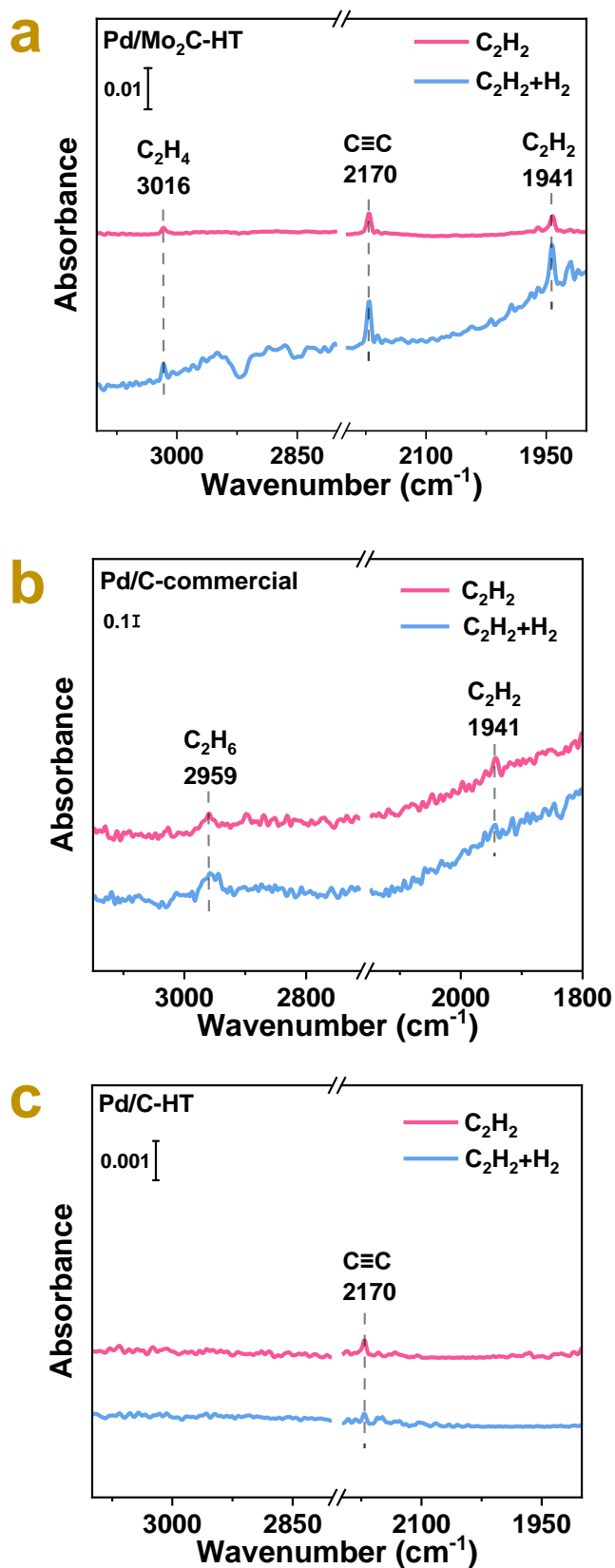


Fig. S19 *In situ* FT-IR spectra during the treatment of the (a) Pd/Mo₂C-HT, (b) Pd/C-commercial, and (c) Pd/C-HT catalysts with C₂H₂ or C₂H₂ + H₂.

Table S1. Textual structure of Pd/C-commercial, Pd/C-HT, Pd/Mo₂C-HT, and Mo₂C samples.

Sample	S_{BET} (m ² /g) ^a	V_{p} (cm ³ /g) ^b
Pd/Mo ₂ C-HT	<5	< 0.1
untreated Mo ₂ C	<5	< 0.1
Pd/C-HT	215.8	0.41
Pd/C-commercial	841.4	0.65

^a Calculated by using the BET method.

^b Single point total pore volume at $P/P_0 = 0.997$.