

Supplementary Materials

Acid-modified Pd-UiO-67 for o-xylene degradation: residual Cl species removal and regulation of Cl-containing byproducts formation

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Supplementary Texts

Supplementary Text 1. Synthesis of acid-modified UiO-67

The acid-modified UiO-67 was synthesized via solvothermal method, using acetic acid as the regulator. Generally, 2.27 mmol $ZrCl_4$, 2.27 mmol 4,4'-Biphenyldicarboxylic acid (BPDC) and 22.7 mmol acetic acid ($ZrCl_4$:BPDC:formic acid molar ratio was 1:1:10) were ultrasonic dissolved in 50 mL DMF. Then, the mixture was continuously ultrasound until dispersed completely. After that, the mixed solution was transferred into a Teflon reactor and crystallized at 120 °C for 24 h. Finally, the obtained white crystal, named U-ace, was centrifuged and washed with DMF and ethanol three times and then dried at 70 °C for 12 h.

Supplementary Text 2. Synthesis of the supported Pd catalysts

The supported Pd catalysts were prepared by a traditional wet-impregnation method. Taking the preparation of U-ace supported Pd catalyst as the example, 1.0 g of the U-ace was placed in a porcelain element dish and 3.13 mL of DMF solution of palladium acetate ($Pd(OAc)_2$, 0.03 mol/L) was added into the porcelain element dish under stirring until uniformly mixed. After that, the mixture was first impregnated at ambient temperature for 12 h and then dried in an oven at 70 °C for another 12 h. Finally, the catalyst named Pd-U-ace could be acquired after reducing under H_2 atmosphere at 200 °C for 2 h with a heating rate of 10 °C/min. Pd-U-ace-SN, Pd-U-ace-SN-F and Pd-U-ace-NH could be prepared using U-ace-SN, U-ace-SN-F and U-ace-NH as the supports, respectively, via the similar processes.

Supplementary Text 3. Characterizations

Physical-chemical properties of the as-prepared catalysts were characterized by many techniques, including X-ray diffraction (XRD), Fourier transform infrared (FT-IR), N_2 adsorption-desorption, UV-vis diffuse reflectance spectra (UV-vis DRS), 1H nuclear magnetic resonance (1H NMR), thermogravimetry (TG), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and TEM mapping, and X-ray photoelectron spectroscopy (XPS). Meanwhile, the degradation intermediates were determined by a thermal desorption-gas

chromatograph-mass spectrometer (TD-GC-MS). The detailed information is list as the follows.

XRD: The XRD patterns of the sample were obtained on a Bruker D8 Advance X-ray diffractometer using Cu K α under the conditions of 40 kV accelerating voltage and 40 mA emission current. The scanning range was 5-80° with a scanning rate of 5°/min.

FT-IR: The FT-IR spectra were collected on a Thermo Fisher Nicolet iS50 infrared spectrometer with a resolution ratio and scanning times of 4 and 64, respectively.

N₂ adsorption-desorption: The N₂ adsorption-desorption curves of the catalysts were determined on a Quantachrome autosorb-iQ-2MP apparatus at -196 °C. Before analysis, the samples were outgassed under a vacuum at 105 °C for 12 h for purification. The Brunauer-Emmett-Teller (BET) model and was utilized to calculate the specific surface area, and the pore size distributions were generated by the Density-functional- theory (DFT) and Barrett-Joyner-Halenda (BJH) method according to the desorption branch of the N₂ adsorption-desorption curve.

UV-vis DRS: UV-vis DRS was performed on a UV-vis spectrometer (UV-2600, Shimadzu, Japan) using BaSO₄ as the internal standard.

¹H NMR: Dissolution/¹H NMR spectra were obtained on an Agilent 600 MHz NMR spectrometer. The sample was pretreated for digestion with the following steps: 1 mg sample and 40 μ L hydrochloric acid were sonicated for 5 min, and 0.7 mL DMSO-d₆ was added to obtain a clear solution. The relative molar ratios ($\frac{\text{Benz.}}{\text{BPDC}} \times m_R$) were used to identify the organic components in all modified UiO-67 samples.

$$\frac{\text{Benz.}}{\text{BPDC}} \times m_R = \left(\frac{\text{Benz. } H_b \text{ Int.}}{N_{\text{HBenz.}}} \times \frac{N_{\text{HBPDC}}}{(\text{BPDC} + \text{Benz. } H_a) \text{ Int.} - \text{Benz. } H_b \text{ Int.}} \right) \quad (1)$$

where Benz. H_a Int. and Benz. H_b Int. are the numerical values of the ¹H NMR integrals that are obtained on the benzoate H_a and H_b signals, respectively, and N_{HBenz.} and N_{HBPDC} are the numbers of equivalent protons that contribute to the ¹H NMR signals of benzoate and H₂BPDC, respectively, per molecule.

TG: The TG curves are obtained on a PerkinElmer STA8000 simultaneous thermal analyzer under the atmosphere of air. Heating rate: 10 °C/min; Temperatures: 30-800 °C. The number of linker defects was calculated by the following formula (2):

$$x = 6 - \frac{W_{\text{Exp.}}}{W_{\text{LTheo.}} + \left(\frac{\text{Benz.}}{\text{BPDC}}\right)^{\text{mR}} \times W_{\text{BTheo.}}} \quad (2)$$

where $W_{\text{Exp.}}$ is the magnitude of the actual weight loss, $W_{\text{Ltheo.}}$ is the theoretical weight loss magnitude per BPDC linker that is lost from the Zr_6 formula unit, and $W_{\text{Btheo.}}$ is the theoretical weight loss magnitude per benzoate ligand that is lost from the Zr_6 formula unit.

TEM, HRTEM and TEM mapping: TEM, HRTEM and TEM mapping were obtained on FEI Talos F200S Super-X-ray energy disperse spectroscopy.

XPS: XPS was performed on THERMO ESCALAB 250XZ. The binding energies were calibrated internally by the carbon deposit C1 s at 284.8 eV.

TD-GC-MS: Typically, the organic gas collection-GC-MS method is used to analyze the organic compounds in the gas phase during the toluene and/or acetone degradation process. The outlet by-products are first collected through the Tenax-TA tube and the captured gas is then released into a thermal desorption (TD) apparatus (TurboMatri 350, PerkinElmer) equipped with a GC-MS analyzer (7890A GC/5975C MS, Agilent). Desorption condition: The Tenax-TA tube was desorbed at 280 °C for 10 min. The desorbed gas is enriched in the collector at 5 °C. Then, the collector is rapidly heated to 300 °C at a rate of 40 °C/min and kept for 6 min. Finally, the gas is introduced to GC-MS for detection. GC-MS testing condition: column box temperature 40 °C, ion source temperature 230 °C, four-stage rod temperature 150 °C. Programming heating: the initial temperature was 40 °C, kept for 5 min, then rose to 180 °C at the rate of 5 °C/min, kept for 5 min.

Supplementary Text 4. Catalytic performance test

Calculation of the o-xylene conversion (X_{ox}) and CO_2 yield (X_{CO_2}): o-Xylene conversion (X_{ox}) and CO_2 yield (X_{CO_2}) were calculated by formulas (3, 4).

$$X_{\text{ox}} = (C_{\text{out}} - C_{\text{in}})/C_{\text{in}} \times 100\% \quad (3)$$

$$X_{\text{CO}_2} = C_{\text{CO}_2}/8C_{\text{in}} \times 100\% \quad (4)$$

where C_{in} and C_{out} were the inlet and outlet o-xylene conversion, respectively. The C_{CO_2} was the outlet CO_2 concentration.

Kinetic Study: For the kinetic study, o-xylene oxidation under excessive oxygen should

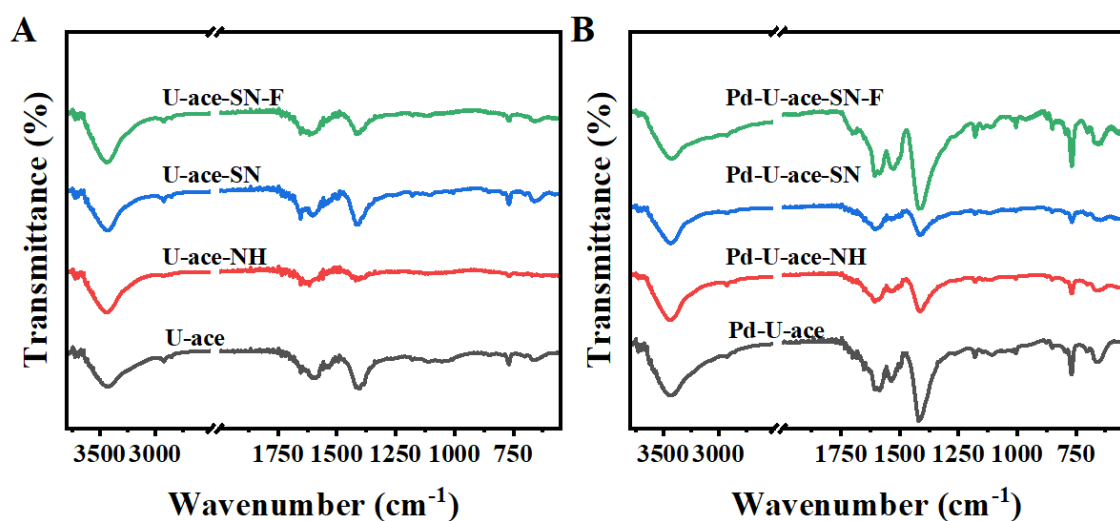
obey a first-order reaction mechanism for the o-xylene molecular, following the equation (5):

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (5)$$

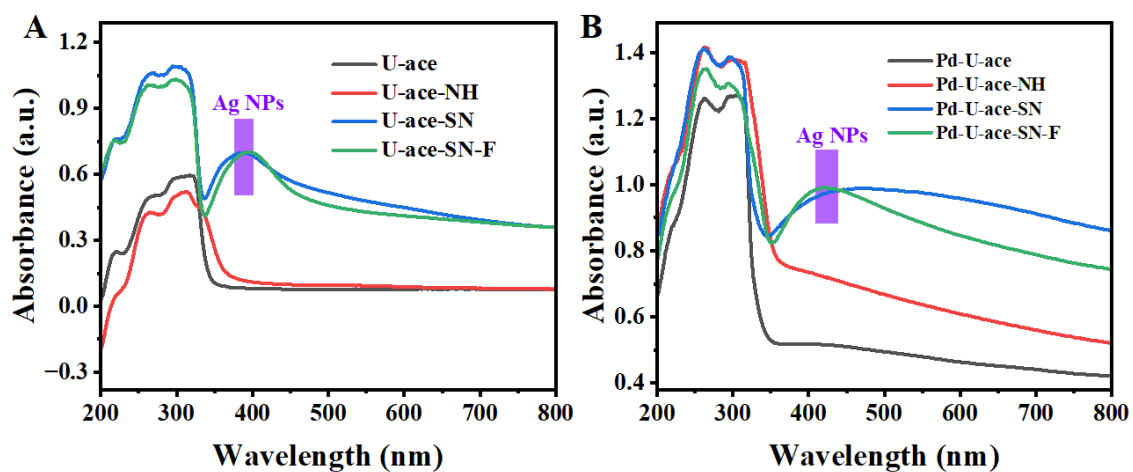
where k, E_a , and A refer to rate constant (s^{-1}), apparent activation energy (kJ/mol), and pre-exponential factor, respectively. R and T represent gas constant (J/(mol·k)) and corresponding temperature (K), respectively. Arrhenius plots derived from the formula (6) are applied to the calculation of E_a at lower conversion (less than 20%).

Water Resistance Test: For the water resistance test, at a certain temperature, the water vapor (5.0 and 10 vol.%) was introduced by an Ar flow.

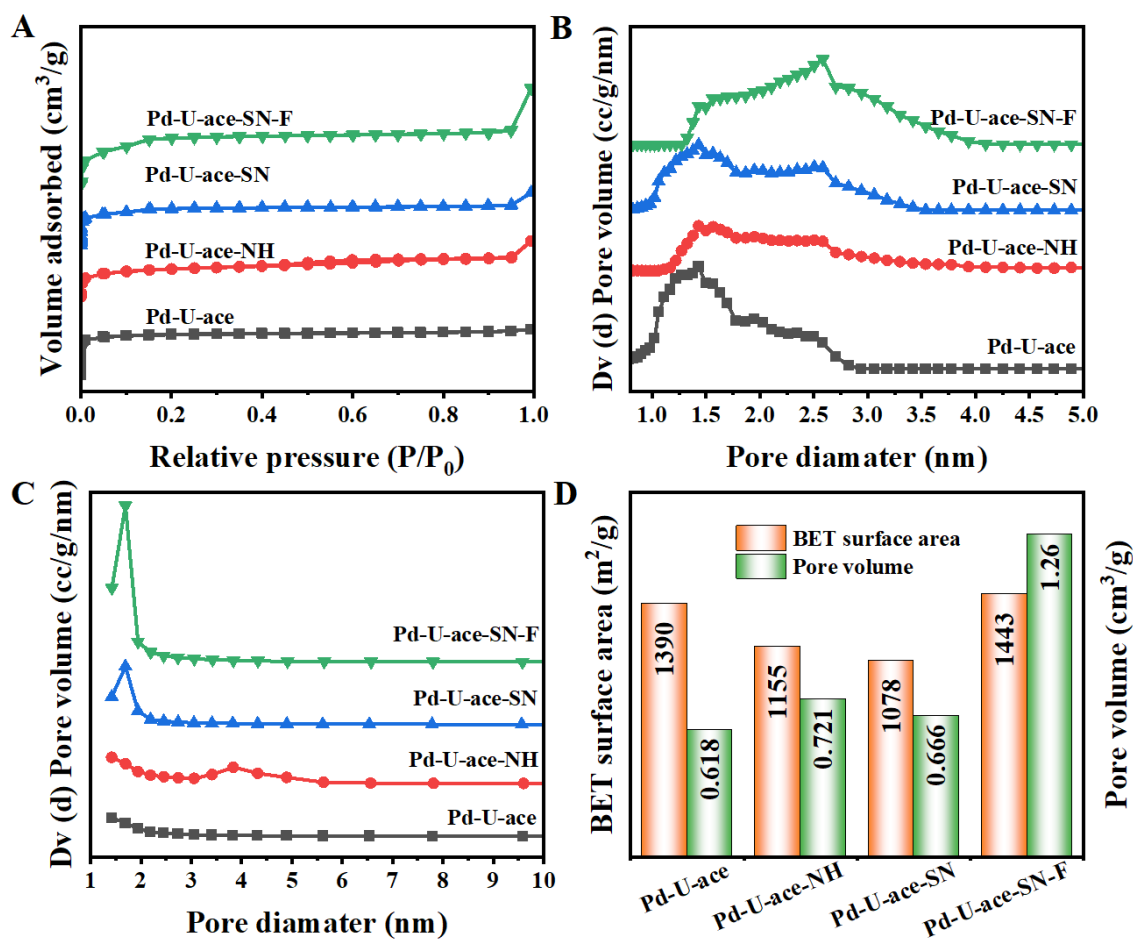
Supplementary Figures



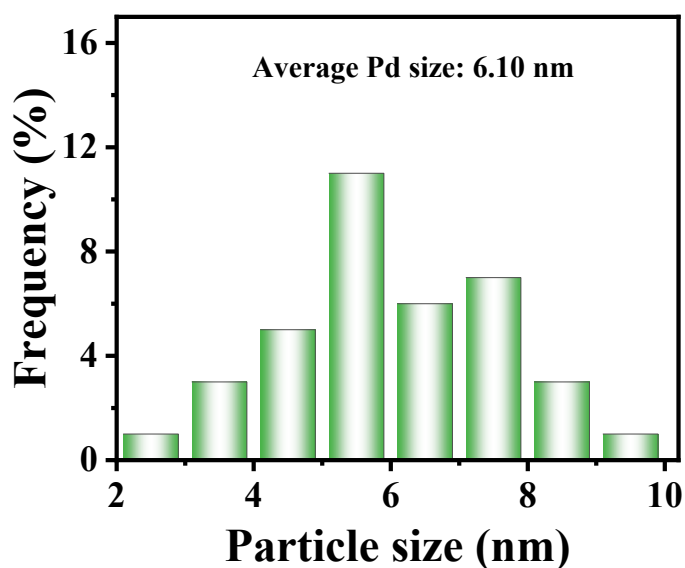
Supplementary Figure 1. The FT-IR spectra of U-ace^[1] and the different conditions pretreated U-ace (A), and the corresponding supported Pd catalysts (B).



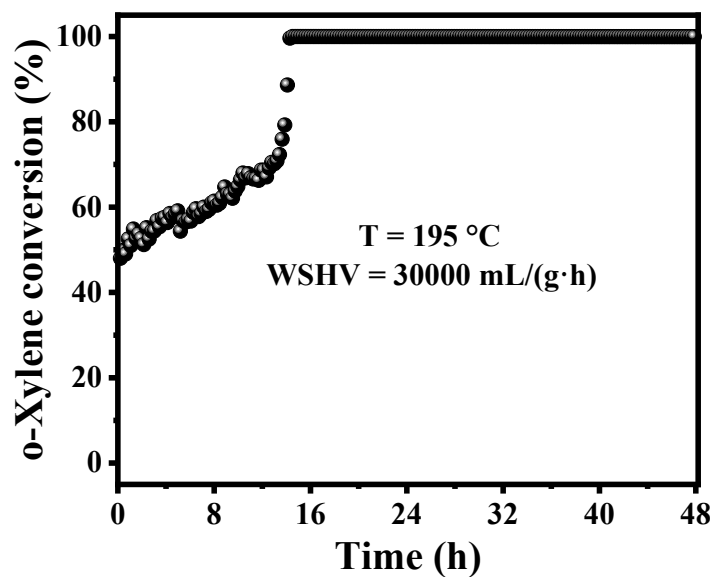
Supplementary Figure 2. The UV-Vis spectra of U-ace^[1] and the different conditions pretreated U-ace (A), and the corresponding supported Pd catalysts (B).



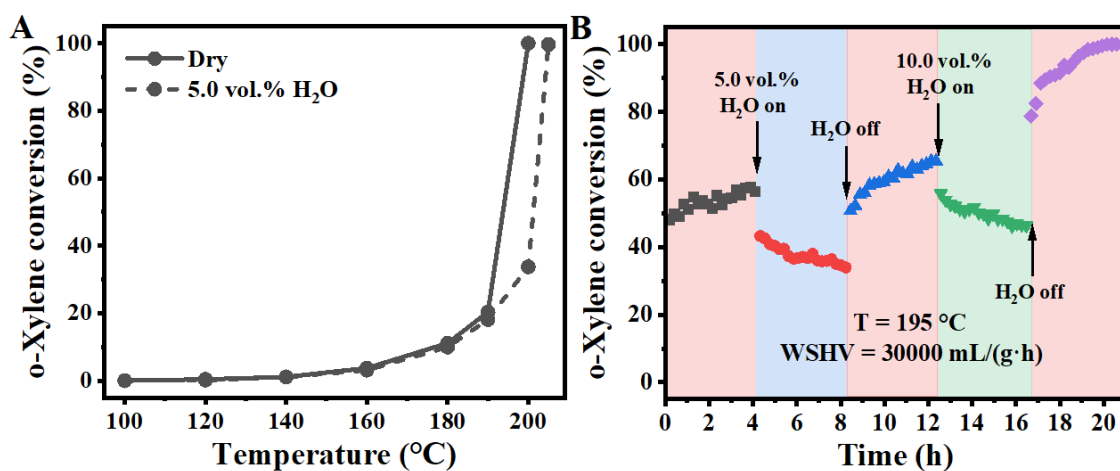
Supplementary Figure 3. N_2 adsorption-desorption curves (a), pore size distributions calculated by DFT (b) and BJH (c) method and the corresponding BET surface area and pore volume (d) of Pd-U-ace^[1], Pd-U-ace-NH, Pd-U-ace-SN and Pd-U-ace-SN-F.



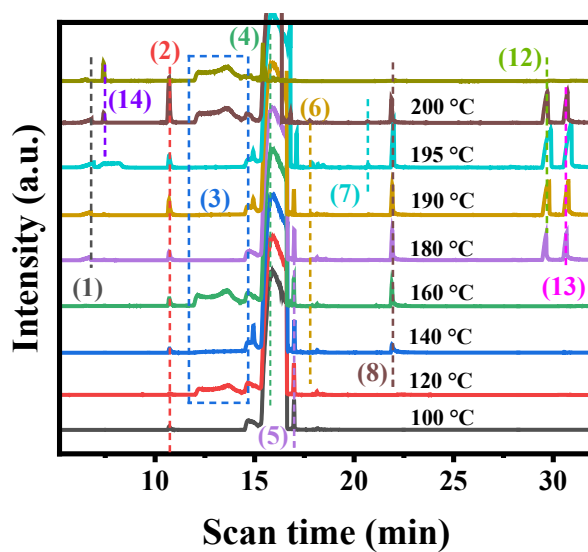
Supplementary Figure 4. Distribution of Pd size in Pd-U-ace-NH.



Supplementary Figure 5. Stability of Pd-U-ace-NH for o-xylene degradation.

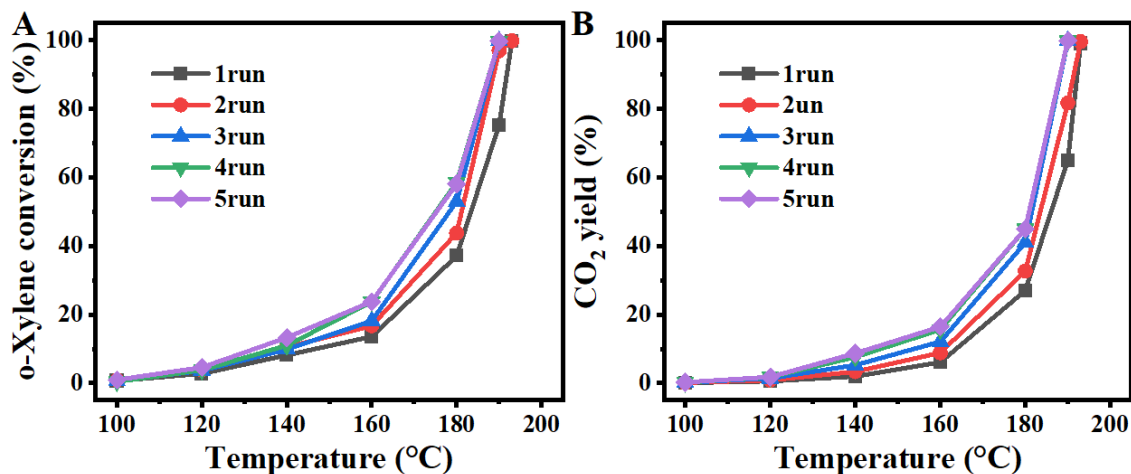


Supplementary Figure 6. The temperature-dependent (A) and time-dependent (B) o-xylene oxidation over Pd-U-ace-NH.

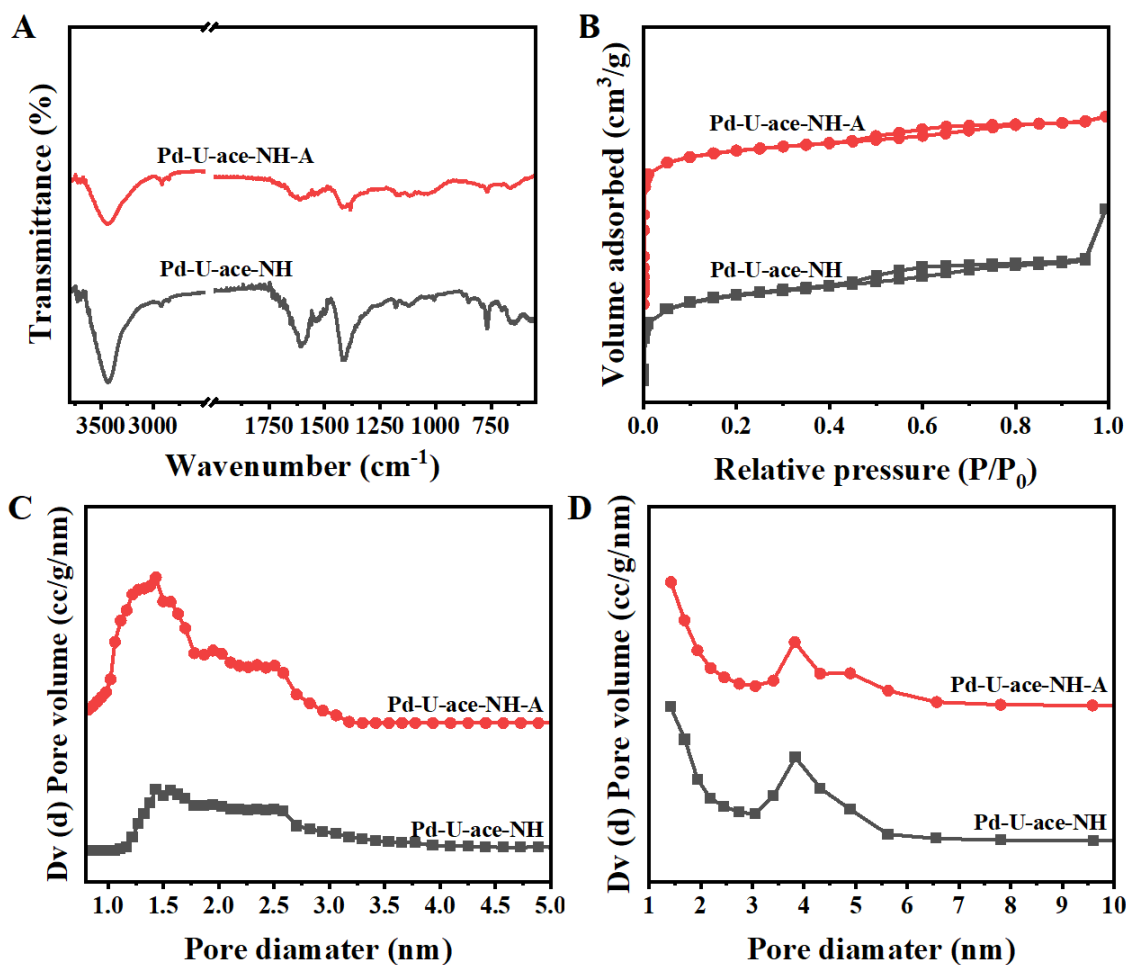


Supplementary Figure 7. TD-GC-MS total ion current chromatograms of

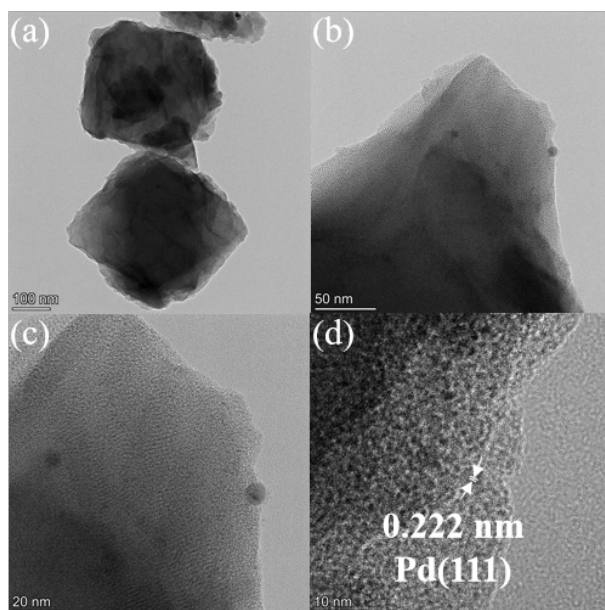
Pd-U-ace-NH for o-xylene degradation in the presence of 5.0 vol.% H₂O (The corresponding products of serial numbers are summarized in **Supplementary Table 3**).



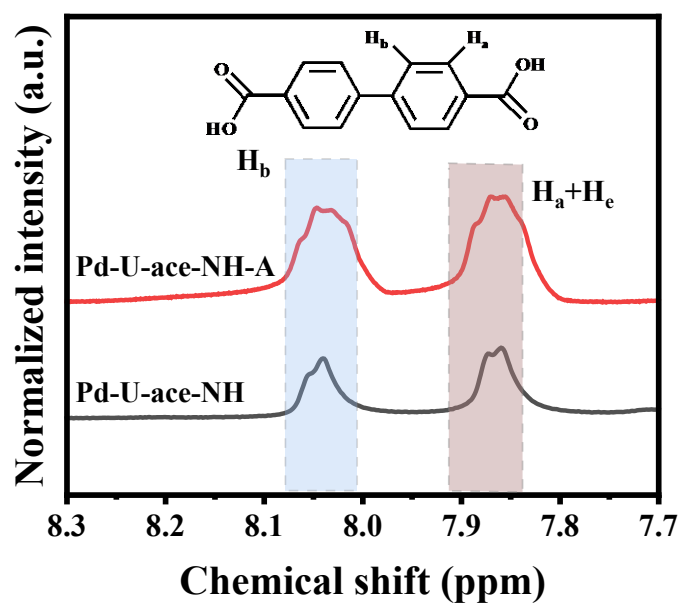
Supplementary Figure 8. Reusability of Pd-U-ace-NH for o-xylene degradation: (A) o-xylene conversion and (B) CO₂ yield.



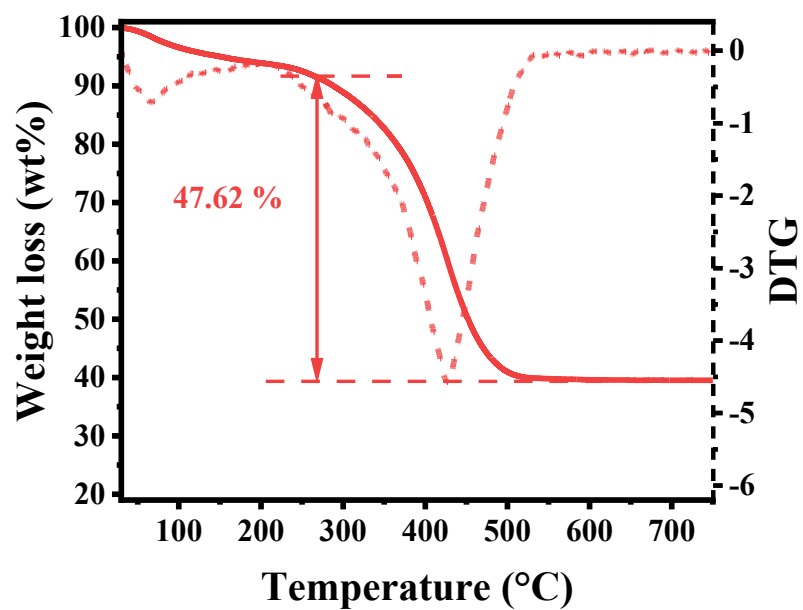
Supplementary Figure 9. FT-IR spectra (A), N₂ adsorption-desorption curves (B), pore size distributions calculated by DFT (C) and BJH (D) methods of Pd-U-ace before and after reaction.



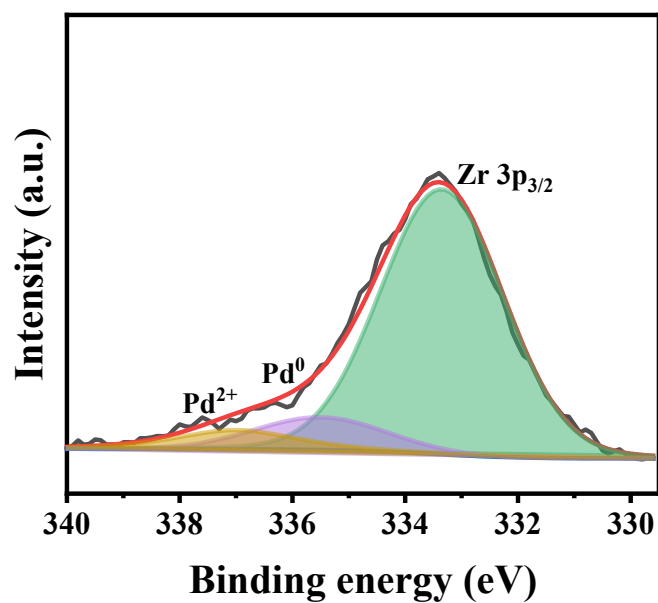
Supplementary Figure 10. TEM (a-c) and HRTEM (d) images of Pd-U-ace-NH after reaction.



Supplementary Figure 11. ^1H NMR patterns of Pd-U-ace-NH before and after reaction.



Supplementary Figure 12. TG and DTG patterns of Pd-U-ace-NH after reaction.



Supplementary Figure 13. Pd 3d XPS spectra of Pd-U-ace-NH after reaction.

Supplementary Tables

Supplementary Table 1. Physicochemical parameters of the supported Pd catalysts.














Samples	S _{BET} (m ² /g)	V (cc/g)	D (nm)	Defective linker numbers	Metal loading (Pd, wt.%)	XPS
						Pd ⁰ / (Pd ²⁺ + Pd ⁰)
Pd-U-ace ^[1]	1390	0.618	1.0-2.9	3.24	1.46	0.76
Pd-U-ace-NH	1155	0.721	1.1-4.0	2.89	1.44	0.52
Pd-U-ace-SN	1078	0.666	1.0-3.6	3.88 [#]	1.41	0.68
Pd-U-ace-SN-F	1443	1.260	1.4-4.0	2.67	1.48	0.73

[#] The apparent defect value of Pd-U-ace-SN cannot be directly compared with others due to the AgCl impurity phase.

Supplementary Table 2. Catalytic performance of Pd-U-ace, Pd-U-ace-NH, Pd-U-ace-SN and Pd-U-ace-SN-F for o-xylene degradation.

Samples	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	E _a (kJ/mol)
Pd-U-ace ^[1]	142	169	181	38.7
Pd-U-ace-NH	177	194	199	81.1
Pd-U-ace-SN	168	190	196	74.2
Pd-U-ace-SN-F	152	183	192	65.2

Supplementary Table 3. Intermediate products of o-xylene degradation over Pd-U-ace^[1], Pd-U-ace-NH, Pd-U-ace-SN, Pd-U-ace-SN-F and Pd-U-ace-NH in the presence of 5.0 vol.% H₂O detected by TD-GC-MS (+: Detected; -: Not detected).

No.	Compound name	Molecular formula	Molecular structure	Catalysts				Pd-U-ace-NH in 5.0 vol.% H ₂ O
				Pd-U-ace	Pd-U-ace-NH	Pd-U-ace-SN	Pd-U-ace-SN-F	
1	Acetic acid	C ₂ H ₂ O ₂		+	-	+	+	+
2	Toluene	C ₇ H ₈		+	+	+	+	+
3	p-Xylene	C ₈ H ₁₀		+	+	+	+	+
4	o-Xylene	C ₈ H ₁₀		+	+	+	+	+
5	Cumene	C ₉ H ₁₂		+	+	+	+	+
6	2-Chlorotoluene	C ₇ H ₇ Cl		+	+	+	+	+
7	3,4-Dimethylfuran-2,5-dione	C ₆ H ₆ O ₃		+	+	+	+	+
8	2-Methylbenzoic acid	C ₈ H ₈ O ₂		+	+	+	+	+
9	4-Chloro-1,2-dimethylbenzene	C ₈ H ₉ Cl		+	-	+	-	-
11	2-Methylbenzyl acetate	C ₁₀ H ₁₂ O ₂		+	-	-	-	-
12	Phthalic anhydride	C ₈ H ₄ O ₃		+	+	+	+	+
13	Phthalide	C ₈ H ₆ O ₂		+	+	+	+	+
14	Benzene	C ₆ H ₆		-	+	+	+	+

Supplementary Table 4 Physicochemical parameters of Pd-U-ace-NH before and after reaction.

Samples	S_{BET} (m^2/g)	V (cc/g)	D (nm)	Defective linker numbers	XPS
					$\text{Pd}^0/(\text{Pd}^{2+} + \text{Pd}^0)$
Pd-U-ace-NH	1155	0.721	1.1-4.0	2.89	0.52
Pd-U-ace-NH-A	1571	0.775	1.4-4.0	3.12	0.61

REFERENCES

1. Bi, F.; Feng, X.; Huang, J.; Wei, J.; Wang, H.; Du, Q.; Liu, N.; Xu, J.; Liu, B.; Huang, Y.; Tang, L.; Zhang, X. Unveiling the Influence Mechanism of Impurity Gases on Cl-Containing Byproducts Formation during VOC Catalytic Oxidation. *Environ. Sci. Technol.* **2025**, *59*, 15526-15537. **DOI:** 10.1021/acs.est.5c05940