Supporting Information

Room-temperature tandem condensation-hydrogenation catalyzed by C_3N_4 nanosheet-supported Pd nanoparticles

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Characterizations

Powder X-ray diffraction (XRD) was performed on a Bruker D8A25 diffractometer with Cu *K*α radiation (λ = 1.54184 Å) operating at 30 kV and 25 mA. N_2 adsorption was carried out at −196 °C using an auto-adsorption analyzer (Micromeritics, 3Flex). Before adsorption measurements were taken, the samples were degassed at 250 °C overnight. The total pore volume was determined from the aggregation of N_2 vapor adsorbed at a relative pressure of 0.99. The specific surface area was calculated using the BET method, and the pore size distributions were measured using BJH analysis from the desorption branch of the isotherms. X-ray photoelectron spectra (XPS) were recorded on a PerkinElmer PHI ESCA system. Transmission electron microscopy (TEM) images were acquired using a Tecnai G2 F20 electron microscope operated at 200 kV. Inductively coupled plasma mass spectroscopy (ICP-MS, X Series II, Thermo Scientific) was performed to determine the actual palladium content in catalysts. The samples were dissolved in perchloric acid under boiling until the solid was completely dissolved.

CO_2 Temperature Programmed Desorption (TPD) experiments were carried out on a Micromeritics 3Flex instrument equipped with a mass spec detector. Typically, the sample (ca.100 mg) was pretreated under a flow of He (50 mL/min) at 200 °C for 1 h. Then the sample was cooled to RT under a flow of He and adsorbed CO_2 for 30 min. Then the sample was purged with He (50 mL/min) at RT for 30 min. The TPD data were collected from RT to 400 °C at a heating rate of 10 °C/min in a flow of He.

CO chemisorption was conducted at 35 °C using the Micromeritics 3Flex instrument. The first isotherm was performed after evacuation at 200 °C for 30 min using a turbomolecular pump. Subsequently, the second isotherm was conducted after evacuation at 35 °C for 1 h. The difference between the two isotherms extrapolated to zero pressure gave the amount of the irreversibly adsorbed CO.

Table S1. Pore structure of C_3N_4-based materials.

Samples	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_p (nm)
C_3N_4	16	0.078	12
C_3N_4-NH_2	138	0.550	43
Pd/C_3N_4-NH_2	118	0.486	36

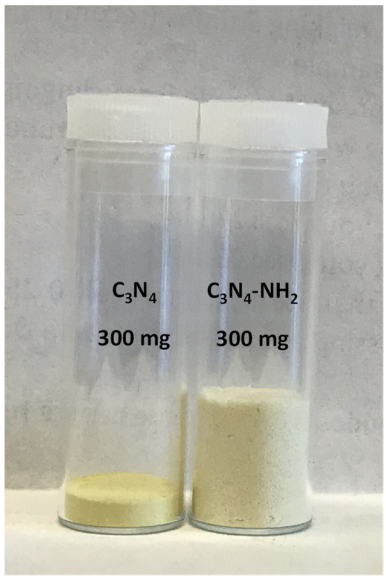

Figure S1. Digital photographs of C_3N_4 and C_3N_4-NH_2.

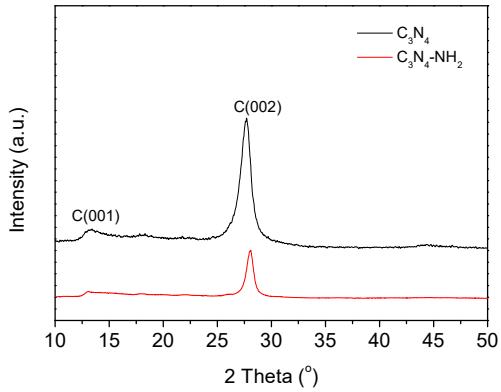

Figure S2. XRD patterns of C_3N_4-based materials.

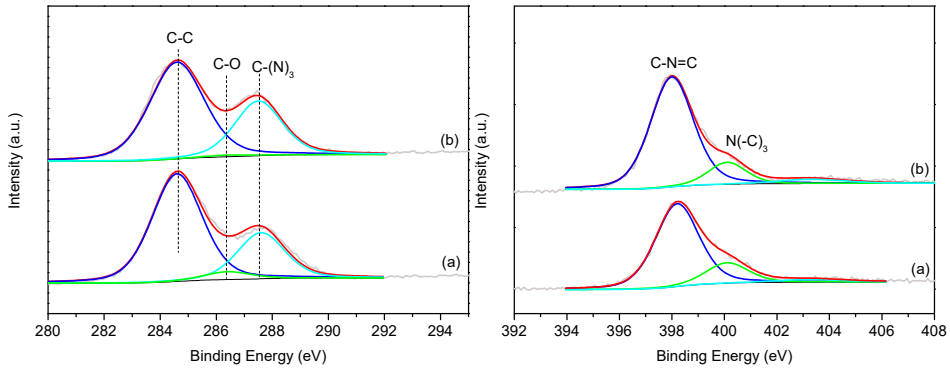

Figure S3. C1s and N1s XPS spectra of (a) Pd/C_3N_4 and (b) Pd/C_3N_4-NH_2.

Table S2. Surface composition of Pd/C_3N_4 and Pd/C_3N_4-NH_2 catalysts calculated from XPS.

Catalysts	C atom composition (%)		
	C-C	C-O	C-$(N)_3$
Pd/C_3N_4	69.8	4.7	25.5
Pd/C_3N_4-NH_2	64.3	0.9	34.7

Table S3. Element composition of Pd/C_3N_4 and Pd/C_3N_4-NH_2 catalysts.

Catalysts	Surface atom composition (%)[a]				Pd loading (wt%)[b]	D_{Pd} (%)[c]	d_{Pd} (nm)[c]
	C	O	N	Pd			
Pd/C_3N_4	73.8	8.3	15.0	0.39	2.3	16.7	6.7
Pd/C_3N_4-NH_2	67.1	7.5	22.8	0.33	2.4	28.9	3.9

[a] Atomic concentrations were detected in XPS analysis.

[b] Detected *via* ICP, the value was the percentage of Pd relative to the mass of C.

[c] Detected by CO chemisorption.

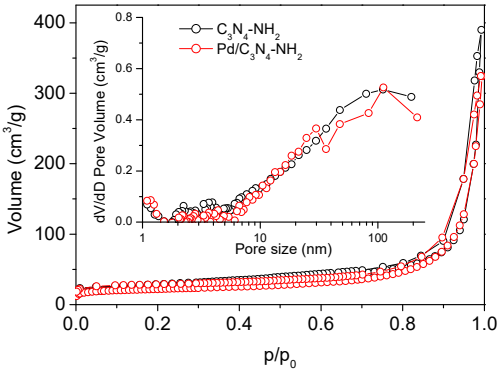

Figure S4. N_2 sorption isotherms and the size distributions of C_3N_4-NH_2 and Pd/C_3N_4-NH_2.

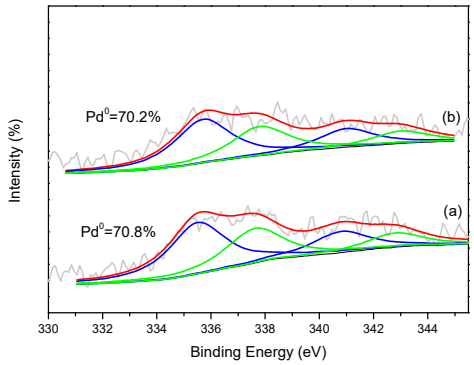

Figure S5. Pd 3d XPS spectra of (a) Pd/C_3N_4 and (b) Pd/C_3N_4-NH_2.

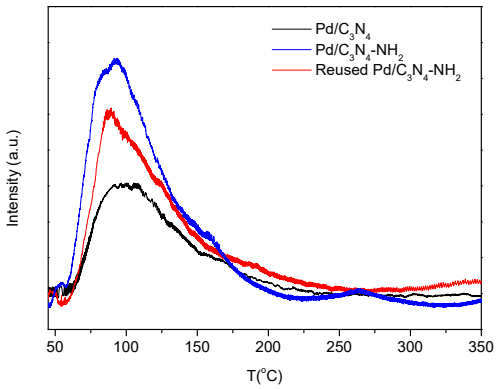

Figure S6. CO_2-TPD profiles of Pd/C_3N_4, Pd/C_3N_4-NH_2 and reused Pd/C_3N_4-NH_2 catalysts.

Table S4. Basicity measured by CO_2-TPD and surface N composition measured by XPS for Pd/C_3N_4, Pd/C_3N_4-NH_2 and reused Pd/C_3N_4-NH_2 catalysts.

Catalysts	Basicity by CO_2-TPD (μmol/g)	N atom composition (%)		
		C-N=C	$N(-C)_3$	N-O
Pd/C_3N_4	42.0	77.5	18.7	3.8
Pd/C_3N_4-NH_2	72.9	80.9	14.2	4.9
Reused Pd/C_3N_4-NH_2	64.4	81.8	14.9	3.3

Table S5. One-step condensation-hydrogenation towards cyclohexanone over 5%Pd/C_3N_4-NH_2.

Entry	Catalyst	T	H_2	Con.	Selectivity (%)			P2 Yield
		(h)	(MPa)	(%)	P1	P2	P3	(%)
1	5%Pd/C_3N_4-NH_2	4	2	88.1	44.8	55.2	0	39.5

Reaction conditions: Catalyst (2.5 mg), cyclohexanone (0.1 mmol), malononitrile (0.2 mmol), EtOH (2mL), 23 °C.

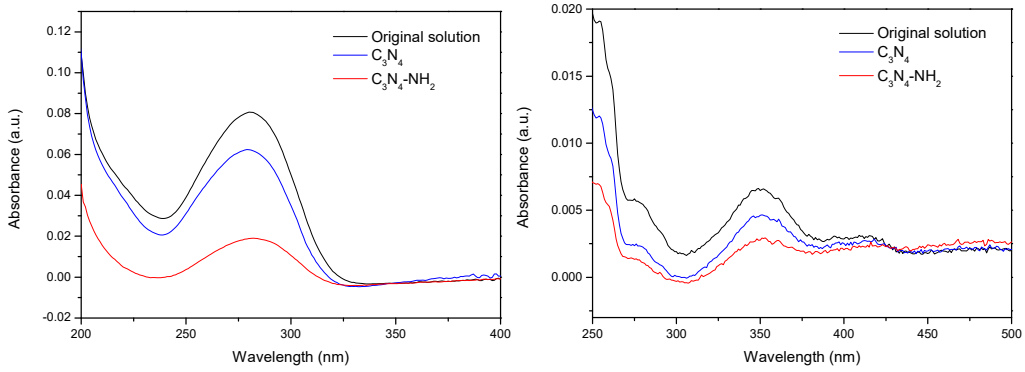

Figure S7. UV-vis spectra of (a) cyclohexanone and (b) malononitrile adsorption on C_3N_4 and C_3N_4-NH_2.

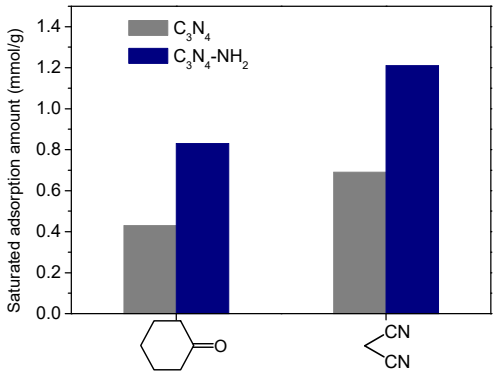

Figure S8. The saturated adsorption amount of cyclohexanone and malononitrile over C_3N_4 and C_3N_4-NH_2.

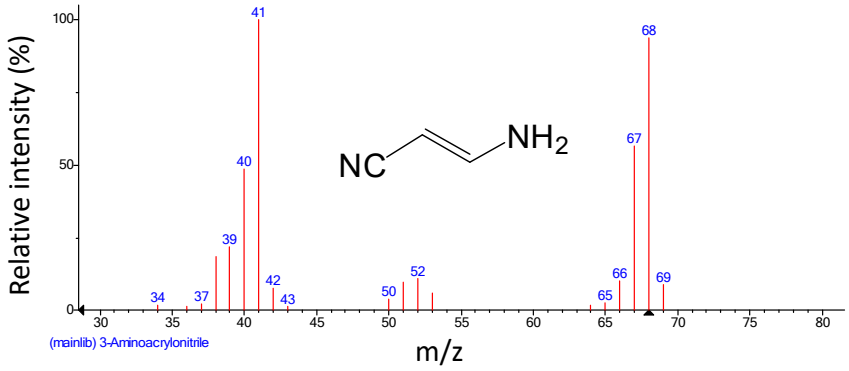

Figure S9. The MS analysis of byproduct from hydrogenation of malononitrile during one-step condensation-hydrogenation. Reaction conditions: Pd/C_3N_4-NH_2 (5mg), cyclohexanone (0.1 mmol), malononitrile (0.2 mmol), EtOH (2mL), 50 ºC, 2 MPa H_2, 4h.

Table S6. One-step condensation-hydrogenation at low hydrogen pressure over Pd/C_3N_4-NH_2.

Entry	Catalyst	T	H_2	Con.	Selectivity (%)			P2 Yield
		(h)	(MPa)	(%)	P1	P2	P3	(%)
1	Pd/C_3N_4-NH_2	2	0.5	89.4	47.9	52.1	0	46.6
2	Pd/C_3N_4-NH_2	28	0.5	99.8	4.5	95.5	0	95.3

Reaction conditions: Catalyst (5 mg), cyclohexanone (0.1 mmol), malononitrile (0.2 mmol), EtOH (2mL), 23 ºC.

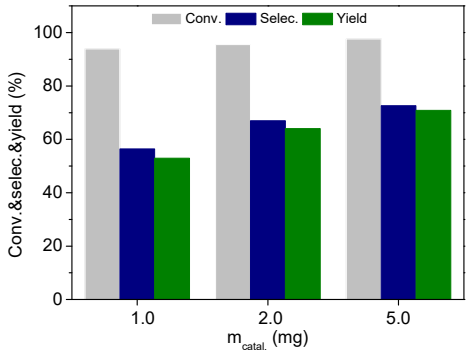

Figure S10. Catalyst loading effect on one-step condensation-hydrogenation reaction. Reaction conditions: Pd/C_3N_4-NH_2, cyclohexanone 0.1 mmol, malononitrile 0.2 mmol, EtOH 2mL, 2 MPa H_2, 23 °C, 2h.

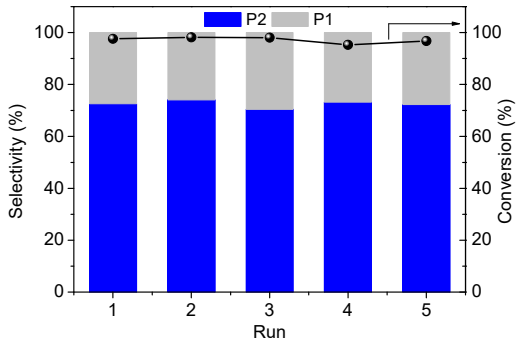

Figure S11. Recycling of Pd/C_3N_4-NH_2 for one-step condensation-hydrogenation reaction. Reaction conditions: catalyst (5mg), cyclohexanone (0.1 mmol), malononitrile (0.2 mmol), EtOH (2mL), 2 MPa H_2, 23 °C, 2h.

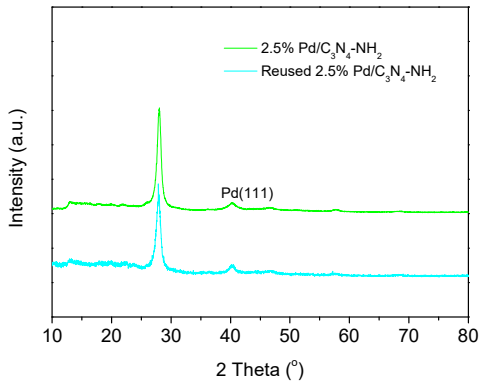

Figure S12. XRD patterns of fresh Pd/C_3N_4-NH_2 and reused Pd/C_3N_4-NH_2 catalysts.

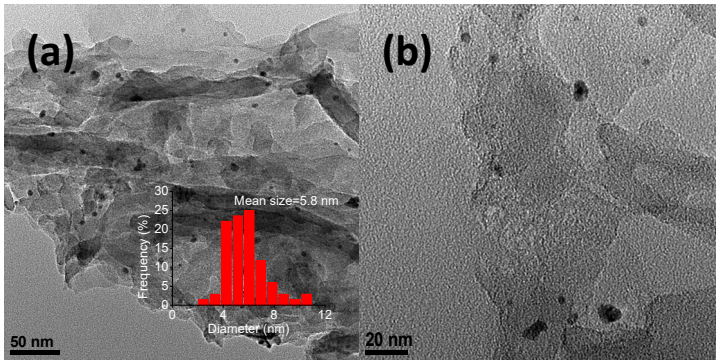

Figure S13. TEM images of recycled Pd/C_3N_4-NH_2.

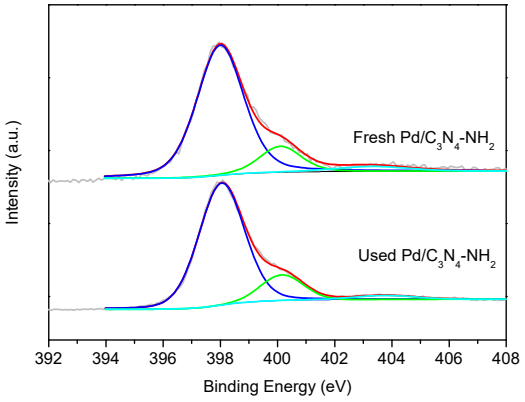

Figure S14. N1s spectra of fresh and reused Pd/C_3N_4-NH_2 catalysts.