

Supporting Information

Long-Range Synergistic Effect between Pt_n Cluster and Zn₁ Single Atom for Efficient Selective Hydrogenations

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1. Methods

1.1 Chemicals

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole (98%), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (37.5%) were purchased from Aladdin Chemical Co. Ltd. (Shanghai, China). P-chloronitrobenzene and other functional nitro compounds were purchased from Macklin Biochemical Co. Ltd. (Shanghai, China). All reagents were used without further purification.

1.2 Catalysts synthesis

ZnO support was prepared as our previous report[1]. Firstly, Pt/ZnO was synthesized by impregnation method with H_2PtCl_6 as Pt precursor. Specifically, 1 g ZnO was impregnated with 1.6 mL acidic H_2PtCl_6 aqueous solution (19 mg Pt/mL) and dried at 25 °C to obtain Pt/ZnO. Then, 0.4 g of Pt/ZnO was dispersed in a mixed solution containing 5 mL ethanol and 10 mL ionic water, denoted as solution A. And 0.8 g 2-methylimidazole(2-MeIM) was dissolved in 20 mL ethanol, denoted as solution B. Then, solution B was dropped into A and stirred for 2 h at 80 °C. After that, the solid was centrifuged, washed twice with ethanol, and dried in vacuum at 60 °C overnight to obtain Pt@ZIF-8. The obtained material was further calcined at 600 °C in nitrogen atmosphere for 4 h at a heating rate of 5 °C/min to obtain Pt@ZIF-8-C600 catalyst. Lastly, the resultant material was washed with HCl solution (0.5 M) at 50 °C for 5 h to etch ZnO particles. The residual solid was adequately washed with deionized water to neutral and dried in vacuum at 60 °C to obtained Pt@ZIF-8-C600-HCl catalyst. The content of metal Pt in this catalyst is 1.7 wt% by ICP measurement, which is lower than that in 3 wt% Pt/ZnO precursor.

Zn₁-N-C sample was prepared by the similar method of Pt@ZIF-8-C600-HCl catalyst except for the impregnation with Pt precursor.

The synthesized method of Pd_n@Zn₁-N-C and Ir_n@Zn₁-N-C catalysts were similar with Pt@ZIF-8-C600-HCl catalyst except for the substitution of Pt precursor with Pd

and Ir precursor.

Pt_{NP}/AC catalyst was prepared by impregnation method with H₂PtCl₆ solution and activated carbon (AC) support.

1.3 Details of characterization method

The Pt content was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, PE optima8000). Specifically, the catalysts were treated with aqua regia and heated to obtain a clear solution, then configured into a suitable concentration for test.

XRD patterns were performed on a D/max 2550 with Cu K α radiation ($\lambda = 0.15406$ nm) with a measurement speed of 2θ of 10 °/min in the range of 5°-80°.

Hydrogen temperature programmed reduction (H₂-TPR) characterization was collected on micromeritics AutoChem II 2920. Typically, 0.05 g catalyst was pretreated at 150 °C for 30 min under He atmosphere. Then, data in the range of 50-800 °C were measured at a heating rate of 10 °C/min under 10 % H₂-Ar mixed gas.

The aberration-corrected high-angle annual dark-filed scanning transmission electron microscopy (AC-HAADF-STEM) analysis was conducted on a FEI Themis Z microscope equipped with spherical aberration corrector and operated at 300 kV, with a guaranteed resolution of 0.06 nm.

The X-ray absorption fine structure (XAFS) spectra, including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), were performed at the beamline 14 W of Shanghai Synchrotron Radiation Facility (SSRF) in China. The output beam was selected by Si(111) monochromator. The energy was calibrated by the Pt foil and Zn foil. Before measurement, the samples were treated under H₂ at 200 °C for 0.5 h, followed by purging with pure Ar until cooled to room temperature. Next, the samples were evacuated and transferred to glove box without exposure to air. The sample was sealed with Kapton films in the glove box before XAFS measurement. Athena software package was employed to process the XAS data.

The attenuated total reflection infrared (ATR-IR) spectroscopy was acquired with

a Thermo Scientific Nicolet iS50 spectrometer equipped with a mercury cadmium telluride (MCT) detector at a resolution of 4 cm^{-1} . Before the experiment, the samples were dispersed in ethanol and treated with ultrasound for 1 h. Then, the suspension was dropwise introduced onto the diamond crystal surface on the instrument at the $65\text{ }^{\circ}\text{C}$ and dried at $100\text{ }^{\circ}\text{C}$ for 4 h. Before data collection, background spectrum was recorded. And then, to get the signal of the adsorbed substrates, the substrate was added the catalysts surface dropwise.

X-ray photoelectron spectroscopy measurements (XPS) were recorded on Thermo Scientific K-Alpha equipped with a mono-chromatized Al $K\alpha$ X-ray source (1486.6 eV). And the data were corrected by the charge of the contaminated carbon (284.8 eV).

The Brunauer-Emmett-Teller (BET) surface area, pore size and pore volume were acquired by analysis of nitrogen adsorption and desorption isotherms with Micromeritics ASAP 2460 built-in software. Before the measurement, degassing was performed at $180\text{ }^{\circ}\text{C}$ for 6 h to remove adsorbed moisture.

1.4 Reaction tests

The selective hydrogenation of p-chloronitrobenzene was selected as probe reaction to investigate different catalysts. In detail, 0.05 g catalyst without reduction treatment, 0.5 mmol substrate, 0.25 mmol 1,3,5-trimethylbenzene (internal standard), as well as 5 mL toluene solvent were put into a 15 mL stainless steel autoclave. Then, the reactor was sealed and purged with H_2 for five times. The reaction was conducted at the conditions of 0.5 MPa and $40\text{ }^{\circ}\text{C}$. The stirring speed was 600 rpm and the particle size of the $\text{Pt}_n@\text{Zn}_1\text{-N-C}$ catalyst was $150\text{ }\mu\text{m}$, which had eliminated the effects of internal/external mass transfer limitations in the selective hydrogenation of p-NB. The products were analyzed by Agilent 7890B gas chromatograph equipped with an HP-5 column and FID detector. As for stability test, the catalyst was centrifuged and washed with ethanol and toluene solvent for three times to remove the adsorbed species and reused in a next run under the same conditions.

In the sulfur compound-resistant hydrogenation experiment, the reaction condition is same except for the addition of thiophene with the mole ratio of thiophene/Pt of 20.

The stability tests of reverse water gas shift reaction (RWGS) over Pt/AC and Pt_n@Zn₁-N-C catalysts were compared. CO₂ reduction activity measurements was carried out in a quartz tube reactor (d = 8 mm) using 0.1g catalysts. Before the reaction, the catalysts were reduced at 200 °C for 2 h in H₂, and subsequently were exposed to the feed gas (CO₂:H₂=1/2.5, 40mL min⁻¹) at 600 °C. Reaction products were analyzed online by gas chromatography a TCD detector. CO₂ conversion, CO selectivity and the specific conversion rate were calculated using the below equations:

$$\text{Conversion}(CO_2\%) = \frac{F_{CO_2,in} - F_{CO_2, out}}{F_{CO_2,in}} \times 100\%$$

$$\text{Selectivity}(CO\%) = \frac{F_{CO, out}}{F_{CO, out} + F_{CH_4,out}} \times 100\%$$

Where the subscript "in" represented the reaction gas entering the reactor, and "out" indicated the gas coming out of the reactor outlet.

2. Results and Discussion

2.1 Figures

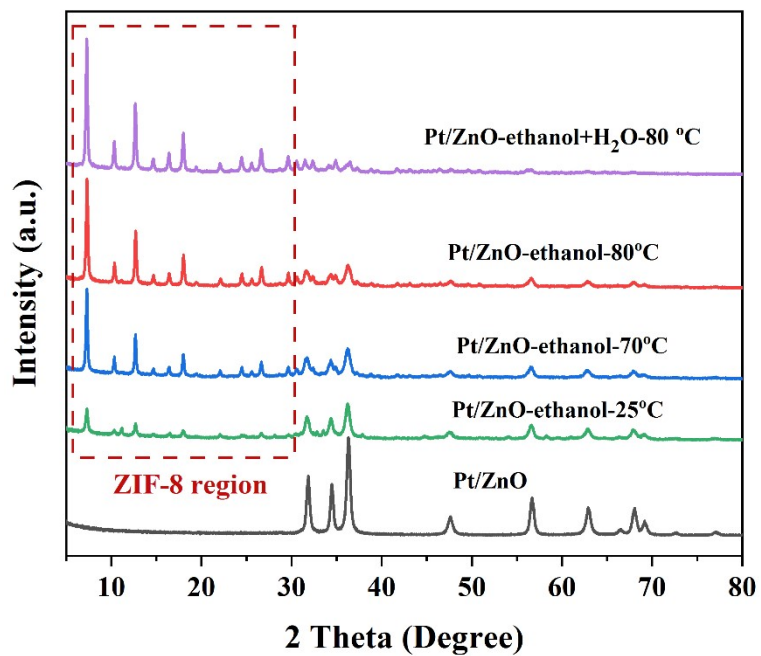


Fig. S1 The XRD patterns of the generation of Pt@ZIF-8 from Pt/ZnO at different etching conditions.

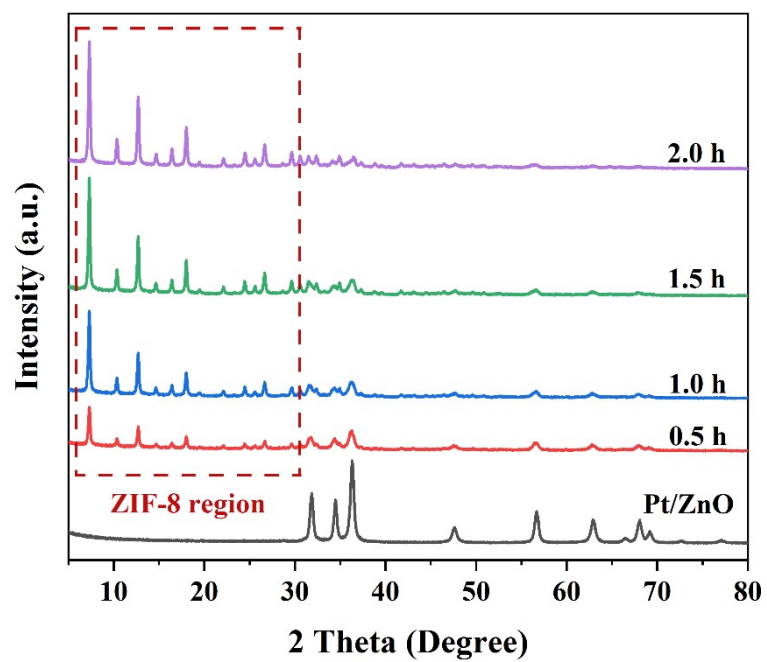


Fig. S2 The XRD patterns of the transformation process of Pt/ZnO to Pt@ZIF-8 at different etching time with the optimal condition at 80 °C in ethanol/H₂O mixed solution.

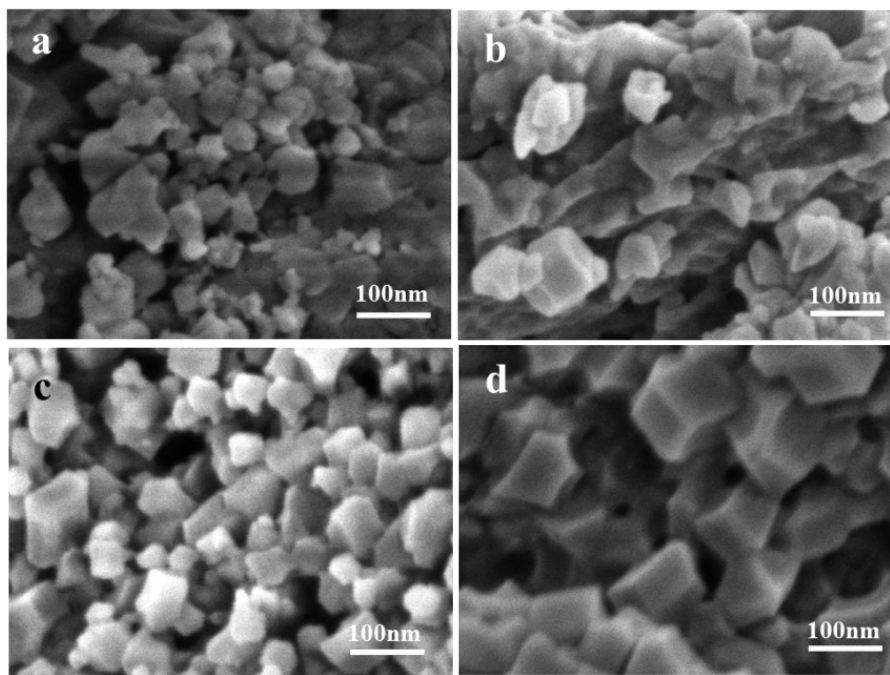


Fig. S3 SEM images of etched Pt/ZnO support at different etching time: (a) 0.5 h, (b) 1 h, (c) 1.5 h, (d) 2 h.

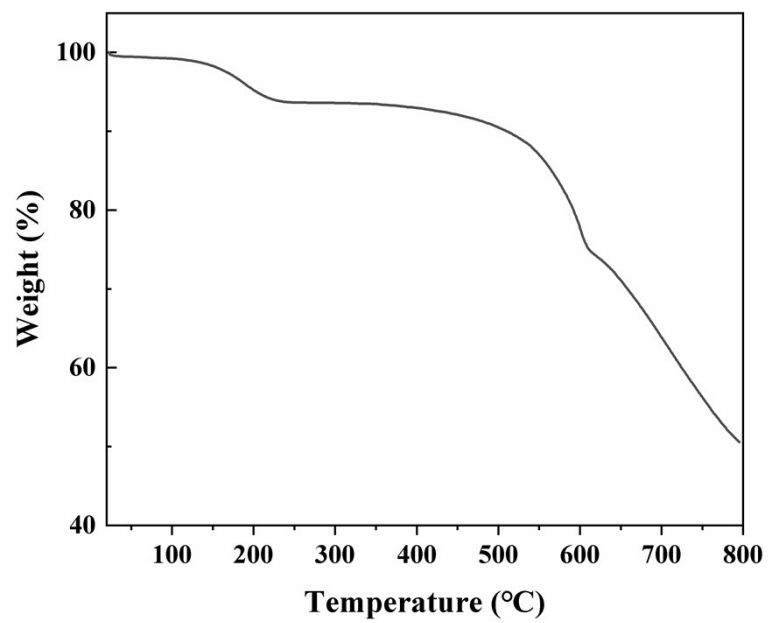


Fig. S4 TG curve of Pt@ZIF-8 sample under N₂ atmosphere.

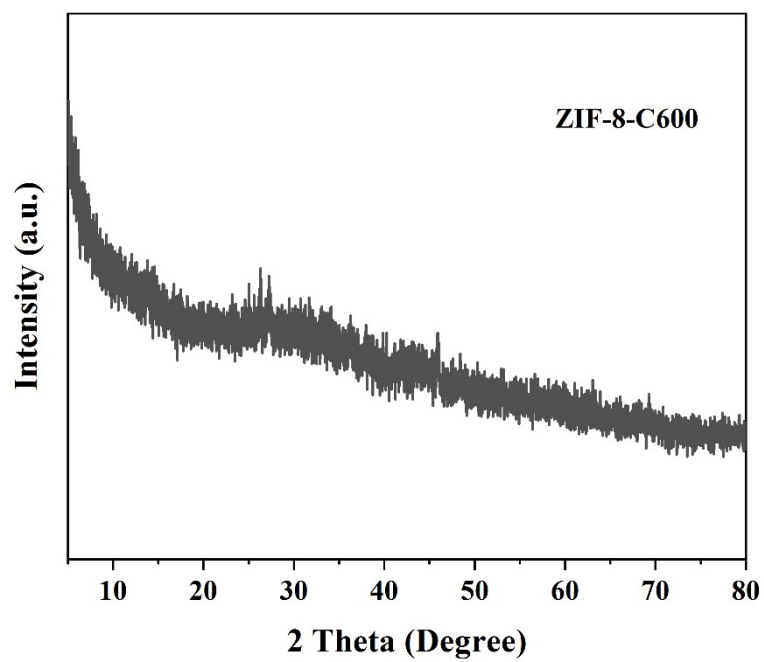


Fig. S5 XRD analysis of ZIF-8-C600 sample.

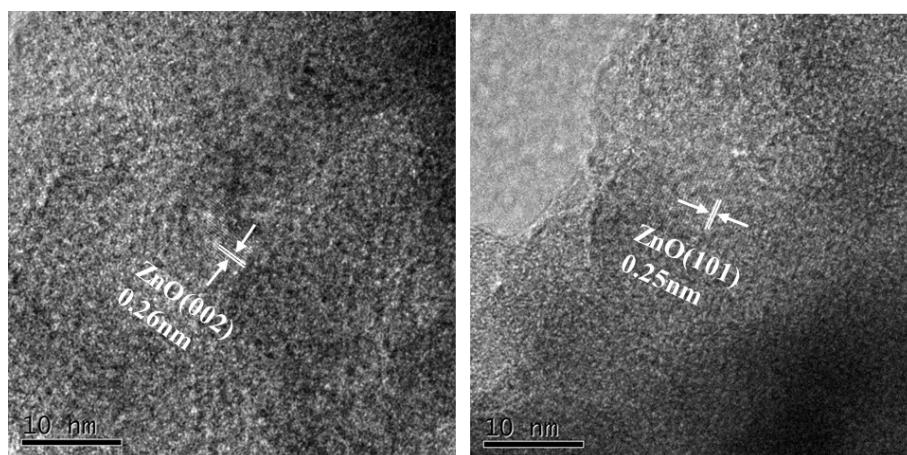
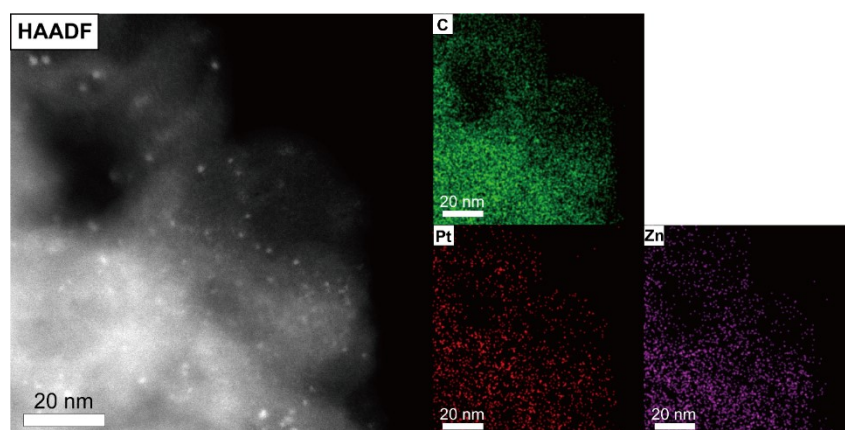
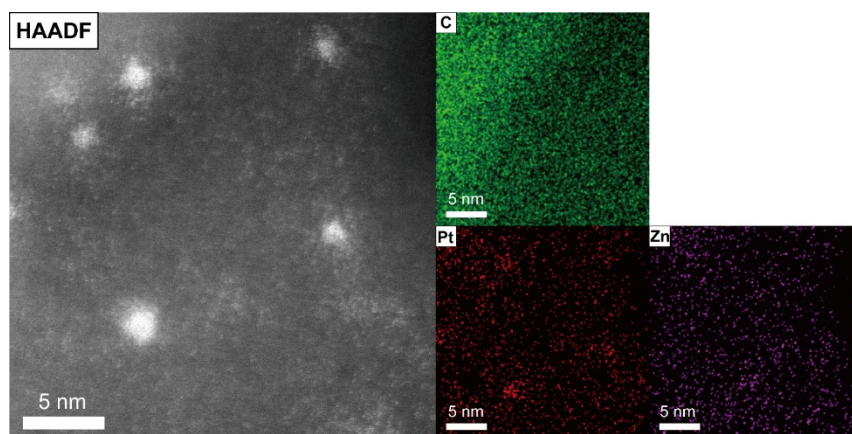


Fig. S6 HRTEM images of Pt@ZIF-8-C600 catalyst, the lattice distances of 0.26 and 0.25 nm are assigned to the (002) and (101) facet of ZnO, respectively.



Element	Family	Atomic Fraction (%)	Atomic Error (%)
C + N	K	98.35	/
Zn	K	1.58	0.25
Pt	L	0.07	0.01

Fig. S7 HAADF-STEM and EDS-Mapping images of $\text{Pt}_n@Zn_1\text{-N-C}$ catalyst.



Element	Family	Atomic Fraction (%)	Atomic Error (%)
C + N	K	99.27	/
Zn	K	0.70	0.10
Pt	L	0.03	0.00

Fig. S8 High-resolution HAADF-STEM and EDS-Mapping images of Pt_n@Zn₁-N-C catalyst.

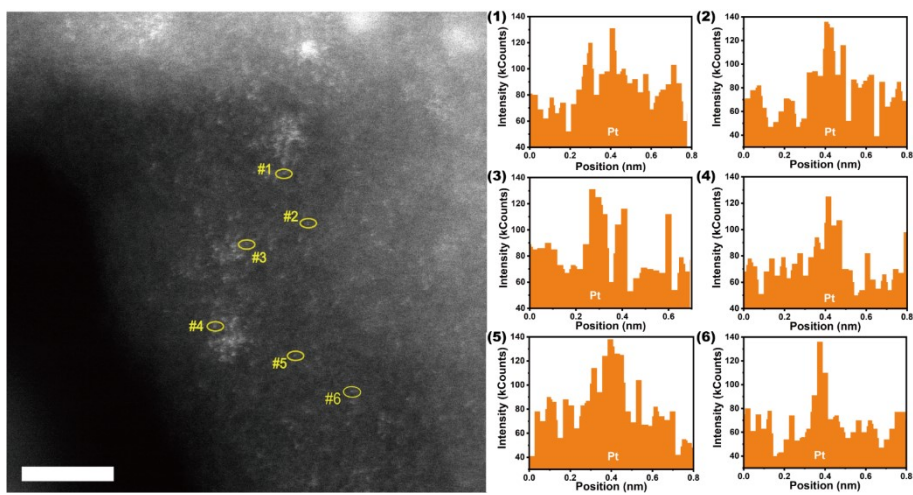
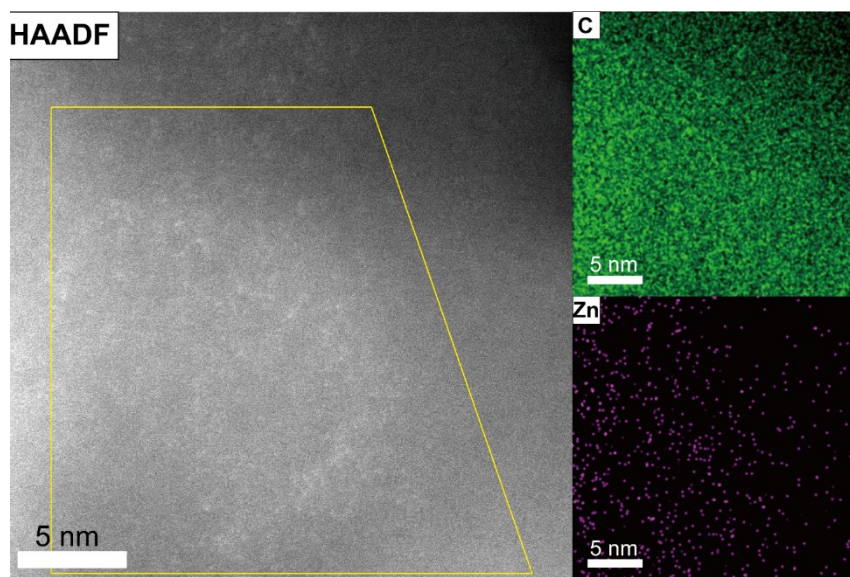


Fig. S9 HAADF-STEM and corresponding image intensity profiles of areas #1-6 in Pt_n@Zn₁-N-C catalyst.



Element	Family	Atomic Fraction (%)	Atomic Error (%)
C + N	K	99.9	/
Zn	K	0.09	0.01
Pt	L	0.01	0.00

Fig. S10 High-resolution HAADF-STEM and EDS-Mapping images of Pt_n@Zn₁-N-C catalyst.

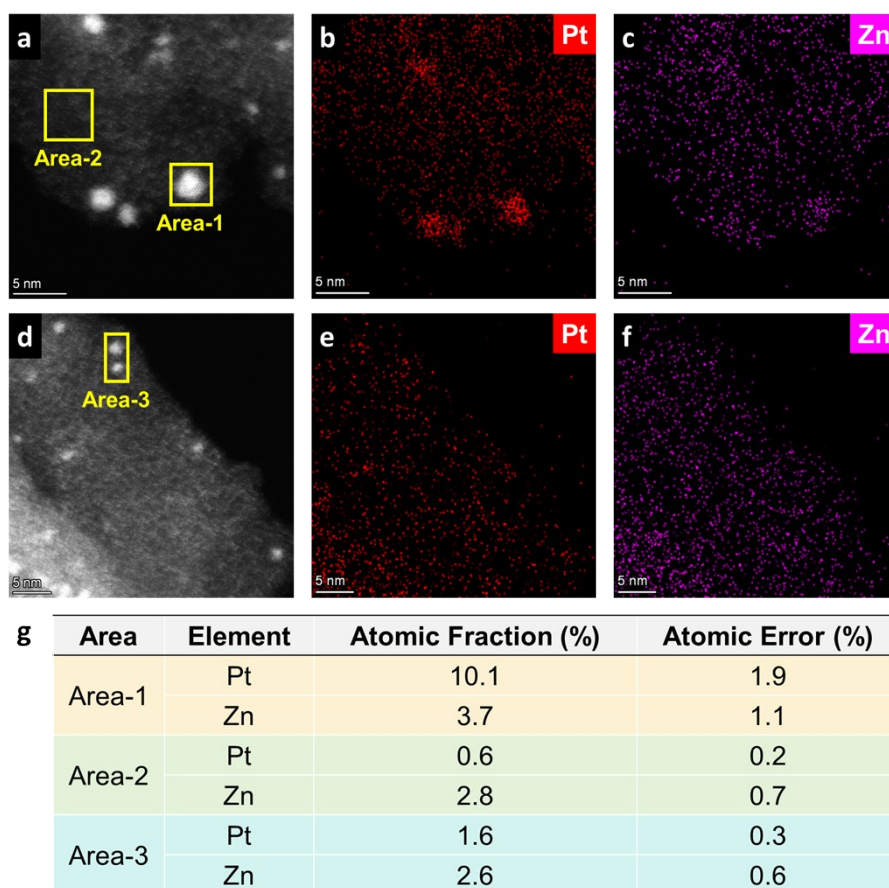


Fig. S11 The AC-HAADF-STEM and corresponding EDS-mapping characterizations of $Pt_n@Zn_1$ -N-C catalyst. (a,d) The AC-HAADF-STEM and (b, c, e, f) corresponding EDS-mapping images of $Pt_n@Zn_1$ -N-C catalyst; (g) The atomic fraction of Pt and Zn species in the square area. In both area-1 and area-3, there apparently are overlap of Pt and Zn signals, indicating the existence of Pt-Zn interaction in the individual Pt_n cluster.

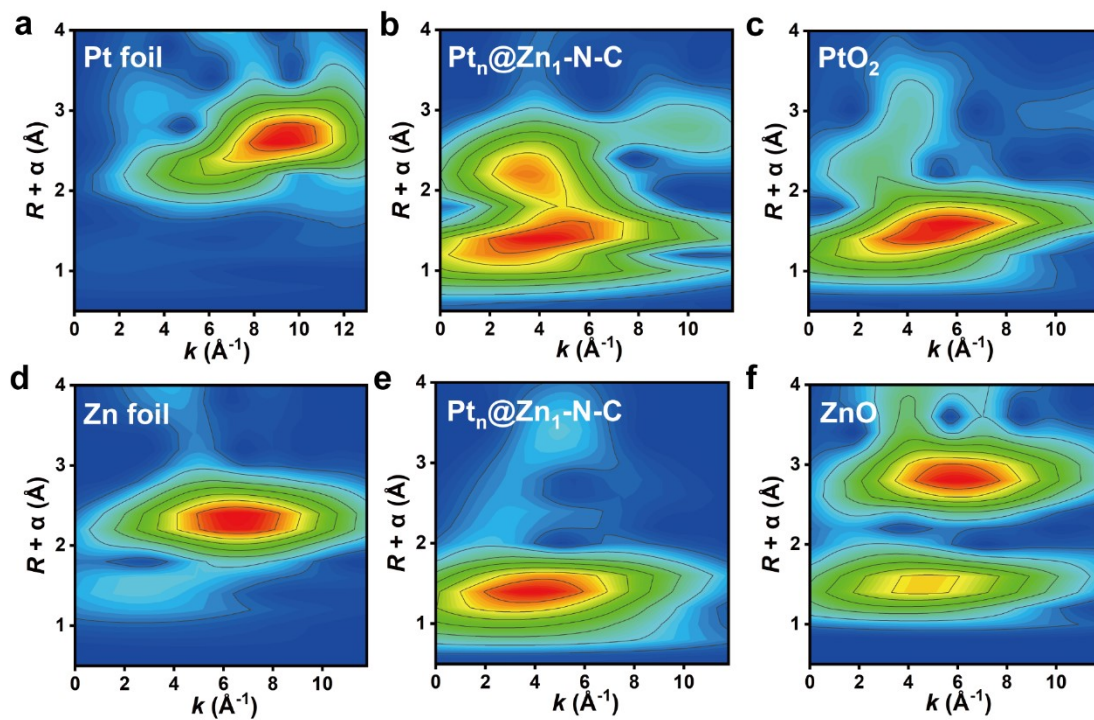


Fig. S12 Wavelet transforms of (a-c) Pt-L_{III} edge and (d-f) Zn K-edge EXAFS spectra of Pt_n@Zn₁-N-C and reference samples.

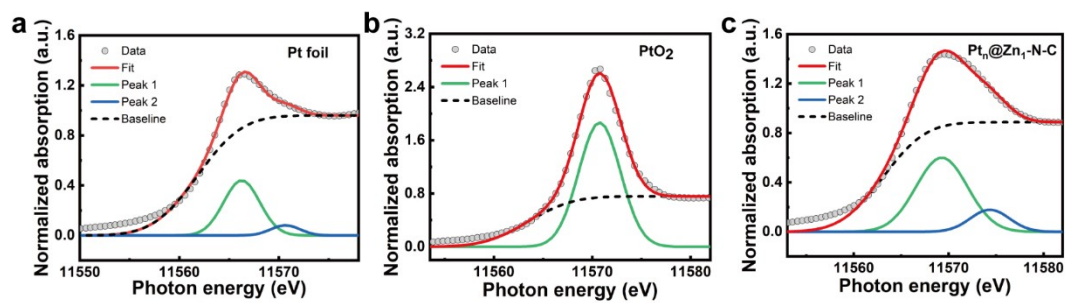


Fig. S13 The simulation of Pt L_{III}-edge XANES spectra of Pt_n@Zn₁-N-C and reference samples.

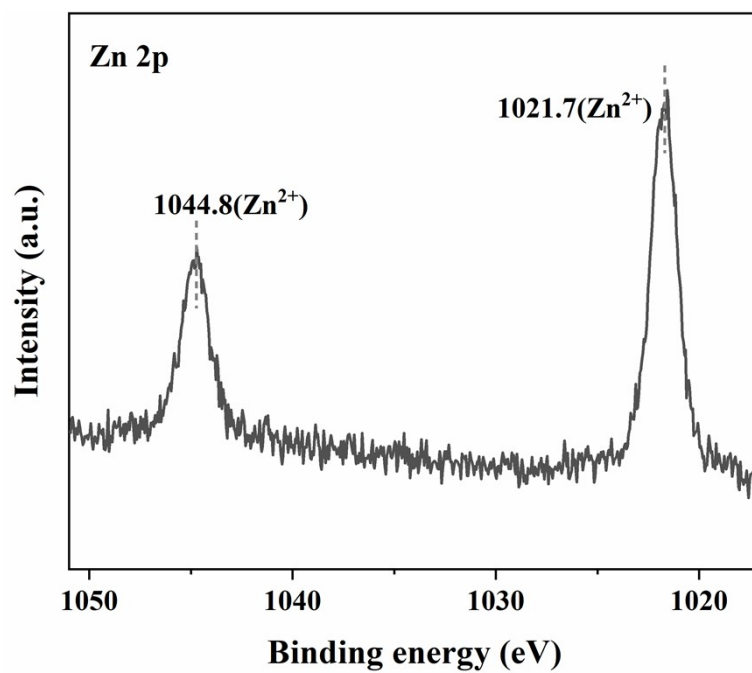


Fig. S14 Zn 2p XPS result of Pt_n@Zn₁-N-C catalyst.

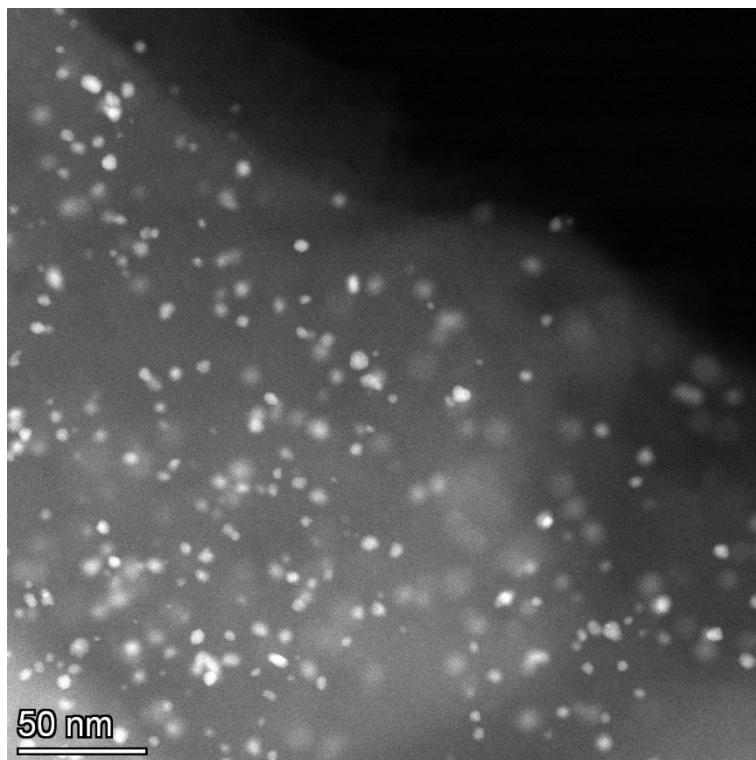


Fig. S15 HAADF-STEM image of Pt_{NP}/AC catalyst.

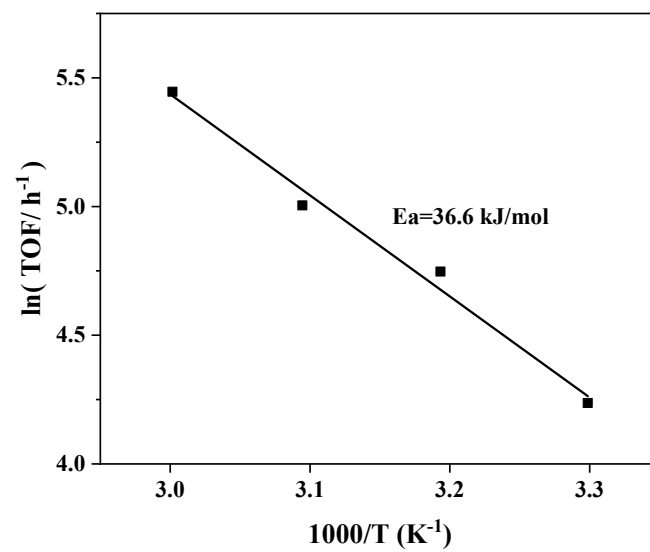


Fig. S16 The apparent activation energy test for the selective hydrogenation of p-nitrochlorobenzene on $\text{Pt}_n@Zn_1\text{-N-C}$.

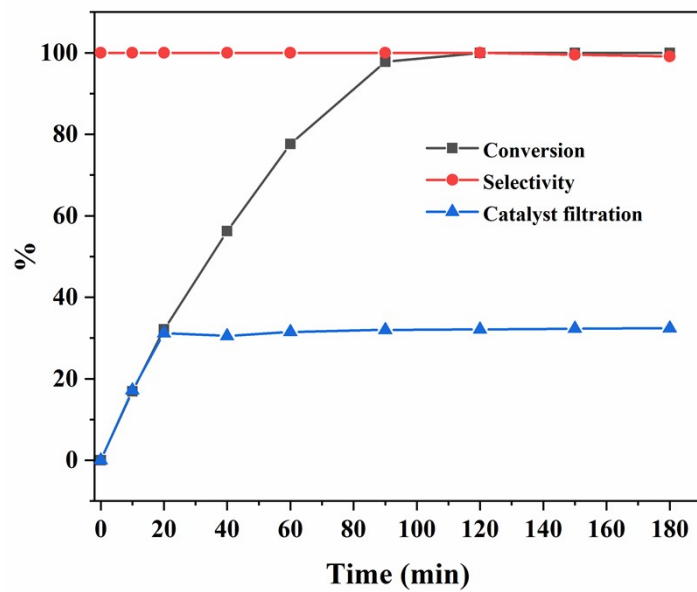


Fig. S17 Kinetic and hot filtration experiments of $\text{Pt}_n@Zn_1\text{-N-C}$ catalyst in *p*-NB hydrogenation reaction.

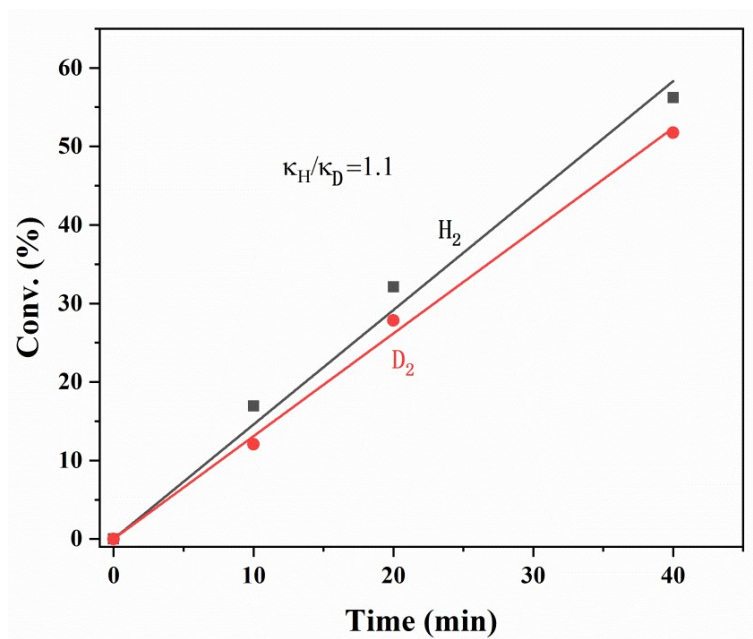


Fig. S18 Kinetic isotopic effect (KIE) results of Pt_n@Zn₁-N-C catalyst in *p*-NB hydrogenation reaction.

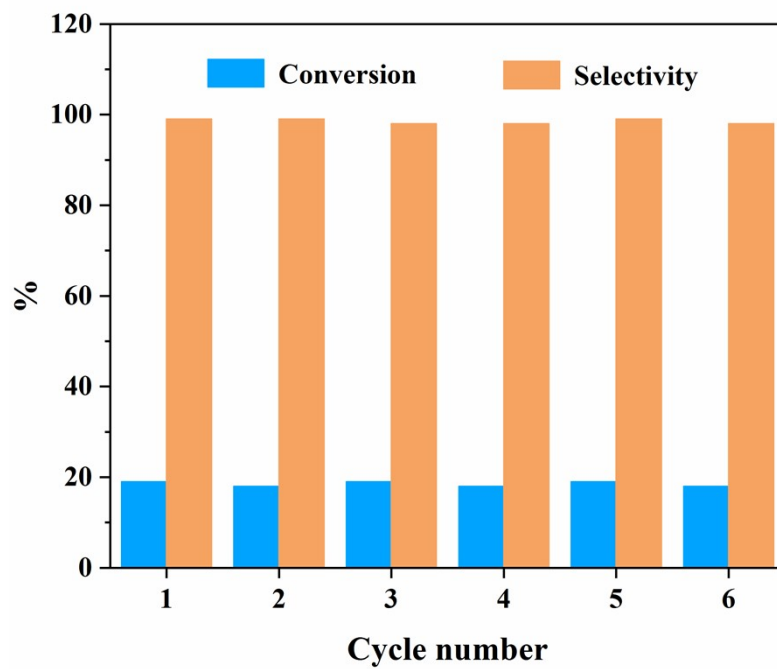


Fig. S19 Recycling tests of p-NB hydrogenation under low conversion.

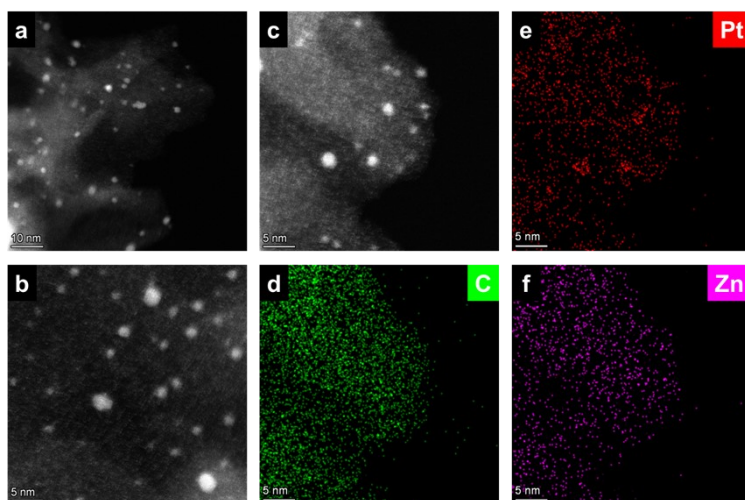


Fig. S20 The HAADF-STEM and corresponding EDS-mapping characterizations of $\text{Pt}_n@Zn_1\text{-N-C}$ -used catalyst. (a-c) The HAADF-STEM images of $\text{Pt}_n@Zn_1\text{-N-C}$ -used catalyst; The EDS-mapping images of (d) C, (e) Pt and (f) Zn elements for $\text{Pt}_n@Zn_1\text{-N-C}$ -used catalyst.

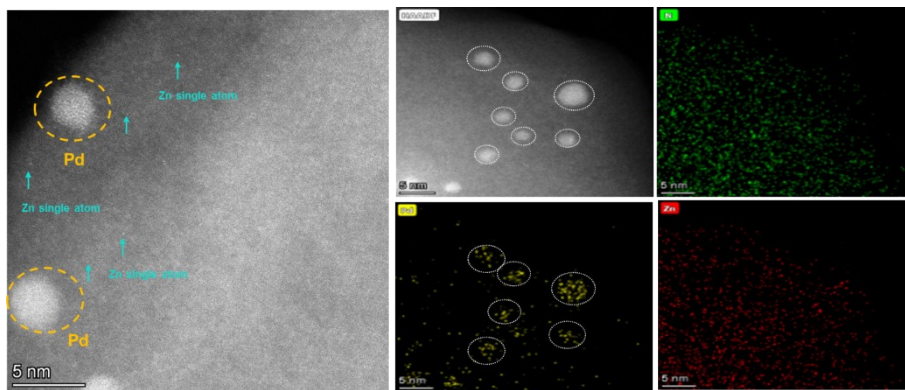


Fig. S21 HAADF-STEM image and EDS mapping of Pd_n@Zn₁-N-C.

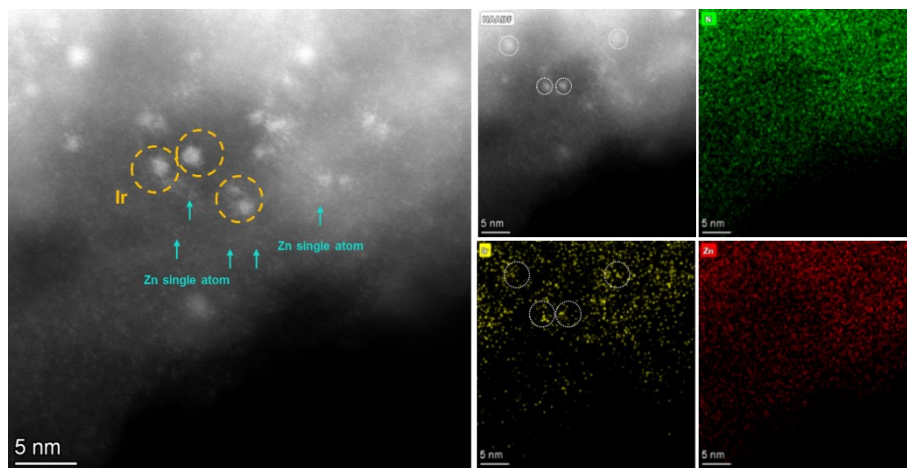


Fig. S22 HAADF-STEM image and EDS mapping of Ir_n@Zn₁-N-C catalyst.

2.2 Tables

Table S1 The fitted EXAFS results of Pt_n@Zn₁-N-C catalyst ^a

Sample	Shell	CN	R (Å)	σ^2 (10 ⁻² Å ²)	ΔE_0 (eV)	r-factor (%)
Pt Foil	Pt-Pt	12.0	2.76	-	-	
	Pt-N/C	2.4	2.01	0.4	8.0	
Pt _n @Zn ₁ -N-C	Pt-Zn	1.1	2.52	0.7	-8.0	0.6
	Pt-Pt	4.8	3.00	1.2	8.0	

^a CN is the coordination number for the absorber-backscatterer pair, R is the average absorber-back scatterer distance, σ^2 is the Debye-Waller factor, and ΔE_0 the inner potential correction. The data range used for data fitting in k-space (Δk) and R-space (ΔR) are 3.0-10.5 Å⁻¹ and 1.0-3.2 Å, respectively. The S_0^2 for Pt L_{III}-edge EXAFS fitting is determined as 0.75.

Table S2 The fitted EXAFS results of Pt_n@Zn₁-N-C catalyst ^a

Sample	Shell	CN	R (Å)	σ^2 (10 ⁻² Å ²)	ΔE_0 (eV)	r-factor (%)
Zn Foil	Zn-Zn	12.0	2.48	-	-	-
Pt _n @Zn ₁ -N-C	Zn-N/C	3.4	2.03	0.4	-2.4	0.3

^a CN is the coordination number for the absorber-backscatterer pair, R is the average absorber-back scatterer distance, σ^2 is the Debye-Waller factor, and ΔE_0 the inner potential correction. The data range used for data fitting in k-space (Δk) and R-space (ΔR) are 3.7-11.5 Å⁻¹ and 1.0-2.0 Å, respectively. The S_0^2 for Zn K-edge EXAFS fitting is determined as 0.75.

Table S3 XPS analysis of the average oxidation state in Pt_n@Zn₁-N-C catalyst.

Pt species	Binding energy (eV)	Content (%)	Average oxidation state
Pt ⁰	71.5	26	+1.5
Pt ²⁺	73.0	74	

Table S4 Nitrogen physisorption analysis of different materials.

Catalysis	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)
Pt@ZIF-8	1124.9	0.61
Pt@ZIF-8-C600	43.8	0.05
Pt _n @Zn ₁ -N-C	397.2	0.29

Table S5 The surface Pt/(C+N) mass ratio analysis for Pt_n@Zn₁-N-C catalyst

Sample	Surface Pt/C atomic ratio	Surface Pt/N atomic ratio	Surface Pt/(C+N) mass ratio
Pt _n @Zn ₁ -N-C	0.016	0.077	0.013

The surface Pt/C and Pt/N atomic ratios were calculated according to equation:

$$n_i/n_j = I_i/I_j \times \sigma_j/\sigma_i \times E_{kj}^{0.5}/E_{ki}^{0.5}$$

i: Pt species; j: C/N species;

n: the numbers of surface atom;

I: the intensity of XPS peak area;

σ : photoionization cross section; $Al_{K\alpha}$: C $I_s = 1.0$, N $I_s = 1.8$, Pt $4f_{7/2} = 8.65$;

E_k : photoelectron kinetic energy;

$E_k = hv (Al_{K\alpha}, hv = 1486.6 \text{ eV}) - BE$ (Binding Energy).

Table S6 The hydrogen chemisorption result of Pt_n@Zn₁-N-C and Pt_{NP}/AC.

Catalyst	The atomic ration of H ₂ consumption to Pt	H/Pt atomic ratio
Pt _n @Zn ₁ -N-C	1.6	3.2
Pt _{NP} /AC	0.7	1.4

Table S7 The catalytic results of Pt_n@Zn₁-N-C catalysts treated with HCl and HNO₃.

Catalyst	Conv. (%)	Sel. (%)
Pt _n @Zn ₁ -N-C (HCl)	97.8	>99
Pt _n @Zn ₁ -N-C (HNO ₃)	95.5	>99

Reaction condition: 40 °C, 0.5 MPa, 0.05 g catalyst, 0.5 mmol *p*-NB, 5 mL toluene, 2 h.

Table S8 The hydrogenation of *p*-NB over Pt_n@Zn₁-N-C catalyst at low temperature.

Catalyst	Time (h)	Conv. (%)	Sel. (%)
Pt _n @Zn ₁ -N-C	4.5	33.3	>99

Reaction condition: 0 °C, 2.0 MPa, 0.05 g catalyst, 0.5 mmol *p*-NB, 5 mL toluene.

Table S9 Catalytic performance comparison with other heterogeneous hydrogenation catalysts

Catalyst	T(°C)	P(MPa)	Con.%	Sel.%	TOF(h ⁻¹)	Note
Pt _n @Zn ₁ -N-C	40	0.5	100	>99	100.5	This work
PVP-1Pt/4Ru	25	0.1	100	99	28.8	[2]
5%Pt/Al ₂ O ₃	27	4	32	50	1872	[3]
Pt/C	50	2	100	85.1	1800	[4]
Pt/Fe ₃ O ₄	60	0.1	100	99	19	[5]
Pt-PVP	60	0.1	100	45.3	212	[5]
<i>pd</i> -Pt/TiO ₂	80	1	100	91.1	-	[6]

Table S10 The hydrogenation of *p*-NB over Ir_n@Zn₁-N-C and Pd_n@Zn₁-N-C.

Catalyst	Time (h)	Conv. (%)	Sel. (%)
Ir _n @Zn ₁ -N-C	1.5	100	>99
Pd _n @Zn ₁ -N-C	6.5	95.0	>99

Reaction condition: 40 °C, 0.5 MPa, 0.05 g catalyst, 0.5 mmol *p*-NB, 5 mL toluene.

3. Reference

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