

Supplementary Information

Selective hydrogenation of nitroaromatics catalyzed by surface Pt-rich high-entropy alloy catalyst at room temperature

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1. Supplementary Figures

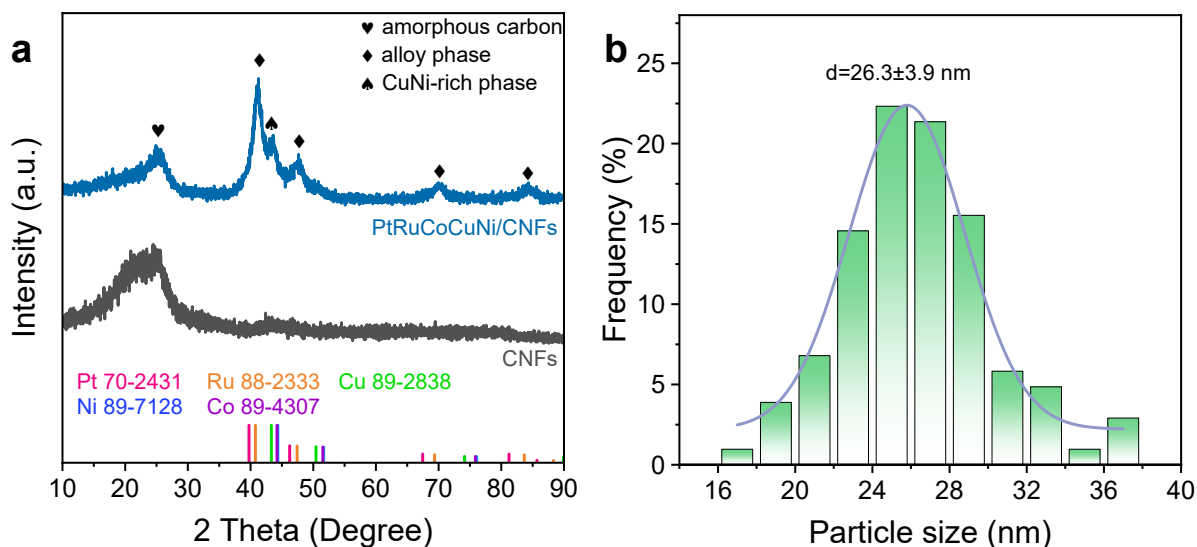


Figure S1. (a) XRD pattern of CNFs and PtRuCoCuNi/CNFs. (b) Particle size distribution of PtRuCoCuNi HEA nanoparticles.

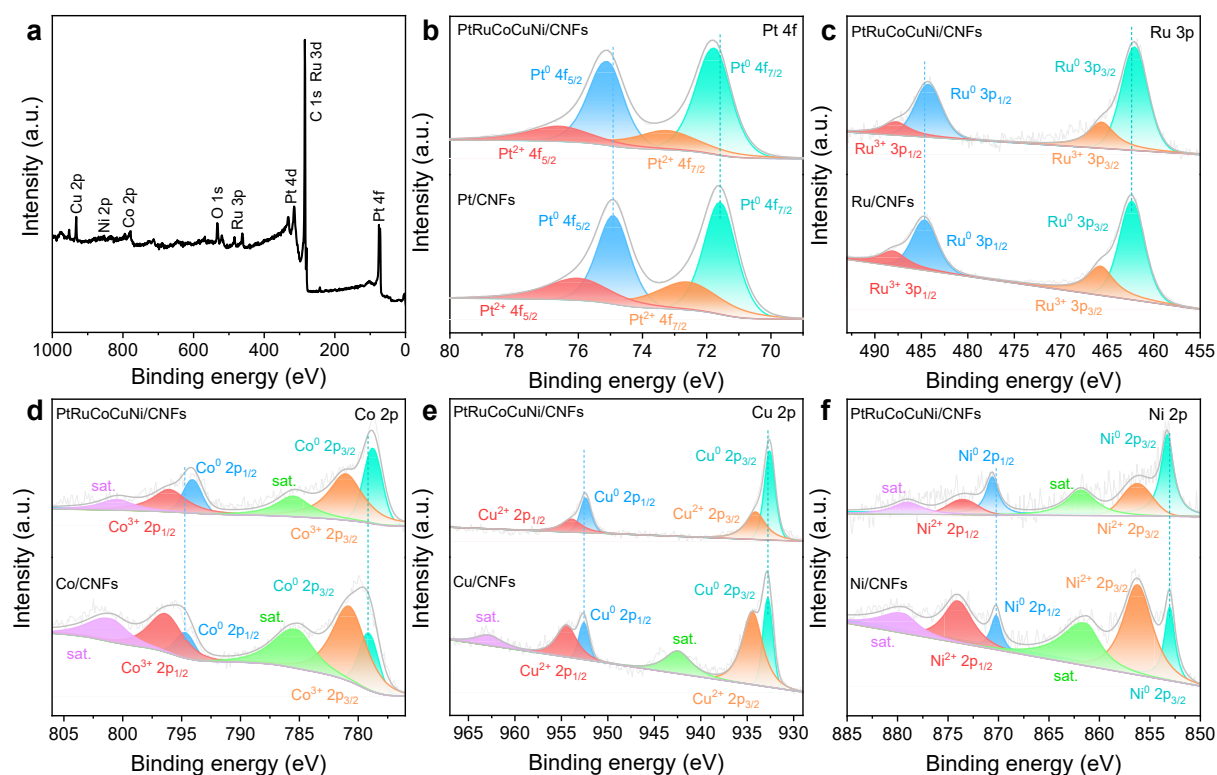


Figure S2. XPS analysis of PtRuCoCuNi/CNFs. (a) full spectra. (b) Pt 4f XPS spectrums. (c) Ru 3p XPS spectra. (d) Co 2p XPS spectra. (e) Cu 2p XPS spectra. (f) Ni 2p XPS spectra.

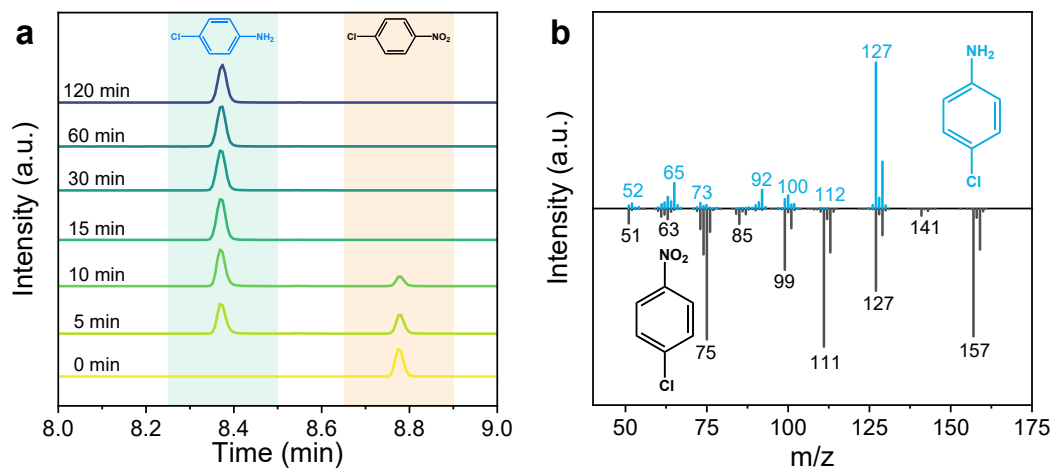


Figure S3. GC-MS analysis of the products after catalytic *p*-CNB hydrogenation by PtRuCoCuNi/CNFs with different reaction times. (a) GC results, (b)MS results.

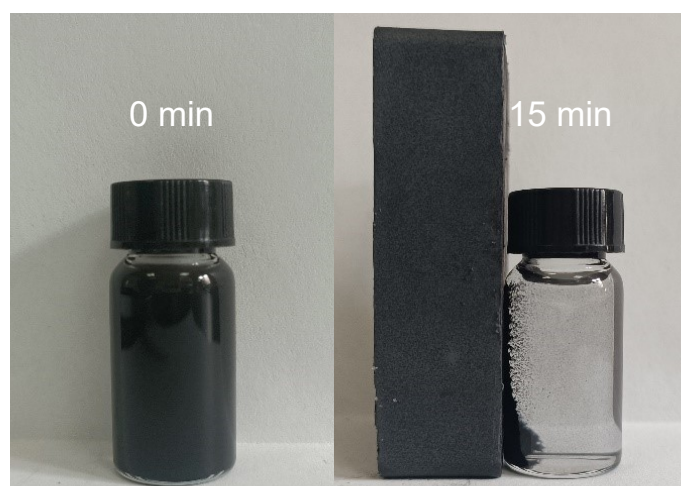


Figure S4. Recyclability of PtRuCoCuNi/CNFs.

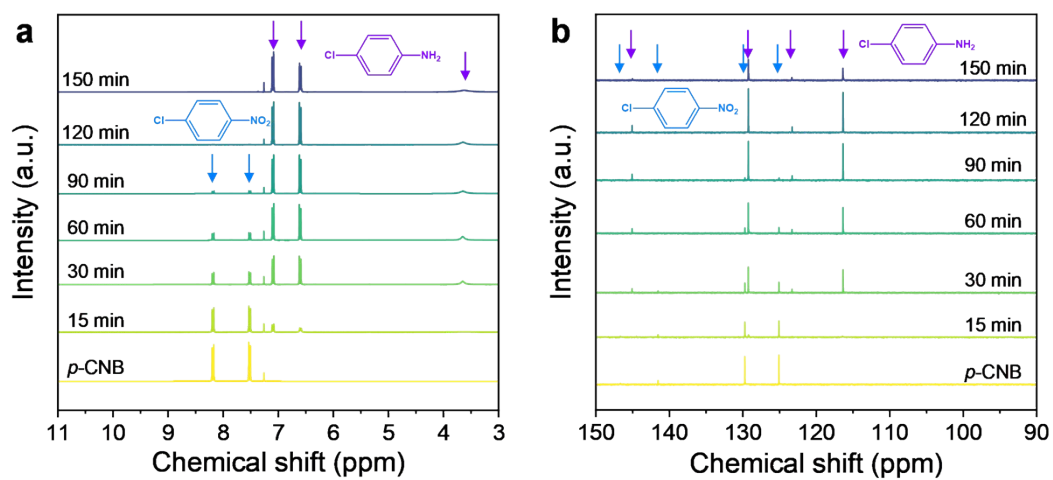


Figure S5. NMR product analysis of *p*-CNB and products with different reaction times. (a) ¹H-NMR. (b) ¹³C-NMR.

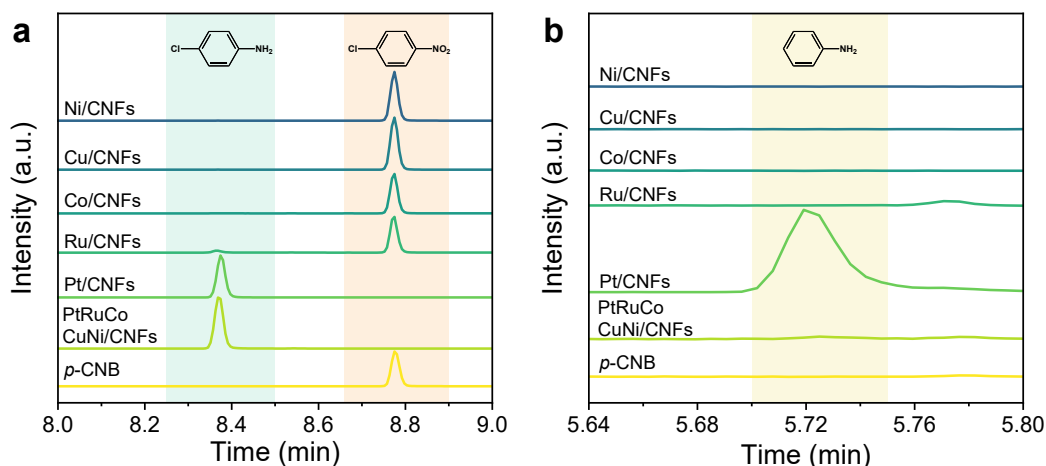


Figure S6. (a) GC analysis of the products after catalytic *p*-CNB hydrogenation by PtRuCoCuNi/CNFs and five monometallic catalysts. (b) Distribution of the by-product aniline.

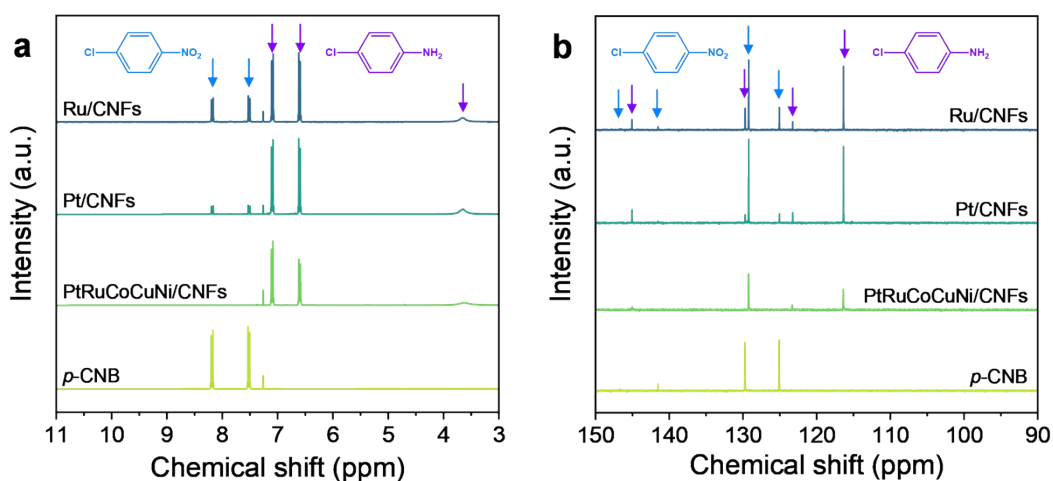


Figure S7. NMR analysis of *p*-CNB before and after hydrogenation with different catalysts. (a) ^1H -NMR. (b) ^{13}C -NMR.

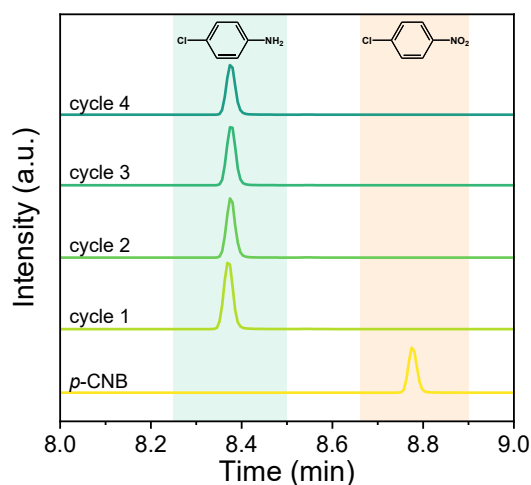


Figure S8. GC results of the products after reuse of PtRuCoCuNi/CNFs. After completion of hydrogenation, the catalyst was washed three times with ethanol and tetrahydrofuran, respectively, and then dried for the next hydrogenation experiment.

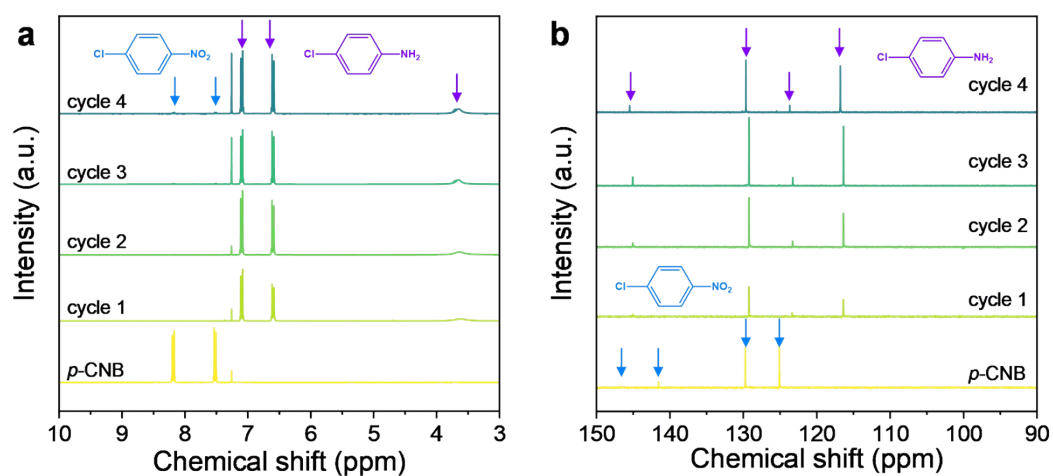


Figure S9. NMR results of the products after reuse of PtRuCoCuNi/CNFs. (a) $^1\text{H-NMR}$. (b) $^{13}\text{C-NMR}$.

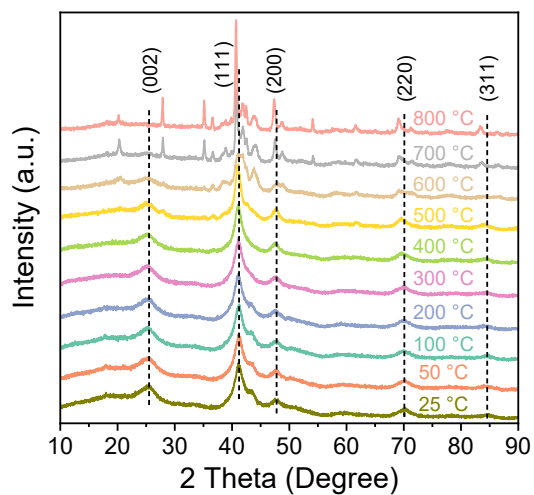


Figure S10. In-situ XRD spectrum of PtRuCoCuNi/CNFs.

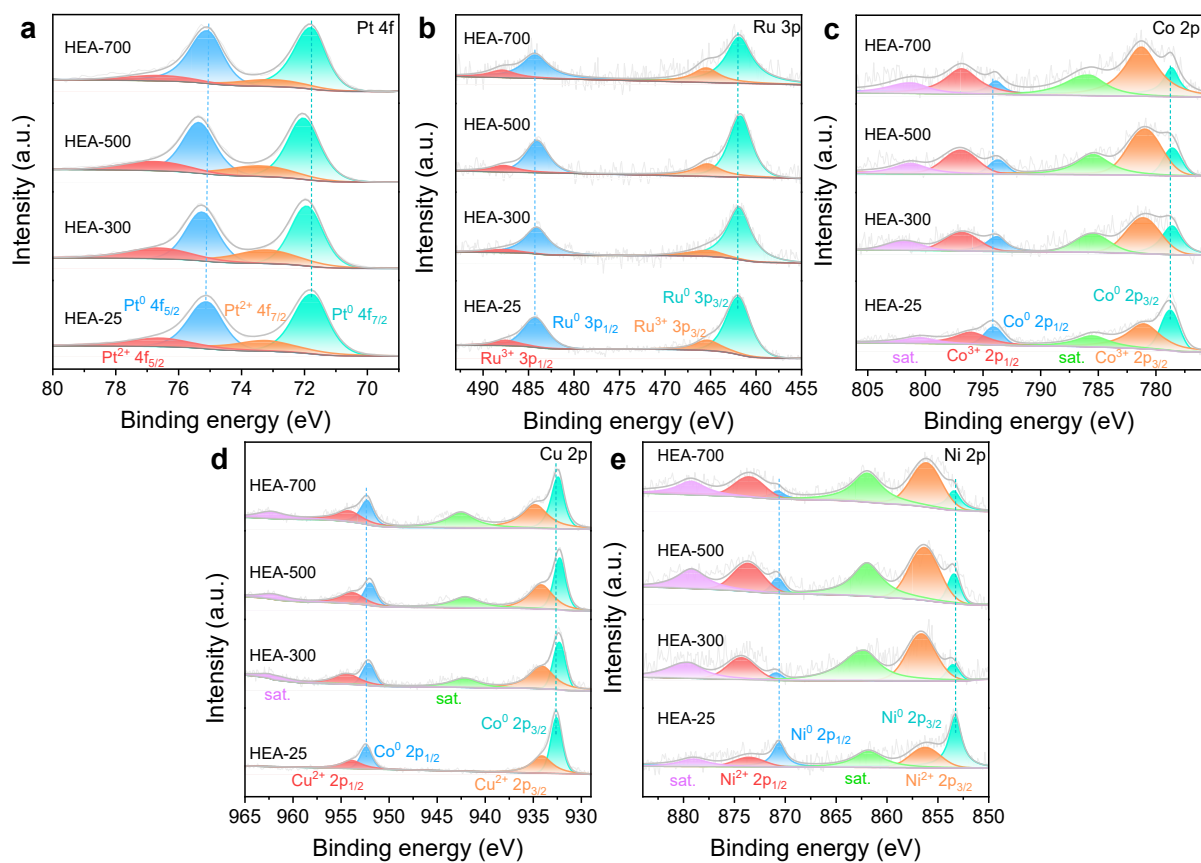


Figure S11. XPS high resolution spectra analysis of HEA-25, HEA-300, HEA-500, HEA-700. (a) Pt4f. (b) Ru3p. (c) Co 2p. (d) Cu 2p. (e) Ni 2p.

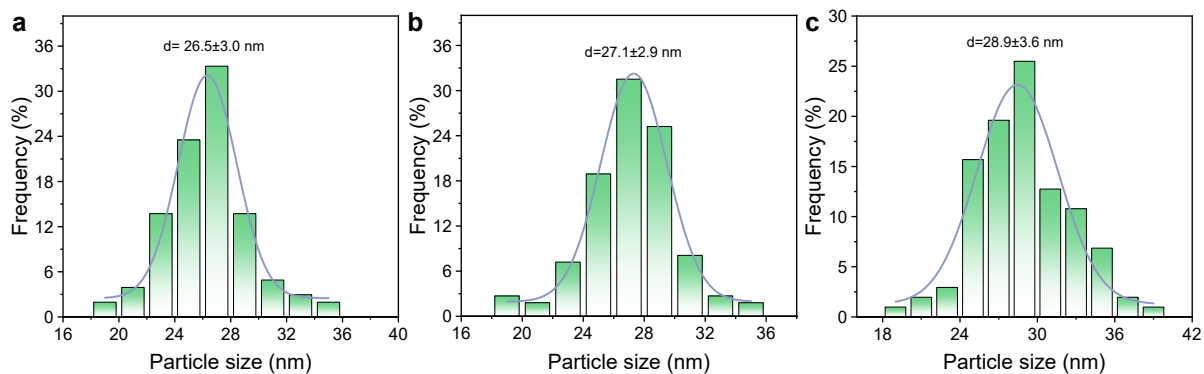


Figure S12. Particle size statistics of (a) HEA-300, (b) HEA-500, (c) HEA-700.

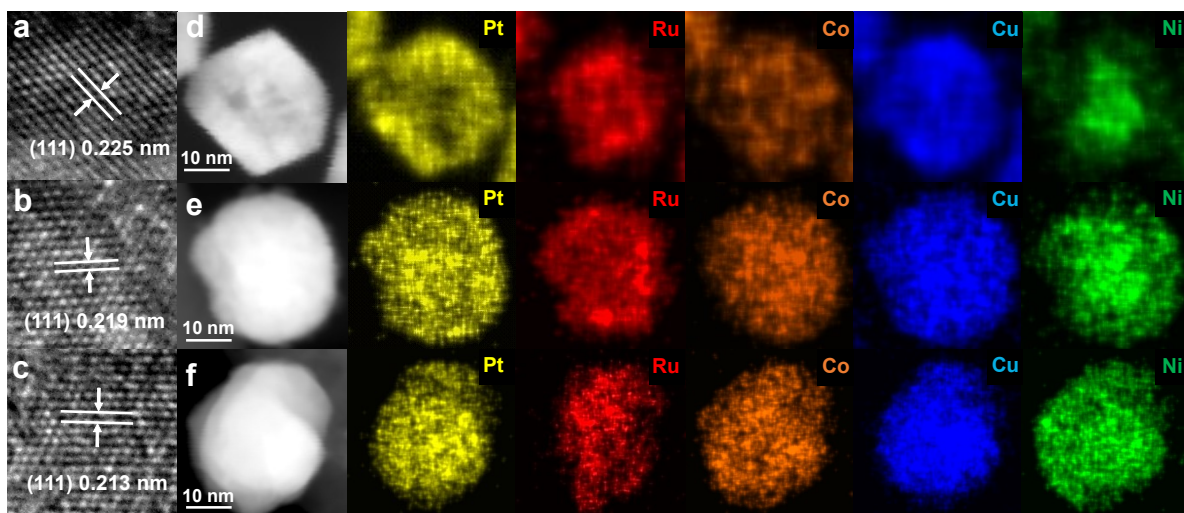


Figure S13. The corresponding elemental mapping of (a) HEA-300, (b) HEA-500, and (c) HEA-700.

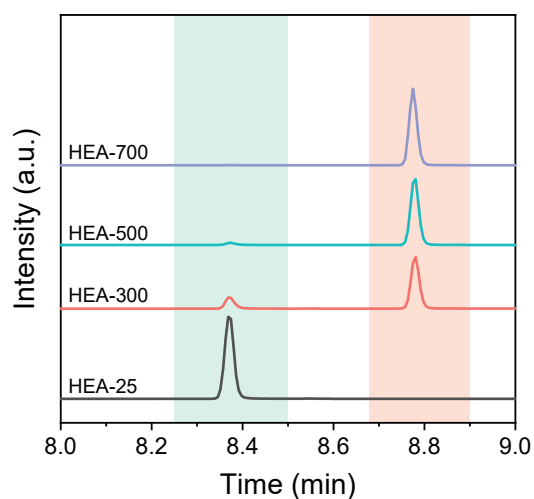


Figure S14. GC-MS results of *p*-CNB hydrogenation products catalyzed using HEA, HEA-300, HEA-500, HEA-700.

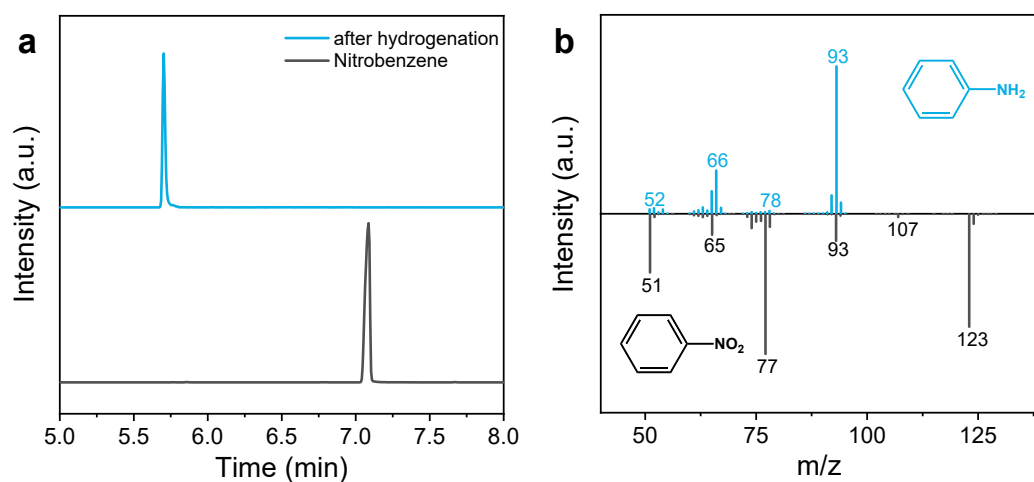


Figure S15. GC-MS results of nitrobenzene before and after hydrogenation. (a) GC results, (b) MS results.

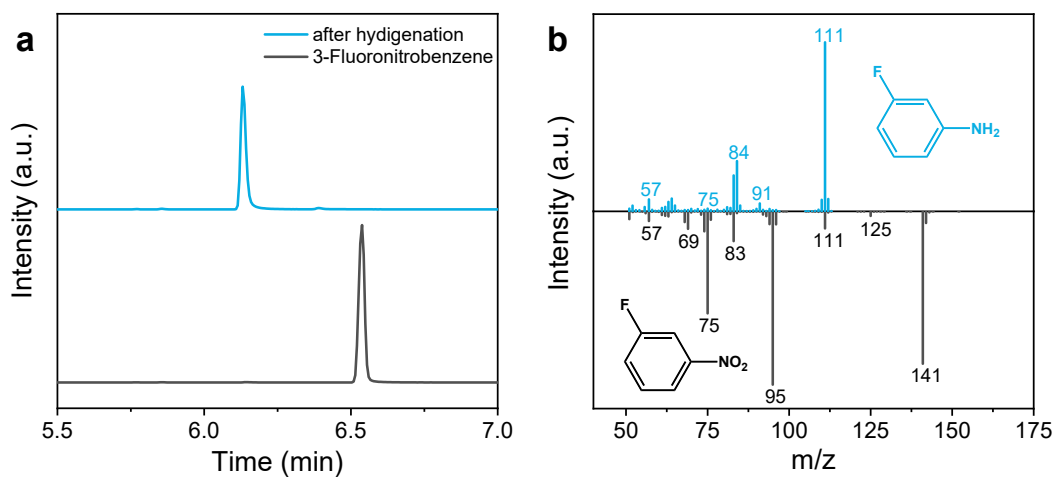


Figure S16. GC-MS results of 3-fluoronitrobenzene before and after hydrogenation. (a) GC results, (b)MS results.

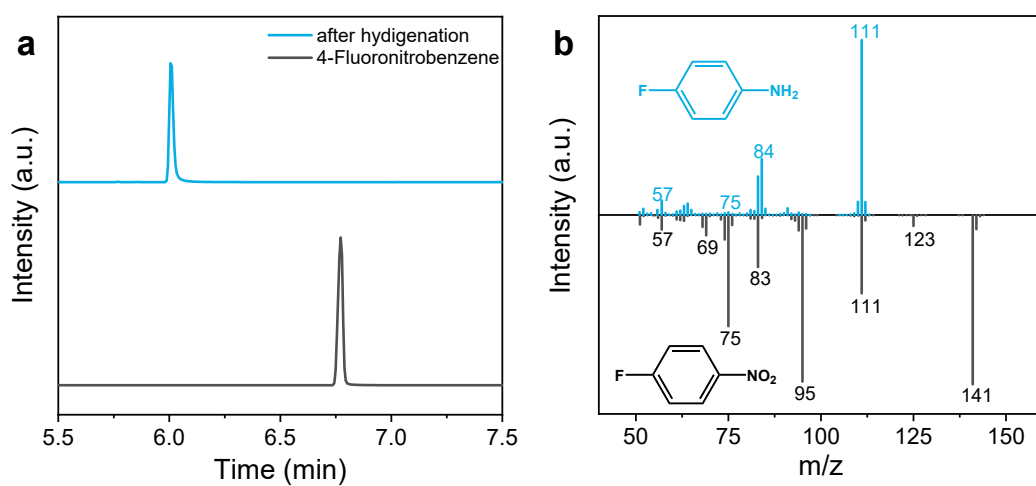


Figure S17. GC-MS results of 4-fluoronitrobenzene before and after hydrogenation. (a) GC results, (b)MS results.

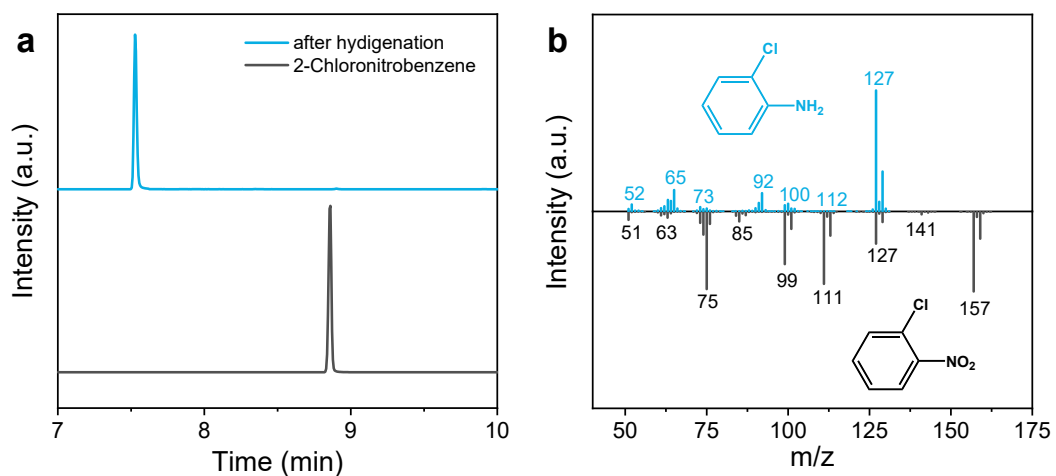


Figure S18. GC-MS results of 2-chloronitrobenzene before and after hydrogenation. (a) GC results, (b)MS results.

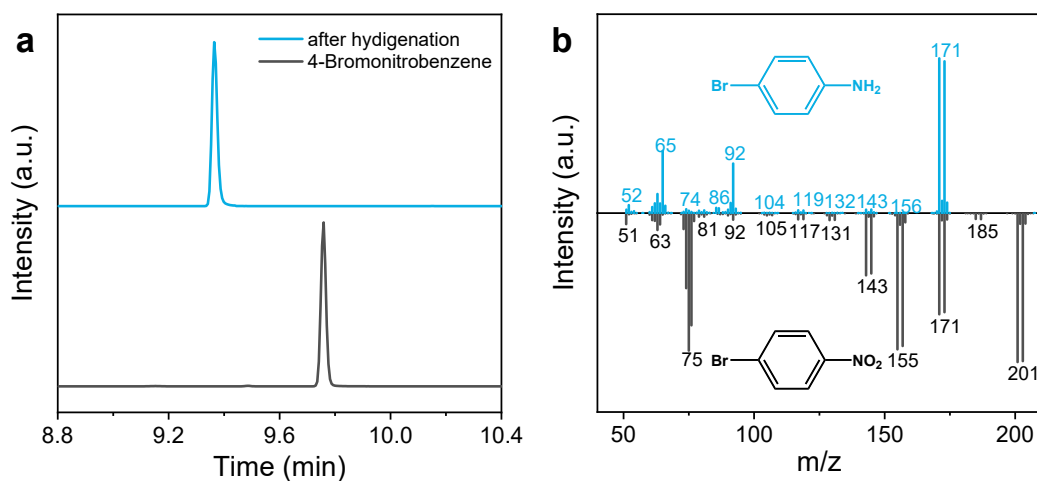


Figure S19. GC-MS results of 4-bromonitrobenzene before and after hydrogenation. (a) GC results, (b)MS results.

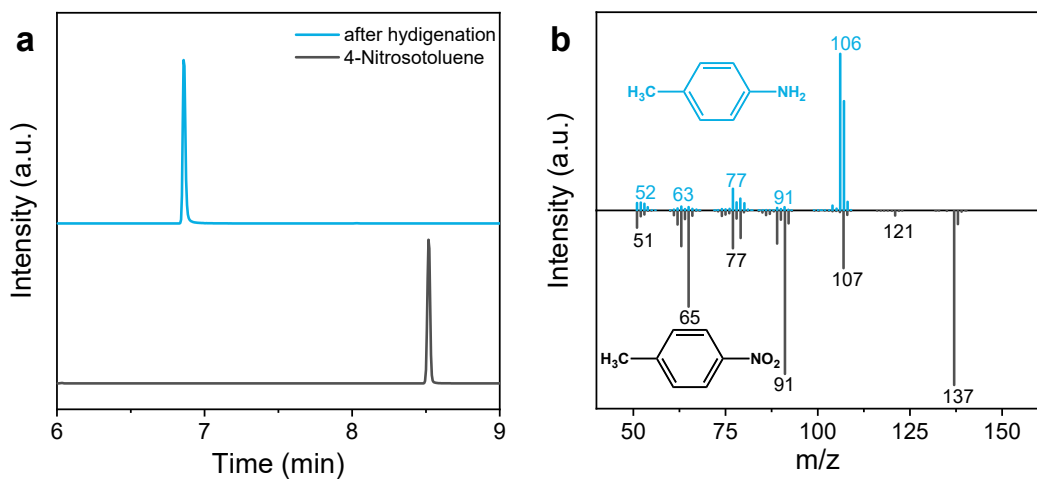


Figure S20. GC-MS results of 4-nitrosotoluene before and after hydrogenation. (a) GC results, (b)MS results.

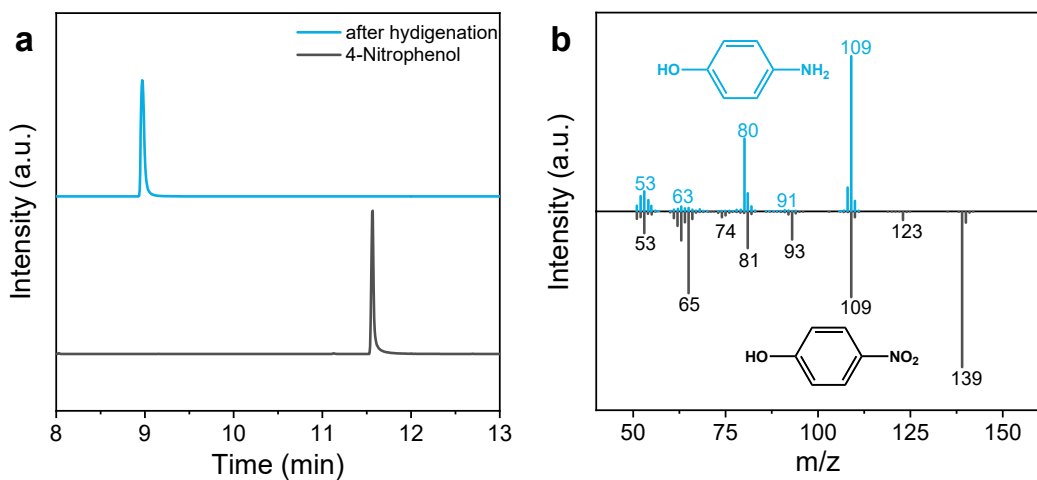


Figure S21. GC-MS results of 4-nitrophenol before and after hydrogenation. (a) GC results, (b)MS results.

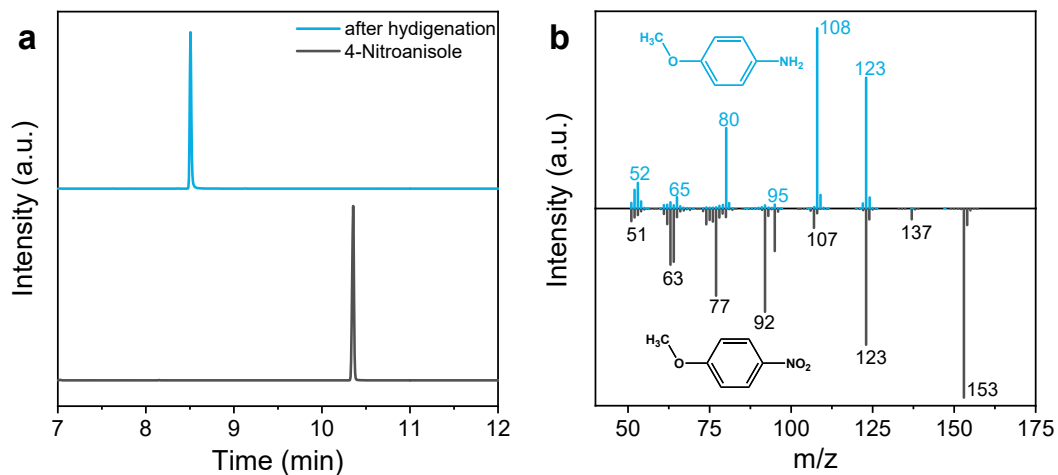


Figure S22. GC-MS results of 4-nitroanisole before and after hydrogenation. (a) GC results, (b)MS results.

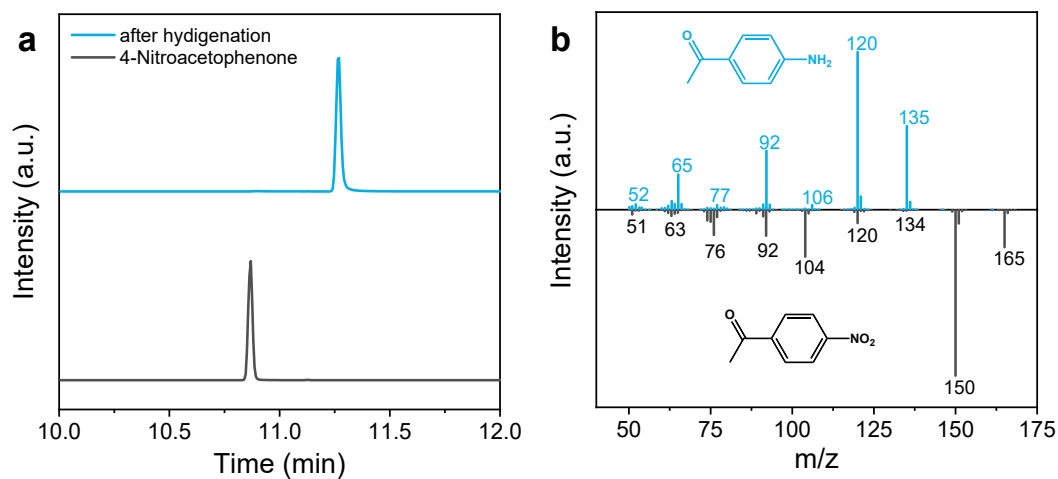


Figure S23. GC-MS results of 4-nitroacetophenone before and after hydrogenation. (a) GC results, (b)MS results.

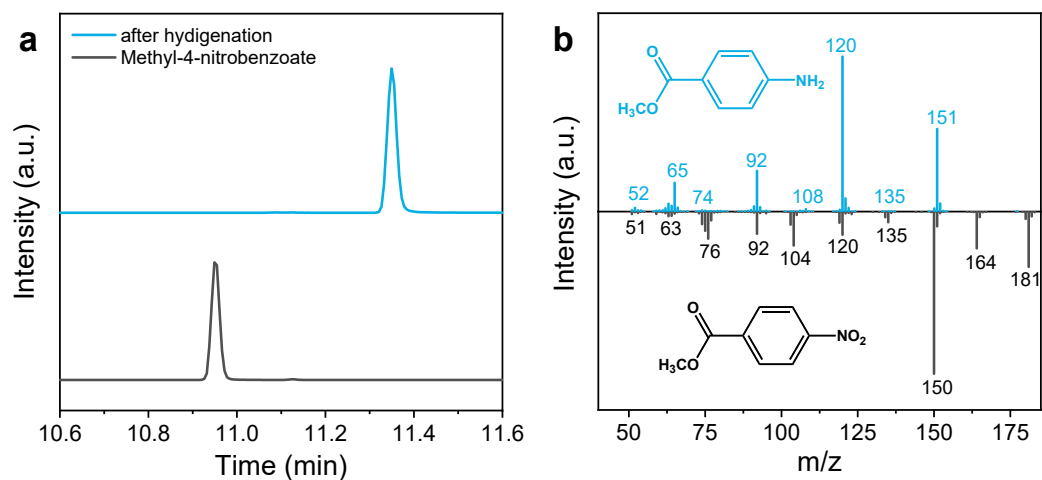


Figure S24. GC-MS results of methyl-4-nitrobenzoate before and after hydrogenation. (a) GC results, (b)MS results.

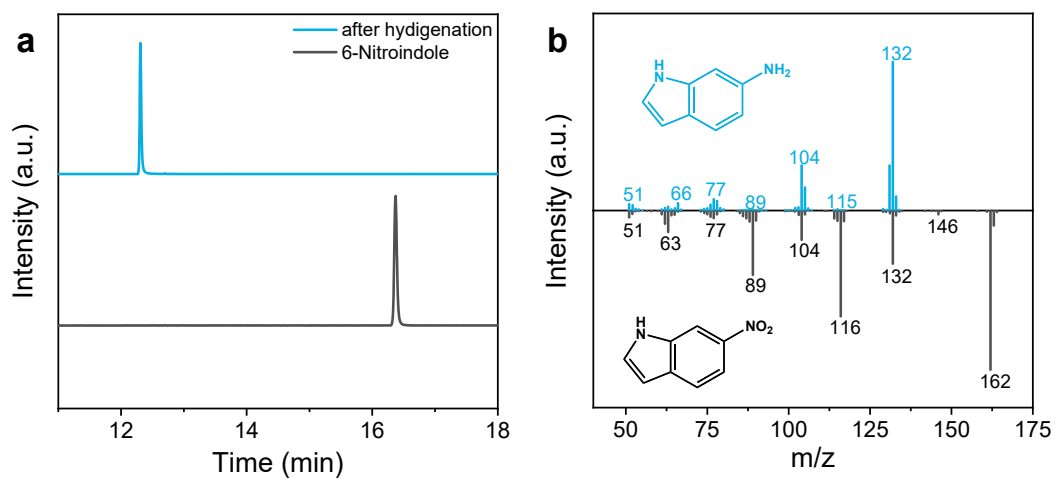


Figure S25. GC-MS results of 6-nitroindole before and after hydrogenation. (a) GC results, (b)MS results.

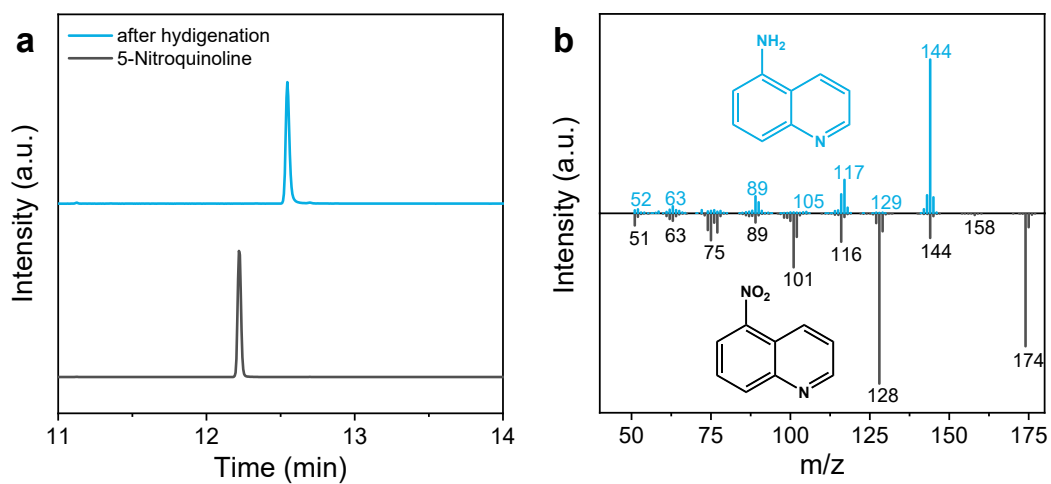


Figure S26. GC-MS results of 5-nitroquinoline before and after hydrogenation. (a) GC results, (b)MS results.

2. Supplementary Tables

Table S1. The (111) facet lattice fringes spacings of Pt, Ru, Cu, Ni, Co monometallic and PtRuCoCuNi/CNFs catalysts.

Crystal facets	PtRuCoCuNi/CNFs (d/nm)	Pt (d/nm)	Ru (d/nm)	Cu (d/nm)	Ni (d/nm)	Co (d/nm)
(111)	0.234	0.227	0.221	0.209	0.204	0.205

Table S2. The total load and mono-metal load of catalysts.

Catalysts	Total load (wt%)	Pt (wt%)	Ru (wt%)	Co (wt%)	Cu (wt%)	Ni (wt%)
PtRuCoCuNi/CNFs	24.46	10.12	5.28	2.85	3.09	3.12
Pt/CNFs	29.89	29.89	/	/	/	/
Ru//CNFs	20.72	/	20.72	/	/	/
Co/CNFs	17.71	/	/	17.71	/	/
Cu/CNFs	18.28	/	/	/	18.28	/
Ni/CNFs	12.01	/	/	/	/	12.01

Table S3. Reaction conditions and catalytic performance of different catalysts in p-CNB hydrogenation reaction

Catalysts	Solvent	T/°C	P/MPa	Con./%	Sel./%	TOF*/h ⁻¹	Ref.
<i>pd</i> -Pt@Cu(0.11)/TiO ₂	ethanol	80	1	100	100	1941.5	1
Fe@C-2	methanol	100	1.15	100	>99	22.9	2
15Cu@SiO ₂	ethanol	110	2	100	99.3	75.4	3
PtCuCo/γ-Al ₂ O ₃	ethanol	60	0.5	99.7	97.3	743.3	4
Pd _{0.53} Cu _{0.47} /NC	ethanol	60	1	100	98.8	1515.2	5
Co ₁ @NC-(SBA)	ethanol	90	1	99	99	32.6	6
Pt ₂ /mpg-C ₃ N ₄	isopropanol	100	1	93	100	623.32	7
Co@CN@HZM	H ₂ O	100	2	69.2	90	29.9	8
Co ₁ /NSC-AT	methanol+ H ₂ O	85	0.5	100	>99	59.9	9
PdsNC/PN-CeO ₂	methanol	80	0.5	70	95.8	744.9	10
Pd/N-CMK-3	/	85	1	100	87	1773.7	11
Pd-MS-50-TMS	/	85	3.45	100	99.9	2529.2	12
NiMo-10.7	/	80	0.1	99.7	96.2	---	13
PtRuCoCuNi/CNFs	ethanol	25	1	100	100	489.4	This work
PtRuCoCuNi/CNFs	/	25	1	100	100	12.2	This work

$$TOF = \frac{n_{p-CNB}}{n_{active\ metal} \times h}$$

*:

Table S4. Change in binding energy of catalyst before and after heat treatment.

	HEA-25	HEA-300	HEA-500	HEA-700
Pt ⁰ 4f _{7/2}	71.77	71.93	72.03	71.79
Ru ⁰ 3p _{3/2}	462.09	461.88	461.67	461.88
Co ⁰ 2p _{3/2}	778.76	778.58	778.59	778.65
Cu ⁰ 2p _{3/2}	932.69	932.30	932.25	932.41
Ni ⁰ 2p _{3/2}	853.28	853.52	853.42	853.42

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