Supporting Information

Ultra-low Temperature Direct reconstruction of Biomass Fermentation Ethanol to Higher Alcohols in Water over Thermostable Hcp-Ni

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Table S1. Chemical compositions and textural properties of the catalysts.

Catalysts	BET Area (m^2/g)	Pore Size (nm)	Ni (wt%)	N (wt%)	Particle size (nm)
hcp/fcc-Ni@C-1/1-450	59	5.1	78.8	2.7	10.0
hcp/fcc-Ni@C-1/2-450	191	2.8	47.9	5.6	4.62
hcp/fcc-Ni@C-1/4-450	158	2.5	26.5	7.9	3.22
hcp/fcc-Ni@C-1/2-400	49	5.3	44.7	7.1	4.13
hcp/fcc-Ni@C-1/2-500	187	2.8	54.9	5.2	4.31
hcp/fcc-Ni@C-1/2-600	175	3.0	62.9	4.2	5.53

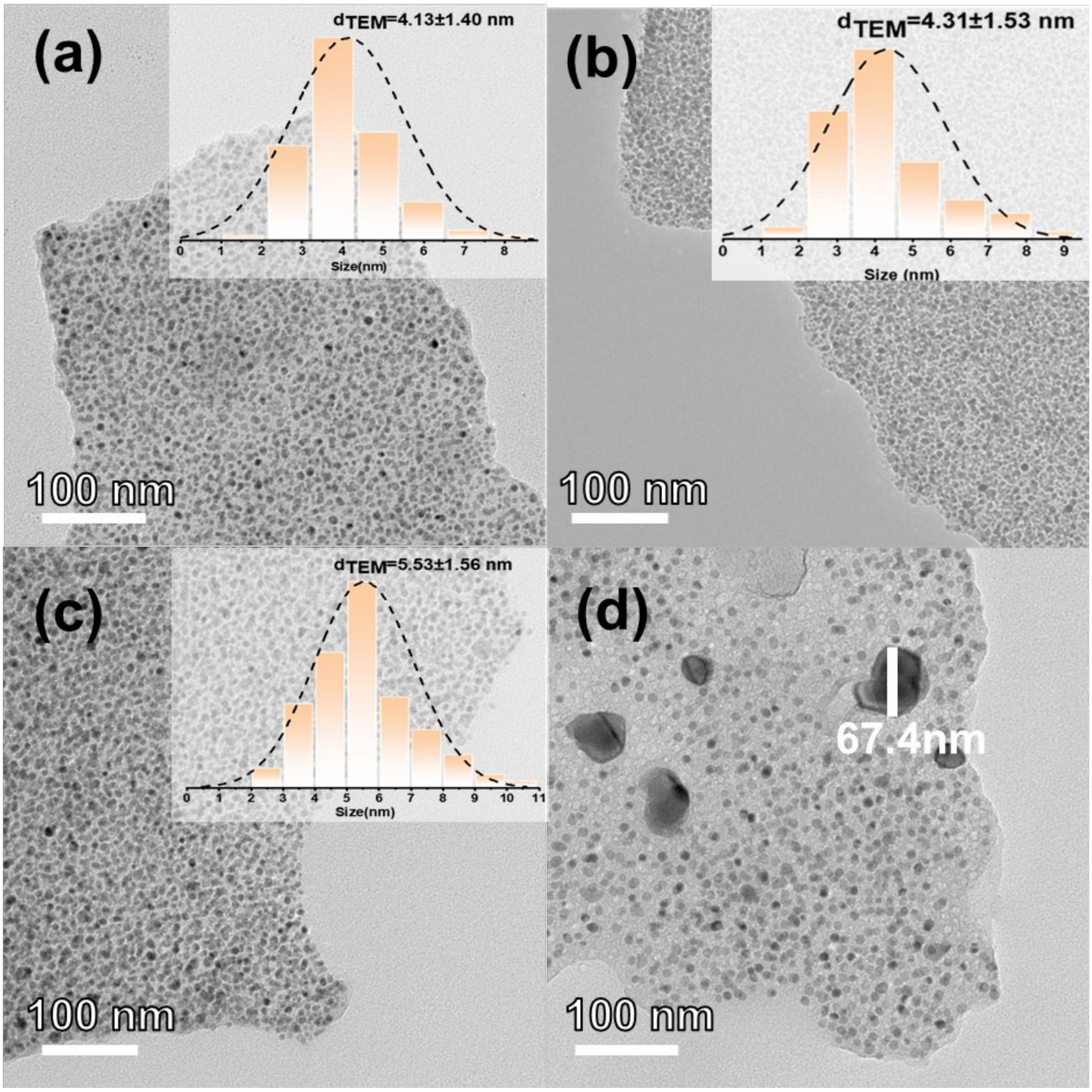

Figure S1. TEM image of hcp/fcc-Ni@C-1/2-T (T=400 ºC, 500 ºC, 600 ºC, 700 ºC)

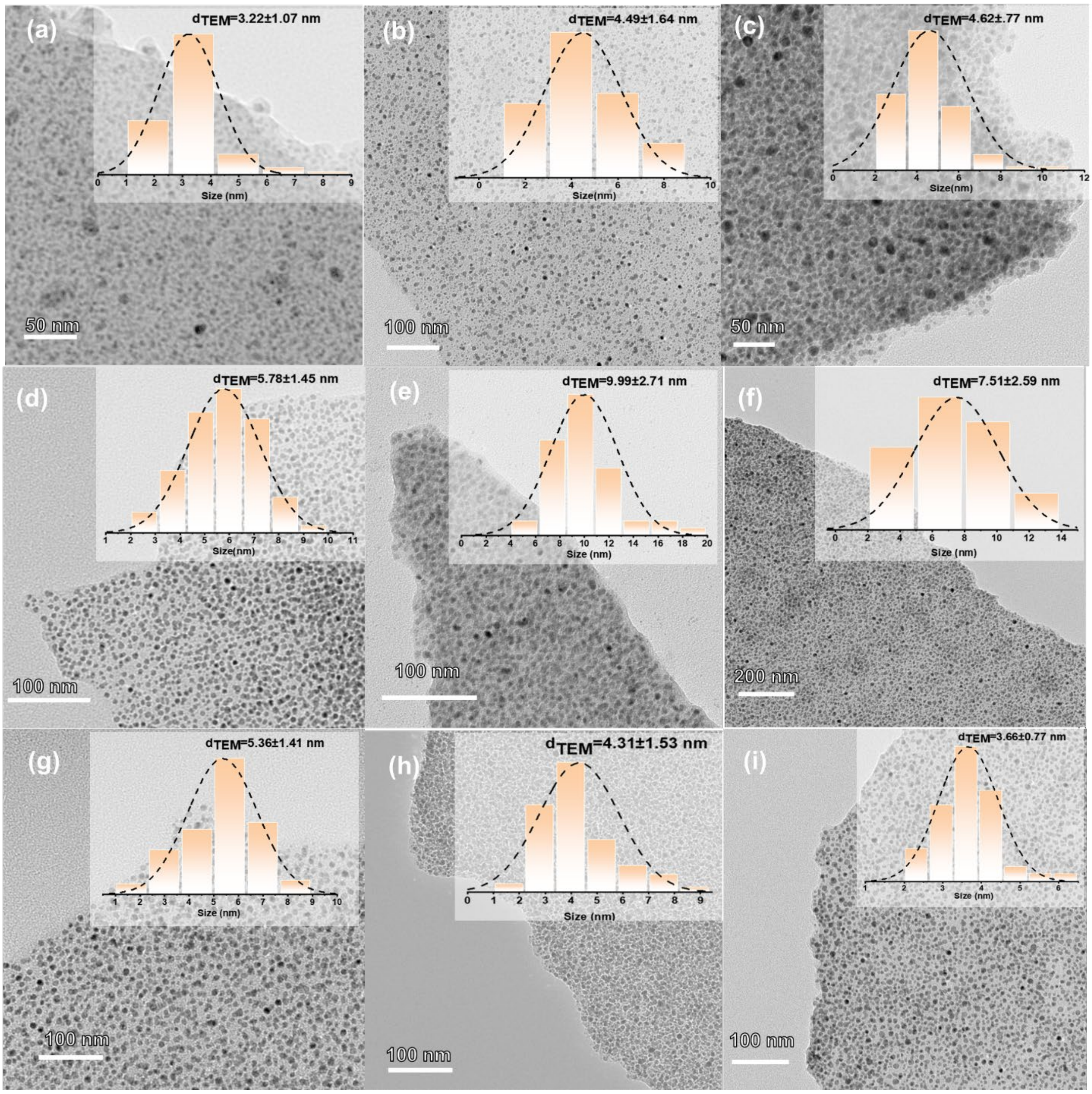

Figure S2. (a-e) TEM image of hcp/fcc-Ni@C-X-450 (1/4, 1/3, 1/2, 1/1.5, 1/1); (f-i) TEM image of hcp/fcc-Ni@C-1/2-500 with different molecular weight of PVP (Mw=8000, 24000, 58000, 1300000)

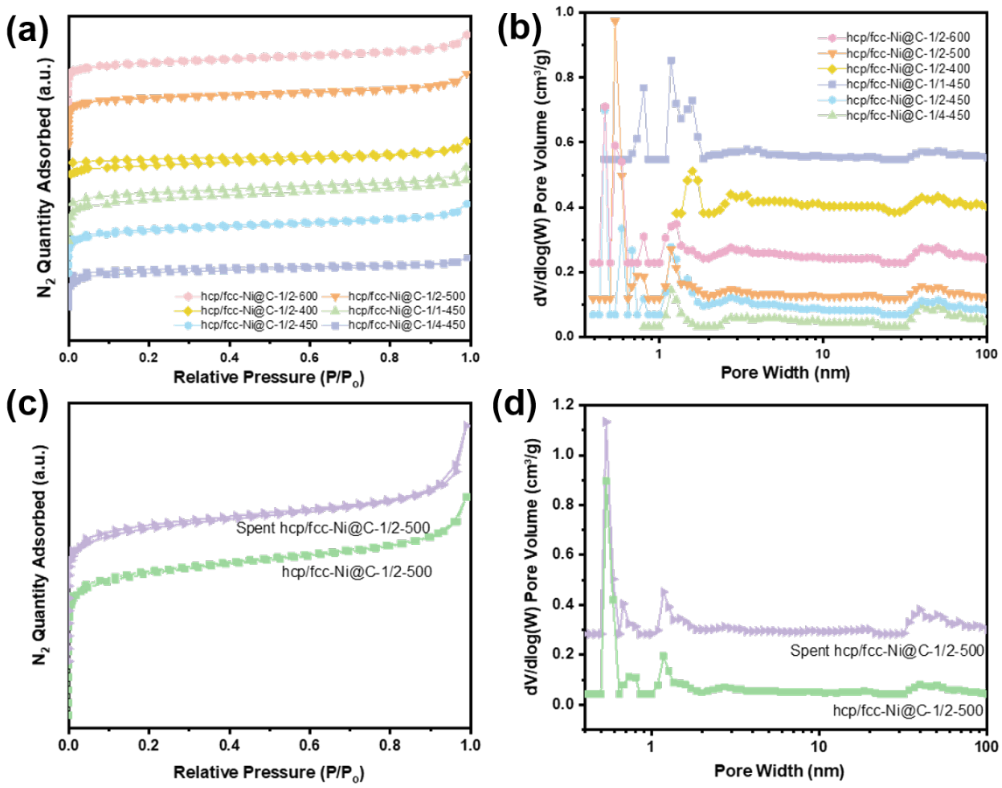

Figure S3. (a) N_2 adsorption/desorption isotherms and (b) pore distributions of hcp/fcc-Ni@C-X-T (X=1/1, 1/2, 1/4; T=400, 450, 500, 600); (c) N_2 adsorption/desorption isotherms and (d) pore distributions of fresh and spent hcp/fcc-Ni@C-1/2-500.

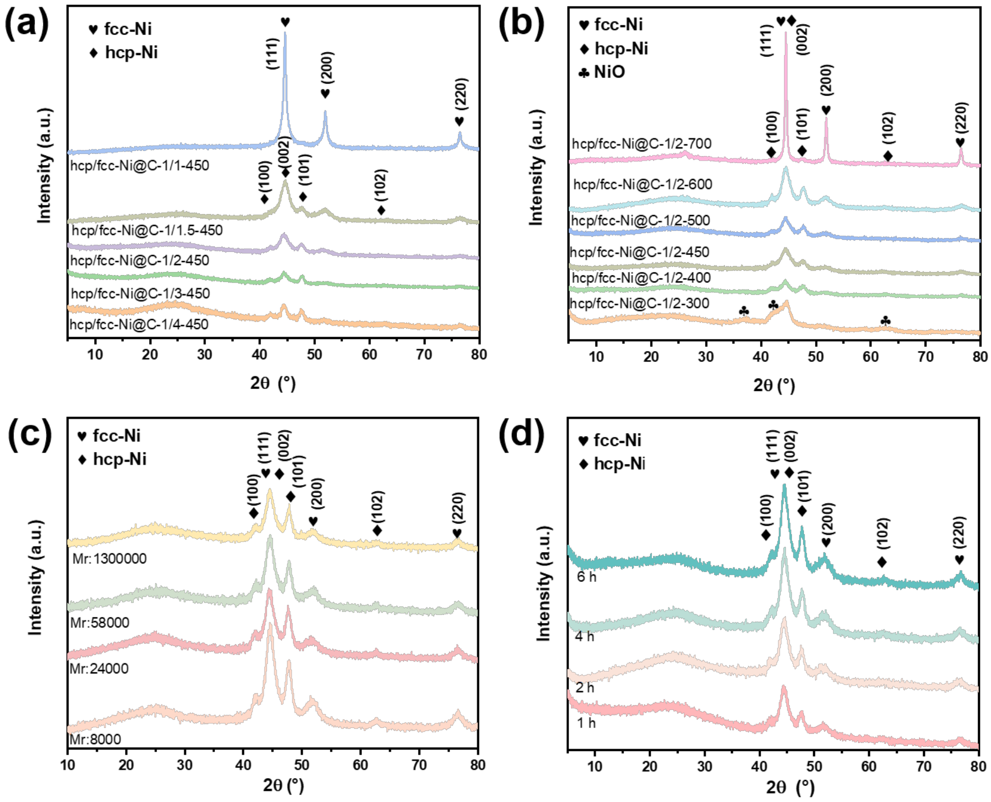

Figure S4. The XRD patterns and XPS spectra of hcp/fcc-Ni@C-X-T catalysts: (a) hcp/fcc-Ni@C-X-450 catalysts with different Ni/PVP molar ratio, (b) hcp/fcc-Ni@C -1/2-T catalysts prepared with different carbonization temperature, (c) hcp/fcc-Ni@C-1/2-500 catalysts with different molecular weight of PVP;(d) hcp/fcc-Ni@C-1/2-500 catalysts with different carbonization duration from 1h to 6h.

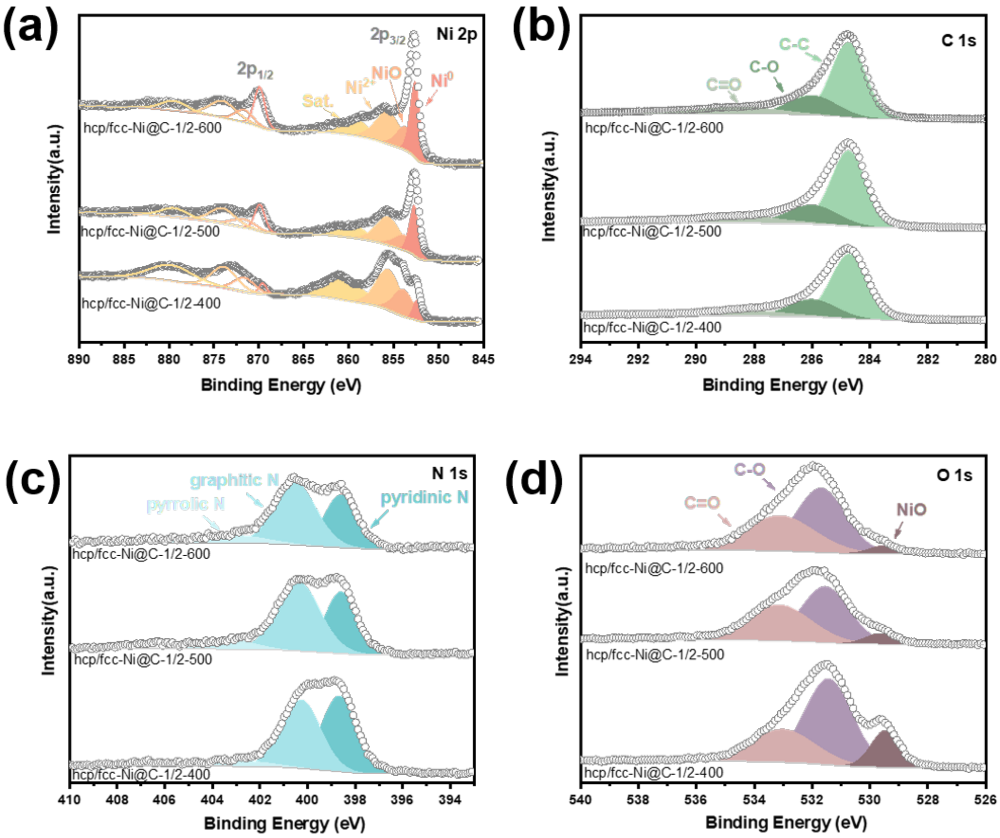

Figure S5. XPS spectra of hcp/fcc-Ni@C-1/2-T catalysts synthesized under different carbonization temperatures: (a) Ni 2p spectra, (b) C 1 s spectra, (c) N 1 s spectra, (d) O 1s spectra.

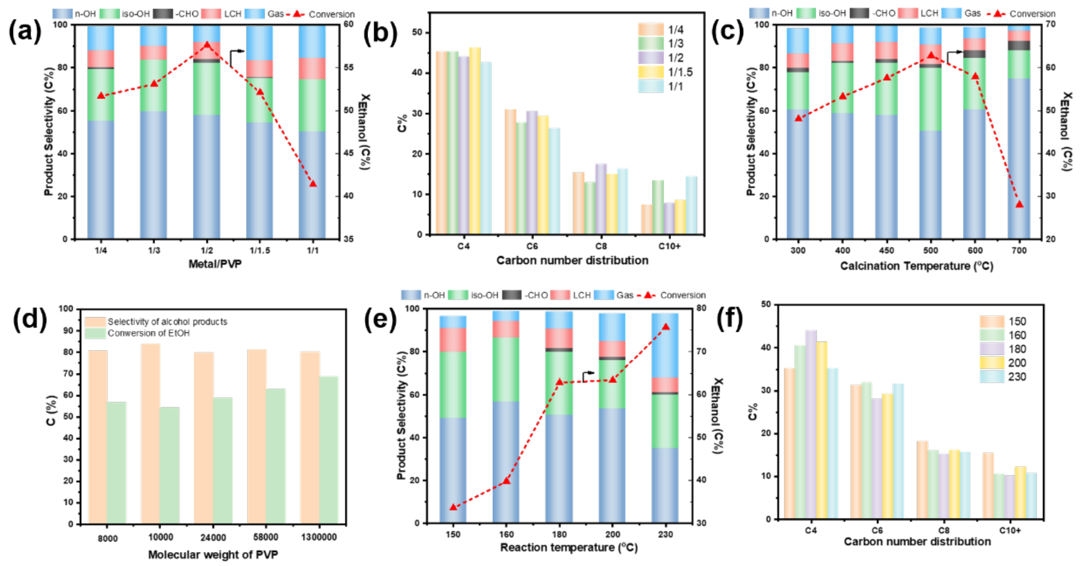

Figure S6. Overall catalytic performance of ethanol aqueous reconstruction over hcp/fcc-Ni@C catalysts (Reaction conditions: 0.3 g catalysts, 0.87 g NaOH, 20g fermentation ethanol solution (50 wt.%); 180 ◦C,12 h: (a) hcp/fcc-Ni@C-X-450 catalysts, (b) carbon number distribution of (a), (c) hcp/fcc-Ni@C-1/2-T catalysts, (d) hcp/fcc-Ni@C-1/2-500 catalysts with different molecular weight of PVP. (e) Catalytic performances of hcp/fcc-Ni@C-1/2-500 catalysts under different reaction temperatures (Reaction conditions: 0.3 g catalysts, 0.87 g NaOH, 20g fermentation ethanol solution (50 wt.%), 150-230 ℃, 12 h. (f) carbon number distribution of (e).

Table S2. Catalytic performance of ethanol aqueous reconstruction over hcp/fcc-Ni@C-1/2-500 catalysts for 10 recycle runs.

Recycle	Conversion (%)	Carbon balance (%)	Selectivity					
			n-OH	iso-OH	CHO	LCH	Gas	Other
1	62.8	86.0	50.5	29.4	1.7	9	8	1.4
2	62.9	90.8	49.2	27.8	1.5	9.6	10.4	1.5
3	63.8	84.9	49	28.1	2	10.9	8.5	1.5
4	64.5	88.7	49.5	28	2.3	8.5	9.5	2.2
5	65.7	85.6	48.1	31.1	2.7	9.6	7.1	1.3
6	65.7	85.3	48.6	31.6	1.8	9.8	7.2	0.9
7	64.5	84.9	49.4	31.1	1.4	9.5	7.5	1.1
8	67.2	86.4	47.8	31.8	1.6	9.5	8.3	1
9	67.8	85.9	47.2	32.3	2	9.5	7.1	1.9
10	65.9	87.6	45.6	32.3	3.3	10.5	6.5	1.9

(Reaction conditions: 0.3 g catalysts, 0.87 g NaOH, 20g fermentation ethanol solution (50 wt.%), 180 ℃ for 12 h. *n/iso*-OH: C4+ n/iso-alcohol, -CHO: C4+ aldehyde, LCH: C6+ hydrocarbons, Gas: H_2, and C1-C4 hydrocarbons)

Table S3. Comparison of catalytic activities in aqueous ethanol reconstruction over hcp/fcc-Ni@C-1/2-500 catalysts, fcc-Ni@C-1/2-500 catalysts and commercial noble metal catalysts

Catalyst	Conversion (%)	Carbon balance (%)	Selectivity					
			n-OH	iso-OH	CHO	LCH	Gas	Other
5% Pd/C	27.1	90.0	36.7	40.2	0	23	0	0.1
5% Pt/C	9.7	91.4	73.3	26	0	0	0.8	0
5% Ru/C	18.6	98.0	47.9	5	0	0	47	0
fcc-Ni@C	38.5	92.5	60.6	23	2.5	7.1	6.8	0
hcp/fcc-Ni@C	52.3	90.8	52.4	30.5	6.5	9.4	0.8	0.4

(Reaction conditions: 0.3 g catalysts, 0.87 g NaOH, 10g fermentation ethanol solution (50 wt.%), 130 ºC for 36 h)

Table S4. Evaluation of hcp/fcc-Ni@C-1/2-500 catalysts activity at near-ambient temperatures with prolonged reaction time.

Reaction temperature (ºC)	Reaction time (h)	Conversion (%)	Carbon balance (%)	Selectivity				
				n-butanol	2-ethyl butanol	n-hexanol	C8+ alcohol	Gas
80	36	5.9	94.4	99.9	0	0	0	0.1
	72	9.1	99.0	62	37.7	0	0	0.3
	108	11.7	95.3	53	24.7	17.9	0	0.4
100	36	9.1	95.4	43.96	21.05	11.08	23.91	0.2
	72	13	91.7	51.45	16.87	9.26	22.42	0.6
	108	17.6	92.1	50.25	15.94	8.5	24.66	0.9

(Reaction conditions: 0.3 g catalysts, 0.87 g NaOH, 10g fermentation ethanol solution (50 wt.%))

Table S5. Evaluation of hcp/fcc-Ni@C-1/2-500 catalysts activity at near-ambient temperature with different concentration of ethanol solution.

Content of EtOH	Conversion (%)	Carbon balance (%)	Selectivity				
			n-butanol	2-ethyl butanol	n-hexanol	C8+ alcohol	Gas
3%	1.2	98.0	100	0	0	0	0
10%	3.1	98.2	100	0	0	0	0
20%	4.6	96.5	62	37.7	0	0	0.05
40%	7.8	93.2	53	24.7	17.9	0	0.3

(Reaction conditions: 0.9 g catalysts, 0.87 g NaOH, fermentation ethanol solution (3-40 wt.%), 80 ºC for 72 h)

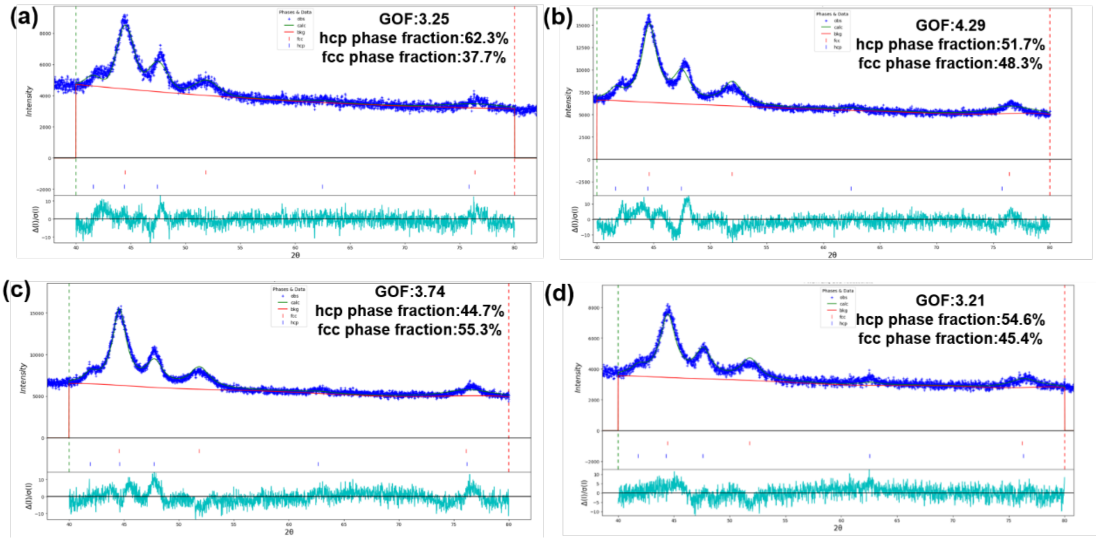

Figure S7. Rietveld refined XRD pattern of hcp/fcc-Ni@C-500 of different calcination time in N_2: (a) 1h, (b) 4h, (c) 6h,; (d) Rietveld refined XRD pattern of spent hcp/fcc-Ni@C-500 after 10 recycles. The legends are: Obs (observed) and Calc (calculated) patterns, diff (difference) plot between Obs and Calc), and bck (background plot).

Table S6. Chemical compositions and textural properties of the spent catalysts.

Samples	BET Area (m^2/g)	Pore Size (nm)	hcp-Ni content (%)
spent-hcp/fcc-Ni@C-1/2/500	176	3.2	54.6
hcp/fcc-Ni@C-1/2/500	187	2.8	60.7

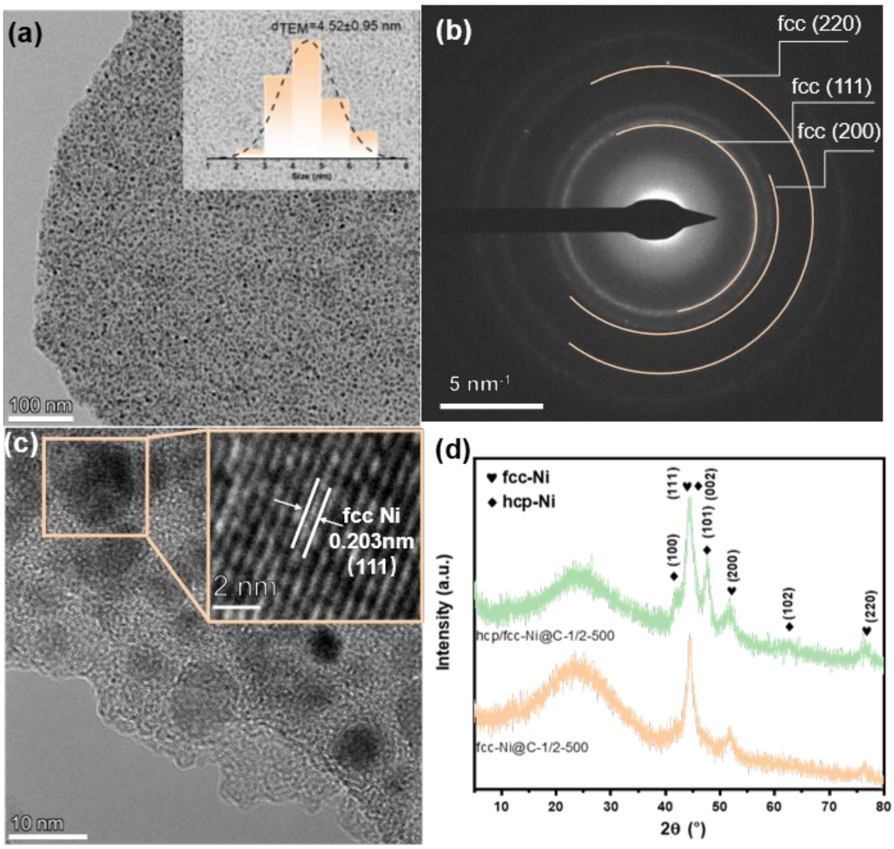

Figure S8. (a) TEM image of fcc-Ni@C-1/2-500; (b) SAED pattern corresponding to (a); (c) HR-TEM image of fcc-Ni@C-1/2-500; (d) The XRD patterns of hcp/fcc-Ni@C-1/2-500 and fcc-Ni@C-1/2-500.

Table S7. Catalytic activities of ethanol upgrading to higher alcohols in reported researches.

Catalyst	Reaction temperature(°C)	EtOH Conv. (C%)	C4+ alcohol Selectivity (C%)	Reference
1.04wt% Ru/Mg_3Al1-LDO-P-A.	350	29.6	82.6	Applied Catalysis B-Environmental,2022. 309.
$Co_{0.15}Mg_{2.85}AlOx$	250	32.9	95.4	Green Chemistry,2023. 25: 2653-2662.
Cu_1Ni_7-PMO	320	47.9	72	ACS Sustainable Chemistry & Engineering,2017. 5: 1738-1746.
[Ru]-6	150	73.4	100	J Am Chem Soc,2016. 138: 9077-9080.
[Mn]-1	160	11.2	92	J Am Chem Soc,2017. 139: 11941-11948.
Ru-5	130	49	96	ACS Catalysis,2023. 13: 5449-5455.
BAP-0.25Ni	200	55.6	90.3	ACS Sustainable Chemistry & Engineering,2022. 10: 3466-3476.
Cu-HAP	250	36.6	86.7	Green Chemistry, Journal of Energy Chemistry,2022. 72: 306-317.
Cu-NiMgAlO	250	30	64.2	Journal of Energy Chemistry,2022. 72: 306-317.
CuMgAl (LDH)	325	59.3	82	ACS Catalysis,2022. 12: 12045-12054.
Ni-MgAlO	275	18.7	85	Journal of Catalysis,2016. 344: 184-193.
Ni-TiO2	210	49.2	69.7	ChemistrySelect,2020. 5: 8669-8673.
10%Ni15%CeO_2/AC	250	27.2	85.6	Industrial & Engineering Chemistry Research,2020. 59: 22057-22067.
[Ru(bipy^{OH})]	80	28	57	Organometallics,2021. 40: 1884-1888.
[(RPNP)-MnBr$(CO)_2$] (R = iPr, Cy, tBu, Ph or Ad)	150	50	50	ACS Catalysis,2018. 8: 997-1002.
Sn-Ni/CS	230	60	86.4	Applied Catalysis B-Environmental,2023. 321.
NiSn/ MgAlO	250	66.9	93.8	ACS Sustainable Chemistry & Engineering,2021. 9: 11269-11279.
NiSn@C(CA)	250	48.1	90.8	Energy Conversion and Management,2021. 249.
NiMo@C-3/1	240	89.4	84.6	Chemical Engineering Journal,2023. 461.
hcp/fcc-Ni@C-1/2-500	180	62.8	79.9	This work
	130	52.3	82.9	
	100	17.6	100	
	80	11.7	100	

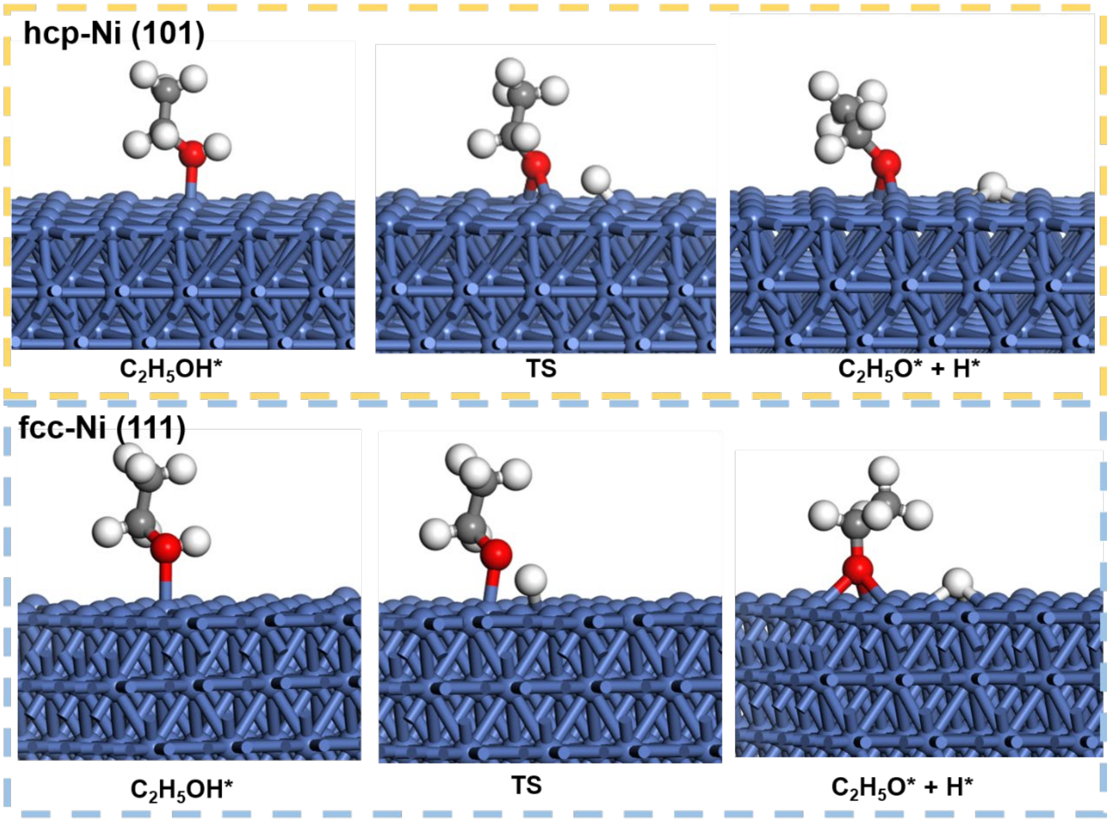

Figure S9. Configuration diagrams of C_2H_5OH*, transition state (TS) and C_2H_5O*+H* for the dehydrogenation and C-C cleavage of ethanol on the hcp-Ni (101) and fcc-Ni (111) models.

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