Electronic Supplementary Information

Pyramidal Ni Nanoparticles with Highly Coordinated Surfaces Enabled by Metal-Support Interaction Regulation for Efficient H$_2$ Production from NH$_3$

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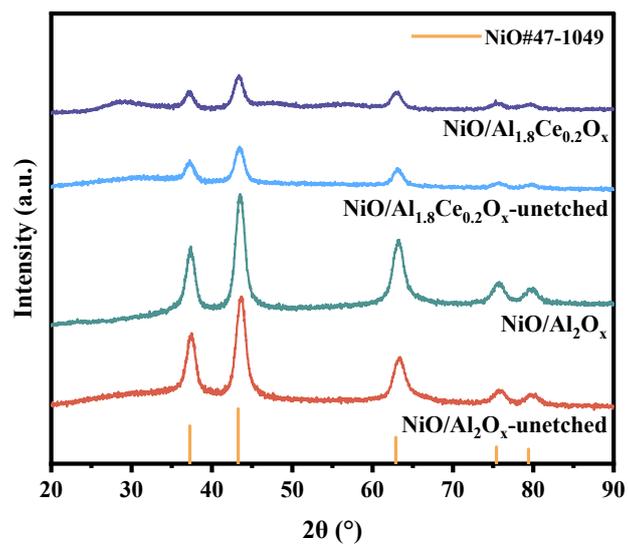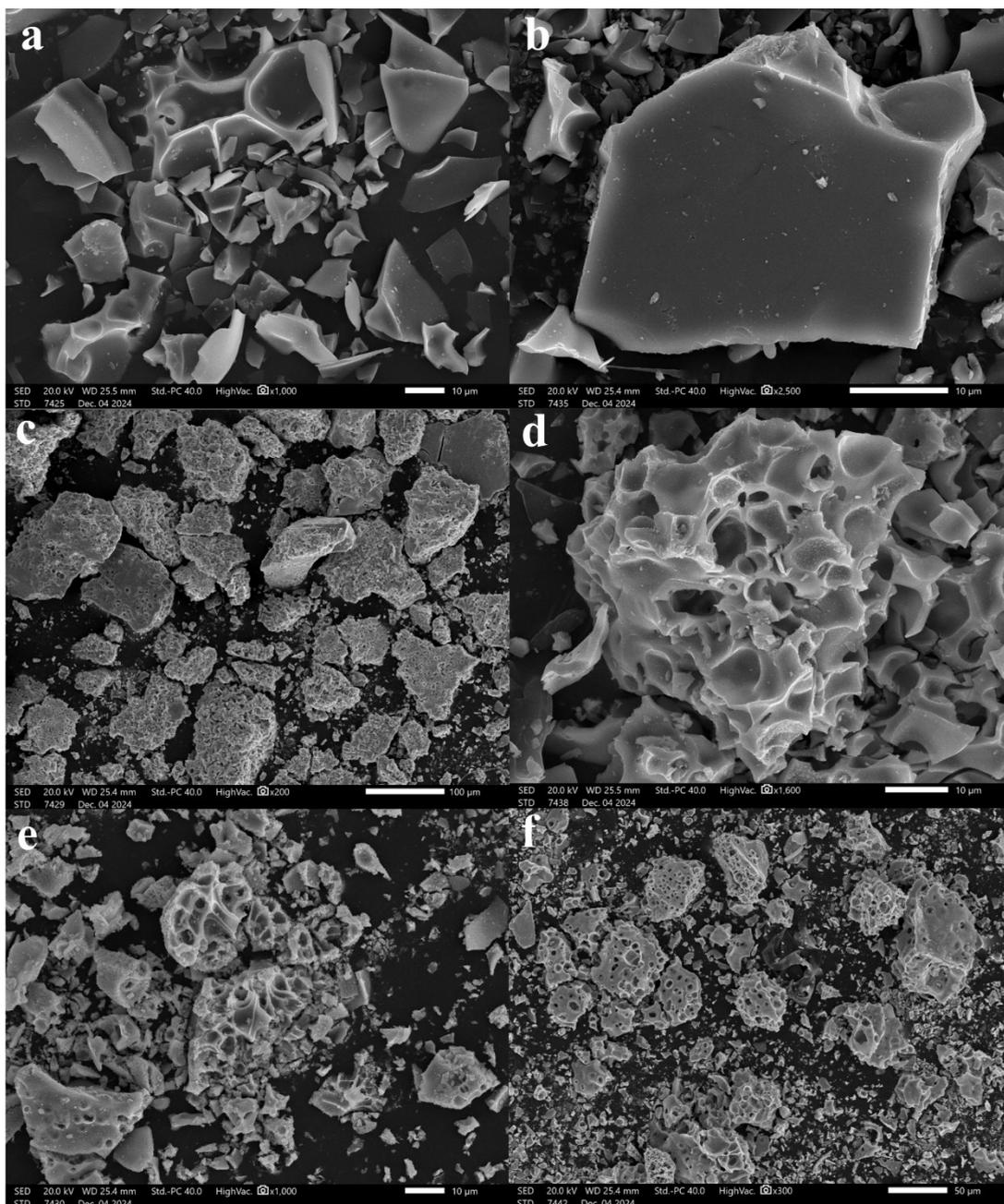

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Email: jkguo@hnu.edu.cn (J.-K. Guo)
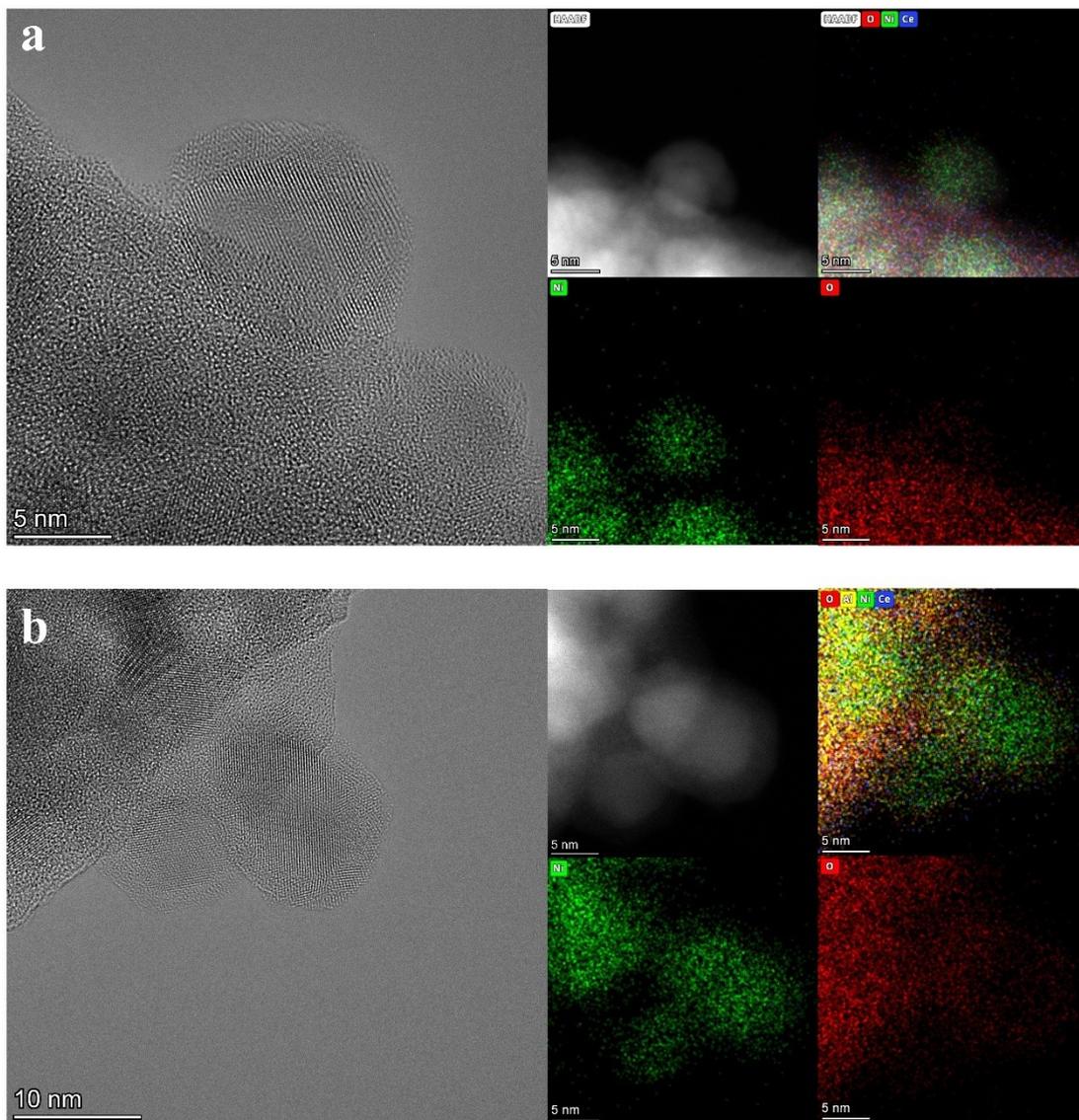
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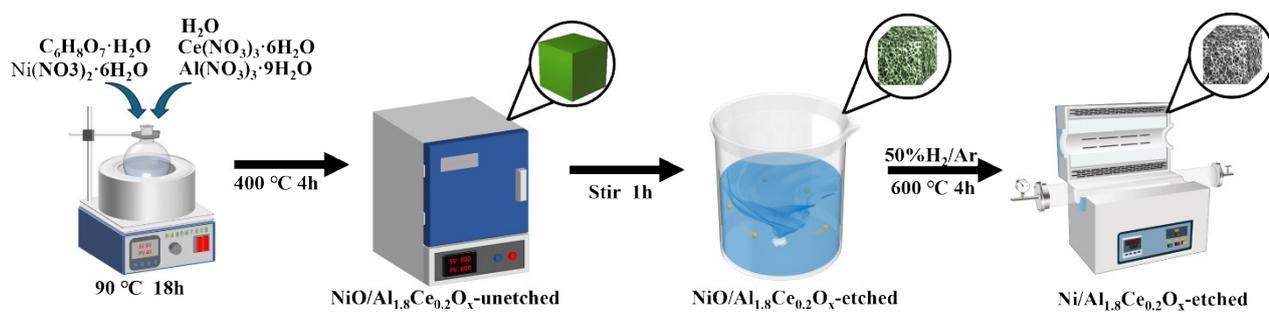
Scheme 1. Catalyst synthesis roadmap.

Figure S1. XRD spectra of oxide precursor before H_2/Ar pre-reduction.

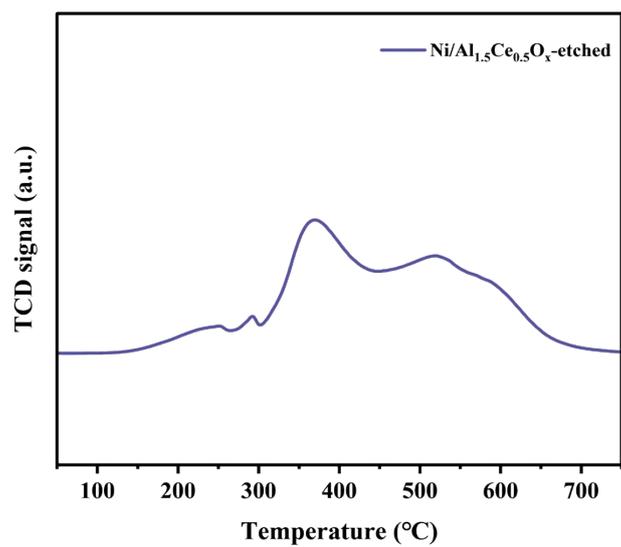**Figure S2.** SEM micrographs of catalysts. (a) Ni/Al_2O_x-unetched; (b) $Ni/Al_{1.8}Ce_{0.2}O_x$-unetched; (c) Before restoration of $Ni/Al_{1.8}Ce_{0.2}O_x$-etched; (d) Ni/Al_2O_x-etched; (e) $Ni/Al_{1.8}Ce_{0.2}O_x$-etched; (f) $Ni/Al_{1.5}Ce_{0.5}O_x$-etched.

Figure S3. HRTEM image and element mapping of Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-unetched.
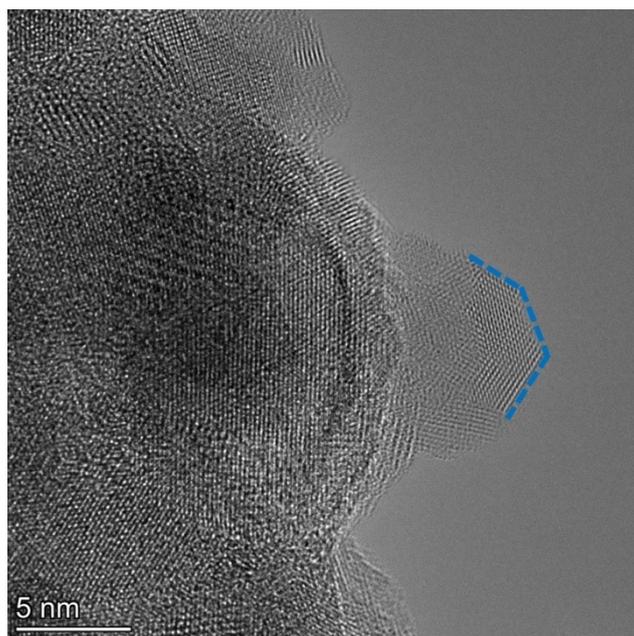
Figure S4. HRTEM image of Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched.

Figure S5. H_2-TPR of $Ni/Al_{1.5}Ce_{0.5}O_x$-etched.
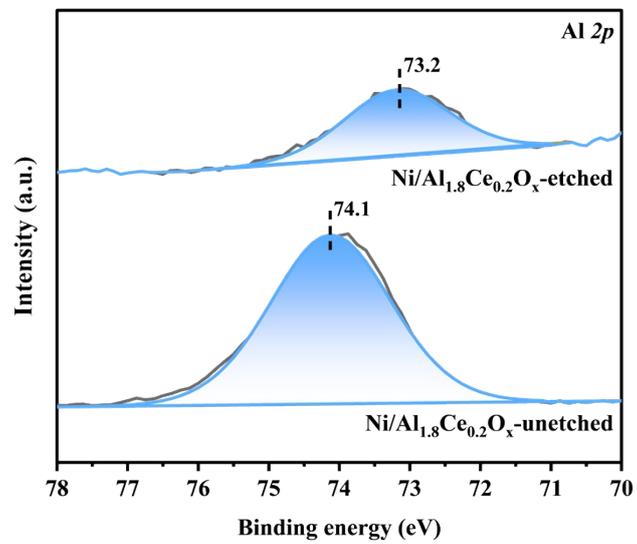
Figure S6. XPS peak deconvolution of Al *2p* spectra.
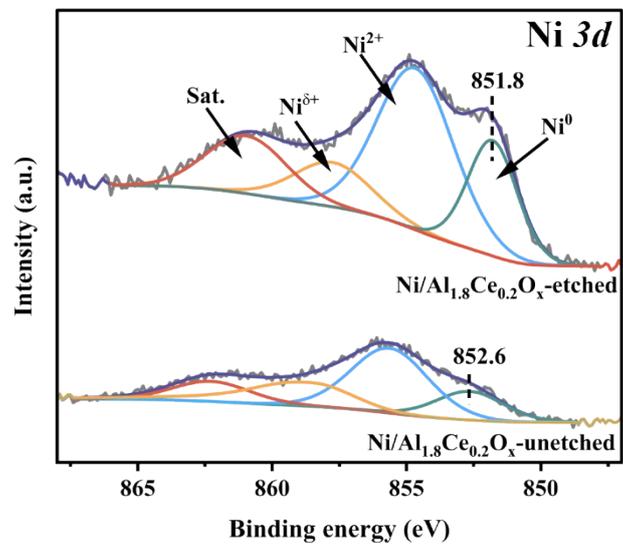
Figure S7. XPS peak deconvolution of Ni *3d* spectra.
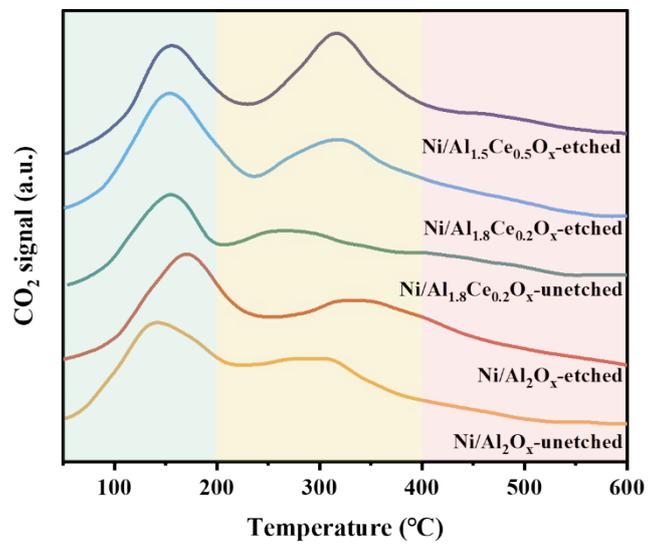
Figure S8. CO_2-TPD profiles.
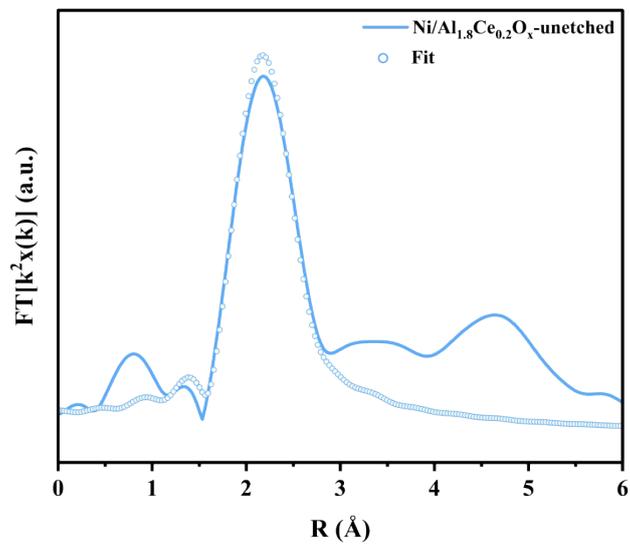
Figure S9. Ni K-edge XANES spectra of Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-untetched.
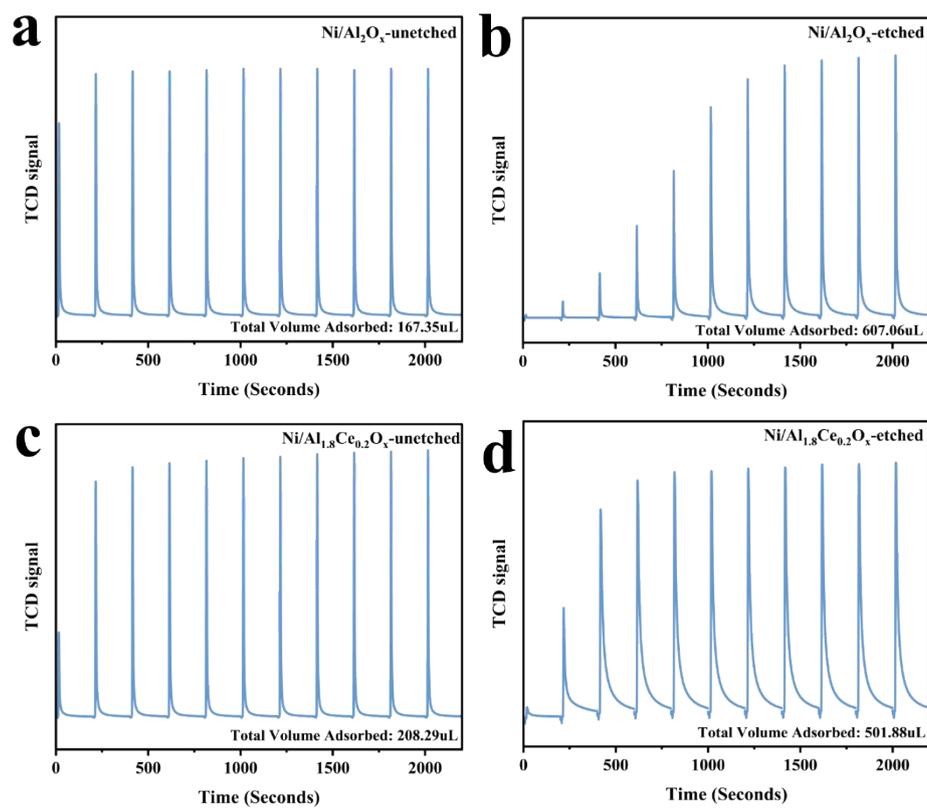
Figure S10. H_2 pulse profiles of (a) Ni/Al$_2$O$_x$-unetched, (b) Ni/Al$_2$O$_x$-etched, (c) Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-unetched,

(d) Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched.
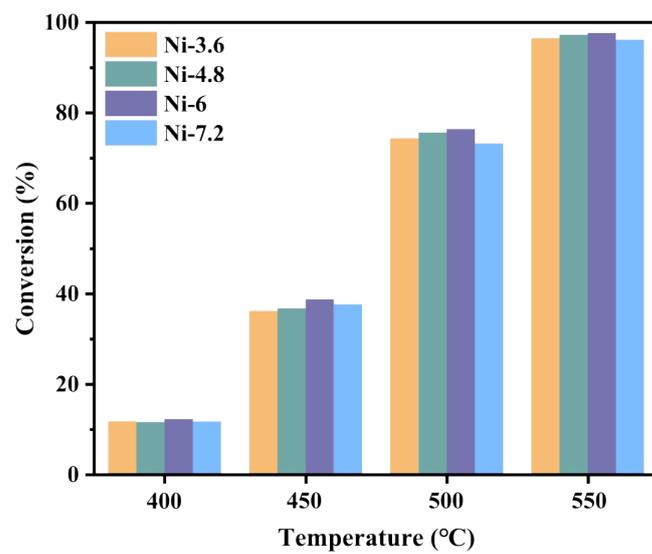
Figure S11. Catalytic performance of $Al_{1.8}Ce_{0.2}O_x$-etched with different Ni contents.
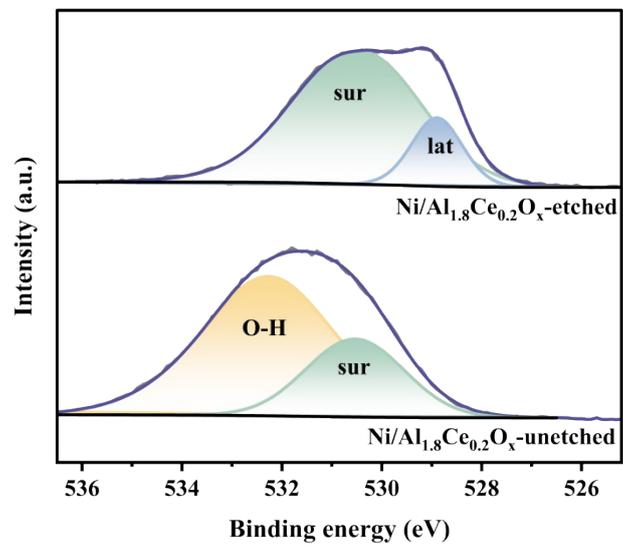
Figure S12. XPS peak deconvolution of O 1*s* spectra.
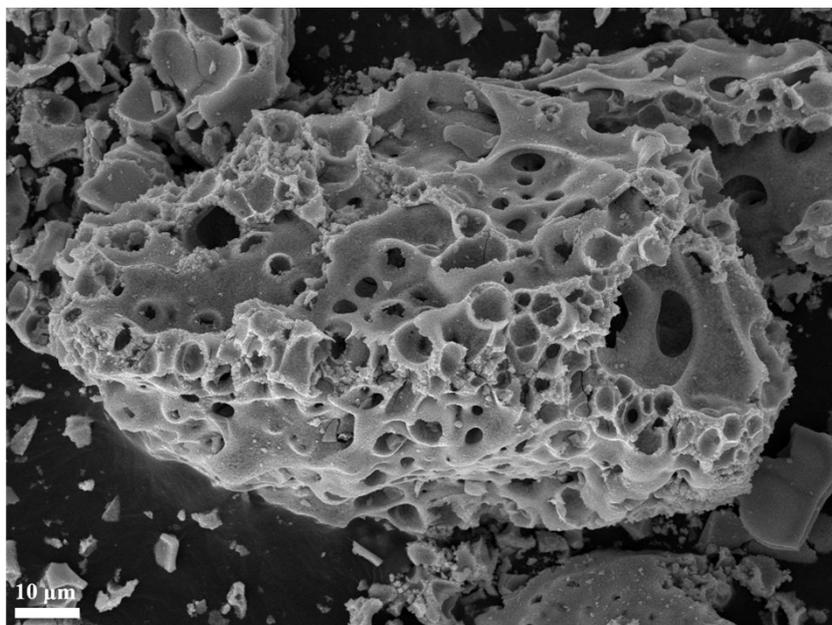
Figure S13. SEM image of Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched after long-term stability testing.
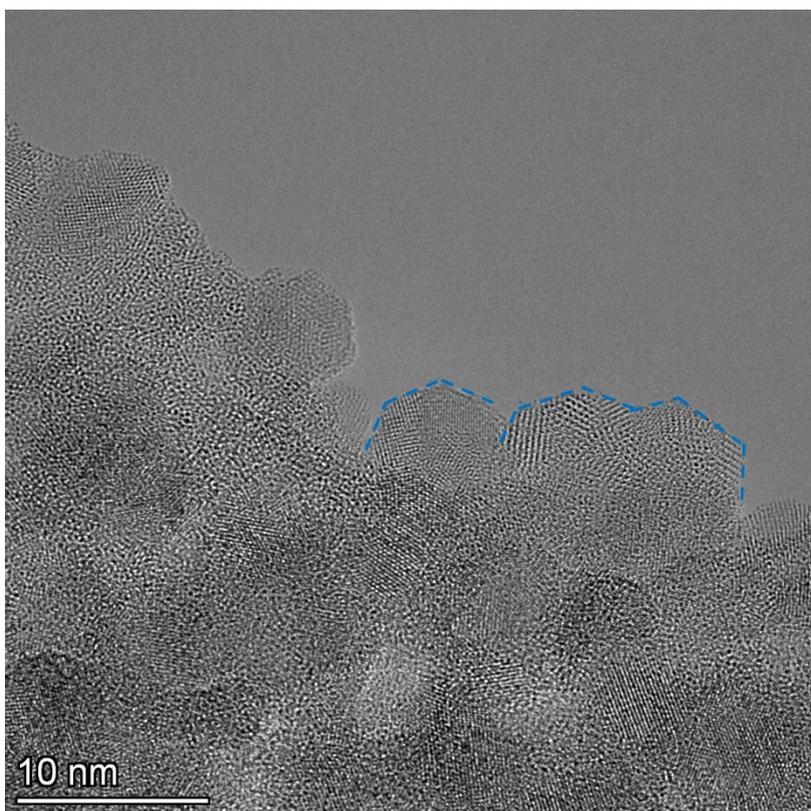
Figure S14. TEM image of Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched after long-term stability testing.
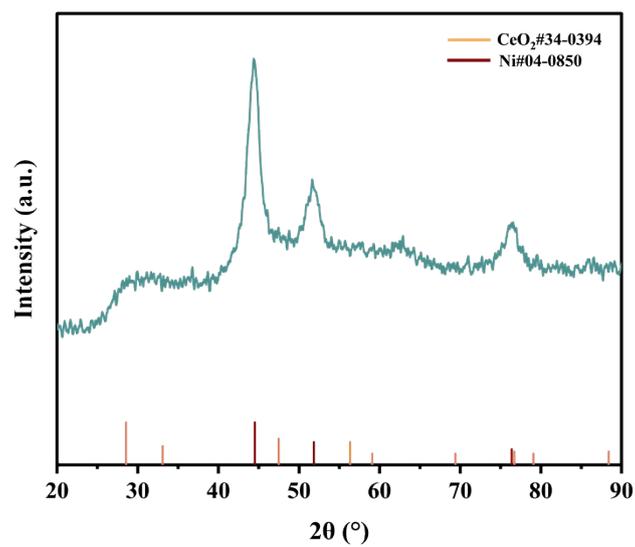
Figure S15. XRD spectra of Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched after long-term stability testing.
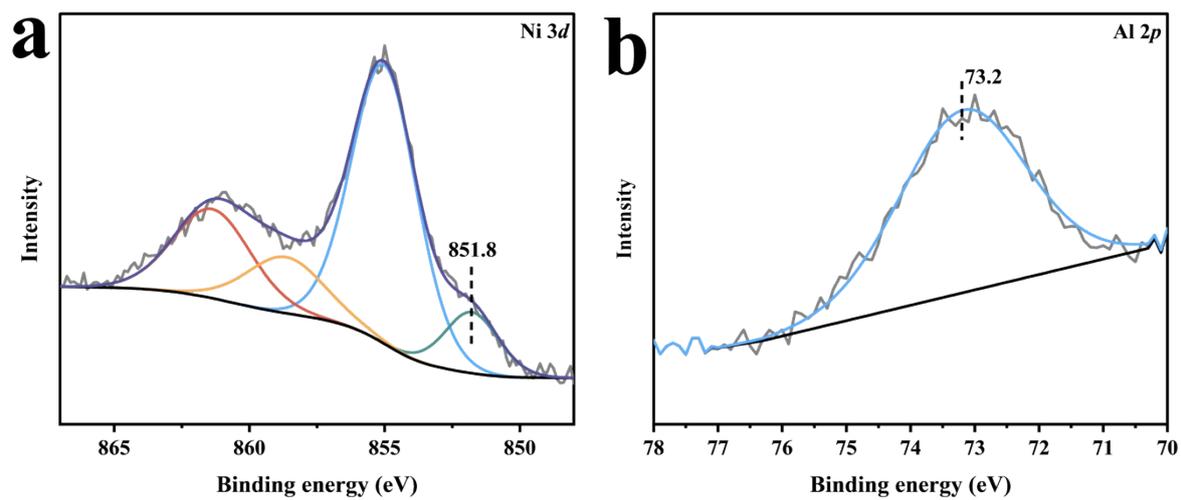
Figure S16. XPS spectra of Ni (a) and Al (b) of Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched after long-term stability testing.
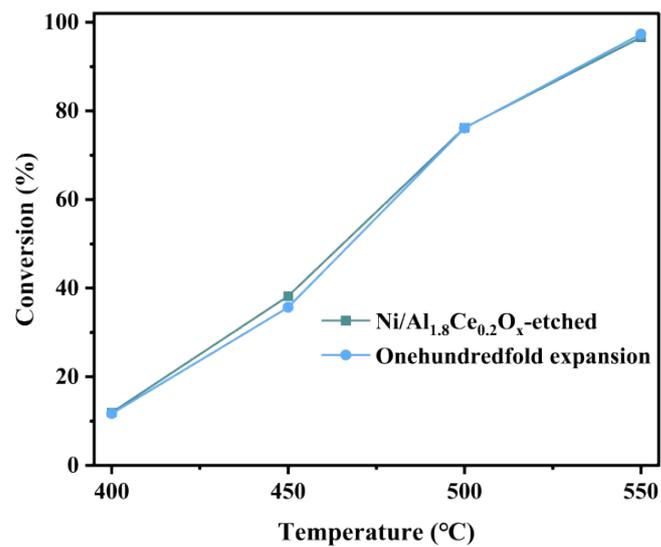
Figure S17. Catalytic performance of catalysts prepared at an enlarged scale.
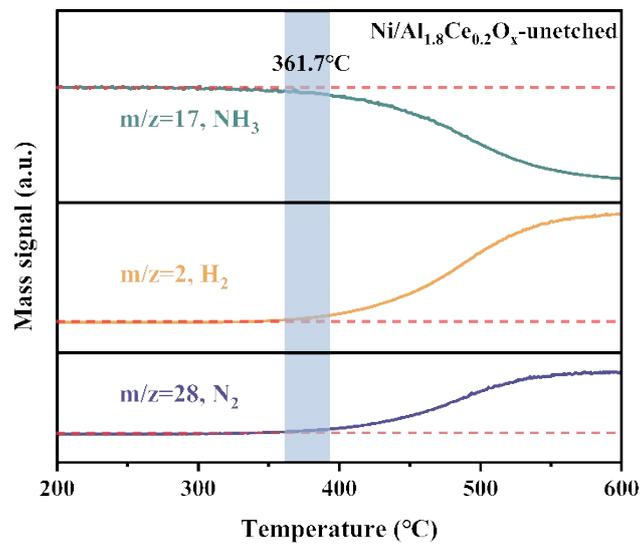
Figure S18. NH_3-TPSR profiles of $Ni/Al_{1.8}Ce_{0.2}O_x$-unetched.
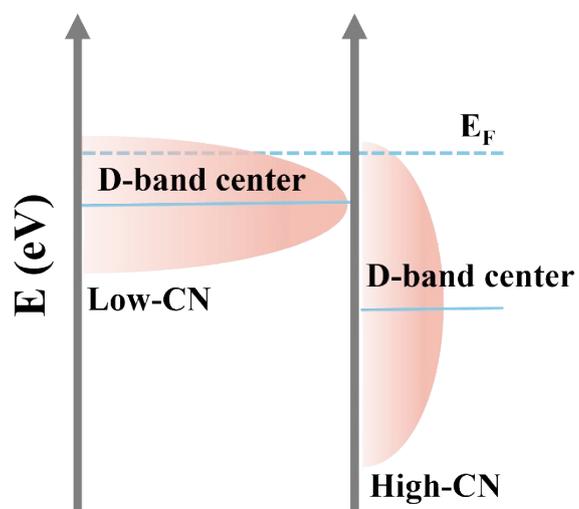
Figure S19. Schematic illustration of d-band center shifts of Ni with different CN.
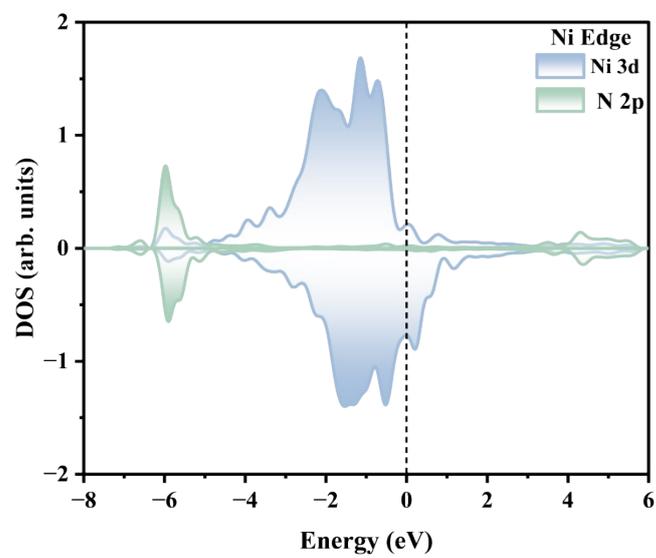
Figure S20. DOS spectra of Ni at edge sites.

Catalysts	Surface area (m$^2 \cdot$g^{-1}) [a]	Pore Volume (cm$^3 \cdot$g^{-1}) [a]	Average pore diameter (nm) [a]	Ni particle size [b]	Ni content (wt.%) [c]
Ni/Al$_2$O$_x$-unetched	96.49	22.17	7.86	9.02	32.00
Ni/Al$_2$O$_x$-etched	89.00	20.45	10.24	12.13	62.87
Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-unetched	92.56	21.27	5.59	11.06	28.93
Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched	45.24	10.39	12.38	13.18	53.31
Ni/Al$_{1.5}$Ce$_{0.5}$O$_x$-etched	31.94	7.34	12.24	14.84	39.96

Table S1. Physicochemical properties of various catalysts.

a. The textural properties of the catalyst were assessed using N$_2$ adsorption desorption isothermal measurements. The surface area was determined by the BET equation. Additionally, the pore volume and pore diameter were derived from the BJH desorption data.

b. The average Ni particle size was calculated by the Scherer equation.

c. The actual composition of the catalyst was determined based on ICP results.

Table S2. Local structure parameters of Ni derived from the EAXFS data.

Sample	Shell	CN[a]	R(Å)[b]	$\sigma^2(10^{-3}Å^2)$[c]	ΔE_0(eV)	R-factor (10^{-2})[d]
Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-unetched	Ni-Ni	6.59	2.54	2.76	-3.00	1.50
Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched	Ni-Ni	6.72	2.54	2.79	-2.64	1.66

a. CN = coordination number;

b. R = distance between absorber and backscatter atoms;

c. σ^2 = Debye-Waller factor;

d. R-factor indicates the goodness of the fit.

Table S3. Comparison of the catalytic performance of the prepared catalysts with reported Ni-based catalysts.

Catalysts	Ni content (wt.%)	Temperature (°C)	WHSV (mL·g_{cat}^{-1}·h^{-1})	conv. (%)	References
Ni/Al$_2$O$_x$-unetched	32.0	550	30000	47.7	This work
Ni/Al$_2$O$_x$-etched	62.9	550	30000	62.5	This work
Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-unetched	28.9	550	30000	55.1	This work
Ni/Al$_{1.8}$Ce$_{0.2}$O$_x$-etched	53.3	550	30000	96.6	This work
Ni/5MgLa	10	500	30000	40.1	1
NALC-60CA	20	550	30000	86.5	2
La$_{0.5}$Sr$_{0.5}$NiO$_3$-δ-600H$_2$	25.6	550	30000	87.7	3
Ni-DML-160	22.6	550	12000	98.0	4
Ni-CeO2(CSCS-3.0)	9.2	550	30000	81.0	5
Ni$_7$Y$_{2.5}$Al$_{0.5}$O$_x$	47.7	550	30000	92.1	6
Ni/SiO$_2$-AEH	-	600	30000	55.0	7
30Ni/SiC-700	-	550	30000	79.6	8
Ni/La$_2$O$_3$	40	550	6000	78.9	9
Ni-Ce/Al$_2$O$_3$	43.4	500	30000	63.9	10
Ni/SBA-15	10	500	30000	49.1	11
Ni/CeO$_2$-BN	10	550	30000	63.0	12
20Ni/Al$_1$Ce$_{0.05}$O$_x$	20	500	6000	50.8	13
CeO$_2$/Ni	59.4	500	30000	72.4	14
Ni/MgO CP	24.9	550	15000	91.0	15
Ni$_x$Mg$_{1-x}$O/CeO$_2$	30.0	525	30000	99.1	16

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