Supporting Information

Solvent-free Oxidation of Benzyl C-H to Ketone with Co-Ni Layered Double Hydroxide as Catalyst using O_2 as Sole Oxidant

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Table S1. ICP-OES results of CoNi-LDH with different feed ratio of Co/Ni.

Sample	Co (wt.%)	Ni (wt.%)	Co:Ni
Co_4Ni-LDH	29.8	18.0	1.7:1
Co_2Ni-LDH	27.3	29.0	0.94:1
CoNi-LDH	22.3	26.0	0.85:1
$CoNi_2$-LDH	18.0	36.8	0.5:1
$CoNi_4$-LDH	12.2	42.5	0.3:1

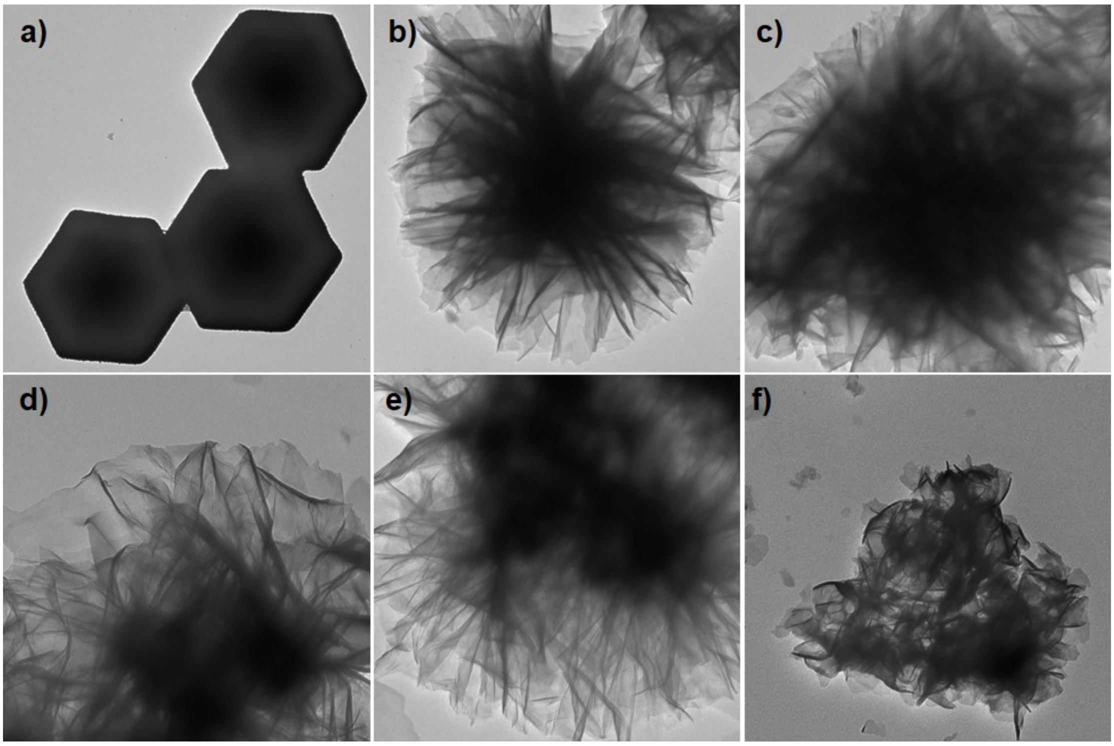

Fig. S1 The representative TEM images of a) ZIF-67; b) Co_4Ni-LDH; c) CoNi-LDH; d) $CoNi_2$-LDH; e) $CoNi_4$-LDH; f) α-$Ni(OH)_2$.

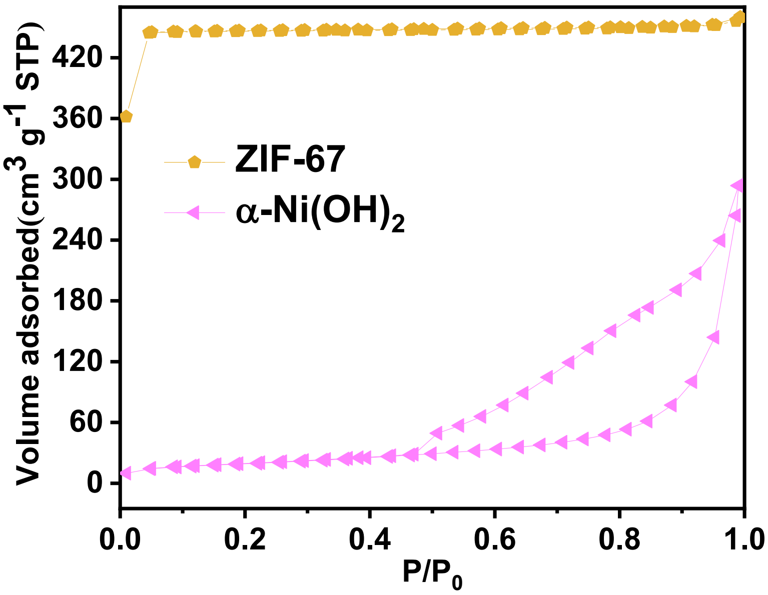

Fig. S2 The N_2 adsorption-desorption isotherm curve of ZIF-67 and α-$Ni(OH)_2$.

Table S2. The specific surface area and pore volume of different samples

Sample	S_{BET} (m^2/g)	Pore Volume（cm^3/g）
ZIF-67	1933	0.699
Co_4Ni-LDH	189	0.104
Co_2Ni-LDH	22.7	0.035
CoNi-LDH	22.3	0.036
$CoNi_2$-LDH	44	0.080
$CoNi_4$-LDH	80.6	0.153
α-$Ni(OH)_2$	68	0.217

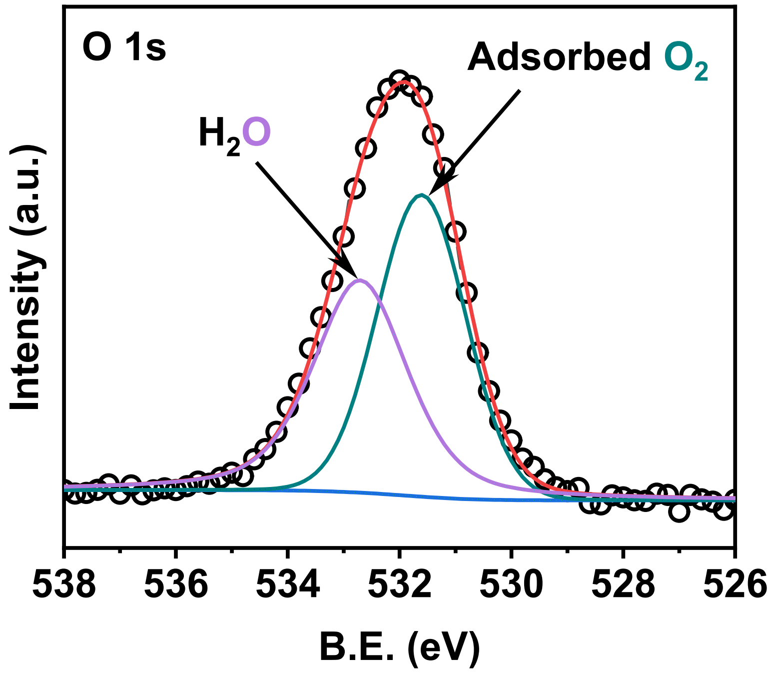

Fig. S3 High-resolution O 1s spectra of ZIF-67.

Table S3. The ratio of O species in different samples determined by XPS.

Sample	M-O	M-OH	H_2O	M-O ratio
ZIF-67	611	30682.51	28054.74	0.01
Co_4Ni-LDH	8000	283045.1	24796.98	0.03
Co_2Ni-LDH	25000	177129.7	30544.36	0.11
CoNi-LDH	36730.16	235192.6	57813.89	0.11
$CoNi_2$-LDH	20466.96	173238.5	118690.8	0.07
$CoNi_4$-LDH	39934.72	247491.2	205154.3	0.08
a-$Ni(OH)_2$	7855.96	268250.4	52122.25	0.02

Table S4. The ratio of Co^{2+} and Co^{3+} in different samples determined by XPS.

Sample	Co^{2+} area	Co^{3+} area	Co^{2+} ratio	Co^{3+} ratio
ZIF-67	51828.07	6299.97	0.89	0.11
Co_4Ni-LDH	61194.77	99003.99	0.38	0.62
Co_2Ni-LDH	25177.73	48177.09	0.34	0.66
CoNi-LDH	33271.16	49438.25	0.40	0.60
$CoNi_2$-LDH	30696.55	28898.63	0.52	0.49
$CoNi_4$-LDH	38750.41	33050.51	0.54	0.46

Table S5. The ratio of Ni^{2+} and Ni^{3+} in different samples determined by XPS.

Sample	Ni^{2+} area	Ni^{3+} area	Ni^{2+} ratio	Ni^{3+} ratio
Co_4Ni-LDH	67236.94	64170.61	0.51	0.49
Co_2Ni-LDH	79638.68	65178.18	0.55	0.45
CoNi-LDH	119331.4	95601.33	0.56	0.44
$CoNi_2$-LDH	114760.4	90981.32	0.56	0.44
$CoNi_4$-LDH	175322.60	162121.60	0.61	0.39
α-$Ni(OH)_2$	168016.3	105427.6	0.52	0.48

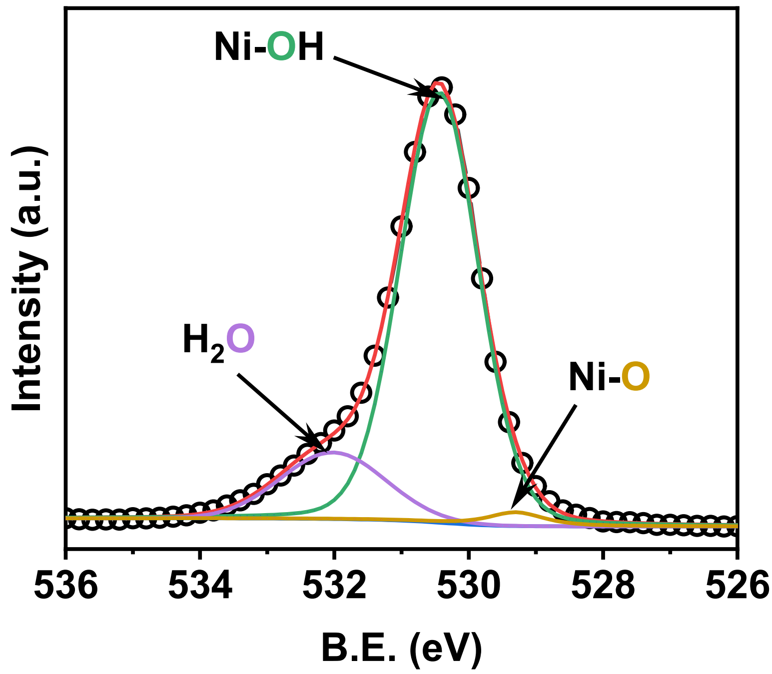

Fig. S4 High-resolution O 1s spectra of α-$Ni(OH)_2$.

Table S6. The effect of the amount of Co_2Ni-LDH as catalyst on the selective oxidation of ethylbenzene.

Entry[a]	Cat. [b]	Con.(%) [c]	Sel.(%) [c]
1	0	2.3	3.4
2	20 mg	49.3	74.6
3	30 mg	69.1	96.8
4	50 mg	63.2	79.2
5	80 mg	11.0	71.2

[a] reaction parameter: 2 mL ethylbenzene, O_2 balloon, 110 ^{o}C and 12 h; [b] the catalyst is Co_2Ni-LDH; [c] conversion and selectivity are determined by GC and GC-MS.

Table S7. The catalytic oxidation of ethylbenzene using Co_2Ni-LDH at 36 h and 48 h.

Entry	Time (h)	Product	Conversion/ Selectivity
1	36	Acetophenone	>99.9%/>99.9%
2	48	Acetophenone	>99.9%/>99.9%

Table S8. Comparison of Co_2Ni-LDH with other reported catalysts in solvent-free oxidation of ethylbenzene with O_2 as sole oxidant.

Catalyst	Condition	Solvent	Product	Conversion / Selectivity	References
Co-SiO_2	120 °C, 1 MPa, O_2	free	Acetophenone	8.3%/ 20.1%	1
Ni-MOF-5	150 °C, 1 atm, O_2	free	Acetophenone	55.3%/ 90.2%	2
Co-N-C	120 °C, 0.8 MPa, O_2	free	Acetophenone	14.1%/ 73.2%	3
Mn-MOF-74	135 °C, 1 atm, O_2	free	Acetophenone	66%/ 89%	4
Ce-BTC	160 °C, 1 atm, O_2	free	Acetophenone	84.99%/ 95.63%	5
mCeO_2:0.05Ni	120 °C, 10 bar, O_2	free	Acetophenone	29%/ 83%	6
mCo_3O_4-0.1NiO	120 °C, 0.6 MPa, O_2	free	Acetophenone	68.0%/ 95.4%	7
Co_2Ni-LDH	120 °C, 1 atm, O_2	free	Acetophenone	97.8%/ 98.8%	This work
Co_2Ni-LDH	130 °C, 1 atm, O_2	free	Acetophenone	>99.9%/ >99.9%	This work

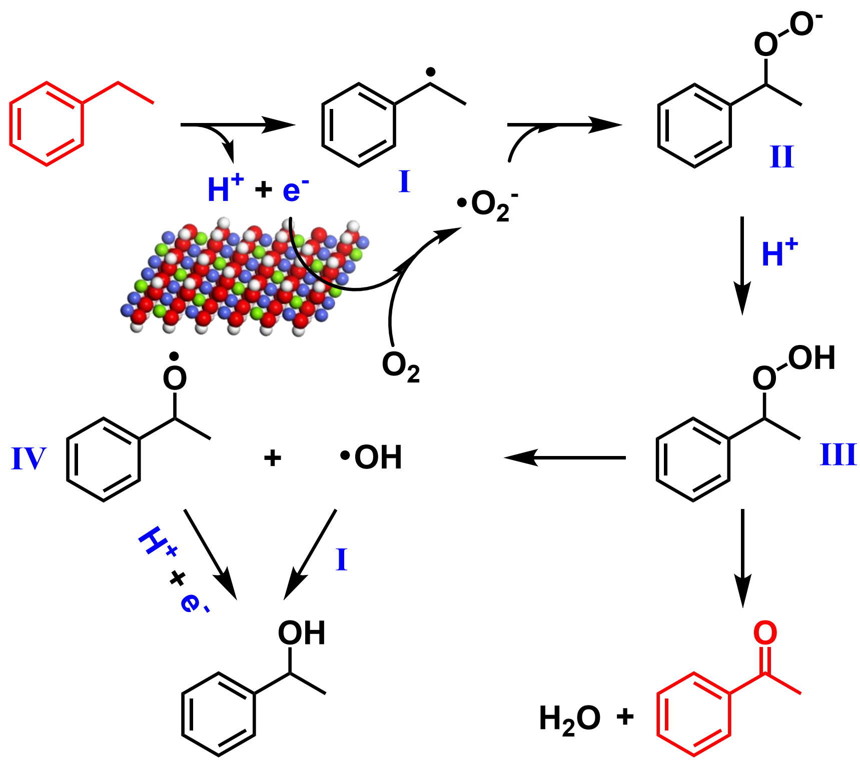

Fig. S5 The proposed mechanism of CoNi-LDH catalysed oxidation of ethylbenzene.

Table S9. The quenching experiment of free radical using scavenger.

Entry[a]	Radical scavenger[b]	Cov.(%) [c]	Sel(%)[c]
1	-	5.7	77.4
2	p-benzoquinone	0	0
3	4-chloro-2-nitrophenol	4.7	60.7
4	tert-butanol	2.6	89.1

[a] reaction parameter: 2 mL ethylbenzene, 30 mg Co_2Ni-LDH, O_2 balloon for 5 minutes, 120 ^{o}C and 24 hours; [b] 2 mmol of radical scavenger; [c] conversion and selectivity are determined by GC and GC-MS.

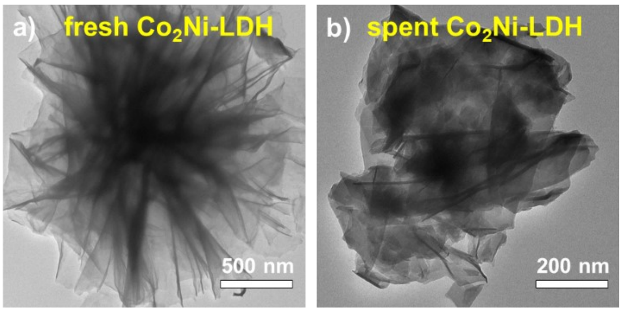

Fig. S6 TEM comparison of a) fresh and b) spent Co_2Ni-LDH catalyst.

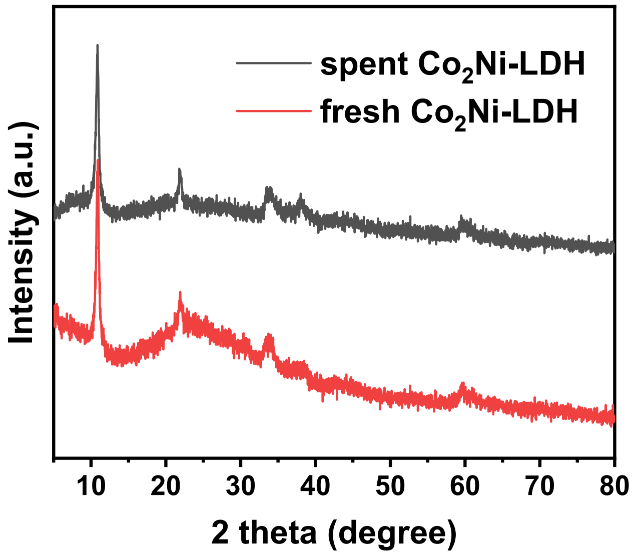

Fig. S7 XRD comparison of fresh and spent Co_2Ni-LDH catalyst.

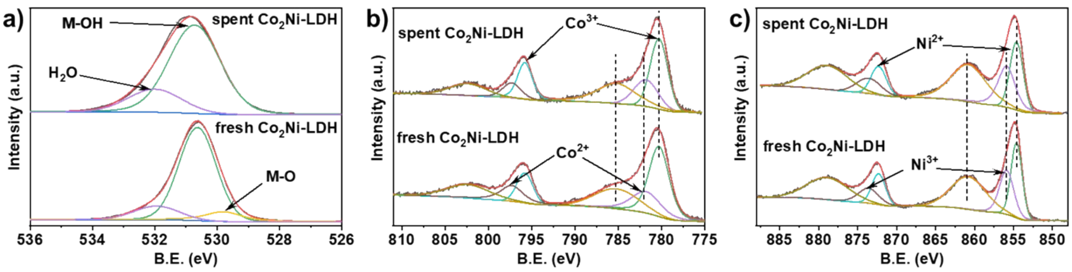

Fig. S8 The XPS comparison of fresh and spent Co_2Ni-LDH: High-resolution a) O1s spectra; b) Co 2p spectra and c) Ni 2p spectra.

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