Supporting Information

Efficient Oxidation of Hindered Amines to Nitroxide Radicals with Hydrogen Peroxide over Layered Double Hydroxide

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Contents

1、Optimisation of Catalytic Conditions（Table S1-S4）

Screening of catalysts

The catalytic performance of different LDHs was first evaluated by adding 5.00 wt% of each catalyst relative to the mass of HTEMP under identical conditions for 8.00 hours. The results are summarised in Table 1.

Table S1 Catalytic performance of different hydrotalcites

Types of catalysts	**Dosage (wt %)**	**Reaction time (h)**	**Con. (%)**	**Sel. (%)**
MgAl-LDH	5.00	8.00	99.9	99.3
CuAl-LDH	5.00	8.00	1.11	/
NiAl-LDH	5.00	8.00	53.0	96.3
CoAl-LDH	5.00	8.00	1.20	/
ZnAl-LDH	5.00	8.00	66.5	99.7
MgFe-LDH	5.00	8.00	14.6	97.7
CuFe-LDH	5.00	8.00	0	/
NiFe-LDH	5.00	8.00	50.0	95.2
CoFe-LDH	5.00	8.00	0.600	/
ZnFe-LDH	5.00	8.00	50.3	98.9
/	/	8.00	0.96	/

Experimental conditions: 5.00 wt% catalyst, 8 equivalents of hydrogen peroxide, 8.00h at 60.0°C

Screening of reaction temperature

The effect of reaction temperature was investigated by conducting reactions at 40.0 °C, 50.0 °C, and 60.0 °C using 8 equivalents of H_2O_2 and 5.00 wt% MgAl-LDH catalyst. After 8 hours, no significant change in conversion or selectivity was observed. The results are showed in Table 2.

Table S2 Effect of reaction temperature

Types of catalysts	**Temperature (°C)**	**Reaction time (h)**	**Con. (%)**	**Sel. (%)**
MgAl-LDH	40.0	8.00	69.3	89.5
MgAl-LDH	50.0	8.00	89.4	93.0
MgAl-LDH	60.0	8.00	99.3	99.1
MgAl-LDH	70.0	8.00	56.2	90.1

Optimisation of hydrogen peroxide dosage

Reactions were carried out using varying amounts of H_2O_2, at 60.0 °C and 5.00 wt% MgAl-LDH catalyst for 8 h. The results are presented in Table 3.

Table S3 Effect of H_2O_2 dosage

Types of catalysts	**H_2O_2 dosage (eq)**	**Reaction time (h)**	**Con. (%)**	**Sel. (%)**
MgAl-LDH	2.00	8.00	69.5	82.1
MgAl-LDH	4.00	8.00	90.1	97.8
MgAl-LDH	6.00	8.00	94.2	98.9
MgAl-LDH	8.00	8.00	99.3	99.1
MgAl-LDH	14.00	8.00	99.9	99.3

Screening of catalyst dosage

An excess of hydrogen peroxide (8 equivalents relative to HTEMP) was used, and the reaction temperature was maintained at 60.0 °C. MgAl-LDH was employed as the catalyst with catalyst dosage from 0.500% to 5.00% shown in table 4. The reaction was monitored by GC, the results are summarised in Table 4.

Table S4 Effect of catalyst dosage

Types of catalysts	**Dosage (wt %)**	**Reaction time (h)**	**Con. (%)**	**Sel. (%)**
MgAl-LDH	0.500	8.00	13.2	92.4
MgAl-LDH	1.00	8.00	55.9	96.3
MgAl-LDH	1.50	8.00	62.9	96.4
MgAl-LDH	2.00	8.00	85.8	96.8
MgAl-LDH	2.50	8.00	88.0	95.1
MgAl-LDH	3.00	8.00	93.7	96.8
MgAl-LDH	3.50	8.00	95.4	97.5
MgAl-LDH	4.00	8.00	96.9	98.8
MgAl-LDH	4.50	8.00	99.7	98.4
MgAl-LDH	5.00	8.00	99.8	99.30

2、Hydroxyl radical capture experiment

Coumarin-3-carboxylic acid of 20.0 mg, MgAl-LDH of 30.0 mg and 15.0 ml of water were added to a 50 mL round-bottomed flask and stirred thoroughly. Subsequently, 6.78 mL 30.0% H_2O_2 was added dropwise to the reaction mixture and stirred at preset temperature for 30.0 min, and the fluorescence emission spectra of the reaction mixture were collected.

3、Superoxide radical capture experiment

NBT of 20.0 mg, MgAl-LDH of 30.0 mg and 15.0 ml of methanol were added to a 50 mL round-bottomed flask and stirred thoroughly. Subsequently, 6.78 mL 30% H_2O_2 was added dropwise to the reaction mixture and stirred at preset temperature for 120 min, and the UV-Vis absorption spectra of the reaction mixture were collected.

4、Singlet oxygen capture experiment

DPBF of 20.0 mg, MgAl-LDH of 30.0 mg and 15.0 ml of methanol were added to a 50 mL round-bottomed flask and stirred thoroughly. Subsequently, 6.78 mL 30% H_2O_2 was added dropwise to the reaction mixture and stirred at preset temperature for 60.0 min, and the UV-Vis absorption spectra of the reaction mixture were collected.

5、Hydroxyl radical quenching experiment

HTEMP (1.57 g, 0.0100 mol), 78.5 mg of MgAl-LDH, and 15.0 mL of methanol were added to a 50 mL round-bottom flask. Subsequently, 30.0% aqueous hydrogen peroxide containing 0.0800 mol H_2O_2 was added, and the reaction mixture was stirred at 60.0 °C for 8.00 hours. The conversion and selectivity were determined by GC and compared with those obtained under identical conditions using water as the solvent.

6、Superoxide radical quenching experiment

HTEMP (1.57 g, 0.0100 mol), p-BQ (20.0 mg, 0.185mmol), 78.5 mg of MgAl-LDH, and 15.0 mL of deionised water were added to a 50 mL round-bottom flask. Subsequently, 30% aqueous hydrogen peroxide containing 0.0800 mol H_2O_2 was added, and the reaction mixture was stirred at 60.0 °C for 8.00 hours. The conversion and selectivity were determined by GC and compared with those obtained under identical aqueous conditions without the addition of p-BQ

7、Singlet oxygen quenching experiment

HTEMP (1.57 g, 0.0100 mol), β-carotene (199 mg,0.370mmol), 78.5 mg of MgAl-LDH, and 15.0 mL of deionised water were added to a 50 mL round-bottom flask. Subsequently, 30% aqueous hydrogen peroxide containing 0.0800 mol H_2O_2 was added, and the reaction mixture was stirred at 60.0 °C for 8.00 hours. The conversion and selectivity were determined by GC and compared with those obtained under identical aqueous conditions without the addition of β-carotene.

8、Preparation of LDH Materials with Various Metal Cations

ZnAl-LDH : $Zn(NO_3)_2{\cdot}6H_2O$ (4.46 g, 15.0 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (1.88 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting slurry was aged at 80.0 °C for 8.00 hours. The precipitate was collected by filtration, thoroughly washed with water, and dried at 80.0 °C for 24.0 hours to afford the ZnAl-LDH with a molar ratio of 3:1.

CuAl-LDH : $Cu(NO_3)_2 \cdot 3H_2O$ (3.63 g, 15.0 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (1.88 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 6 and 7 by the addition rate of solution B. The resulting slurry was aged at 70.0 °C for 8.00 hours. The precipitate was collected by filtration, thoroughly washed with water, and dried at 70.0 °C for 24.0 hours to afford the CuAl-LDH with a molar ratio of 3:1.

NiAl-LDH : $Ni(NO_3)_2 \cdot 6H_2O$ (4.36 g, 15.0 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (1.88 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting slurry was aged at 80.0 °C for 8.00 hours. The precipitate was collected by filtration, thoroughly washed with water, and dried at 80.0 °C for 24.0 hours to afford the NiAl-LDH with a molar ratio of 3:1.

CoAl-LDH : $Co(NO_3)_2·6H_2O$ (4.37 g, 15.0 mmol) and $Al(NO_3)_3·9H_2O$ (1.88 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting mixed solution was aged in a hydrothermal autoclave at 120 °C for 8.00 h. The precipitate was collected by filtration, thoroughly washed with water, and dried at 80.0 °C for 24.0 hours to afford the CoAl-LDH with a molar ratio of 3:1.

MgFe-LDH : $Mg(NO_3)_2·6H_2O$ (3.85 g, 15.0 mmol) and $Fe(NO_3)_3·9H_2O$ (2.02 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting mixed solution was aged in a hydrothermal autoclave at 120 °C for 8.00 h. The precipitate was collected by filtration, thoroughly washed with water, and dried at 80.0 °C for 24.0 hours to afford the MgFe-LDH with a molar ratio of 3:1.

CuFe-LDH : $Cu(NO_3)_2·3H_2O$ (3.63 g, 15.0 mmol) and $Fe(NO_3)_3·9H_2O$ (2.02 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0

mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 6 and 7 by the addition rate of solution B. The resulting slurry was aged at 70.0 °C for 7.00 hours. The precipitate was collected by filtration, thoroughly washed with water, and dried at 70.0 °C for 24.0 hours to afford the CuFe-LDH with a molar ratio of 3:1.

ZnFe-LDH : $Zn(NO_3)_2 \cdot 6H_2O$ (4.46 g, 15.0 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (2.02 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting mixed solution was aged in a hydrothermal autoclave at 120 °C for 8.00 h. The precipitate was collected by filtration, thoroughly washed with water, and dried at 80.0 °C for 24.0 hours to afford the ZnFe-LDH with a molar ratio of 3:1.

NiFe-LDH : $Ni(NO_3)_2 \cdot 6H_2O$ (4.36 g, 15.0 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (2.02 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting slurry was aged at 80.0 °C for 8.00 hours. The precipitate was collected by filtration, thoroughly washed with water, and dried at 80.0 °C for 24.0 hours to afford the NiFe-LDH with a molar ratio of 3:1.

CoFe-LDH : $Co(NO_3)_2\cdot 6H_2O$ (4.37 g, 15.0 mmol) and $Fe(NO_3)_3\cdot 9H_2O$ (2.02 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting mixed solution was aged in a hydrothermal autoclave at 120 °C for 8.00 h. The precipitate was collected by filtration, thoroughly washed with water, and dried at 80.0 °C for 24.0 hours to afford the CoFe-LDH with a molar ratio of 3:1.

9、Preparation of Nitrate-inserted hydrotalcites

$Mg(NO_3)_2\cdot 6H_2O$ (3.85 g, 15.0 mmol) and $Al(NO_3)_3\cdot 9H_2O$ (1.88 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting slurry was aged at 80.0 °C for 8.00 hours. The solid product was separated by filtration, washed thoroughly with deionised water (to remove the base from the catalyst) and then dried at 80.0°C for 24.0 hours.

10、Preparation of hydrotalcites with different magnesium to aluminium ratios

Mg1Al preparation: $Mg(NO_3)_2{\cdot}6H_2O$ (3.85 g, 15.0 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (5.63 g, 15.0 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting slurry was aged at 80.0 °C for 8.00 hours. The solid product was separated by filtration, washed thoroughly with deionised water (to remove the base from the catalyst) and then dried at 80.0°C for 24.0 hours.

Mg4Al preparation: $Mg(NO_3)_2{\cdot}6H_2O$ (5.128 g, 20.0 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (1.88 g, 5.00 mmol) were dissolved in 25.0 mL water to afford solution A. NaOH (3.60 g, 90.0 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) were dissolved in 25.0 mL water to yield solution B. Solutions A and B were simultaneously added dropwise to a four-necked round-bottom flask containing 25.0 mL of water at 25.0 °C under stirring. During the co-precipitation process, the pH of the reaction mixture was maintained between 11 and 12 by the addition rate of solution B. The resulting slurry was aged at 80.0 °C for 8.00 hours. The solid product was separated by filtration, washed thoroughly with deionised water (to remove the base from the catalyst) and then dried at 80.0°C for 24.0 hours.

11、Decomposition of H_2O_2 in the Presence and Absence of LDHs

A 30% aqueous solution of hydrogen peroxide (1 mL, 9.00 mmol) was dissolved in 10.0 mL of water. The experiments were conducted under two conditions: with the addition of 10 mg MgAl–LDH and without LDHs. The reaction vessel was sealed and heated to 60 °C. The gas outlet was connected to an inverted graduated cylinder submerged in water, and the volume of O_2 generated was recorded over time using the water-displacement method.

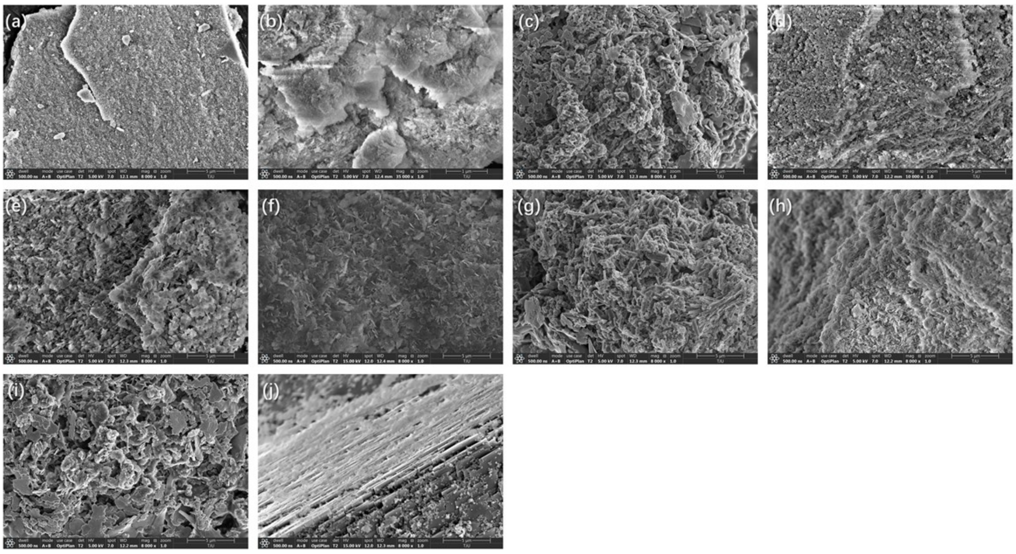
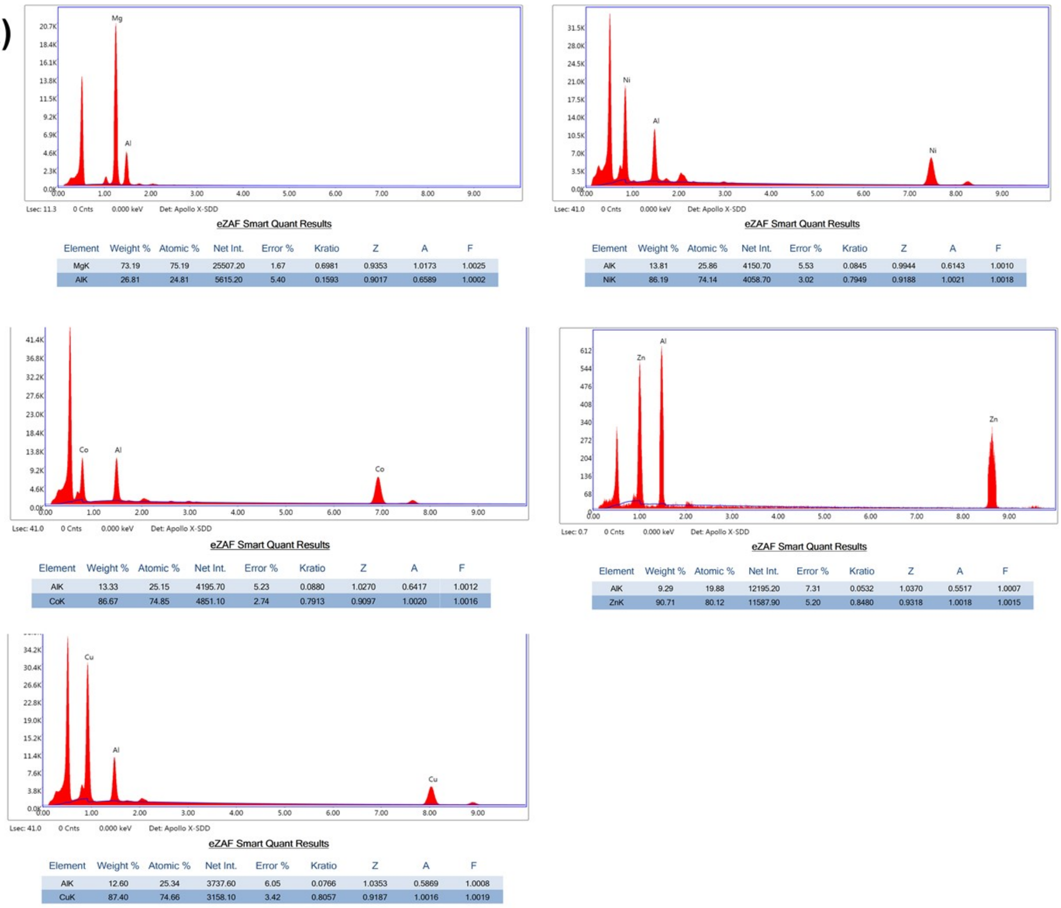


Fig.S1 (a) SEM image of MgAl-LDH (b) SEM image of NiAl-LDH (c) SEM image of CuAl-LDH (d) SEM image of ZnAl-LDH (e) SEM image of CoAl-LDH (f) SEM image of MgFe-LDH (g) SEM image of CuFe-LDH (h) SEM image of NiFe-LDH (i) SEM image of CoFe-LDH (j) SEM image of ZnFe-LDH

(a)



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
MgK	73.19	75.19	25507.20	1.67	0.6981	0.9353	1.0173	1.0025
AlK	26.81	24.81	5615.20	5.40	0.1593	0.9017	0.6589	1.0002

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
AlK	13.81	25.86	4150.70	5.53	0.0845	0.9944	0.6143	1.0010
NiK	86.19	74.14	4058.70	3.02	0.7949	0.9188	1.0021	1.0018

eZAF Smart Quant Results

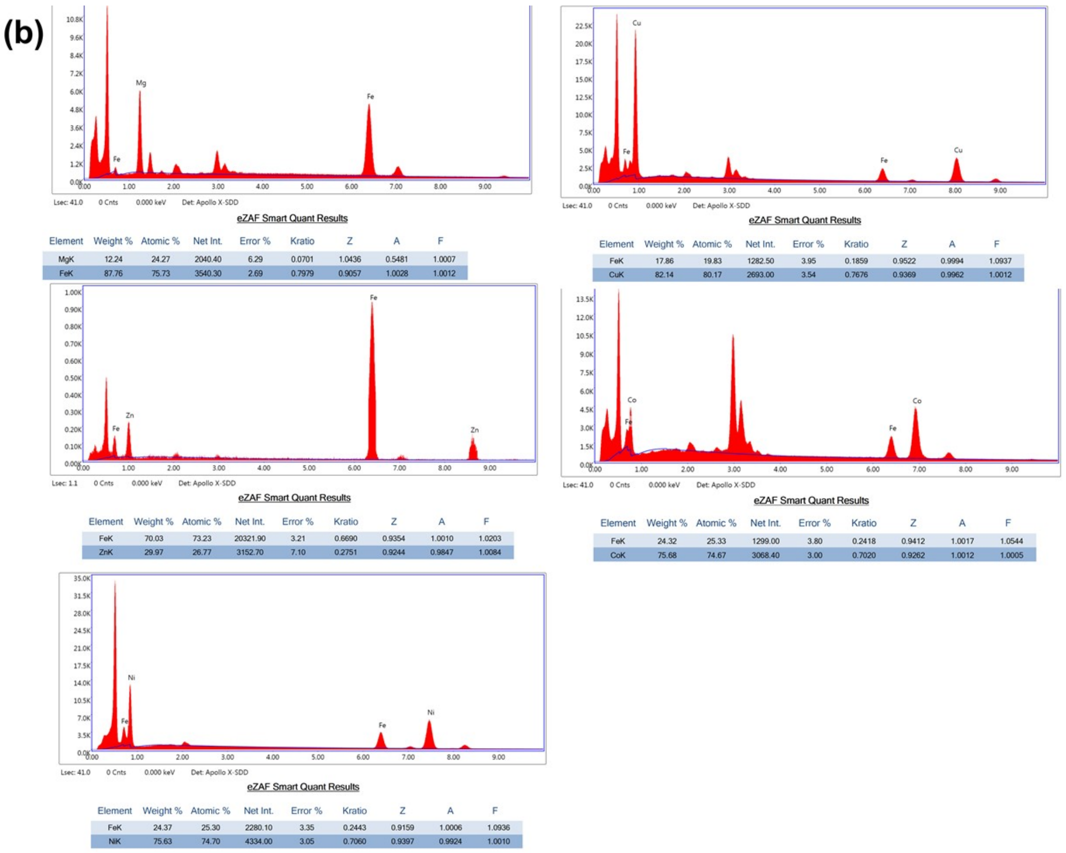
Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
AlK	13.33	25.15	4195.70	5.23	0.0880	1.0270	0.6417	1.0012
CoK	86.67	74.85	4851.10	2.74	0.7913	0.9097	1.0020	1.0016

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
AlK	9.29	19.88	12195.20	7.31	0.0532	1.0370	0.5517	1.0007
ZnK	90.71	80.12	11587.90	5.20	0.8480	0.9318	1.0018	1.0015

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
AlK	12.60	25.34	3737.60	6.05	0.0766	1.0353	0.5869	1.0008
CuK	87.40	74.66	3158.10	3.42	0.8057	0.9187	1.0016	1.0019



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
MgK	12.24	24.27	2040.40	6.29	0.0701	1.0436	0.5481	1.0007
FeK	87.76	75.73	3540.30	2.69	0.7979	0.9057	1.0028	1.0012

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
FeK	17.86	19.83	1282.50	3.95	0.1859	0.9522	0.9994	1.0937
CuK	82.14	80.17	2693.00	3.54	0.7676	0.9369	0.9962	1.0012

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
FeK	70.03	73.23	20321.90	3.21	0.6690	0.9354	1.0010	1.0203
ZnK	29.97	26.77	3152.70	7.10	0.2751	0.9244	0.9847	1.0084

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
FeK	24.32	25.33	1299.00	3.80	0.2418	0.9412	1.0017	1.0544
CoK	75.68	74.67	3068.40	3.00	0.7020	0.9262	1.0012	1.0005

eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
FeK	24.37	25.30	2280.10	3.35	0.2443	0.9159	1.0006	1.0936
NiK	75.63	74.70	4334.00	3.05	0.7060	0.9397	0.9924	1.0010

Fig.S2 (a) EDS Spectrum of Fe-Based LDH. The molar ratio of divalent cations to trivalent iron ions was 3:1. (b) EDS Spectrum of Al-Based LDH The molar ratio of divalent cations to trivalent aluminium ions was 3:1.

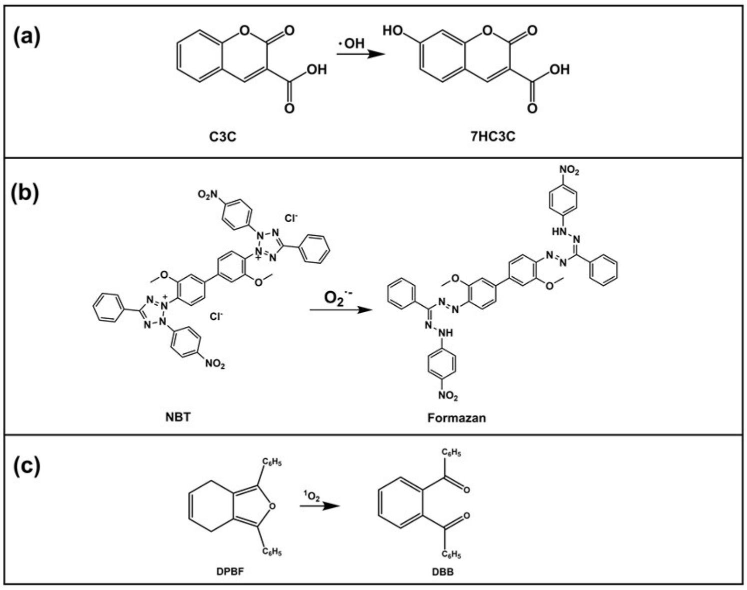


Fig. S3 (a) Reaction equation for C3C capturing hydroxyl radicals (b) Reaction equation for NBT capturing superoxide anions (c) Reaction equation for DPBF capturing singlet oxygen

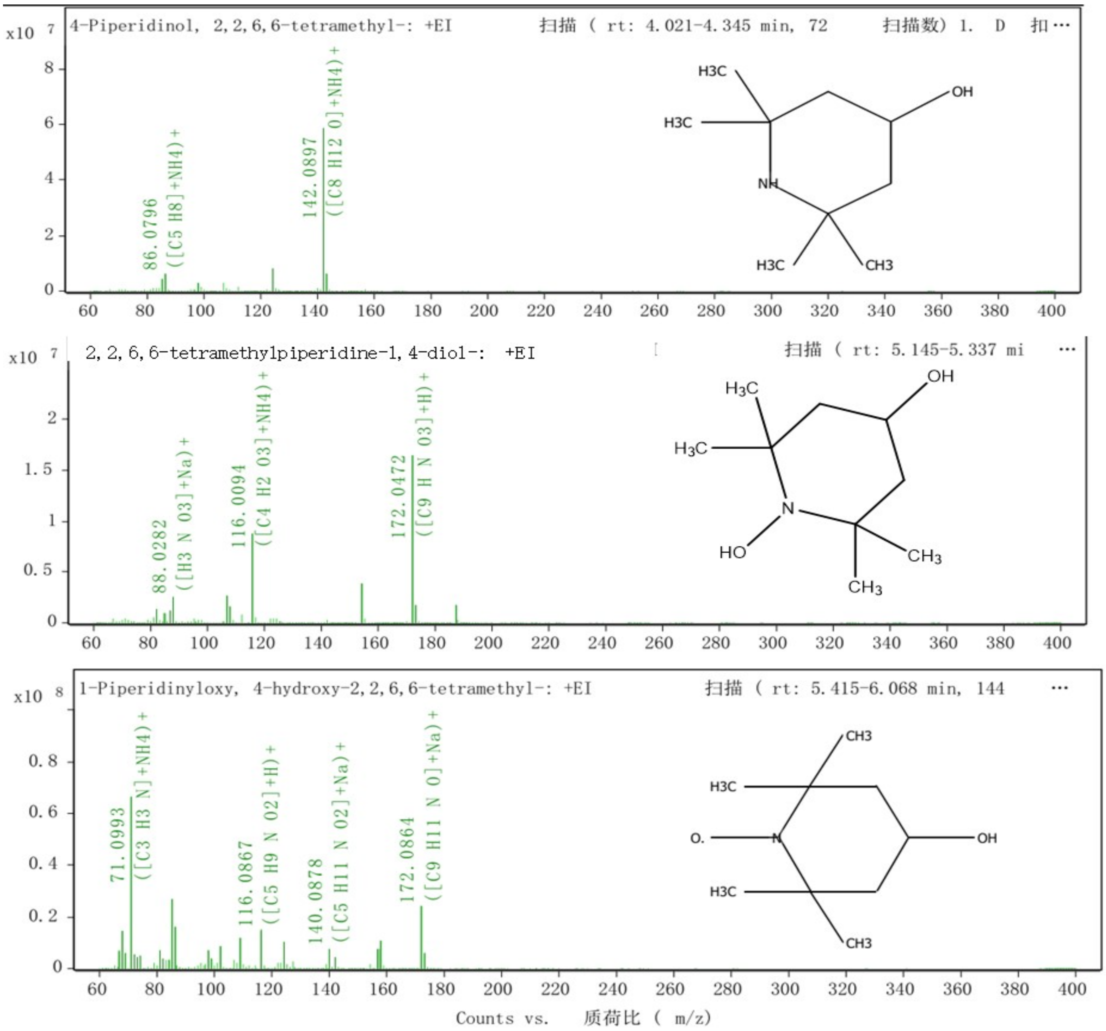


Fig. S4 GC-MS test plot of reaction mixture

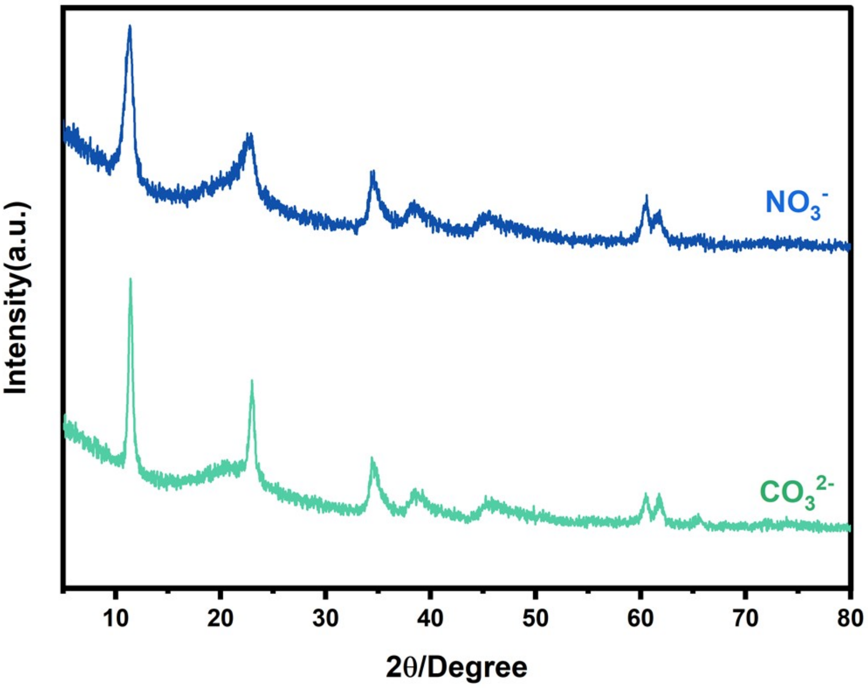


Fig. S5 XRD pattern of nitrate intercalated hydrotalcite

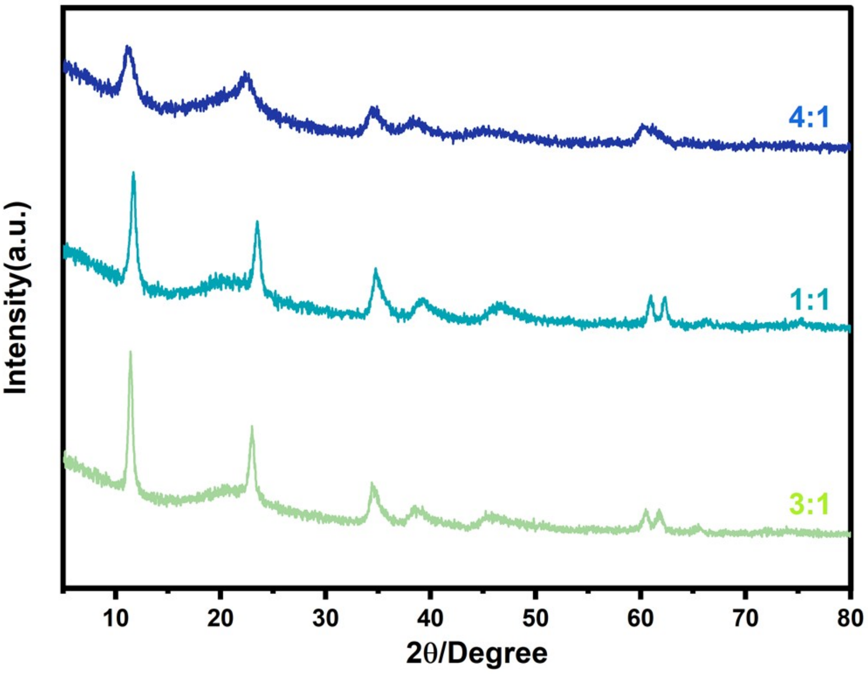


Fig. S6 XRD pattern of hydrotalcites with different Mg-Al ratios

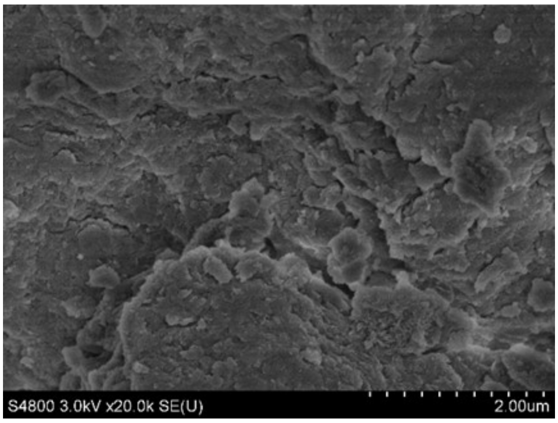


Fig.S7 SEM image of Mg4Al-LDH

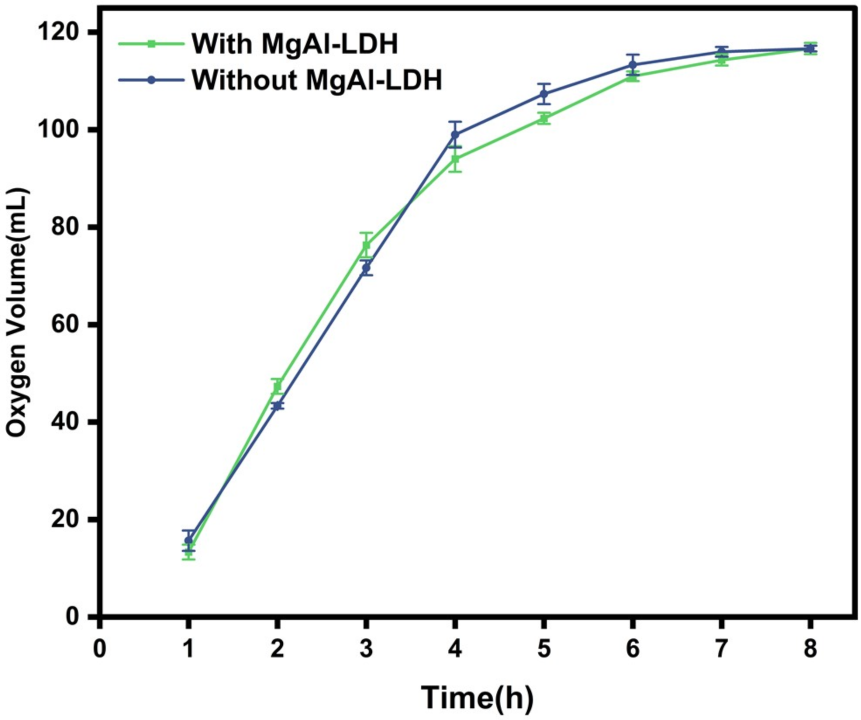


Fig.S8 Time-dependent O_2 evolution from H_2O_2 decomposition with and without MgAl-LDHs, showing nearly identical decomposition rates under the experimental conditions.

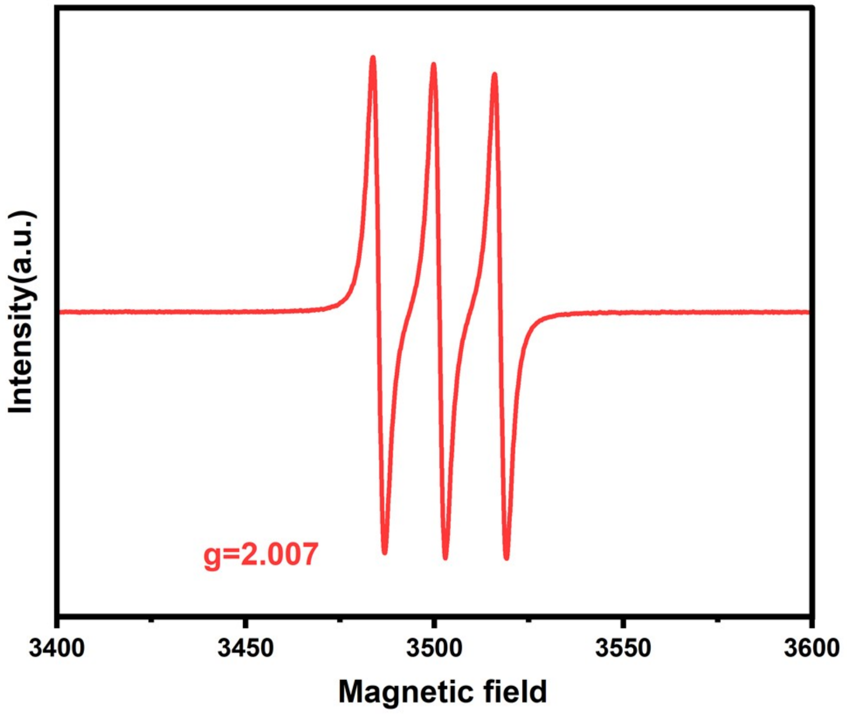


Fig.S9 EPR spectrum of HTEMPO

Table S5 DFT-Calculated Gibbs Free Energies for Different Reaction Pathways

	Delta G (a.u.)	Delta G (kcal/mol)
int1 + $\cdot$OH = int2 + OH^-	0.239076	150.02
int2 + $O_2^{\cdot -}$ = int3 + $HO_2^{\bullet}$	-0.203888	-127.94
int2 + OH^- = int3 + H_2O	-0.274507	-172.26
int3 + $^1O_2$ = int4	-0.048445	-30.40
int4 + int3 = 2 int5	-0.106947	-67.11
int3 + $\cdot$OH = int6	-0.081798	-51.33
int6 + $O_2^{\cdot -}$ = int5 + HO_2^-	0.010707	6.72

Table S6 Catalytic Performance of LDHs with Different Mg/Al Ratios

Types of catalysts	Dosage (wt%)	Con. (%)	Sel. (%)
Mg3Al	5.00	99.9	99.3
Mg4Al	5.00	99.3	98.5
Mg1Al	5.00	79.6	99.2
Mg4Al	2.50	99.9	97.2