

Supplementary Information

Frustrated Lewis Pairs on Metal-cation Vacancies Catalysts

Enhanced the Electroreduction of NO to NH₃

Honghong Yi ^{a, b}, Ruzhu Jia ^a, Xiaolong Tang ^{a, b}, Dongjuan Kang ^a, Qingjun Yu ^{a, b},
Fengyu Gao ^{a, b}, Shunzheng Zhao ^{a, b, *}, Yunpeng Liu ^{c, *}

a. School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China;

b. Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, Beijing 100083, China;

c. Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China.

*** Correspondence to:**

Yunpeng Liu, liuyunpeng@ihep.ac.cn;

Shunzheng Zhao, zhaoshunzheng86@126.com.

I. Supplementary Figures

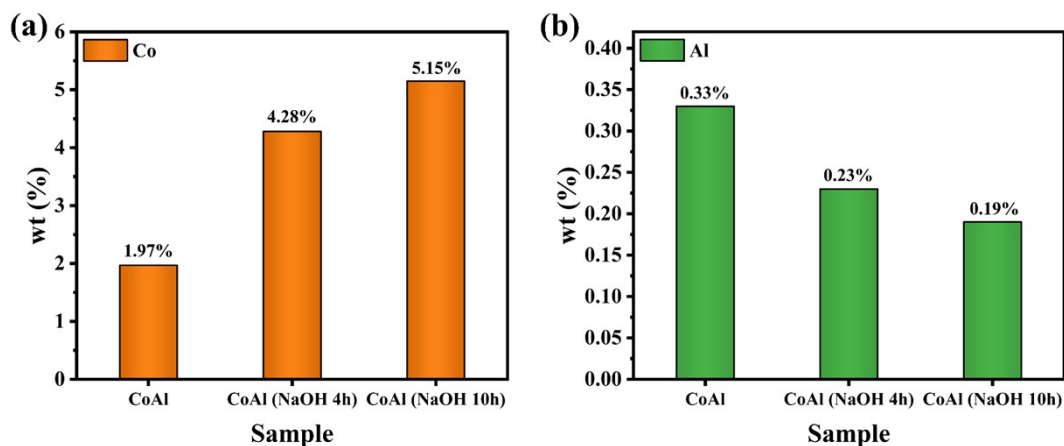


Figure S1. ICP-OES measurement of the percentage content of (a) Co and (b) Al elements in CoAl-LDH nanosheets.

The graph depicts the results of the ICP-OES test, indicating that the Co content gradually increases with prolonged alkaline etching time. Conversely, the Al content exhibits a corresponding decrease. This trend suggests that the etching process effectively removed a portion of the Al sites, thereby creating metal cation defect sites.

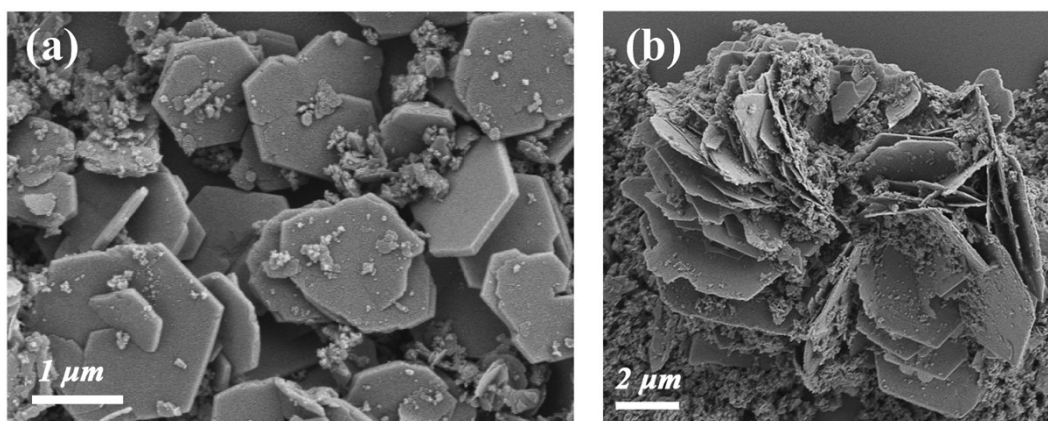


Figure S2. SEM patterns of (a) CoAl (NaOH 4 h) and (b) CoAl (NaOH 10 h) samples.

The CoAl (NaOH 4h) catalyst maintains the lamellar structure, whereas the lamellar structure of the CoAl (NaOH 10h) sample is disrupted and etched into flower-cluster-like shapes.

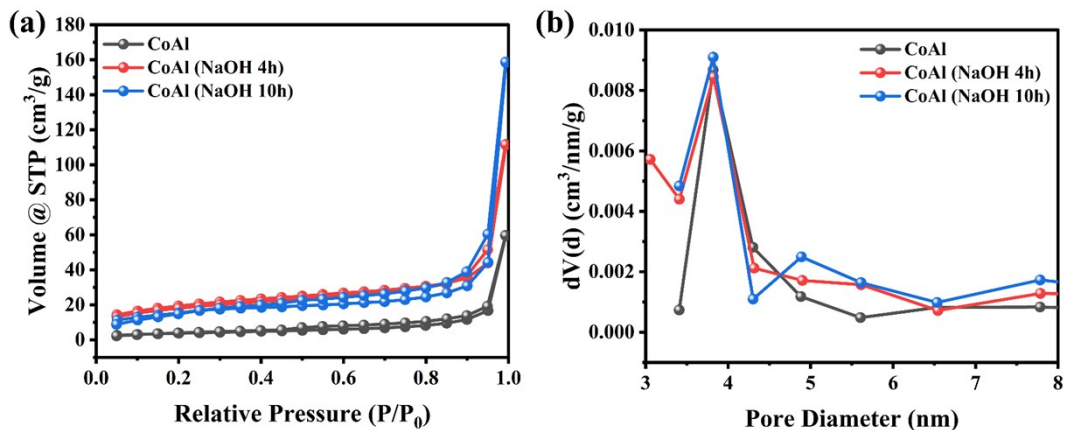


Figure S3. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of catalysts at different alkali etching times.

The N_2 adsorption and desorption experiments demonstrate that all samples exhibit type IV adsorption isotherms, which are characterized by H3-type hysteresis loops, indicative of mesoporous materials. Additionally, the majority of samples display a pore size distribution of approximately 3.82 nm.

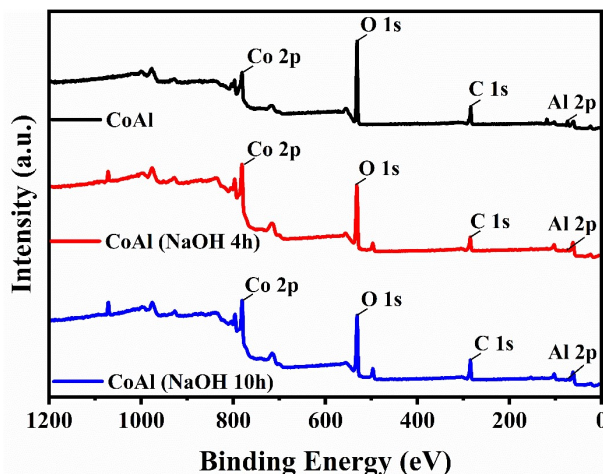


Figure S4. XPS spectrum of pristine CoAl-LDH and alkali etching of CoAl-LDH for various times.

The CoAl-LDH nanosheets are primarily composed of four elements: Co, Al, C, and O.

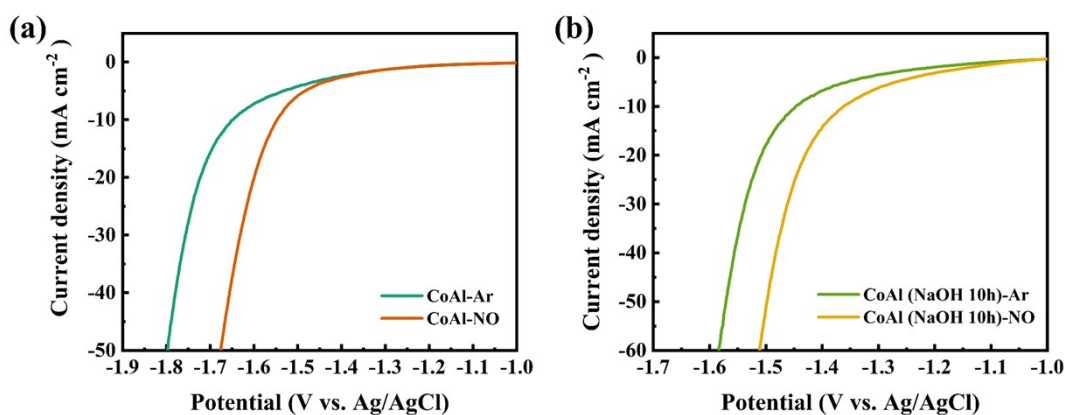


Figure S5. The LSV curves of (a) CoAl and (b) CoAl (NaOH 10h) nanosheets in Ar and NO saturated electrolytes.

The employment of LSV permitted the assessment of the electrocatalytic performance of CoAl-LDH nanosheets. It is noteworthy that the NO-saturated electrolyte yielded a higher current density compared to the Ar-saturated solution, indicating a clear preference for NO reduction.

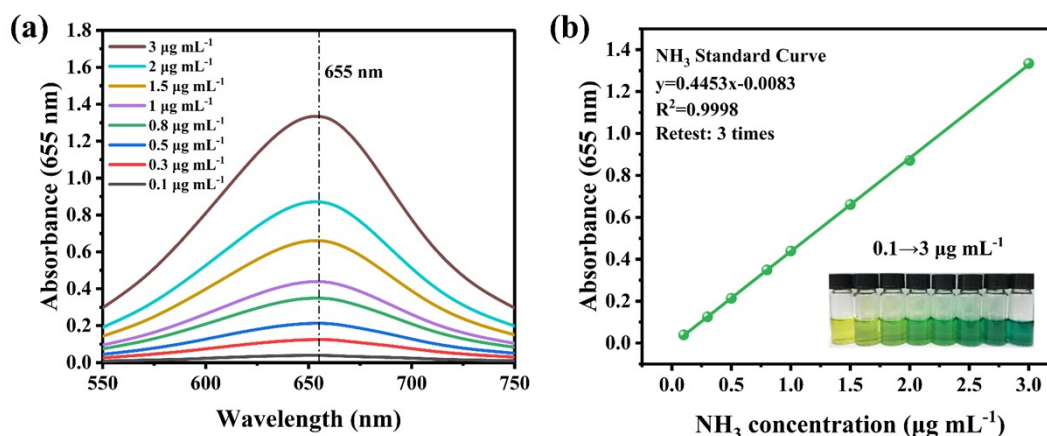


Figure S6. Performance evaluation of electrochemical NH_3 synthesis. (a) UV-Vis absorption spectra of solutions of NH_3 at different concentrations. (b) NH_3 standard curve.

Using indophenol blue spectrophotometry to determine NH_3 concentration, the average of three measurements was taken. The concentration range was $0.1\sim 3 \mu\text{g/mL}$ with an R^2 of 0.9998, indicating excellent linearity.

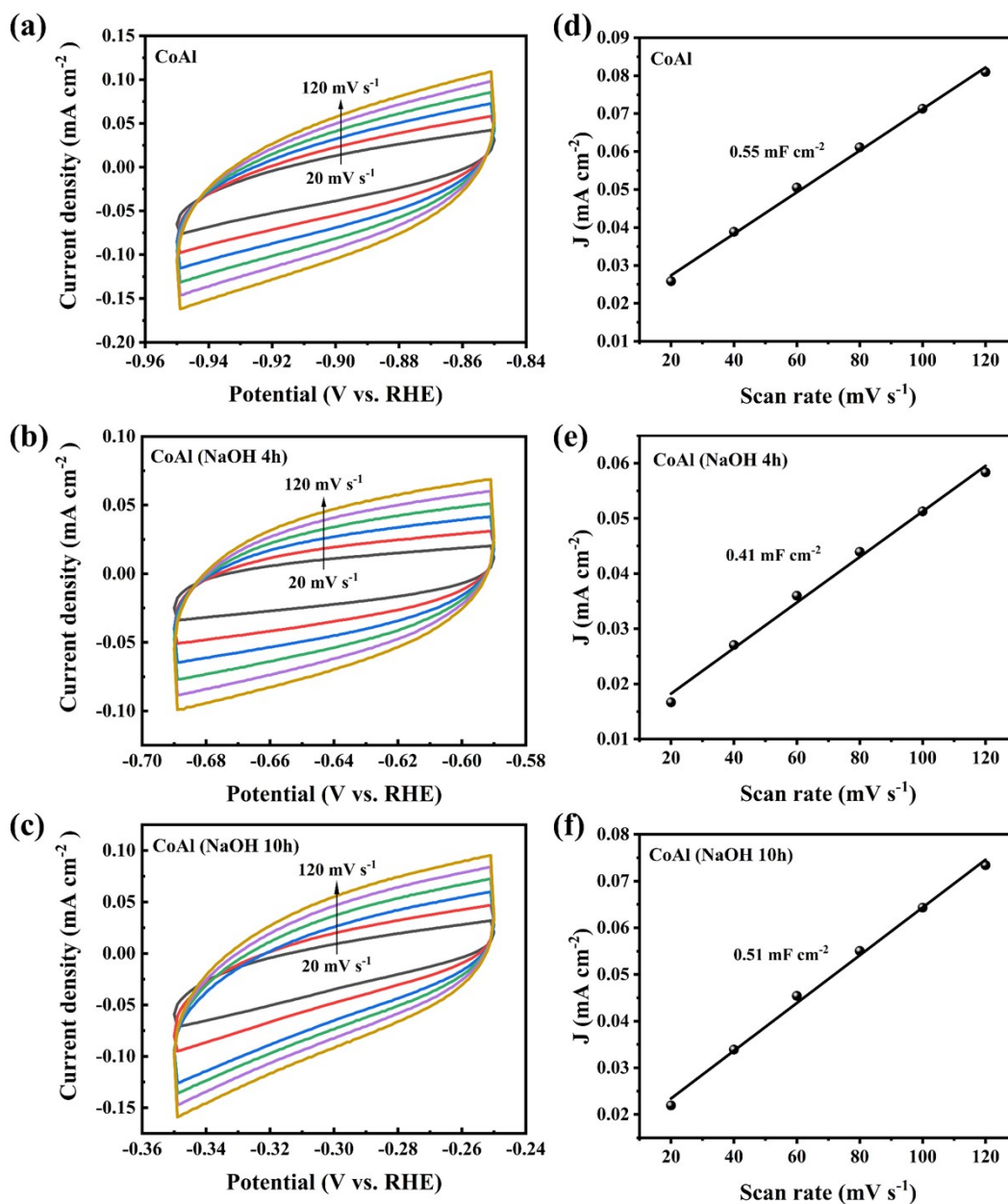


Figure S7. (a-c) CV curves of (a) CoAl, (b) CoAl (NaOH 4 h) and (c) CoAl (NaOH 10 h) at different scan rates. (d-f) The relationships between scan rates and current density for (d) CoAl, (e) CoAl (NaOH 4 h) and (f) CoAl (NaOH 10 h).

The electrochemical active surface area (ECSA) of the catalysts is evaluated by calculating the C_{dl} using the CV data from the non-Faradaic region. The double-layer capacitance (C_{dl}) values derived from fitting the scan rates and current densities for CoAl, CoAl (NaOH 4 h), and CoAl (NaOH 10 h) are 0.55, 0.41, and 0.51 mF cm⁻², respectively. The absence of a significant discrepancy indicates that the ECSA is similar among these samples.

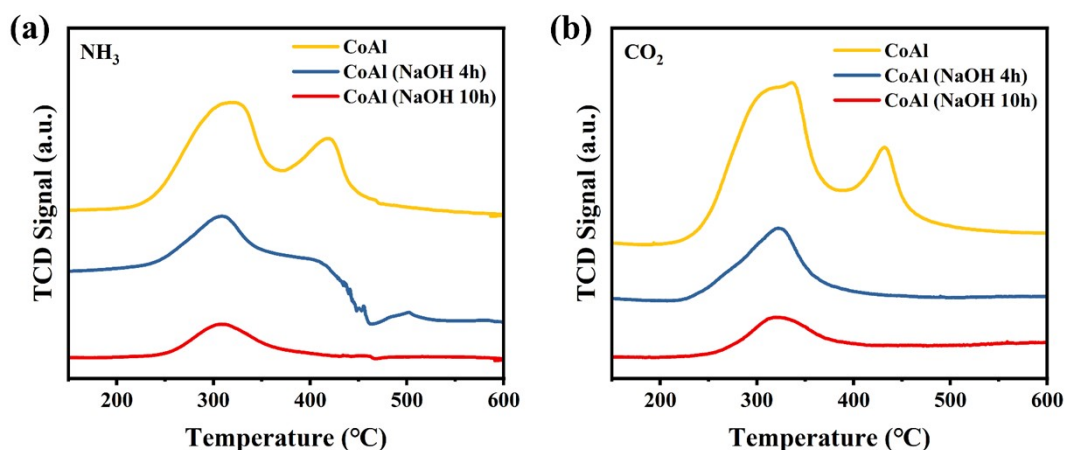


Figure S8. (a) NH_3 and (b) CO_2 TPD profiles of CoAl-LDH nanosheets.

The NH_3 -TPD test results indicated the presence of medium and strong acidic sites in the pristine CoAl samples. Following alkali etching, the strong acidic sites in the CoAl-LDH nanosheets (NaOH 4 h and NaOH 10 h) were no longer present, and the medium-strength acidic sites also exhibited a gradual decrease with the extension of alkali treatment time. The CO_2 -TPD test demonstrated that the trend of alkaline sites in the catalysts was consistent with that observed for acidic sites in the NH_3 -TPD test.

II. Supplementary Tables

Table S1. Structure parameters of CoAl-LDH in pristine and alkali etched for different times.

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter $D_v(d)$ (nm)
CoAl	12.829	0.091	3.818
CoAl (NaOH 4h)	22.840	0.151	3.823
CoAl (NaOH 10h)	25.203	0.228	3.819

Table S2. The white line peak positions of CoAl-LDH in pristine and alkali etched for different times as well as their valence states.

Sample	White line peak positions (eV)	Valence states
CoO	7721.92	2
CoAl	7721.04	1.75
CoAl (NaOH 2h)	7722.47	2.18

CoAl (NaOH 4h)	7722.71	2.26
CoAl (NaOH 6h)	7722.88	2.31
CoAl (NaOH 8h)	7723.26	2.42
CoAl (NaOH 8h)	7723.55	2.51
Co ₂ O ₃	7725.20	3

Table S3. The Co K-edge EXAFS fitting parameters for the first-shell around Co atom of different CoAl samples. The structural parameters of the constructed models are also listed.

Model/Sample	Bond	R (Å)	N	σ^2 (10^{-3} Å ²)	ΔE (eV)	R-factor
CoAl LDH.cif	Co-O	2.076	2			
	Co-O	2.175	4			
Co ₃ Al-HT LDH.cif	Co-O	1.964	2			
	Co-O	2.033	4			
CoAl	Co-O	2.09±0.02	7.2±1.5	7.0±2.0	2.5±0.5	0.008
CoAl (NaOH 2h)	Co-O	1.90±0.02	5.8±1.7	10.0±2.0	-12.4±4.3	0.02
CoAl (NaOH 4h)	Co-O	1.89±0.02	5.6±1.2	8.0±2.0	-14.4±3.9	0.02
CoAl (NaOH 6h)	Co-O	1.90±0.02	5.6±1.4	10.0±2.0	-13.0±3.7	0.018
CoAl (NaOH 8h)	Co-O	1.90±0.02	5.5±1.5	7.0±2.0	-9.2±4.3	0.02
CoAl (NaOH 10h)	Co-O	1.90±0.01	4.7±0.9	4.0±1.0	-5.1±2.0	0.015

N: coordination number; R: bond length; σ^2 : Debye-Waller factor.