

Annealing activated nickel-molybdenum oxide as an efficient electrocatalyst toward benzyl alcohol upgrading

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1. Experimental section

1.1 Synthesis of NiMoO/NF

To synthesize precursor, 2.1 mmol of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.3 mmol of ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) were added into 35 mL deionized water, which was then stirred to be light green. Then, the above solution was transferred into a 50 mL Teflon-lined autoclave, with a piece of 3×3 cm nickel foam (NF) being added as well. (The NF was previously washed via hydrochloric acid, acetone, ultra-pure water and ethanol, respectively.) Then, the autoclave was heated at 150°C for 6 h. After the reaction, the NF covered with NiMoO_4 sample was washed via ultra-pure water and ethanol, respectively. Then, it was dried in vacuum at 60°C for 6 h, with NiMoO/NF being obtained finally.

1.2 Synthesis of NiMoO-Ar/NF

The NiMoO/NF was placed in a tubular furnace under Ar atmosphere. Then, it was heated at 400°C for 2 hours, after which the NiMoO-Ar/NF was fabricated.

1.3 Synthesis of NF-Ar

The NF was placed in a tubular furnace under Ar atmosphere. Then, it was heated at 400°C for 2 hours, after which the NF-Ar was fabricated.

1.4 Characterizations

The phases of the samples were analyzed by X-ray diffraction (XRD, Rigaku Smart Lab), the morphologies of the samples were characterized by Scanning electron microscope scanning electron microscopy (SEM, JEOL JSM-6700F), and the content distribution of elements was characterized by energy dispersive X-ray spectroscopy (EDS, JEOL JSM-6700F). The internal morphology of the material was observed by transmission electron microscope electron spectroscopy (TEM, FEI Talos F200X), and the valence state of the elements and the chemical composition of the surface of the material were analyzed by X-ray electron spectroscopy (XPS, ESCALAB 250).

1.5 Electrochemical tests

The electrochemical test was carried out on an electrochemical workstation (CHI660B) in an H-type cell. The electrocatalytic reaction tests were carried out via a three-electrode system in which Ag/AgCl and carbon rods were used as reference and

counter electrodes, respectively. The electrolyte for OER process was 1 M KOH. While, the electrolyte for BA oxidation was 50 mL of 1 M KOH with 15 mM benzyl alcohol. The Ni foam obtained after the hydrothermal reaction was firstly cut into the small pieces of 1*3 cm. Then the mass loading was evaluated via the difference value between clean Ni foam and Ni foam with catalysts. According to our various parallel tests, we found that the mass loading was about 1.51 mg/cm². Then the Ni foam electrode was fixed via the electrode holder with GC collector with 1*1 cm² was immersed into the electrolyte. The catalyst was first fully activated and stabilized by 100 Cyclic voltammetry (CV) at a scanning rate of 50 mV s⁻¹. Linear sweep voltammetry (LSV) was used to plot the polarization curves at the scanning rate of 5 mV s⁻¹. The AC impedance value was recorded at the frequency from 0.1 mHz to 100 kHz, with an amplitude being 5 mV. The potential was converted to the RHE scale according to the Nernst equation:

$$E_{(\text{RHE})} = E_{(\text{Ag}/\text{AgCl})} + 0.059 \times \text{pH} + 0.197$$

GC detection was performed by Agilent gas chromatograph under the following conditions: injection temperature (180°C), oven temperature (80°C for 3 min, 10°C/min to 220°C for 5 min), detector temperature (220°C). After the electrooxidation reaction, 1 mL of the reaction solution was taken out, which was extracted via 1 mL of ethyl acetate. Then, 10 uL of the about solution was injected for gas phase detection. The conversion rate of benzoic acid (Equation 1), selectivity (Equation 2), yield (Equation 3), and Faraday efficiency (Equation 4) were calculated according to the following equation:

$$\text{Conversion (\%)} = \frac{\text{mol of reacted benzyl alcohol}}{\text{mol of initail benzyl alcohol}} \times 100\%$$

(1)

$$\text{Selectivity (\%)} = \frac{\text{mol of benzoic acid production}}{\text{mol of reacted benzyl alcohol}} \times 100\%$$

(2)

$$\text{yield (\%)} = \frac{\text{mol of benzoic acid production}}{\text{mol of initail benzyl alcohol}} \times 100\%$$

(3)

$$FE(\%) = \frac{nzF}{Q} \times 100\% \quad (4)$$

where n is the number of moles of benzoic acid, z denotes the moles of electrons per mole of benzyl alcohol ($z = 4$), F is the Faraday constant (96485C mol^{-1}), and Q is the charge passed through the electrode.

2. Structure characterization of NiMoO/NF and NiMoO-Ar/NF

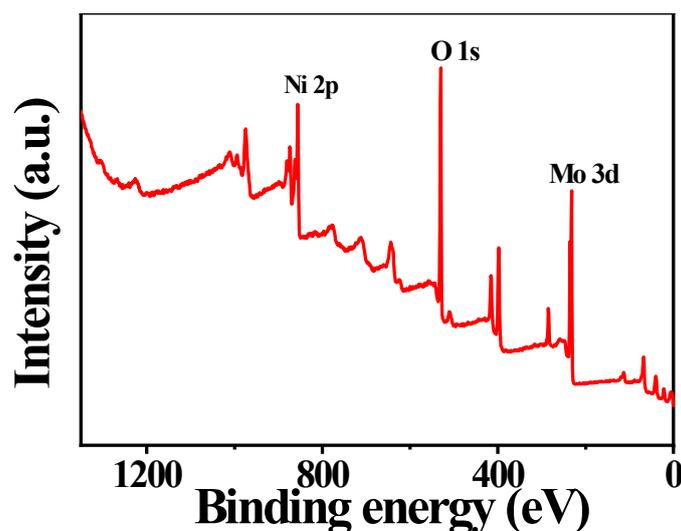


Fig. S1 The full XPS spectra of NiMoO-Ar/NF.

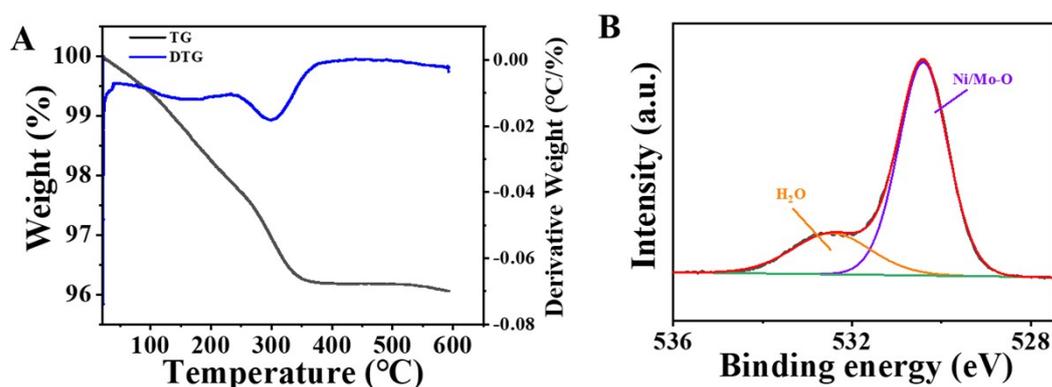


Fig. S2 (A) TG and DTG curves of NiMoO/NF. (B) O 1s spectra of NiMoO/NF.

As for the TG as shown in Fig. S2A, it can be seen that a mass loss at about 350°C was observed, which should mainly be ascribed to the loss of water content in the NiMoO₄·xH₂O. This weight loss is consistent with the literature, confirming the existence of lattice water in the precursor.¹ As for the O 1s spectra of NiMoO/NF as shown in Fig. S2B, it can be obtained that the peak attributed to the metal-oxygen bonding and the absorbed water appeared at 530.4 eV and 532.5 eV, respectively. This is similar with the NiMoO-Ar/NF catalyst as shown in Fig. 2D in the manuscript.

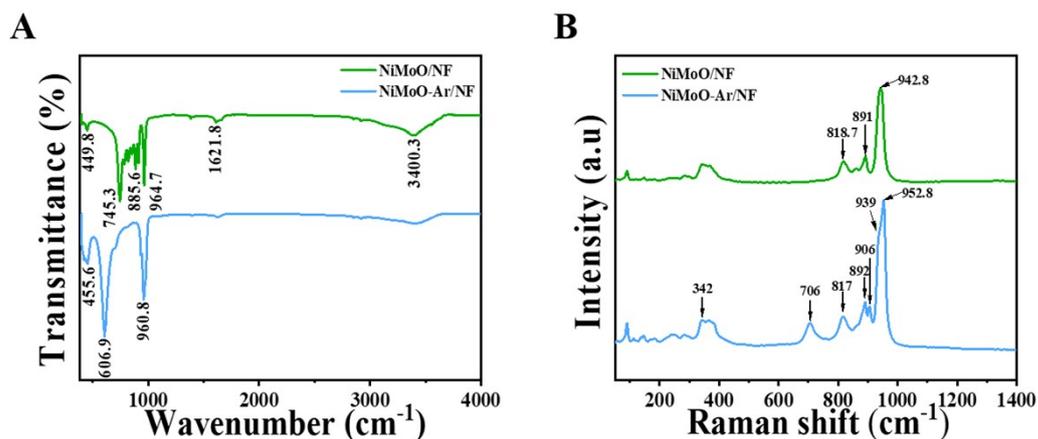


Fig. S3 (A) FTIR spectra of NiMoO/NF and NiMoO-Ar/NF. (B) Raman spectra of NiMoO/NF and NiMoO-Ar/NF.

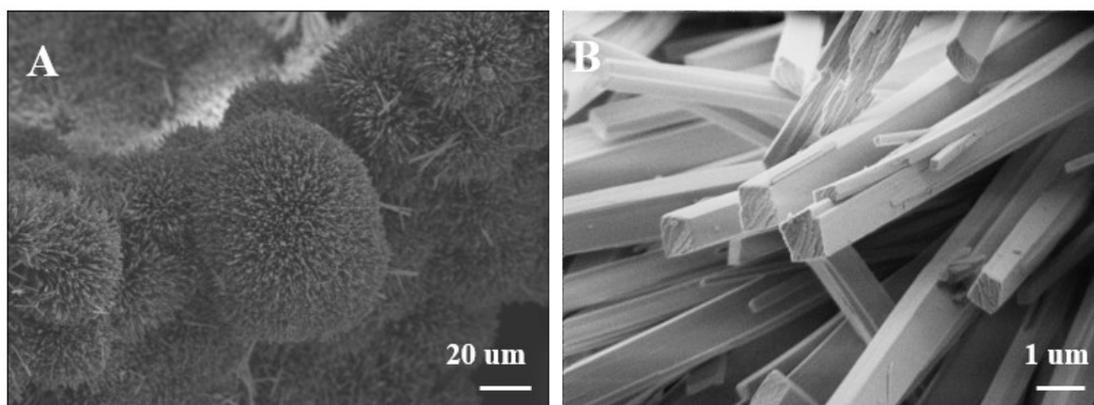


Fig. S4 A and B SEM images of NiMoO/NF.

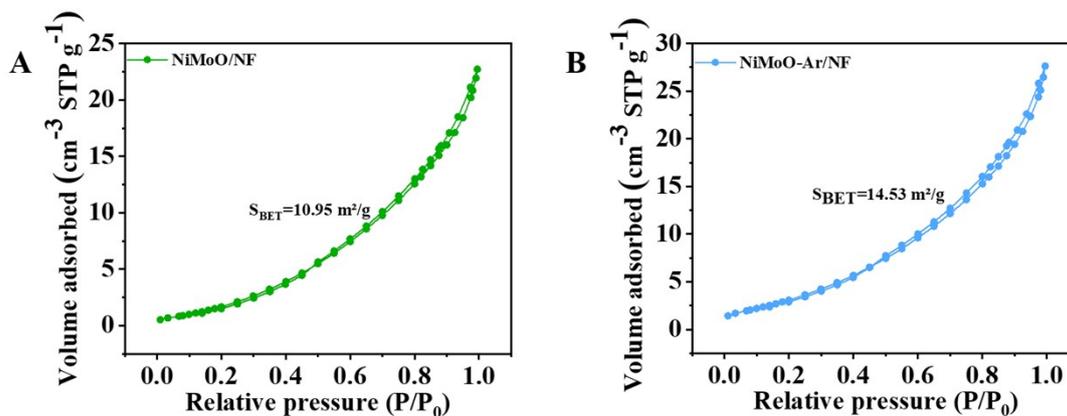


Fig. S5 Nitrogen adsorption-desorption isotherms for NiMoO/NF (A) and NiMoO-Ar/NF (B).

3. Electrochemical characterization

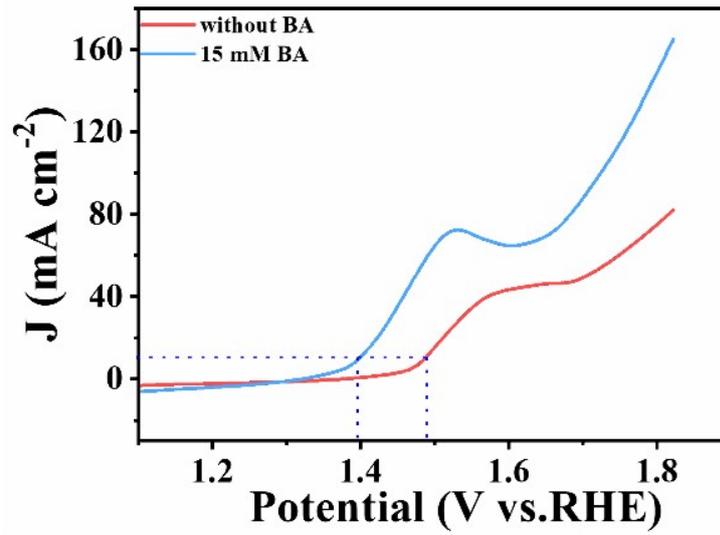


Fig. S6 Polarization curves of NiMoO-Ar/NF in 1 M KOH electrolyte with and without 15 mM BA.

Table S1. Fitting parameters of equivalent circuits for various catalytic materials.

	R_s/Ω	R_{ct}/Ω	CPE-T	W-1
NiMoO-Ar/NF	1.022	1.45	0.252	0.12
NiMoO/NF	0.943	10.42	0.016	0
NF	0.916	16.98	0.018	0

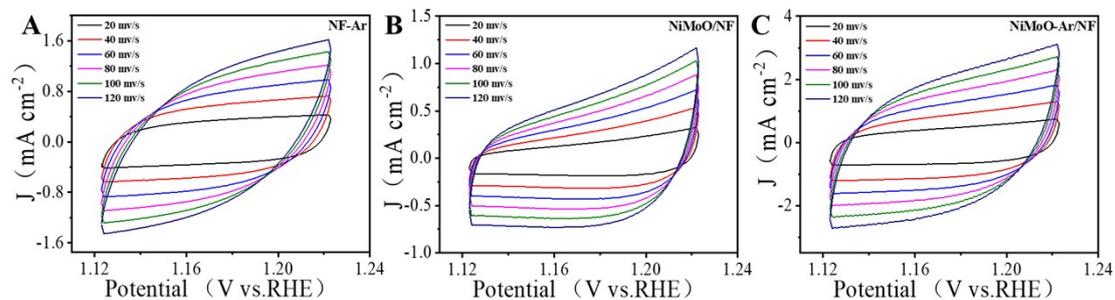


Fig. S7 CV curves of NF-Ar (A), NiMoO/NF(B) and NiMoO-Ar/NF (C) in 1M KOH with 15mM BA at various scan rates.

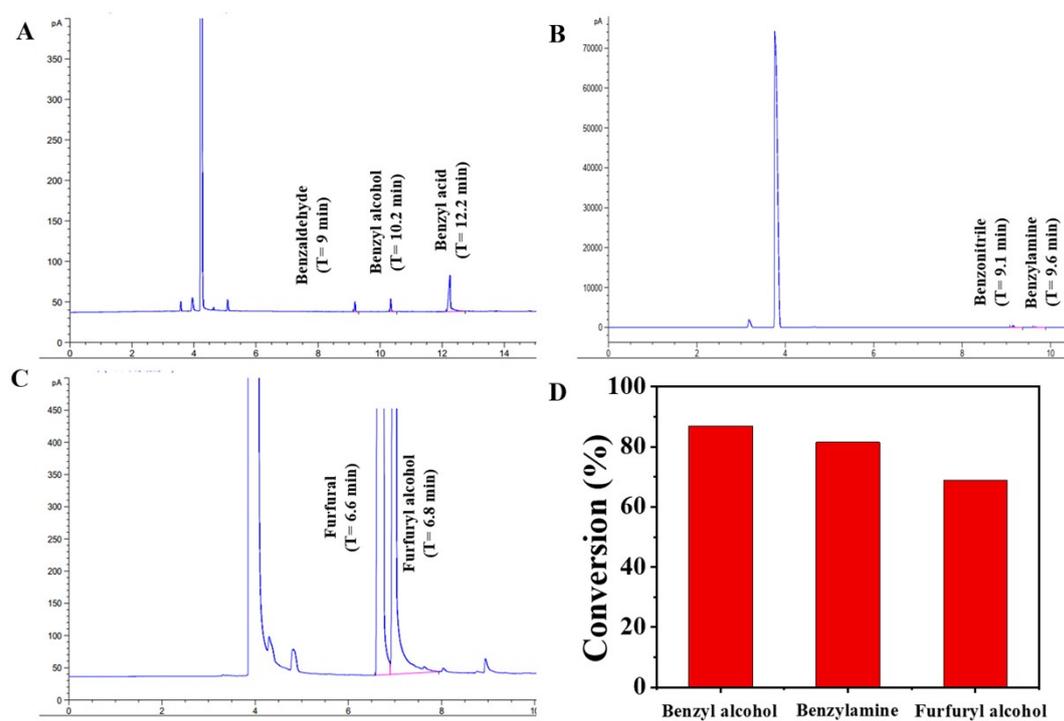


Fig. S8 Gas Chromatogram of the electrolyte after the electrocatalytic oxidation of benzyl alcohol (A), benzylamine (B) and furfuryl alcohol (C). (Reaction at 1.5 V for 2h) (D) The conversion comparison of these three organic substrate.

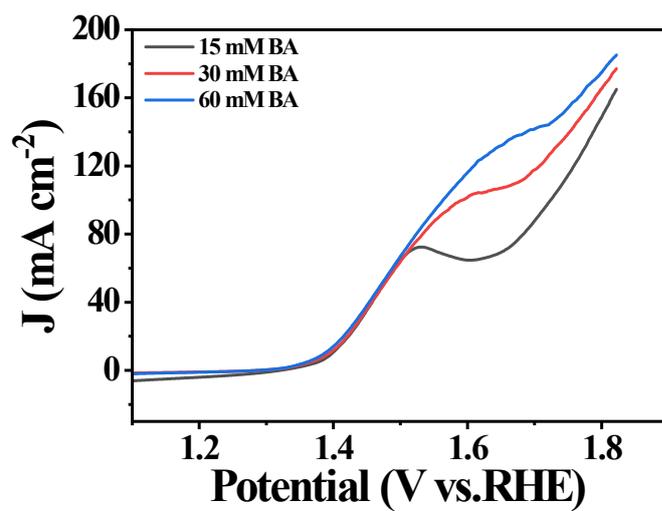
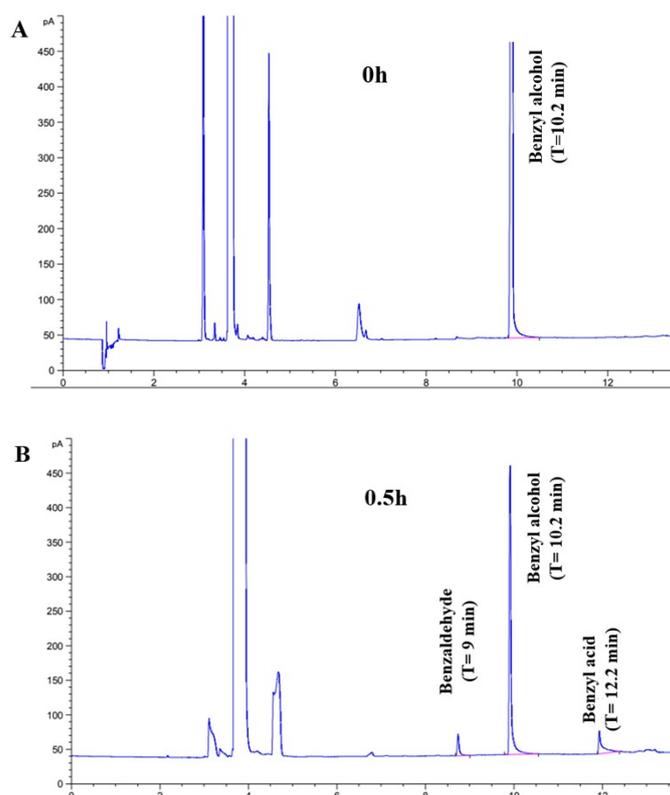


Fig. S9 LSV testing at electrolyte with higher benzyl alcohol concentration.



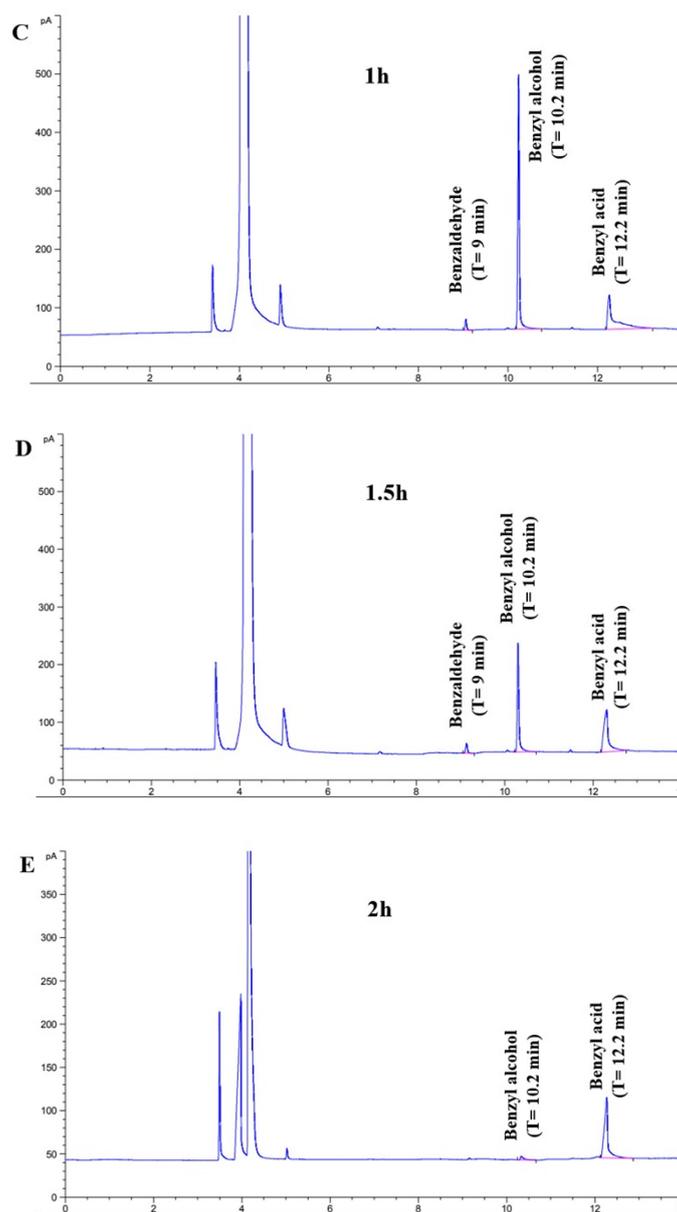
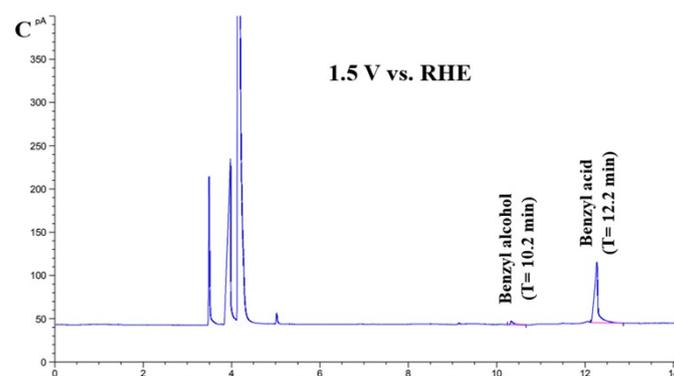
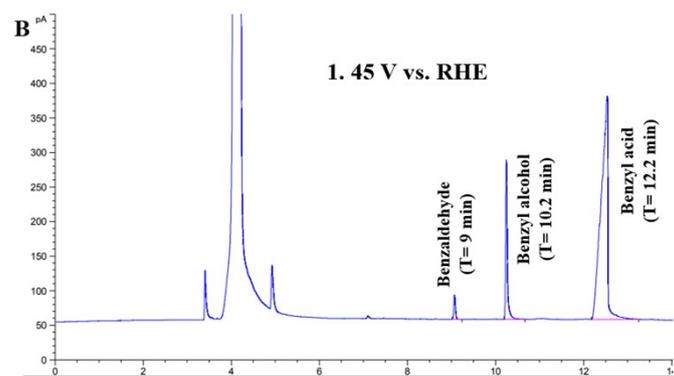
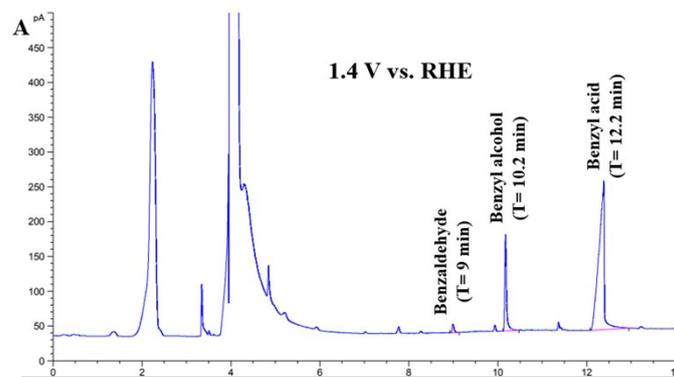


Fig. S10 Gas chromatogram corresponding to the change in peak area of the product at different times at 1.5 V vs. RHE.

Table S2 The peak area values of BC, BA and benzaldehyde (BH) after reaction.

Reaction time/h	peak area of BH		peak area of BA/%		peak area of BC	
	/%		/%		/%	
0	0		100		0	
0.5	6.33		81.25		12.41	
1	2.82		63.09		34.09	

1.5	4.45	46.64	48.91
2	0	5.73	94.27



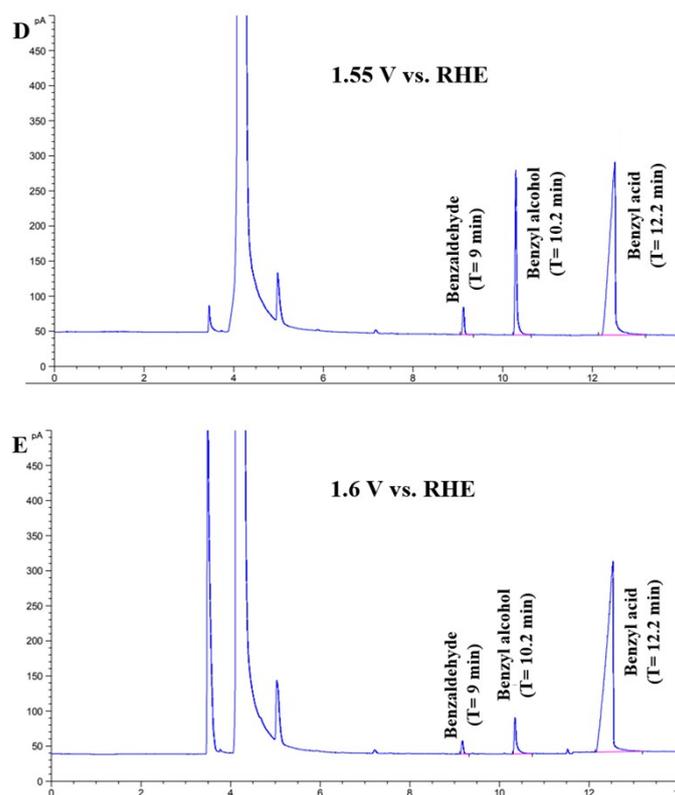


Fig. S11 GC chromatograms of electrolyte after 2h reaction under various potentials.

Table S3 The peak area values of BA, BC and BH after reacting with different voltages for the same time.

Voltage/V vs. RHE	peak area of BH/%	peak area of BA/%	peak area of BC/%
1.40	1.67	17.08	81.25
1.45	2.19	14.53	83.27
1.50	0	5.73	94.27
1.55	3.70	20.46	75.84
1.60	1.74	5.93	92.33

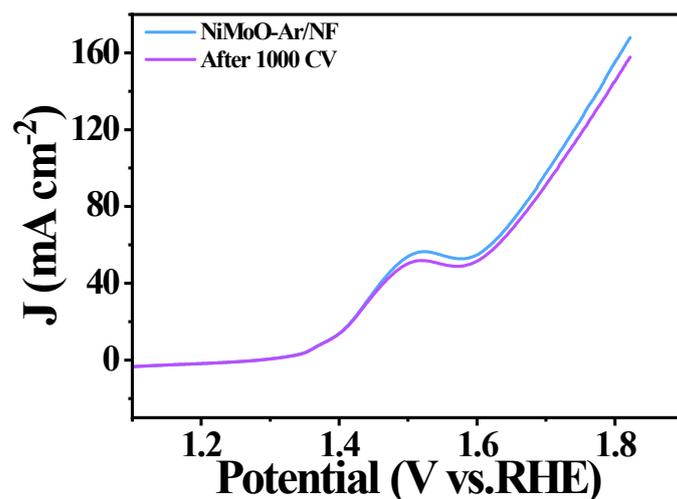


Fig. S12 Comparison of polarization curves of NiMoO-Ar/NF before and after 1000 CV cycles.

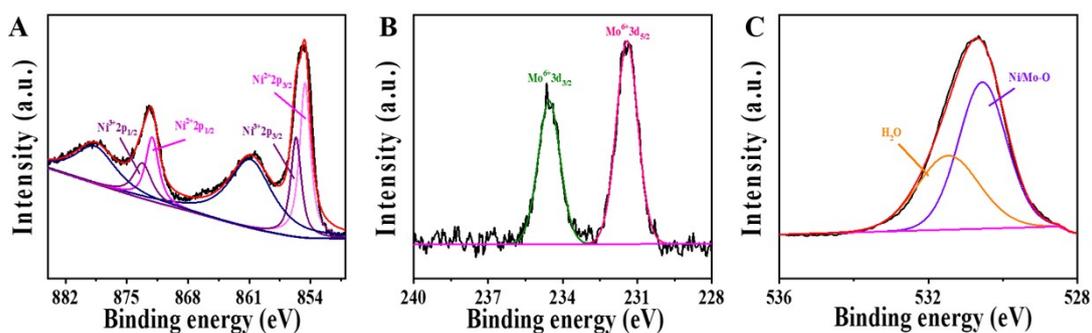


Fig. S13 XPS after NiMoO-Ar/NF 1000 CV cycle test.

Table S4. Comparison with other electrocatalysts.

Catalyst materials	Current density at 1.5 V vs. RHE (mA cm ⁻²)	Con.(%)	Sel. (%)	FE(%)
NiMoO-Ar/NF (this work)	65	94.27	100%	91.25
A-Ni-Co-H/NF ²	400	100	100	94.2

NC@CuCo ₂ Nx/CF ³	200	97.25	98	81.3
CC@NiO/Ni ₃ S ₂ ⁴	89	99	98	94
N-Mo-Ni/NF ⁵	Over 600	99.1	98.2	98.7
NiSe ⁶	200	99	99	99

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