#### **Supporting Information**

# Maximizing the Synergistic Effect of CoNi Catalyst on α-MoC for Robust Hydrogen Production

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#### Materials

**Chemicals:** Ammonium paramolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), cobalt chloride (CoCl<sub>2</sub>·6H<sub>2</sub>O), hydrochloric acid (38%), nitric acid (60%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ammonia borane was purchased from 9ding Chemistry. Gas: ammonia gas, 15% CH<sub>4</sub> / 85% H<sub>2</sub>, 0.5% O<sub>2</sub> in Ar, 20% CH<sub>4</sub> / 80% H<sub>2</sub>, Ar were purchased from Haikeyuanchang Gas Co. Ltd.

## **Preparation of catalysts**

**1. MoO<sub>3</sub> precursor:** The MoO<sub>3</sub> precursor was prepared by the decomposition of ammonium paramolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O) under the temperature of 773 K for 4 hours.

**2.**  $\alpha$ -MoC support: The pure phase  $\alpha$ -MoC was prepared by the temperature programed nitridation and carbonization of MoO<sub>3</sub>. Typically, 800 mg of MoO<sub>3</sub> was put in the quartz tube reactor and the temperature was risen from room temperature to 973 K with the rate of 5 K/min under the flow of 160 mL/min pure ammonia gas, then maintained at 973 K for 2 hours. After dropped to room temperature, the same procedure was performed at the atmosphere of 20% CH<sub>4</sub> / 80% H<sub>2</sub> with the flow rate of 125 mL/min. After the temperature dropped to room temperature, the sample was passivated by 0.5% O<sub>2</sub> in Ar with the flow rate of 55 mL/min.

**3.** *a*-MoC supported transition metals:  $\alpha$ -MoC supported Co, Ni were prepared by the impregnation method. Typically, 150 mg of  $\alpha$ -MoC was dispersed by 15 mL deionized water in a 50 mL single neck flask, then the required amount of 0.2 M Co<sup>2+</sup>, Ni<sup>2+</sup> aqueous solution or mixed solutions (for bimetal catalysts) were added into the flask. The air was replaced 3 times with pure Ar by double row tube and the solution in the flask was further stirred for 2 hours. After that, water was separated by the rotary evaporator at the temperature of 308 K, and the powder was collected. The collected samples were reactivated by 15% CH<sub>4</sub> / 85% H<sub>2</sub> at the temperature of 863 K for 2 hours with the flow rate of 30 mL/min before activity test.

## **Evaluation of catalytic performance**

**1. General procedure:** Before the reaction, the just activated catalyst was carefully transferred into a 50 mL two necked flask containing 5 mL deionized water at 298 K. A gas burette filled with water was connected to the reaction flask to measure the volume of released hydrogen. The reaction started when 5 mL aqueous ammonia borane (NH<sub>3</sub>·BH<sub>3</sub>, AB) solution was injected into the reactor by using a syringe. The volume of the generated hydrogen was monitored by recording the displacement of water in the gas burette. The reaction was completed when there was no more gas generated.

The same procedure was performed by replacing the neutral water with aqueous NaOH solutions to study the influence of base conditions on the activity of catalysts.

2. Kinetics study: The same procedure was performed at different concentrations of AB, catalysts and temperatures to determine the reaction kinetics and Activation Energy ( $E_a$ ) value in this reaction system.

**3. Durability test:** The procedure for the durability test was same as described above. 50 mg catalyst was dispersed in 5 mL 0.5 M NaOH aqueous solution at 298 K, then 1.0 mmol AB was dissolved in another 5 mL 0.5 M NaOH aqueous solution and injected into the reactor. After the completion of reaction, another 1.0 mmol of AB in 5 mL 0.5 M NaOH aqueous solution was injected directly into the reaction system for the next run. After 10 times of running, the catalyst was collected by centrifugation and washed by deionized water for 3 times, then dispersed in the 0.5 M NaOH aqueous solution for the 11<sup>th</sup> running.

**4. Calculation method:** The turnover frequency (TOF) reported here was based on the total amount of active metals. The equation for TOF calculation is given below:

$$TOF = \frac{V_{H2}}{22.4 V_s C_{ca} t}$$

 $V_{H2}$  was the total volume of hydrogen generated,  $V_s$  was the volume of solution (10 mL in this report),  $C_{ca}$  was the concentration of active metals in catalyst, and *t* was the time for the completion of reaction. The unit of TOF used in this study was mol<sub>H2</sub>· mol<sup>-1</sup><sub>CoNi</sub>· min<sup>-1</sup>.

5. Water adsorption and surface reaction: Firstly, 100 mg catalysts were put in an 8 mm quartz tube and activated by 15%  $CH_4 / 85\% H_2$  at the temperature of 863 K for 2 hours with the flow rate of 30 mL/min before activity test. After activation, the samples for testing were purged in inert gas in order to remove any chemisorbed surface species. Then the activated samples were exposed to 30 mL/min 2% H<sub>2</sub>O/Ar at 298 K with mass spectrometer collecting the signals of m/z=2, m/z=18 and m/z=40.

### Structural characterizations

**TEM:** STEM images and EDS element maps were collected by an aberration corrected JEM-ARM300F instrument. The samples were firstly activated then passivated by 0.5% O<sub>2</sub> in Ar, and dispersed by ethanol before being dropped onto TEM grid. The atomic resolution Z-contrast HAADF-STEM images and EELS spectrum images (SIs) were performed on a Nion HERMES-100 under 60 kV accelerating voltage. The TEM specimen prepared by ultramicrotomy is about 30 nm thickness. The convergence angle used in all characterization is 32 mrad. The collection angles of bright field (BF) and high angle annular dark field (HAADF) images are 0-9 and 75-210 mrad, respectively. Because Co and Ni have lower atomic numbers than that of Mo, it is hard to determine the highly dispersed Co and Ni species on  $\alpha$ -MoC by Z-contrast HAADF-STEM imaging. By taking advantage of electron energy loss spectroscopy analysis in aberration corrected STEM, it is possible to separately map the distribution of Co and Ni elements on  $\alpha$ -MoC particles even at the atomic scale. However, the performance of

electron energy loss spectroscopy (EELS) with high spatial resolution is still limited by the poor signal to noise ratio (SNR), indicating that denoising methods are imperative to extract the weak characteristic signals from the experimental data. In this research, denoising process was performed by principal component analysis (PCA) in HyperSpy library.<sup>1</sup> PCA method can decompose the three-dimensional EELS SI to several components and index them by their mathematical significance. The components whose significance are higher than a threshold are regarded as principal components, while the others are regarded as random noise. The denoised data were reconstructed by the principal components. The demonstrated EELS results in this research are PCA processed, unless specified. In addition, because the energy dispersion of low-dispersion setting is non-linear at the two ends of the spectrometer prism, we have recalibrated the energy axis of the as-acquired SIs by matching the onsets of the Co and Ni L-edges with the standard data<sup>2</sup> in order to correct the energy deviation caused by the spectrometer artifact. This energy recalibration, however, does not affect the chemical mappings presented in this manuscript.

**Others:** XRD patterns were collected on a Rigaku X-ray diffractometer operated at 40 kV and 100 mA, using Cu K<sub>a</sub> radiation. The in-situ XPS analysis was performed by using an Axis ultra-imaging photoelectron spectrometer. The samples after impregnation were made into small disks (6 mm diameter) and held on the sample holder, then activated in the pretreatment chamber of the XPS spectrometer under a flow of 15% CH<sub>4</sub> / 80% H<sub>2</sub> at 863 K for 2 hours. The samples were introduced directly into an ultrahigh-vacuum chamber for XPS measurement after activation without exposure to air. XAFS measurements were carried out at the BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF, 3.5 GeV, 250 mA in maximum, Si (111) double-crystals). All the samples were pre-activated in a mixture of 15% CH<sub>4</sub> / 80% H<sub>2</sub> at 863 K for 2 hours and carefully scaled under argon protection in a glove box.

Catalysts	ICP results of Co+Ni (wt%)
0.5Co0.5Ni/α-MoC	0.7
1.0Co1.0Ni/α-MoC	1.5
1.5Co1.5Ni/α-MoC	2.2
2.0Co2.0Ni/α-MoC	3.0
2.5Co2.5Ni/α-MoC	4.8

Table S1 ICP results of CoNi/ $\alpha$ -MoC catalysts with different active metal loadings.

Note: The catalysts in this report were named as  $xCoyNi/\alpha$ -MoC which means the loading of Co was x wt%, Ni

was y wt%.



**Figure S1** (A) Full XPS spectrum of 1.5Co1.5Ni/α-MoC, and high resolution XPS spectra of elements (B) Mo, (C) C, (D) Ni, and (E) Co. The binding energies of Ni 2p and Co 2p were compared with the standard binding energies of metallic Ni<sup>0</sup> and Co<sup>0</sup> from *Handbook of X-ray Photoelectron Spectroscopy*.<sup>3</sup>



Figure S2 Least square EXAFS fitting curves of Ni K edge in (A) 3Ni/a-MoC and (B) 1.5Co1.5Ni/a-MoC, Co

K edge in (C) 1.5Co1.5Ni/α-MoC and (D) 3Co/α-MoC.



**Figure S3** Wavelet transform analysis of Ni K edge in (A) 3Ni/α-MoC and (B) 1.5Co1.5Ni/α-MoC, Co K edge

in (C)  $1.5Co1.5Ni/\alpha$ -MoC and (D)  $3Co/\alpha$ -MoC.



**Figure S4** 3D wavelet transform analysis of Ni K edge in (A) 3Ni/α-MoC and (B) 1.5Co1.5Ni/α-MoC, Co K edge in (C) 1.5Co1.5Ni/α-MoC and (D) 3Co/α-MoC.

	Ni-Ni			Ni-C				
3Ni/α-MoC (Ni K-edge)	C.N.	$\sigma^{2/*10^{-3}}(Å^2)$	$E_0/eV$	R/Å	C.N.	σ <sup>2</sup> /*10 <sup>-3</sup> (Å <sup>2</sup> )	${\rm E_0/eV}$	R/Å
	0.5	5	-2.3	2.53±0.01	2.9	4.61	-2.3	2.08±0.02
	Ni-Ni、Ni-Co				Ni-C			
1.5Co1.5Ni/α-MoC (Ni K-edge)	C.N.	σ <sup>2</sup> /*10 <sup>-3</sup> (Å <sup>2</sup> )	$E_0/eV$	R/Å	C.N.	$\sigma^{2/*10^{-3}}(\text{\AA}^2)$	${\rm E}_{_0}/{\rm eV}$	R/Å
(in Reduge)	0.5	3	-0.4	2.50±0.02	3.1	2.56	-0.4	2.08±0.02
1.5Co1.5Ni/α-MoC (Co K-edge)	Со-Ni、Со-Со			Co-C				
	C.N.	σ <sup>2</sup> /*10 <sup>-3</sup> (Å <sup>2</sup> )	$E_0/eV$	R/Å	C.N.	$\sigma^{2/*10^{-3}}(\text{\AA}^2)$	${\rm E_0/eV}$	R/Å
	0.4	3	3.7	2.50±0.03	3.3	8.41	3.7	2.12±0.01
3Co/α-MoC (Co K-edge)	Со-Со			Co-C				
	C.N.	σ <sup>2</sup> /*10 <sup>-3</sup> (Å <sup>2</sup> )	$E_0/eV$	R/Å	C.N.	σ <sup>2</sup> /*10 <sup>-3</sup> (Å <sup>2</sup> )	$E_0/eV$	R/Å
	2.2	6	-2.3	2.49±0.01	1.7	9.97	-2.3	2.13±0.01

# corresponding to Figure S2.



Figure S5 HAADF-STEM images and EDS mapping results of  $1.5Co1.5Ni/\alpha$ -MoC.



**Figure S6** (a) Representative high resolution STEM-BF image of  $1.5Co1.5Ni/\alpha$ -MoC. (b) HAADF image collected simultaneously with (a). (c) Overlay of the distribution of Co and Ni elements on  $\alpha$ -MoC particles. (d) Overlay of the Co and Ni EELS maps. A region of a pair of contacted Co and Ni atoms is highlight in the overlay and enlarged at the upper right panel. The corresponding pixel index is shown at the lower right panel. (e) PCA processed and (f) raw EEL spectra extracted from the pixels in the enlarged area of (d) with the corresponding numbers. Ni signal is almost located in the '3' pixel and Co signal is mainly detected in the adjacent '4' pixel, indicating that the single Ni atom is contacted with the Co atom.



**Figure S7** Zoom-in (a) BF and (b) HAADF image of 3Co/α-MoC. (c) Overlay of the distribution of Co on α-MoC particles. (d) The Co-L edge EELS map. A single Co atom is highlighted in the map and the region is enlarged in the upper right panel. The corresponding pixel index of the enlarged image is at the lower right panel. (e) PCA processed and (f) raw EEL spectra extracted from the corresponding numbered pixels in the enlarged area of (d). The signal of Co is accredited to a single Co atom, since it is nearly confined in the central pixel ('3').



**Figure S8** Zoom-in (a) BF and (b) HAADF images of  $3Ni/\alpha$ -MoC. (c) Overlay of the distribution of Ni on  $\alpha$ -MoC particles. (d) Ni-L edge EELS map. A Ni single atom is highlighted in the map and the region is enlarged at the upper right panel. The pixel in the enlarged image is indexed in the lower right illustration. (e) PCA processed and (f) raw EEL spectra extracted from the corresponding numbered pixels in (d). It is clear that a single Ni atom is located in the central pixel ('3').



Figure S9 Isotopic experiment of catalytic hydrolysis of AB by 1.5Co1.5Ni/α-MoC in H<sub>2</sub>O and D<sub>2</sub>O. Conditions:

10~mL 0.1 M AB, 25 °C, 50 mg catalyst.



Figure S10  $H_2$  (m/z = 2, by mass spectrosopy) formation from water reaction (30 mL/min 2%  $H_2$ O/Ar at 298 K)

on the activated  $\alpha\text{-MoC}$  and 1.5Co1.5Ni/ $\alpha\text{-MoC}$  catalysts, respectively.



**Figure S11** Duration of the catalytic hydrogen production from hydrolysis of AB and the corresponding TOF values of CoNi/α-MoC with different loadings of CoNi. The ratio of Co:Ni was controlled as 1:1.

The synergistic effect between Co and Ni atoms can be further evaluated by changing the total metal loadings of Co and Ni from 1% to 5% while maintaining the Co / Ni ratio to 1. The volcano relationship between the TOF values with the total metal loadings of CoNi was observed and the  $1.5Co1.5Ni/\alpha$ -MoC exhibited the highest activity. In comparison, the TOF value of  $0.5Co0.5Ni/\alpha$ -MoC was  $36.1 \text{ mol}_{H2}^{-1} \text{ mol}^{-1}_{CoNi}^{-1}$  which is similar to that of monometallic Co(Ni)/ $\alpha$ -MoC, indicating the synergistic effect between Co and Ni atoms was almost disappeared at low metal loadings. While at the high loading condition, the TOF of 2.5Co2.5Ni/a-MoC also dropped significantly to the value of  $36.8 \text{ mol}_{H2}^{-1} \text{ mol}^{-1}_{CoNi}^{-1}$  min<sup>-1</sup>, probably related to the loss of the density of active metal sites.



Figure S12 Duration of the catalytic hydrogen production from hydrolysis of AB and the corresponding TOF

values of  $1.5Co1.5Ni/\alpha$ -MoC in the presence of 0-1.0 M NaOH aqueous solution.



**Figure S13** (A) Time dependent hydrogen production curves of 1.5Co1.5Ni/α-MoC with different concentration of AB for hydrogen production from hydrolysis of AB, (B) Calculated reaction order. Conditions: neutral water, 25 °C, 50 mg catalyst.



**Figure S14** (A) Time dependent hydrogen production curves of 1.5Co1.5Ni/α-MoC with different concentration of AB for hydrogen production from hydrolysis of AB. (B) Calculated reaction order. Conditions: 25 °C, 50 mg catalyst, 10 mL 0.5 M NaOH.



**Figure S15** (A) Time dependent hydrogen production curves by different amount of 1.5Co1.5Ni/α-MoC for hydrogen production from hydrolysis of AB. (B) Calculated reaction order. Conditions: 25 °C, 10 mL 0.1 M AB in 0.5 M NaOH.



Figure S16 (A) Time dependent hydrogen production curves of  $1.5Co1.5Ni/\alpha$ -MoC at different temperature for hydrogen production from hydrolysis of AB. (B)Calculated activation energy (E<sub>a</sub>). Conditions: neutral water, 50 mg catalyst, 10 mL 0.1 M AB.



Figure S17 (A)Calculated activation energy ( $E_a$ ), and time dependent hydrogen production curves of  $\alpha$ -MoC supported (B) 1.5Co1.5Ni, (C) 3Ni, (D) 3Co at different temperatures for hydrogen production from hydrolysis of AB. Conditions: 20 mg catalyst, 10 mL 0.1 M AB in 0.5 M NaOH.



**Figure S18** (A) Time dependent hydrogen production curves of  $\alpha$ -MoC and  $\beta$ -MoC supported CoNi catalysts for hydrogen production from hydrolysis of AB with or without the presence of NaOH. (B) The corresponding TOF values of catalysts and conditions in (A). Conditions: 25 °C, 10 mL 0.1 M AB, 50 mg catalyst.

Catalysts	T / °C	Additives	$TOF/ \\ mol_{H2} \cdot mol^{\text{-1}}{}_{active \ metal} \cdot \ min^{\text{-1}}$	Ref
Ni-Co-P	25 °C	NaOH	109.4	4
Co NPs@PCC	25 °C		90.1	5
Ni/ZIF-8	25 °C	NaOH	85.7	6
Cu <sub>x</sub> Co <sub>1-x</sub> O	25 °C		70.0	7
NiMo/graphene	25 °C		66.7	8
Co/MIL-101	25 °C		51.4	9
NiCo <sub>2</sub> O <sub>4</sub> /Ti	25 °C		50.1	10
Ni <sub>2</sub> P	25 °C		40.7	11
Ni/CNTs	25 °C		26.2	12
CuCo@MIL-101	25 °C		19.6	13
PEI-GO <sub>3D</sub> /Co	25 °C		18.5	14
Ni/SiO <sub>2</sub>	25 °C		13.2	15
Ni <sub>3</sub> FeN@SiO <sub>2</sub>	25 °C		14.2	16
Ni/C	25 °C		8.8	17
Co@N-C-700	25 °C		5.6	18
Cu/RGO	25 °C		3.6	19
Commercial Pt/C	25 °C		83.3	20
CoNi/a-MoC	25 °C		128.5	This work
CoNi/a-MoC	25 °C	NaOH	321.3	This work

Table S3 Summary of recent reports on noble metal free catalysts for hydrogen production from AB.

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