Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Enhanced ammonia synthesis performance of ceria-supported bimetallic catalyst by changing Co and Mo segregation

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Characterization

XRD analysis was performed on a PANalytical X'Pert3 powder diffractometer with Cu Kα radiation. The texture of catalysts was obtained by Micromeritics ASAP 2020 apparatus at −196 ºC. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained by a FEI Tecnai G2 F30 microscope. Aberration-corrected HAADF-STEM images were measured by a FEI TIan G2 60-300 microscope. Raman spectra of samples were acquired on an InVia Reflex Raman microscope equipped with a 532 nm laser.

X-ray photoelectron spectroscopy (XPS) spectrum of catalysts was collected an ESCALAB 250Xi photoelectron spectrometer. Specifically, Sample was reduced at 500 °C for 6 h in 75%H_2/25%N_2 mixture in a pretreatment chamber attached to the spectrometer. Then, the C1s peak of adventitious carbon was regulated to the binding energy at 284.6 eV.

Hydrogen temperature-programmed reduction (H_2-TPR) of sample was performed on a Micromeritics AutoChem II 2920. 100 mg of catalyst was purged in Ar at 150 °C for 1 h and then cooled to 50 °C. Afterward, the sample was heated from 50 °C to 600 °C in 10% H_2/Ar mixture. Temperature-programmed desorption of hydrogen experiments (H_2-TPD) and Temperature-programmed desorption of nitrogen experiments (N_2-TPD) were carried out on the same instrument. After reduced in H_2 at 500 °C for 6 h, catalyst was purged and cooled to 400 °C in Ar. Then hydrogen or nitrogen was added to sample for 1 h and cooled to 50 °C. Afterwards, the sample was heated in Ar flow to 600 °C, and the mass signals were obtained.

Calculations of ammonia synthesis rate:

The ammonia synthesis rate is calculated by the concentration of ammonium ion, which is examined using an ion chromatography (Thermo Scientific, ICS-600) equipped with the Dionex IonPac^{TM}CS16 column and DS5 conductivity detector. The ammonia synthesis rate is calculated by the following formula:

$$r = \frac{C * V * 3600}{T * M_N * m_{cat}}$$

r: ammonia synthesis rate (mol g^{-1} h^{-1});

C: concentration of ammonium ion (mg L^{-1});

V: liquid volume in gas absorption tube (mL);

T: absorption time (s);

M_N: relative atomic mass of nitrogen atom (14);

m_{cat}: quality of the catalyst (g).

Mass and Heat Transfer Calculations for Ammonia Synthesis over Mo/Co-C

Mears Criterion for External Diffusion (Fogler, Elements of Chemical Reaction Engineering, 4th edition, p841; Mears, Ind. Eng. Chem. Process Des. Dev. 1971, 10, 541–547)

If $C_M = \frac{(-r_A^{'})\rho_b Rn}{k_c C_{Ab}} < 0.15$, then external mass transfer effects can be neglected.

$-r_A^{'}$ = reaction rate of nitrogen, kmol/kg-cat·s

n = reaction order with respect to N_2.

R = catalyst particle radius, m

ρ_b = bulk density of catalyst bed, kg/m^3

C_{Ab} = bulk gas concentration of nitrogen, kmol/m^3

k_c = mass transfer coefficient, m/s

$C_M = \frac{(-r_A^{'})\rho_b Rn}{k_c C_{Ab}}$ = [2.2 x 10^{-7} kmol-N_2/kg-cat·s][910 kg/m^3][3 x 10^{-4} m][0.69]/([1.7 m/s]*[0.045 kmol/m^3])= **5.4 x 10^{-7} <0.15**

Generally, according to the Mears Criterion, when the calculation value for C_M is below 0.15, the external diffusion limitations can be neglected during the kinetic experiments. In our case, the C_M is **5.4 x 10^{-7}**, indicating that the external diffusion limitations of the kinetic experiments could be neglected.

Weisz-Prater Criterion for Internal Diffusion (Fogler, Elements of Chemical Reaction Engineering, 4th edition, p839)

If $C_{WP} = \frac{(-r_A^{'})\rho_c R^2}{D_e C_{As}} < 1$, then internal mass transfer effects can be neglected.

$-r_A^{'}$ = reaction rate of nitrogen, kmol /(kg-cat·s)

ρ_c = solid catalyst density (kg m^{-3})

R = catalyst particle radius, m

ρ_c = bulk density of catalyst bed, kg/m^3

C_{Ab} = bulk gas concentration of nitrogen, kmol/m^3

k_c = mass transfer coefficient, m/s

D_e = effective gas-phase diffusivity (m^2 s^{-1})

$$C_{WP} = \frac{(-r_A^{'})\rho_c R^2}{D_e C_{As}}$$ = [2.2 x 10^{-7} kmol-N_2/kg-cat·s] × [4×10^3 kg-cat/m^3] × [3 x 10^{-4} m]^2 / ([3.34 x 10^{-6} m^2/s] × [0.045 kmol/m^3]) = **$5.3 \times 10^{-4} < 1$**

Generally, according to the Mears Criterion, when the calculation value for C_{WP} is below 1, the internal diffusion limitations can be neglected during the kinetic experiments. In our case, the C_{WP} is **$5.3 \times 10^{-4} < 1$**, indicating that the internal diffusion limitations of the kinetic experiments could be neglected.

Mears Criterion for External (Interphase) Heat Transfer (Fogler, Elements of Chemical Reaction Engineering, 4th edition, p842)

$$C_{MH} = \left| \frac{-\Delta H_r(-r_A^{'})\rho_b RE}{h_t T_b^2 R_g} \right| < 0.15$$

[136.9 kJ/mol× 2.2 x 10^{-7} kmol-N_2/kg-cat·s × 910 kg-cat/m^3 ×3 x 10^{-4} m× 150 kJ/mol] / [185.3 kJ/m^2.K.s × 673^2 K^2× 8.314 ×10^{-3} kJ/mol.K]=**$9.4 \times 10^{-6} < 0.15$**

Generally, according to the Mears Criterion, when the calculation value for C_{MH} is below 0.15, the heat transfer effect can be neglected during the kinetic experiments. In our case, the C_{MH} is **9.4×10^{-6}**, indicating that the heat transfer effect can be neglected in the kinetic experiments.

Mears Criterion for Combined Interphase and Intraparticle Heat and Mass Transport (Mears, Ind. Eng. Chem. Process Des. Dev. 1971, 10, 541–547)

$$\frac{\left(-r_A^{'}\right)\rho_b R^2}{D_e C_{Ab}} < \frac{1+0.33\gamma\chi}{|n-r_b\beta_b|(1+0.33n\omega)}$$

$$\gamma = \frac{E}{R_g T_s};\ \gamma_b = \frac{E}{R_g T_b};\ \beta_b = \frac{(-\Delta H_r) D_e C_{Ab}}{\lambda T_b};\ \chi = \frac{(-\Delta H_r)\left(-r_A^{'}\right)R}{h_t T_b};\ \omega = \frac{\left(-r_A^{'}\right)R}{k_c C_{Ab}}$$

γ = Arrhenius number;

β_b = heat generation function;

λ = catalyst thermal conductivity, W/m.K;

χ = Damköhler number for interphase heat transport

ω = Damköhler number for interphase mass transport

$\frac{\left(-r_A^{'}\right)\rho_b R^2}{D_e C_{Ab}}$ = [2.2 x 10^{-7} kmol-N_2/kg-cat·s × 910 kg-cat/m^3× (3 x 10^{-4})^2 m^2]/ ([3.34 x 10^{-6} m^2/s] × [0.045 kmol/m^3]) = **12.0×10^{-5}**

$$\frac{1+0.33\gamma\chi}{|n-r_b\beta_b|(1+0.33n\omega)} = \mathbf{1.1}$$

Left member < Right member

Generally, according to the Mears Criterion, when the calculation value for $\frac{\left(-r_A^{'}\right)\rho_b R^2}{D_e C_{Ab}}$ is lower than that for $\frac{1+0.33\gamma\chi}{|n-r_b\beta_b|(1+0.33n\omega)}$, the interphase and intraparticle heat and mass transfer effect can be neglected during the kinetic experiments.

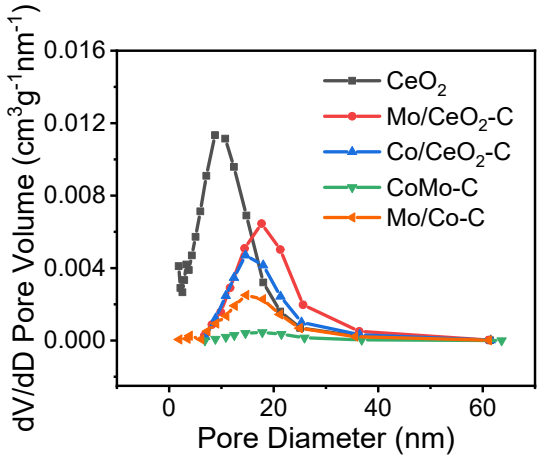

Fig. S1 Pore size distribution curves of samples.

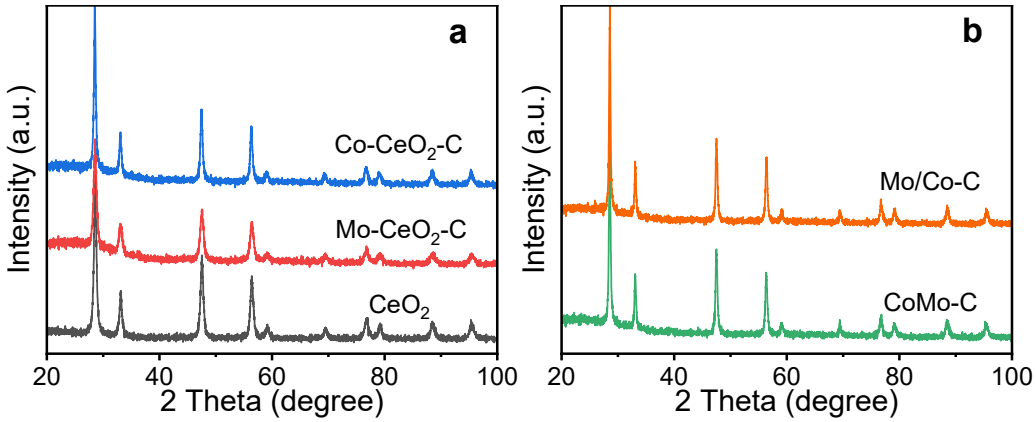

Fig. S2 XRD pattern of various samples.

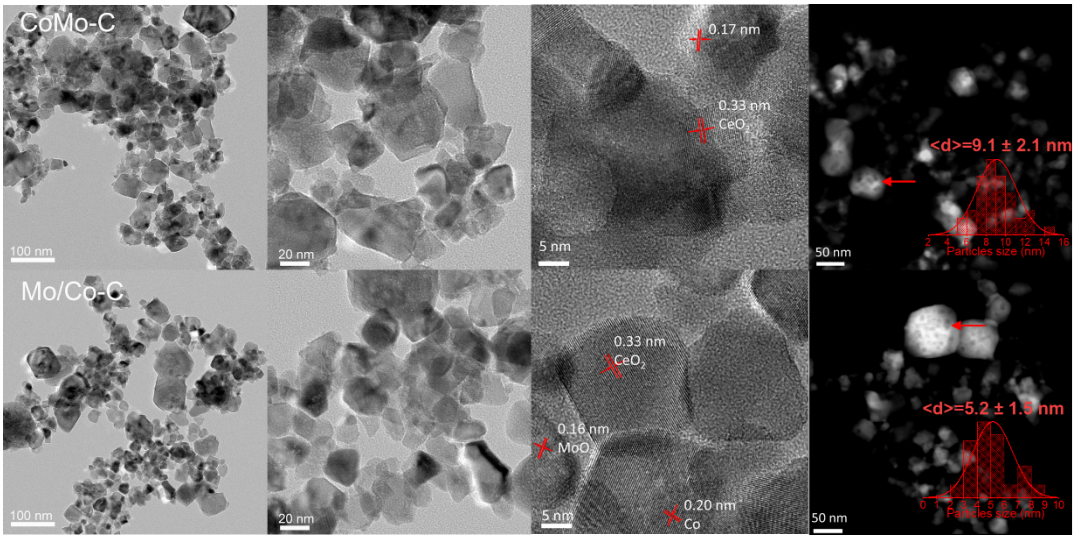

Fig. S3 TEM images and Co-Mo particle size distribution in the inset.

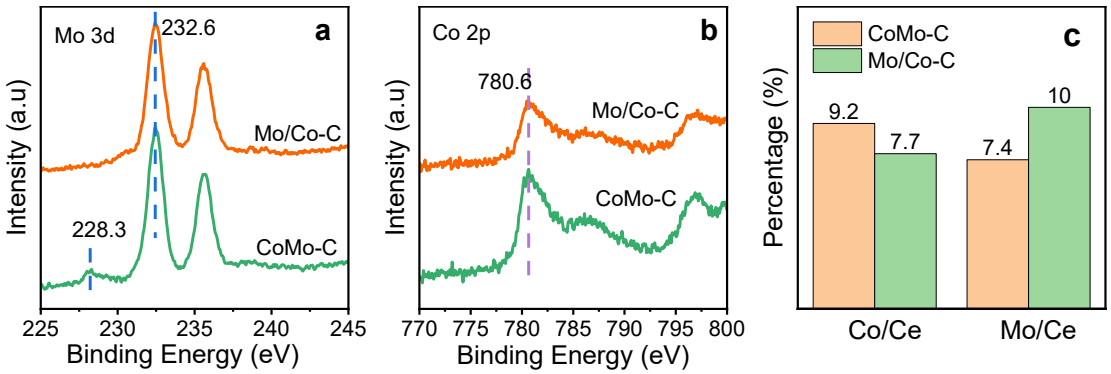

Fig. S4 XPS spectra of the as-prepared samples: (a) Mo 3d, (b) Co 2p and (c) the percentage of Co/Ce and Mo/Ce.

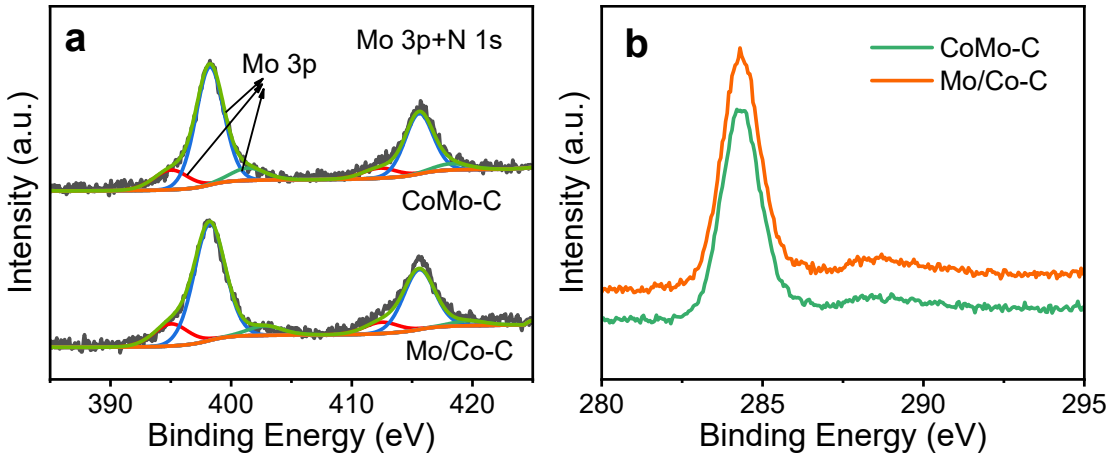

Fig. S5 XPS spectra of the as-prepared samples: (a) Mo 3p+N 1s, (b) C 1s.

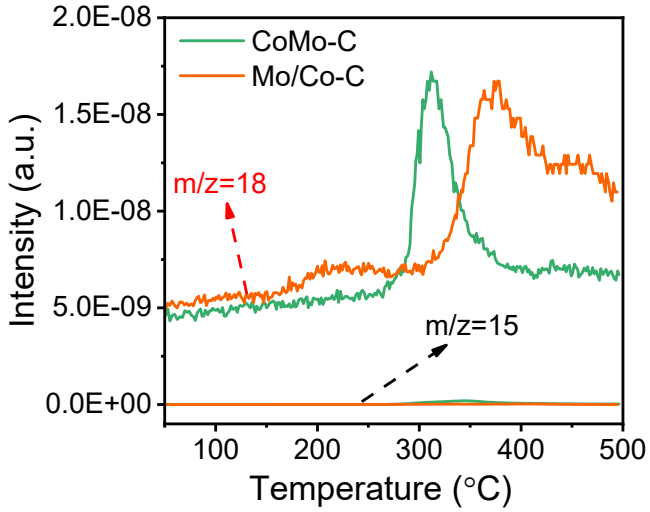

Fig. S6 MS signals of m/z=18 and m/z=15 during H_2-TPR.

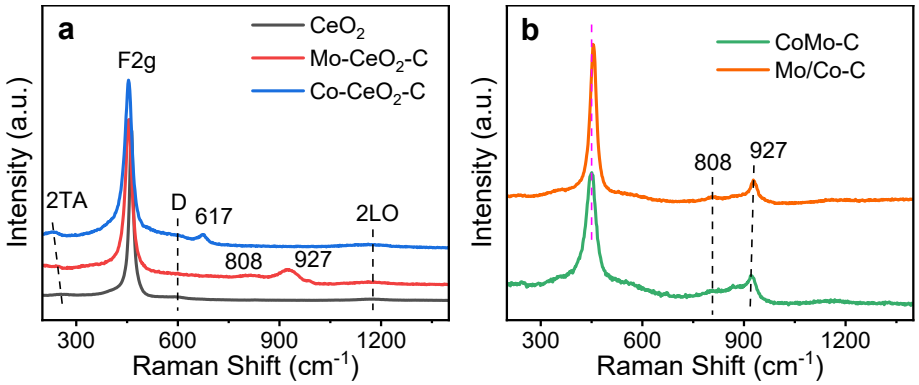

Fig. S7 Raman spectra of various samples.

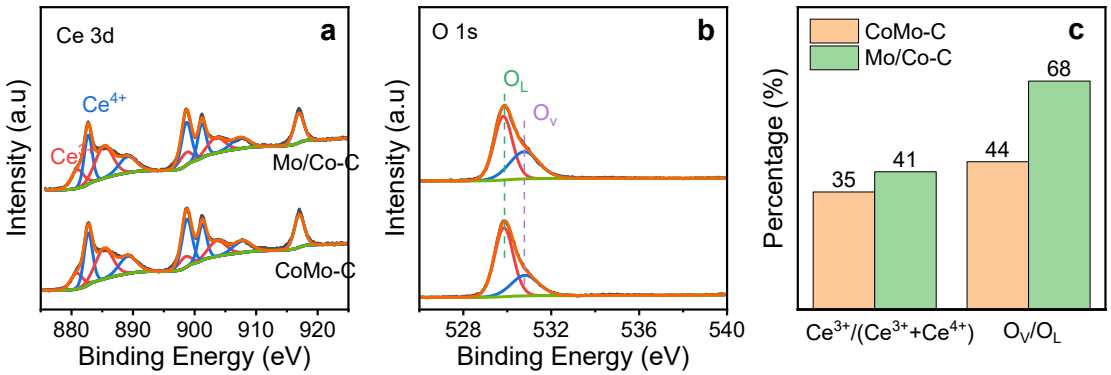

Fig. S8 XPS spectra of the reduced catalysts: (a) Ce 3d, (b) O 1s and (c) the ratios of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ and O_V/O_L.

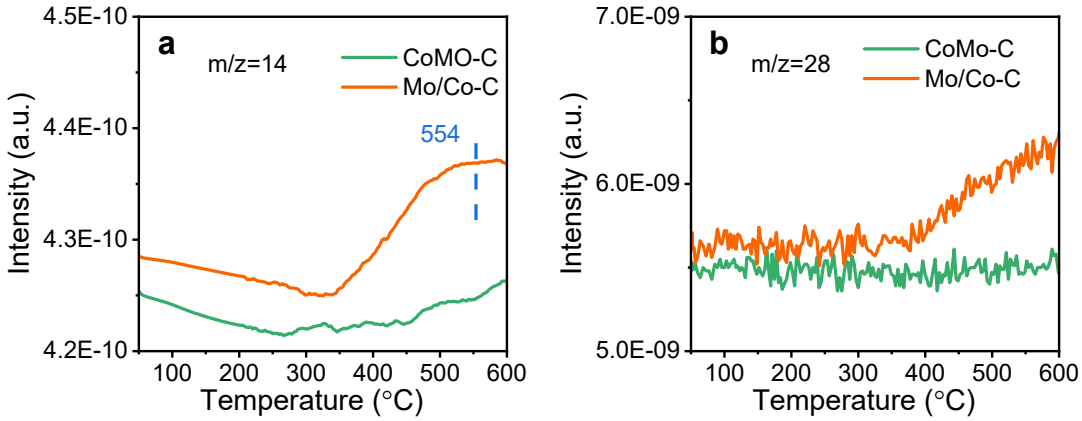

Fig. S9 MS signals of (a) m/z=14 and (b) m/z=28 during N_2-TPD.

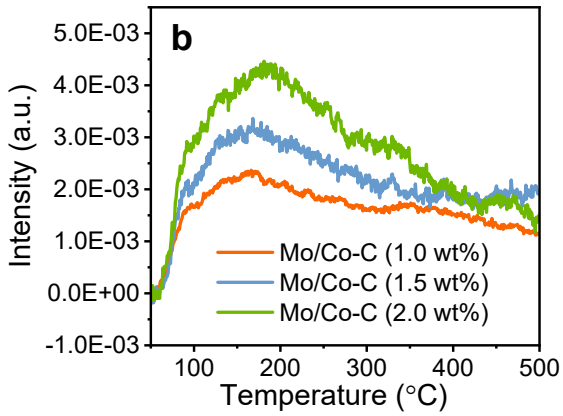

Fig. S10 H_2-TPD profile over catalysts with different Co loadings.

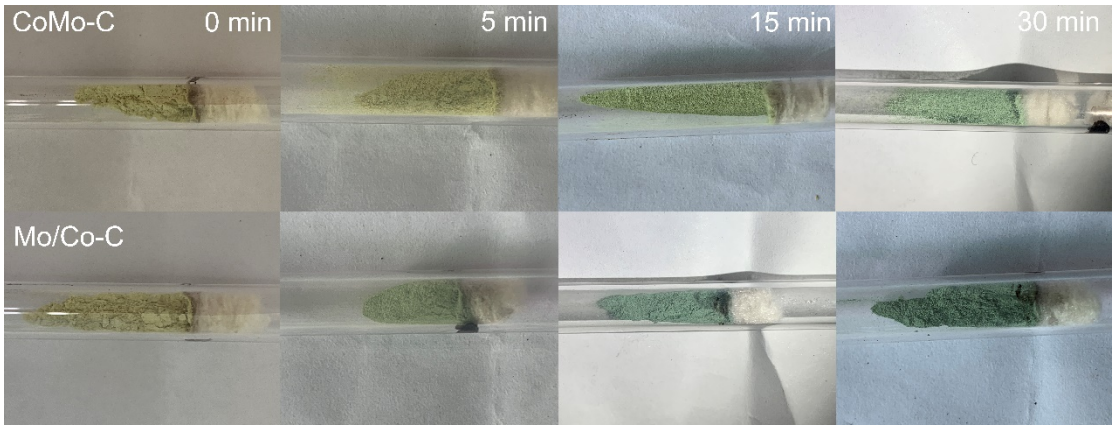

Fig. S11 **Color change photographs of the mixtures.** Photographs of samples made with WO_3 mixed with the catalysts before treatment (0 min) and after treatment with H_2 at 300°C for 5 min, 15 min and 30 min.

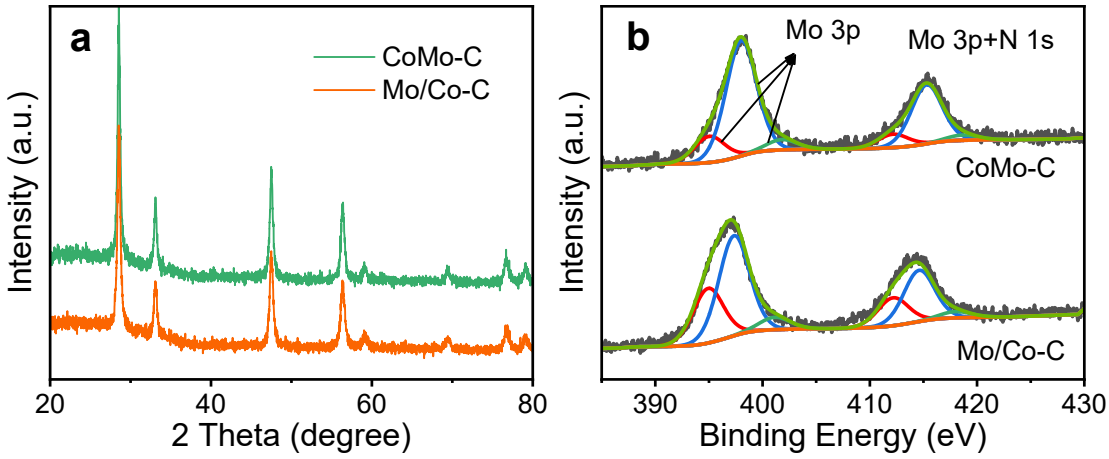

Fig S12 XRD pattern of used catalysts and Mo 3p+N 1s spectrum of catalysts with treatment in N_2-H_2 mixture.

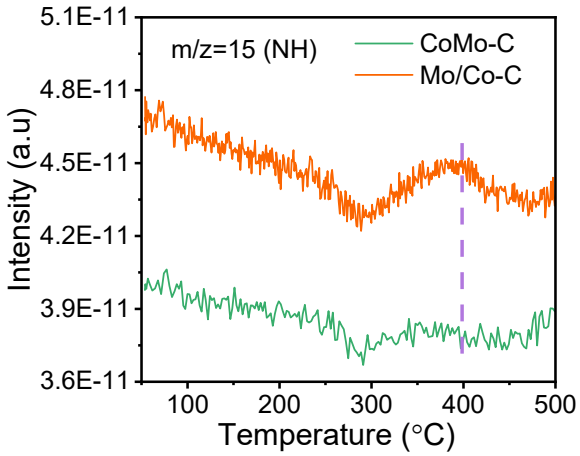

Fig. S13 MS signals of a m/z=15 (NH) during TPSR over catalysts pre-adsorbed with D_2.

Table S1 Catalytic performance of various Co-Mo catalysts.

Samples	Rate ($\mu mol\ g^{-1}\ h^{-1}$)	Ea ($kJ\ mol^{-1}$)	Reaction conditions	SV ($mL\ g^{-1}\ h^{-1}$)	Ref.
CoMo-C	909	88	1 MPa, 400 °C	36000	This
Mo/Co-C	1563	56	1 MPa, 400 °C	36000	work
Mo/Co-C (0.5wt%)	1026	53	1 MPa, 400 °C	36000	This
Mo/Co-C (1.5wt%)	1525	58	1 MPa, 400 °C	36000	work
Mo/Co-C (2.0wt%)	1558	55	1 MPa, 400 °C	36000	This
Mo/Co-C (2.5wt%)	1653	55	1 MPa, 400 °C	36000	Work
Mo (8.3wt%)/Co-C	1597	-	1 MPa, 400 °C	36000	This
Mo (10.9wt%)/Co-C	1625	-	1 MPa, 400 °C	36000	Work
$CoMo_T$-c	895	-	1 MPa, 400 °C	36000	This
Mo_T/Co-C	1605	-	1 MPa, 400 °C	36000	work
CoMo-C	1545	-	1 MPa, 400 °C	72000	This
Mo/Co-C	3282	-	1 MPa, 400 °C	72000	work
Mo/Co-H	1288	57	1 MPa, 400 °C	36000	1
Co/CeO_2	689	-	1 MPa, 400 °C	36000	1
Mo/CeO_2	203	-	1 MPa, 400 °C	36000	1
$CoMo/CeO_2$	481	61	1 MPa, 400 °C	36000	1
$Co\text{-}Mo/CeO_2$	2840	61	0.9 MPa, 400 °C	72000	2-3

Table S2 Textural properties of CeO_2 and CeO_2 supported Co-Mo catalysts.

Samples	Surface area ($m^2\ g^{-1}$)	Pore volume (cm^3g^{-1})	Average pore size (nm)	Co (wt%)	Mo (wt%)
CeO_2	45	0.15	9	-	-
Mo/CeO_2-C	16	0.10	19	-	5.46
Co/CeO_2-C	13	0.07	18	0.95	-
CoMo-C	1	0.01	19	1.01	5.56
Mo/Co-C	12	0.04	13	0.96	5.72

References

1. Fang, B.; Qi, Z.; Liu, F.; Zhang, C.; Li, C.; Ni, J.; Lin, J.; Lin, B.; Jiang, L., Activity enhancement of ceria-supported Co-Mo bimetallic catalysts by tuning reducibility and metal enrichment. *J. Catal.* **2022,** *406*, 231-240.

2. Tsuji, Y.; Kitano, M.; Kishida, K.; Sasase, M.; Yokoyama, T.; Hara, M.; Hosono, H., Ammonia synthesis over Co-Mo alloy nanoparticle catalyst prepared via sodium naphthalenide-driven reduction. *Chem Commun (Camb)* **2016,** *52* (100), 14369-14372.

3. Tsuji, Y.; Ogasawara, K.; Kitano, M.; Kishida, K.; Abe, H.; Niwa, Y.; Yokoyama, T.; Hara, M.; Hosono, H., Control of nitrogen activation ability by Co-Mo bimetallic nanoparticle catalysts prepared via sodium naphthalenide-reduction. *J. Catal.* **2018,** *364*, 31-39.