Supporting Information

Enhanced ammonia synthesis activity of carbon-supported Mo catalyst by Mo carburization

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1. Experimental section

1.1. Preparation of Samples

Preparation of thermally modified carbon. Thermally modified carbon was prepared by the previous reported method.[1] Commercial activated carbon (AC, Fujian Xinsen Carbon. Co., Ltd.) was heated in Ar at 1900 °C for 2 h, and then oxidized in steam at 430 °C for 30 h. The resulting carbon was named as "C", and the surface area of C was 713 m^2 g^{-1}.

Synthesis of MoO_x/C. Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) as Mo precursors, were introduced on C by incipient wetness impregnation, the weight ratio of Mo to C was 20 wt.%, and the sample was named as "the as-prepared MoO_X/C". The as-prepared sample was reduced in N_2-H_2 at 500 °C for 6 h, and the reduced sample was named as MoO_X/C.

Synthesis of Mo_2C/C catalysts. The as-prepared MoO_x/C was heated at 400 °C for 1 h with a heating rate of 10 °C min^{-1} in H_2. Subsequently, the sample continues to be heated from 400 to 700 °C at a rate of 1 °C min^{-1} and held for 4 h. The sample drop to room temperature and then switch the gas to 0.5 %O_2/Ar and keep it for 10 h to passivate the sample, and the resulting sample was named as "the as-prepared Mo_2C/C". The as-prepared sample was reduced in N_2-H_2 at 500 °C for 6 h, and the reduced sample was named as Mo_2C/C.

1.2. Characterization

X-ray diffraction (XRD) patterns were obtained in a PANalytical X'Pert3 Powder diffractometer

instrument with Cu Kα radiation (λ=0.154 32 nm). Nitrogen absorption-destruction isotherms were measured at −196 °C on ASAP 2020M instrument. Raman spectra were obtained using 532 nm laser by InVia Reflex Raman microscope equipped.

For Thermogravimetric analysis (TGA), 10 mg sample was heated to 500 °C under the 3.3 % N_2−10 % H_2−Ar gas mixture for 2 h and record the sample quality information by Setsys Evolution (Setaram) thermal analyzer.

The XPS results of the catalysts were collected using ESCALAB 250 X-ray photoelectron spectrometer. Before the measurements, the samples were reduced at 500 °C for 1h in a flow of 3.3 % N_2−10 % H_2−Ar mixture (30 ml min^{-1}) in the pretreatment chamber. After cooling down to 50 °C, the sample was transferred into the analysis chamber during which the samples do not contact air. Binding energy calibration was performed using adventitious carbon (284.6 eV) before data processing.

The D/H exchange experiment was carried out on Micromeritics AutoChem II 2920 equipment. First, 100 mg sample was raised to 500 °C at 10 °C min^{-1} in hydrogen atmosphere and maintained for 2 h and then purged with Ar for 30 min and cooled down to 400 ℃. After that, the gas was changed to D_2 and keep sample at 400 °C for 60 min. After reduce the temperature to 50 °C in D_2 and continue to maintain it for 60 min, the mass signals were recorded by a Hiden Analytical HPR-20 spectrometer while changing the gas to 3.3 % N_2–10 % H_2–Ar gas mixture. Temperature-programmed surface reaction (TPSR) was performed after the D/H exchange. The sample temperature was heated to 600 °C at 10 °C min^{-1} and record the mass spectrometry signal.

Temperature-programmed desorption of hydrogen or nitrogen (H_2-TPD or N_2-TPD) experiments was 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. Afterwards, hydrogen or nitrogen was added to sample for 1 h and cooled to 50 °C. Finally, the sample was heated in Ar flow to 600 °C, and the TCD signals were obtained.

1.3. Evaluation of catalytic performance

Catalytic reactions were conducted in a continuous fixed-bed flow (inner diameter = 12 mm). The catalyst was reduced by temperature programmed reduction program 500 °C in N_2-H_2 (1:3) atmosphere for 6 h, then ammonia synthesis activity test was carried out under the set conditions (each condition was stable for at least 2 h). Afterward the outlet gas of the reactor was absorbed by

fixed volume of dilute sulfuric acid aqueous solution. The ammonia synthesis rate was calculated based on the concentration of ammonium ion in the solution by ion chromatography. The reproducibility of the reaction rate was confirmed 3 times and the error range was ±5%.

1.4. Reaction order

To measure the reaction orders with respect to N_2 and H_2, 0.2 g of catalyst was loaded into the reactor and the gas flow rate was fixed at 120 mL min^{-1}. The ammonia synthesis tests are carried out under the conditions without mass transport or heat transfer limitations, and the detailed mass transport and heat transfer calculations based on the best-performing Mo_2C/C have been given above. The ammonia concentration in the outlet gas is lower than 5% under the adopted condition, and thus the change in the ammonia partial pressure would exert a negligible influence on the measured partial pressures of nitrogen and hydrogen. In view of this, the influence of the ammonia partial pressure on the reaction orders of N_2 and H_2 is slight. The constituent gases of the reactant (N_2, H_2, Ar) were as follows in volume fraction (10%, 50%, 40%), (20%, 50%, 30%) and (34%, 50%, 16%) for N_2 order, (20%, 30%, 50%), (20%, 50%, 30%) and (20%, 80%, 0) for H_2 order. The NH_3 order was obtained by changing the flow rate of a stoichiometric H_2–N_2 gas mixture (60–240 mL min^{-1}). The kinetic experiments were carried out far from equilibrium conditions, and the reaction orders were calculated according to the metho ds described elsewhere.[2] The reaction orders were estimated by using the following Eqs:

$$r = kP_{N2}^{\alpha}P_{H2}^{\beta}P_{NH3}^{\gamma} \quad (1)$$

$$r = \frac{1}{W}\frac{dy_0}{d(\frac{1}{q_0})} \quad (2)$$

$$my_0^{m-1}dy_0 = Cd(\frac{1}{q_0}) \quad (3)$$

$$C = k_2P_{N2}^{\alpha}P_{H2}^{\beta} \quad (4)$$

Where r is the ammonia synthesis rate, α, β, and γ are the reaction orders with respect to N_2, H_2, and NH_3, respectively. P_{N2}, P_{H2}, and P_{NH3} are the partial pressures of N_2, H_2, and NH_3, respectively. And W, y_0 and q_0 represent the catalyst mass, molar fraction of ammonia in the outlet gas and relationship between flow rate.

1.5 Mass and Heat Transfer Calculations for Ammonia Synthesis over Mo_2C/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

$C_M = \frac{(-r_A^{'})\rho_b Rn}{k_c C_{Ab}}$ = [2.7 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])= **6.7 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 **6.7 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})

$C_{WP} = \frac{(-r_A^{'})\rho_c R^2}{D_e C_{As}}$ = [2.7 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]) = **6.5 × 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 **6.5 × 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× 2.7 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]=**2.2×10^{-10} < 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 **2.2×10^{-9}**, 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)

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

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

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

$\frac{(-r_A^{'})\rho_b R^2}{D_e C_{Ab}}$ = [2.7 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]) = **1.5×10^{-4}**

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

Left member < Right member

Generally, according to the Mears Criterion, when the calculation value for $\frac{(-r_A^{'})\rho_b R^2}{D_e C_{Ab}}$ 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.

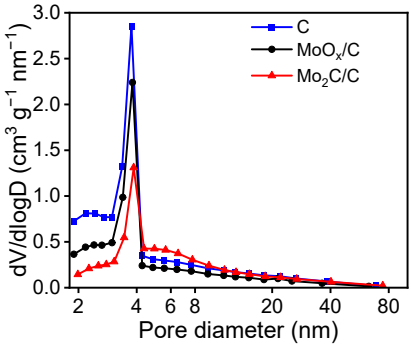

Fig. S1 Pore size distribution map of C, MoO_xC/C and Mo_2C/C.

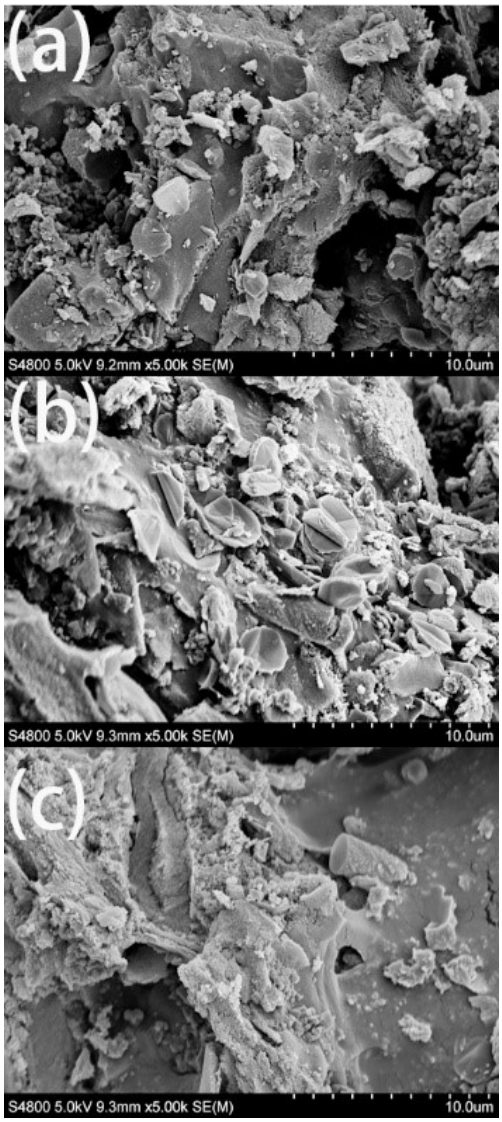

Fig. S2 SEM images of (a) C, (b) MoO_x/C, (C) Mo_2C/C.

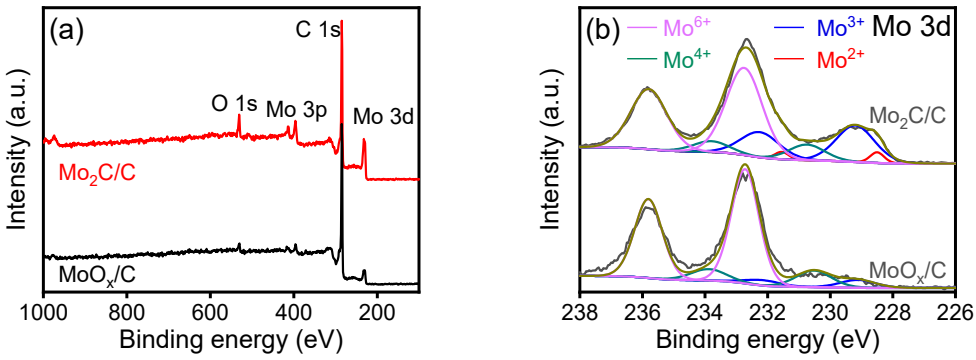

Fig. S3 (a) XPS survey spectra and (b) Mo 3d XPS spectra of the as-prepared Mo catalysts without hydrogen treatment.

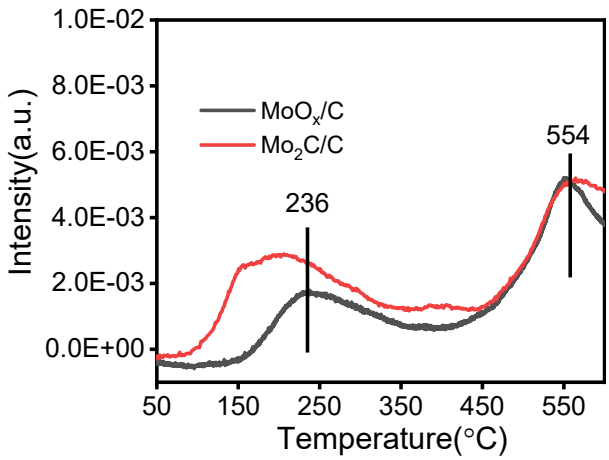

Fig. S4 N_2-TPD profiles of Mo catalysts.

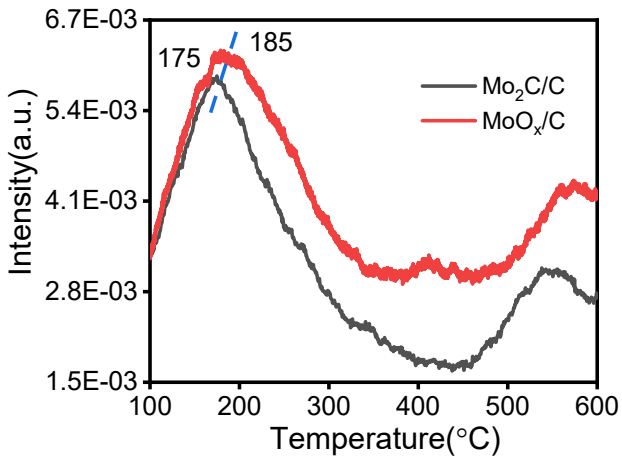

Fig. S5 H_2-TPD profiles of Mo catalysts.

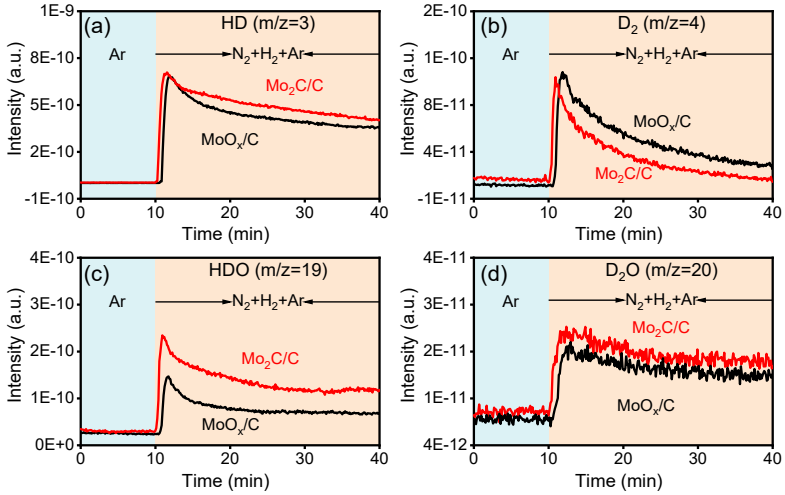

Fig. S6 The mass signals of HD, D_2, HDO, and D_2O with time during the D/H exchange reaction at 50 °C.

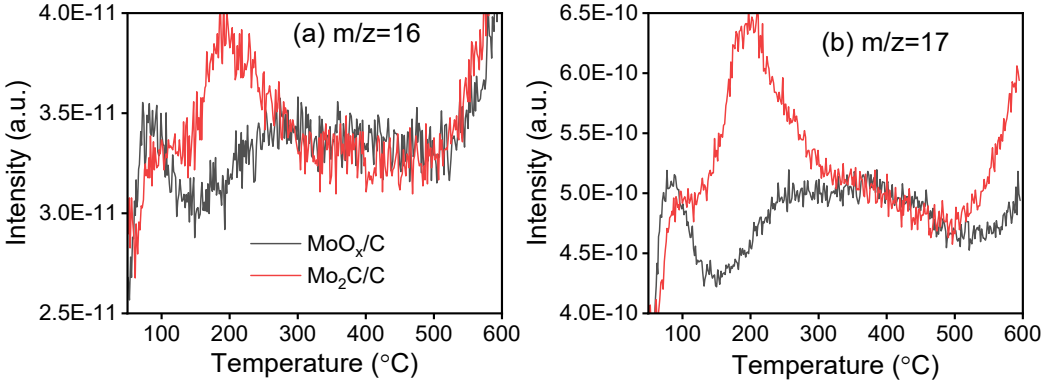

Fig. S7 Evolution profiles of NH_2 (m/z=16) and NH_3 (m/z=17) during TPSR study in the 3.3% N_2−10% H_2−Ar mixture.

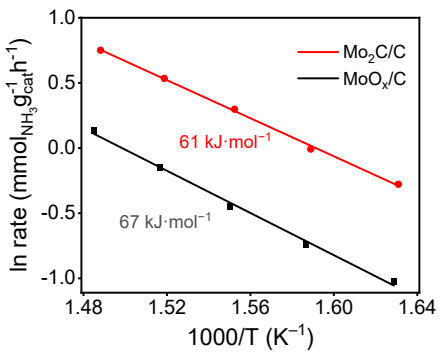

Fig. S8 Arrhenius plots of ammonia synthesis for MoO_x/C and Mo_2C/C.

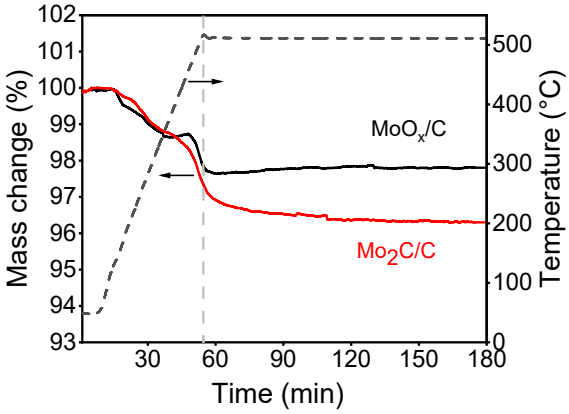

Fig. S9 TG profiles of Mo catalyst in 3.3 %N_2–10 %H_2–Ar gas mixture.

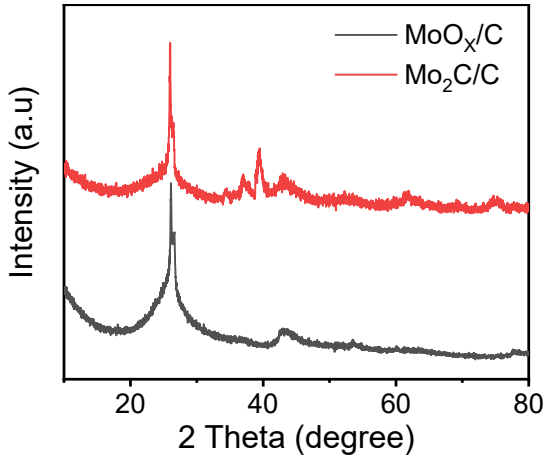

Fig. S10 XRD patterns of used catalysts.

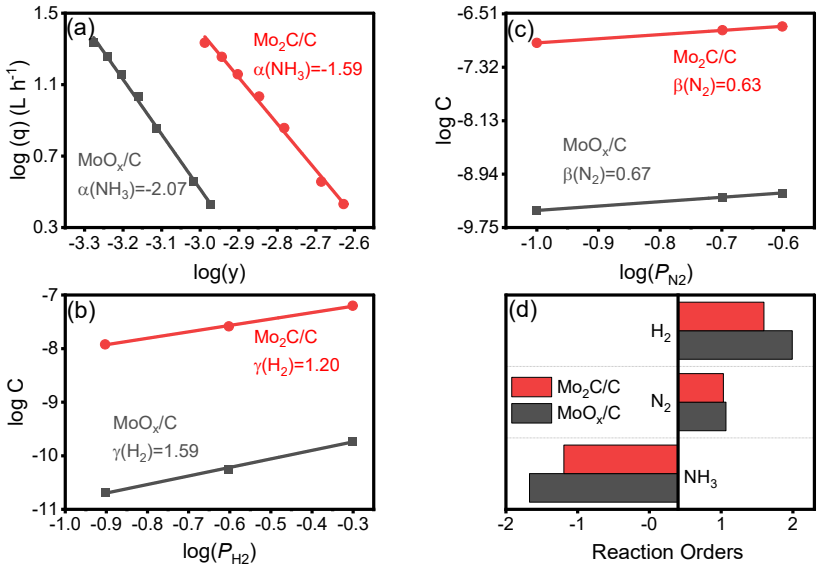

Fig. S11 Graphs for calculating reaction orders with respect to (a) NH_3, (b) H_2, (c) N_2 and (d) H_2, N_2 and NH_3 reaction orders, and the reproducibility of the reaction rate is confirmed 3 times and the error range is ±5%.

Table S1 Textural properties of MoO_xC/C and Mo_2C/C catalysts.

Sample	Surface area ($m^2\ g^{-1}$)	Pore Volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)	I_D/I_G
C	713	0.64	3.7	1.45
MoO_x/C	424	0.41	3.9	1.22
Mo_2C/C	272	0.36	5.2	0.85

Table S2 CO chemisorption results and particle sizes obtained by TEM measurements.

Samples	CO quantity[a] ($\mu mol/g_{cat}$)	Dispersion[a] (%)	Particle size[b] (nm)
MoO_X/C	11.6	0.66	8.1
Mo_2C/C	22.8	1.28	10.1

[a] obtained by CO chemisorption;

[b] obtained by TEM measurement (more than 100 particles).

Table S3 Ammonia synthesis activities of Mo catalysts.

Samples	Rate (mmol g_{cat}^{-1} h^{-1})	Ea (kJ mol^{-1})	Reaction conditions	SV (mL g^{-1} h^{-1})	Ref.
MoO_x/C	1.05	67	1 MPa, 400 °C	36 000	This
Mo_2C/C	1.95	61	1 MPa, 400 °C	36 000	Work
γ-Mo_2N	0.29	51	1 MPa, 400 °C	9 000	3
β-Mo_2C	1.70	53	1 MPa, 400 °C	9 000	4
Co_3Mo_3N	1.07	57	1 MPa, 400 °C	9 000	
Co-Mo/CeO_2	2.84	--	0.9 MPa, 400 °C	72 000	5
Mo/Co-CeO_2	2.72	57	1 MPa, 400 °C	72 000	6
Mo/Co-CeO_2	1.29	57	1 MPa, 400 °C	36 000	6
CoMo/CeO_2	0.48	61	1 MPa, 400 °C	36 000	6

Table S4 The Mo loading of Mo catalysts obtained by ICP analysis and N content obtained by Elemental Analysis.

Samples	Mo loading (wt%)	N content (wt%)
MoO_X/C	16.5	< 0.3
Mo_2C/C	15.6	< 0.3
Used MoO_X/C	16.8	< 0.3
Used Mo_2C/C	15.2	< 0.3

References:

1. B. Lin, K. Wei, X. Ma, J. Lin and J. Ni, *Catalysis Science & Technology*, 2013, **3**, 1367–1374.
2. (a) R. Kojima and K.-i. Aika, *Applied Catalysis A: General*, 2001, **218**, 121–128; (b) Y. Tsuji, K. Ogasawara, M. Kitano, K. Kishida, H. Abe, Y. Niwa, T. Yokoyama, M. Hara and H. Hosono, *J. Catal.*, 2018, **364**, 31-39.
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