

## Electronic Supplementary Information

### Unsaturated Mo in $\text{Mo}_4\text{O}_4\text{N}_3$ for efficiently catalytic transfer hydrogenation of nitrobenzene using stoichiometric hydrazine hydrate

Shicheng Luo<sup>a</sup>, Yu Long<sup>a\*</sup>, Kun Liang<sup>a</sup>, Jiaheng Qin<sup>a</sup>, Yi Qiao<sup>b</sup>, Jing Li<sup>c</sup>, Guangxue Yang<sup>a</sup>, Jiantai Ma<sup>a\*</sup>

<sup>a</sup> State Key Laboratory of Applied Organic Chemistry (SKLAOC), Gansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China.

<sup>b</sup> Lanzhou Petrochemical Research Center, Petrochemical Research Institute, Petrochina, Lanzhou 730060, PR China.

<sup>c</sup> State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Ningxia University, Yinchuan 750021, PR China

\*Corresponding author:

E-mail: majiantai@lzu.edu.cn; longyu@lzu.edu.cn; Tel: +86-931-8912577.

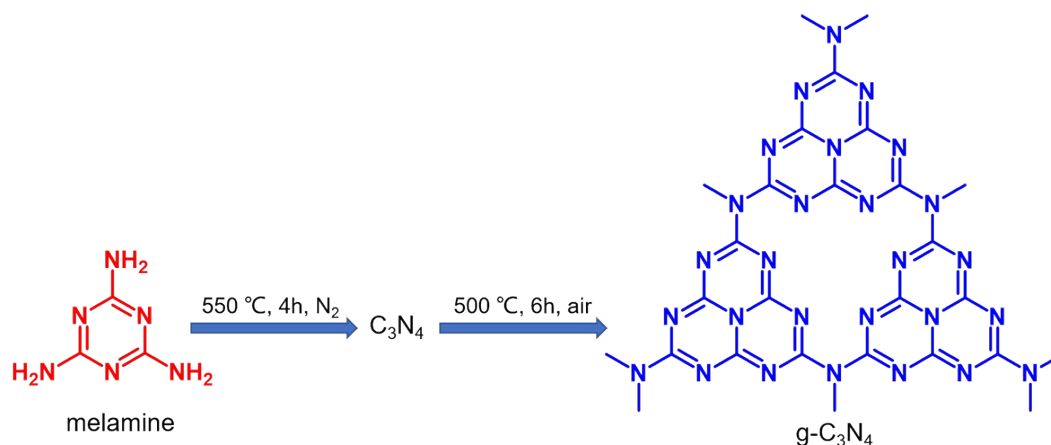
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## EXPERIMENTAL SECTION

### Reagents and chemicals

Ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, 99%, w/w), Molybdenum (IV) oxide (MoO<sub>2</sub>, 99%, w/w) and Molybdenum (VI) oxide (MoO<sub>3</sub>, 99%, w/w) were purchased from Macklin Biochemical Co., Ltd, Shanghai. Melamine, hydrazine hydrate, nitrobenzene and other nitroarenes were purchased from DAMAO Chemical Reagent Factory, Tianjin. Deionized water was used throughout the experiments. All chemicals were of analytical grade and used as received without further purification.

### Synthesis of g-C<sub>3</sub>N<sub>4</sub>



**Scheme S1.** Reaction path for the formation of g-C<sub>3</sub>N<sub>4</sub> from melamine.

### Characterizations

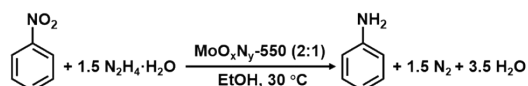
The crystallographic structure of the solid samples was investigated at room temperature using powder X-ray diffraction (XRD, Rigaku D/max-2400 diffractometer, Cu-K $\alpha$  radiation,) at a scanning rate of 10°·min<sup>-1</sup>. The morphology of the samples was captured by transmission electron microscopy (TEM, Tecnai G2 F30, 300 kV), and high-resolution transmission electron microscopy (HRTEM/EDX, Tecnai G2 F30, 300 kV). Hitachi S4800 system was adopted to gain scanning electron microscopy (SEM) images. Chemical bonding information of the samples was acquired with Fourier transform infrared spectroscopy (FT-IR, Nicolet NEXUS 670) using the potassium

bromide (KBr) pellet technique. About 1 mg of sample was diluted with 100 mg of KBr powder to make the KBr pellets. FT-IR spectrum was generated after 32 scans with a resolution of  $4\text{ cm}^{-1}$  from  $400$  to  $4000\text{ cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) was performed on the PHI-5702 instruments with an Mg anode (Mg K $\alpha$  hu = 1253.6 eV) at a base pressure of  $5\times 10^{-8}$  mbar. The revision of the binding energies (BE) was implemented with the C 1s peak of extraneous C at 284.6 eV. As for the NH<sub>3</sub>-TPD experiments, the sample (50 mg) was pretreated under Ar at 100 °C for 30 min. After cooling to 50 °C and being flushed in Ar flow for 30 min, the sample was exposed to repeated 10% NH<sub>3</sub>/Ar pluses until saturation. Subsequently, the temperature rose to 1073 K at a ramping rate of  $10\text{ °C}\cdot\text{min}^{-1}$ . The final NH<sub>3</sub>-TPD profiles were obtained by applying subtraction treatment between the adsorbed curve with blank curve without adsorbing any probe molecular. The gas detection was performed on the GC-9A gas chromatograph from Shimadzu, Japan.

### **Catalyst activity test**

The general procedure for aniline transfer hydrogenated from nitrobenzene with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O is as follows: a mixture of nitrobenzene (0.5 mmol), catalyst (20 mg) and solvent (1 mL) was added into a quartz tube. Then, 0.75 mmol of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (80% w/w.) was injected rapidly into the reaction tube. The mixture was allowed to stir at 303 K for a certain time. After the reaction, the crude mixture was diluted with ethanol and filtered, the product mixtures were detected by GC-MS (GC-MS, Agilent 5977E) with an HP-5 capillary column.

The reaction conditions were further studied. 82% yield of the aniline was gained within 30 minutes, and the yield reached up to 93% when the reaction time was extended to 40 minutes (Table S1, entries 1 and 2). Eventually, nitrobenzene was completely transferred to aniline within 50 minutes (Table S1, entry 3). Additionally, when reaction temperature was cooled down to 20 °C or the usage amount of catalyst was decreased to 10 mg, the aniline yield was 71% and 66% respectively. (Table S1, entry 4 and 5).

**Table S1** Optimization of the reaction conditions.<sup>a</sup>

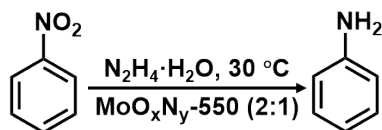
Entry	Catalyst	Time (min)	T (°C)	Conv. (%)	Sel. (%) <sup>b</sup>
1	MoO <sub>x</sub> N <sub>y</sub> -550 (2:1), 20 mg	30	30	82	>99
2	MoO <sub>x</sub> N <sub>y</sub> -550 (2:1), 20 mg	40	30	93	>99
3	MoO <sub>x</sub> N <sub>y</sub> -550 (2:1), 20 mg	50	30	>99	>99
4	MoO <sub>x</sub> N <sub>y</sub> -550 (2:1), 20 mg	50	20	71	>99
5	MoO <sub>x</sub> N <sub>y</sub> -550 (2:1), 10 mg	50	30	66	>99
6 <sup>c</sup>	MoO <sub>x</sub> N <sub>y</sub> -550 (2:1), 20 mg	50	30	>99	>99

<sup>a</sup> Conditions: nitrobenzene (0.5 mmol), catalyst (20 mg), N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (0.75 mmol), ethanol (1 mL), 30 °C, air, 1200 rpm.

<sup>b</sup> Determined by GC-MS using n-hexadecane as an internal standard.

<sup>c</sup> Under N<sub>2</sub> atmosphere.

The solvent effect was investigated (Table S2). By contrast with the non-polar solvents, all the polar solvents were more favorable to the reaction. On the other hand, as an aprotic solvent, THF also shows excellent performance among the aprotic solvents (Table S1, entry 4), which is verified by the literature report.<sup>1</sup> The disadvantage of non-polar solvent may be caused by the poor solubility of the hydrazine hydrate and inferior dispersibility of the catalyst. In view of the activity, toxicity and cost, ethanol is exactly the ideal solvent for this reaction.

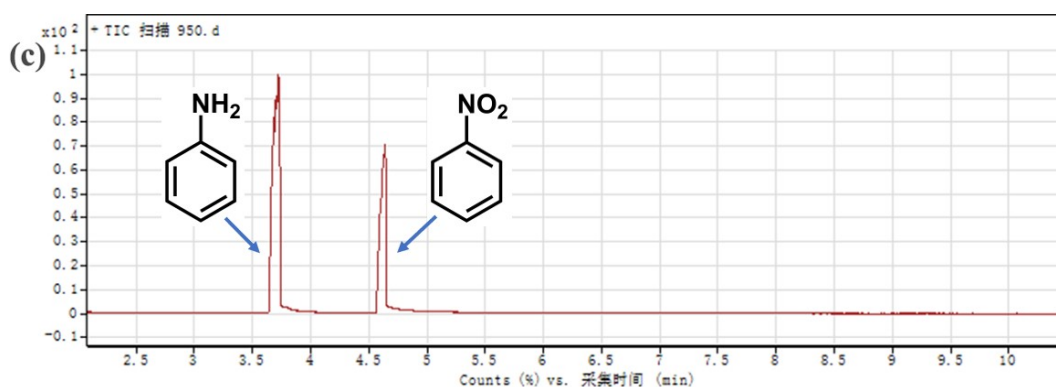
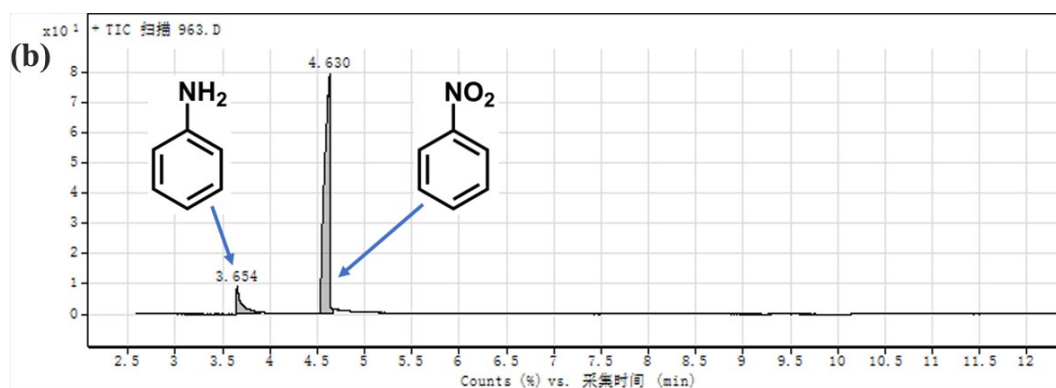
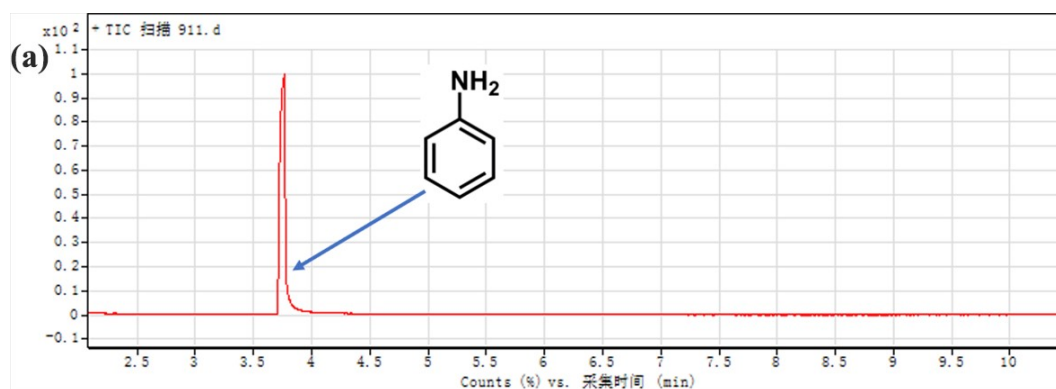
**Table S2** Influence of the solvent.<sup>a</sup>

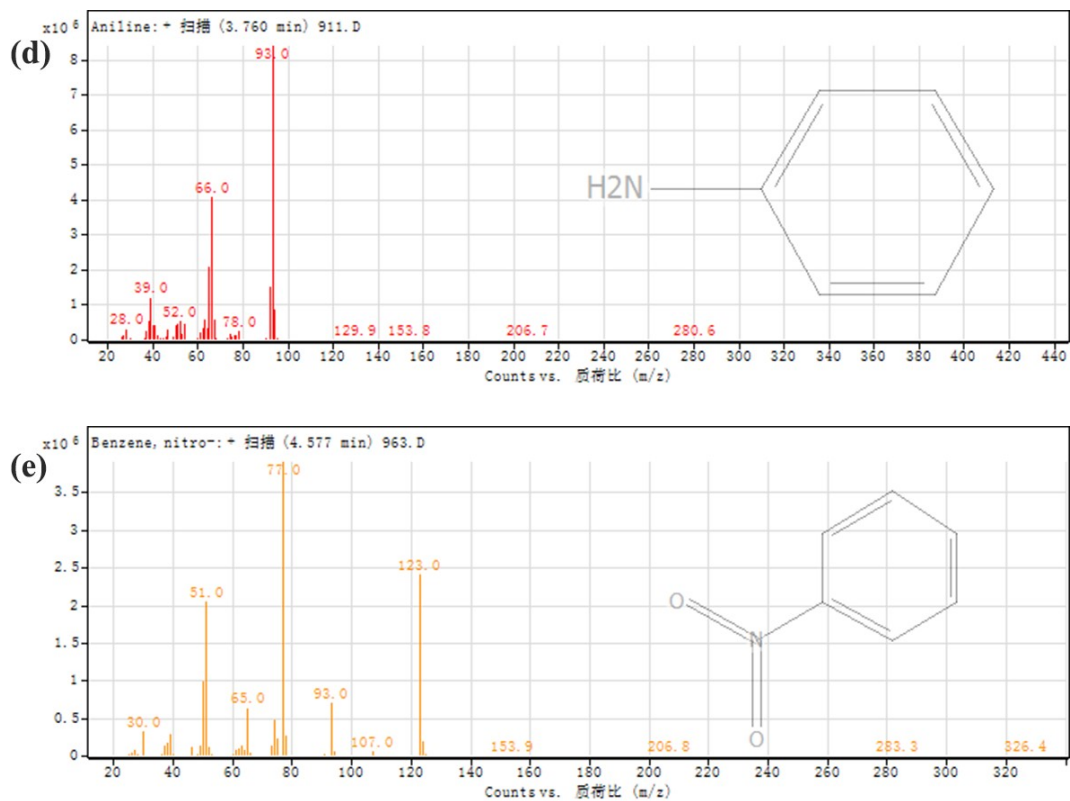
Entry	Solvent	Conv. (%)	Sel. (%) <sup>b</sup>
1	H <sub>2</sub> O	88	>99
2	Ethylacetate	43	>99
3	THF	83	>99
4	DMF	39	>99
5	Toluene	37	>99
6	Acetonitrile	27	>99
7	Dichloromethane	33	>99
8	MeOH	94	>99
9	<i>i</i> -PrOH	90	>99
10 <sup>c</sup>	None	>99	>99

<sup>a</sup> Conditions: nitrobenzene (0.5 mmol), N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (0.75 mmol), MoO<sub>x</sub>N<sub>y</sub>-550 (2:1) (20 mg), solvent (1 mL), 30 °C, 50 min, air, 1200 rpm.

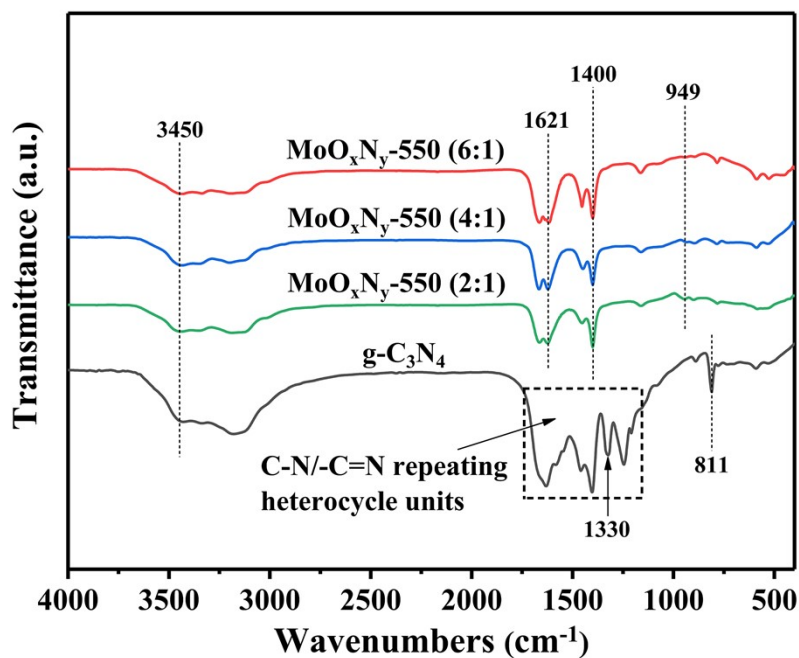
<sup>b</sup> Determined by GC-MS using n-hexadecane as an internal standard.

<sup>c</sup> Conditions: nitrobenzene (10 mmol), N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (18 mmol), catalyst (400 mg), solvent-free, 30 °C, 1 h, air, 1200 rpm.





**Fig. S1** Gas chromatograms of reactions (a) Table 2, entry 2. (b) Table 1, entry 8 and (c) Table S1, entry 5. And mass spectra of (d) aniline and (e) nitrobenzene.



**Fig. S2** FT-IR spectra of g-C<sub>3</sub>N<sub>4</sub> and Mo-based materials.

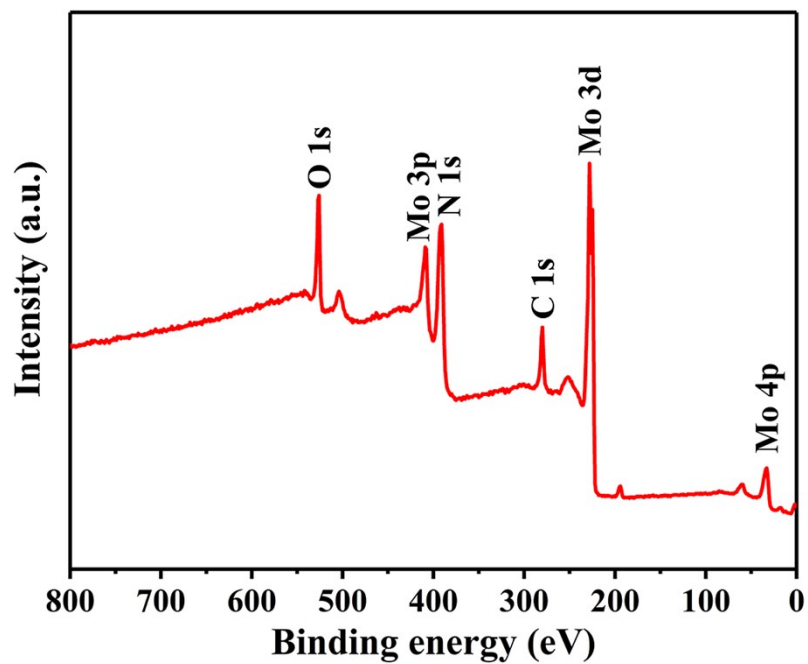


Fig. S3 Wide-scan XPS spectrum of  $\text{Mo}_4\text{O}_4\text{N}_3$  catalyst.

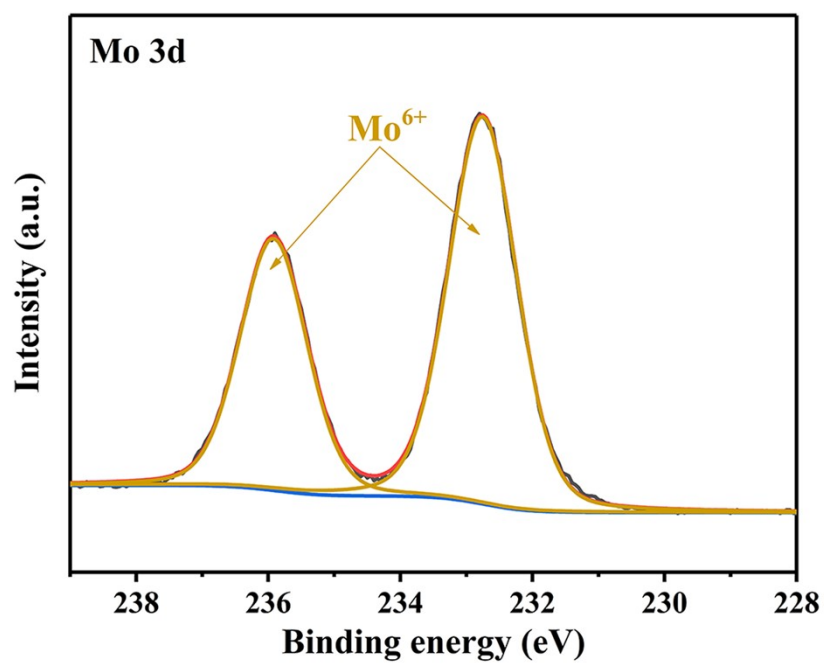
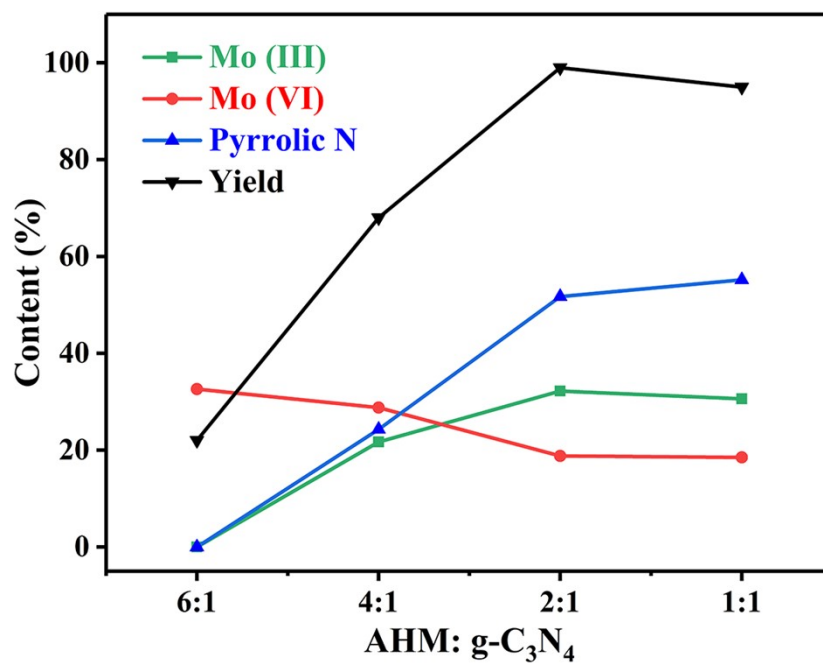
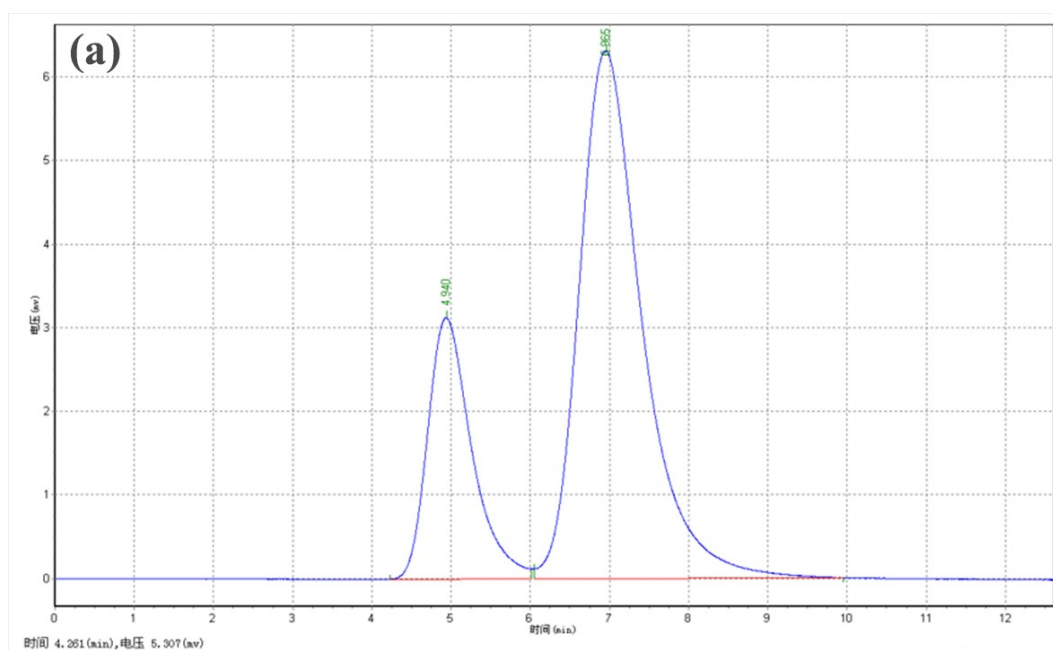


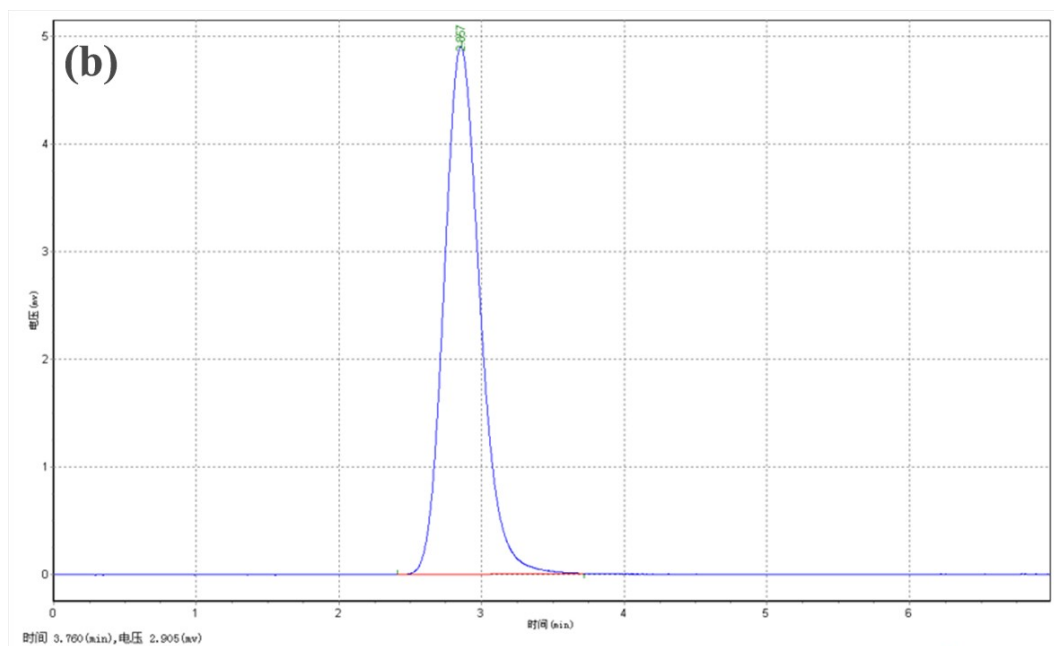
Fig. S4 Mo 3d XPS spectrum of  $\text{MoO}_x\text{N}_y\text{-RT (2:1)}$



**Fig. S5** The relationships between different states of elements and reactivity on MoO<sub>x</sub>N<sub>y</sub>-550 (6:1), MoO<sub>x</sub>N<sub>y</sub>-550 (4:1), MoO<sub>x</sub>N<sub>y</sub>-550 (2:1) and MoO<sub>x</sub>N<sub>y</sub>-550 (1:1) catalysts.







**Fig. S6** The gas chromatograms of (a) mixed gas phases collected from NH<sub>3</sub>-TPD testing program of Mo<sub>4</sub>O<sub>4</sub>N<sub>3</sub> catalyst. And (b) Standard H<sub>2</sub> gas phase.

**Table S3** The peak information of NH<sub>3</sub>-TPD testing program of Mo<sub>4</sub>O<sub>4</sub>N<sub>3</sub> catalyst

Peak	Retention time (min)	Peak Height	Peak area	Content (%)
1	4.940	3129.12	121026.11	25.76
2	6.965	6311.98	348812.56	74.24

### Notes and references

1. G. Wienhofer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R. Llusar and M. Beller, *J. Am. Chem. Soc.*, 2011, **133**, 12875-12879.