Supplementary Information (SI) for Chemical Communications.

Supporting Information for "Mo-V/g-C_3N_4 with strong electron donating capacity and abundant oxygen vacancies for low-temperature aerobic oxidative desulfurization"

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1 Experimental

1.1 Materials

Ammonium metavanadate (NH_4VO_3), melamine, ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), sodium borohydride ($NaBH_4$), dibenzothiophene (DBT), benzoquinone (BQ), n-tetradecane($C_{14}H_{30}$), decahydronaphthalene ($C_{10}H_{18}$), dimethyl sulfoxide (DMSO) were all of analytical grade and purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All chemicals used were of analytical grade and could be used without further purification. Deionized water was used for all experiments. O_2 (99.9%), N_2 (99.9%) and H_2 (5%)/N_2(95%) were purchased from Panjin Tongyu Gas Co., Ltd.

1.2 Catalyst preparation

10 g of melamine was weighed and placed into a ceramic boat, spread evenly, and covered with a lid. The boat was transferred into a tube furnace. Prior to heating, N_2 gas was purged through the furnace for 30 min to ensure complete nitrogen atmosphere. Subsequently, under continuous N_2 flow, the temperature was raised to 550°C at a heating rate of 5°C/min and maintained at 550°C for 4 h. After cooling to room temperature, the bulk yellow solid was collected, ground into powder, and labeled as the g-C_3N_4 support.

0.029 g of ammonium molybdate tetrahydrate and 0.078 g of ammonium metavanadate were dissolved in 10 mL of deionized water. The mixture was stirred at 60°C for 30 min until a yellow solution was formed. Then 1 g of the prepared g-C_3N_4 support was added to the solution, and stirred at 60°C for 2 h. The resulting slurry was centrifuged, washed, and dried in an oven at 100°C for 10 h. Then the obtained powder was calcined in the tube furnace. Under air flow, the temperature was raised to 400°C at 5°C/min and held for 3 h, and then cooled to room temperature. Then a reducing gas mixture (5% H_2, 95% N_2) was purged for 30 min to ensure a fully reducing environment. Under continuous 5% H_2 gas flow, the temperature was increased to 400°C at 5°C/min and maintained for 3 h to get the 350°C Mo-V/g-C_3N_4. 350°C Mo-V/g-C_3N_4 and 450°C Mo-V/g-C_3N_4 can be obtained by adjusting the temperature (calcination and reduction) to 350°C and 450°C, respectively.

150 mg of the 400°C Mo-V/g-C_3N_4 was dispersed in 50 mL of 0.25 M $NaBH_4$ solution and stirred at room temperature for varying durations (1 h, 3 h, 5 h, or 7 h). The solids were then centrifuged, filtered, and dried to get the corresponding catalysts.

1.3 Characterization

Crystal phases were analyzed by X-ray diffraction (XRD, Lab XRD- 7000s) equipped with Cu Kα radiation at the voltage of 120 kV and a current of 100 mA, recorded with 2θ varying from 10 to 90° with a scanning speed of 5°/min. TEM and HRTEM were performed on Tecnai G2 F30 produced by FEI Company. The chemical composition and functional groups of sorbents were investigated with the help of FTIR spectrometer (PerkinElmer, USA) carried out by a Spectrum 3 system. X-ray photoelectron spectroscopy (XPS) (ESCALAB250Xi, Thermo Fisher Scientific, UK) was performed on a VG ESCALAB MKII X-ray photoelectron spectrometer equipped with a monochromatic Al Kα X-ray source. Electron paramagnetic resonance (EPR) was performed using a Bruker model A200–9.5/12 paramagnetic resonance spectrometer.

1.4 Oxidative desulfurization experiments

The oxidative desulfurization reaction was conducted in an oil bath at 80°C. The internal standard method was employed to study the conversion rate of dibenzothiophene (DBT) during the reaction, thereby evaluating the desulfurization performance of the catalysts. DBT was dissolved in decahydronaphthalene to prepare a simulated oil of 500 ppm. To accurately quantify the DBT concentration before and after the reaction, n-tetradecane was added as an internal standard at a fixed concentration prior to the reaction. The reaction was carried out in a 50 mL two-necked flask. 20 mL of the prepared simulated oil and 30 mg of catalyst were added to the flask. The mixture was heated and stirred at 80°C under continuous oxygen flow. Samples (0.5 mL) were withdrawn at reaction times of 0 h, 2 h, 4 h, 6 h and 10 h. After 10 h, the oxygen flow was stopped, and the system was cooled to room temperature. The withdrawn samples were filtered through a membrane filter to remove the catalyst. The DBT content in the samples (before, during, and after the reaction) was analyzed by gas chromatography (GC). The conversion rate at each time point was calculated using the internal standard method.

The gas chromatograph (GC) analysis was performed using an Agilent 7820A instrument (Agilent Technologies Inc., USA) equipped with a flame ionization detector (FID) and a capillary column (30 m length, 320 μm inner diameter, 0.25 μm film thickness). The temperature program for separation was initiated at 110°C and held for 1 min, followed by a gradual increase to 250°C at a rate of 10°C/min. Both the injector and detector temperatures were maintained at 300°C throughout the analysis. The carrier gas flow rate and split ratio were optimized to ensure precise quantification of dibenzothiophene (DBT) in the simulated oil samples, with n-tetradecane serving as the internal standard for calibration.

DBT conversion was calculated as follow:

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

Turnover Frequency (TOF, h^{-1}) was calculated as follow:

$$TOF(h^{-1}) = \frac{S_{conv} \times C_0 \times V_{oil}/t}{m \times \omega^1/M_{m1} + m \times \omega^2/M_{m2}}$$

S_{conv}: DBT conversion;

C_0: initial sulfur content, mol L^{-1} ;

V_{oil}: volume of model oil added, L;

t: reaction time, h;

m: mass of catalyst dosage, g;

ω_1: Mo content in the catalyst;

ω_2: V content in the catalyst;

M_{m1}: atomic mass of Mo, 95.94 g mol^{-1}.

M_{m2}: atomic mass of V, 50.94 g mol^{-1}.

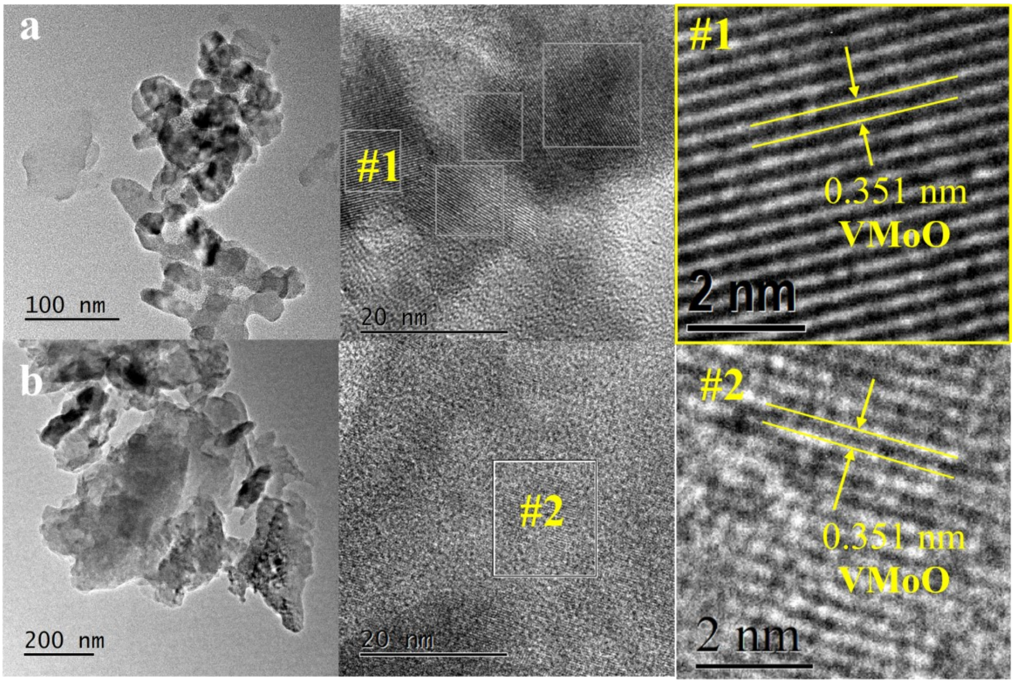

Fig. S1 TEM and HRTEM images of (a) 400°CMo-V/g-C_3N_4 and (b) 400°CMo-V/g-C_3N_4+$NaBH_4$.

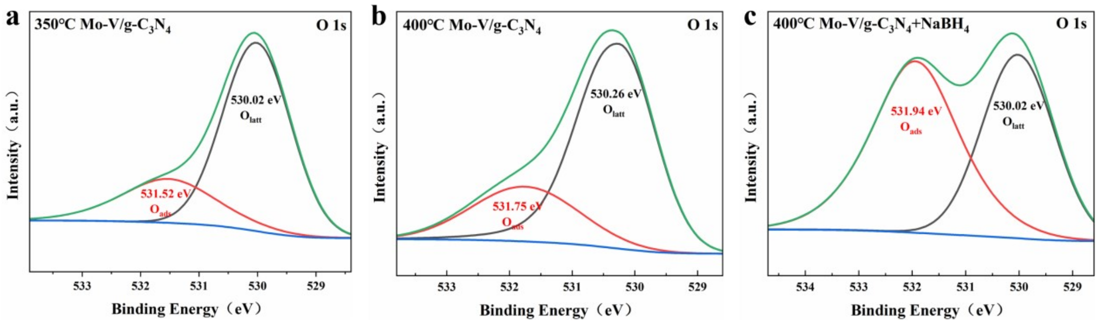

Fig. S2 XPS spectra of O 1s for Mo-V/g-C_3N_4 reduced at (a) 350°C, (b) 400°C, and (c) 400°C+$NaBH_4$ reduction.

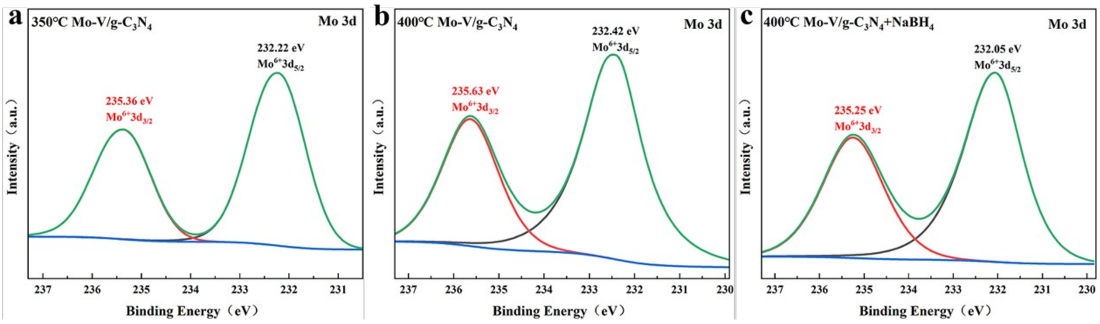

Fig. S3 XPS spectra of Mo 3d for Mo-V/g-C_3N_4 reduced at (a) 350°C, (b) 400°C, and (c) 400°C+$NaBH_4$ reduction.

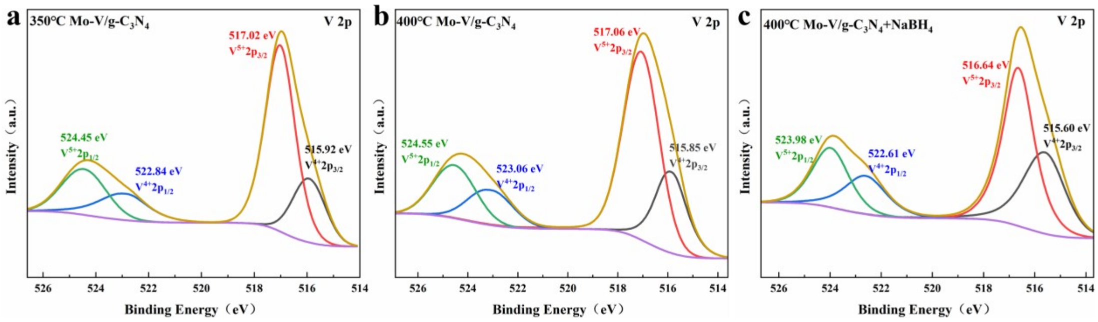

Fig. S4 XPS spectra of V 2p for Mo-V/g-C_3N_4 reduced at (a) 350°C, (b) 400°C, and (c) 400°C+$NaBH_4$ reduction.

Fig. S5 The proposed catalytic mechanism.

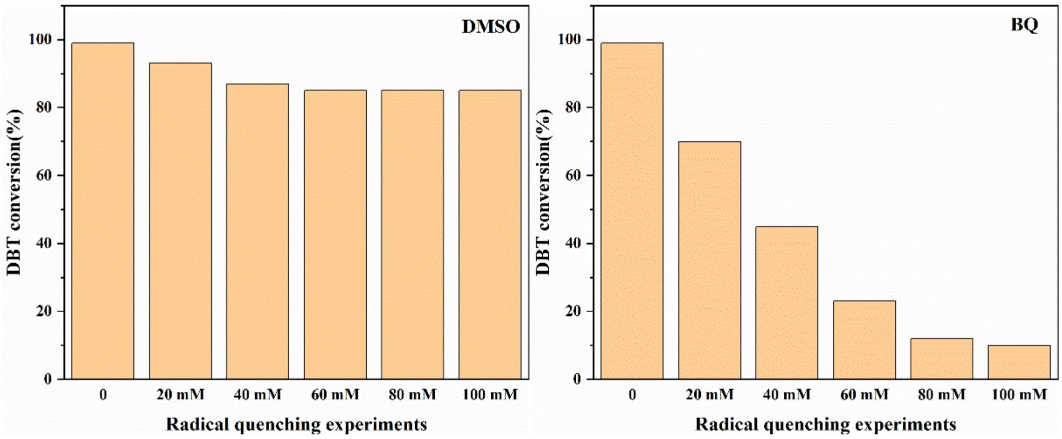

Fig. S6 The radical quenching experiments with different quencher concentrations.

Table S1 Percentage of different valence states of catalyst V at different calcination temperatures and after $NaBH_4$ reduction.

catalyst	V^{4+}	V^{5+}	V^{4+}/V^{5+}
350°C Mo-V/g-C_3N_4	28	72	0.38
400°C Mo-V/g-C_3N_4	32	68	0.48
400°C Mo-V/g-C_3N_4+$NaBH_4$	41	59	0.70

Table S2 The activity comparison of Mo-V/g-C_3N_4 with the reported metal oxide catalysts.

Catalyst	Reaction temperature (°C)	Conversion (%)	Ref
Mo-V/g-C_3N_4	**80**	**100**	**This work**
[C_4VIM]PMoV_2	120	100	1
Co-Fe-Mo	120	100	2
CoMo nanosheet	100	100	3
V-BNO	125	100	4
Co-Mo-O	100	83	5
Ce-Mo-O	100	100	6
MoOx/MC-600	120	100	7
C_8V/g-BN	120	100	8
V_2O_5/BNNS	120	99.6	9

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