Electronic Supplementary Information

Preparation of Co-Mo-O ultrathin nanosheets with outstanding catalytic performance in aerobic oxidative desulfurization

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S1. Experimental Section

Materials Reagents. Ammonium molybdate tetrahydrate and ((NH₄)₆Mo₇O₂₄·4H₂O, 95%), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, 99%), hexamethylenetetramine (HMT, 99%), dibenzothiophene (DBT, 98%), 4, 6-dimethyl 97%), dibenzothiophene (4,6-DMDBT, benzothiophene (BT, 98%) and decahydronaphthalene (99%), ethanol (99%) were purchased from Tianjin Fuchen Reagent Co., Ltd (China). Nitrogen (99%) was purchased from Yantai Feifei Special Gas Co., Ltd. (China).

Catalyst preparation. A coprecipitation method was employed to prepare the Co-Mo-O ultrathin nanosheets. 3 mM CoCl₂·6H₂O, 3/7 mM (NH₄)₆Mo₇O₂₄·4H₂O and 90 mM HMT were dissolved in pure water, heated to boiling under nitrogen protection, and kept for 4 hours with constant stirring. After the reaction completed, the precipitations were separated and washed by centrifugation, and then dried at 60 °C over night. The solid were calcined at a temperature of 500 °C for 4 hours to obtain a bimetallic oxide catalyst. By contrast, a bare Co-O oxide was also prepared without adding of (NH₄)₆Mo₇O₂₄·4H₂O in the preparation process.

Characterization. The morphologies of the catalysts were characterized by a field emission scanning electron microscopy (SEM, SU8010, BRUKER). X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2500V powder X-ray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm). Transmission electron microscopy (TEM) micrographs were taken with a transmission electron microscope (Talos F200X, FEI). The Fourier Transform infrared (FT-IR) spectra measurements were performed on a Nicolet is50 (Thermo Fisher Nicolet, United States). X-ray photoelectron spectroscopy (XPS) data were obtained with an electron spectrometer (EscaLab Xi+, Thermo fisher). The specific surface areas of the samples were measured on a Surface Area and Porositiy Analyzer (ASAP 2460, Micromeritics).

Oxidation of sulfur compounds. Sulfide (DBT, BT or 4,6-DMDBT) was dissolved in decahydronaphthalene to reach 500 ppm of sulfur content. In desulfurization experiments, 20 mL of model oil and 20 mg of catalyst was charged into a 50 mL threenecked flask equiped with a gas injection, a refulx tube and a sampling port for liquid. The flask was then immersed in an oil bath which was preheated to the desired reaction temperature and stirred at 200 rpm. Air was passed through a silica gel column to remove moisture, and then was bubbled into the flask under atmospheric pressure to start the reaction. Samples were taken from the liquid phase at intervals, and GC-FID (Agilent 7890A; HP-5, FID: Agilent) was used to quantify the conversion of sulfides. Each experiment was repeated at least three times.

Reuse of catalysts. After each AODS cycle, the solid phase was separated from the reaction system by centrifugation, and 10 mL of methanol was added to dissolve the oxidation products. The catalyst was then dried under vacuum and subjected to a new reuse cycle. The methanol solution was analyzed by GC-MS to determine the evolution of sulfide speciation.

S2. Characterization of precursors.



Fig. S1. SEM images of the Co-O precursor.



Fig. S2. SEM images of the Co-Mo-O precursor.



Fig. S3. HRTEM image of the Co-Mo-O precursor.

S3. XPS characterization



Fig. S4 XPS survey curves of (a) Co-O nanosheets and (b) Co-Mo-O nanosheets.



Fig. S5 High-resolution Co 2p curves of (a) Co-O and (b) Co-Mo-O nanosheets.

As shown in the high-resolution Co 2p curves of the Co-O and Co-Mo-O nanosheets (Fig. S5), double peaks of 2p3/2 and 2p1/2 levels can be clearly distinguished. By setting the 2p3/2 and 2p1/2 area ratio as 2:1, the spectra were successfully fitted. The 2p3/2 component of the Co-O nanosheets contained two peaks at 778.9 and 780.4 eV, which were attributed to Co(II) and Co(III) in Co₃O₄ species, respectively. As for the Co-Mo-O nanosheets, an extra peak was observed at 778.0 eV, which was attributed to Co(II) in CoMoO₄.



Fig. S6 High-resolution Mo 3d curve of Co-Mo-O nanosheets.

The characteristic Mo 3d doublet composed of the 3d5/2 and 3d3/2 levels resulting from spin-orbit coupling. As shown in Fig. S6, the high-resolution XPS spectrum was divided into four peaks. Peaks at 233.3 and 230.1 eV were assigned to Mo(V), while peaks at 233.9 and 230.8 eV were attributed to Mo(IV).

S4. SEM image of the bulk Co-Mo-O



Fig. S7 SEM image of the bulk Co-Mo-O synthesized according to literature.

S5. Investigation of reaction kinetics.



Fig. S8 Fitting of the kinetic data with pseudo-first-order model.



Fig. S9. Calculation of activation energy with Arrhenius equation.

Kinetic Equation:

The reaction rate of DBT oxidation with air as an oxidant is expressed as

$$-\frac{dC_{DBT}}{dt} = kC_{oxy}C_{DBT}$$

where, C_{oxy} and C_{DBT} were the concentrations of oxygen and DBT in the reaction system. *k* was the reaction rate constant (h⁻¹).

For the O_2 was excessive, the equation was simplified as

$$-\frac{dC_{DBT}}{dt} = k'C_{DBT}$$

Where k' is the apparent rate constant (h⁻¹).

Then, the activation energy (Ea, KJ/mol) was calculated by

$$\ln k' = -\frac{Ea}{RT} + C$$

S6. Influence of reaction parameters on catalytic performances



Fig. S10 Influence of catalyst dosage on DBT conversion. Reaction conditions: T = 100°C, $V_{oil} = 20$ ml, initial S-content = 500 ppm, air was bubbled in at ambient pressure with the flow rate of 30 mL/min.

The influence of catalyst dosage on desulfurization performance was illustrated in Fig. S9. As the amount of catalyst increases, the desulfurization effect increases because the more catalyst provides more contact opportunities for the sulfide and the catalyst, while the desulfurization efficiency was not very sensitive to the dosage of the Co-Mo-O nanosheets. It was observed during the reaction that, when employ a large amount of catalyst, the dispersion of catalyst was not well due to the limited reaction space.



Fig. S11 Reactivities of different sulfides over the Co-Mo-O nanosheets.

Since various thiophenic compounds existed in the fuel system, the catalytic experiments on the other two thiophene substances (4,6-DMDBT and BT) have been carried out. As shown in Fig. S10, the conversion versus time curve of 4,6-DMDBT basically coincided with that of DBT, which suggests their similar reactivities. The reactivity of BT was lower, reaching the conversion of 84.5 % at 8 hours. For the three sulphides, electron densities of S atoms decreased in the order of 4,6-DMDBT \approx DBT > BT, which is consistent with the results obtained in this work. The results further evidenced that the oxidation of thiophenic compounds follows the electrophilic addition principle. As shown in Fig. S11-S13, the thiophenic compounds were all converted to their corresponding sulfones.

S7. Characterization of oxidation products.



Fig. S12 Mass spectrometry of dibenzothiophene sulfone (DBTO₂).



Fig. S13 Mass spectrometry of 4,6-dimethyldibenzothiophene sulfone (4,6-

DMDBTO₂).



Fig. S14 Mass spectrometry of benzothiophene sulfone (BTO₂).

S8. Characterization of catalysts before and after reused



Fig. S15 FT-IR spectra of the Co-Mo-O nanosheets before and after recycled.



Fig. S16 SEM image of the Co-Mo-O nanosheets after recycled.

S9. Comparation of catalytic performances with different catalysts

| Entry | Catalyst | Substrate | Oxidant | Reaction conditions ^a | Conversion | Ref |
|-------|--|-----------|----------------|----------------------------------|------------|--------------|
| 1 | Co-Mo-O nanosheets | DBT | Air | 100 °C, 10 mg/20 mL, 4 h | 100% | This work |
| 2 | $(NH_4)_5H_6PV_8Mo_4O_{40}$ | DBT | O ₂ | 100 °C, 20 mg, 6 h | 88.4% | 1 |
| 3 | r-GO | DBT | O ₂ | 140 °C, 5 mg/25 mL, 4 h | 100% | 2 |
| 4 | MoO _x /MC-600 | DBT | O ₂ | 120 °C, 10 mg, 8 h | 100% | 3 |
| 5 | Се-Мо-О | DBT | O ₂ | 100 °C, 100 mg, 6 h | 100% | 4 |
| 6 | (Cu-Co)(salen)Y | DBT | O ₂ | 100 °C, 200 mg, 4 h | 97.6% | 5 |
| 7 | MFM-300(V) | DBT | O ₂ | 120 °C, 0.75 g/L, 5 h | 99.6% | 6 |
| 8 | Ch _x Na _{5-x} IMo ₆ O ₂₄ | DBT | O ₂ | 100 °C, 0.1 mmol/6 mL, 5 h | 100% | 7 |
| 9 | MIL-101 | DBT | O ₂ | 120 °C, 500 mg/L, 15 h | 100% | 8 |

 Table S1 Comparation of catalytic performances with different catalysts.

^{*a*} Reaction conditions: reaction temperature, catalytic dosage/model oil volume, reaction time.

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