

Effect of Mn doping on the structure and oxidative desulfurization properties of Co-V-O binary metal oxides

DONG Zhehan¹, WANG Hongli², LI Xiuping³, ZHAO Rongxiang^{1,*}

¹ School of Petrochemical Engineering, Liaoning Petrochemical University, Fushun 113001, China;

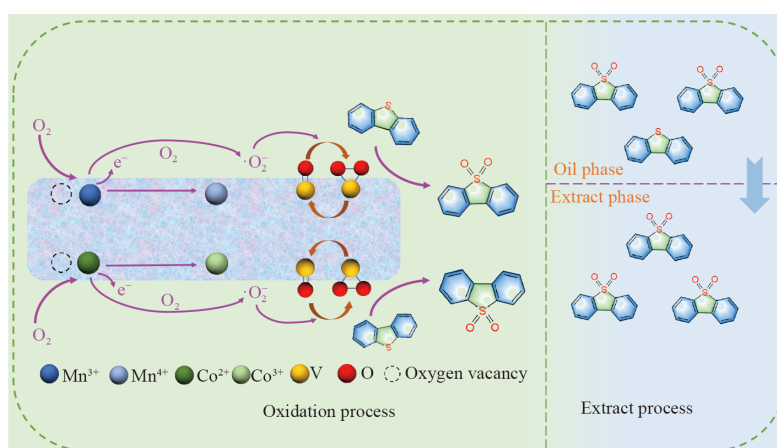
² Shandong Jinchuang Gold and Silver Smelting Co., Ltd. Yantai 265600, China;

³ School of Science, Liaoning Petrochemical University, Fushun 113001, China

Abstract: The sulfur dioxide produced by the combustion of sulfur-containing aromatic compounds in fuels is a major contributor to atmospheric pollution. Due to its mild reaction conditions and excellent efficiency in removing aromatic sulfides, oxidative desulfurization has become a crucial complement to hydrodesulfurization technology. Metal doping represents an effective strategy for modulating the electronic structure of catalysts and enhancing their catalytic performances. In this study, Mn-doped Co-V-O metal oxide (Mn-Co-V-O) was successfully synthesized *via* a reflux method followed by high-temperature calcination. The structure, morphology, and surface chemical composition of Mn-Co-V-O were systematically characterized using FT-IR, XRD, SEM, XPS and UV-vis DRS. The oxidative desulfurization (ODS) performance of the catalyst toward dibenzothiophene (DBT) was evaluated using oxygen as a green oxidant. Results indicated that Mn doping significantly enhanced the ODS activity of Mn-Co-V-O compared to the undoped Co-V-O. Under optimized reaction conditions, the direct removal rate of DBT reached 81.6%. When combined with an extraction process, the desulfurization rate was further increased to 98.0%. Mechanistic studies revealed that Mn doping effectively increased the surface oxygen vacancy concentration, facilitating the activation of oxygen to generate superoxide radicals ($\cdot\text{O}_2^-$). Free radical trapping experiments confirmed that $\cdot\text{O}_2^-$ served as the key active species responsible for the selective oxidation of DBT to DBTO₂. This study provides an important reference for the design of highly efficient metal oxide catalysts applicable to deep oxidative desulfurization in the future.

Mn doping effectively increased the surface oxygen vacancy concentration, facilitating the activation of oxygen to generate superoxide radicals ($\cdot\text{O}_2^-$). Free radical trapping experiments confirmed that $\cdot\text{O}_2^-$ served as the key active species responsible for the selective oxidation of DBT to DBTO₂. This study provides an important reference for the design of highly efficient metal oxide catalysts applicable to deep oxidative desulfurization in the future.

Key words: Co-V-O; aerobic oxidation desulfurization; DBT; oxygen vacancy; superoxide radical



Sulfur oxide emissions from fuel-powered vehicles significantly contribute to the atmospheric pollution^[1–2]. Accordingly, controlling sulfur-containing compounds at the source has become a global priority^[3–4]. In China, the National V standard for gasoline and diesel stipulates a sulfur content limit below 10 $\mu\text{g/g}$. Currently, hydrodesulfurization (HDS) remains the dominant technology in petroleum refining^[5–8], primarily owing to its high efficiency in removing aliphatic sulfur compounds.

However, HDS operates under severe conditions (high temperature and pressure), requires highly active catalysts, and exhibits limited effectiveness toward aromatic sulfur compounds due to steric hindrance^[9]. These drawbacks have motivated extensive research efforts to develop alternative and more efficient desulfurization technologies.

Oxidative desulfurization (ODS) has emerged as a promising complementary technology to HDS, by virtue of its mild reaction conditions, low energy consumption, and

Received: 2025-11-18; Revised: 2025-12-16

Foundation items: Supported by the Mentoring Program Projects from Liaoning Natural Science Foundation (2019-ZD-0064).

* Corresponding author. E-mail: zylhxr@126.com.

DOI: 10.1016/S1872-5813(26)60658-5 CSTR: 32157.14.2097-213X.2026.JFCT.0013 Associated Data DOI: 10.57760/sciencedb.j00124.00394

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

notably high efficiency in removing aromatic sulfur compounds that are resistant to HDS^[10–11]. In ODS systems, both the oxidant and the catalyst play decisive roles in determining overall performance. Hydrogen peroxide is commonly employed as an oxidant due to its low cost, environmental compatibility, and the formation of water as the sole byproduct. Despite these advantages, its use is associated with practical challenges, such as equipment corrosion and potential explosion hazards. In contrast, molecular oxygen has attracted considerable interest as an alternative oxidant because of its abundance, low cost, intrinsic safety, and environmental benignity, with water typically being the primary oxidation product^[12–13]. However, activating the inherently stable triplet ground state of molecular oxygen under mild conditions remains a significant challenge, highlighting the critical need for the development of highly active and efficient catalysts for oxygen-mediated oxidative desulfurization.

In recent years, transition metal oxides have been widely investigated as catalysts for ODS due to their tunable oxidation states, structural stability, and ease of recovery^[14]. However, single-component metal oxides often suffer from limited catalytic activity. To enhance their performances, two primary strategies have been adopted: increasing the specific surface area and introducing heterometal ions into the catalyst structure. Such doping approaches can effectively modulate the electronic structure and surface physicochemical properties of the catalyst, thereby enhancing their performances. For example, Liu et al.^[15] incorporated Fe into MoO_x and demonstrated that Fe ions precisely regulated the electronic structure of Mo sites, significantly raising the surface oxygen vacancy concentration. After optimizing the dopant content, the catalyst exhibited excellent activity, achieving full conversion of various sulfur compounds. Uematsu et al.^[16] doped Mo ions into MnO₂ and observed that the introduction of high-valence transition-metal cations, particularly Mo⁶⁺, notably shortened the fiber length of MnO₂, leading to the formation of aggregates composed of ultrafine nanocrystals. This structural evolution increased the specific surface area and the number of exposed active sites, enabling efficient oxidation of various sulfides into the corresponding sulfoxides and sulfones. Similarly, An et al.^[17] reported that Mn doping effectively altered the electronic structure and surface atomic composition of NiMoO₄, resulting in an increased oxygen vacancy density and enhanced O₂ activation capability.

In the field of ODS, vanadium-based catalysts, such as 2D-2D V₂O₅/BNNS and V₂O₅, have shown promising desulfurization performance^[18–19]. Cobalt-based catalysts have also been extensively studied. For example, Murata et al.^[20] achieved 97% sulfur removal from diesel using cobalt acetate or cobalt chloride as catalysts, with aldehydes serving as sacrificial agents. Wei et al.^[21] synthesized a Co/KIT-6 catalyst, which reached a desulfurization rate of 98% in model oil with cyclohexanone peroxide employed as the oxidant. Similarly, Deng et al.^[22] prepared a Co/SBA-15 catalyst by loading cobalt oxide onto SBA-15 and

achieved a notable sulfur removal efficiency of 99.5% at room temperature.

Considering that Co-V-O can be regarded as a composite metal oxide comprising of cobalt oxide and vanadium oxide, it is reasonable to expect that such materials to demonstrate favorable ODS activity. In this work, both Co-V-O and Mn-doped Co-V-O catalysts were synthesized *via* a reflux-calcination method. The crystalline structure, morphology, elemental valence states, and optical properties of the prepared catalysts were systematically characterized using XRD, SEM, XPS, FT-IR and UV-vis DRS. The results confirm the successful incorporation of Mn into the Co-V-O lattice. The ODS performance of the catalysts was evaluated using dibenzothiophene (DBT) in model oil as the substrate. The effects of Mn doping content, reaction temperature, catalyst dosage, oxygen flow rate, and different sulfur compounds on the desulfurization efficiency were investigated. Furthermore, the stability of the catalyst was examined, and a preliminary reaction mechanism for the ODS process was proposed.

1 Experimental

1.1 Preparation of catalysts

Manganese(II) chloride tetrahydrate (MnCl₂·4H₂O, ≥ 99.0%), ammonium metavanadate (NH₄VO₃, ≥ 99.5%), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, ≥ 99.0%), hexamethylenetetramine (HMT, ≥ 99.5%), DBT (≥ 99.0%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, ≥ 98.5%), and benzothiophene (BT, 98.0%) were purchased from Aladdin Reagent Co., Ltd. Decahydronaphthalene (≥ 98.0%), *p*-benzoquinone (≥ 99.0%), and isopropanol (≥ 99.7%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Oxygen (≥ 99.99%) was supplied by Fushun Oxygen Plant.

The catalysts were synthesized through a typical procedure as follows: MnCl₂·4H₂O (0.03 g), NH₄VO₃ (2.32 g), CoCl₂·6H₂O (0.952 g), and hexamethylenetetramine (7.0 g) were dissolved in 160 mL of deionized water under stirring. The mixture was stirred at 80 °C for 4 h and then centrifuged. The precipitate was collected, washed three times with deionized water, dried at 100 °C for 4 h, and ground into a fine powder. Finally, the powder was calcined in a muffle furnace at 400 °C for 2 h to obtain the catalyst with a Mn-to-Co molar ratio of 1 : 15, denoted as Mn-Co-V-O(1 : 15). For comparison, Mn-Co-V-O(1 : 10) and Mn-Co-V-O(1 : 20) were synthesized by adjusting the amount of MnCl₂·4H₂O to 0.04 and 0.02 g, respectively. The Co-V-O catalyst was prepared under identical conditions without the addition of MnCl₂·4H₂O.

1.2 Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a NEXUS 870 spectrometer (Thermo Nicolet, USA). X-ray diffraction (XRD) patterns were obtained using a D8

Advance diffractometer (Bruker, Germany). Scanning electron microscopy (SEM) was performed on a Philips XL 30 microscope (Philips, Netherlands). X-ray photoelectron spectroscopy (XPS) measurements were conducted with a K-Alpha spectrometer (Thermo Fisher Scientific, USA). UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded on a TU-1901 spectrophotometer (Shanghai Yuanxi, China) in the range of 200–800 nm, with a scan step of 5 nm at room temperature, using barium sulfate as a reference. Electron paramagnetic resonance (EPR) spectra were measured on a Bruker EMXplus spectrometer. The sulfur content in oils was determined using a WK-2D coulometric analyzer (Jiangsu Jiangdian, China).

1.3 Catalytic evaluation

1.437 g of DBT was ultrasonically dissolved in 1000 mL of decahydronaphthalene to prepare a model oil with a sulfur content of 250 µg/g. The ODS experiments were carried out in a 250 mL three-necked flask equipped with a condenser. Typically, 20 mL of tetralin-based model oil and a predetermined amount of the Mn-Co-V-O catalyst were added to the reactor. The reaction was performed under a constant flow of oxygen at a specified temperature. During the process, 0.1 mL aliquots of the upper oil layer were collected at 20 min intervals. After reaction completion, all collected oil samples were centrifuged to remove residual catalyst particles. The sulfur content in the clarified samples was then quantified using a WK-2D coulometric analyzer. The desulfurization rate (η) was calculated using the following equation:

$$\eta = [(A - B)/A] \times 100\% \quad (1)$$

where η is the desulfurization rate (%), and A and B represent the sulfur contents in the model oil at the initial time and at time t , respectively (µg/g).

2 Results and discussion

2.1 Morphology, structure and composition characterization

The FT-IR spectra of the samples are shown in Figure 1(a). The absorption bands observed at 3448 and 1639 cm^{-1} are assigned to the O–H stretching and bending vibrations, respectively. Peaks located at 931 and 812 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of VO_4 units^[23], while the band at 653 cm^{-1} is attributed to the bending vibration of Co–O bonds^[24], and the band at 420 cm^{-1} arises from the Co–O stretching mode^[25]. It can be noted that the positions of these characteristic absorption bands remained largely unchanged after Mn doping; however, the band at 812 cm^{-1} becomes broader. This broadening indicates an increased structural disorder around the VO_4 tetrahedra, likely due to lattice distortion induced by the incorporation of Mn ions.

The XRD patterns of the samples are shown in Figure 1(b).

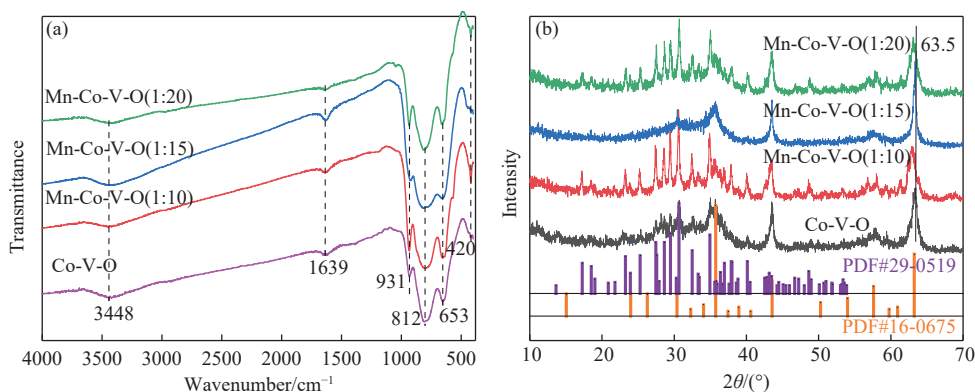
All characteristic diffraction peaks can be indexed to $\text{Co}_2\text{V}_2\text{O}_7$ (PDF#29-0519) and $\text{Co}_3\text{V}_2\text{O}_8$ (PDF#16-0675), indicating that the samples exhibit a mixed-phase structure composed of these two crystalline phases. Furthermore, after Mn doping, the diffraction peak at $2\theta \approx 63.5^\circ$ shifts to a lower angle, suggesting lattice expansion likely due to the incorporation of Mn ions into the host framework.

The morphological features of Co-V-O and Mn-Co-V-O(1:15) were analyzed by SEM. As shown in Figure 2(a), Co-V-O exhibits a uniform assembly of block-like structures. The corresponding SEM image of Mn-Co-V-O(1:15) in Figure 2(b) indicates that the overall morphology remains largely unchanged after Mn doping. Furthermore, elemental mapping results of Mn-Co-V-O(1:15) presented in Figures 2(c)–(f), reveal a homogeneous spatial distribution of Mn, Co, V and O throughout the sample, confirming the successful incorporation of Mn into the Co-V-O framework.

The surface elemental composition and chemical states of Co-V-O and Mn-Co-V-O(1:15) were further investigated by XPS spectra, as shown in Figure 3. The survey spectra in Figure 3(a) confirm the presence of Co, V and O in both samples, while Mn is detected exclusively in Mn-Co-V-O(1:15), indicating the successful incorporation of Mn into the catalyst structure. Figure 3(b) presents the Mn 2*p* XPS spectrum of Mn-Co-V-O(1:15). The peaks located at 653.2, 641.1 and 647.4 eV correspond to Mn 2*p*_{1/2}, Mn 2*p*_{3/2} and satellite peaks (Sat), respectively. In the Mn-Co-V-O catalyst, Mn exhibits mixed valence states: the peaks at 655.01 and 644.1 eV are assigned to Mn^{4+} , those at 653.5 and 642.4 eV to Mn^{3+} , and those at 652.3 and 640.9 eV to Mn^{2+} ^[26]. The presence of Mn^{4+} can induce structural defects, thereby promoting oxygen mobility within the lattice, and thereafter enhancing the catalyst's oxidative capability^[27].

The Co 2*p* XPS spectra are shown in Figure 3(c). Both Co-V-O and Mn-Co-V-O(1:15) exhibit characteristic peaks corresponding to Co 2*p*_{1/2}, Co 2*p*_{3/2}, and two satellite peaks. For Mn-Co-V-O(1:15), the fitted peaks at 796.6 and 780.5 eV are assigned to Co^{3+} , those at 798.1 and 782.1 eV to Co^{2+} , and the signals at 803.3 and 786.7 eV correspond to satellite peaks^[28]. Compared with Co-V-O, no significant peak shift in binding energy is observed for Mn-Co-V-O(1:15), however, notable changes in peak areas are evident. Specifically, the $\text{Co}^{3+}/(\text{Co}^{2+} + \text{Co}^{3+})$ ratio increases from 38.8% in Co-V-O to 46.8% in Mn-Co-V-O(1:15), suggesting that Mn doping promotes electron transfer and lead to an elevated concentration of Co^{3+} species.

Figure 3(d) shows the V 2*p* XPS spectra. Both samples display characteristic peaks for V 2*p*_{1/2} and V 2*p*_{3/2}. In Co-V-O, the fitted peaks at 524.2 and 516.7 eV are assigned to V^{4+} 2*p*_{1/2} and 2*p*_{3/2}, respectively, while those at 524.8 and 517.5 eV correspond to V^{5+} . For Mn-Co-V-O(1:15), the V^{4+} 2*p*_{1/2} and 2*p*_{3/2} peaks are located at 524.0 and 516.8 eV and the V^{5+} peaks appear at 525.3 and 517.6 eV^[29], showing slight shifts compared to the undoped sample. The relative peak area of V^{4+} increases from 64.1% in Co-V-O to 69.5% in Mn-Co-V-O(1:15), indicating that Mn doping promotes the formation and stabilization of V^{4+} species.



be attributed to enhanced molecular collisions that facilitate the reaction and improve the desulfurization performance^[35]. However, when the temperature is further increased to 120 °C, the desulfurization rate declines to 60.0%. This is likely resulted from solvent volatilization, which compromises reaction stability, along with increased energy consumption^[36]. Consequently, 110 °C is identified as the optimal reaction temperature.

Under the optimized conditions (110 °C, oxygen flow rate of 150 mL/min), the influence of catalyst dosage on the desulfurization performance was studied using 20 mL of DBT model oil, as shown in Figure 5(c). As the catalyst

amount increases from 0.02 to 0.03 g, the DBT removal efficiency after 100 min increases from 45.2% to 81.6%, owing primarily to the greater availability of active sites, which accelerates the ODS reaction^[37]. However, further increasing the catalyst loading to 0.04 and 0.05 g leads to reduced desulfurization efficiencies of 56.4% and 50.4%, respectively. This can be attributed to particle agglomeration at higher catalyst loadings, which diminishes the effective surface area, restricts contact with DBT molecules, and hampers the mass transfer of reactants and products^[38]. Therefore, the optimal catalyst dosage is determined to be 0.03 g.

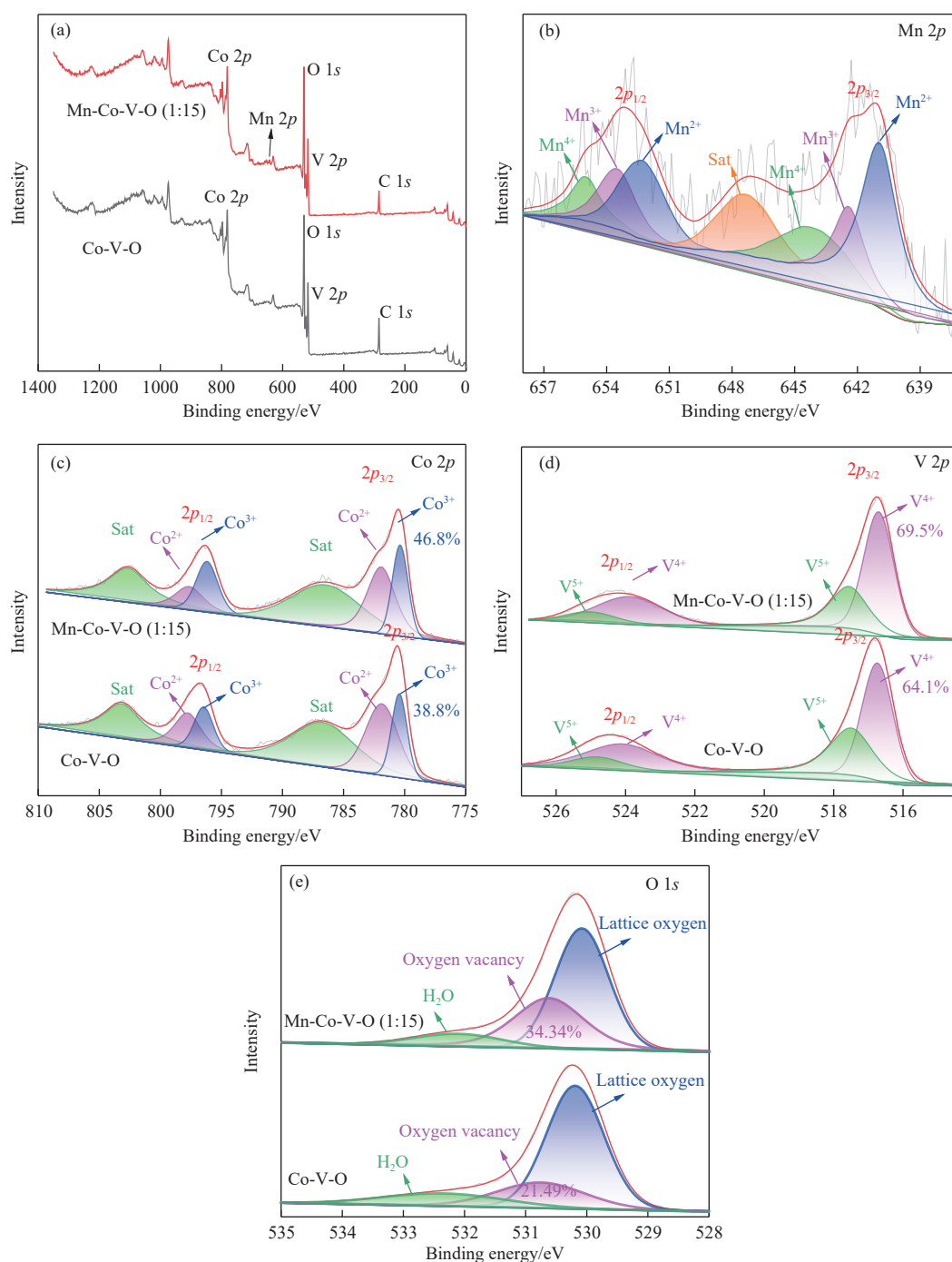


Fig. 3 XPS spectra (survey (a), Mn 2p (b), Co 2p (c), V 2p (d), O 1s (e)) of Co-V-O and Mn-Co-V-O(1:15)

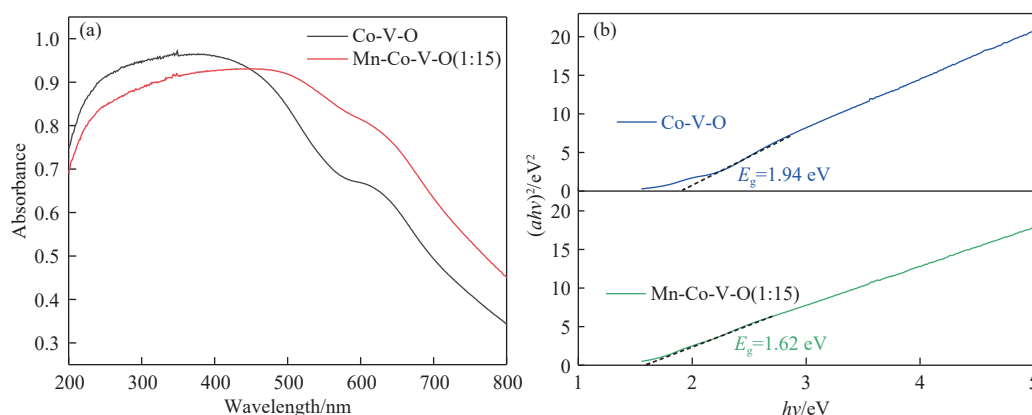


Fig. 4 UV-vis DRS (a) and bandgap widths (b) of Co-V-O and Mn-Co-V-O(1:15)

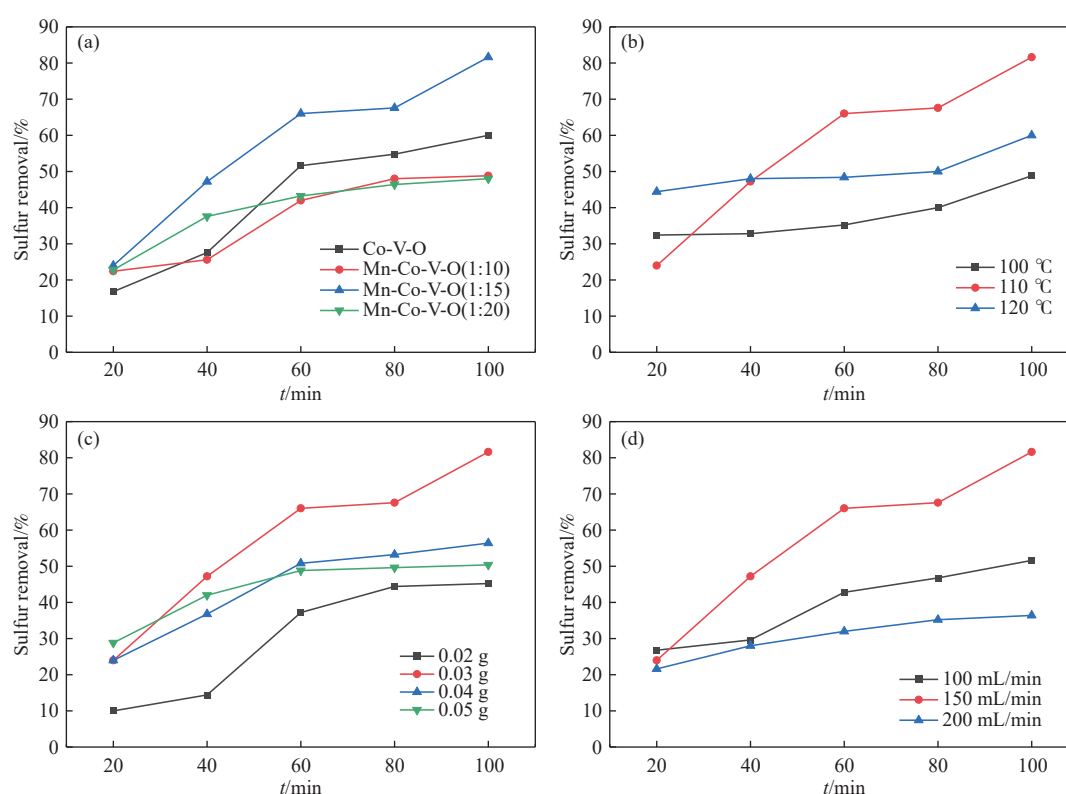


Fig. 5 Mn doping (a), reaction temperature (b), catalyst dosage (c), oxygen flow rate (d) on desulfurization rate

The effect of oxygen flow rate on DBT removal was examined at 110 °C using 0.03 g of Mn-Co-V-O(1:15) and 20 mL of model oil, as shown in Figure 5(d). As the oxygen flow rate increases from 100 to 150 mL/min, the desulfurization rate increases from 51.6% to 81.6%. This improvement is attributed to enhanced gas-liquid mass transfer under moderate oxygen flow, which promotes the reaction between oxygen and DBT. However, further increasing the oxygen flow rate to 200 mL/min results in a decrease in the desulfurization rate to 36.4%. Excessive gas flow shortens the residence time, limiting sufficient oxygen dissolution and diffusion into the liquid phase, thereby reducing gas-liquid contact efficiency and the overall desulfurization performance^[39]. Therefore, an oxygen flow rate of 150 mL/min is determined to be optimal.

2.3 Effect of oxidation-extraction coupling on desulfurization rate

The desulfurization rate in the ODS process alone remains limited. To further improve sulfur removal, after the oxidation step, 5 mL of oxidized model oil was mixed with 5 mL of polyethylene glycol 200 (PEG-200) extractant and stirred at room temperature for 10 min. As shown in Figure 6(a), the desulfurization rate increases from 81.6% to 98.0%, in contrast to a mere 45.0% achieved by extraction alone. This result demonstrates that a synergistic oxidation-extraction strategy enables deep desulfurization.

Practical fuels typically contain various sulfur compounds. Following the oxidation step under optimized conditions, 5 mL of the oxidized upper oil layer was

extracted with 5 mL of PEG-200 for 10 min. The sulfur content in the upper oil phase was subsequently determined. As shown in Figure 6(b), the desulfurization efficiencies of DBT, BT and 4,6-DMDBT are 98.0%, 60.0%, and 86.8%, respectively, indicating that the Mn-Co-V-O (1:15) catalyst in the ODS-extraction system can effectively remove diverse sulfur species. The differences in removal efficiency are primarily due to differences in the electron cloud density at the sulfur atom and molecular steric hindrance. Generally, a higher electron cloud density facilitates sulfur removal^[40]. The electron cloud densities of 4,6-DMDBT, DBT and BT are 5.760, 5.758 and 5.739, respectively^[41]. BT, with the lowest electron cloud density, exhibits the poorest removal. Although 4,6-DMDBT possesses the highest electron density, the two methyl groups in its structure induce significant steric hindrance, which explains its lower desulfurization rate compared with DBT.

The presence of olefins and aromatics in real fuels may also influence the desulfurization process. Toluene and cyclohexene were used as representative compounds to investigate their effects on the removal of DBT. Under optimized reaction conditions, 1 mL of toluene or cyclohexene was added to the reaction mixture prior to extraction. As shown in Figure 6(c), the desulfurization efficiencies for DBT reach 79.2% and 98.8%, respectively. The lower efficiency observed in the toluene system may be attributed to competitive oxidation of toluene, which consumes a portion of the active oxidative species^[41]. Overall, the aerobic ODS system exhibits only limited interference from

olefins and aromatics, demonstrating its potential for deep desulfurization of fuels containing such components.

Following the reaction, the catalyst was recovered by washing successively with distilled water and anhydrous ethanol, and then drying. The reusability of the recycled catalyst was evaluated under the optimal reaction conditions. As shown in Figure 6(d), the desulfurization rate decreases from 98.0% to 93.2% after repeated use. The observed decline in catalytic activity can be primarily attributed to a partial loss of catalyst material during the recovery process, as well as the adsorption or accumulation of oxidation products within the catalyst pores, which reduces the accessibility of the active sites.

The recovered catalyst was further analyzed by FT-IR spectroscopy. As shown in Figure 7(a), the characteristic absorption bands of the fresh and recovered catalysts are essentially identical, indicating that the catalyst framework remains intact after the reaction. However, additional absorption bands are observed at 1155 and 1251 cm^{-1} , which correspond to dibenzothiophene sulfone (DBT_2O_2). This confirms the adsorption of sulfur-containing oxidation products on the catalyst surface. To remove these residual sulfur species, the recovered catalyst was calcined at 400 $^{\circ}\text{C}$ for 2 h and subsequently analyzed by XRD. The XRD pattern of the regenerated catalyst, shown in Figure 7(b), exhibits diffraction peaks that are highly consistent with those of the fresh catalyst. This demonstrates good structural stability of the catalyst throughout the reaction and regeneration processes.

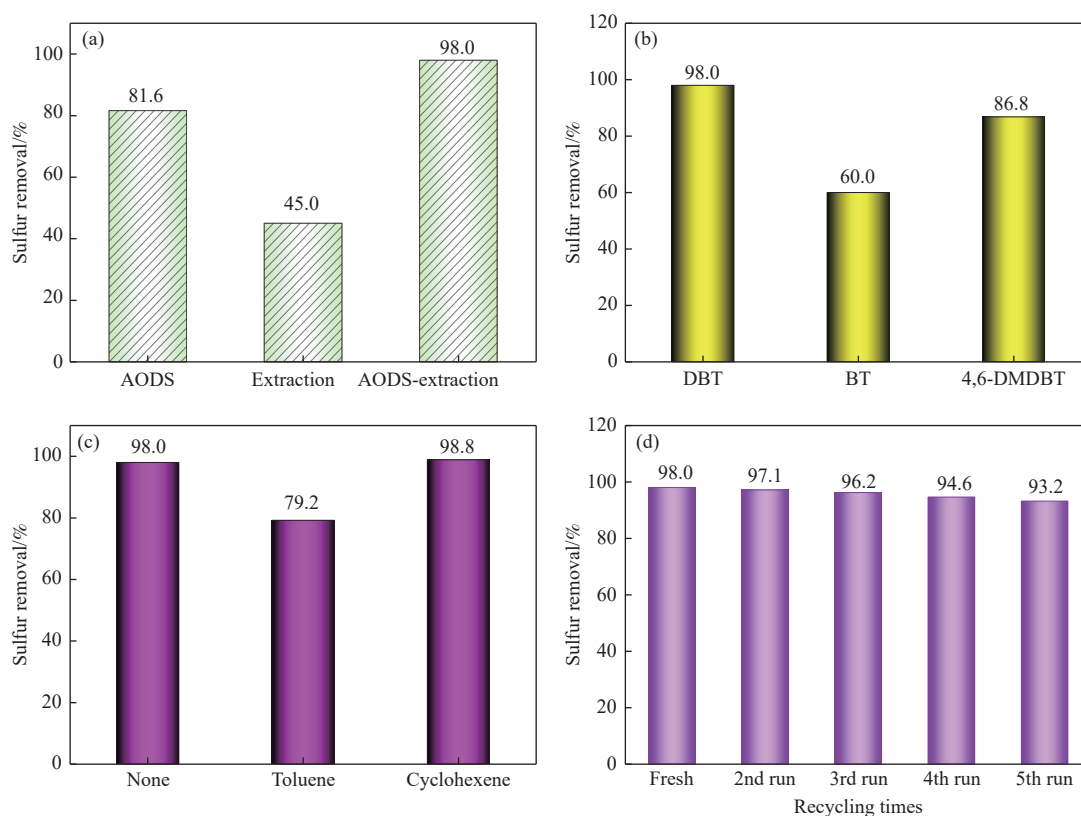


Fig. 6 Oxidation and extraction combination (a), various sulfur compounds (b), toluene and cyclohexene (c), recycling time (d) on desulfurization rate

The ODS performance of the catalyst was further benchmarked against previously reported systems. As summarized in Table 1, the present catalyst exhibits a comparatively high desulfurization rate under milder reaction conditions. Notably, it achieves efficient sulfur removal at lower temperatures and with shorter reaction times compared to other catalysts, underscoring its favorable energy efficiency and practical potential for industrial application.

2.4 Oxidation-extraction desulfurization mechanism

Radical trapping experiments were performed to identify the key active species in the aerobic ODS process. Under the optimized conditions, *p*-benzoquinone (BQ, 0.02 g) a superoxide radical ($\cdot\text{O}_2^-$) scavenger, or isopropanol (IPA, 24 μL), a hydroxyl radical ($\cdot\text{OH}$) scavenger, was separately added to the reaction system. As shown in Figure 8(a), the desulfurization rate drops sharply to 49.6% with BQ, whereas it remains almost unaffected (97.8%) with IPA. These results demonstrate that superoxide radicals ($\cdot\text{O}_2^-$), rather than hydroxyl radicals ($\cdot\text{OH}$), are the predominant active species driving the ODS reaction. Further confirmation was obtained from the EPR spectroscopy (Figure 8(b)), which displays characteristic signals attributable to $\cdot\text{O}_2^-$, directly evidencing its *in situ* generation during the reaction. The formation of these reactive oxygen

species can be attributed to the enhanced activation of molecular oxygen over the Mn-doped Co-V-O catalyst, promoted by its high oxygen vacancy concentration and the synergistic redox cycling among Mn, Co and V species.

Figure 9 schematically illustrates the proposed desulfurization mechanism over the Mn-Co-V-O(1:15) catalyst. The left part of the diagram depicts the oxidation process, while the right part illustrates the extraction step. During the oxidation stage, Mn^{3+} and Co^{2+} species in the Mn-Co-V-O (1:15) catalyst are oxidized to Mn^{4+} and Co^{3+} via electron loss. Concurrently, molecular oxygen accepts these electrons and is activated to form superoxide radicals ($\cdot\text{O}_2^-$) as reactive intermediates. These $\cdot\text{O}_2^-$ species then interact with the V active sites on the catalyst surface, promoting the conversion of $\text{V}=\text{O}$ bonds into peroxovanadate intermediates. Such highly oxidative intermediates subsequently facilitate the stepwise oxidizing of DBT to its corresponding DBTO₂. The introduction of Mn dopants substantially increases the oxygen vacancy concentration, which enhances the adsorption and activation of molecular oxygen on the catalyst surface and promotes $\cdot\text{O}_2^-$ formation. Consequently, the overall rate of aerobic ODS is significantly improved. In the extraction stage, based on the “like dissolves like” principle, polyethylene glycol (PEG) acts as an effective extractant to selectively transfer the polar oxidation product DBTO₂ from the oil phase into the extraction phase, thereby achieving deep desulfurization.

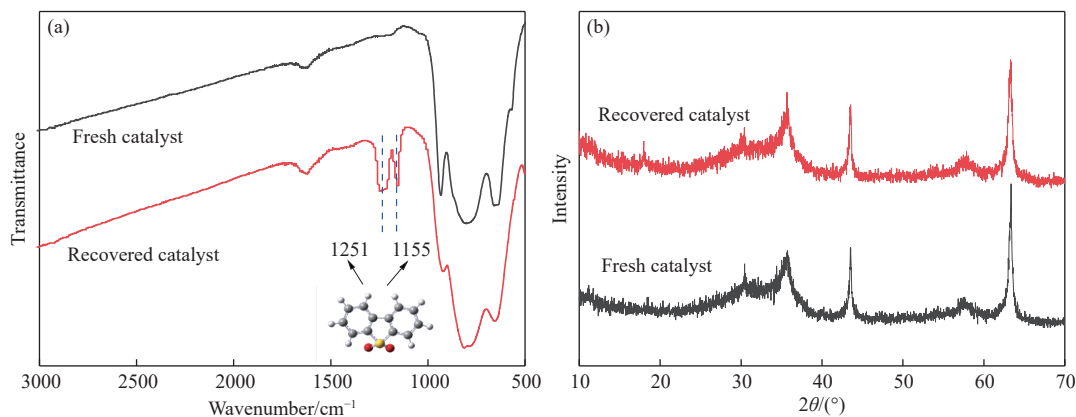


Fig. 7 FT-IR (a) and XRD (b) of the fresh and recovered catalysts

Table 1 Sulfur removal with different metal-based catalysts

Catalyst	<i>t</i> /min	<i>t</i> /°C	Catalyst amount/g	Sulfur removal/%	Ref.
[Bpy]PMoVn	480	110	0.02	65.5 (petroleum coke)	[42]
MoO ₃ /LaTiO _x	150	130	0.02	100 (4,6-DMDBT)	[43]
30%HPA-CeO ₂	240	70	0.03	52.5 (petroleum coke)	[44]
Mo@CeO ₂	480	100	—	61.2 (petroleum coke)	[45]
FeMoO _x /LaTiO _y	60	130	0.02	100 (4,6-DMDBT)	[46]
MoO ₃ /La ₂ O ₂ CO ₃	120	130	0.04	100 (4,6-DMDBT)	[47]
VO _x /TiO ₂	180	80	—	100 (4,6-DMDBT)	[48]
V ₂ O ₅ /TiO ₂	120	120	0.02	100 (DBT)	[49]
Mn-Co-V-O	100	110	0.03	98 (DBT)	this work

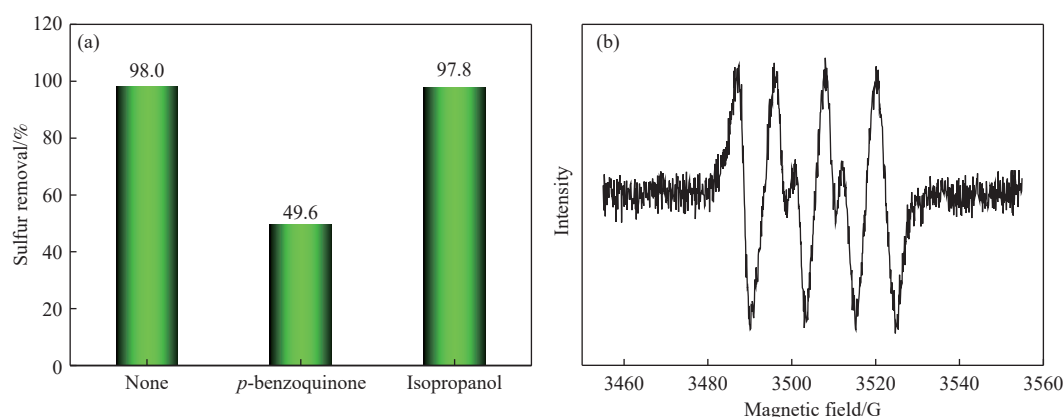


Fig. 8 Free radical capture experiment (a) and EPR spectroscopy (b)

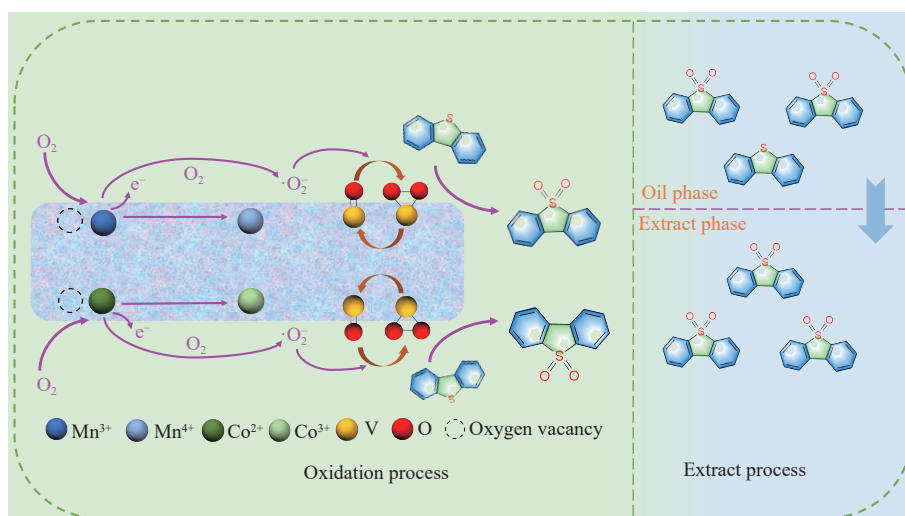


Fig. 9 Desulfurization mechanism diagram of Mn-Co-V-O(1:15)

3 Conclusions

In this study, Mn doping was introduced into the Co-V-O system to significantly enhance desulfurization performance by modulating the oxygen vacancy concentration and electronic structure. Experimental results demonstrated that under the optimal conditions of a reaction temperature of 110 °C, catalyst dosage of 0.03 g, oxygen flow rate of 150 mL/min and 20 mL of model oil, a desulfurization rate of 81.6% could be achieved. Notably, when oxidative desulfurization was combined with extraction, the removal efficiency of DBT was further increased to 98.0%, significantly surpassing that of the undoped Co-V-O catalyst. These results indicated that Mn doping effectively increased the concentration of oxygen vacancy, thereby improving the catalytic desulfurization performance. Radical trapping experiments further confirmed that $\cdot\text{O}_2^-$ are generated in the presence of the catalyst and molecular oxygen, which played a crucial role in the efficient oxidation of DBT to DBTO₂.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] ZHAO Y, LI X P, ZHAO R X. Highly efficient oxidative desulfurization with titanium sulfate as catalyst in phenol based deep eutectic solvent[J]. Chin J Chem Eng, 2021, 72(8): 4391–4400.
- [2] WU P W, DENG C, LIU F, et al. Magnetically recyclable high - entropy metal oxide catalyst for aerobic catalytic oxidative desulfurization[J]. Chin J Catal, 2023, 54(11): 238–249.
- [3] LIU F, YU J, QAZI A B, et al. Metal-based ionic liquids in oxidative desulfurization: A critical review[J]. Environ Sci Technol, 2021, 55(3): 1419–1435.
- [4] ZHAO R, LI X, SU J, et al. Preparation of WO₃/g-C₃N₄ composites and their application in oxidative desulfurization[J]. Appl Surf Sci, 2017, 392: 810–816.
- [5] WANG Y, HUA M Q, ZHOU S H, et al. Regulating the coordination environment of surface alumina on NiMo/Al₂O₃ to enhance ultra-deep hydrodesulfurization of diesel[J]. Appl Catal B: Environ, 2024, 357: 124265.
- [6] LIU J, LIU Y F, WANG Y, et al. Regulating the electron affinity of NiMo/Al₂O₃ to enhance ultra-deep hydrodesulfurization of diesel[J]. Appl Catal B: Environ, 2025, 378: 125565.
- [7] ZHOU S H, PAN Y, WANG Y, et al. Structure-reactivity relationship of Fe-triggered NiMoS active phase for ultradeep

- hydrodesulfurization of diesel[J]. *Chem Eng Sci*, 2025, 317: 122071.
- [8] ZHOU S H, WU Z J, LIU J X, et al. Modifying the active phase structure of $\text{Ni}_2\text{P}/\text{Al}_2\text{O}_3$ by Ga introduction for improved hydrodesulfurization of diesel[J]. *Chem Eng J*, 2024, 479: 147776.
- [9] HARUNA A, MERICAN Z M A, MUSA S G. Recent advances in catalytic oxidative desulfurization of fuel oil—A review[J]. *J Ind Eng Chem*, 2022, 112: 20–36.
- [10] AHMADIAN M, ANBIA M. Oxidative desulfurization of liquid fuels using polyoxometalate-based catalysts: A review[J]. *Energy Fuels*, 2021, 35(13): 10347–10373.
- [11] LIM X B, ONG W J. A current overview of the oxidative desulfurization of fuels utilizing heat and solar light: From materials design to catalysis for clean energy[J]. *Nanoscale Horiz*, 2021, 6(8): 588–633.
- [12] ZHANG M, LIAO W, WEI Y, et al. Aerobic oxidative desulfurization by nanoporous tungsten oxide with oxygen defects[J]. *ACS Appl Nano Mater*, 2021, 4(2): 1085–1093.
- [13] LIU X Y, LI X P, ZHAO R X. $\text{Ce}_2(\text{MoO}_4)_3$ as an efficient catalyst for aerobic oxidative desulfurization of fuels[J]. *Pet Sci*, 2022, 19(2): 861–869.
- [14] SHAFIQ I, SHAFIQUE S, AKHTER P, et al. Recent breakthroughs in deep aerobic oxidative desulfurization of petroleum refinery products[J]. *J Clean Prod*, 2021, 294: 125731.
- [15] LIU Y, BAI J, SONG Y, et al. Oxygen vacancy engineering of molybdenum oxide nanobelts by Fe ion intercalation for aerobic oxidative desulfurization[J]. *ACS Appl Nano Mater*, 2021, 4(12): 13379–13387.
- [16] UEMATSU T, MIYAMOTO Y, OGASAWARA Y, et al. Molybdenum-doped $\alpha\text{-MnO}_2$ as an efficient reusable heterogeneous catalyst for aerobic sulfide oxygenation[J]. *Catal Sci Technol*, 2016, 6(1): 222–233.
- [17] AN X, JIANG W, HE J, et al. Modulating electronic characteristics of nickel molybdate via an effective manganese-doping strategy to enhance oxidative desulfurization performance[J]. *Inorg Chem*, 2022, 61(51): 21067–21075.
- [18] WANG C, QIU Y, WU H, et al. Construction of 2D-2D $\text{V}_2\text{O}_5/\text{BNNS}$ nanocomposites for improved aerobic oxidative desulfurization performance[J]. *Fuel*, 2020, 270: 117498.
- [19] ZOU Y, WANG C, CHEN H, et al. Scalable and facile synthesis of V_2O_5 nanoparticles via ball milling for improved aerobic oxidative desulfurization[J]. *Green Energy Environ*, 2021, 6(2): 169–175.
- [20] MURATA S, MURATA K, KIDENA K, et al. A novel oxidative desulfurization system for diesel fuels with molecular oxygen in the presence of cobalt catalysts and aldehydes[J]. *Energy fuels*, 2004, 18(1): 116–121.
- [21] WEI S, HE H, CHENG Y, et al. Preparation, characterization, and catalytic performances of cobalt catalysts supported on KIT-6 silicas in oxidative desulfurization of dibenzothiophene[J]. *Fuel*, 2017, 200: 11–21.
- [22] DENG C, LI J, KANG L, et al. Efficient Co/SBA-15 catalyst for aerobic oxidative desulfurization at mild reaction temperature[J]. *Mol Catal*, 2022, 530: 112567.
- [23] TANG Y, ZHOU J, LIU J, et al. Facile synthesis of cobalt vanadium oxides and their applications in lithium batteries[J]. *Int J Electrochem Sci*, 2013, 8(1): 1138–1145.
- [24] ZHANG L, CHANG S, LU X, et al. Vapor phosphorus-coated cobalt vanadate as a high-performance anode for a lithium-ion battery[J]. *J Solid State Electrochem*, 2022, 26(4): 917–927.
- [25] ZHENG X Q, CAO X C, ZHANG Y, et al. Tunable dual cationic redox couples boost bifunctional oxygen electrocatalysis for long-term rechargeable Zn-air batteries[J]. *J Colloid Interface Sci*, 2022, 628: 922–930.
- [26] AO R, MA L P, GUO Z Y, et al. La-Co-Mn perovskite (LCMO) for NO and HgO oxidation: Experimental and DFT investigations of adsorption processes[J]. *Colloids Surf A Physicochem Eng Asp*, 2024, 695: 134324.
- [27] WANG J Z, GUO Z Y, LIU M Y, et al. CoMoO_4 nanoparticles decorated ultrathin nanoplates constructed porous flower as an electrocatalyst toward overall water splitting and Zn-air batteries[J]. *Renewable Energy*, 2023, 212: 751–760.
- [28] WU F F, YU C H, LIU W X, et al. Large-scale synthesis of Co-V-O hexagonal microplatelets under ambient conditions for highly reversible lithium storage[J]. *J Mater Chem A*, 2015, 3(32): 16728–16736.
- [29] GUO J Z, CHU L, WANG L Y, et al. Self-templated fabrication of $\text{CoMoO}_4\text{-Co}_3\text{O}_4$ hollow nanocages for efficient aerobic oxidative desulfurization[J]. *Appl Surf Sci*, 2022, 579: 152251.
- [30] LIU Y Z, DENG C, WU P W, et al. High-entropy zeolitic imidazolate framework for efficient oxidative desulfurization of diesel fuel: Towards complete sulfur removal and valuable sulfone production[J]. *Fuel*, 2024, 359: 130375.
- [31] AN X, XU L C, XU L X, et al. Boosting catalytic oxidative desulfurization performance over yolk-shell nickel molybdate fabricated by defect engineering[J]. *Inorg Chem*, 2023, 62(23): 9199–9208.
- [32] LIU Z Y, XU J, LI Y R, et al. High performance photocatalytic based on Ce doped CoWO_4 : Controllable synthesis and enhanced photocatalytic activity[J]. *Catal Lett*, 2018, 148(10): 3205–3213.
- [33] SHEN C, WANG Y J, XU J H, et al. Oxidative desulfurization of DBT with H_2O_2 catalysed by TiO_2 /porous glass[J]. *Green Chem*, 2016, 18(3): 771–781.
- [34] ZHAO D S, WANG J L, ZHOU E P. Oxidative desulfurization of diesel fuel using a Brønsted acid room temperature ionic liquid in the presence of H_2O_2 [J]. *Green Chem*, 2007, 9(11): 1219–1222.
- [35] ESEVA E, AKOPYAN A, SCHEPINA A, et al. Deep aerobic oxidative desulfurization of model fuel by Anderson-type polyoxometalate catalysts[J]. *Catal Commun*, 2021, 149: 106256.
- [36] QIU L, CHENG Y, YANG C P, et al. Oxidative desulfurization of dibenzothiophene using a catalyst of molybdenum supported on modified medicinal stone[J]. *RSC Adv*, 2016, 6(21): 17036–17045.
- [37] MOKHTARI B, AKBARI A, OMIDKHAH M. Superior deep desulfurization of real diesel over MoO_3 /silica gel as an efficient catalyst for oxidation of refractory compounds[J]. *Energy Fuels*, 2019, 33(8): 7276–7286.
- [38] LI H M, ZHU W S, WANG Y, et al. Deep oxidative desulfurization of fuels in redox ionic liquids based on iron chloride[J]. *Green Chem*, 2009, 11(6): 810–815.

- [39] CAO Y, WANG H X, DING R M, et al. Highly efficient oxidative desulfurization of dibenzothiophene using Ni modified MoO₃ catalyst[J]. Appl Catal A: Gen, 2020, 589: 117308.
- [40] LÜ H Y, DENG C G, REN W Z, et al. Oxidative desulfurization of model diesel using [(C₄H₉)₄N]₆Mo₇O₂₄ as a catalyst in ionic liquids[J]. Fuel Process Technol, 2014, 119: 87–91.
- [41] XIONG Y H, CHEN B C, XU T T, et al. Modulation of C=O groups concentration in carbon-based materials to enhance peroxymonosulfate activation towards degradation of organic contaminant: Mechanism of the non-radical oxidation pathway[J]. Environ Res, 2025, 275: 121442.
- [42] WANG Y, LUAN H, GONG J H, et al. Mechanochemical driven oxidative desulfurization of high-sulfur petroleum coke over [Bpy]PMoVn coupled with amide-based binary deep eutectic solvents[J]. Chem Eng Sci, 2025, 304: 121021.
- [43] CHENG H F, WU Y, SHAO S J, et al. Regulating the metal-support interaction of MoO₃/LaTiO_x to enhance ultra-deep aerobic oxidative desulfurization of diesel[J]. Chem Eng J, 2025, 519: 165375.
- [44] LI F X, WANG Y, LI F M, et al. Efficient oxidative desulfurization of high-sulfur petroleum coke over polyoxometalates HPA coupled CeO₂[J]. Surf Interfaces, 2025, 70: 106821.
- [45] ZHANG W F, SHEN Y G, LI F M, et al. Effective oxidative desulfurization of high-sulfur petroleum coke over 4A zeolite reinforced Mo@CeO₂[J]. Surf Interfaces, 2025, 72: 107137.
- [46] ZHANG F R, YAN Y, LIU F, et al. Regulating the Fe/Mo ratio of FeMoO_x/LaTiO₃ to boost aerobic oxidative desulfurization of diesel[J]. J Fuel Chem Technol, 2025, 53: 1255–1268.
- [47] SHAO S J, LIU H, WANG X D, et al. Unveiling the structure-performance of MoO₃/La₂O₂CO₃ for ultra-deep aerobic oxidative desulfurization of diesel[J]. Chem Eng J, 2024, 495: 153654.
- [48] CHENG H F, ZHANG Z T, ZHANG L, et al. Crystal-plane-engineered TiO₂-anchored vanadium single atoms and clusters for boosting ultradeep aerobic oxidative desulfurization of diesel[J]. Inorg Chem, 2024, 63: 1488–1498.
- [49] LIU J X, ZHANG L, ZHU J Y, et al. Size-dependent surface electronic structure of V₂O₅/TiO₂ for ultra-deep aerobic oxidative desulfurization of diesel[J]. Chem Eng Sci, 2023, 275: 118749.

Mn 掺杂对 Co-V-O 二元金属氧化物结构和氧化脱硫性能的影响

董哲涵¹, 王泓力², 李秀萍³, 赵荣祥^{1,*}

(1. 辽宁石油化工大学 石油化工学院, 辽宁 抚顺 113001; 2. 山东金创金银冶炼有限公司, 山东 烟台 265600;

3. 辽宁石油化工大学 理学院, 辽宁 抚顺 113001)

摘要: 燃油中硫化物的燃烧排放是加剧大气污染的重要诱因之一。氧化脱硫技术因反应条件温和、对芳香族硫化物脱除效率优异, 已成为传统加氢脱硫技术的重要补充手段。金属元素掺杂是精准调控催化剂电子结构、进而提升其催化性能的有效策略, 本研究采用回流-高温煅烧耦合方法制备了锰掺杂钴钒复合金属氧化物(Mn-Co-V-O); 借助傅里叶变换红外光谱(FT-IR)、X 射线衍射(XRD)、扫描电子显微镜(SEM)、X 射线光电子能谱(XPS)及紫外-可见吸收光谱(UV-vis)等多种表征手段, 分析了该催化剂的晶体结构、微观形貌及表面化学组成。以分子氧为氧化剂, 本研究对 Mn-Co-V-O 催化剂的二苯并噻吩(DBT)氧化脱硫性能开展了评价。结果表明, 相较于未掺杂的 Co-V-O 催化剂, Mn 元素的引入可显著提升其催化活性; 在优化反应条件下, DBT 的直接脱除率可达 81.6%, 与萃取工艺联用后脱硫效率进一步提升至 98.0%。机理探究结果表明, Mn 掺杂可有效提升催化剂表面氧空位浓度, 进而促进分子氧活化生成超氧自由基($\cdot\text{O}_2^-$); 自由基捕获实验证实, $\cdot\text{O}_2^-$ 是实现 DBT 选择性氧化为二苯并噻吩砜(DBTO₂)的关键活性物种。本研究为深度氧化脱硫用高效金属氧化物催化剂的设计与开发提供了重要的理论依据与技术参考。

关键词: Co-V-O; 有氧氧化脱硫; DBT; 氧空位; 超氧自由基

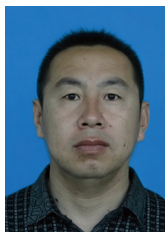
中图分类号: TQ028.8

文献标识码: A

作者简介:



董哲涵(2001), 硕士研究生, 研究方向为氧化脱硫, dongzh0505@163.com。



赵荣祥(1971), 博士, 教授, 研究方向为清洁燃料生产, zylhzrx@126.com。