Relationship between the structure and catalytic performance of MoS$_2$ with different surfactant-assisted syntheses in the hydrodesulfurization reaction of 4,6-DMDBT

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Surfactants are important factors in the hydrothermal synthesis of MoS$_2$ with different morphologies. Herein, we report the synthesis of MoS$_2$ via the hydrothermal method combined with a single-source precursor with the assistance of different surfactants (CTAB/SDS/SDBS). The synthesis mechanisms of MoS$_2$ with different morphologies and their effects on 4,6-DMDBT in hydrodesulfurization (HDS) have been systematically studied. MoS$_2$-CTAB was prepared by the adsorption of molybdate radicals, nucleation and formation. MoS$_2$-SDS and MoS$_2$-SDBS were synthesized via four steps, namely, adsorption, insertion, exfoliation and assembly, and the relationship between the morphology-structure-performance of MoS$_2$ in the hydrodesulfurization of 4,6-DMDBT was investigated. It was established that the desulfurization rate of MoS$_2$, HYD ratio and selectivity of the MoS$_2$ increased in the order: MoS$_2$-SDBS > MoS$_2$-CTAB > MoS$_2$-SDS, which exhibited a positive correlation with the average number of layers and dispersion, and a negative correlation with the average slab length and the ratio of the Mo edge/corner sites of MoS$_2$. Among all the MoS$_2$, MoS$_2$-SDBS exhibited the best HDS performance.

Introduction

Energy is an important driving force for the development of human society and diesel is widely used as a primary energy source in the world at present. However, significant harm is done to the environment on burning diesel, which contains a large number of sulfur compounds.$^1$ Thus, controlling the sulfur content of diesel is needed to reduce air pollution and also satisfy the increasingly strict regulations.$^{2,3}$ The removal of 4,6-dimethylbenzothiophene (4,6-DMDBT), which is the most difficult sulfur compound of diesel oil, is highly desirable. To date, hydrodesulfurization (HDS) remains one of the principal techniques for achieving this goal.$^{4,6}$ Molybdenum disulfide (MoS$_2$) is considered to be an excellent catalyst for the HDS reaction because of its active sites including edge and corner sites exposed by its layered structure.$^7$

Different preparation methods have different effects on the morphology and structure of molybdenum disulfide, which further affect its catalytic activity. The methods of preparation of MoS$_2$ have been quite developed, e.g., the hydrothermal method, chemical vapor deposition (CVD), precipitation method and precursor thermolysis.$^{8,9}$ The morphology and crystallinity of MoS$_2$ are substantially affected by different preparation methods. For example, Li et al.$^9$ synthesized hollow MoS$_2$ microspheres composed of nanoflakes by the hydrothermal method. Lee et al.$^{10}$ used MoO$_3$ and S as reducing agents to prepare single-layer MoS$_2$ films by CVD. Hu et al.$^{11}$ synthesized MoS$_2$ (x = 3–20) in an ethanol–water solution by the precipitation method, and it was calcined in hydrogen at different temperatures to obtain MoS$_2$ with different morphologies. Wang et al.$^{12}$ synthesized MoS$_2$ and MoO$_3$ hierarchical nanostructures using a single-source molecular precursor.

Single-source molecular precursors refer to a single-source molecule containing all the elements required in order to form the final product, which means fewer irrelevant elements in reaction systems; the use of such precursors combined with the hydrothermal method could gain products in a more moderate way. For example, Wang et al.$^{12}$ prepared molybdenum sulfide nanoclusters using Mo([C$_2$H$_5$]$_2$NCS)$_2$O as the single-source molecule by the hydrothermal method. Judging by current research, this combination method is relatively uncommon in the preparation of MoS$_2$. Moreover, there is a lack of micro-level understanding of the HDS reaction of MoS$_2$ and related materials, and how to establish the morphology-structure-activity relationship between MoS$_2$ and HDS for 4,6-DMDBT. In other words, the numbers of layers and active sites of MoS$_2$ are estimated by characterization, and the catalytic performance, being directly and systematically related to HDS performance, is seldom studied. Therefore, we have proposed a strategy that combines the reaction product of silver...
diethylthiocarbamate (DDTC) and ammonium paramolybdate (NH₄)₆Mo₇O₂₄·4H₂O as the single-source precursor with the hydrothermal method to prepare different morphologies of MoS₂, assisted by different surfactants. The products were characterized by XRD, SEM, BET, Raman spectroscopy. All the different morphologies of MoS₂ as catalysts showed different HDS activities and desulphurization rates with 4,6-DMDBT for varied micro-structures of MoS₂.

Experimental

Materials

(NH₄)₆Mo₇O₂₄·4H₂O, HO–NH₂·HCl, diethylthiocarbamic acid sodium salt (DDTC), NH₄OH, SDS, CTAB, SDBS, KI (AR) were purchased from Sinopharm Group Chemical Reagents Co. Ltd. 4, 6-DMDBT was obtained from Shanghai Vauquet, and decalin was obtained from Macklin. The above reagents were used without further purification.

Preparation of MoS₂

MoS₂ was prepared by hydrothermal synthesis with the assistance surfactants (CTAB/SDS/SDBS). In a typical procedure, the experiment consists of two steps. First, the precursor was synthesized by the following steps. (NH₄)₆Mo₇O₂₄·4H₂O and DDTC, in a molar ratio of Mo : S = 1 : 4, were dissolved in 100 mL deionized water, stirred with a magnetic stirrer for 5 h then allowed to react for 12 h as the molybdenum source and sulfur source, respectively. The products were washed several times with deionized water and anhydrous ethanol and were then transferred and dried in a vacuum dryer at 60 °C for 5 h.

Second, MoS₂ was prepared as follows. The precursor (1.275 g) and hydroxylamine hydrochloride (2.085 g) were dissolved in 30 mL of deionized water, and then SDS, CTAB and SDBS, three different kinds of surfactants, were respectively added to the hydrothermal system under vigorous stirring. The mixed solutions were then transferred to 100 mL hydrothermal reactors and heated at 220 °C for 24 h. After cooling to room temperature, black powders were obtained, which were washed several times with deionized water and ethanol. The final catalysts were obtained after drying under vacuum at 60 °C for 12 h and were denoted as “MoS₂-x”, where x indicates the different surfactants.

Characterization

The crystalline structures of the samples were detected by a SmartLab X-ray powder diffractometer (XRD) with Cu Kα radiation operated at 40 kV and 30 mA; the diffraction angle (2θ) ranged from 5° to 80°, and the scanning rate was 10° min⁻¹. XRD spectra were analyzed using MDI Jade 6.

Before the FT-IR analysis, the KBr was dried in an oven at 120 °C for 12 h. Small amounts of the dry samples were mixed with KBr and pressed into pellets, and were measured on an FT-IR spectrometer (NICOLET I50).

The surface morphologies of the samples were recorded by S-4800 scanning electron microscopy (SEM). Secondary electron imaging was conducted and the surface morphologies and element distributions were obtained by observing the samples at low voltage.

High-resolution transmission electron microscopy (HRTEM) characterization was performed on a JEM-2100 transmission electron microscope. Before characterization, tiny samples were dispersed in absolute ethanol by ultrasound, and a small number of liquid droplets were put on the copper mesh to be tested after volatilization. We acquired 25 representative pictures, including 400 slabs and 150 independent layered areas obtained from different regions of each catalyst. The average stacking number (ΔN) and average slab length (ΔL) were respectively calculated using the following equations:

$$
\Delta N = \frac{\sum_{i=1}^{n} x_i N_i}{\sum_{j=1}^{n} x_j}
$$

$$
\Delta L = \frac{\sum_{i=1}^{n} x_i L_i}{\sum_{j=1}^{n} x_j}
$$

where i is the total number of MoS₂ slabs. Nᵢ and Lᵢ represent the stacking layer number and length of MoS₂, respectively, and xᵢ is the number of MoS₂ slabs with Nᵢ layers of length Lᵢ.

The Mo edge/corner ratio of the MoS₂ slab [(fₑ/fₐ)Mo] was gained by the following equation:

$$
(f_e)_{Mo} = \frac{\text{Mo}}{\text{Mo} + \text{Ni}} = \frac{5 \Delta L}{3.2} - 1.5
$$

where Moₑ is the number of edge sites and Moₓ is the number of corner sites.

N₂ adsorption–desorption (BET) isotherms were obtained on a QUADRASORB evo-2 automatic microporous physical adsorption instrument. The principle is that the surface of the sample is physically adsorbed with nitrogen at a low temperature to calculate the specific surface area and pore size distribution. The specific surface area of the sample was calculated by the BET (Brunauer–Emmett–Teller) formula. The pore size distribution was modeled by BJH (Barrett–Joyner–Halenda) analysis. The samples were vacuum degassed at 250 °C for 3 h before testing, and subsequently transferred to the analysis station for adsorption–desorption at −196 °C.

Raman spectra were obtained on a confocal inVia micro Raman spectrometer produced by Renishaw, UK. Monochromatic light was scattered on the sample and the structural information of the samples was gained after calculating the wavelength of the scattered light. Generally speaking, the wavelength was mainly located in the range of molecular vibration, rotation and electronic level transition in the molecular system.

HDS of 4,6-DMDBT on the prepared MoS₂

A mixture of 4,6-DMDBT and decalin (0.4 wt% S) was used as the simulated diesel oil to test the catalytic activity of MoS₂; the test was performed in a microform high-pressure autoclave (200 mL). First, 70 mL of simulated diesel oil and 0.6 g catalyst were
poured into the autoclave. The reactor was installed according to the operation and the gas tightness of the device was good before reaction, then hydrogen was injected three times into the autoclave to replace the air in the autoclave until it was discharged. The reaction conditions were as follows: H_2, 3 MPa, 300 °C, 500 rpm, 5 h. After the reaction was finished, the power was turned off, and the gas discharged from the reactor was fed into the saturated NaOH solution when the temperature dropped to room temperature.

Analysis of the total sulfur content of the solution after the HDS reaction was tested on a WK-2D microcoulomb comprehensive instrument, Jiangfen, from Jiangsu. The hydrocarbon composition was determined using a Pano A90 gas chromatograph equipped with an HP-5 (30 m × 0.32 mm × 0.25 µm) and FID detector for quantitative analysis; the qualitative analysis was carried out using a Trace 1310-ISQ LT GC-MS equipped with an HP-5.

The desulfurization ratio was calculated by the following equations:

\[ D_s = \frac{X_0 - X_s}{X_0} \]

where \( X_s \) and \( X_0 \) represent the total sulfur contents before and after the reaction, respectively.

The ratio of the product content of the HYD pathway to that of the DDS pathway was expressed by calculating the product selectivity \( S \). The formula is as follows:

\[ S = \frac{S_{\text{HYD}}}{S_{\text{DDS}}} = \frac{S_{\text{THDMBCH}} + S_{\text{DMBCH}} + S_{\text{MCHT}}}{S_{\text{DMBP}}} \]

where \( S_{\text{THDMBCH}}, S_{\text{DMBCH}}, S_{\text{MCHT}}, S_{\text{DMBP}} \) represent the contents of THDMBCH, DMBCH, MCHT, DMBP in solution after HDS reaction.

Results and discussion

**XRD results**

The preparation of the precursors was the first step in the preparation of MoS_2. To determine the composition of the precursors, XRD characterization was conducted as shown in Fig. 1. Upon comparison with the standard card PDF 25-1978\#, it was concluded that the precursor was MoO_2 (DDTC)_2, the complex of ammonium paramolybdate and DDTC. The formation mechanism of the precursor is as follows:

\[ 20H^+ + \text{MoO}_2\text{O}_2^{6-} + 14\text{DDTC}^- \rightarrow \text{MoO}_4^{2-} (\text{DDTC})_2 + 10\text{H}_2\text{O} \]

In the hydrothermal reaction, MoO_2 (DDTC)_2 decomposed into MoO_4^{2-}, then the O^{2-} was replaced by S^{2-} and MoS_2 was obtained.\^\footnote{16}

The XRD patterns of the three types of MoS_2-X, with MoO_2 (DDTC)_2 as the precursor, are shown in Fig. 2. The peaks of the three types of MoS_2 are similar, all exhibiting weak crystals of MoS_2 synthesized according to different surfactant-assisted hydrothermal methods. The MoS_2 peaks with 2θ at 34° and 57° were detected but not obvious in the three MoS_2, and were attributed to the (100) and (110) planes of 2H-MoS_2 (JCPDS card no.75–1539), respectively, which indicated that the three MoS_2-

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**Fig. 1** The XRD spectra of the precursor.

**Fig. 2** XRD patterns of MoS_2-CTAB, MoS_2-SDS, MoS_2-SDBS.

**Fig. 3** FT-IR spectra of the samples. (a) MoS_2-CTAB; (b) MoS_2-SDS; (c) MoS_2-SDBS.
X had the same arrangement of atoms in basal planes of 2H-MoS$_2$. Moreover, the (002) peaks represented the accumulation of the S–Mo–S layers along the c-axis; since only weak van der Waals forces connect the MoS$_2$ layers, it is very easy to insert heteroatoms between the layers. A weak peak at 9° was observed instead of the (002) peak at 14° for MoS$_2$-CTAB, MoS$_2$-SDS and MoS$_2$-SDBS as compared to the pristine 2H-MoS$_2$. This indicated that the (002) peaks moved forward, which was attributed to the increase in the interlayer spacing caused by the addition of surfactants, demonstrating that there were few stacking layers of MoS$_2$. On the whole, the effects of the three surfactants on the crystalline form and intensities of MoS$_2$-X in the hydrothermal reaction were slight, and all the MoS$_2$ exhibited poor crystallinity, consistent with the previous results of the synthesis of MoS$_2$ using the hydrothermal method.

Fig. 4  SEM micrographs of the MoS$_2$-CTAB (a and b), MoS$_2$-SDBS (c and d), MoS$_2$-SDS (e and f).

Fig. 5  FETEM images of the MoS$_2$-CTAB (a), MoS$_2$-SDBS (b), MoS$_2$-SDS (c).
FT-IR analysis

The FT-IR spectra of MoS₂-CTAB (a), MoS₂-SDS (b), MoS₂-SDBS (c) are given in Fig. 3. The peaks at 3434 cm⁻¹ and 1630 cm⁻¹ for the three samples were assigned to the N–H stretching vibrations and C=S stretching vibrations of the amide bond from the precursor, respectively.²² The stronger intensity of MoS₂-SDBS was because of the effect of the C=C bond from the benzene ring in SDBS. The peaks at 2917 cm⁻¹ and 2850 cm⁻¹ were assigned to the stretching vibration modes of C–H from the surfactants (CTAB, SDS, SDBS).²³ The C–H stretching vibration intensity was stronger in MoS₂-CTAB than in the others, which was attributed to CTAB having the most C–H groups. The characteristic peaks of −SO₂ from MoS₂-SDBS appeared at about 1103 cm⁻¹ and 1249 cm⁻¹. In Fig. 3(c), the peak at 945 cm⁻¹ was strengthened, which indicated that there was a strong coordination effect between MoS₂ and SDBS rather than simple adsorption and modification.²⁴

SEM results

The SEM micrographs of the synthesized MoS₂ with three surfactants are provided in Fig. 4. The introduction of three surfactants in the synthesis process gave rise to remarkable morphological changes in the MoS₂. Some irregularly shaped particles with sizes ranging from 300 to 3000 nm were detected. MoS₂-CTAB exhibited smooth, ball-like particles with sizes ranging from 400 to 2800 nm and larger; the particles were evenly dispersed and less agglomerated. This was attributed to the larger steric hindrance caused by the hydrophilic functional group ((CH₃)₃N⁺) of CTAB, which led to the larger size of the micelles formed by CTAB. In addition, the selective adsorption of CTA⁺ on the specific crystal surface of the nuclei of MoS₂ limited the growth of the nuclei of MoS₂ and hindered its reunion in the hydrothermal process, thus increasing its dispersion. The size of the MoS₂ formed by CTAB as the template was fairly large;²⁵ its average size was 1.2 μm and the range of mean sizes was 700–900 nm. MoS₂-SDBS exhibited rough, ball-like particles that were greatly aggregated; there were hardly any single ball-like structures. The average particle size was 800 nm in the range from 300 nm to 1.5 μm. MoS₂-SDS exhibited a flower-like morphology with many stacked nanosheets, and the average thickness of the nanosheets was 15 nm, which indicated substantial aggregation.

FETEM results

HRTEM studies were carried out in order to acquire more information regarding the distribution and structure of MoS₂ as catalysts. The HRTEM images in Fig. 5 further show the specific outlines of the morphology of MoS₂ prepared by heating at 220 °C for 24 h and adding CTAB, SDS and SDBS, respectively. It was found that the fringes of the three samples were arranged in a relatively disorderly manner, which may have been caused by cracks on the crystal plane. Those disorders led to the disorder of the interlayer arrangement, which resulted in the poor crystallinity of MoS₂, entirely consistent with the XRD results. Typical MoS₂ fringes with layer stacking spacing of 0.63 nm were visible on all the samples, in accordance with the characteristic crystalline MoS₂ basal plane (002).²⁶,²⁷ The dislocations and distortions on the surface between different fringes indicated that the structure of MoS₂ was defective and the existence of defects means the exposure of more active sites of MoS₂.

| Table 1 | HRTEM statistics of MoS₂-CTAB, MoS₂-SDS and MoS₂-SDBS |
|---------|--------------------------------------------------------|
| Catalysts | \( \Delta N \) | \( \Delta L \) | \( D \) | \( f_{0f} \) |
| MoS₂-CTAB | 3.31 | 1.94 | 3.22 | 1.53 |
| MoS₂-SDS | 2.95 | 2.35 | 3.16 | 2.45 |
| MoS₂-SDBS | 3.62 | 1.89 | 3.26 | 1.45 |

| Table 2 | Specific surface area, pore volume and pore diameter of MoS₂-CTAB, MoS₂-SDS and MoS₂-SDBS |
|---------|-------------------------------------------------|
| Samples | MoS₂-CTAB | MoS₂-SDS | MoS₂-SDBS |
| Specific surface area (m² g⁻¹) | 28 | 33 | 59 |
| Pore volume (cm³ g⁻¹) | 0.13 | 0.11 | 0.17 |
| Pore diameter (nm) | 3.82 | 3.82 | 3.82 |
The distribution of the slab length and the layer numbers of the MoS₂-X are presented in Fig. 6. The values of the average slab length, layer number and $f_{c/f_{bmo}}$ are shown in Table 1. By changing the type of surfactant, the synthesized MoS₂ showed differences in slab length and layer number. The number of layers in MoS₂-X was between 1 and 8, and the slab length was mostly within 7 nm. For all the MoS₂ samples, the slab lengths were mostly between 1 and 2 nm and the number of layers was mostly 3. MoS₂-SDS, MoS₂-CTAB, and MoS₂-SDBS accounted for 34.5%, 47.25%, and 38.25% of the total, respectively. With this as the demarcation point, the slab length first increased and then decreased. The percentage of MoS₂ slabs with less than 5 layers exceeded 87.5% and the percentage of MoS₂ slabs shorter than 4.0 nm exceeded 75%. As listed in Table 1, the average slab lengths of MoS₂-SDS, MoS₂-CTAB, and MoS₂-SDBS were 2.35, 1.94, and 1.89 nm, the average numbers of layers were 2.95, 3.31, and 3.62 nm, the dispersions were 3.16, 3.22, and 3.26, and the values of $f_{c/f_{bmo}}$ were 2.45, 1.53, and 1.45, respectively. There were three layers for MoS₂-CTAB, and MoS₂-SDBS, and MoS₂-SDS had greater than three layers. The results, combined with the analysis results from Raman spectroscopy, are in good agreement with the FETEM results, suggesting that the distribution of MoS₂ slabs was finely adjusted by adding different surfactants.

**BET results**

The specific surface area of MoS₂ affects its catalytic performance to some extent. It was found that the specific surface areas of all the MoS₂ synthesized by adding different surfactants were in the order of MoS₂-SDBS > MoS₂-SDS > MoS₂-CTAB. From Table 2, the pore size followed the sequence of MoS₂-CTAB > MoS₂-SDBS > MoS₂-SDS, and pore volume was of the order MoS₂-SDBS > MoS₂-CTAB > MoS₂-SDS. MoS₂-SDBS had the largest specific surface area and pore volume of 59.47 m² g⁻¹ and 11 cm³ g⁻¹, respectively. The N₂ adsorption–desorption and pore size distribution of MoS₂ with different morphologies are illustrated in Fig. 7. The adsorption and desorption isotherms were classified as all delayed rings of type H3, which are associated with slit-shaped pores formed by the accumulation of plate-like particles and the existence of mesoporous structures, but there was no saturated adsorption platform. At 3–5 nm, this is consistent with the results of SEM characterization.

**Raman results**

Raman spectroscopy is an effective method for characterizing the interface quality of 2H-MoS₂. As layered materials with incomplete crystalline structures, the interface quality was affected by strain, defects and dislocation. The Raman spectra of the MoS₂ samples are displayed in Fig. 8. All the MoS₂ samples exhibited typical bands in the E₁²g (378–382 cm⁻¹) and A₁g (404–408 cm⁻¹) ranges; both the A₁g peak and the E₁²g peak had blue-shifts, and the bands were attributed to the interlayer displacement of Mo and S atoms and outside vibrations of the Mo–S bond along the c-axis. Comparing the three morphologies of MoS₂, the interaction intensity between the adjacent layers of MoS₂-CTAB was the weakest. The low-angle displacement of the vibration peak position of E₁²g was caused by interlayer dislocations or intra-layer defects of Mo and S atoms in crystalline MoS₂-CTAB and MoS₂-SDBS, which could lead to greater exposure of edge active sites.²⁸,²⁹ The distance between A₁g and E₁²g ($d = r(A₁g) − r(E₁²g)$) increased with the increasing layer number of MoS₂.²⁸ MoS₂-CTAB displayed two peaks at 376 cm⁻¹ (E₁²g) and 403 cm⁻¹ (A₁g), and $d = 27$ cm. MoS₂-SDS displayed two peaks at 381 cm⁻¹ (E₁²g) and 406 cm⁻¹ (A₁g) ($d = 25$ cm). MoS₂-SDBS displayed two peaks at 378.5 cm⁻¹ (E₁²g) and 403 cm⁻¹ (A₁g) ($d = 24.5$ cm). Raman spectroscopy demonstrated that the average

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**Fig. 7** Adsorption–desorption isotherms and pore volume distribution curves of MoS₂-CTAB (a), MoS₂-SDBS (b), MoS₂-SDS (c).

**Fig. 8** Raman spectra of MoS₂-CTAB, MoS₂-SDS, MoS₂-SDBS.
layers of MoS$_2$-SDS and MoS$_2$-SDBS were three layers, in agreement with the HRTEM results.

The formation mechanism of MoS$_2$

According to the above characterization and results, MoO$_4^{2-}$ was acidic (pH < 4) in aqueous solution and existed in the form of MoO$_4^{2-}/$C$_0$ and DDTC/C$_0$; the O$_2$/C$_0$ in MoO$_4^{2-}/$C$_0$ was easily replaced by S$_2$/C$_0$ because of the weak Mo–O bond in MoO$_4^{2-}$. MoO$_4^{2-}$ aggregated to form polymolybdate, and hydroxylamine hydrochloride was used as the reducing agent to reduce Mo(VI) to Mo(IV). During the hydrothermal reaction, DDTC/C$_0$ reacted with polymolybdate to form polytetrathiomolybdate, and the nucleus of MoS$_2$ was finally formed by oxidation and reduction. The addition of surfactants resulted in different morphologies and structures of MoS$_2$, and the surfactants also acted as templates in the hydrothermal processes. The insertion of surfactant into the layered structure of MoS$_2$ led to the formation of nanosheets. These nanosheets aggregated on SDS/SDBS-formed micelles and grew into flower-like morphologies. When CTAB/SDS/SDBS was added to the reaction, the reaction mechanism was as given in Fig. 9(a) and (b). From Fig. 9(a), with CTAB as the cationic surfactant, MoO$_4^{2-}$ was adsorbed on it as a template to produce a smooth spherical morphology. When SDS and SDBS were added to the reaction system as anionic surfactants, the formation mechanism of MoS$_2$ was similar. Specifically, the nanosheets were easier to grow along the (002) plane because this plane is the thermodynamically stable plane of MoS$_2$ nanosheets. Fig. 9(b) shows the mechanism with SDS/SDBS as surfactants. During the reaction, SDS and SDBS were dissolved in water to form micelles; then, MoO$_4^{2-}$ was adsorbed onto the surface of the micelles. A large number of nanosheets were formed at the same time, and then those nanosheets were exfoliated and assembled into spheres under the action of the surfactants. In addition, the head-to-base ratio of SDBS is larger and more easily agglomerated to form micelles, as compared to SDS, which may explain why the morphology of MoS$_2$-SDS is flower-like and MoS$_2$-SDBS is rough-ball-like.

Catalytic activity

The hydrodesulfurization of 4,6-DMDBT can be divided into the hydrodesulfurization path (HYD) and the direct desulfurization path (DDS). HDS products of 4,6-DMDBT mostly contain THDMDBT, MCHT, DMBCH and DMBP. THDMDBT, MCHT and DMBCH are HYD products and DMBP are DDS products. The hydrogenation intermediate THDMDBT in the HYD pathway breaks the C–S bond to form MCHT, which is further hydrogenated to form DMBCH. In the DDS pathway, the C–S

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| Catalysts | Desulfurization (%) | HYD ratio (%) | Path selectivity |
|-----------|---------------------|---------------|-----------------|
| MoS$_2$-CTAB | 58.5 | 37.1 | 1.6 |
| MoS$_2$-SDS | 44.6 | 26.3 | 1.1 |
| MoS$_2$-SDBS | 95.9 | 90.1 | 15.5 |

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Fig. 9 Schematic diagram of formation mechanism of MoS$_2$-CTAB (a), MoS$_2$-SDBS and MoS$_2$-SDS (b).

Fig. 10 Schematic diagram of the hydrodesulfurization path of 4,6-DMDBT.

Fig. 11 XRD patterns of MoS$_2$-SDBS before and after HDS.
The catalystic performances of MoS2-X in the HDS of simulated diesel oil (0.4 wt% S content of 4,6-DMBT/decalin) are set out in Table 3. MoS2-SDBS exhibited the best HDS performance, with highest desulphurization, HYD ratio and selectivity, combined with FETEM analysis, the results showed that MoS2-SDBS had more active catalytic sites, which included edge sites and corner sites and this can be attributed to its shortest average slab length, average layer number and the smallest value of \((f_e/f_c)_{Mo}\). The BET results showed that MoS2-SDBS had the largest specific surface area among the three MoS2. A comprehensive comparison of the results of HRTEM and BET analyses showed that they were accordant. The order of the \(D_N\) and \((f_e/f_c)_{Mo}\) values of MoS2 with three morphologies from large to small is MoS2-SDS > MoS2-CTAB > MoS2-SDBS, while the order of \(D_N\) and dispersion are the opposite, MoS2-SDBS > MoS2-CTAB > MoS2-SDS. Many studies have shown that HDS catalysts with shorter slab length, higher stacking and greater dispersion have better catalytic performance because more active sites are exposed. Therefore, the catalytic activities of the three MoS2 can be inferred as follows: MoS2-SDBS > MoS2-CTAB > MoS2-SDS. The shortest slab length, the smallest value ratio of Mo edge sites to corner sites and the greatest dispersion of MoS2-SDBS determine that it has the most active sites and the larger corner position as compared to the other two catalysts, which ultimately led to the best HDS performance. The desulphurization rate of MoS2-X was arranged in the order of MoS2-SDBS > MoS2-CTAB > MoS2-SDS. According to BET and HRTEM results, the specific surface area and pore volume of MoS2-SDS were larger than those of MoS2-CTAB and MoS2-SDBS. This may be the point of the higher desulphurization rate of MoS2-SDS. From the analysis results, the desulphurization rate of 4,6-DMBT was influenced greatly by the average slab length, followed by the average number of layers and finally the value of \((f_e/f_c)_{Mo}\). In addition, the HYD ratio and selectivity of MoS2-X were in the order of MoS2-SDBS > MoS2-CTAB > MoS2-SDS. The three MoS2 as catalysts preferred to react along the HYD path. The \((f_e/f_c)_{Mo}\) value of MoS2 was negatively correlated with the degree of hydrogenation. It was reported that the corner sites on the MoS2 are favorable for HYD reactions and the edge sites on the MoS2 promote HDS reactions because the corner sites are more favorable for the adsorption and dissociation of molecular hydrogen into ionic hydrogen. The values of \((f_e/f_c)_{Mo}\) were calculated in combination with HRTEM: \(f_e/f_c\) (MoS2-SDBS) > \(f_e/f_c\) (MoS2-CTAB) > \(f_e/f_c\) (MoS2-SDS), which exhibited the same trends as the HYD ratio and selectivity of MoS2-X. These results can be reviewed as the reason the HYD ratio and selectivity of MoS2-CTAB are higher as compared to MoS2-SDS. In conclusion, the desulphurization rate of MoS2-X is positively correlated with the average number of layers and the HYD ratio and selectivity are positively correlated with the average slab length, and the ratio of the Mo edge/corner.

### Reuse rate of MoS2-SDBS

MoS2-SDBS has the best catalytic activity of three catalysts; its morphology, structure and reuse in the HDS process have been studied. Fig. 11 compares the XRD spectra of MoS2-SDBS before and after the HDS reaction. MoS2-SDBS, after HDS reaction, exhibited higher crystallinity than it did before the HDS reaction, which may be due to the high temperature during the reaction. Fig. 12 shows SEM micrographs of MoS2-SDBS after the HDS reaction; the morphology changed from rough, spherical particles before the reaction to granular particles that just stuck together after the reaction. MoS2-SDBS after the HDS reaction was used as a catalyst for HDS to explore the reuse rate; the result showed that the desulphurization of the catalyst was 78.7% as compared with MoS2-SDBS without HDS. The desulphurization rate was reduced by 17.9%, which showed that its reuse rate had decreased.

### Conclusions

Three types of MoS2 were synthesized for use as catalysts by the combination of the precursor method and the hydrothermal method and were used in HDS to assess their catalytic activity. The results are as follows. The smooth-surfaced and ball-like, rough-surfaced and ball-like, and flower-like morphologies of MoS2 were prepared with the assistance of different surfactants (CTAB/SDBS/SDS). The TEM images showed that in general, the average slab length and the ratio of edge/corner of the MoS2 increased remarkably in the following order: MoS2-SDBS > MoS2-CTAB > MoS2-SDS. The average number of layers was in the order MoS2-SDBS > MoS2-SDS > MoS2-CTAB. When MoS2-DMPB was replaced by MoS2-SDS...
was used as the catalyst in hydrodesulfurization, the desulfurization rate of the MoS\textsubscript{2} increased in the order MoS\textsubscript{2}-SDS > MoS\textsubscript{2}-CTAB, which exhibited a positive correlation with the average number of layers and dispersion of MoS\textsubscript{2}. The HYD ratio and selectivity of the MoS\textsubscript{2} increased in the order MoS\textsubscript{2}-SDS > MoS\textsubscript{2}-CTAB > MoS\textsubscript{2}-SDS, which exhibited a negative correlation with the average slab length and the ratio of Mo edge/corner sites of MoS\textsubscript{2}. The results showed that MoS\textsubscript{2}-SDS exhibited the highest HDS performance among the three catalysts because it had the shortest average slab length, highest Mo ratio of edge to corner, and highest dispersion and specific surface area. The HDS performance of the reused MoS\textsubscript{2}-SDS was lower than that of the original MoS\textsubscript{2}-SDS.

**Conflicts of interest**

There are no conflicts to declare.

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