Dendritic Micro-Mesoporous Composites with Center-Radial Pore Assembled by TS-1 Nanocrystal for Enhancing Hydrodesulfurization Activities of Dibenzothiophene and 4,6-Dimethyldibenzothiophene

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ABSTRACT

A novel dendritic composite (TD) with an open center-radial pore structure using TS-1 nanocrystals as microporous precursors were synthesized successfully by a facile method. TS-1 nanocrystals were embedded into the framework of dendritic mesoporous silica nanospheres (DMSNs) to form Si-O-Ti bonds, which was beneficial to generate more S vacancies of MoS$_2$ active phases. NiMo/TD-2 catalyst had a larger surface area and higher metal-support-interaction (MSI), resulting in a higher sulfidation and dispersion degrees of MoS$_2$ active phases over the sulfided NiMo/TD-2 catalyst, which was consequently favored to improve the HDS activity of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT). Furthermore, the NiMo/TD-2 catalyst with SiO$_2$/TiO$_2$ molar ratio of 150 exhibited higher hydrodesulfurization (HDS) performances of DBT and 4,6-DMDBT than other NiMo/TD catalysts and the commercial NiMo/Al$_2$O$_3$ catalyst. Moreover, the NiMo/TD-2 catalyst possessed higher Brønsted (B) and lewis (L) acid sites, thus promoted the hydrogenation (HYD) of DBT and the isomerization (ISO) of 4,6-DMDBT.

KEYWORDS

Dendritic composite; TS-1 nanocrystal; Dibenzothiophene; 4,6-dimethyl dibenzothiophene; Hydrodesulfurization

1. INTRODUCTION

As environmental laws and regulations for transportation fuels becomes stricter, the production of ultralow-sulfur fuels has received increasing attention to improve the fuel quality and to reduce the exhaust emission [1-5]. To achieve these goals, the refractory sulfur compounds, such as DBT and 4,6-DMDBT must be removed from
the transportation fuels [6-10], in which 4,6-DMDBT is one of the most challenging species to be removed from the raw oils due to its high steric resistance [11-14]. However, the hydrogenation of the phenyl ring could alleviate the steric hindrance of methyl substitutes at the 4 and 6 positions near to sulfur atom through the conformational change of the planar phenyl ring [15-17]. While the most commonly used catalysts for HDS at present in industry are based on alumina supported NiMo or CoMo materials [18-20], they fail to meet the latest fuel standards because of their low hydrogenation performance and high metal-support interaction (MSI) [21, 22].

It has been demonstrated that the HDS performance of the catalysts can be improved by designing novel carriers with high hydrogenation capacity and suitable MSI [23-27]. Recently, a new class of mesoporous materials, dendritic mesoporous silica nanoparticles (DMSNs), were synthesized, which showed a high potential on the applications in gene/protein/drug delivery or storage, medical, disease diagnosis and heterogeneous catalysis because of their center-radial pore structures, short diffusion paths, open three-dimensional dendritic pores and highly accessible surfaces [28-32]. The pore diameters of DMSNs increase gradually from inside to outside so that the active metals do not block the pore entrances, making the active sites of the catalyst more accessible [33]. It is also well known that HDS activity is highly influenced by the acidity of the catalyst that can enhance the hydrogenation or isomerization of the reactants [34]. Thus, pure silica materials have intrinsic limitations in the HDS reaction due to their low acidity, low MSI and poor hydrothermal stability [35], but zeolites, such as Beta, ZSM-5, TS-1 and Y-zeolites, are candidates for the hydrofining reactions as they have high acidities and high hydrothermal stabilities [36-38]. Among these zeolites, TS-1 exhibits some superior characteristics, including small crystal sizes of approximately 100 nm, which can be assembled easily into corresponding micro-mesoporous composites [39]. It is also conceivable that such TS-1 zeolites from the ammonium type template (tetrapropylammonium hydroxide, TPAOH) does not require the ammonium exchange step for the preparation of HDS catalysts, potentially leading to a shorter synthesis time and a lower synthetic cost. Ramirez et al. found that titanium (IV)
species in the NiMo/TS-1 HDS catalysts can be converted into trivalent titanium (III) ions during the reaction, and the d-electron can be embedded into the Mo species, reducing the Mo-S interaction and creating more S vacancies of MoS$_2$ phases [40]. However, the small pore sizes of the TS-1 zeolite limit the diffusion of the reactants and products in the pores, impeding the application in the HDS reaction.

Some of the issues of small pore channels of zeolites, weak acidity, and poor thermal stability of pure mesoporous silica, were addressed by a micro-mesoporous composite strategy. Indeed, it was found that NiMo/Beta-KIT-6 catalysts displayed a higher conversion in the HDS of DBT than those of the pure Beta zeolite and KIT-6 supported NiMo catalysts [35]. NiMo/ZSM-5-SBA-16 catalysts with uniform morphology also exhibited superior ISO performance and HDS activity for the HDS of 4,6-DMDBT [41]. However, these catalysts require complicated fabrication processes which greatly limit their practical application.

Herein, we report a facile method for the preparation of dendritic micro-mesoporous TS-1/DMSNs composites (TD) with center-radial pore assembled by TS-1 nanocrystals without the requirement of the ammonium ion exchange. The corresponding NiMo/TD series catalysts with different SiO$_2$/TiO$_2$ molar ratios were synthesized and applied in the HDS of DBT and 4,6-DMDBT. The new NiMo/TD catalysts not only greatly saved the time and cost during the synthesis, but also showed a higher conversion than those of commercial NiMo/Al$_2$O$_3$ catalysts and other micro-mesoporous material supported NiMo catalysts in literature [25, 41].

2. EXPERIMENTAL

2.1 Synthesis of TD supports and the corresponding NiMo catalysts

The synthesis scheme and protocol of TD series composites are described in Supporting Information. TD series composites with different SiO$_2$/TiO$_2$ molar ratios (100/150/200/400/800) were noted as TD-1, TD-2, TD-3, TD-4 and TD-5 respectively. The preparation method of the NiMo catalysts are described in Supporting Information. The corresponding NiMo catalysts were denoted as NiMo/TD-1, NiMo/TD-2, NiMo/TD-3, NiMo/TD-4, NiMo/TD-5, NiMo/DNSNs and NiMo/Al$_2$O$_3$. 
2.2 Characterization of the supports and catalysts

The characterization of X-ray diffraction (XRD), Nitrogen adsorption/desorption, $^{29}\text{Si}$ MAS NMR, Scanning electron microscopy (SEM), Fourier transform infrared (FTIR), Pyridine adsorption FTIR (Py-FTIR), Raman spectra, X-ray photoelectron spectroscopy (XPS), and Transmission electron microscope (TEM) were introduced in Supporting Information.

High-resolution transmission electron microscope (HRTEM) images were taken on a FEI F20 apparatus. Average stacking number ($N_{av}$) and average staking length ($L_{av}$) were calculated from more than 300 MoS$_2$ stacks using the following formulae [42]:

$$L_{av} = \frac{\left(\sum_{i=1}^{n} n_i l_i\right)}{\sum_{i=1}^{n} n_i}$$

(1)

$$N_{av} = \frac{\left(\sum_{i=1}^{n} n_i N_i\right)}{\sum_{i=1}^{n} n_i}$$

(2)

where $l_i$ is the stacking length and $N_i$ is the stacking number of MoS$_2$.

Dispersion degree ($f_{Mo}$) of MoS$_2$ stacking was calculated using the following formula [43]:

$$f_{Mo} = \frac{M_{edge}}{M_{total}} = \frac{\sum l_i\left(6n_i-6\right)}{3n_i^2-3n_i+1}$$

(3)

where $n_i$ is the quantity of Mo atom along one side of the MoS$_2$ slab, which can be calculated from the formula ($l_i=3.2(2n_i-1)$).

2.3 Catalytic performance evaluation

The HDS performance of the as-prepared catalysts was carried out in a continuous fixed bed reaction tube using DBT or 4,6-DMDBT (500 ppm S dissolved in cyclohexane) as the feedstock. A series of catalysts were presulfided at 8.0 h$^{-1}$, 340 °C, 4.0 MPa, and 600 mL mL$^{-1}$ for 4 h before activity evaluation by using the solution of 2.5 wt.% CS$_2$ in cyclohexane to be the presulfiding agent. Subsequently, the HDS reaction was performed at 340 °C, 4.0 MPa, and 200 mL mL$^{-1}$ with modulating the weight hour space velocity (WHSVs) in the range of 10-100 h$^{-1}$. Conversions of DBT and 4,6-DMDBT HDS reactions were calculated using the following formula [44]:

$$HDS\text{ }(\%) = \frac{S_f - S_p}{S_f} \times 100\%$$

(4)
Where $S_f$ is the sulfur content of feed, and $S_p$ is the sulfur content of product, which can be detected in a RPP-2000SN sulfur analyzer.

Assuming that DBT and 4,6-DMDBT HDS reactions follow the pseudo-first-order reaction kinetics, the rate constants could be deduced through following formula [45]:

$$k_{HDS} = \frac{F}{m} \ln \left( \frac{1}{1 - \tau} \right)$$

(5)

Turn-over frequency ($TOF$, h$^{-1}$) of DBT or 4,6-DMDBT HDS reactions was calculated using following formula [46]:

$$TOF = \frac{(F \times \tau)/(n_{Mo} \times f_{Mo})}{m}$$

(6)

Where $k_{HDS}$ is DBT or 4,6-DMDBT HDS reaction rate constant (mol·g$^{-1}$·h$^{-1}$), $F$ is molar flow rate of reactants (mol·h$^{-1}$), $m$ is the mass of the catalysts (g), $\tau$ is conversion, and $n_{Mo}$ is Mo amount of the loaded catalyst (mol).

3. RESULTS

3.1 Characterization of series TD composites

3.1.1 XRD

The wide-angle XRD spectra of the series TD composites and the pure TS-1 are exhibited in Figure 1. As can be seen from the figure, all the TD composites and the pure TS-1 show the MFI-type characteristic peaks attributed to (011), (020), (051), (303), (313), and (532) planes of TS-1 zeolite at $2\theta = 7.8-8.7^\circ$ and 22-25$^\circ$ [47]. The peak intensities of the series materials decrease in the trend of TS-1 > TD-1 > TD-2 > TD-3 > TD-4 > TD-5, manifesting that the amounts of TS-1 nanocrystal in the series composites decrease in the same order.

3.1.2 TEM and HAADF-STEM-EDS of the Supports

The TEM images are taken to observe the pore structures of the series TD composites and the pure DMSNs, then the relevant images are displayed in Figure 2. TD series composites and the pure DMSNs show dendritic structures with center-radial pore channels. Moreover, TD series composites present uniform particle
sizes at about 200 nm, which also exhibit an increasing tendency with more TS-1 nanocrystals introduced into the composites as compared with the pure DMSNs (about 150 nm).

HAADF-STEM and EDS mapping images are taken to investigate the Ti element distributions in the TD-2 composite, and the corresponding images are presented in Figure 3. As can be seen in the mapping images, the Ti species are evenly distributed in the framework of TD-2 composite, indicating that TS-1 nanocrystals are incorporated into the framework of DMSNs successfully. Titanium species in NiMo/TD series catalysts can create more S vacancies of MoS$_2$ active phases, which is beneficial to enhance the DBT and 4,6-DMDBT HDS performance.

3.1.3 $^{29}$Si NMR

To further prove that TS-1 nanocrystals have been embedded into the DMSNs framework, $^{29}$Si NMR of TD-2, TD-3, and the pure DMSNs are performed, and the corresponding spectra are displayed in Figure 4. The characteristic peak appearing at -112 nm (Q4) is ascribed to Si(-O-)$_4$ species with no silanol group (SiOH) [48]. The characteristic peak that appears at -102 nm (Q3) is attributed to Si(OH)(-O-)$_3$ species with one silanol group. The characteristic peaks of TD-2 and TD-3 composites attributed to Si(OH)(-O-)$_3$ species at -102 nm are weaker than that of the pure DMSNs, which is due to the substitution of hydrogen in the Si(OH)(-O-)$_3$ of pure DMSNs by Ti element of TS-1, manifesting that DMSNs and TS-1 nanocrystal are composited together by Si-O-Ti bonds in the TD-2 and TD-3 composites. Furthermore, the intensity of the characteristic peaks attributed to Si(-O-)$_4$ species in the TD-2 and TD-3 composites is relatively higher than the pure DMSNs, suggesting that more Si-O-Ti bonds are formed after the substitution of the hydrogen of silanol in the DMSNs by Ti elements of TS-1.

3.1.4 FTIR

In order to further confirm whether DMSNs and TS-1 in the series TD composites are composited by Si-O-Ti bond, FTIR spectra of the series TD composites and the pure TS-1 nanocrystal were performed as shown in Figure 5. The
characteristic peaks at 808 and 1068 cm$^{-1}$ are attributed to symmetric and asymmetric stretching vibrations of Si-O-Si bond, respectively [49]. The peak intensity of Si-O-Si bond of TD series composites and the pure TS-1 nanocrystal increases along with the trend of TS-1 < TD-1 < TD-2 < TD-3 < TD-4 < TD-5. The characteristic peak at 1640 cm$^{-1}$ is attributed to the surface silanol groups. The peak intensity of surface silanol groups of TD series composites and the pure TS-1 nanocrystal also increases in the same trend as Si-O-Si bond. The characteristic peaks at 948 cm$^{-1}$ are attributed to Si-O-Ti bond [50]. The peak intensity of Si-O-Ti bond in TD series composite is stronger than that of the pure TS-1 nanocrystal after the introduction of mesoporous DMSNs, manifesting that DMSNs and TS-1 nanocrystal is composited with Si-O-Ti bonds.

3.1.5 SEM

SEM images were taken to investigate the morphologies of series TD composites and the pure TS-1 nanocrystal, and the corresponding pictures are displayed in Figure 6. The series TD composites present characteristic spherical particles with uniform dimensions at about 200 nm. However, TD-1 composite with more TS-1 nanocrystal addition showed two independent phases of TS-1 nanocrystal and DMSNs, indicating that some TS-1 nanocrystals were not incorporated into DMSNs. Series TD composites also have the wrinkled surfaces, which can increase the specific surface areas of the TD composites and improve the dispersion degrees of the active phases on the surface of the support. It can also be clearly seen that series TD composites has large pore channels, which can reduce the diffusion resistance of the reactants in the mass transfer process.

3.1.6 N$_2$ physisorption

N$_2$ adsorption-desorption isotherms and pore size distribution patterns of the series TD supports and the pure DMSNs are shown in Figure 7(A) and (B), respectively. Figure 7(A) displays that the isotherms of TD series supports and pure DMSNs display type IV curves with a H2 hysteresis loop, the characteristics of mesoporous textures. Moreover, Figure 7(B) displays series TD composites exhibits two peaks at about 5 nm and 28 nm respectively, while the pure DMSNs only show
one peak at about 24 nm. The extremum probable pore size of series TD composites become even bigger with the introduction of TS-1 nanocrystal.

The relevant properties of TD series composites and the pure DMSNs are listed in Table 1. Compared with other TD composites and the pure DMSNs, TD-2 composite shows the largest specific surface area and pore volume which can promote the dispersion of active metals. The average pore sizes of series TD composites is slightly smaller than the pure DMSNs, while the pore size differences between the series TD composites are not significant.

3.2 Characterization of series NiMo/TD Catalysts.

3.2.1 Py-FTIR spectra

Py-FTIR spectra were performed to investigate the acidity properties of the catalysts, and the relevant spectra of NiMo/TD series catalysts are shown in Figure 8. The Py-FTIR spectra obtained by degassing at 200 °C and 350 °C are attributed to the acid quantities of the total acids, the medium, and strong acids, respectively [51]. The acidic parameters of NiMo/TD series catalysts are summarized in Table 2. As can be seen from Table 2, the quantities of total acid and the medium and strong acid decrease with the following trend of NiMo/TD-1 > NiMo/TD-2 > NiMo/TD-3 > NiMo/TD-4 > NiMo/TD-5, among which NiMo/TD-2 catalyst presents the highest amount of B acid.

3.2.2. Raman spectra

Raman spectra can be used to investigate the existing mode of active metals on the surface of the oxide and sulfided catalysts, and the relevant spectra of NiMo/TD series catalysts are shown in Figure 9. As shown in Figure 9, the characteristic peaks at 826 and 955 cm\(^{-1}\) are ascribed to the vibration of NiMoO\(_4\) species [52]. The wide characteristic peaks at 890-1000 cm\(^{-1}\) are attributed to the stretching vibrations of Mo=O bonds, which are generally the products of the weak MSI and easier to be sulfided for forming more active phases [53]. The peak intensities at 890-1000 cm\(^{-1}\) increase in the trend of NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-1 < NiMo/TD-3 < NiMo/TD-2, manifesting that NiMo/TD-2 catalyst has more active species that are easy to be sulfided, consequently beneficial to the improvement of HDS activity.
3.2.3. XPS spectra

XPS was used to determine the sulfidation degree of the active metals on the series sulfided NiMo/TD catalyst. The XPS fitting standards of the series sulfided NiMo/TD catalyst was described in our previous work [42], and the corresponding spectra was shown in Figure 10. The Mo3d statistical results of the series sulfided NiMo/TD catalysts are summarized in Table 3. The sulfidation degrees of the series sulfided NiMo/TD catalysts increase in NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-1 < NiMo/TD-3 < NiMo/TD-2. NiMo/TD-2 catalyst shows the highest sulfidation degree, which can provide more active sites for HDS reaction. Moreover, these results are consistent with the previous Raman results.

3.2.4. HRTEM images

The stacking layers and stacking lengths of MoS$_2$ species of the series NiMo/TD catalysts could be visually observed from HRTEM images. The representative images with stacking layer distributions and stacking length distribution of each catalyst are displayed in Figure 11. The stacking states of MoS$_2$ species on the series NiMo/TD catalysts show the tendency of higher stack number and longer stack length with the increasing contents of TS-1 nanocrystals. The statistical results of MoS$_2$ species of the series NiMo/TD catalysts are listed in Table 4. As shown from the data in Table 4, $L_{av}$ and $N_{av}$ of MoS$_2$ stacking increase with the trend of NiMo/TD-1 < NiMo/TD-2 < NiMo/TD-3 < NiMo/TD-4 < NiMo/TD-5, while $f_{Mo}$ values increase in the opposite order. NiMo/TD-2 catalyst has a relatively high dispersion degree and a comparatively low stacking number and stacking length of MoS$_2$ species, which are conducive to exposing more active sites and finally improving the desulfurization activity.

3.3 HDS of DBT

The DBT HDS evaluation results of the series NiMo/TD catalysts and the commercial NiMo/Al$_2$O$_3$ are shown in Figure 12. It can be seen from Figure 12 that the conversion of NiMo/TD series catalysts increase with the decrease of WHSV values. DBT HDS activities of the series NiMo/TD catalysts increase with the trend of
NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-1 < NiMo/TD-3 < NiMo/TD-2. The NiMo/TD-2 catalyst shows the highest DBT HDS activity compared to other NiMo/TD catalysts. Compared with the commercial NiMo/Al₂O₃ catalyst, the series dendritic NiMo/TD catalysts have more obvious advantages in DBT HDS reaction especially at higher WHSV, which are derived from the lower diffusion resistance of the reactant and product molecules inside the open dendritic pore structures in the mass transfer process.

GC-MS was performed to testify the product distributions of DBT HDS reaction over the series NiMo/TD catalysts. The statistical results of DBT HDS product distribution over NiMo/TD catalysts are shown in Table 5. The DBT HDS reaction mechanism over the series NiMo/TD catalysts could be inferred from the main products, and the possible mechanisms were presented in Figures S2 (in Supporting Information). DBT proceeds chemical reactions along with two main paths, one is direct desulfurization (DDS), in which the sulfur atom is removed directly from the reactant molecule; and another is hydrogenation route (HYD), in which the benzene ring was hydrogenated first and then removes the sulfur atom. As shown in Table 5, the HYD/DDS ratios increase in the trend of NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-3 < NiMo/TD-2 < NiMo/TD-1. The L acids of the series NiMo/TD catalysts favor HYD route of DBT HDS reaction. The relevant $k_{HDS}$ and TOF values were summarized in Table 5. The $k_{HDS}$ and TOF values of DBT HDS of the series NiMo/TD catalysts increase with the trend of NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-1 < NiMo/TD-3 < NiMo/TD-2.
3.4 HDS of 4,6-DMDBT

The 4,6-DMDBT HDS evaluation results of the series NiMo/TD catalysts and the commercial NiMo/Al₂O₃ are shown in Figure 13. It can be seen from Figure 12 that 4,6-DMDBT HDS activities of the series NiMo/TD catalysts increase in the sequence of NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-1 < NiMo/TD-3 < NiMo/TD-2, while NiMo/TD-2 catalyst shows the highest 4,6-DMDBT HDS activity compared with other NiMo/TD catalysts and the commercial NiMo/Al₂O₃.

The statistical results of 4,6-DMDBT HDS product distribution over the series NiMo/TD catalysts are shown in Table 6. The 4,6-DMDBT HDS reaction mechanism over the series NiMo/TD catalysts could be deduced from the main products, and the possible mechanisms are presented in Figures S4 (in Supporting Information). 4,6-DMDBT reacts in three pathways, DDS, HYD, and ISO route, in which 4,6-DMDBT is first isomerized into 3,7-DMDBT, then it further reacts along with HYD and DDS paths.

As shown in Table 6, the selectivities for ISO route increase according to the following sequence of NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-1 < NiMo/TD-3 < NiMo/TD-2. The B acids of NiMo/TD series catalysts favor to the ISO route of 4,6-DMDBT HDS reaction, which can alleviate the steric resistance of 4,6-DMDBT in the reaction process and improve the 4,6-DMDBT HDS activity. The relevant $k_{HDS}$ and TOF values of 4,6-DMDBT HDS are listed in Table 6. The $k_{HDS}$ and TOF values of 4,6DMDBT HDS of the series NiMo/TD catalysts increase in NiMo/TD-5 < NiMo/TD-4 < NiMo/TD-1 < NiMo/TD-3 < NiMo/TD-2.
4. DISCUSSION

Dendritic TD composites with different SiO$_2$/TiO$_2$ ratios were synthesized by the two-step hydrothermal crystallization method. The TD composite does not require ammonium ion exchange prior to the synthesis of the corresponding NiMo catalyst, which can save a lot of synthesis time and cost. Moreover, the NiMo/TD-2 catalyst shows superior HDS activity of DBT and 4,6-DMDBT, which is due to its large pore volume, large specific surface area, strong acidity, relatively open dendritic pore structure, and good metal dispersion.

DMSNs and TS-1 nanocrystals were composited through Si-O-Ti bonds (Figure 3, 4, and 5), which gives dendritic TD composites the advantage of both the open channel structure of DMSNs and the strong acidity and high hydrothermal stability of TS-1 nanocrystal. The open center-radial dendritic pore structure (Figure 2) of series NiMo/TD catalysts can eliminate the diffusion resistance of the reactants and products in the mass transfer process and increase the accessibility of the reactants to the active metals. The strong acidity (Figure 8) can promote the HYD path of DBT (Table 5) and the ISO path of 4,6-DMDBT (Table 6), which was beneficial to the reduction of the steric hindrance of reactants, thus making the removal of sulfur atoms in reactants easier [54, 55].

The TD composites with a wrinkled surface (Figure 6) have a large specific surface area, which is conducive to promoting the dispersion (Figure 11 and Table 4) of the active metal on the surface. Compared with other TD composites, TD-1 composite with more TS-1 nanocrystal addition showed two independent phases of TS-1 nanocrystal and DMSNs (Figure 6), indicating that some TS-1 nanocrystal was not embedded into DMSN materials, which was not conducive to the improvement of HDS activity of DBT and 4,6-DMDBT.

Titanium species in series NiMo/TD catalysts can be converted into trivalent titanium ions during the HDS process, so that free d-electrons can be embedded into the Mo species, reducing the Mo-S interaction and creating more S vacancies. NiMo/TD-2 catalyst possesses higher Si-O-Ti species (Figures 3, 4, and 5), which can generate more S vacancies and promoting HDS activity of DBT and 4,6-DMDBT.
MSIs of series NiMo/TD catalysts increase with the increase of TS-1 addition amount (Figure 9). Higher MSI can promote the dispersion (Figure 11 and Table 4) of the active metal on the surface of series TD composites, which is conducive to exposing more active sites, thus improving the HDS activity of DBT and 4,6-DMDBT.

The sulfidation degree of series NiMo/TD catalysts can directly affect the HDS activity of DBT and 4,6-DMDBT. NiMo/TD-2 catalyst presented the highest sulfurization degree (Figure 9, 10, and Table 3), which was beneficial to the improvement of HDS activity of DBT and 4,6-DMDBT.

The NiMo/TD-2 catalyst presents higher HDS activity than other NiMo/TD catalysts and commercial NiMo/Al₂O₃ catalyst, which is mainly due to the synergistic effect of open center-radial dendritic pore structure and wrinkle surface of TD-2 composite, higher B acid content and suitable MSI of oxide NiMo/TD-2 catalyst, higher sulfidation degree and relatively high dispersion degree of sulfided NiMo/TD-2 catalyst.

5. CONCLUSION

Series novel TD composites with an open center-radial dendritic pore structure was synthesized by a facile method. DMSNs and TS-1 nanocrystals were composited through Si-O-Ti bonds, which can create more S vacancies. Compared with the zeolites used in previous composites, TS-1 nanocrystal has a smaller particle size to facilitate the assembly of mesoporous materials. Moreover, H-type TS-1 can be directly obtained without the ammonium ion exchange, which can save the time and cost of synthesizing TD composite. The NiMo/TD-2 catalyst with uniform center-radial dendritic pore structure, higher Si-O-Ti species, higher B acid site and higher specific surface area showed the highest HDS activity of DBT and 4,6-DMDBT than other NiMo/TD catalysts and NiMo/Al₂O₃ catalyst.
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![Figure 1. Wide angle XRD spectra of series materials.](image-url)
Figure 2. TEM images of TD series composites and the pure DMSNs.
Figure 3. HAADF-STEM and EDS mapping images of TD-2 composite.
Figure 4. $^{29}$Si NMR spectra of TD-2, TD-3 and the pure DMSNs.
Figure 5. FTIR graphs of the series TD composites and the pure TS-1 nanocrystal.
Figure 6. SEM images of series TD composites and the pure TS-1 nanocrystal.
Figure 7. (A) N$_2$ physisorption isotherms and (B) pore size distribution patterns of series TD composites and the pure DMSNs.
Figure 8. Py-FTIR spectra of the series catalysts after degassing at (A) 200 °C and (B) 350 °C: (a) NiMo/TD-1; (b) NiMo/TD-2; (c) NiMo/TD-3; (d) NiMo/TD-4 and (e) NiMo/TD-5.
Figure 9. Raman spectra of the series oxide catalysts.
Figure 10. Mo3d XPS results of the series catalysts: (a) NiMo/TD-1; (b) NiMo/TD-2; (c) NiMo/TD-3; (d) NiMo/TD-4 and (e) NiMo/TD-5.
Figure 11. HRTEM images of the series sulfided catalysts: (a) NiMo/TD-1; (b) NiMo/TD-2; (c) NiMo/TD-3; (d) NiMo/TD-4; (e) NiMo/TD-5 and (f) stacking length distribution.
Figure 12. HDS reaction evaluation of DBT over series catalysts: (a) NiMo/TD-1; (b) NiMo/TD-2; (c) NiMo/TD-3; (d) NiMo/TD-4; (e) NiMo/TD-5 and (f) NiMo/Al$_2$O$_3$. 
Figure 13. HDS reaction evaluation of 4.6-DMDBT over series catalysts: (a) NiMo/TD-1; (b) NiMo/TD-2; (c) NiMo/TD-3; (d) NiMo/TD-4; (e) NiMo/TD-5 and (f) NiMo/Al₂O₃.

Table 1. Textural properties of the series materials.

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Table 2. Acidic parameters of the series catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Amount of acid sites (μmol g⁻¹)</th>
<th>200 °C</th>
<th>350 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L</td>
<td>B</td>
<td>L+B</td>
</tr>
<tr>
<td>NiMo/TD-1</td>
<td>119</td>
<td>7</td>
<td>126</td>
</tr>
<tr>
<td>NiMo/TD-2</td>
<td>104</td>
<td>10</td>
<td>114</td>
</tr>
<tr>
<td>NiMo/TD-3</td>
<td>97</td>
<td>8</td>
<td>105</td>
</tr>
<tr>
<td>NiMo/TD-4</td>
<td>86</td>
<td>3</td>
<td>89</td>
</tr>
<tr>
<td>NiMo/TD-5</td>
<td>71</td>
<td>2</td>
<td>73</td>
</tr>
</tbody>
</table>
### Table 3. Mo3d XPS statistical results of series NiMo/TD catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mo$^{4+}$</th>
<th></th>
<th>Mo$^{5+}$</th>
<th></th>
<th>Mo$^{6+}$</th>
<th></th>
<th>$S_{Mo}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ar. % a</td>
<td>ar.% (eV)</td>
<td>ar. % (eV)</td>
<td>ar. % (eV)</td>
<td>ar. % (eV)</td>
<td>S$_{Mo}$ b</td>
<td></td>
</tr>
<tr>
<td>NiMo/TD-1</td>
<td>39</td>
<td>26 (229.0)</td>
<td>3</td>
<td>2</td>
<td>18</td>
<td>12</td>
<td>65</td>
</tr>
<tr>
<td>NiMo/TD-2</td>
<td>44</td>
<td>29 (232.1)</td>
<td>1</td>
<td>1</td>
<td>15</td>
<td>10</td>
<td>73</td>
</tr>
<tr>
<td>NiMo/TD-3</td>
<td>42</td>
<td>27 (230.1)</td>
<td>2</td>
<td>1</td>
<td>17</td>
<td>11</td>
<td>69</td>
</tr>
<tr>
<td>NiMo/TD-4</td>
<td>37</td>
<td>25 (232.2)</td>
<td>4</td>
<td>3</td>
<td>19</td>
<td>13</td>
<td>62</td>
</tr>
<tr>
<td>NiMo/TD-5</td>
<td>35</td>
<td>23 (230.1)</td>
<td>5</td>
<td>3</td>
<td>20</td>
<td>14</td>
<td>58</td>
</tr>
</tbody>
</table>

**Note:**

- a ar. % represents the area percentage of the peak.
- $b S_{Mo}= Mo_{sulfidation} = Mo^{4+}/(Mo^{4+}+Mo^{5+}+Mo^{6+})$. 
Table 4. MoS$_2$ stacking statistical results of series NiMo/TD catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$L_{av}$ (nm)</th>
<th>$N_{av}$</th>
<th>$f_{Mo}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/TD-1</td>
<td>3.7</td>
<td>2.6</td>
<td>0.34</td>
</tr>
<tr>
<td>NiMo/TD-2</td>
<td>3.9</td>
<td>2.7</td>
<td>0.33</td>
</tr>
<tr>
<td>NiMo/TD-3</td>
<td>4.3</td>
<td>3.1</td>
<td>0.30</td>
</tr>
<tr>
<td>NiMo/TD-4</td>
<td>4.7</td>
<td>3.6</td>
<td>0.28</td>
</tr>
<tr>
<td>NiMo/TD-5</td>
<td>5.2</td>
<td>4.2</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Table 5. Catalytic performances for DBT HDS over series NiMo/TD catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)(^a)</th>
<th>(k_{HDS}) (10(^{-4})mol g(^{-1}) h(^{-1}))</th>
<th>TOF(^b) (h(^{-1}))</th>
<th>HYD</th>
<th>DDS</th>
<th>HYD/DDS ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>THDBT</td>
<td>CHEB</td>
<td>PHDi</td>
</tr>
<tr>
<td>NiMo/TD-1</td>
<td>49.1</td>
<td>11.6</td>
<td>4.6</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>NiMo/TD-2</td>
<td>48.9</td>
<td>12.7</td>
<td>5.1</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>NiMo/TD-3</td>
<td>49.4</td>
<td>12.1</td>
<td>4.8</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>NiMo/TD-4</td>
<td>50.3</td>
<td>10.5</td>
<td>4.4</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>NiMo/TD-5</td>
<td>49.6</td>
<td>8.1</td>
<td>4.1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^a\) Obtained at about 50% of total conversion of DBT HDS by adjusting the WHSVs (340 °C, 4.0 MPa, and 200 mL mL\(^{-1}\)).

\(^b\) Number of reactants that have reacted per hour and per Mo atom.

HYD: THDBT + CHEB + PHDi + CHB + CPMB + CPMCH; DDS: BP.
Table 6. Catalytic performances for HDS of 4,6-DMDBT over different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$k_{HDS}$&lt;sup&gt;b&lt;/sup&gt; (10&lt;sup&gt;-4&lt;/sup&gt; mol·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>TOF&lt;sup&gt;b&lt;/sup&gt; (h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Product selectivity (%)</th>
<th>HYD</th>
<th>DDS</th>
<th>ISO</th>
<th>Total ISO</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/TD-1</td>
<td>50.4</td>
<td>6.9</td>
<td>2.0</td>
<td>4,6-THDMDBT + 4,6-HHDMDBT</td>
<td>6</td>
<td>49</td>
<td>7</td>
<td>32</td>
</tr>
<tr>
<td>NiMo/TD-2</td>
<td>49.8</td>
<td>8.4</td>
<td>2.6</td>
<td>3,3'-DMCHB</td>
<td>5</td>
<td>45</td>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>NiMo/TD-3</td>
<td>49.5</td>
<td>8.0</td>
<td>2.3</td>
<td>3,3'-DMBCH</td>
<td>6</td>
<td>47</td>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>NiMo/TD-4</td>
<td>50.1</td>
<td>7.4</td>
<td>1.8</td>
<td>3,3'-DMBP</td>
<td>7</td>
<td>51</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>NiMo/TD-5</td>
<td>50.5</td>
<td>6.1</td>
<td>1.4</td>
<td>4,4'-DMBP + Iso-MIPT</td>
<td>8</td>
<td>55</td>
<td>8</td>
<td>27</td>
</tr>
</tbody>
</table>

<sup>a</sup> Obtained at about 50% of total conversion of 4,6-DMDBT HDS by adjusting the WHSVs (340 °C, 4.0 MPa, and 200 mL mL<sup>-1</sup>).<sup>b</sup>

<sup>b</sup> Number of reactants that have reacted per hour and per Mo atom.

HYD: 4,6-THDMDBT + 4,6-THDMDBT + 3,3'-DMCHB + 3,3'-DMBCH; DDS: 3,3'-DMBP; Total ISO: 4,4'-DMBP + Iso-MIPT.
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[46] X. Wang, J. Fan, Z. Zhao, Z. Chen, P. Zheng, J. Li, Y. Li, L. Han, A. Duan, C. Xu,


