Structural Screening and Design of Dendritic Micro-Mesoporous Composites for Efficient Hydrodesulfurization of Dibenzothiophene and 4,6-Dimethyldibenzothiophene

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ABSTRACT

Novel dendritic micro-mesoporous TS-1/dendritic mesoporous silica nanoparticles (DMSNs) composites (TD) were assembled by TS-1 nanocrystals with ultrasmall particle size and strong acidity. TS-1 seeds and DMSNs were composited via the Ti-O-Si chemical bond, which stimulate on the generation of Brønsted (B) and Lewis (L) acid. The spillover d-electrons produced by The Ti element of TS-1 seeds produced a spillover of d-electrons, which could interact with the surface of MoS₂ phases, thereby reducing Mo-S interactions and creat sulfur vacancies that are favorable for dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) hydrodesulfurization (HDS) reactions. The increased B&L acid amount of NiMo/TD-2.0 with Cetyltrimethylammonium bromide/Sodium salicylate molar ratio of 2.0 played a important role in facilitating the hydrogenation (HYD) route of DBT HDS and the isomerization (ISO) route of 4,6-DMDBT HDS, which is more favorable to the reduction of steric hindrance of DBT and 4,6-DMDBT reactants in the HDS reaction process. The NiMo/TD-2.0 catalyst exhibited the highest turn-over frequency (TOF) value and HDS reaction rate constant (k_{HDS}) of DBT and 4,6-DMDBT due to its ultrasmall particle size, uniform spherical dendritic morphology, strong B&L acidities and good stacking degree.

KEYWORDS

Dendritic composite; TS-1 seed; Ultrasmall particle size; Dibenzothiophenes; Hydrodesulfurization

1. INTRODUCTION

Strict environmental laws and regulations have been implemented in the world to reduce the emission of toxic gases from transportation fuels.¹⁻⁷ Sulfur-containing species in transportation fuels are intrinsic to produce SO₂ after combustion in the engine.^{8, 9} In order to reduce the environmental impact, HDS of sulfur-containing species in transportation fuels is considered one of the main approaches.^{10, 11} As the

typical stubborn sulfocompounds, DBT and 4,6-DMDBT are usually taken as the feedstock in the study of ultra-deep HDS of transportation fuels.¹²⁻¹⁷ Traditional HDS catalysts of alumina supported tungsten or molybdenum promoted by nickel or cobalt have been identified unable to meet the requirements of the latest ultra-deep HDS due to their high metal-support interaction (MSI) and low hydrogenation activity.¹⁸⁻²²

In order to ultra-deep removal of sulfur in transportation fuels, design of new HDS catalytic materials and catalysts for realizing high efficiency of hydrogenolysis of sulfides is needed.²³⁻²⁷ Mesoporous materials are widely used in the catalysis processes because of their excellent physicochemical properties of surface area and pore structure. In particular, DMSNs have received considerable attraction owing to their open three-dimensional dendritic pores and center-radial pore structures, which can provide highly accessible surfaces and short diffusion paths during the catalytic reaction.²⁸⁻³² However, pure DMSNs are unsuitable for applications in the HDS reactions due to its weak acidity and inferior hydrothermal stability.^{33, 34} These issues could be addressed by introducing microporous zeolites such as ZSM-5, Beta, Y and TS-1 into mesoporous materials due to their good acidities and superior hydrothermal stabilities.³⁵⁻³⁷ While among all the zeolites, TS-1 shows outstanding properties such as small crystal size, low cost, facile method and active Ti atom framework, which can reduce the cost of catalyst and improve the activity of catalyst simultaneously,^{38, 39} the synthesis of dendritic micro-mesoporous TD composites assembled by TS-1 nanocrystals with superior structural properties, such as uniform morphology, large pore diameter and small particle size, still faces a considerable challenge. Moreover, it is very difficult but necessary to regulate both the structural and acidic properties at the same time.

Herein, a series of dendritic TD composites with superior texture properties and acidities were successfully designed and screened. Various characterization methods were carried out on TD composites and the relevant NiMo/TD catalysts were examined to investigate the impact of structural and acidic properties on DBT and 4,6-DMDBT HDS reactions. The novel NiMo/TD catalyst with relatively small particle size (~90 nm), uniform morphology and high acidity showed the highest TOF

value and k_{HDS} for DBT and 4,6-DMDBT. The relationship between the structural and acidic properties and the HDS performance and selectivity was presented.

2. EXPERIMENTAL

2.1 Synthesis of supports

2.1.1 Synthesis of TS-1 nanocrystal

The synthesis procedure of TS-1 nanocrystal with the $\text{SiO}_2/\text{TiO}_2$ molar ratios of 25 is as follows. 40 g of tetraethyl orthosilicate (TEOS), 2.64 g tetrabutyl titanate, and 46.72 g TPAOH (25wt. %) were added to 11.68 g of deionized water. The solution was agitated to dissolve for 1 hour in an ice water bath, then switched to a water bath at 70 °C for 3 hours. 48 g of isopropanol was added to the mix and agitated for 1 hour. The resulting mixture was moved to a 200 ml autoclave at 170 °C for four days. Finally, TS-1 nanocrystal was obtained by centrifugation, washing, and drying.

2.1.2 Synthesis of TD supports.

Firstly, 0.82 g triethanolamine (TEA) was added in 300 ml deionized water and stirred at 80 °C for 30 minutes. Secondly, a certain amount (1.255/2.51/4.56/9.12/13.68 g) of cetyltrimethylammonium bromide (CTAB) and 2.02 g sodium salicylate (NaSal) were added and kept stirring for 1 hour. Thirdly, 48.0 g TEOS (28.4 w % SiO_2) was added dropwise and agitated for 30 minutes, then 1.86 g of the as-synthesized TS-1 nanocrystal was added and kept stirring for 1.5 hours. Fourthly, the resulting mixture was transferred to a 500 ml autoclave at 100 °C for 4 h. Finally, TD series composites ($\text{SiO}_2/\text{TiO}_2$ molar ratios of 200) were prepared by adjusting the CTAB/NaSal molar ratios (0.25/0.5/1.0/2.0/3.0) and noted as TD-x, which x represents the CTAB/NaSal molar ratios. Pure DMSN material was taken as the reference support, which was prepared under the similar conditions to TD material and only without addition of TS-1 nanocrystals in the third step.

2.2 Preparation of the corresponding catalysts.

NiMo catalysts with 15.0 wt% MoO_3 and 3.5 wt% NiO were manufactured through stepwise incipient wetness impregnation of the series supports (TD-x, pure DMSNs and commercial Al_2O_3) using ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$)

and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). The as-prepared catalysts were labeled as NiMo/TD-0.25, NiMo/TD-0.5, NiMo/TD-1.0, NiMo/TD-2.0, NiMo/TD-3.0, NiMo/DNSNs and NiMo/ Al_2O_3 .

2.3 Characterization and catalytic evaluation

The analytical methods of XRD, ^{29}Si MAS NMR, SEM, H_2 -TPR, Py-FTIR, XPS, HRTEM and the catalytic performance evaluation methods were introduced in the supporting information. And the calculation methods of average stacking number (N_{av}), average staking length (L_{av}), dispersion degree (f_{Mo}) of MoS_2 stacking, k_{HDS} and TOF of HDS reaction were described in the previous papers.⁴⁰⁻⁴⁴

3. RESULTS

3.1 Characterization of supports

3.1.1 XRD

Figure 1. Wide angle XRD spectra of the various supports.

Figure 1 shows the XRD patterns of various TD materials and TS-1 zeolite. All the TD composites display five characteristic peaks from 7.8 – 8.7° to 22 – 25° , which are indicative of (011), (020), (051), (303), (313), and (532) reflections of TS-1 zeolite.⁴⁵ Compared with the pure TS-1 zeolite, the peak intensities decrease with the addition of TS-1 seed, manifesting that some of the TS-1 seeds are embedded into the skeleton

of DMSNs.

3.1.2 SEM

The SEM pictures of the various materials are presented in Figure 2. All the series TD composites show uniform wrinkled surfaces. The changes in particle sizes of TD composites can also be observed from these images. The particle sizes decrease from 350 nm to 75 nm with the increase of CTAB/NaSal molar ratios. Compared to DMSNs, TD-2.0 and TD-3.0 possess smaller particle size. Moreover, we can also find that the partial wrinkled surfaces of wrinkled TD-0.25 particles are covered, which is not conducive to the diffusion of reactants and product molecules in the pore channel. The increase in CTAB/NaSal molar ratios creates more micelles; thus more nuclei are generated, which cause in the formations of the dendritic TD composites with smaller sizes.³¹

Figure 2. SEM images of the various materials.

3.1.3 TEM and HAADF-STEM-EDS

Figure 3. TEM images of various materials.

The TEM images of various TD materials with diverse particle sizes and TS-1 zeolite are exhibited in Figure 3. TS-1 zeolite has irregular square structure. All the series TD composites show uniform dendritic spherical particles and open center-radial pore structures. After adjusting the CTAB/NaSal molar ratios, the particle sizes of dendritic TD supports directly decrease from 350 nm of TD-0.25 to 90 nm of TD-2.0 and continuing to shrink down to 75 nm of TD-3.0. When the CTAB/NaSal molar ratio is small, the partial surfaces of dendritic TD-0.25 particles are covered, which may lead to the blockage of the pore channels.

Figure 4. HAADF-STEM and EDS pictures (Ti, Si, O) of TD-2.0 support.

In order to study the distributions of Ti species in TD-2.0 support, HAADF-STEM and EDS mappings were carried out and the relevant images are presented in Figure 4. It can be found that the Ti elements are uniformly dispersed in the dendritic pore channels, manifesting that TS-1 seeds are successfully embedded into the DMSNs framework. More Ti elements in the framework of the series TD supports can produce more sulfur vacancies and provide electrons for the active metal, which are conducive to the improvement of the catalytic HDS activity.³⁸

3.1.4 FTIR

The FTIR spectra of series supports are presented in Figure 5. Two characteristic peaks at the positions of 808 and 1068 cm^{-1} can be ascribed to the stretching vibrations of Si-O-Si bond, correspondingly.⁴⁶ The characteristic peaks at 1640 cm^{-1} are ascribed to silanol (Si-OH). The characteristic peaks at 948 cm^{-1} are assigned to

the Si-O-Ti bond.⁴⁷ TD-2.0 possesses less silanol groups, fewer Si-O-Si and more Si-O-Ti bonds than other TD supports and TS-1 seed, suggesting that more TS-1 seed are embedded into the DMSNs framework via Si-O-Ti bonds.

Figure 5. FTIR patterns of various supports.

3.1.5 ²⁹Si NMR

The ²⁹Si NMR patterns of series materials with various particle sizes are exhibited in Figure 6. The first peak at the position of -102 ppm (Q3) is ascribed to Si(OH)(-O-)₃ substance. The second peak at -112 ppm (Q4) is attributed to Si(-O-)₄ substance.⁴⁸ The peak intensity of the series TD supports at the position of -102 ppm (Q3) is lower than that of DMSNs material. Combined with the results from FTIR, the H element of the Si(OH)(-O-)₃ of DMSNs may be replaced by Ti element of TS-1 during the introduction of TS-1 seed. Moreover, TD-2.0 support possesses more Si(-O-)₄ and less Si(OH)(-O-)₃ groups than those of TD-0.25, TD-3.0 and DMSNs, indicating more Si-O-Ti species are generated in the TD-2.0 framework.

Figure 6. ^{29}Si NMR patterns of various materials.

3.1.6 N_2 physisorption

Figure 7. (A) N_2 adsorption-desorption isotherms and (B) pore size distributions of TD materials and DMSNs.

Figure 7(A) and 7(B) display the N_2 adsorption-desorption isotherms and pore size distributions of TD materials and DMSNs. N_2 adsorption-desorption isotherms show that TD materials and DMSNs display type-IV curves with H2 hysteresis loops. The hysteresis loops of TD-0.25 and TD-3.0 are very narrow, which means the N_2 adsorption amount is limited because of these two supports' relatively low surface areas. Figure 7(B) shows that the mesoporous structures are maintained after the addition of TS-1 seeds. The pore size distributions of TD-2.0 are more concentrative

than TD-0.25 and TD-3.0 supports.

Table 1. Textural parameter of various materials.

Samples	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	$S_{\text{EXT}}^{\text{a}}$ ($\text{m}^2 \text{ g}^{-1}$)	$S_{\text{MIC}}^{\text{b}}$ ($\text{m}^2 \text{ g}^{-1}$)	V_{mes} ($\text{cm}^3 \text{ g}^{-1}$)	d_{BJH} (nm)
TD-0.25	303	195	108	0.95	17.5
TD-0.5	426	291	135	1.47	17.6
TD-1.0	548	378	170	1.73	16.7
TD-2.0	575	396	179	1.77	16.3
TD-3.0	392	274	118	0.94	11.9
DMSNs	415	415	415	1.67	20.4
TS-1	276	184	92	0.63	-

^a t-Plot extremal surface area.

^b t-Plot microporous surface area.

The texture parameter of various TD materials and DMSNs are displayed in Table 1. As CTAB/NaSal molar ratios increase, the corresponding BET surface areas and pore volumes of various TD materials increase firstly from TD-0.25 (303 $\text{m}^2 \cdot \text{g}^{-1}$, 0.95 $\text{cm}^3 \cdot \text{g}^{-1}$) to TD-2.0 (575 $\text{m}^2 \cdot \text{g}^{-1}$, 1.77 $\text{cm}^3 \cdot \text{g}^{-1}$), then decrease to TD-3.0 (392 $\text{m}^2 \cdot \text{g}^{-1}$, 0.94 $\text{cm}^3 \cdot \text{g}^{-1}$). TD-2.0 presents the highest surface area and pore volume, and relatively concentrative pore size distribution among these TD supports, DMSNs and TS-1 zeolite, which are conducive to promoting the distribution of MoS_2 species to improve the HDS performance.

3.1 Characterization of the series NiMo Catalysts.

3.2.1 H_2 -TPR

Figure 8. H₂-TPR curves of various catalysts.

The MSI for different catalysts can be obtained from H₂-TPR. The corresponding H₂-TPR spectra for various catalysts are displayed in Figure 8. The H₂-TPR patterns of series NiMo/TD catalysts display two peaks. The low reduction temperature peak is corresponding to the reduction of Mo⁶⁺ to Mo⁴⁺. The high reduction temperature peak is assigned to the reduction step of Mo⁴⁺ to Mo⁰.⁴⁹ The reduction temperatures of the two peaks increase following the sequence of NiMo/TD-2.0 < NiMo/TD-1.0 < NiMo/TD-3.0 < NiMo/TD-0.5 < NiMo/TD-0.25. NiMo/TD-2.0 catalyst shows lower H₂ reduction temperature than other NiMo/TD catalyst, suggesting that NiMo/TD-2.0 possesses more active sites that are easy to be reduced and presulfurized.

3.2.2 Py-FTIR

Figure 9. Py-FTIR patterns of various materials at (A) 200 °C and (B) 350 °C.

Table 2. Acidity of the series NiMo catalysts.

Catalysts	Amount of acid sites ($\mu\text{mol g}^{-1}$)							
	200 °C				350 °C			
	L	B	L+B	B/L	L	B	L+B	B/L
NiMo/TD-0.25	58.3	1.1	59.4	0.02	16.5	0	16.5	0
NiMo/TD-0.5	67.4	2.4	69.8	0.04	20.6	1.2	21.8	0.06
NiMo/TD-1.0	91.2	5.1	96.3	0.06	25.4	1.9	27.3	0.07
NiMo/TD-2.0	112.5	6.3	118.8	0.06	33.1	3.1	36.2	0.09
NiMo/TD-3.0	78.6	2.9	81.5	0.04	22.4	1.3	23.7	0.06

Py-FTIR patterns were applied to study NiMo supported catalysts' acidic properties, which are presented in Figure 9. The patterns acquired through degassing at 200 °C and 350 °C are assigned to the total acids, and the medium and strong acids, correspondingly.⁵⁰ The corresponding quantification results are listed in Table 2. The total acid amounts, the medium and strong acid amounts increase following the sequence of NiMo/TD-0.25 < NiMo/TD-0.5 < NiMo/TD-3.0 < NiMo/TD-1.0 < NiMo/TD-2.0. NiMo/TD-2.0 catalyst has the most B & L acid, which facilitating to the HDS reaction along with the HYD path and the ISO path.

3.2.3 Raman

Figure 10. Raman patterns of various catalysts.

Raman spectra of various NiMo supported catalysts are displayed in Figure 10. The characteristic peaks at 826 cm^{-1} are assigned to NiMoO_4 species.⁵¹ The characteristic peaks at 955 cm^{-1} are attributed to $\text{Mo}_8\text{O}_{26}^{4-}$ species,⁵² which are easy to be reduced and presulfurized. The wide peaks in the region of $890\text{--}1000\text{ cm}^{-1}$ are assigned to Mo=O bonds, which are considered as the active species for HDS reaction.⁵³ According to Figure 10, the peak intensities of Mo=O bonds increase following the sequence of $\text{NiMo/TD-3.0} < \text{NiMo/TD-0.25} < \text{NiMo/TD-0.5} < \text{NiMo/TD-1.0} < \text{NiMo/TD-2.0}$. NiMo/TD-2.0 possesses more active sites that are easy to be reduced and presulfurized, which is in accordance with H_2 -TPR result.

3.2.4 XPS

Figure 11. XPS spectra of various catalysts. (a) NiMo/TD-0.25 ; (b) NiMo/TD-0.5 ; (c) NiMo/TD-1.0 ; (d) NiMo/TD-2.0 and (e) NiMo/TD-3.0

XPS spectra for obtaining the sulfurization degree for active metals of the spent NiMo/TD catalysts are presented in Figure 11. The peak-differentiating and imitating method for various sulfide $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$ species are referred to the reported work.⁵⁴ The proportions of different Mo species over various catalysts are listed in Table 3. It presents that the proportion of MoS_2 (Mo^{4+}) increase following the sequence of NiMo/TD-3.0 (49 %) < NiMo/TD-0.25 (60 %) < NiMo/TD-0.5 (62 %) < NiMo/TD-1.0 (66 %) < NiMo/TD-2.0 (68 %). This result manifests that

NiMo/TD-2.0 possess higher proportion of active MoS₂ phases than other NiMo/TD catalysts, which is in accordance with H₂-TPR and Raman result.

Table 3. The proportions of different Mo species of various catalysts.

Catalysts	Mo ⁴⁺		Mo ⁵⁺		Mo ⁶⁺		S _{Mo} ^b
	ar. % ^a	ar. %	ar. %	ar. %	ar. %	ar. %	
	(229.1	(232.2	(230.1	(233.2	(232.5	(235.6	
	eV)	eV)	eV)	eV)	eV)	eV)	
NiMo/TD-0.25	36	24	2	1	22	15	60
NiMo/TD-0.5	37	25	2	1	21	14	62
NiMo/TD-1.0	40	26	1	1	19	13	66
NiMo/TD-2.0	41	27	1	1	18	12	68
NiMo/TD-3.0	29	20	3	2	27	19	49

Note: ^a ar. % represents the area percentage of the peak.

^b S_{Mo} = Mo_{sulfidation} = Mo⁴⁺/(Mo⁴⁺+Mo⁵⁺+Mo⁶⁺).

3.2.5 HRTEM

HRTEM photographs of series NiMo supported catalysts, as shown in Figure 12, present different stacking degree of MoS₂ active phases. The stacking layer distributions and stacking length distribution of MoS₂ for various NiMo supported catalysts are presented in Figure 12. The percentage of MoS₂ species with higher stacking layers and higher stacking lengths display a declining trend with the increase of the CTAB/NaSal molar ratios. When the molar ratios of CTAB/NaSal are higher than 2.0, the percentage of MoS₂ species with higher stacking layers and higher stacking lengths exhibit increasing tendencies. Moreover, the *N_{av}*, *L_{av}* and *f_{Mo}* for MoS₂ phases are tabulated in Table 4. The *f_{Mo}* of active MoS₂ of various sulfide catalysts increase following the sequence of NiMo/TD-3.0 < NiMo/TD-0.25 < NiMo/TD-0.5 < NiMo/TD-1.0 < NiMo/TD-2.0. Above all, NiMo/TD-2.0 catalyst shows the highest dispersion degree, the shortest stacking lengths, and the appropriate stacking layers, which are beneficial for improving the HDS activity.

Figure 12. HRTEM photographs of various sulfide catalysts: (a) NiMo/TD-0.25; (b) NiMo/TD-0.5; (c) NiMo/TD-1.0; (d) NiMo/TD-2.0; (e) NiMo/TD-3.0 and (f) stacking length distribution.

Table 4. *Lav* and *Nav* of MoS₂ species.

Catalyst	<i>Lav</i> (nm)	<i>Nav</i>	<i>f</i> _{Mo}
NiMo/TD-0.25	4.4	3.8	0.26
NiMo/TD-0.5	3.9	3.3	0.32
NiMo/TD-1.0	3.5	2.9	0.35
NiMo/TD-2.0	3.3	2.8	0.37
NiMo/TD-3.0	4.7	4.1	0.24

3.2 HDS of DBT

The DBT HDS conversions of various NiMo supported catalysts are presented in Figure 13. During the WHSVs decrease from 100 to 10 h⁻¹, the conversion rates of DBT over NiMo/TD catalysts increase following the sequence of NiMo/TD-3.0 < NiMo/TD-0.25 < NiMo/TD-0.5 < NiMo/TD-1.0 < NiMo/TD-2.0. And NiMo/TD-2.0 exhibits the highest DBT conversion among these NiMo/TD catalysts, the reference catalysts of NiMo/DMSNs, NiMo/TS-1 and NiMo/Al₂O₃. When the CTAB/NaSal molar ratio continues to increase, the DBT conversion over NiMo/TD-3.0 decreases to some extent, which can be ascribed to its poor structural properties.

Figure 13. DBT HDS conversion over various NiMo catalysts: (a) NiMo/TD-0.25; (b) NiMo/TD-0.5; (c) NiMo/TD-1.0; (d) NiMo/TD-2.0; (e) NiMo/TD-3.0 (f) NiMo/DMSNs; (g) NiMo/TS-1 and (h) NiMo/Al₂O₃.

For exploring the reaction pathway of DBT HDS, the products were analyzed using Gas Chromatography-Mass Spectrometer (GC-MS). The reaction mechanisms (Figures S2, Supporting Information) of DBT HDS can be proposed based on the

product distributions. DBT undergoes direct desulfurization (DDS) pathway to remove the sulfur atom from the reactants directly. Another route proceeds HYD to remove the sulfur after the hydrogenation of the benzene ring. The DBT HDS product distributions of series NiMo catalysts are illustrated in Table 5. The HYD/DDS ratios of DBT over series sulfide catalysts increase following the sequence of NiMo/TD-3.0 < NiMo/TD-0.25 < NiMo/TD-0.5 < NiMo/TD-1.0 < NiMo/TD-2.0. Moreover, the k_{HDS} and TOF values of DBT on various sulfide catalysts also increase in the same sequence as above. NiMo/TD-2.0 presents the highest k_{HDS} , TOF values and HYD/DDS ratio compared with other catalysts.

Table 5. DBT HDS results of various NiMo/TD catalysts.

Catalyst	Conversion (%) ^a	k_{HDS} (10 ⁻⁴ mol g ⁻¹ h ⁻¹)	TOF ^b (h ⁻¹)	Product selectivity (%)							
				HYD						DDS	HYD/DDS ratio
				THDBT	CHEB	PHDi	CHB	CPMB	CPMCH	BP	
NiMo/TD-0.25	50.4	8.3	3.6	1	2	1	25	3	1	67	0.49
NiMo/TD-0.5	50.1	10.6	4.4	2	2	1	28	4	2	61	0.64
NiMo/TD-1.0	49.8	12.5	5.0	3	3	1	32	5	2	54	0.85
NiMo/TD-2.0	49.6	13.1	5.3	3	4	1	34	6	3	49	1.04
NiMo/TD-3.0	50.3	7.6	3.1	1	1	1	22	3	1	71	0.41

^a Acquired the total DBT HDS conversion of 50% through modulating WHSVs (340 °C, 4.0 MPa, and 200 mL mL⁻¹).

^b Number of converted reactants per hour and per Mo atom.

HYD: Tetrahydrodibenzothiophene (THDBT) + Cyclohexenylbenzene (CHEB) + Isophenyl hexadiene (PHDi) + Cyclohexylbenzene (CHB) + Cyclopentylmethylbenzene (CPMB) + Cyclopentylmethylcyclohexane (CPMCH); DDS: Biphenyl (BP).

3.3 HDS of 4,6-DMDBT

The 4,6-DMDBT HDS conversions of various catalysts are presented in Figure 14. During WHSVs decreasing from 100 to 10 h^{-1} , the conversion rates of 4,6-DMDBT on various NiMo catalysts increase following the sequence of $\text{NiMo/TD-3.0} < \text{NiMo/TD-0.25} < \text{NiMo/TD-0.5} < \text{NiMo/TD-1.0} < \text{NiMo/TD-2.0}$. Especially, NiMo/TD-2.0 displays the highest 4,6-DMDBT HDS performance among these NiMo/TD catalysts, the reference NiMo/DMSNs, NiMo/TS-1 and NiMo/ Al_2O_3 catalyst. The 4,6-DMDBT HDS conversion of NiMo/TD-3.0 decreases to some extent with the increase of the molar ratios of CTAB/NaSal.

Figure 14. 4,6-DMDBT HDS conversion of various NiMo catalysts: (a) NiMo/TD-0.25; (b) NiMo/TD-0.5; (c) NiMo/TD-1.0; (d) NiMo/TD-2.0; (e) NiMo/TD-3.0; (f) NiMo/DMSNs; (g) NiMo/TS-1 and (h) NiMo/ Al_2O_3 .

In order to explore the 4,6-DMDBT HDS reaction route of series NiMo catalysts, the products were analyzed by GC-MS. The reaction mechanisms (Figures S3, Supporting Information) of 4,6-DMDBT HDS can be proposed according to the product distribution. 4,6-DMDBT undergoes three reaction pathways to remove the sulfur from the reactants. Firstly, DDS pathway means the sulfur removed from reactants directly. Secondly, HYD removes sulfur after the hydrogenation of benzene ring. Thirdly, ISO pathway proceeds the sulfur removal along with HYD and DDS routes after the alkyl substitutes in 4,6-DMDBT molecule are isomerized to further positions at first, i.e., to produce 3,7-DMDBT and 2,8-DMDBT. The product distribution of 4,6-DMDBT HDS on various NiMo catalysts is illustrated in Table 6.

The 4,6-DMDBT ISO ratios of series NiMo catalysts increase following the sequence of NiMo/TD-3.0 < NiMo/TD-0.25 < NiMo/TD-0.5 < NiMo/TD-1.0 < NiMo/TD-2.0. Moreover, the k_{HDS} and TOF of 4,6-DMDBT on various sulfide catalysts also increase following the sequence of NiMo/TD-3.0 < NiMo/TD-0.25 < NiMo/TD-0.5 < NiMo/TD-1.0 < NiMo/TD-2.0. NiMo/TD-2.0 displays the highest k_{HDS} , TOF values and ISO ratio than other NiMo catalysts and reference NiMo/Al₂O₃ catalysts.

Table 6. 4,6-DMDBT HDS results of various NiMo/TD catalysts.

Catalyst	Conversion (%) ^a	k_{HDS} (10 ⁻⁴ mol·g ⁻¹ ·h ⁻¹)	TOF ^b (h ⁻¹)	Product selectivity (%)						Total ISO
				HYD			DDS	ISO		
				4,6-THDMDBT+ 4,6-HHDMDBT	3,3'-DMCHB	3,3'-DMBCH	3,3'-DMBP	4,4'-DMBP	Iso-MIPT	
NiMo/TD-0.25	49.6	6.9	2.0	7	49	10	9	20	5	25
NiMo/TD-0.5	50.1	8.0	2.3	6	46	9	9	23	7	30
NiMo/TD-1.0	50.4	8.4	2.6	6	44	8	8	26	8	34
NiMo/TD-2.0	49.8	8.6	2.7	5	43	8	7	28	9	37
NiMo/TD-3.0	50.2	6.1	1.4	7	52	11	10	16	4	20

^a Acquired the total 4,6-DMDBT HDS conversion of 50% through modulating WHSVs (340 °C, 4.0 MPa, and 200 mL mL⁻¹).

^b Number of converted reactants per hour and per Mo atom.

HYD: 4,6-tetrahydrodimethyldibenzothiophene (4,6-THDMDBT) + 4,6-hexahydrodimethyldibenzothiophene (4,6-HHDMDBT) + 3,3'-dimethylcyclohexylbenzene (3,3'-DMCHB) + 3,3'-dimethylbicyclohexyl (3,3'-DMBCH); DDS: 3,3'-dimethylbiphenyl (3,3'-DMBP); Total ISO: 4,4'-dimethylbiphenyl (4,4'-DMBP) + Isomethylisopropyltetralin (Iso-MIPT)

4. DISCUSSION

Dendritic TD composites with superior structural and acidic properties were successfully screened and designed. NiMo/TD-2.0 catalyst with ultrasmall particle size, uniform spherical dendritic morphology, suitable MSI, strong B&L acidity and good stacking degree exhibit outstanding DBT and 4,6-DMDBT HDS activities. Combined with the systematical characterizations and activity assessments, the structure-function relationship is addressed as follows:

Firstly, the superior structural properties of dendritic TD supports contribute a lot to the diffusion of refractory DBT and 4,6-DMDBT reactants. The ultrasmall particle size (~90 nm) of NiMo/TD-2.0 catalyst is not only beneficial to the uniform disperse of active metals due to its high surface areas ($575 \text{ m}^2\cdot\text{g}^{-1}$), but also in favor of reducing the diffusion resistance and improving the accessibility of MoS_2 to DBT and 4,6-DMDBT molecules due to its short diffusion paths between the reactants and the active metals.

Secondly, Ti elements of TS-1 seeds can release d-electrons by changing the valence states during the HDS reaction. The spillover d-electron moves to the surface of the MoS_2 phases, thereby reducing Mo-S interactions and creating sulfur vacancies that are more favorable for DBT and 4,6-DMDBT HDS reaction.

Thirdly, the open dendritic pore structures (Figure 3) of the various TD materials can lower the diffusion resistance when the reactants and products diffuse through the pore channel, thus improving the DBT and 4,6-DMDBT performance of NiMo/TD catalysts (Figure 13 and 14). The uniform wrinkled surfaces (Figure 2) of the series TD supports can enhance the specific surface areas of the materials, facilitate the distribution of the metal species of the NiMo/TD catalyst surface and expose more active sites for DBT and 4,6-DMDBT HDS reactions. Moreover, the introduction of TS-1 seeds can boost the hydrothermal stability and mechanical strength of the NiMo/TD catalyst, thus extending the catalyst's shelf life.

Fourthly, TS-1 seeds and DMSNs were composited via Ti-O-Si chemical bond (Figures 4, 5, and 6), which positively affected the generation of B&L acid (Figure 9). The increased B&L acid amount of NiMo/TD-2.0 plays a crucial role in promoting

the HYD route of DBT HDS (Table 5) and the ISO route of 4,6-DMDBT HDS (Table 6), which would be more favorable to the reduction of steric hindrance of DBT and 4,6-DMDBT reactants in the HDS reaction process.

Fifthly, NiMo/TD-2.0 catalyst possesses suitable MSI and more active species that are easy to be reduced and sulfurized (Figures 8 and 10), which is conducive to the production of MoS₂ phases with the highest sulfurization degree (Figure 11), highest dispersion degree, the shortest stacking lengths and the appropriate stacking layers (Figure 12), thus increasing the k_{HDS} and TOF of DBT and 4,6-DMDBT HDS (Tables 5 and 6).

5. CONCLUSION

Novel dendritic NiMo/TD-2.0 catalyst with ultrasmall particle size and more robust B&L acidity are successfully prepared via a facile method. The ultrasmall particle size of NiMo/TD-2.0 catalyst can lower the diffusion resistance and improve the accessibility of MoS₂ to DBT and 4,6-DMDBT reactant molecules. Moreover, the spillover d-electrons from TS-1 are beneficial to produce more sulfur vacancies of MoS₂ species. The promotion of HYD route for DBT HDS and the ISO route for 4,6-DMDBT is favorable to the improvement of HDS activity on the NiMo/TD-2.0 catalyst. NiMo/TD-2.0 showed the highest k_{HDS} and TOF values for DBT and 4,6-DMDBT than those of other NiMo/TD and reference NiMo/Al₂O₃ catalysts.

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Supporting Information

Characterization of the supports and catalysts; catalytic performance evaluation; chemicals needed in the experiments; TOF comparison of previous papers; preparation of TS-1/DMSNs composites with different particle size; HDS results of 4,6-DMDBT; possible reaction network of DBT HDS; possible reaction network of 4,6-DMDBT HDS; isomerization of 4,6-DMDBT to 3,7-DMDBT.

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