

Electronic Supplementary Material

Mass-transfer-enhanced hydrodesulfurization of dibenzothiophenes over yolk-shell micro-mesoporous catalysts

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Experimental Section

According to HRTEM images, average staking length (L_{av}) and stacking number (N_{av}) were calculated by the following formula:

$$L_{av} = \left(\sum_{i=1}^n n_i l_i \right) / \sum_{i=1}^n n_i, \quad (S1)$$

$$N_{av} = \left(\sum_{i=1}^n n_i N_i \right) / \sum_{i=1}^n n_i, \quad (S2)$$

Where l_i and n_i is assigned as the stacking length and stacking number of MoS₂, respectively. And N_i is the number of stacks with l_i length and n_i layers.

The dispersion degree of MoS₂ active phase (f_{Mo}) is defined as the ratio of the total number of Mo atoms (Mo_{total}) and the total number of Mo atoms at the edge (Mo_{edge}),

which can be calculated according to the formula (S3).

$$f_{Mo} = \frac{Mo_{edge}}{Mo_{total}} = \frac{\sum_{i=1}^t (6n_i - 6)}{\sum_{i=1}^t (3n_i^2 - 3n_i + 1)}, \quad (S3)$$

Where n_i refers to the number of Mo atoms at the edge of MoS₂, which can be calculated by the length of each MoS₂ slab ($n_i = L/0.64 + 0.5$), and t indicates the total number of slabs

The HDS activities of NiMo/TY_xS_y catalysts were indicated by the conversions, which could be evaluated by the equation (S4):

$$\text{HDS conversion (\%)} = \frac{S_f - S_p}{S_f} \times 100\%, \quad (S4)$$

where S_f and S_p is the sulfur content (ppm) in the feedstock and product, respectively.

The k_{HDS} and TOF values were further calculated for comparing the catalytic performance according to the following formula:

$$k_{HDS} = \frac{F}{m} \ln \left(\frac{1}{1 - \eta} \right), \quad (S5)$$

$$TOF = \frac{F \times \eta}{Mo_{edge}} = \frac{F \times \eta}{n_{Mo} \times f_{Mo}}, \quad (S6)$$

where F represents the feeding velocity of flow (mol·s⁻¹), m is the catalyst mass (g), η is the conversion of DBT and 4,6-DMDBT, Mo_{edge} is the number of Mo atoms at the edge (mol), n_{Mo} is the total number of Mo atoms in the catalyst (mol), and f_{Mo} is the dispersion degree of MoS₂ stacking.

Table S1 Pore structural parameters of TY_xS_y supports

Samples	S_{BET} (m ² ·g ⁻¹)	V_{total} (cm ³ ·g ⁻¹)	d_{BJH} (nm)
TY ₅₀ S ₂₆	527	0.67	5.6
TY ₃₅ S ₂₀	543	0.77	6.1
TY ₂₁ S ₁₆	598	0.79	6.3
TY ₁₀ S ₁₃	642	0.84	6.8
TY ₃ S ₇	567	0.87	7.5
TY ₀ S ₃	615	0.92	8.0

Table S2 The amounts of acid determined by Py-FTIR of NiMo/TY_xS_y series catalysts

Catalysts	Amount of acid sites (μmol g ⁻¹)							
	200 °C				350 °C			
	B	L	B+L	B/L	B	L	B+L	B/L
NiMo/TY ₅₀ S ₂₆	10.0	8.5	18.3	1.20	0.9	2.9	3.8	0.31
NiMo/TY ₃₅ S ₂₀	10.2	8.4	18.6	1.21	1.0	3.1	4.1	0.32
NiMo/TY ₂₁ S ₁₆	11.8	8.8	20.6	1.34	2.1	4.0	6.1	0.53
NiMo/TY ₁₀ S ₁₃	15.1	7.5	22.6	2.01	3.3	4.5	7.8	0.73
NiMo/TY ₃ S ₇	12.4	6.3	18.7	1.94	2.3	4.7	7.0	0.49
NiMo/TY ₀ S ₃	11.0	5.8	16.8	1.90	1.3	3.9	5.2	0.33

Table S3 XPS statistical results of Mo 3d in NiMo/TY_xS_y catalysts

Catalysts	Mo ⁴⁺		Mo ⁵⁺		Mo ⁶⁺		S _{Mo} ^b
	ar. % ^a	ar.%	ar. %	ar. %	ar.%	ar.%	
	(229.0	(232.1	(230.1	(233.2	(232.5	(235.6	
	eV)	eV)	eV)	eV)	eV)	eV)	
NiMo/TY ₅₀ S ₂₆	27	18	15	10	18	12	45
NiMo/TY ₃₅ S ₂₀	28	18	6	4	26	18	46
NiMo/TY ₂₁ S ₁₆	32	21	12	8	16	11	53
NiMo/TY ₁₀ S ₁₃	41	27	9	6	10	7	68
NiMo/TY ₃ S ₇	36	24	9	5	16	11	60

NiMo/TY ₀ S ₃	29	19	10	7	21	14	48
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Note: ^a ar. % means the area percent of XPS peaks.

$$^b S_{\text{Mo}} = \text{Mosulfidation} = \text{Mo}^{4+}/(\text{Mo}^{4+} + \text{Mo}^{5+} + \text{Mo}^{6+}).$$

Table S4 Catalytic performance and products statistics in DBT HDS

Catalyst	Conversion (%)	k_{HDS} (10^{-7} mol· g $^{-1}$ ·s $^{-1}$)	TOF (10^{-4} s $^{-1}$)	Product selectivity (%)							
				HYD						DDS	HYD/DDS
				THDBT	PHDi	CHB	DCH	CPMB	CPMCH	BP	ratio
NiMo/TY ₅₀ S ₂₆	30.0	1.3	5.3	2.6	-	34.3	1.1	1.6	0.7	59.7	0.68
NiMo/TY ₃₅ S ₂₀	30.1	1.5	5.5	5.7	-	33.1	0.2	0.3	0.3	60.4	0.65
NiMo/TY ₂₁ S ₁₆	29.7	1.9	6.7	6.1	0.2	28.8	0.4	1.9	0.6	62.0	0.61
NiMo/TY ₁₀ S ₁₃	30.1	2.6	7.5	6.2	0.5	26.1	0.4	2.1	0.5	64.2	0.56
NiMo/TY ₃ S ₇	30.1	2.2	7.1	7.2	0.3	27.4	0.4	2.1	0.4	62.2	0.60
NiMo/TY ₀ S ₃	29.9	1.7	5.9	9.7	0.3	25.4	0.4	2.1	0.5	61.6	0.62

Note: Activity evaluation conditions: 340 °C, 4.0 MPa, H₂/Oil=200 mL·mL⁻¹.

k_{HDS} and TOF values were calculated at low conversions (<20%).

Product selectivities were detected at about 30% conversions.

Table S5 Catalytic performance and products statistics in 4,6-DMDBT HDS

Catalyst	Conversion (%)	k_{HDS} (10^{-7} mol· g ⁻¹ ·s ⁻¹)	TOF (10^{-4} s ⁻¹)	Product selectivity (%)							Total
				HYD			DDS	ISO			
				4,6-	3,3'-	3,3'-	3,3'-	4,4'-	4,4'-	Iso-	
				THDMDBT	DMCHB	DMBCH	DMBP	DMBP	DMBCH	MIPT	
NiMo/TY ₅₀ S ₂ 6	29.9	1.1	4.4	55.2	3.7	0.5	35.8	3.2	1.5	0.1	4.8
NiMo/TY ₃₅ S ₂ 0	30.3	1.2	4.6	54.4	4.2	1.6	33.0	3.7	1.9	1.2	6.8
NiMo/TY ₂₁ S ₁ 6	30.1	1.6	5.5	48.7	5.6	1.7	33.1	5.7	3.2	2.0	10.9
NiMo/TY ₁₀ S ₁ 3	30.0	2.1	6.1	50.6	6.2	1.3	22.9	9.8	5.8	3.4	19.0
NiMo/TY ₃ S ₇	29.7	1.8	5.6	47.3	12.0	0.8	26.6	6.4	3.9	3.0	13.3
NiMo/TY ₀ S ₃	30.3	1.4	4.8	45.0	15.4	0.3	29.1	5.4	2.1	2.7	10.2

Note: Activity evaluation conditions: 340 °C, 4.0 MPa, H₂/Oil=200 mL·mL⁻¹.

k_{HDS} and TOF values were calculated at low conversion (<20%).

Product selectivities were detected at about 30% conversions.

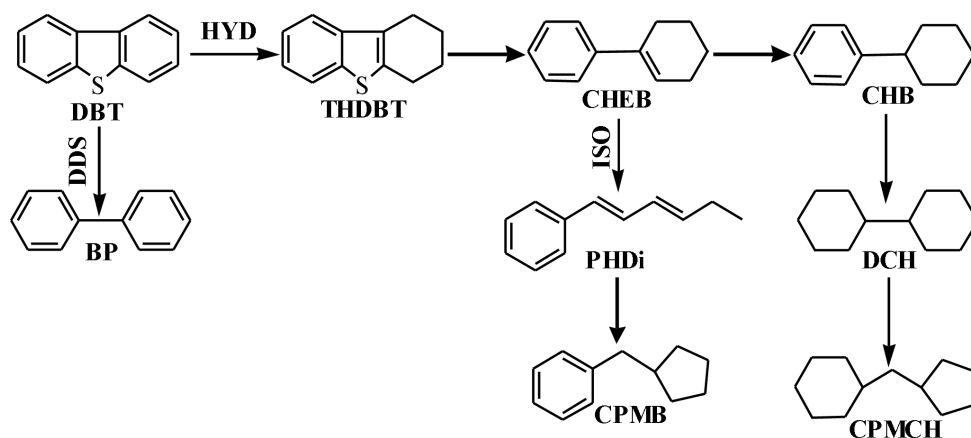


Fig. S1 DBT HDS reaction network over the NiMo/TY_xS_y catalysts

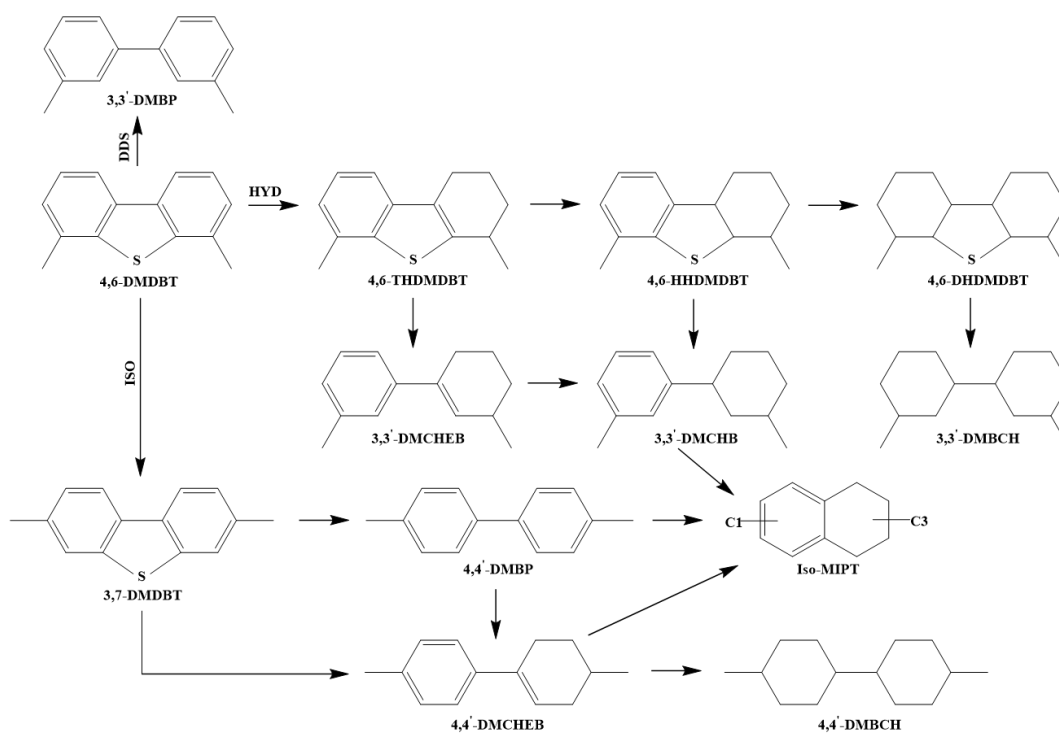


Fig. S2 4,6-DMDBT HDS reaction network over the NiMo/TY_xS_y catalysts

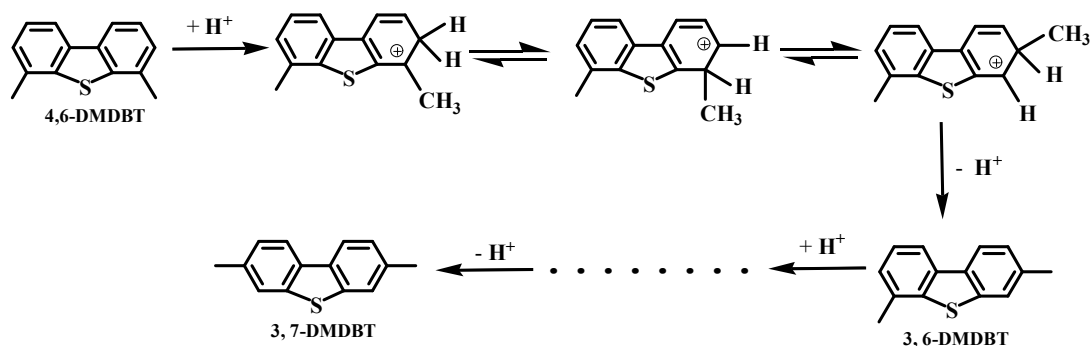


Fig. S3. Isomerization of 4,6-DMDBT to 3,7-DMDBT over series NiMo/TY_xS_y catalysts

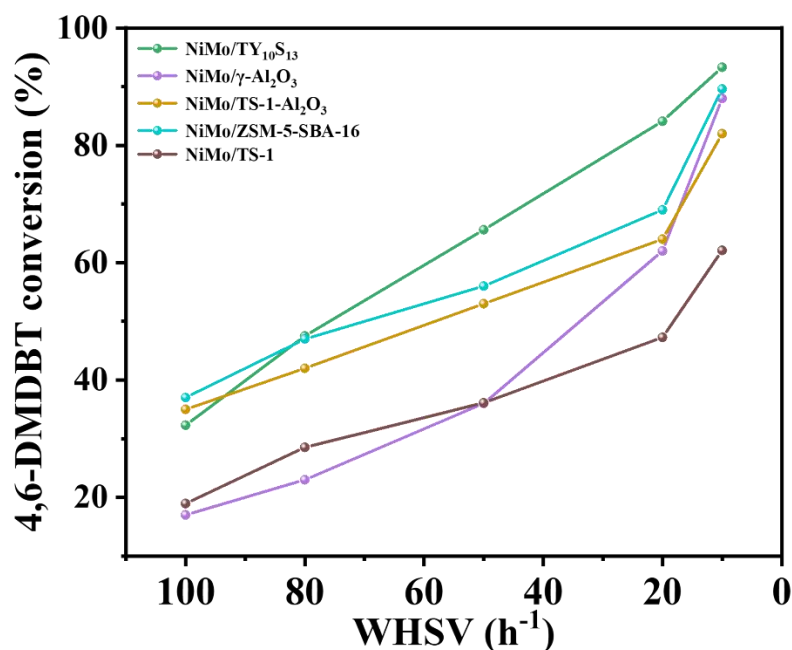


Fig. S4. 4,6-DMDBT HDS performance over different catalysts

In order to visually compare the actual HDS performance of the synthesized catalyst, the 4,6-DMDBT HDS activity of the NiMo/TY₁₀S₁₃ catalyst was compared with those reported in the literature, and the results are presented in Fig. S4. As shown in the figure, the as-prepared NiMo/TY₁₀S₁₃ catalyst exhibits high 4,6-DMDBT HDS activity, achieving a desulfurization degree of 93.3% at WHSV of 10 h⁻¹. Compared with the NiMo/TS-1 catalyst prepared from pure microporous TS-1 (*Carbon Resources Conversion*, 2025, 8(1): 100299), the desulfurization degree increased by approximately 31.2%. At WHSV of 100 h⁻¹, the desulfurization degree increased from 18.9% to 32.3%. Compared with the reported micro-mesoporous composite catalysts, including NiMo/TS-1-Al₂O₃ (*Journal of Catalysis*, 2024, 435: 115576) and NiMo/ZSM-5-SBA-16 (*Energy & Fuels*, 2018, 32(5): 6204-12), the micro-mesoporous composite catalyst prepared from TS-1 and yolk-shell SiO₂ exhibits superior HDS catalytic performance. Furthermore, the catalyst prepared in this work also

demonstrates better catalytic activity than the commercial NiMo/ γ -Al₂O₃ catalyst

(*Journal of Catalysis*, 2017, 356: 269-82).