Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Synthesis of Co-Mo sulfide catalyst with hollow structure for highly efficient hydrodesulfurization of dibenzothiophene

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Experimental Section

Synthesis of Co-Mo precursors. All chemicals purchased from Aladdin Industrial Corporation were directly used without further purification. Typically, 4.0 mmol of $Co(CH_3COO)_2{\cdot}4H_2O$ and 0.57 mmol of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were dissolved into 100 ml of deionized water at room temperature, resulting in a clear red solution. Then 100 ml of ethanol was added into the above solution. Afterward, the resultant solution was heated to 85 °C in a hot bath and maintained for 4 h under refluxing conditions. During this process, a purple precipitate was formed increasingly. After the reaction, the precipitate was collected by filtration, washed with deionized water for several times, and then dried in air at 80 °C overnight.

Synthesis of Co-Mo sulfide nanotubes. Co-Mo sulfide nanotubes can be synthesized through a facile sulfurization process at low temperature. In a typical procedure, 0.4 g of Co-Mo precursors was put into a 100 ml stainless steel autoclave with mechanical stirring, followed by the addition of 40 g of sulfurizing agent (an ethanol solution containing 3.0 wt.% carbon disulfide). Prior to sulfurization, the reactor was purged three times with H_2 to replace the air inside. Then the precursors were sulfurized at 160 °C and 2.0 MPa H_2 (initial pressure at room temperature) for 6 h with a stirring rate of 600 r/min. After that, the sulfides were collected by filtration, washed with ethanol for three times, and then dried in a vacuum at 60 °C for 8 h. The obtained Co-Mo sulfide nanotubes then were calcined at 400 °C for 4 h under N_2 atmosphere at a flow rate of 80 ml/min.

Synthesis of Co-Mo sulfide nanorods. To verify the superiority of nanotubes, the Co-Mo sulfide nanorods without hollow structure, as a reference catalyst, were prepared via a conventional method. Typically, a certain amount of the as-prepared Co-Mo precursors were calcined at 400 °C for 4 h in air to produce Co-Mo composite oxides. Then 0.4 g of the oxides were sulfurized at 350 °C and 3.0 MPa H_2 (initial pressure at room temperature) for 6 h, using 40 g of decalin solution containing 3.0 wt.% carbon disulfide as sulfurizing agent. This process was also carried out in a 100 ml stainless

steel autoclave with a stirring rate of 600 r/min. After the sulfurization, the sulfides were collected by filtration, washed with cyclohexane for three times, and then dried in a vacuum at 60 °C for 8 h.

Materials characterization. The crystalline structure of the samples was examined by X-ray diffraction (XRD) on a Brucker AXS-D8 Advance powder diffractometer with a Cu Kα radiation source (λ = 1.5406 Å) at a voltage of 40 kV and a current of 40 mA. The morphology and inner structure of the samples were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100UHR). The textural property of the samples were obtained from N_2 adsorption/desorption isotherms measured on a Quantachrome AutoSorb-6B analyzer at -196 °C. Prior to measurements, all of the samples were degassed at 140 °C in vacuum for 6 h. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volumes and pore size were determined by the Barrett–Joyner–Halenda (BJH) method from desorption branch of the isotherms. The reducibility of sulfide samples was detected by H_2-TPR measurements with a Micromeritics AutoChem II 2920 instrument. The hydrogen consumption was measured with a thermal conductivity detector during this process. The surface elemental composition of sulfurized samples was analyzed by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi, Thermo spectrometer equipped with a monochromatic X-ray source of Al Kα under ultra-high vacuum (3-2 $\times 10^{-6}$ Pa) and a hemispherical analyzer. The binding energies (BE) were internally calibrated by the reference deposit C1s binding energy (BE), respectively.

Hydrodesulfurization reaction tests. The activity tests were carried out in a 100 ml stainless steel autoclave with mechanical stirring. The decline solution containing 2.0 wt.% DBT was selected as model reactants. In a typical experiment, 40.0 g of reactant was charged into the reactor, together with 0.2 g of the Co-Mo sulfide samples. Prior to the reaction, the reactor was purged three times with H_2 to exchange the air inside. The reaction was carried out at 300 °C and 2.0 MPa H_2 (initial pressure at room

temperature) for 4 h with a stirring rate of 600 r/min. The liquid product was collected by centrifugation and analyzed on an Agilent 7890 GC-MS instrument equipped with a HP-5MS column.

The HDS activity of the catalysts was estimated as follow:

$$x_{\mathrm{DBT}}(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

where x_{DBT} is the conversion of DBT (%), C_0 is the DBT content in the feedstock (wt.%) and C_t is the DBT content in the product (wt.%).

The apparent reaction rate was calculated using the following equation:[1]

$$r = \frac{F}{m} \cdot x_{\mathrm{DBT}}$$

where r is the apparent reaction rate (mol/g_{cat}·s), F is the molar flow rate of the reactant (mol/s), x_{DBT} is the conversion of DBT (%), and m is the catalyst weight (g).

The rate constant of the pseudo-first-order reaction of DBT hydrodesulfurization was determined using the following equation:[1]

$$k = \frac{F}{mC} \cdot \ln \frac{1}{1 - x_{DBT}}$$

where k is the pesudo-first-order rate constant (L/g_{cat}·s), F is the molar flow rate of the reactant (mol/s), m is the catalyst weight (g), C is DBT molar concentration (mol/L), and x_{DBT} is the conversion of DBT (%) determined by kinetics experiments.

The TOF value (s^{-1}) for the HDS of DBT was calculated using the following equation:[2]

$$TOF = \frac{F \cdot x_{DBT} \cdot Mr_{Co}}{m \cdot C_{CoMoS} \cdot 3600}$$

where F is the molar flow rate of the reactant (mol/s), x_{DBT} is the conversion of DBT (%), Mr_{Co} is the molar mass of cobalt (58.9 g/mol), m is the catalyst weight (g), C_{CoMoS} is the effective Co content in the CoMoS phase (wt.%) determined by XPS, which can be calculated as follows:[2]

$$C_{CoMoS} = [CoMoS] \times C(Co)_T$$

where $C(Co)_T$ represents the effective concentration of cobalt determined by XPS (wt.%).

$$[CoMoS](\%) = \frac{A_{CoMoS}}{A_{Co_9S_8} + A_{CoMoS} + A_{Co^{2+}}} \times 100$$

where [*CoMoS*] is the relative amount of CoMoS, A_x represents the peak area of species x.

$$C(j)_T(\%) = \frac{A_j / S_j}{\sum_{i=1\cdots n} A_i / S_i} \times 100$$

where $C(j)_T$ is the absolute content of species *j*, A_i is the measured area of species *i* and S_i is the sensitivity factor of the atom related to species *i* (provided by the manufacturer).

References:

[1] D. Genuit, P. Afanasiev, M. Vrinat, J. Catal. 2005, 235, 302-317.

[2] P.A. Nikulshin, D.I. Ishutenko, A.A. Mozhaev, K.I. Maslakov, A.A. Pimerzin, J. Catal. 2014, 312, 152-169.

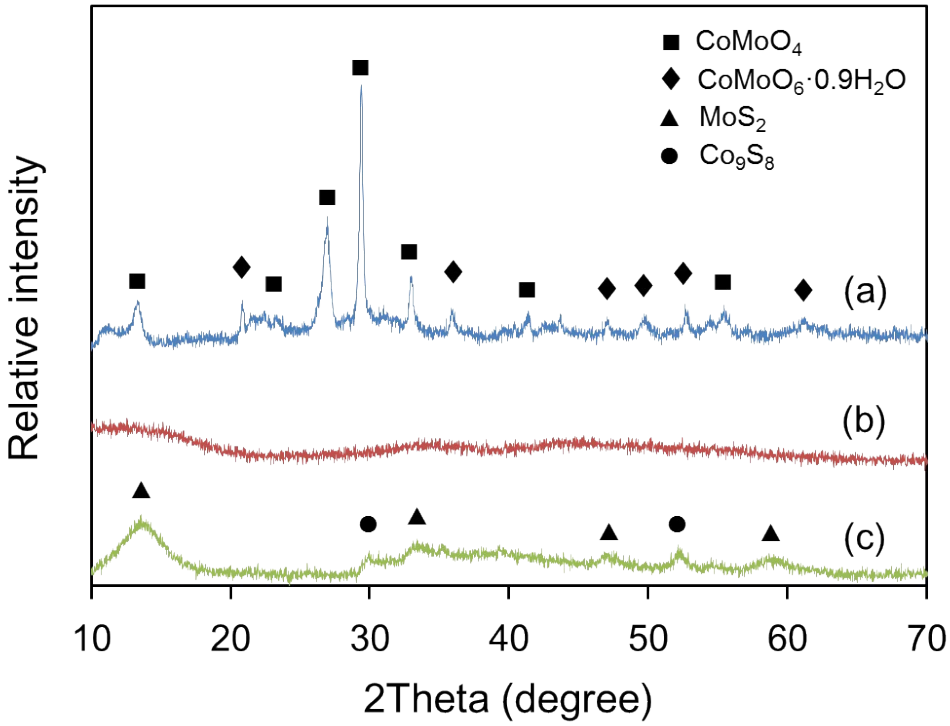


Figure S1. XRD patterns of (a) Co-Mo precursor, (b) fresh Co-Mo sulfide sub-microtubes, and (c) calcined Co-Mo sulfide sub-microtubes.

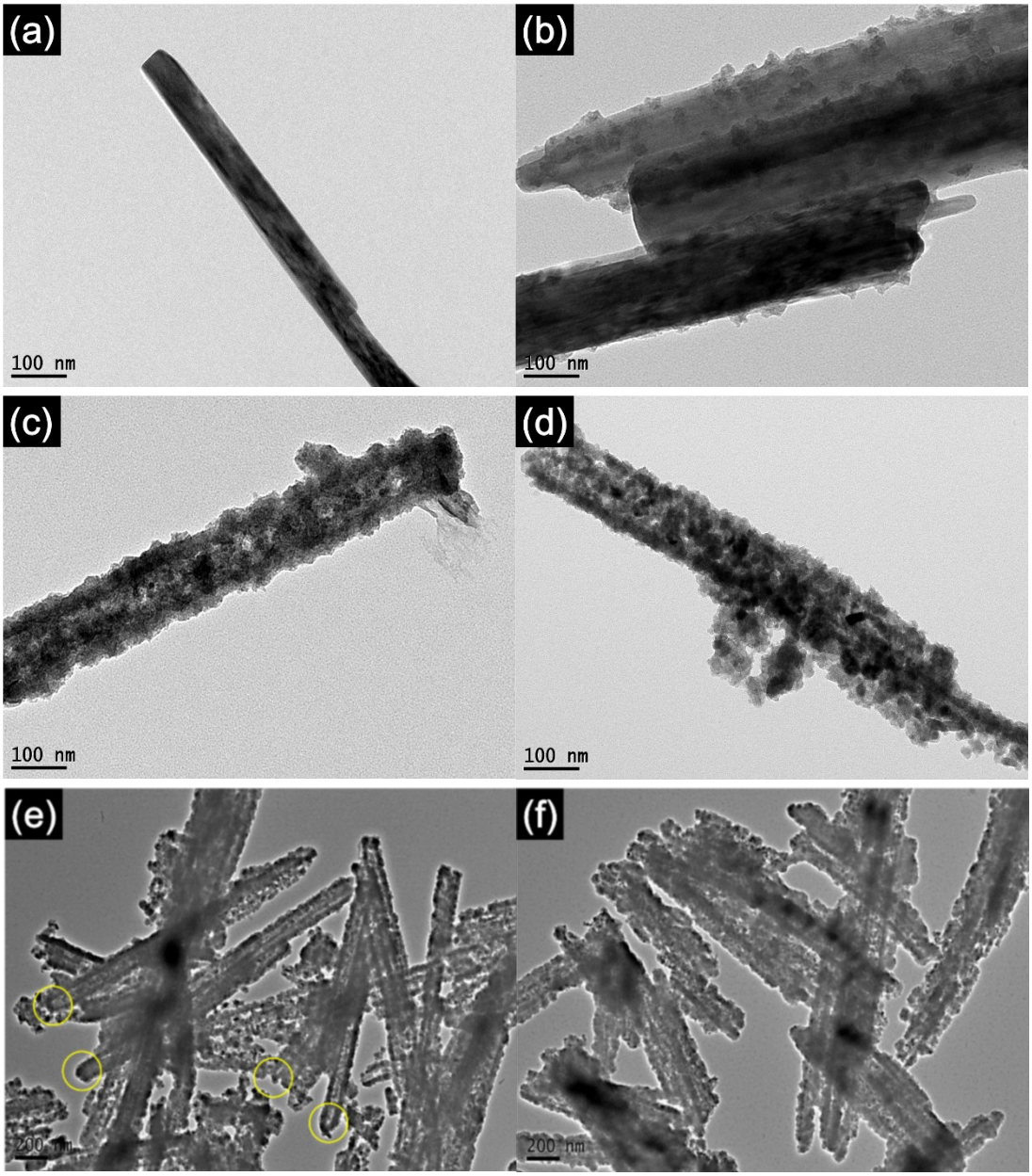


Figure S2. TEM images of the samples sulfurized at 160 °C for different durations: (a) Co-Mo precursor, (b) 0 h, (c) 0.5 h, (d) 1.0 h, (e) 1.5 h, and (f) 3.0 h. The duration means the holding time under sulfurization conditions for each process.

The structural evolution of the Co-Mo precursor during the sulfurization reaction were investigated to understand the formation process of tube-like structure. The duration of the sulfurization varied from 0 to 3.0 h, where 0 h means that the reaction system was heated to 160 °C and then cooled down to room temperature immediately, and the evolution of morphology and crystalline structure against the duration are shown in Figure S2 and S3. Prior to the sulfurization, the morphology of the Co-Mo precursor is quadrangular with a smooth surface (Figure S2a). Then the reactor was

heated from room temperature to 160 °C within about 25 min. In this short duration, the Co-Mo precursor started to be sulfurized, and sulfide Co-Mo nanoparticles were generated on the surface of sub-microrods (Figure S2b). Due to the short time, the crystalline structure of the sub-microrods does not change markedly except that the intensity of diffraction peaks became weak (Figure S3b). With increasing the duration, the surface sulfide Co-Mo nanoparticles grew up, and hollow structures appeared inside the sub-microrods (Figure S2c). At this time, the crystalline structure of the sub-microrods was destroyed and all diffraction peaks disappeared completely (Figure S3c), indicating that the Co-Mo precursor has been well sulfurized. After the sulfurization for 1.0 h, more hollow structures appeared inside the rod-like particles (Figure S2d), and the morphology of the rod-like particles have been changed from quadrangular to cylindrical. In terms of crystalline structure, although there are several weak and broad diffraction peaks in the XRD pattern, the sample is still amorphous in nature (Figure S3d). Further increasing the sulfurization time made the formed hollow structures connect with each other to create an integrated space in the interior of the Co-Mo sulfide particles, however, the ends of the particles have not yet open completely and some of them still closed (see the yellow circles marked in Figure S2e). Until the sulfurization continued for 3.0 h, the Co-Mo sulfides with open-ended tube-like structures were obtained (Figure S2f). During this stage, the crystalline structure of the sample had nearly no change (Figure S3e and S3f).

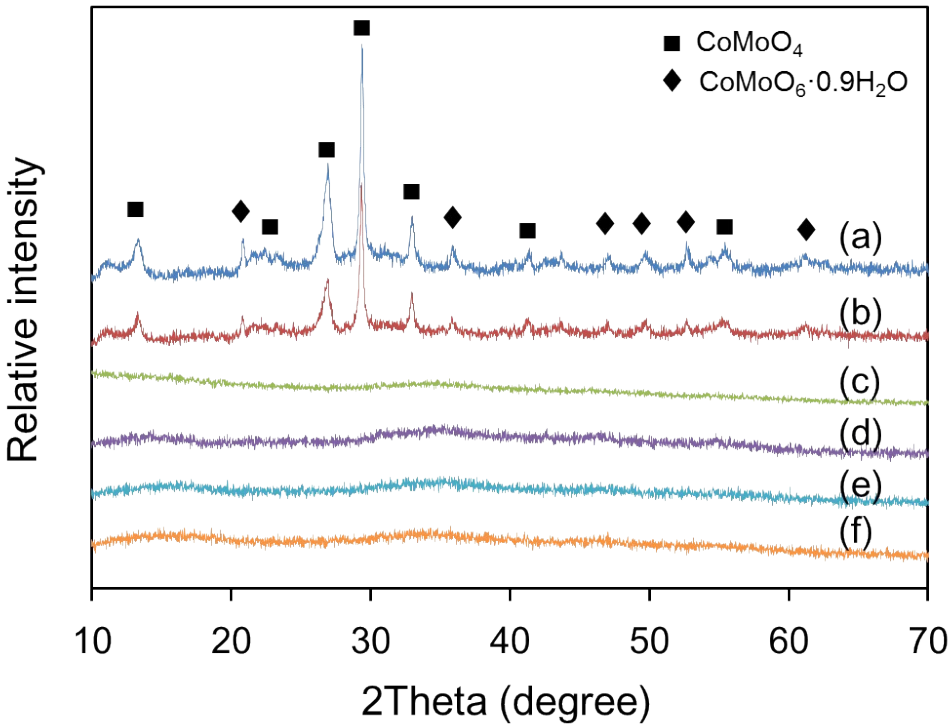


Figure S3. XRD patterns of the samples sulfurized at 160 °C for different durations: (a) Co-Mo precursor, (b) 0 h, (c) 0.5 h, (d) 1.0 h, (e) 1.5 h, and (f) 3.0 h. The duration means the holding time under sulfurization conditions for each process.

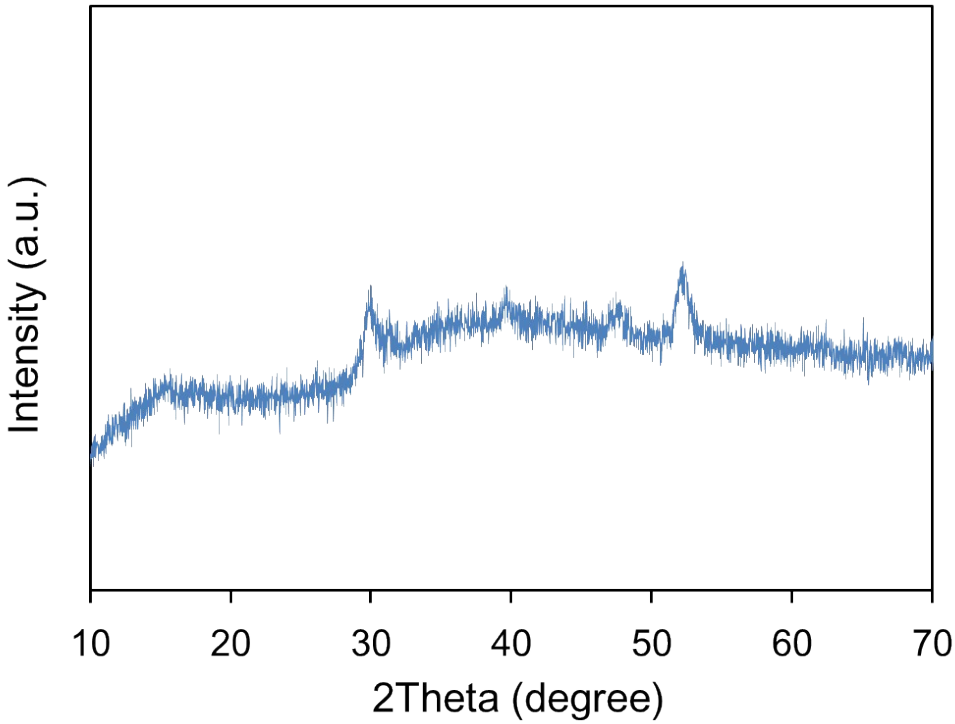


Figure S4. XRD pattern of the Co-Mo sulfide sample sulfurized in decalin at 160 °C.

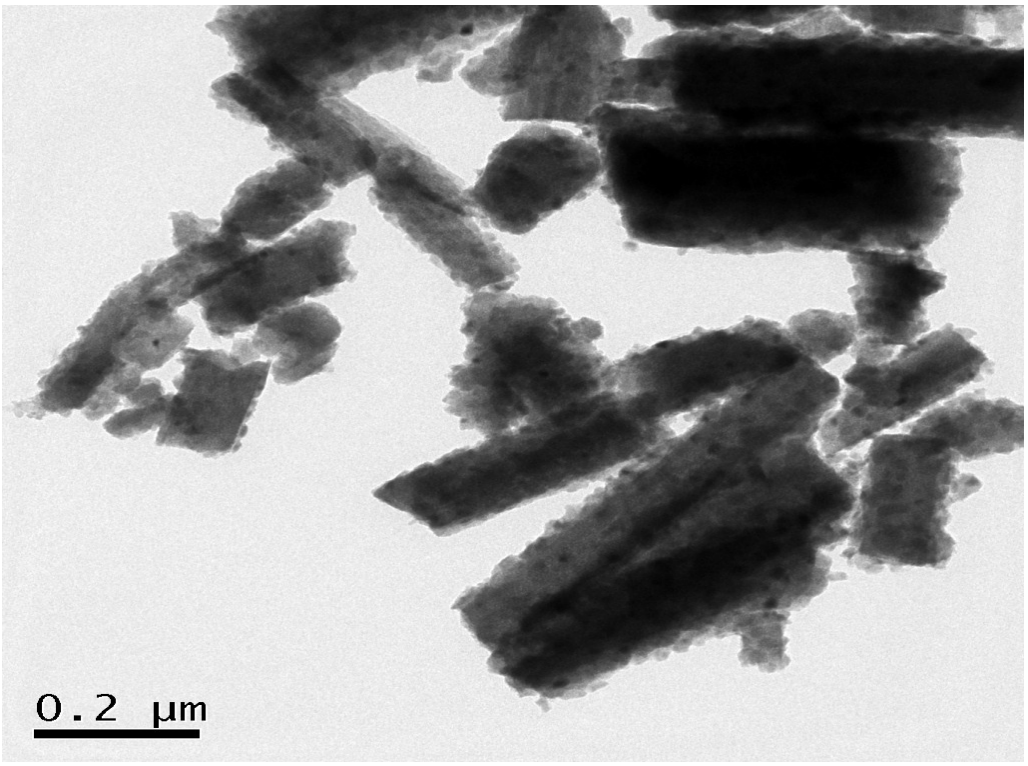


Figure S5. TEM image of the Co-Mo sulfide sample sulfurized in decalin at 160 °C.

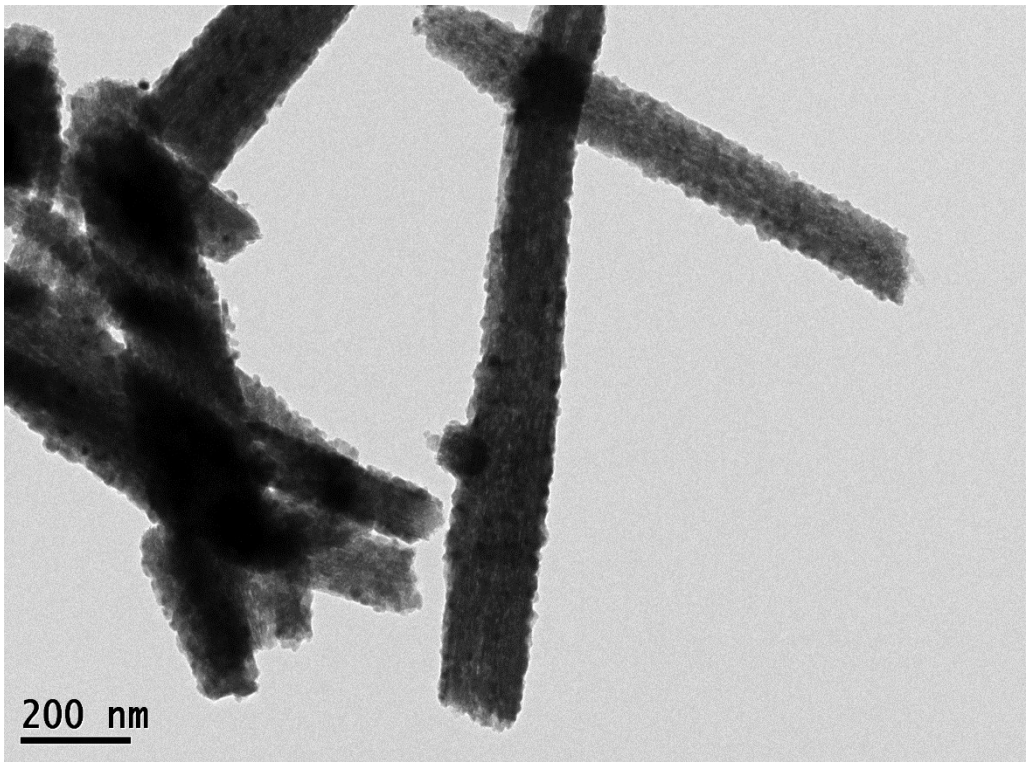


Figure S6. TEM image of the calcined Co-Mo sulfide sub-microrods.

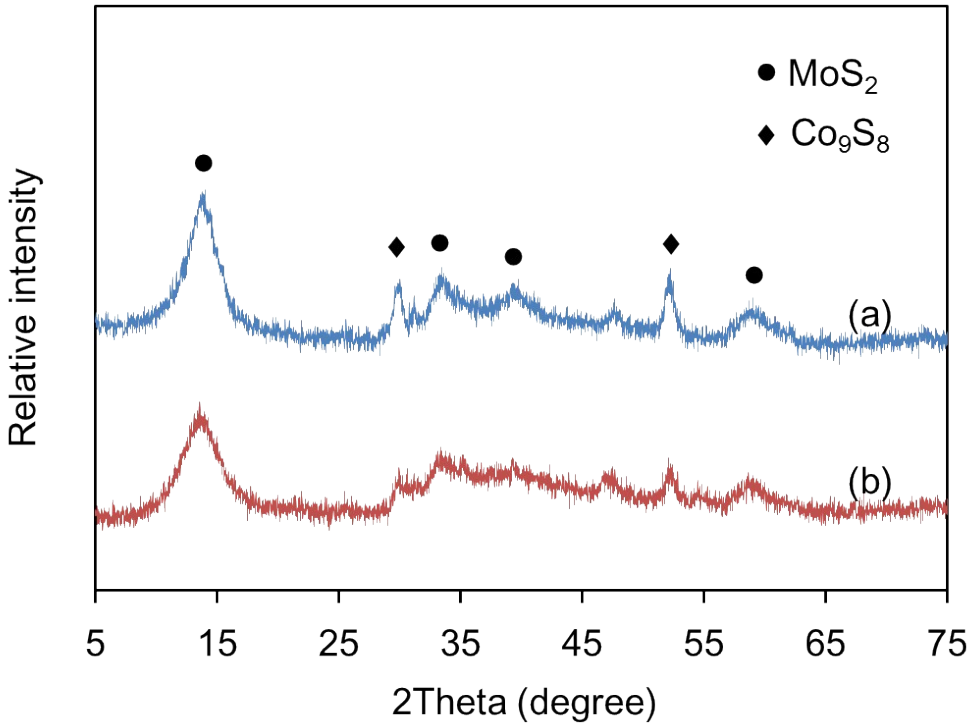


Figure S7. XRD patterns of the calcined Co-Mo sulfide (a) sub-microrods and (b) sub-microtubes.

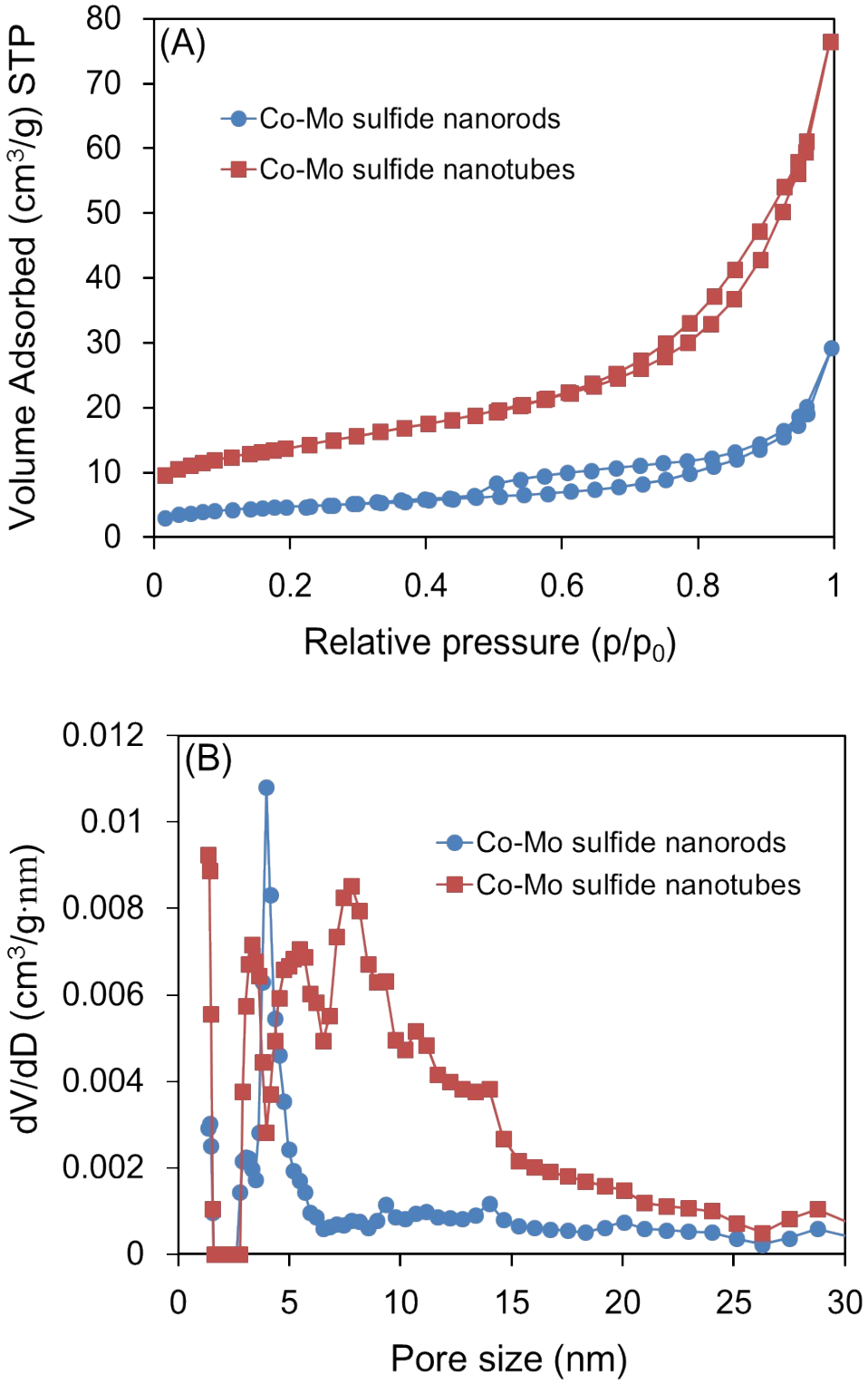


Figure S8. N_2 adsorption-desorption isotherms (A) and pore size distributions (B) of the calcined Co-Mo sulfide sub-microrods and sub-microtubes.

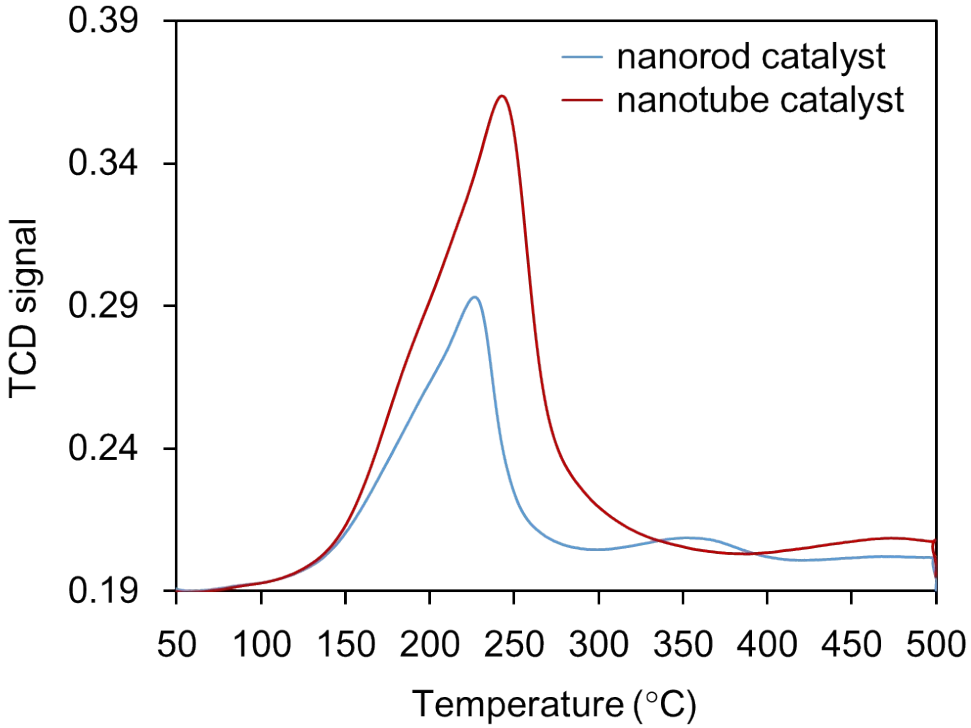


Figure S9. H_2-TPR profiles of the catalysts with different nanostructures.

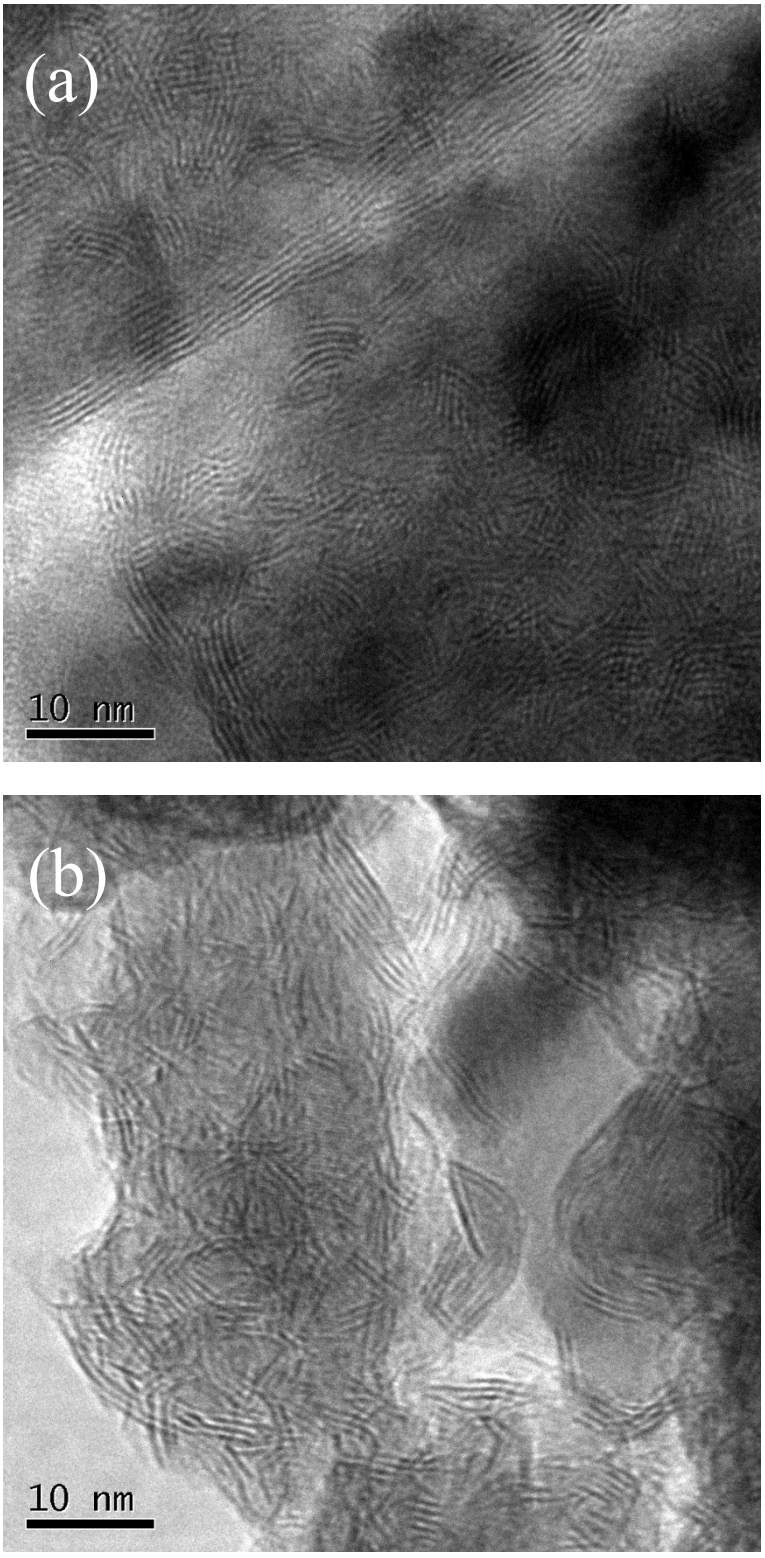


Figure S10. HRTEM images of (a) sub-microrod catalyst and (b) sub-microtube catalyst.

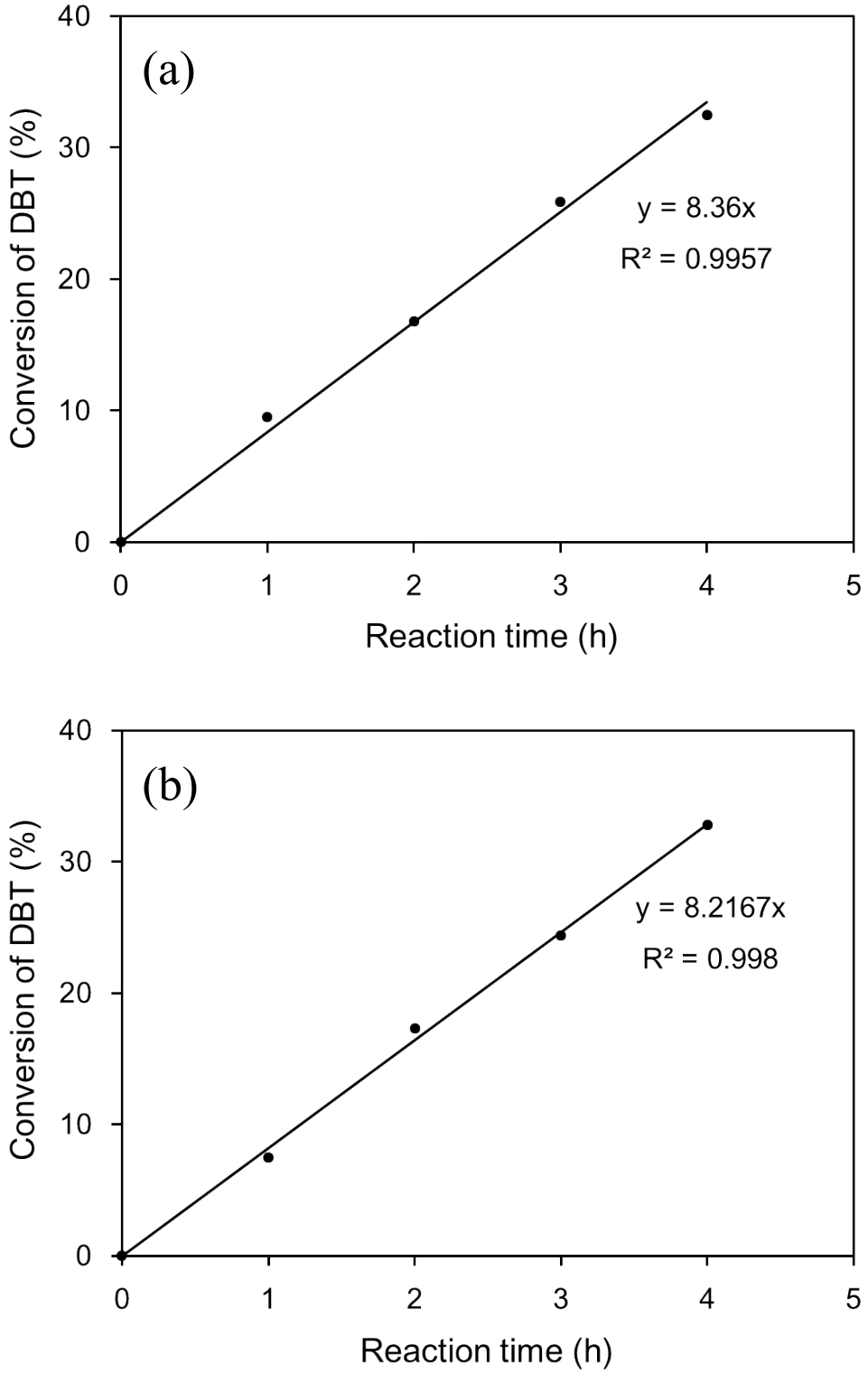


Figure S11. Conversion of DBT versus reaction time over (a) Co-Mo sub-microtube catalyst and (b) Co-Mo sub-microrod catalyst. Reaction conditions: (a) DBT (0.8 g), decalin (39.2 g), catalyst (0.025 g), temperature (300 °C), H_2 pressure (2.0 MPa), and stirring rate (600 r/min); (b) DBT (0.8 g), decalin (39.2 g), catalyst (0.2 g), temperature (300 °C), H_2 pressure (2.0 MPa), and stirring rate (600 r/min).

Table S1. Metal distributions for cobalt and molybdenum species present at the surface of sulfided catalysts measured by XPS.

Catalyst	Co (at.%)	Mo (at.%)	S (at.%)	S/(Co+Mo)	C_{CoMoS} (wt.%)	Co distribution (rel.%)			Mo distribution (rel.%)	
						Co_9S_8	CoMoS	Co^{2+}	MoS_2	Mo^{5+}/Mo^{6+}
CoMo sub-microrod catalyst	15.36	5.37	34.5	1.66	7.4	23.1	20.7	56.2	96.3	3.7
CoMo sub-microtube catalyst	8.27	14.63	37.6	1.64	5.1	20.6	32.2	47.2	88.7	11.3

Table S2. Comparison of catalytic activity of various catalysts in the HDS of DBT.

Catalyst	Conditions	HDS activity for DBT				Refs.
		Apparent reaction rate		Rate constant k	TOF ×	
		× 10^7 (mol/g_{cat}·s)	× 10^5 (mol/mol_{metal}·s)	× 10^6 (L/g_{cat}·s)	10^3 (s^{-1})	
Co-Mo sulfide sub-microtube	Autoclave T = 300 °C P_{H2} = 2.0 MPa	**40.3**	**55.4**	**41.1**	**4.65**	This work
NiMoW	Autoclave T = 350 °C P_{H2} = 3.4 MPa	17.1				[1]
CoMoW	Autoclave T = 320 °C P_{H2} = 5.5 MPa	0.85				[2]
NiMoW		3.02				
CoMoW	Autoclave T = 340 °C P_{H2} = 7.0 MPa		16.9			[3]
NiMo			33.9			
NiMoW-HHD	Micro-reactor T = 330 °C P_{H2} = 4.0 MPa	4.13			0.89	[4]

Reference:

[1] Y. Gochi, C. Ornealas, F. Paraguay, S. Fuentes, L. Alvarez, J.L. Rico, G. Alonso-Núñez, Catal. Today 2005, 107-108, 531-536.

[2] S.L. Amaya, G. Alonso-Núñez, T.A. Zepeda, S. Fuentes, A. Echavarría, Appl. Catal. B: Environ. 2014, 148-149, 221-230.

[3] Y.E. Licea, R. Grau-Crespo, L.A. Palacio, A.C. Faro Jr., Catal. Today 2017, 292, 84-96.

[4] S. Shan, H. Liu, Y. Yue, G. Shi, X. Bao, J. Catal. 2016, 344, 325-333.

Table S3. The characteristics of the morphology of (Co)MoS_2 slabs.[a]

Catalyst	Average slab length (nm)	Average stacking number	f_e	f_c	f_c/f_e
CoMo sulfide sub-microrod	6.29	4.55	17.2	2.1	0.12
CoMo sulfide sub-microtube	4.99	3.82	20.7	3.3	0.16

[a] The calculation formulas are listed as follows:

$\overline{\mathrm{L}} = \frac{\sum l_i}{n}$, $\overline{\mathrm{L}}$: the average slab length of (Co)MoS_2 slabs; n : the total number of slabs; l_i : the length of slab *I*.

$\overline{\mathrm{N}} = \frac{\sum n_i N_i}{n}$, $\overline{\mathrm{N}}$: the average stacking number of (Co)MoS_2 slabs; n_i : the number of stacks with N_i layers.

$\mathrm{n}_i^{'} = \frac{10 \times \overline{L} / 3.2 + 1}{2}$, $\mathrm{n}_i^{'}$: the number of Mo atoms along one side of a (Co)MoS_2 slab.

$M_e = (6n_i^{'} - 12)\overline{N}$, M_e : the number of Mo atoms at edge sites.

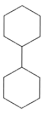
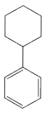
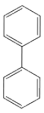
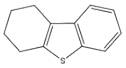
$M_c = 6\overline{N}$, M_c : the number of Mo atoms at corner sites.

$M_T = (3n_i^{'2} - 3n_i^{'} + 1)\overline{N}$, M_T : the total number of Mo atoms.

$f_e = M_e / M_T \times 100$, f_e : the fraction of Mo atoms at the edge sites.

$f_c = M_c / M_T \times 100$, f_c : the fraction of Mo atoms at the corner sites.

Table S4. Product distribution of DBT hydrodesulfurization under different reaction durations.[a]

Catalyst	Reaction duration (h)	Product distribution (wt. %)			
					
Co-Mo sub-microrods	1	8.2	5.5	78.2	8.1
	2	5.3	5.6	82.5	6.6
	3	2.1	6.4	87.6	3.9
	4	-	6.8	89.2	3.0
Co-Mo sub-microtubes	1	7.9	9.7	75.6	6.8
	2	6.6	10.2	77.5	5.7
	3	4.6	12.7	78.3	4.4
	4	2.1	17.8	76.8	3.3

[a] Reaction conditions: catalyst (0.2 g), DBT (0.8 g), decalin (39.2 g), reaction temperature (300 °C), initial H_2 pressure (2.0 MPa), stirring rate (600 rpm).