

## Supplementary Material

The critical role of solvent polarity in the preparation of tube-like Co-Mo sulfide catalysts for the hydrodeoxygenation of stearic acid

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## Materials characterization

The crystalline phases of the precursors and sulfides were characterized by X-ray diffraction on a Bruker AXS-D8 Advance powder diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), a voltage of 40 kV, a current of 40 mA, and a  $2\theta$  range between  $5^\circ$  and  $60^\circ$ . The textural properties were determined by N<sub>2</sub> adsorption-desorption on a Micromeritics ASAP 2020 apparatus. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volumes and pore sizes were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherms. The microscopy analyses were conducted by scanning electron microscopy (SEM, FEI Quanta200) and high-resolution transmission electron microscopy (HRTEM, JEM-2100).

The chemical structure of the composites was analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific ESCALAB 250Xi spectrometer with a monochromatic Al K $\alpha$  X-ray source under ultrahigh vacuum ( $3.2 \times 10^{-6} \text{ Pa}$ ) and a hemispherical analyzer. Gaussian-Lorentzian functions and nonlinear squares fitting algorithms were applied for peak fitting. The C 1 s peak (from adventitious carbon) at 284.6 eV was used as a reference. The binding energies were reproducible within  $\pm 0.2$  eV. The composition of the surface elements was determined by fitting and integrating the Co 2p, Mo 3d, S 2p, C 1 s and O 1 s bands and converting these values to atomic ratios using theoretical sensitivity factors provided by the manufacturer of the XPS apparatus.

To investigate the relationship between the morphology of the (Co)MoS<sub>2</sub> phase and hydrodesulfurization activity, at least ten representative HRTEM images were captured from different parts of each catalyst. The average slab length ( $\bar{L}$ ) and stacking number ( $\bar{N}$ ) of (Co)MoS<sub>2</sub> slabs over the catalyst were measured based on at least 200 slabs for each catalyst. The (Co)MoS<sub>2</sub> slabs are assumed to be perfectly hexagonal; therefore, the related morphology parameters of the (Co)MoS<sub>2</sub> slabs can be calculated as follows<sup>1</sup>:

$$\bar{L} = \frac{\sum_{i=1}^t l_i}{t} \quad (1)$$

where  $\bar{L}$  is the average slab length of (Co)MoS<sub>2</sub> slabs (nm),  $t$  is the total number of slabs, and  $l_i$  is the length of slab  $i$  (nm).

$$\bar{N} = \frac{\sum_{i=1}^t N_i}{t} \quad (2)$$

where  $\bar{N}$  is the average stacking number of (Co)MoS<sub>2</sub> slabs and  $N_i$  is the number of layers of slab  $i$ .

$$n_i = \frac{10 \times l_i / 3.2 + 1}{2} \quad (3)$$

$$f_e = \frac{\sum_{i=1}^t 6n_i - 12}{\sum_{i=1}^t 3n_i^2 - 3n_i + 1} \quad (4)$$

$$f_c = \frac{6t}{\sum_{i=1}^t 3n_i^2 - 3n_i + 1} \quad (5)$$

where  $n_i$  is the number of Mo atoms along one side of a (Co)MoS<sub>2</sub> slab,  $f_e$  is the fraction of Mo atoms at the edge sites, and  $f_c$  is the fraction of Mo atoms at the corner sites.

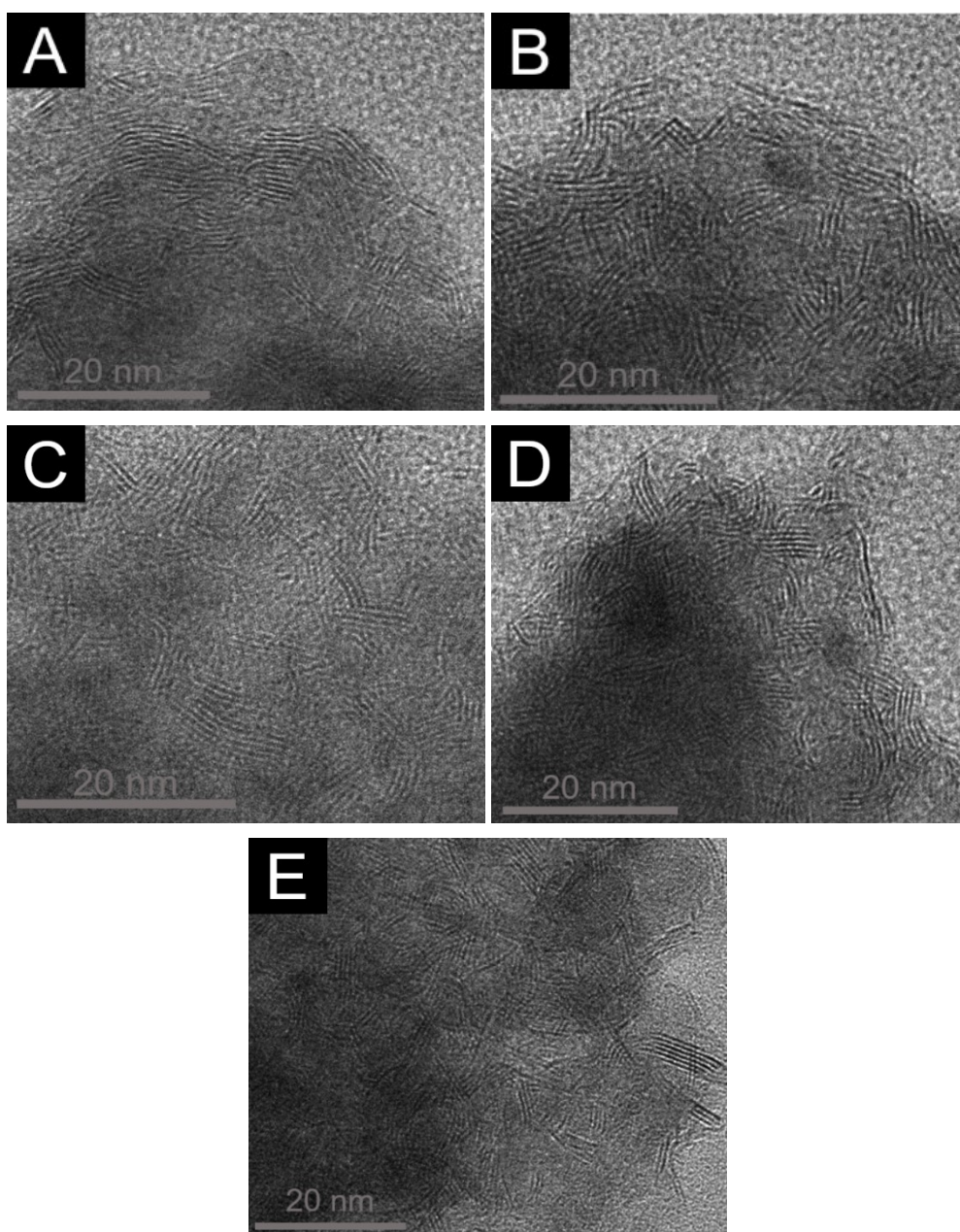


Fig. S1 HRTEM images of (A) Cat-B, (B) Cat-P, (C) Cat-E, (D) Cat-M and (E) Cat-W.

Table S1. Empirical Parameters of the Solvent Polarity  $E_T(30)^2$ .

No.	Solvent	$E_T(30)/\text{kcal}\cdot\text{mol}^{-1}$
1	deionized water	63.1
2	methanol	55.4
3	ethanol	51.9
4	n-propanol	50.7
5	n-butanol	49.7

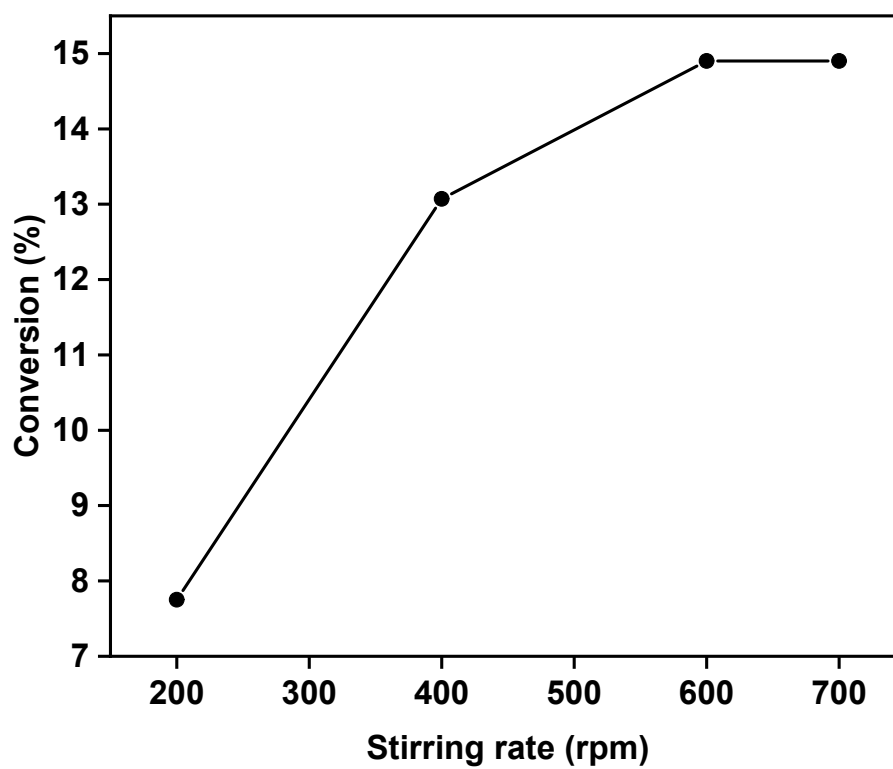


Fig. S2. Effect of stirring rate on the conversion of SA over Cat-M catalysts. Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial  $\text{H}_2$  pressure (3.0 MPa), reaction temperature (240 °C), and reaction duration (4 h).

Table S2. Effects of pre-sulfurization solvents with different polarities on SA conversion and product selectivity.

Catalyst	Conv. <sup>[a]</sup>	Selectivity (wt.%)						
	(%)	C <sub>17</sub>	C <sub>17=</sub>	C <sub>18</sub>	C <sub>18=</sub>	C <sub>17-CHO</sub>	C <sub>18-OH</sub>	C <sub>36-e</sub>
Cat-W	23.2	0.9	2.7	1.7	3.8	8.7	21.7	60.5
Cat-M	29.2	1.5	4.1	2.2	5.6	4.0	18.7	63.9
Cat-E	25.1	1.4	4.3	2.3	5.1	4.1	18.7	64.1
Cat-P	23.9	1.2	4.3	2.2	5.2	4.1	19.0	64.0
Cat-B	15.1	1.5	6.1	2.0	6.0	5.4	14.9	64.1

[a] Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial H<sub>2</sub> pressure (3.0 MPa), reaction temperature (260 °C), stirring rate (700 rpm), and reaction duration (4 h).

Table S3. Effects of pre-sulfurization solvents with different polarities on SA conversion and product selectivity.

Catalyst	Conv. <sup>[a]</sup>	Selectivity (wt.%)						
	(%)	C <sub>17</sub>	C <sub>17=</sub>	C <sub>18</sub>	C <sub>18=</sub>	C <sub>17-CHO</sub>	C <sub>18-OH</sub>	C <sub>36-e</sub>
Cat-W	35.7	1.2	3.6	2.3	6.8	4.2	16.4	65.5
Cat-M	45.2	2.4	4.8	3.3	8.3	2.5	18.7	60.0
Cat-E	43.4	2.2	5.4	3.2	8.5	2.3	17.3	61.1
Cat-P	39.1	2.4	4.7	3.4	9.0	2.4	18.6	59.5
Cat-B	37.1	2.4	4.7	2.7	9.2	2.4	19.2	59.4

[a] Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial H<sub>2</sub> pressure (3.0 MPa), reaction temperature (280 °C), stirring rate (700 rpm), and reaction duration (4 h).

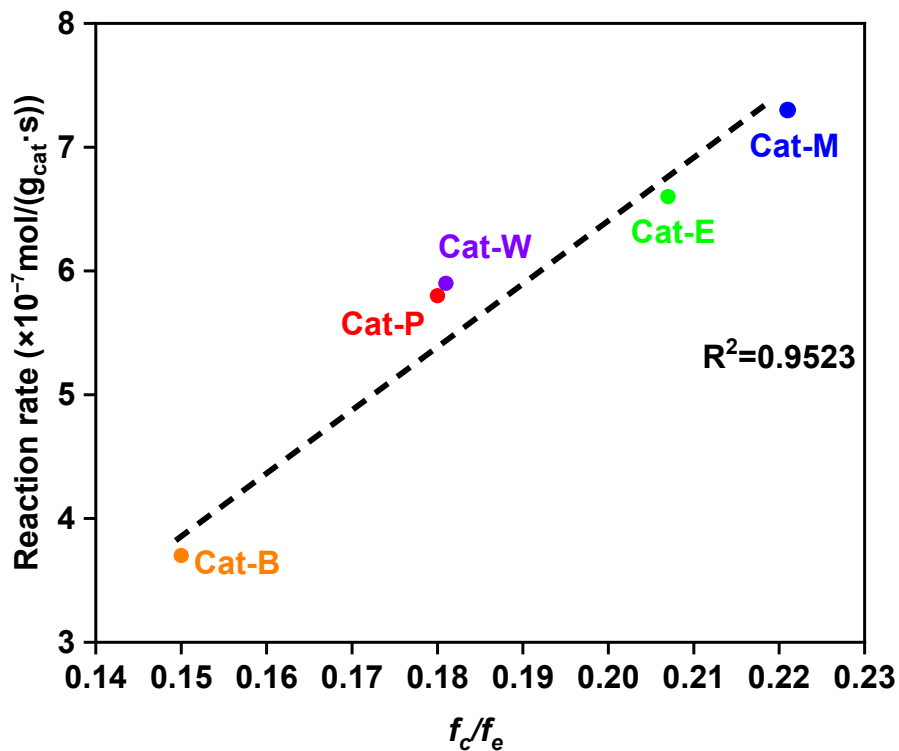


Fig. S3. The relationship between HDO activity and the ratio of corner and edge sites of Mo atoms in catalysts. Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial H<sub>2</sub> pressure (3.0 MPa), reaction temperature (240 °C), stirring rate (700 rpm), and reaction duration (4 h).

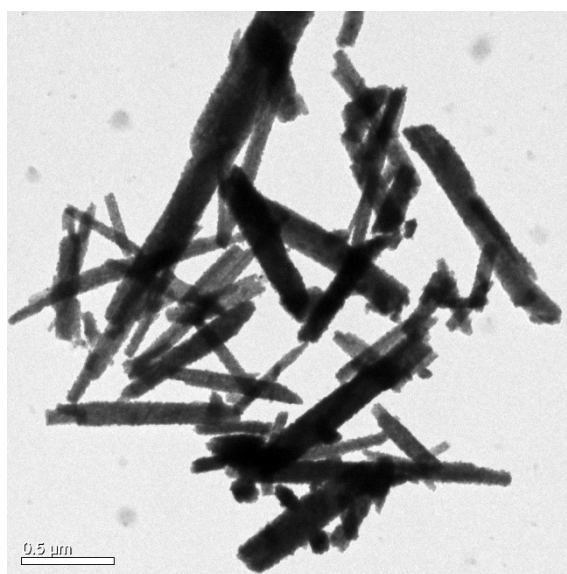


Fig. S4. TEM images of rod-like CoMo sulfide.

Table S4. Comparison of the catalytic activity of different types of catalysts in SA hydrodeoxygenation<sup>[a]</sup>.

Catalyst	Conv. (%)	Selectivity (wt.%)							
		C <sub>17</sub>	C <sub>17=</sub>	C <sub>18</sub>	C <sub>18=</sub>	C <sub>17-CHO</sub>	C <sub>18-OH</sub>	C <sub>36-e</sub>	Others <sup>[b]</sup>
Cat-M	98.0	22.0	-	74.6	-	-	0.3	0.1	3.0
r-CoMoS <sup>[c]</sup>	92.4	20.9	10.9	26.2	15.4	-	3.1	23.2	0.3
CoMoS/ $\gamma$ - Al <sub>2</sub> O <sub>3</sub> <sup>[d]</sup>	96.4	17.6	4.6	49.3	19.7	-	5.3	3.0	0.5

[a] Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial H<sub>2</sub> pressure (3.0 MPa), reaction temperature (300 °C), stirring rate (700 rpm), and reaction duration (12 h).

[b] Includes alkane isomerization and cracking products.

[c] The catalyst was prepared by pre-sulfurization of the CoMoO<sub>4</sub> precursor in a n-dodecane solution (containing 2.0 wt.% carbon disulfide) at 350 °C and 2.0 MPa H<sub>2</sub> for 6 h.

[d] The catalyst was prepared by the incipient wetness impregnation method, and the loading amount of metal oxides (MoO<sub>3</sub> + CoO) was 25.0 wt.%. Before the activity test, the catalyst was pre-sulfurized under the same conditions as [c].

Table S5. Reusability of Cat-M Catalysts.

No.	Conv. <sup>[a]</sup> (%)	Selectivity (wt.%)						
		C <sub>17</sub>	C <sub>17=</sub>	C <sub>18</sub>	C <sub>18=</sub>	C <sub>17-CHO</sub>	C <sub>18-OH</sub>	C <sub>36-e</sub>
1	63.4	1.5	2.6	3.0	5.3	0.7	12.2	38.1
2	62.2	1.5	2.5	2.8	5.2	0.6	12.4	38.2
3	62.3	1.5	2.5	2.9	5.0	0.6	11.9	37.0
4	63.1	1.5	2.5	2.8	5.0	0.6	11.8	36.9
5	62.7	1.5	2.4	2.8	4.9	0.6	11.8	36.7

[a] Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial H<sub>2</sub> pressure (3.0 MPa), reaction temperature (280 °C), stirring rate (700 rpm), and reaction duration (6 h).



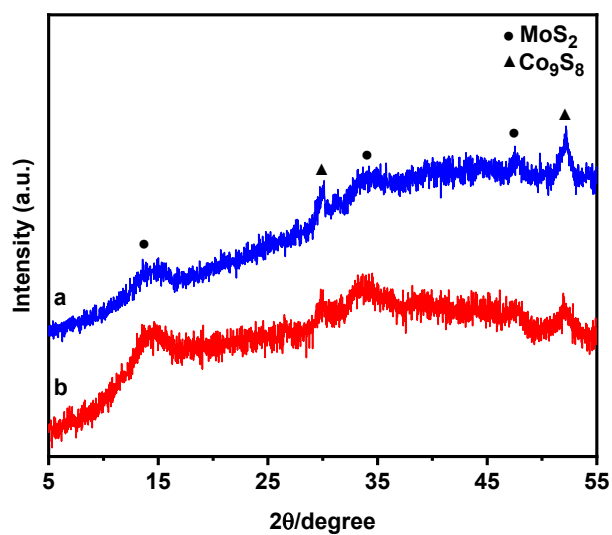


Fig.S5. XRD patterns of the Cat-M before (a) and after reaction (b).

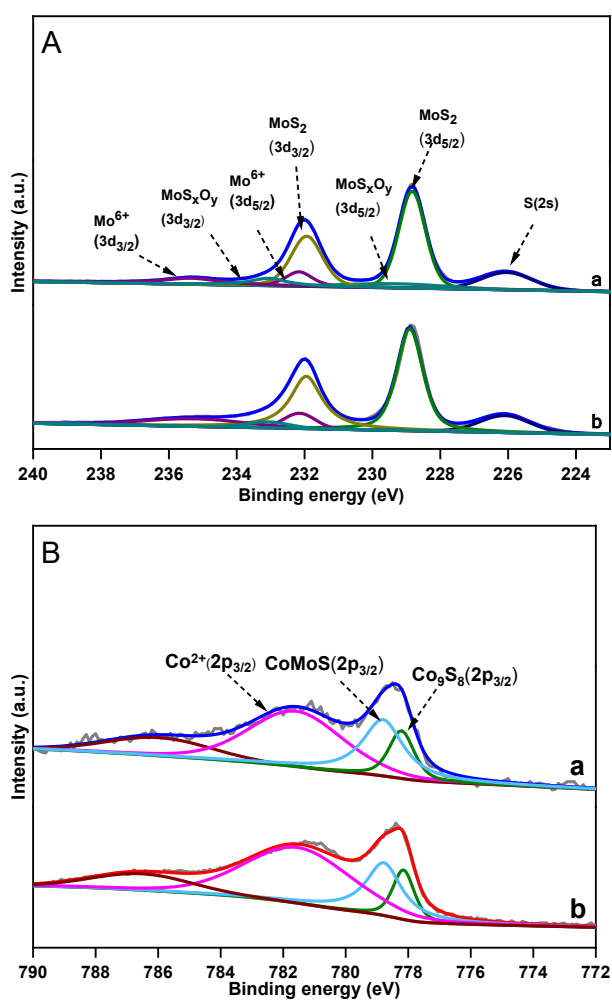


Fig.S6. (A) The Mo 3d spectra of the Cat-M before (a) and after reaction (b); (B) Co 2p spectra of the Cat-M before (a) and after reaction (b).

Table S6. Compositional distribution of cobalt and molybdenum present on the surface of Cat-M catalyst before and after the reaction.

Catalyst	Mo distribution (at. %)		Co distribution (at. %)		
	MoS <sub>2</sub>	Mo <sup>6+</sup> /Mo <sup>5+</sup>	Co <sub>9</sub> S <sub>8</sub>	CoMoS	Co <sup>2+</sup>
Fresh Cat-M	71.5	28.5	18.1	31.8	50.1
Used Cat-M	70.3	29.7	17.9	31.1	51.0

## References

1. M. Li, H. Li, F. Jiang, Y. Chu and H. Nie, *Catal. Today*, 2010, **149**, 35-39.
2. C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319-2358.