Supporting information

Three-dimensionally ordered macro-mesoporous CoMo bulk catalysts with superior performance in hydrodesulfurization of thiophene

Guoliang Chen[a,b], Wenpeng Xie[a], Qinghong Li[a], Wentai Wang[c], Liancheng Bing[a], Fang Wang[a], Guangjian Wang[a], Chunyan Fan[b], Shaomin Liu[b], Dezhi Han[a,*]

[a] State Key Laboratory Base of Eco-chemical Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China
[b] WA School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[c] Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China
***Corresponding author:** D. Han (handzh@qust.edu.cn)*

Chemicals and materials

Cobalt(Ⅱ) nitrate hexahydrate ($(Co(NO_3)_2{\cdot}6H_2O)$, 98%), Hexaammonium heptamolybdate tetrahydrate ($(NH_4)_6MO_7O_{24}{\cdot}4H_2O$), 99%), Polyethylene glycol 400 ($(H(OCH_2CH_2)_nOH)$, 99% donated PEG 400), Cyclohexane ((C_6H_{12}), 99%), Octane ((C_8H_{18}), 98%), Carbon disulfide ((CS_2), 99%), Ethanol pure ((C_2H_6O), 99%) were purchased from sinopharm chemical reagent (Shanghai, China). The thiophene ((C_4H_4S), 98%) was obtained from Fluka (Buchs, Switzerland) and the Pluronic® F-127 ($(C_3H_6O{\cdot}C_2H_4O)_x$, donated F 127) was purchased from Sigma (St. Louis, MO, USA). These reagents were used as received without any further purification.

The analysis of TG and DTG

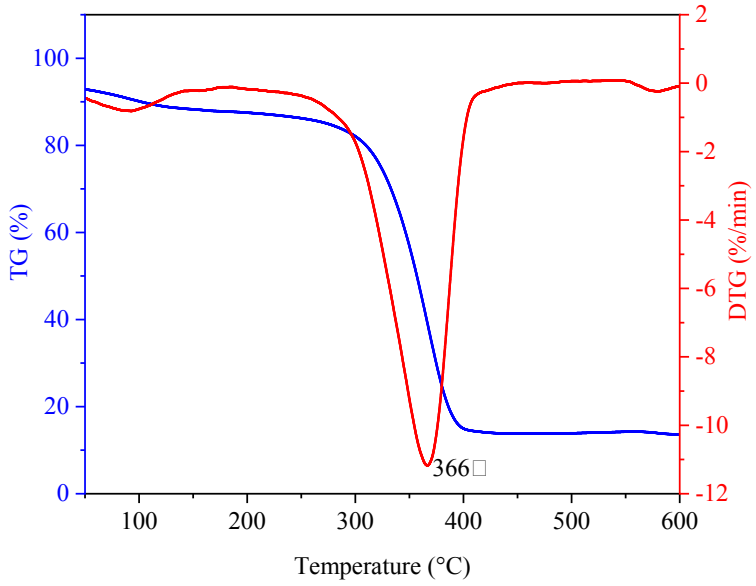

Figure S1 The TG and DTG curves of catalyst precursor/CCT intermediate composite.

The calculation of MoS_2 dispersion

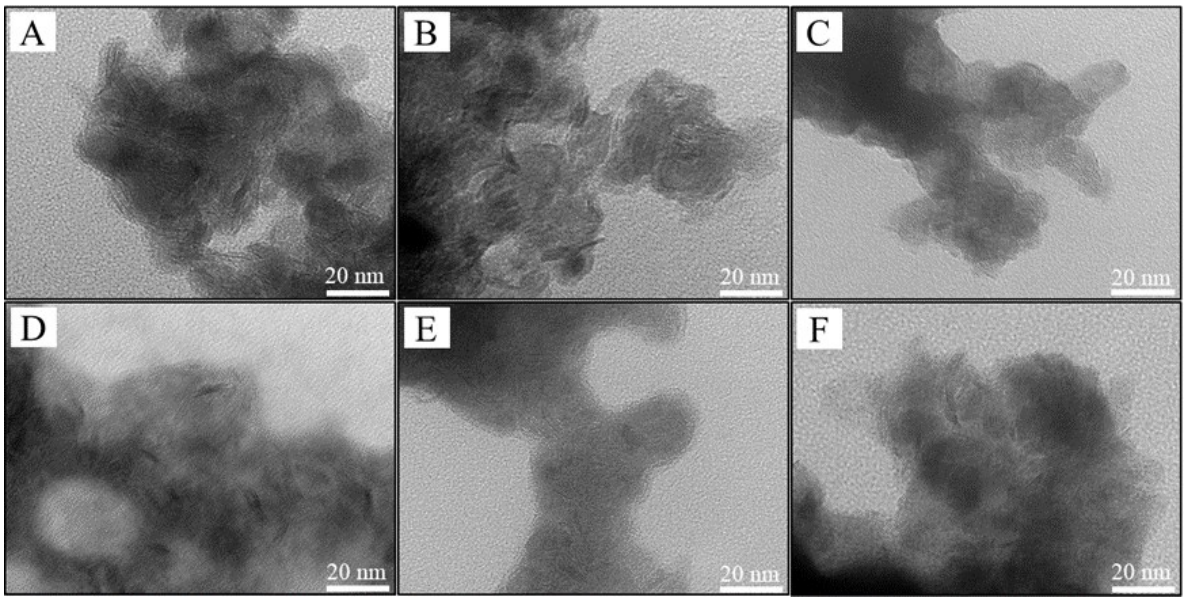

Figure S2 The HRTEM images of the prepared CoMo bulk catalysts with three-dimensionally ordered macroporous structure

(A: CoMo; B: CoMo-PEG; C: CoMo-F127; D: CoMo-PF-1; E: CoMo-PF-2; F: CoMo-PF-3)

According to the literature[1, 2], the average length ($\bar{L}$), the dispersion of MoS_2 (D), and the average stacking number ($\bar{N}$) of MoS_2 slabs are expressed by the following equation:

$$\bar{L} = \frac{\sum_{i=1}^{n} x_i M_i}{\sum_{i=1}^{n} x_i} \quad \text{(E-1)}$$

$$\bar{N} = \frac{\sum_{i=1}^{n} x_i N_i}{\sum_{i=1}^{n} x_i} \quad \text{(E-3)}$$

$$D = \frac{\sum_{i=1\ldots t} 6n_i - 6}{\sum_{i=1\ldots t} 3n^2{}_i - 3n_i + 1} \quad \text{(E-2)}$$

Where x_i is the number of MoS_2 slabs possessing L_i length or N_i number of layers and M_i is the length or layer number of MoS_2 slabs in each stack. Where n_i is the number of Mo atoms along one side of the MoS_2 slab determined from its length and t is the total number of slabs in the TEM micrographs.

Table S1 MoS_2 dispersion calculated from TEM micrographs

Catalyst	Slabs of MoS_2 per 1000nm^2	Average length $\bar{L}$ (nm)	Average stacking number $\bar{N}$	Dispersion of MoS_2 D
CoMo	40	7.8	4.4	0.16
CoM-PEG	32	7.0	4.0	0.17
CoMo-F127	31	5.8	3.9	0.21
CoMo-PF-1	30	5.0	3.3	0.24
CoMo-PF-2	33	6.0	3.7	0.20
CoMo-PF-3	35	7.2	3.9	0.17

Table S2 Comparative study of thiophene conversion available in the literatures for HDS catalysts

Catalyst	Reaction conditions temperature (°C), pressure (bar)	Thiophene conversion	Reference
NiMo-3	350,1	90%	***Energy & Fuels***, 2018, 32(2): 2183-2196.
5.0-$NiSO_4$/γ-Al_2O_3	350,20	89%	***Energy & Fuels***, 2013, 27(6): 3394-3399.
CoMo/γ-Al_2O_3	270,10	91.9%	***Applied Catalysis A: General***, 2017, 533: 99-108.
Rod-CoMo	270,10	95.6%	***Applied Catalysis A: General***, 2017, 533: 99-108.
3DOM CoMo	360,30	99.2%	***Fuel Processing Technology***, 2020, 199: 106268.
CoMoNi/ γ-Al_2O_3(novel)	290,25	87%	***Chemical Engineering Journal***, 2011, 172(1): 444-451.
CoMoNi/A(N-S)	330,35	80%	***Chinese Journal of Chemical Engineering***, 2014, 22(4): 383-391.
NiMoW/CNT-PUP500	160,1	100%	***Advanced Powder Technology***, 2019, 30(3): 502-512.
S-E	300,30	99.48%	***Catalysis Letters***, 2018, 148(5): 1309-1314.

NiMo-AP (15 wt% Mo)	400,1	83.4%	***RSC advances***, 2015, 5(124): 102652-102662.
CoMo-PF-1	360,10	99.4%	This work

References

[1] P.A. Nikulshin, V.A. Salnikov, A.V. Mozhaev, et al. Relationship between active phase morphology and catalytic properties of the carbon-alumina-supported Co (Ni) Mo catalysts in HDS and HYD reactions. ***Journal of catalysis***, 2014, 309: 386-396.

[2] M Li, H Li, F Jiang, et al. The relation between morphology of (Co) MoS_2 phases and selective hydrodesulfurization for CoMo catalysts. ***Catalysis Today***, 2010, 149: 35-39.