

**Electronic Supplementary Information for**

**Ni-modified MoS<sub>2</sub> nanoflake arrays with stepped sites on carbon  
nanotubes for efficient hydrodesulfurization of coal-to-liquid fuel**

Jisheng Xu,<sup>a</sup> Chengxiang Shi,<sup>\*a</sup> Zhou rong Xiao,<sup>a</sup> Ruijie Gao,<sup>a</sup> Yueting Li,<sup>a</sup> Xiangwen Zhang,<sup>ab</sup>  
Lun Pan<sup>ab</sup> and Ji-Jun Zou<sup>\*ab</sup>

- a. Key Laboratory for Green Chemical Technology of the Ministry of Education, School of  
Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.*
- b. Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin  
300072, China*

*Corresponding author. E-mail: cxshi@tju.edu.cn; jj\_zou@tju.edu.cn;*

*Tel: +86-22-27892340*

---

## 1 Chemicals

Ammonium heptamolybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, NMO), nickel nitride hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, NNO), citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, CA), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), decalin, carbon disulfide (CS<sub>2</sub>) and thiourea were purchased from Aladdin Reagent Co., Ltd. The carboxyl (-COOH) modified multi-wall carbon nanotubes (TNSMC3, >98%) and the CNTs water dispersant (TNWDIS) were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences and used as received without further treatment. TNSMC3 is a kind of short-length high purity multiwall carbon nanotubes with a -COOH content of 2.00 wt% (length: 10~30 μm, outer diameter: 10~20 nm, inner diameter: 5~10 nm). TNWDIS is a kind of non-ionic surfactant that consists of aromatics rings and hydrophilic groups connected by long straight alkanes without the addition of poisonous alkylphenol ethoxylates.. Coal-to-liquid fuel (CTL) was obtained from Shanxi Lu'an Coal-based Synthetic Fuel Co., Ltd.

## 2 Preparation of the catalysts

### 2.1 Synthesis of the water dispersion of 2 wt% COOH-MWCNTs

1.500 g TNWDIS was first dissolved in 96.500 g warm water at 60 °C under stirring. Then, 2.000 g CNTs was added and thoroughly mixed using magnetic stirrer for 2 h. After that, a 250 W cell disrupter equipped with an ultrasound probe was applied to uniformly disperse the mixed solution for 30 min, in which the probe was immersed into the mixture and an ice water bath was applied to remove the heat.

### 2.2 Hydrothermal sulfurization

A certain amount of water was added in a 100 mL autoclave, after which 1.537 g CA ((CA/(Mo+Ni))<sub>mol</sub>=2), 0.565 g NMO, 0.233 g NNO ((Mo/Ni)<sub>mol</sub>=4) and 0.914 g thiourea ((S/(Mo+Ni))<sub>mol</sub>=3) were added. The mixture was stirred to form a homogeneous solution. Then x mL of the aforementioned CNTs dispersion was added dropwise to the solution under vigorous agitation. The whole system was maintained at a constant volume of 70 mL by adjusting the dosage (70-x mL) of water used at the beginning. The hydrothermal treatment was applied in an electro-heating jacket with magnetic stirring of 600 rpm at 220°C for 24 h. After natural cooling to room temperature, the suspension was washed repeatedly and successively with water and ethanol followed by centrifugation for several times. The precipitate was dried overnight at 60°C in a vacuum oven.

### 2.3 Gas sulfurization

---

The dried samples were tableted, crushed and sieved to be 20~40 mesh granules, then underwent a gas sulfurization procedure in the fixed bed with pumping in sulfurizing oil (2 wt% CS<sub>2</sub> in decalin, 0.3 mL/min) and inputting of H<sub>2</sub> (150 mL/min) at 280°C and 3.0 MPa for 3 h. The sample was taken out after natural cooling and drying with flowing N<sub>2</sub> (100 mL/min), and named as NiMoS-x (x = 2, 4, 6, 8). The catalysts without the addition of CNTs, CA or both of them were named as NiMoS-NCT, NiMoS-NCA (the dosage of CNTs dispersion is 4 mL) or NiMoS-NN respectively.

### 3 Characterization

XRD patterns were recorded using PANalytical X'Pert Pro X-ray diffractometer equipped with a Cu K $\alpha$  radiation at 40 kV and 40 mA at a scanning rate of 5 °/min. Nitrogen adsorption–desorption isotherms were measured with a Micrometrics ASAP 2460 physisorption analyzer at 77K. The specific surface areas of the samples were calculated using the Bunauer-Emmett-Teller (BET) method and the pore size distributions of the samples were calculated by the BJH method from adsorption branch. SEM images were observed using a Hitachi S-4800 field-emission scanning electron microscope. TEM analysis was carried out using a JEOL JEM-2100F transmission electron microscope with a field-emission gun operating at 200 kV. Raman spectra were collected with a Renishaw inVia microscopy equipped with a Neodymium Yttrium Aluminum garnet (Nd YAG) laser (532 nm). X-ray photoelectron spectrum (XPS) analysis was conducted with a ThermalFisher Thermo ESCALAB 250XI multifunctional imaging electron spectrometer equipped with Al K $\alpha$  radiation. The bulk contents of Ni and Mo were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis (VARIAN Vista MPX) with an automatic microwave digestion instrument to decompose the carbonaceous samples in aqua regia.

### 4 Catalytic performance evaluation

The HDS activities were evaluated in a stainless steel high-pressure fixed-bed tubular reactor with an inner diameter of 6 mm. 300 mg catalyst (20~40 mesh) was mixed with SiC (20~40 mesh) to reach a 5 cm bed height. Decalin containing DBT (500 ppm of sulfur) was applied as the model oil and was pumped to the reactor. The flow rate of H<sub>2</sub> was set to keep a H<sub>2</sub>/oil ratio of 500 (vol/vol). The reaction pressure was 3.0 MPa, the heating rate was 5 °C/min, the oil feed rate was 0.3 mL/min and the liquid hourly space velocity was calculated to be 12.7 h<sup>-1</sup> unless specified otherwise. The temperature of catalyst bed was monitored by a high temperature thermocouple tied closely to the outer

surface of the tube. The liquid product was collected after the system reaching the steady state. Besides, a SiC (20~40 mesh) diluted commercial W-Mo-Ni catalyst (300 mg, 20~40 mesh, FH-98) was used for comparison, which experienced a pre-sulfurization procedure with 2 wt% CS<sub>2</sub> in decalin as sulfide agent and 120 mL/min H<sub>2</sub> at 320°C, 3.0 MPa and H<sub>2</sub>/liquid = 400 (vol/vol). A Shinadzu GCMS-QP2020 was applied to identify the products. The product distribution was analyzed by an offline Shimadzu 2010plus gas chromatograph (GC) equipped with a flame ionization detector and a RxiTM-5ms column.

By assuming that the reaction follows pseudo-first order kinetics model, and using the area normalization method to calculate the conversion of DBT ( $X_A$ , %), the catalytic HDS rate constants ( $k_{HDS}$ , L mol<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) and the apparent activity energy ( $E_a$ , kJ mol<sup>-1</sup>) were obtained by the following equations:

$$k_{HDS} = \frac{F_{A0} \ln(1 - X_A)}{C_{A0} W_{cat}},$$

$$\ln(k_{HDS}) = -\frac{E_a}{R} \frac{1}{T} + C,$$

where  $F_{A0}$  is the molar feed rate of the model oil (mol h<sup>-1</sup>),  $C_{A0}$  is the concentration of DBT in the model oil (mol L<sup>-1</sup>),  $W_{cat}$  is the dosage of catalyst (g<sub>cat</sub>),  $T$  is the reaction temperature (K),  $R = 8.314$  kJ mol<sup>-1</sup> K<sup>-1</sup>, and  $C$  is a constant.

For test of the ultra-deep desulfurization ability of NiMoS-4, 4,6-dimethyldibenzothiophene was dissolved in decalin with a sulfur content of 500 ppm as the model oil. Harsher reaction conditions (340°C, 3 MPa, H<sub>2</sub>/oil = 500 and LHSV = 12.7 h<sup>-1</sup>) was applied.

## 5 the effects of reaction conditions to hydrodesulfurization of model oil

As shown in Fig S4 and the inserted table, various reaction conditions were tested for the hydrodesulfurization of model oil, such as reaction temperature, reaction pressure and the volumetric ratio of hydrogen to model oil (H<sub>2</sub>/oil). Test 1-4 indicates that with the increase of reaction temperature from 250°C to 280°C, the hydrodesulfurization reactivity enhanced significantly, and a DBT conversion as high as 96.9% was achieved at 280°C, 3 MPa, H<sub>2</sub>/oil = 500 and LHSV = 12.7 h<sup>-1</sup>. Test 7-9 shows the effect of reaction pressure on the conversion of DBT. Hydrogen was known to participate in the reaction and benefit for transfer of sulfur in DBT to H<sub>2</sub>S and saturation of phenyl groups. A gradual raise in conversion when reaction pressure was increased from 2 MPa to 4 MPa suggests that the NiMoS-4 are not very sensitive to it, indicating less

operation cost may realize when this catalyst is applied in industry with lower reaction pressure. The increase of  $H_2$ /oil has a complex influence to the reaction. On one hand, it is beneficial for the removal of heats to inhibit coking and the increase of hydrogen partial pressure to increase the reaction rate. On the other hand, the increasing flowrate results in the decline of contact time between reactant molecules and catalyst. Various  $H_2$  flowrates were taken in Test 7 and Test 10-12 to explore the influence of  $H_2$ /oil and it shows that the activity improved slightly when  $H_2$ /oil was raised from 400 to 600. Therefore, it can be concluded that the reaction is not very sensitive to the undulation of  $H_2$ /oil between 400 and 600 and it is favorable for the stable output of the hydrotreated oil.

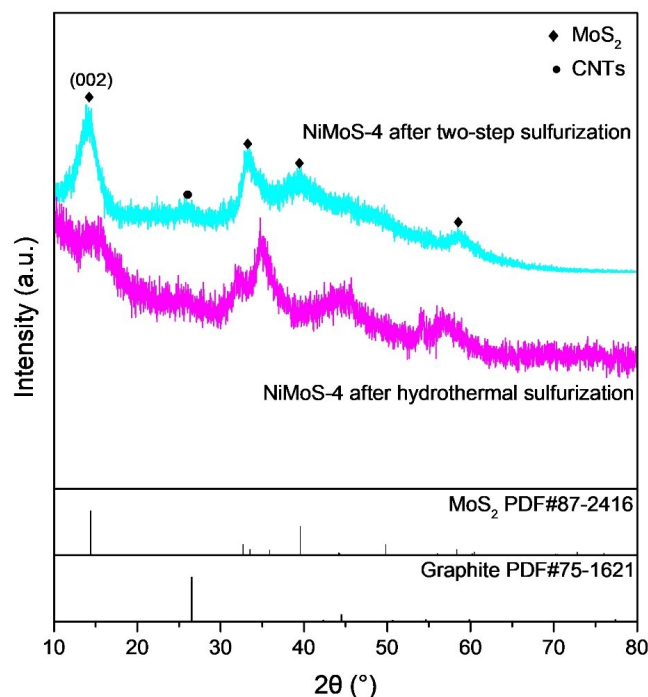


Fig. S1 XRD patterns of hydrothermal synthesized NiMoS-4 and NiMoS-4 after two-step sulfurization.

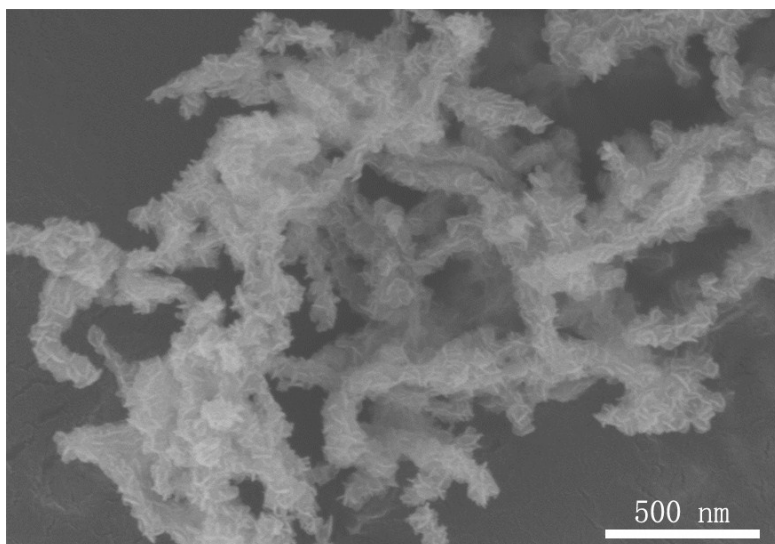


Fig. S2 TEM image of hydrothermal treated NiMoS-4.

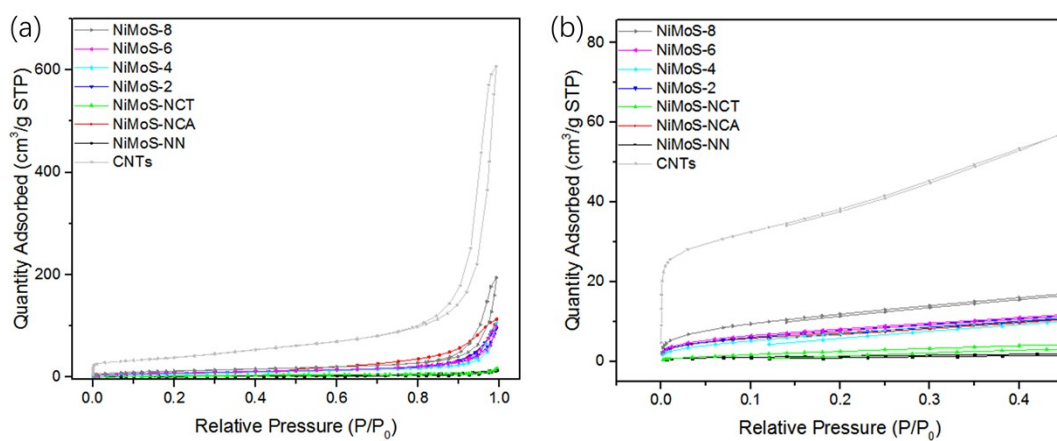


Fig. S3  $N_2$  adsorption-desorption curves of the samples (a) and the enlarged part at lower relative pressure (b).

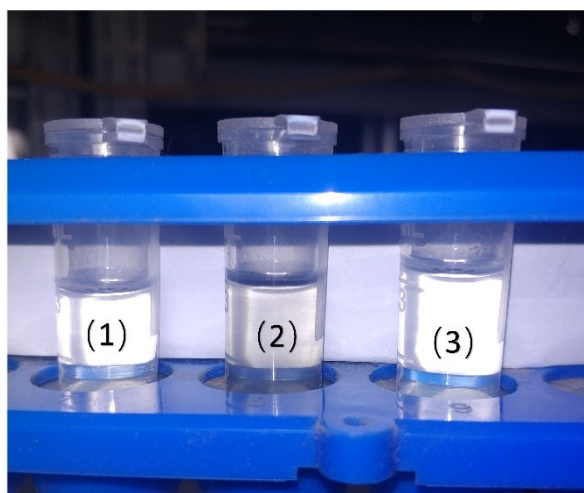


Fig. S4 Digital photographs of the model oil (1), the oil treated by NiMoS-NCT (2), and the oil treated by NiMoS-4 (3) (280°C, 3.0 MPa, 0.3 g catalyst,  $H_2/oil = 500$  (vol/vol), LHSV = 12.7  $h^{-1}$ ).

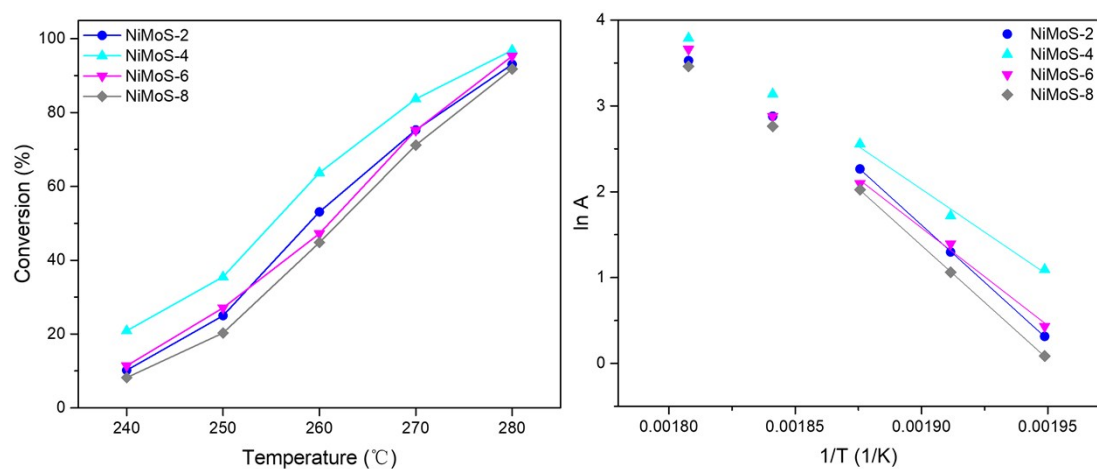
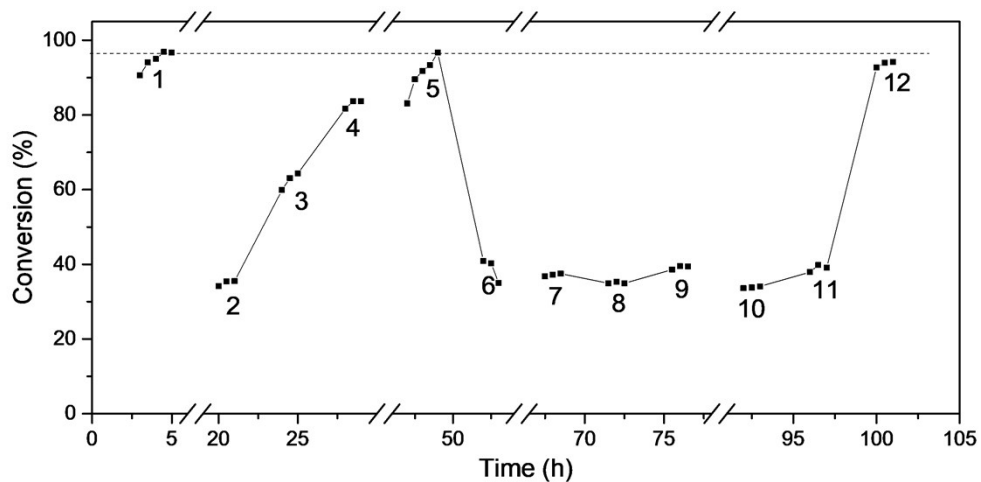


Fig. S5 The variation of the conversion of DBT along with the increase of reaction temperature (240~280°C, 3.0 MPa, 0.3 g catalyst,  $H_2/oil = 500$  (vol/vol), LHSV = 12.7  $h^{-1}$ ) and the fitting curves adopting the pseudo-first order reaction apparent kinetics for NiMoS-x.



Temperature (°C)	1	2	3	4	5	6	7	8	9	10	11	12
Pressure (MPa)	280	250	260	270	280	250	250	250	250	250	250	280
Oil (mL/min)	3	3	3	3	3	3	3	2	4	3	3	3
H <sub>2</sub> (mL/min)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	150	150	150	150	150	150	150	150	150	120	180	150

Fig. S6 The long-time running performance of NiMoS-4 sample under changeable reaction conditions.

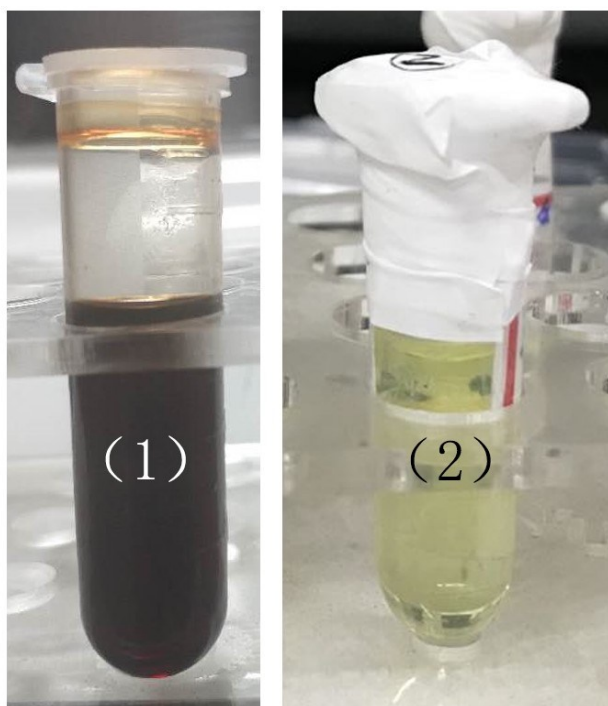


Fig. S7 Digital photographs of the untreated CTL oil (1) and the CTL oil hydrodesulfurized by NiMoS-4 (2) (340°C, 5.0 MPa, 0.3 g catalyst, H<sub>2</sub>/oil = 500 (vol/vol), LHSV = 12.7 h<sup>-1</sup>).



Table S1 The specific surface areas, the contents of Mo and Ni measured by XPS and ICP-OES, the average diameters of the CNTs-supported structures, the average lengths of the nanoflake arrays, and the calculated apparent activation energies measured at 240~260 °C.

Samples <sup>a</sup>	NN	NCA	NCT	2	4	6	8
XPS results (surface)							
Mo/wt%	48.6	22.5	41.6	32.3	29.0	26.3	30.6
Ni/wt%	3.6	1.6	6.3	4.7	4.4	3.8	5.9
Mo/Ni <sub>(mol)</sub>	8.25	14.5	4.01	4.23	4.05	4.25	3.18
ICP-OES results (bulk)							
Mo/wt%	52.3	47.5	29.3	30.5	32.2	31.8	33.5
Ni/wt%	7.9	7.5	5.0	4.9	5.2	5.2	5.2
Mo/Ni <sub>(mol)</sub>	4.04	3.90	3.55	3.85	3.82	3.74	3.97
S <sub>BET</sub> <sup>b</sup> /m <sup>2</sup> g <sup>-1</sup>	5	27	12	19	30	47	72
Diameter/nm <sup>c</sup>	--	--	--	138	89	70	63
Length/nm <sup>c</sup>	--	--	--	41	32	27	23
E <sub>a</sub> /kJ mol <sup>-1</sup>	--	--	--	221.9	166.3	189.3	220.4

<sup>a</sup> "NiMoS-" in the names of samples was omitted. <sup>b</sup> S<sub>BET</sub> was measured using the tableted and crushed samples (20~40 mesh). <sup>c</sup> Diameter and length were counted and averaged referred to SEM and TEM images.

Table S2 The metal contents of the catalysts of the reported articles and this work

Catalysts	Metal contents	
1 Co-Mo/CNT	6.7 wt% Mo, 2.9 wt% Co	[1]
2 NiMo/MWCNTs	12 wt% Mo, 3 wt% Ni	[2]
3 Co-Mo/CNTs	6.7 wt% Mo, 1.6 wt% Co	[3]
4 carbon nanofiber supported NiMo	12 wt% Mo, 4 wt% Ni	[4]
5 Ni-Mo-W/MWCNT	12 wt% Mo, 4 wt% Ni, 6 wt.% W	[5]
6 Co-Mo/CNT	8.0 wt% Mo, 3.4 wt% Co	[6]
7 CoMo/CNT	8.0 wt% Mo, 2.5 wt% Co	[7]
8 S_CNT_Mo_Co	19 wt% Mo, 1.7 wt% Co	[8]
9 Ni-Mo-S/CNT	8.0 wt% Mo, 1.6 wt% Ni	[9]
10 NiMoS-4	32.2 wt% Mo, 5.2 wt% Ni	this work

Table S3 The composition of the coal-to-liquid fuel

Boiling range	Aromatics	Cycloalkanes	Paraffins	Others	Sulfur content*	Sulfur content (treated oil)*
°C	wt%	wt%	wt%	wt%	ppm	ppm
110~360	30~40	30~40	15~25	~5	439.0	8.4

\* The sulfur contents of the coal-to-liquid fuel before and after hydrodesulfurization were measured by an Analytical Jena multi EA 5000 elemental analyzer.

## References

- 1 H. Shang, C. Liu, Y. Xu, J. Qiu and F. Wei, *Fuel Process. Technol.*, 2007, **88**, 117.
- 2 I. Eswaramoorthi, V. Sundaramurthy, N. Das, A. K. Dalai and J. Adjaye, *Appl. Catal., A*, 2008, **339**, 187.
- 3 J. Zhang, W. Yin, H. Shang and C. Liu, *J. Nat. Gas Chem.*, 2008, **17**, 165.
- 4 Z. Yu, L. E. Fareid, K. Moljord, E. A. Blekkan, J. C. Walmsley and D. Chen, *Appl. Catal., B*, 2008, **84**, 482.
- 5 D. M. Nejad, N. Rahemi and S. Allahyari, *React. Kinet., Mech. Catal.*, 2016, **120**, 279.
- 6 W. Ahmed, H. S. Ahmed, H. S. El-Sheshtawy, N. A. Mohamed and A. I. Zahrana, *J. Fuel Chem. Tech.*, 2016, **44**, 853.
- 7 M. I. Mohammed, A. A. Abdul Razak and M. A. Shehab, *Arabian J. Sci. Eng.*, 2016, **42**, 1381.
- 8 J. Whelan, M. S. Katsiotis, S. Stephen, G. E. Luckachan, A. Tharalekshmy, N. D. Banu, J.-C. Idrobo, S. T. Pantelides, R. V. Vladea, I. Banu and S. M. Alhassan, *Energy Fuels*, 2018, **32**, 7820.
- 9 S. Liu, Q. Jin, Y. Xu, X. Fang, N. Liu, J. Zhang, X. Liang and B. Chen, *Fuel*, 2018, **232**, 36.