

Supplementary materials

Reactivity of Sulfur and Nitrogen Compounds of FCC Light Cycle Oil in Hydrotreating over CoMoS and NiMoS Catalysts

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Fig. S1. The structure of heterocyclic aromatic compounds with labeled C atoms: (a) benzothiophene, (b) dibenzothiophene, and (c) carbazole.

Fig. S2. N₂ adsorption isotherm plot of (a) CoMoS and (b) NiMoS

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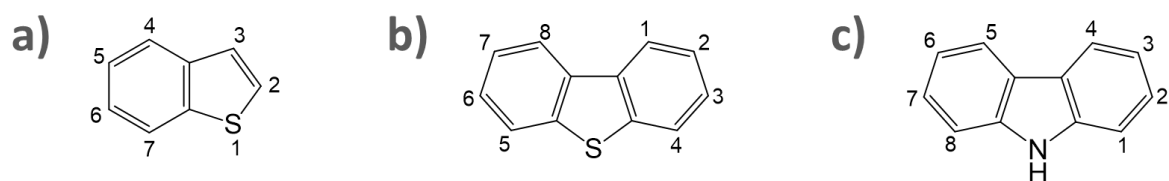


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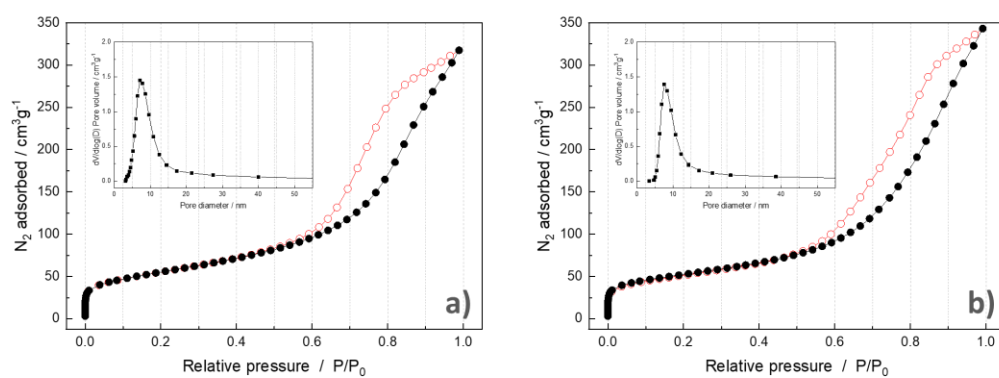


Fig. S2. N₂ adsorption isotherm plot of (a) CoMoS and (b) NiMoS

Table S1. Composition and properties of light cycle oil (LCO)

Physical properties		LCO
API		13.5
S / ppm		3930
N / ppm		550
Color (ASTM)		L2.5
Aromatics / wt. %	Total	74.3
	Mono	14.3
	Di	40.6
	Tri+	19.4
Cetane Index		24.9
Distillation / °C	IBP/5/10	225/256/262
	30/40/50	284/292/308
	60/90/95	325/398/-
	EP	-

Table S2. Sulfur distribution of LCO

#	Compounds	Formula	ppm	Fraction / %	#	Compounds	Formula	ppm	Fraction / %
1	benzothiophene	C ₈ H ₆ S	28	0.7	15	1-methyl dibenzothiophene	C ₁₃ H ₁₀ S	50	1.26
2	7-methyl benzothiophene	C ₉ H ₈ S	48	1.23	16	4-ethyl dibenzothiophene	C ₁₄ H ₁₂ S	38	0.97
3	2-methyl benzothiophene	C ₉ H ₈ S	40	1.02	17	4,6-dimethyl dibenzothiophene	C ₁₄ H ₁₂ S	89	2.28
4	5-/6-methyl benzothiophene	C ₉ H ₈ S	57	1.46	18	2,4-dimethyl dibenzothiophene	C ₁₄ H ₁₂ S	115	2.92
5	3-/4-methyl benzothiophene	C ₉ H ₈ S	80	2.03	19	2,6-/3,6-dimethyl dibenzothiophene	C ₁₄ H ₁₂ S	214	5.45
6	2,6-dimethyl benzothiophene	C ₁₀ H ₁₀ S	12	0.31	20	2,8-/2,7-/3,7-dimethyl dibenzothiophene	C ₁₄ H ₁₂ S	108	2.74
7	4,5-dimethyl benzothiophene	C ₁₀ H ₁₀ S	114	2.91	21	1,4-/1,6--dimethyl dibenzothiophene	C ₁₄ H ₁₂ S	87	2.22
8	2,4-dimethyl benzothiophene	C ₁₀ H ₁₀ S	25	0.65	22	4-ethyl,6-methyl dibenzothiophene	C ₁₅ H ₁₄ S	33	0.83
9	3,5-dimethyl benzothiophene	C ₁₀ H ₁₀ S	51	1.29	23	2,4,6-trimethyl dibenzothiophene	C ₁₅ H ₁₄ S	133	3.4
10	2,3-dimethyl benzothiophene	C ₁₀ H ₁₀ S	38	0.96	24	2,4,8-/2,4,7-trimethyl dibenzothiophene	C ₁₅ H ₁₄ S	64	1.63
11	2,5,7-trimethyl benzothiophene	C ₁₁ H ₁₂ S	26	0.67	25	1,4,6-trimethyl dibenzothiophene	C ₁₅ H ₁₄ S	58	1.48
12	dibenzothiophene	C ₁₂ H ₈ S	182	4.64	26	1,4,8-trimethyl dibenzothiophene	C ₁₅ H ₁₄ S	30	0.76
13	4-methyl dibenzothiophene	C ₁₃ H ₁₀ S	251	6.39	27	3,4,6-trimethyl dibenzothiophene	C ₁₅ H ₁₄ S	47	1.2
14	2-/3-methyl dibenzothiophene	C ₁₃ H ₁₀ S	287	7.3					

Table S3. Nitrogen distribution of LCO


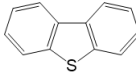
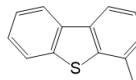
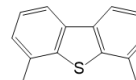
#	Compounds	Formula	ppm	Fraction / %	#	Compounds	Formula	ppm	Fraction / %
1	carbazole	C ₁₂ H ₉ N	24	4.43	11	3,5-dimethyl carbazole	C ₁₄ H ₁₃ N	8	1.38
2	1-methyl carbazole	C ₁₃ H ₁₁ N	35	6.28	12	dimethyl carbazole	C ₁₄ H ₁₃ N	12	2.24
3	2-methyl carbazole	C ₁₃ H ₁₁ N	18	3.25	13	2,4-dimethyl carbazole	C ₁₄ H ₁₃ N	18	3.3
4	3-methyl carbazole	C ₁₃ H ₁₁ N	22	4.07	14	2,5- dimethyl carbazole	C ₁₄ H ₁₃ N	13	2.37
5	4-methyl carbazole	C ₁₃ H ₁₁ N	22	3.96	15	trimethyl carbazole	C ₁₅ H ₁₅ N	17	3.05
6	1,8-dimethyl / 1-ethyl carbazole	C ₁₄ H ₁₃ N	16	2.86	16	trimethyl carbazole	C ₁₅ H ₁₅ N	20	3.71
7	1,4-dimethyl carbazole	C ₁₄ H ₁₃ N	27	4.87	17	trimethyl carbazole	C ₁₅ H ₁₅ N	3	0.48
8	1,5-dimethyl carbazole	C ₁₄ H ₁₃ N	22	3.95	18	trimethyl carbazole	C ₁₅ H ₁₅ N	32	5.8
9	2,6-/2,7-dimethyl carbazole	C ₁₄ H ₁₃ N	30	5.51	19	trimethyl carbazole	C ₁₅ H ₁₅ N	18	3.27
10	1,2-dimethyl carbazole	C ₁₄ H ₁₃ N	8	1.54	20	tri+ methyl carbazole		100	18.11

Table S4. Physical properties of the support and catalysts

Samples	Condition	BET surface area			Pore volume		ICP / wt%		
		/ m ² g ⁻¹			/ cm ³ g ⁻¹				
		S _{total}	S _{micro} ^{a)}	S _{meso} ^{b)}	V _{micro} ^{a)}	V _{meso} ^{c)}	Ni	Mo	Al
γ-Al ₂ O ₃	As calcined	248.3	14.9	233.4	0.004	0.766			-
CoMoS/γ-Al ₂ O ₃	Sulfided	198	13.7	184.3	0.005	0.495	6.1	16	78.0
NiMoS/γ-Al ₂ O ₃	Sulfided	187.4	12.9	174.5	0.004	0.531	6.6	16.7	76.7

^{a)} Calculated by *t*-plot method.^{b)} S_{total} - S_{micro}^{c)} V_{total} - V_{micro}

Table S5. Group of S compounds in LCO and hydrotreated LCO at 613K

	^a Total HDS Conversion / %	^b Sulfur Group 1 HDS conversion / %		^c Sulfur Group 2 HDS conversion / %		^d Sulfur Group 3 HDS conversion / %		^e Sulfur Group 4 HDS conversion / %	
			Total Group 1		Total Group 2		Total Group 3		Total Group 4
CoMoS ₂ : 0.0 h	14.58	91.36	49.38	8.11	8.38	0.64	3.28	0.02	0.64
CoMoS ₂ : 0.5 h	34.91	96.17	89.51	27.82	29.59	6.23	12.07	2.54	6.66
CoMoS ₂ : 1.0 h	42.67	99.99	95.36	47.58	42.10	8.30	15.61	2.70	7.87
CoMoS ₂ : 1.5 h	49.52	99.99	97.32	65.09	52.70	12.01	21.27	2.98	10.37
CoMoS ₂ : 2.0 h	55.71	99.99	98.69	80.75	62.00	17.76	27.14	4.20	12.57
CoMoS ₂ : k / 10 ⁻¹ h ⁻¹	3.6	N/D	N/D	4.8	3.2	0.60	1.0	0.12	0.40
NiMoS ₂ : 0.0 h	20.64	87.70	64.98	11.99	14.76	1.05	4.81	1.70	1.98
NiMoS ₂ : 0.5 h	41.06	93.16	92.69	40.48	41.01	9.28	15.59	1.99	6.45
NiMoS ₂ : 1.0 h	53.14	93.75	95.47	73.24	60.11	18.82	25.59	3.25	9.30
NiMoS ₂ : 1.5 h	61.40	96.96	96.53	87.88	69.17	34.00	38.34	3.83	14.33
NiMoS ₂ : 2.0 h	67.69	97.98	96.80	97.96	73.59	50.27	51.22	9.29	21.87
NiMoS ₂ : k / 10 ⁻¹ h ⁻¹	4.3	N/D	N/D	5.9	5.4	1.4	2.2	0.21	0.80

$$^a \text{Total HDS conversion (\%)} = \left[1 - \frac{\text{Sulfur in product (wt\%)}}{\text{Sulfur in feed (wt\%)}} \right] \times 100$$

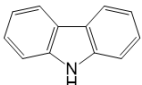
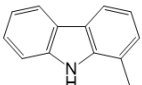
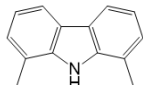
$$^b \text{Sulfur Group 1 HDS conversion (\%)} = \left[1 - \frac{\text{SG 1 in product (wt\%)}}{\text{SG 1 in feed (wt\%)}} \right] \times 100$$

$$^c \text{Sulfur Group 2 HDS conversion (\%)} = \left[1 - \frac{\text{SG 2 in product (wt\%)}}{\text{SG 2 in feed (wt\%)}} \right] \times 100$$

$$^d \text{Sulfur Group 3 HDS conversion (\%)} = \left[1 - \frac{\text{SG 3 in product (wt\%)}}{\text{SG 3 in feed (wt\%)}} \right] \times 100$$

$$^e \text{Sulfur Group 4 HDS conversion (\%)} = \left[1 - \frac{\text{SG 4 in product (wt\%)}}{\text{SG 4 in feed (wt\%)}} \right] \times 100$$

Table S6. Group of N compounds in LCO and hydrotreated LCO at 613K

	^a Total HDN Conversion / %	^b Nitrogen Group 2 HDN conversion / %		^c Nitrogen Group 3 HDN conversion / %		^d Nitrogen Group 4 HDN conversion / %	
			Total Group 2		Total Group 3		Total Group 4
CoMoS ₂ : 0.0 h	0.82	0.51	0.99	0.27	0.55	0.37	0.52
CoMoS ₂ : 0.5 h	2.02	0.94	2.64	0.58	1.07	0.44	0.89
CoMoS ₂ : 1.0 h	3.22	1.86	4.42	0.94	1.39	0.57	1.03
CoMoS ₂ : 1.5 h	4.89	4.57	6.70	2.91	2.20	0.84	1.21
CoMoS ₂ : 2.0 h	5.97	5.53	8.24	3.29	2.59	1.02	1.44
CoMoS ₂ : k (10 ⁻² h ⁻¹)	1.80	2.40	3.00	1.20	0.60	0.24	0.30
NiMoS ₂ : 0.0 h	1.44	8.31	4.92	3.53	4.43	0.01	0.90
NiMoS ₂ : 0.5 h	8.31	21.12	16.00	14.97	14.14	0.13	6.64
NiMoS ₂ : 1.0 h	13.22	30.19	25.20	19.49	20.25	0.55	9.48
NiMoS ₂ : 1.5 h	20.73	41.51	29.92	24.29	23.71	1.01	11.10
NiMoS ₂ : 2.0 h	24.27	46.20	34.50	27.18	27.12	2.13	13.16
NiMoS ₂ : k (10 ⁻² h ⁻¹)	10.20	20.40	13.80	10.20	10.20	0.60	4.80

$$^a \text{ Total HDN conversion (\%)} = \left[1 - \frac{\text{Nitrogen in product (wt\%)}}{\text{Nitrogen in feed (wt\%)}} \right] \times 100$$

$$^b \text{ Nitrogen Group 2 HDN conversion (\%)} = \left[1 - \frac{\text{NG2 in product (wt\%)}}{\text{NG2 in feed (wt\%)}} \right] \times 100$$

$$^c \text{ Nitrogen Group 3 HDN conversion (\%)} = \left[1 - \frac{\text{NG3 in product (wt\%)}}{\text{NG3 in feed (wt\%)}} \right] \times 100$$

$$^d \text{ Nitrogen Group 4 HDN conversion (\%)} = \left[1 - \frac{\text{NG4 in product (wt\%)}}{\text{NG4 in feed (wt\%)}} \right] \times 100$$

Table S7. Rate constants during HDN of CBZ and HDS of DBT over the NiMoS

Reaction	Rate constants (k_{1N}) of 100ppmN CBZ / h^{-1}	Rate constants (k_{2N}) of 500ppmS DBT / h^{-1}	Rate constants (k_{3N}) of 100ppmN CBZ & 500ppmS DBT / h^{-1}	Rate of change / %
CBZ \rightarrow THC (k_{11})	3.30	-	2.46	-25.45
THC \rightarrow BCH (k_{12})	4.08	-	1.08	-73.53
THC \rightarrow CHA (k_{13})	0.84	-	0.36	-57.14
CHA \rightarrow CHB (k_{14})	9.66	-	3.00	-68.94
CHB \rightarrow BCH (k_{15} , k_{23} , k_{33})	2.82	0.9	2.76	-
DBT \rightarrow BP (k_{21})	-	12.9	11.10	-13.95
BP \rightarrow CHB (k_{22})	-	3.42	1.02	-70.18