Supporting Information

Self-assembly of hierarchically porous ZSM-5/SBA-16 with different morphologies and its high isomerization performance for hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene

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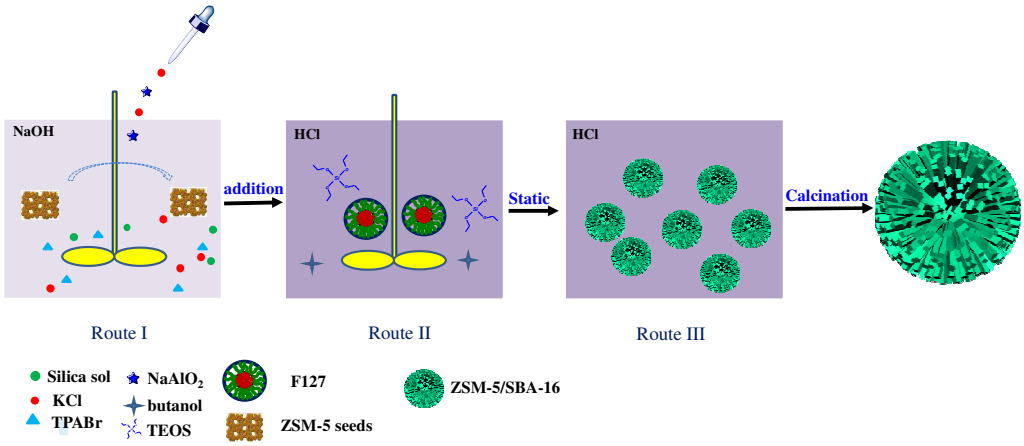

Scheme S1. Preparation of ZSM-5/SBA-16 composite materials with different morphologies.

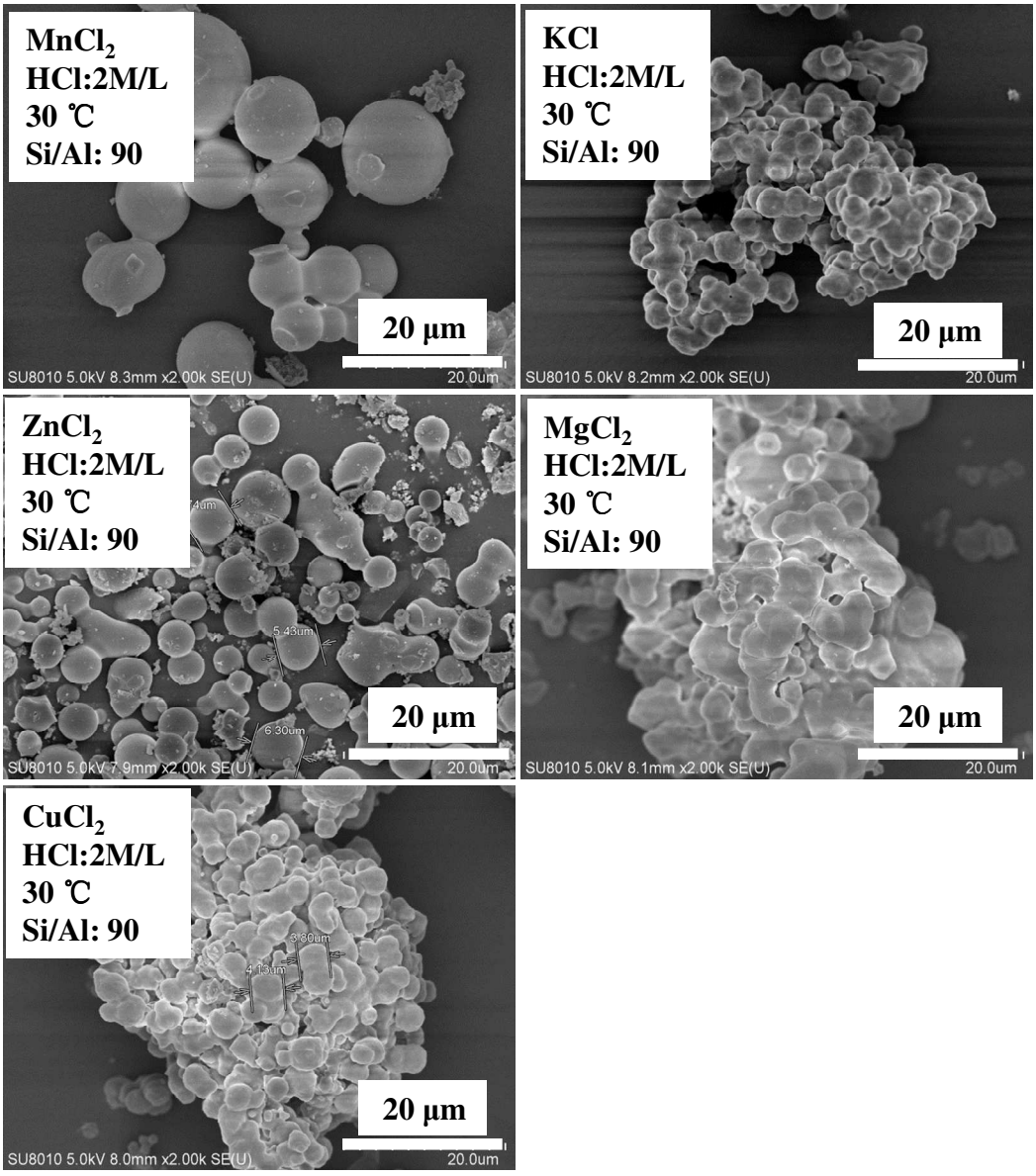

Figure S1. SEM images of the series ZS materials by modulating different inorganic salts.

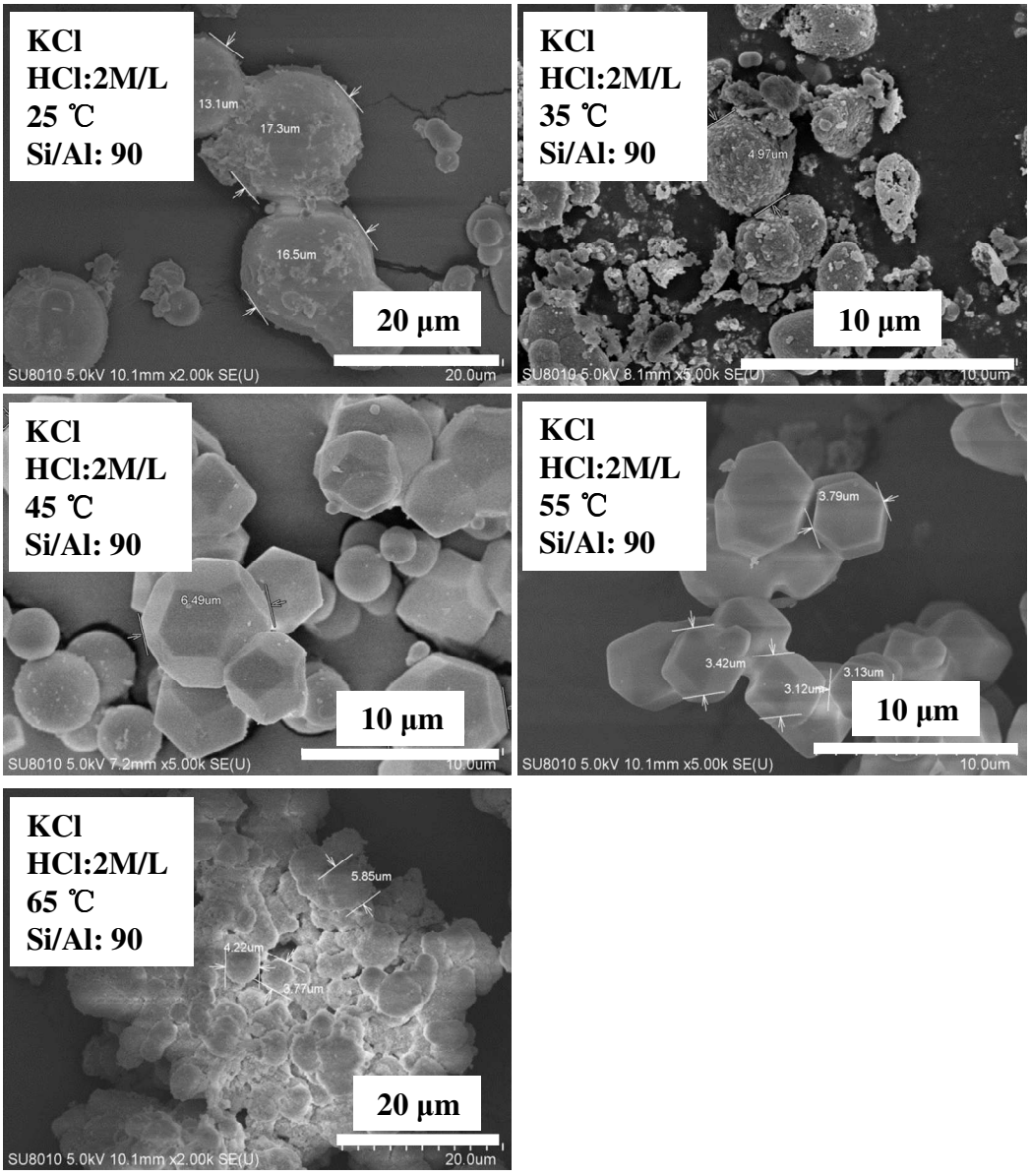

Figure S2. SEM images of the series ZS materials by modulating different aging temperatures.

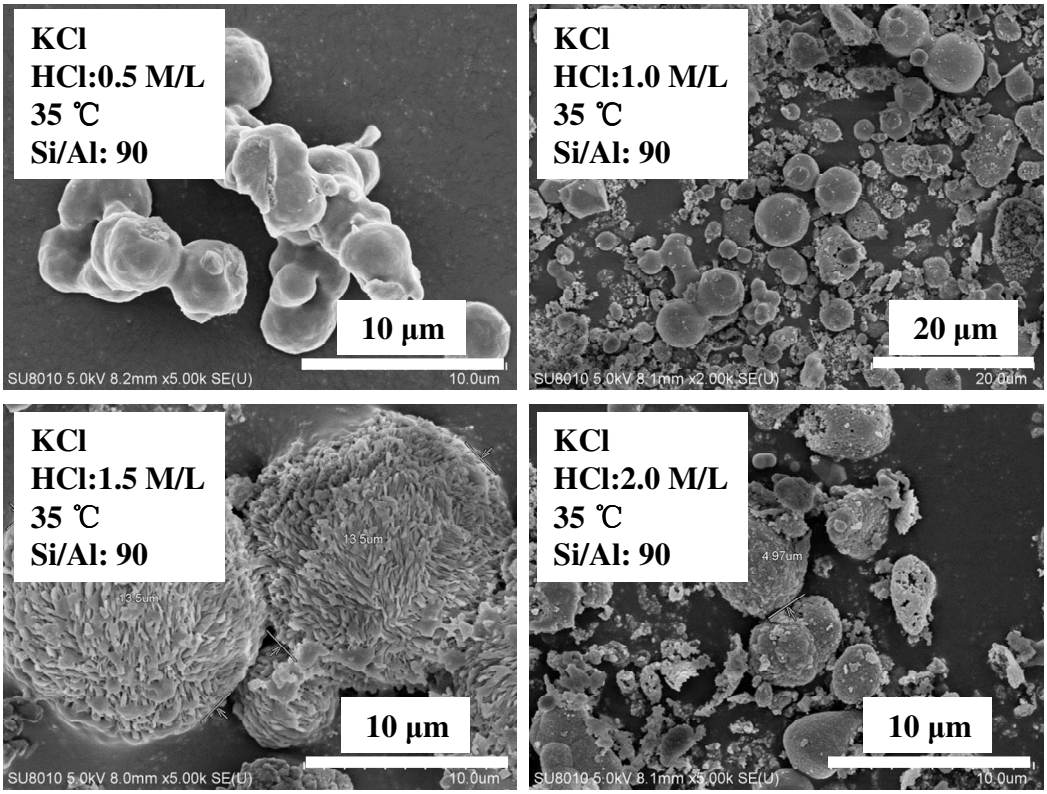

Figure S3. SEM images of the series ZS materials by modulating different concentrations of HCl.

Table S1. Chemicals needed in the experiments.

Drug names	Formula	Grade	Manufacture factory
	NaOH	AR	Sinopharm Chemical Reagent
	HCl	AR	Sinopharm Chemical Reagent
	$NaAlO_2$	AR	Sinopharm Chemical Reagent
TEOS	$Si(OC_2H_5)_4$	AR	Sinopharm Chemical Reagent
	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	AR	Sinopharm Chemical Reagent
	$Ni(NO_3)_2\cdot 6H_2O$	AR	Sinopharm Chemical Reagent
DBT	$C_{12}H_8S$	99 wt%	Adamas-beta Reagent Co. Ltd.
4,6-DMDBT	$C_{14}H_{12}S$	99 wt%	Adamas-beta Reagent Co. Ltd.
F127	$EO_{106}PO_{70}EO_{106}$	AR	Sigma-Aldrich Reagent Co. Ltd.

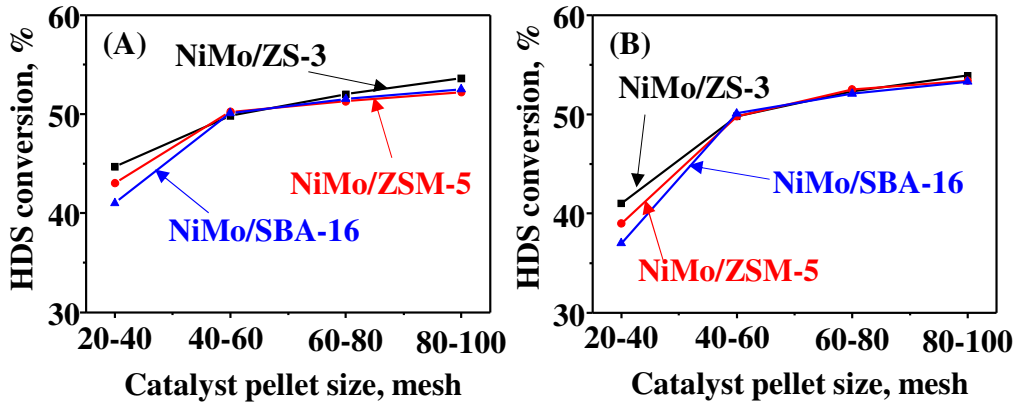

Figure S4. Relationship between desulfurization efficiency and particle size

(A) HDS of DBT; (B) HDS of 4,6-DMDBT

The reaction conditions were the conditions which could obtain the DBT and 4,6-DMDBT HDS conversions of 50%. According to our previous work (Ind. Eng. Chem. Res. 2017, 56, 10018-10027), the internal diffusion, the channeling effect, heat transfer effect, axial diffusion effect and axial heat conduction effect can all be ignored in this DBT and 4,6-DMDBT HDS reaction systems. When the particle size is less than 40-60 mesh, the DBT and 4,6-DMDBT HDS conversions show little change, indicating that the effect of the internal diffusion can be eliminated. Therefore, in this DBT and 4,6-DMDBT HDS reaction systems, at the DBT and 4,6-DMDBT HDS conversions of about 50%, the mass transfer can all be ignored.

Table S2. Textural properties of the series ZS supports.

Samples	S_{BET} (m^2 g^{-1})	V_{mes} (cm^3 g^{-1})	d_{BJH} (nm)
ZS-1	647.42	0.41	4.16
ZS-2	747.61	0.51	4.19
ZS-3	751.96	0.52	4.23
ZS-4	768.21	0.54	4.30
ZS-5	792.62	0.56	4.31
SBA-16	842.16	0.66	4.05
NiMo/ZS-1	432.27	0.36	4.11
NiMo/ZS-2	468.74	0.42	4.12
NiMo/ZS-3	483.29	0.43	4.14
NiMo/ZS-4	489.16	0.43	4.15
NiMo/ZS-5	497.58	0.46	4.17

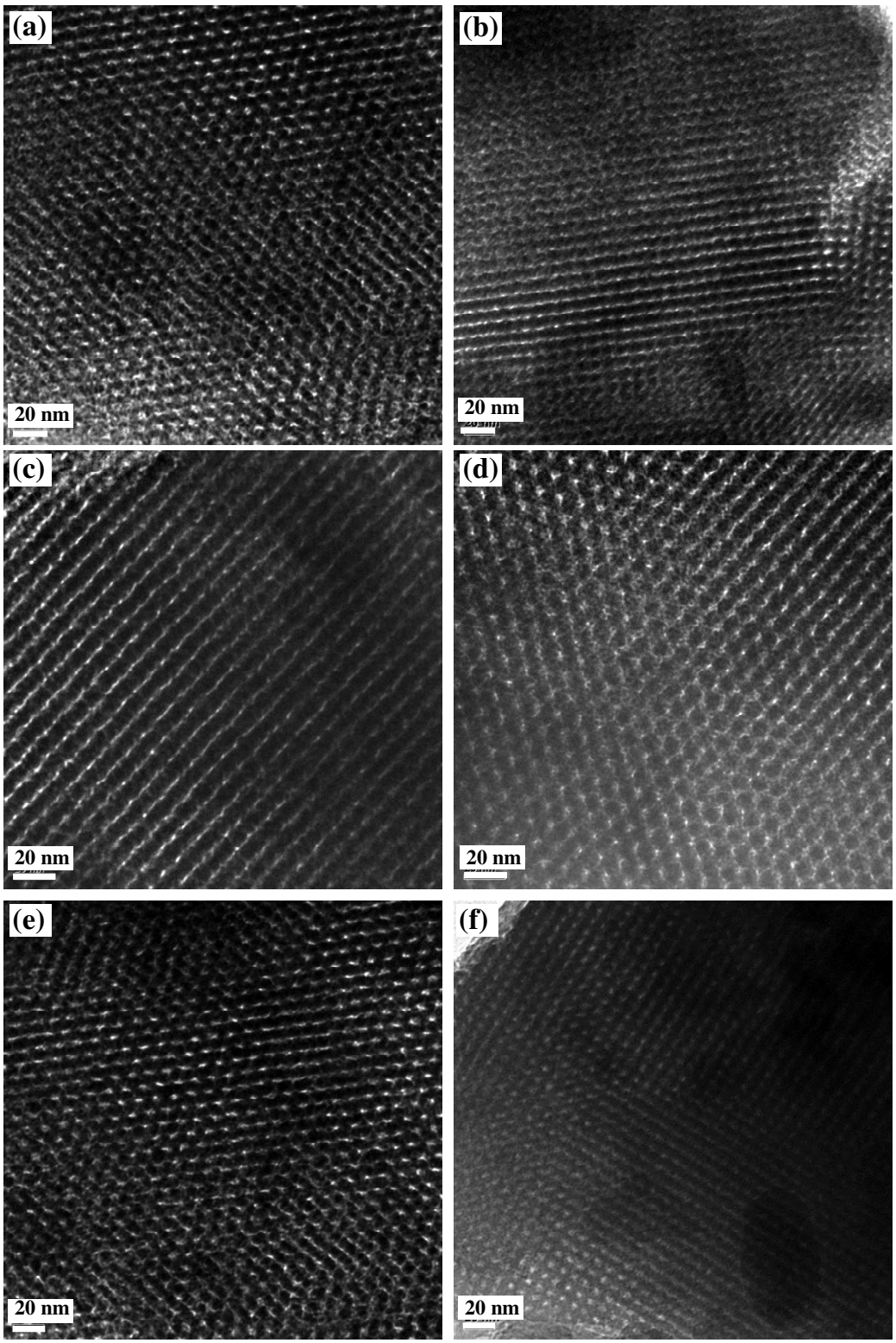

Figure S5. TEM images of the series ZS and pure SBA-16 supports. (a) ZS-1, (b) ZS-2, (c) ZS-3, (d) ZS-4, (e) ZS-5, (f) SBA-16.

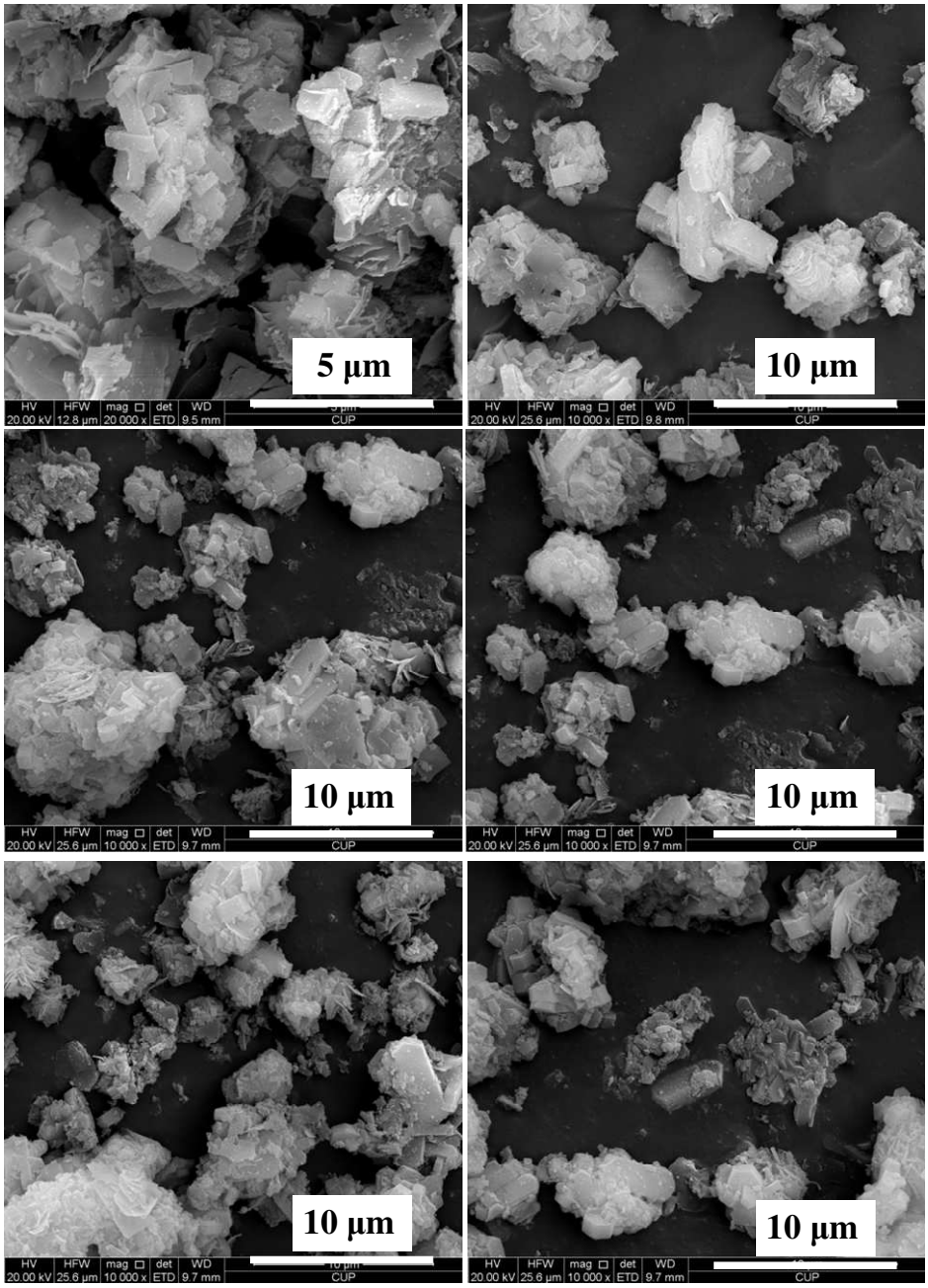

Figure S6. SEM images of pure ZSM-5 zeolite.

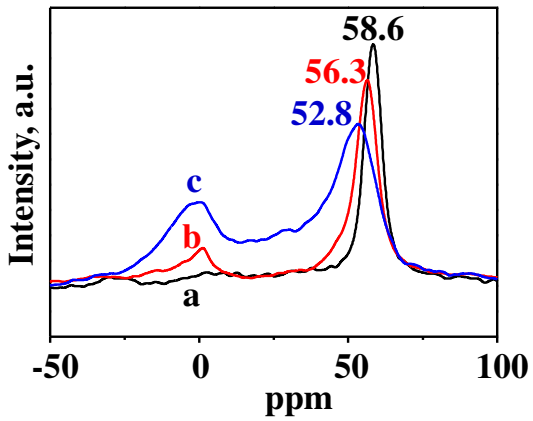

Figure S7. ^{27}Al NMR spectra of the series materials. (a) ZSM-5, (b) ZS-3, (c) Al-SBA-16.

Al-SBA-16 materials with the Si/Al molar ratio of 20 were synthesized by the post alumination synthesized method using the pure mesoporous silicas SBA-16 as precursor material.

^{27}Al MAS NMR spectra were obtained to study the coordination information of Al atoms. The signal centered at about 54 ppm was assigned to the tetrahedral (framework Al species) coordinated aluminum atoms. [1] As shown in Figure S7 (a), the signal centered at 58.6 ppm was assigned to the Al atoms incorporated into the framework of the pure ZSM-5 zeolite. The signal centered at 52.8 ppm (Figure S7 (c)) was assigned to the Al atoms incorporated into the framework of the SBA-16 material. For the ZS-3 composite material (Figure S7 (b)), the chemical shift (56.3 ppm) was between 52.8 ppm and 58.6 ppm, indicating that partial Al species were introduced in the SBA-16 framework. The incorporation of the Al atoms into the SBA-16 framework resulted in the changes of the B/L ratios.

(1) Hannus, I.; Kónya, Z.; Nagy, J.; Lentz, P.; Kiricsi, I. Appl. Catal. B **1998**, 17, 157-166.

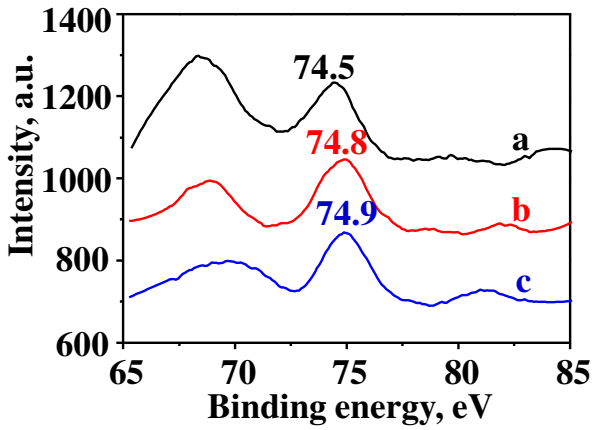

Figure S8. Al 2p XPS spectra of the series catalysts. (a) NiMo/ZSM-5, (b) NiMo/ZS-3, (c) NiMo/Al-SBA-16.

Al-SBA-16 materials with the Si/Al molar ratio of 20 were synthesized by the post alumination synthesized method using the pure mesoporous silicas SBA-16 as precursor material.

Furthermore, XPS was used for measuring the chemical state of the surface chemical composition. For Al 2p spectra, the binding energy at about 74.5 eV related to Al species that were bonded to ZSM-5 zeolite or SBA-16 material.[2] For the ZS-3 composite material (Figure S8 (b)), the binding energy (74.8 eV) was between 74.5 eV and 74.9 eV, indicating that partial Al species were introduced in the SBA-16 framework, which was in accordance with the ^{27}Al MAS NMR spectra.

(2) Sánchez-Sánchez, M.; Navarro, R.; Fierro, J. Int. J. Hydrogen Energy **2007**, 32, 1462-1471.

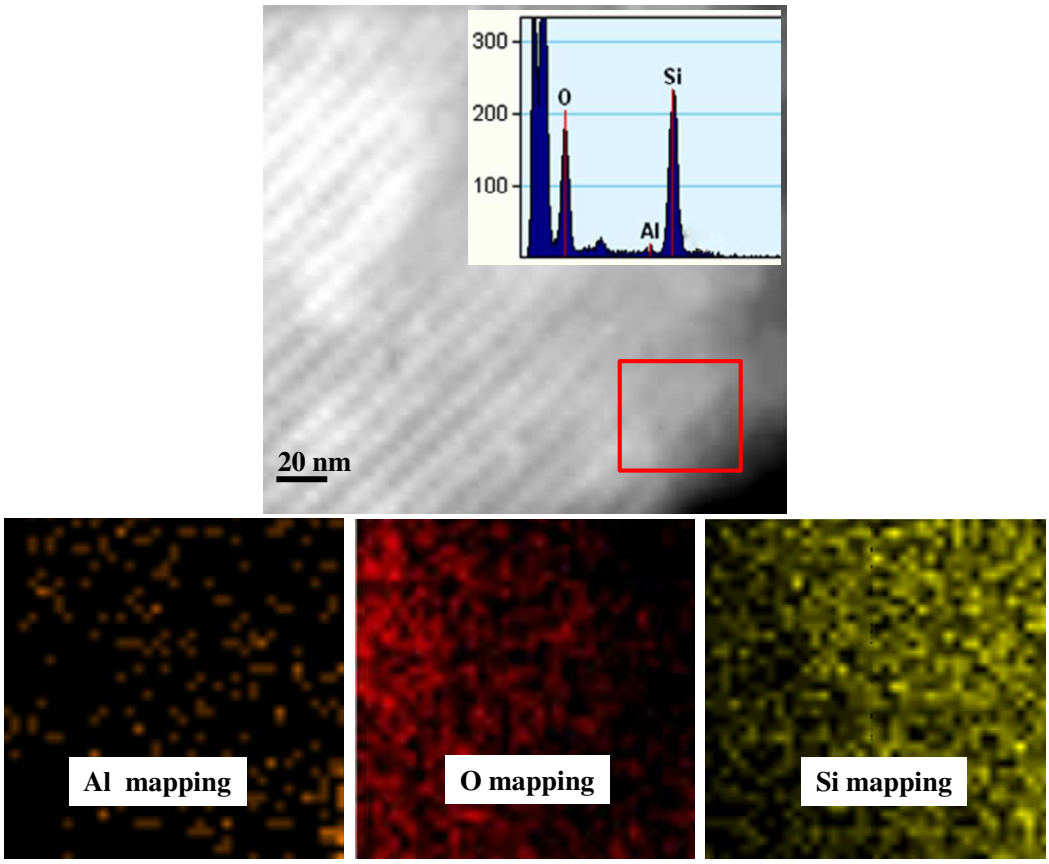

Figure S9. HAADF-STEM and EDX elemental mapping images of ZS-3.

In addition, the Al mapping image (Figure S9) of ZS-3 material showed that the Al element was widely distributed in ZSM-5/SBA-16 composite material, revealing that the primary and secondary building units of ZSM-5 zeolites were the construction units of ZSM-5/SBA-16.

Table S3. B and L acid amounts obtained from series oxide catalysts.

Catalysts	Amount of acid sites (μmol g^{-1})							
	200 °C				350 °C			
	L	B	L+B	B/L	L	B	L+B	B/L
NiMo/ZS-1	173	35	208	0.20	111	22	133	0.20
NiMo/ZS-2	159	33	192	0.21	75	16	91	0.21
NiMo/ZS-3	134	31	165	0.23	52	13	65	0.25
NiMo/ZS-4	124	21	145	0.17	42	8	50	0.19
NiMo/ZS-5	115	16	131	0.14	22	4	26	0.18
NiMo/ZSM-5	192	47	239	0.24	133	37	170	0.28

Table S4. Mo3d XPS results obtained from series sulfide catalysts.

Catalysts	Mo^{4+}		Mo^{5+}		Mo^{6+}		S_{Mo} [b]
	ar. % [a] (229.1 eV)	ar.% (232.2 eV)	ar. % (230.1 eV)	ar. % (233.2 eV)	ar.% (232.5 eV)	ar.% (235.6 eV)	
NiMo/ZS-1	34	22	3	2	23	16	56
NiMo/ZS-2	38	25	2	1	21	13	63
NiMo/ZS-3	41	28	0	0	19	12	69
NiMo/ZS-4	32	22	4	3	24	16	54
NiMo/ZS-5	31	21	8	5	21	14	52
NiMo/ZS-M	30	19	12	8	19	12	49

Note: [a] ar. % means the area percent of XPS peak.

[b] $S_{Mo}= Mo_{sulfidation} = Mo^{4+}/(Mo^{4+}+Mo^{5+}+Mo^{6+})$.

Table S5. Ni2p XPS results obtained from the sulfide NiMo catalysts.

Catalysts	NiMoS		NiS_x		Ni (II)	
	BE (eV)	ar.%	BE (eV)	ar. %	BE (eV)	ar.%
NiMo/ZS-1	855.2	81.6	853.1	8.2	857.2	10.2
NiMo/ZS-2	855.3	87.6	853.2	5.1	857.2	7.8
NiMo/ZS-3	855.1	91.3	853.2	3.2	857.1	5.5
NiMo/ZS-4	855.3	76.1	853.2	9.7	857.2	14.2
NiMo/ZS-5	855.2	71.5	853.1	11.3	857.2	17.2
NiMo/ZS-M	855.1	66.2	853.2	14.5	857.3	19.3

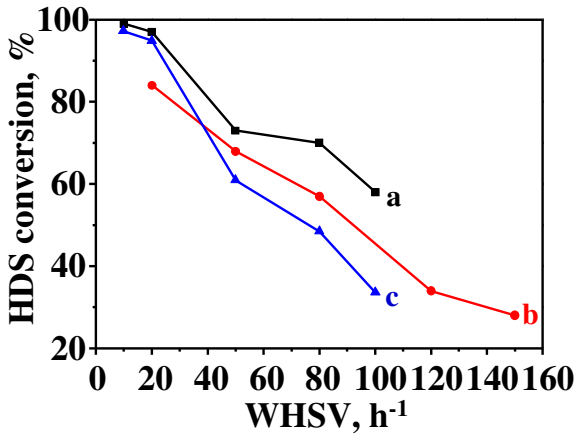

Figure S10. DBT HDS results at different WHSVs (340 °C, 4 MPa, 200 mL/mL).

(a) NiMo/ZS-3, (b) NiMo/Al-SBA-16 and (c) NiMo/Al_2O_3.

The as-obtained NiMo/Al-SBA-16 catalysts were from that NiMo/S-38 reported in the literature (Chemical Engineering Science 155, 2016, 141-152) and the commercial Al_2O_3 catalysts were obtained from Aluminum Corporation of China Limited.

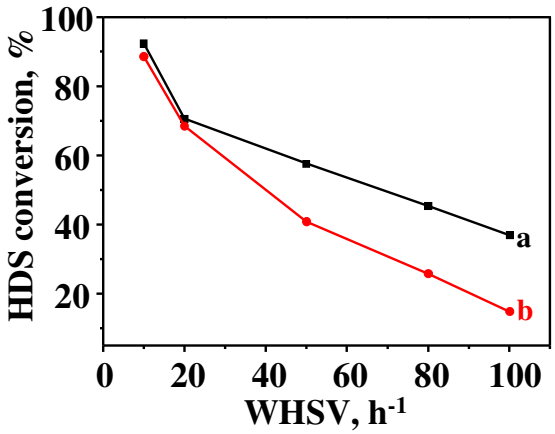

Figure S11. 4,6-DMDBT HDS results at different WHSVs (340 ^{o}C, 4 MPa, 200 mL/mL).

(a) NiMo/ZS-3 and (b) NiMo/Al_2O_3.

The commercial Al_2O_3 catalysts were obtained from Aluminum Corporation of China Limited.

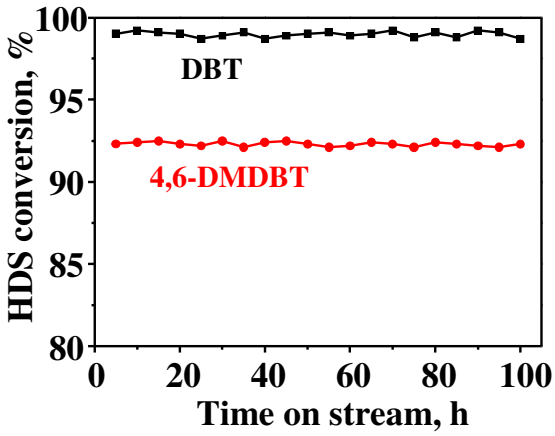

Figure S12. DBT and 4,6-DMDBT HDS results with time on stream over NiMo/ZS-3 (340 ^{o}C, 4 MPa, 200 mL/mL and 10 h^{-1}).

The long-period (100 h) DBT and 4,6-DMDBT HDS reactive experiments were complemented. The HDS results of DBT and 4,6-DMDBT with long time on stream over NiMo/ZS-3 catalyst (@340 ^{o}C, 4 MPa, 200 mL/mL and 10 h^{-1}). From Figure S5, the DBT and 4,6-DMDBT HDS desulfurization degree were maintain at 98.7 and 92.3 at 100 h, indicating that the NiMo/ZS-3 catalyst possessed good DBT and 4,6-DMDBT HDS catalytic stabilities.

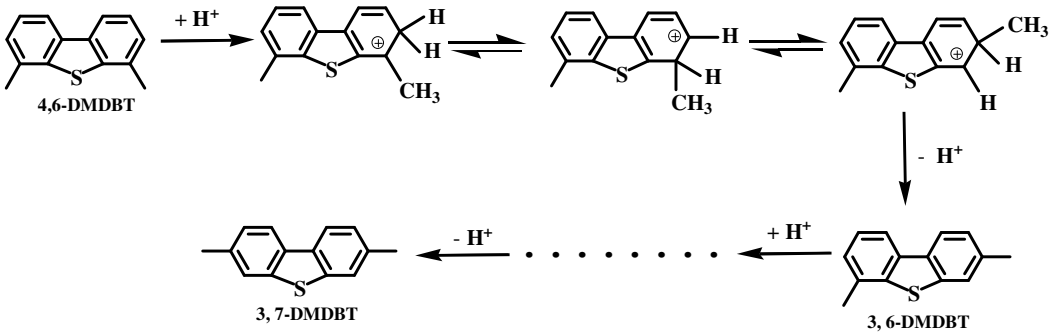

Figure S13. ISO of 4,6-DMDBT to 3,7-DMDBT over acidic catalyst.

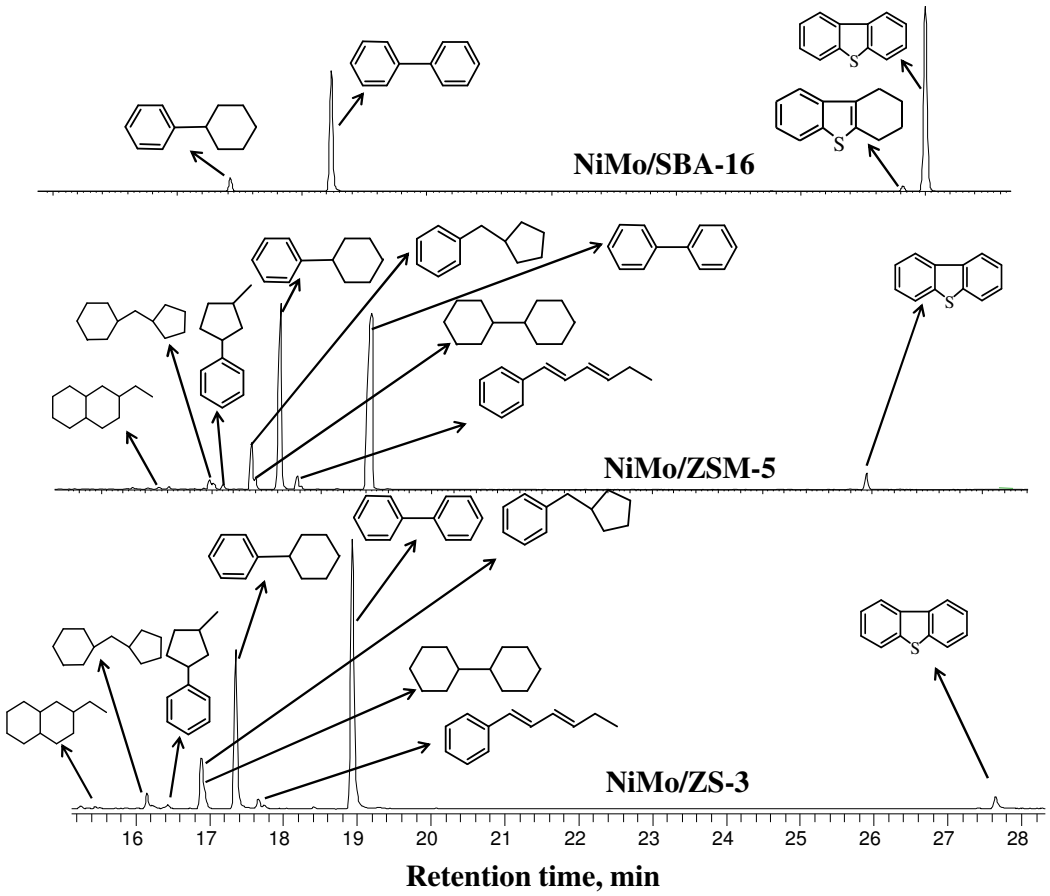

Figure S14. The DBT HDS product distributions over various catalysts.

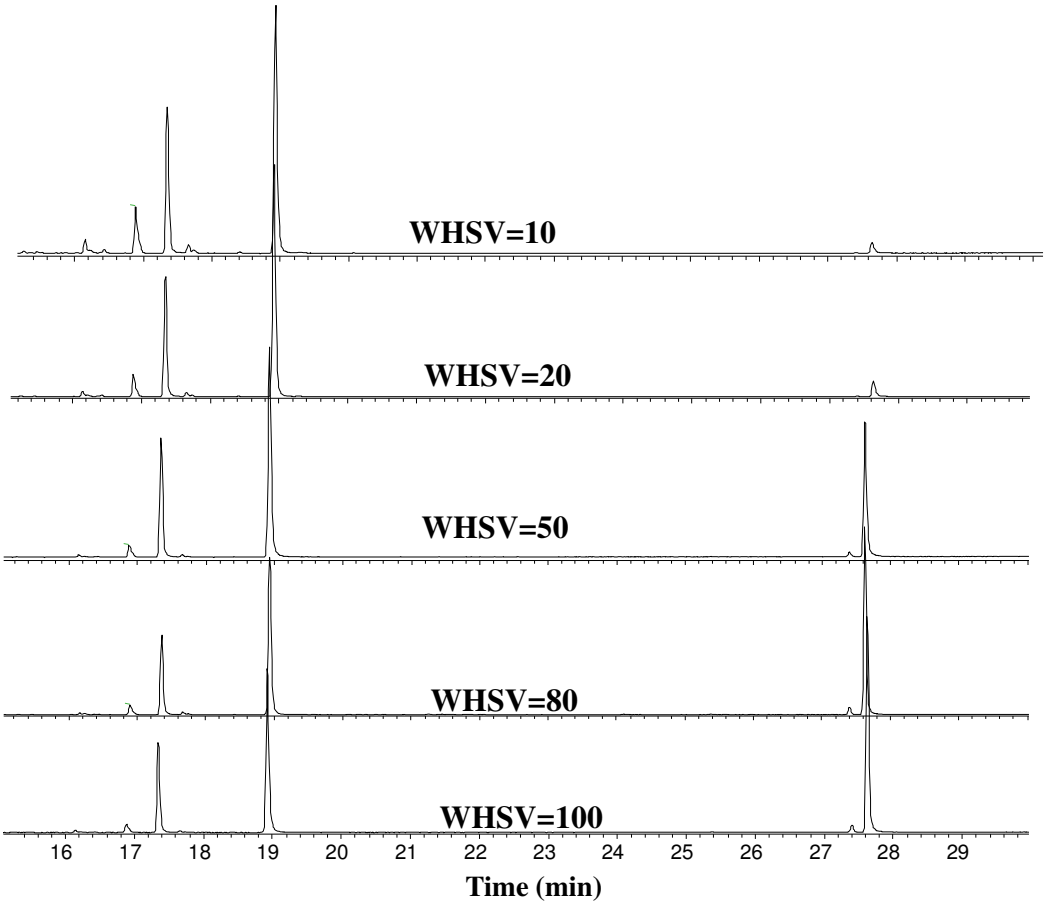

Figure S15. The DBT HDS product distributions over NiMo/ZS-3 at different WHSVs.

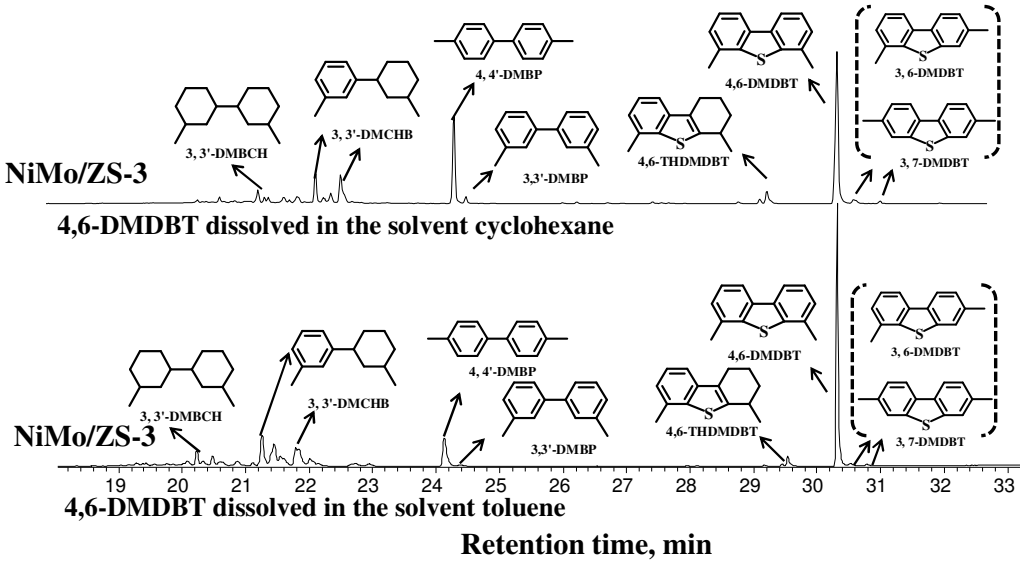

Figure S16. 4,6-DMDBT HDS product distributions of NiMo/ZS-3.

The toluene and methyl cyclohexane were not detected in the 4,6-DMDBT HDS over NiMo/ZS-3 catalyst.

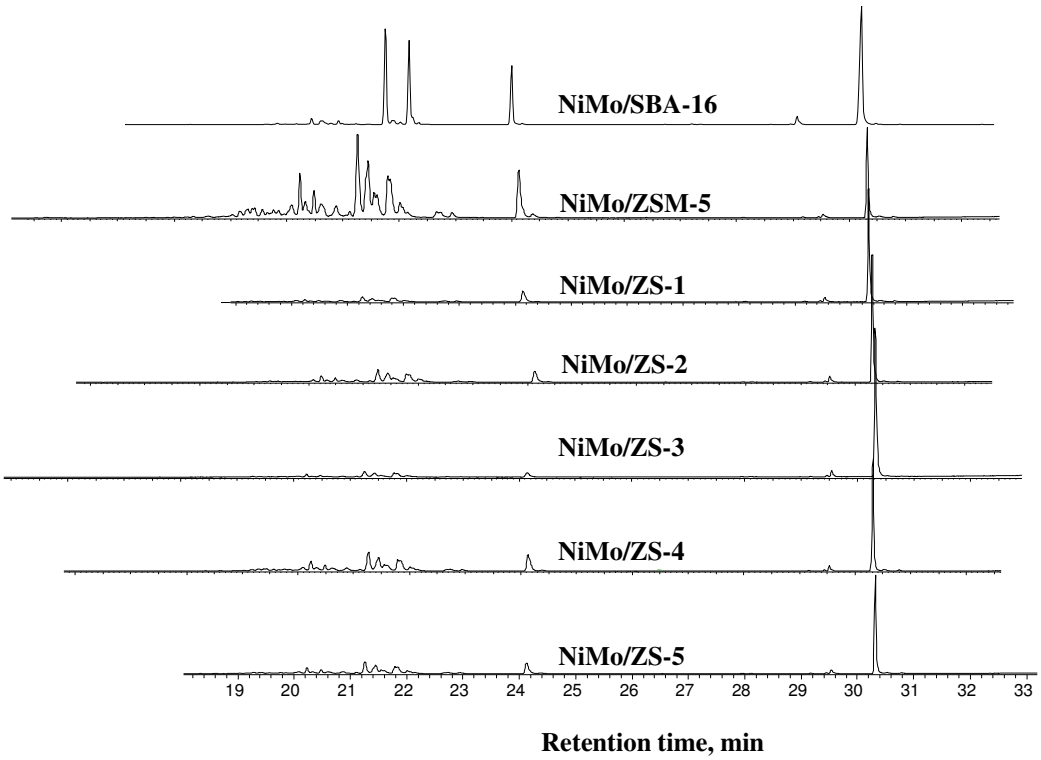

Figure S17. 4,6-DMDBT HDS product distributions of various catalysts.

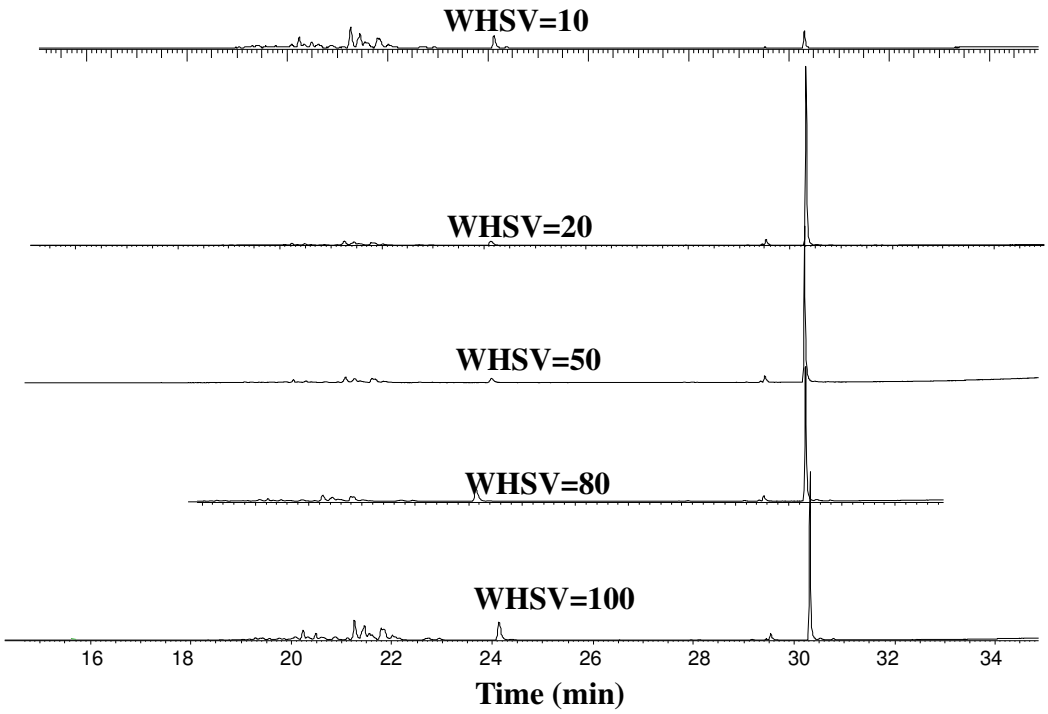

Figure S18. 4,6-DMDBT HDS product distributions of NiMo/ZS-3 at different WHSVs.