Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information (ESI) for:

Insight into the effect of non-stoechiometric sulfur over NiMoS hydrodesulfurization catalyst

Weikun Lai, Yingrui Xu, Yuhong Ren, Lefu Yang, Jinbao Zheng, Xiaodong Yi* and Weiping Fang*

National Engineering Laboratory for Green Chemical Productions of Alcohols-ethers-esters, State Key Laboratory for Physical Chemistry of the Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. Fax/Tel: +86-592-2186291; E-mail: wpang@xmu.edu.cn; xdyi@xmu.edu.cn.

Results

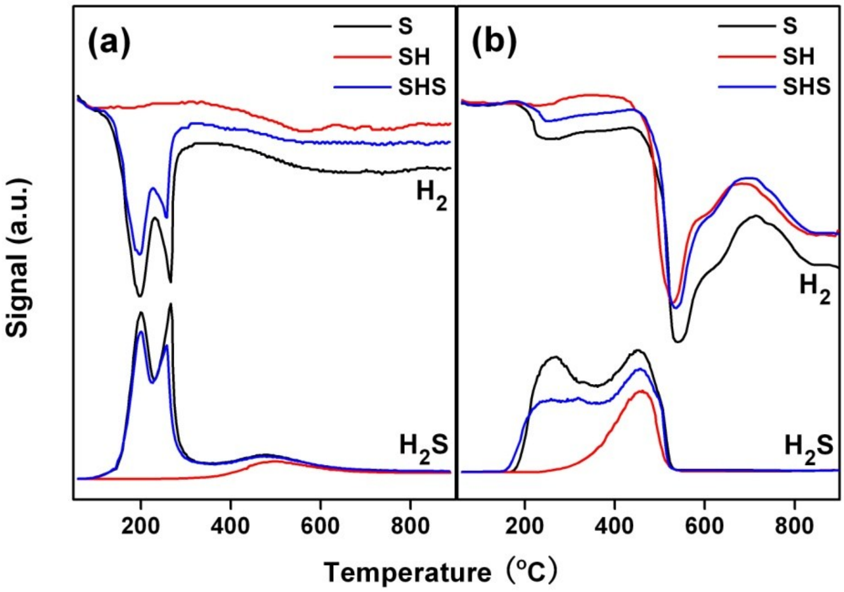

Fig. S1 Temperature-programmed reduction curves (mass spectrometry detection) of sulfide $NiMo/Al_2O_3$ (a) and NiMo (b) samples. -S: sulfide, -SH: reduced after presulfidation, -SHS: sulfurized again after presulfidation and reduction.

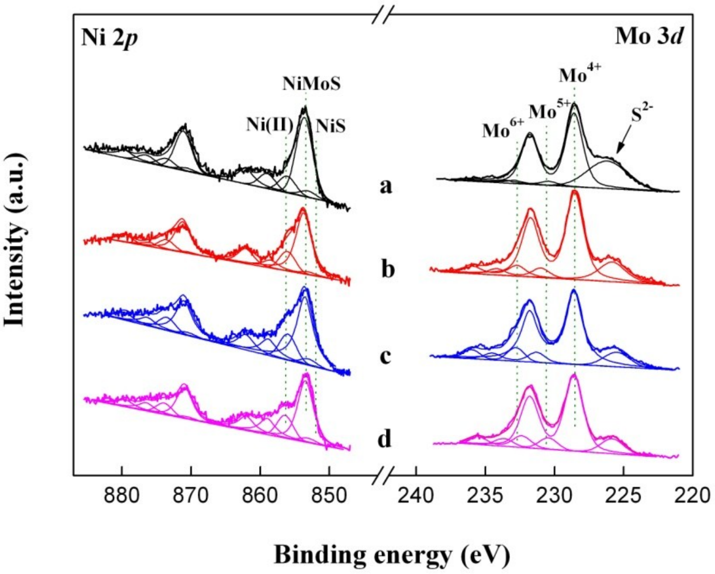

Fig. S2 Ni 2*p* and Mo3*d* XPS spectra of the $NiMo/Al_2O_3$ catalysts and their decomposition. (a: NiMoAl-S, b: NiMoAl-S-spent, c: NiMoAl-SH, d: NiMoAl-SH-spent)

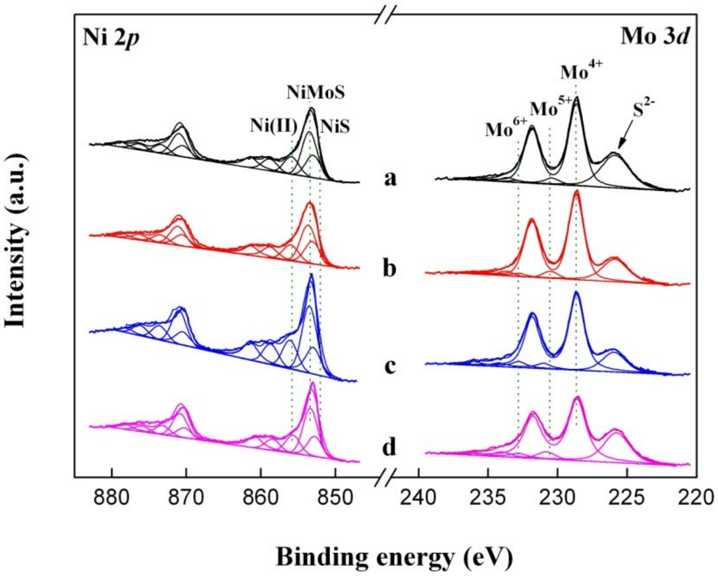

Fig. S3 Ni 2*p* and Mo3*d* XPS spectra of the NiMo catalysts and their decomposition.

(a: NiMo-S, b: NiMo-S-spent, c: NiMo-SH, d: NiMo-SH-spent)

Ni 2*p* and Mo 3*d* XPS spectra of the samples are shown in Fig. S2 and Fig. S3, and the decomposition results can be seen in Table S1 and Table S2. It can be observed that molybdenum can exist as MoS_2 (Mo^{4+}), which is located at 228.6±0.1 eV. Mo^{6+} species located at 232.8±0.2 eV is obviously a Mo oxide species that has not been sulfurized. The last phase is an intermediate state Mo oxysulfide (MoO_xS_y, Mo^{5+}), which appears at 230.6±0.2 eV. Otherwise, a broad peak at 226.0 eV is assigned to S 2*s* and subtracted from the total spectrum of Mo 3*d*. As shown in Fig. S2 and Fig. S3, Ni $2p_{3/2}$ binding energy is 853.6±0.1 eV, which corresponds to Ni in the Ni-Mo-S structure. The peak at 856.1±0.2 eV corresponds to Ni(II) oxide species ($NiAl_2O_4$, NiO_x), Ni also may exist as NiS_x (Ni_3S_2, Ni_9S_8, NiS), which is located at 853.0±0.1 eV. The remaining two broad peaks to the envelopes are satellite lines of the corresponding Ni species.

Table S1 XPS parameters of the different contributions of Mo 3*d* obtained for the sulfide NiMo/Al_2O_3 and unsupported NiMo catalysts

Sample	Mo^{IV}		Mo^{V}		Mo^{VI}	
	BE (eV)	%atom.	BE (eV)	%atom.	BE (eV)	%atom.
NiMoAl-S	228.6	90.1	230.4	5.3	232.9	4.6
NiMoAl-S-spent	228.6	81.1	231.0	8.4	232.7	10.5
NiMoAl-SH	228.6	80.3	231.0	9.3	232.8	10.4
NiMoAl-SH-spent	228.6	78.5	230.5	10.2	232.6	11.3
NiMo-S	228.7	89.5	230.4	7.8	232.9	2.7
NiMo-S-spent	228.7	89.4	230.5	6.3	232.8	4.3
NiMo-SH	228.6	85.4	231.0	7.0	232.8	7.6
NiMo-SH-spent	228.6	84.9	230.8	8.6	232.8	6.5

Table S2 XPS parameters of the different contributions of Ni 2*p* obtained for the sulfide NiMo/Al_2O_3 and unsupported NiMo catalysts

Sample	NiMoS		NiS_x		Ni (II)	
	BE (eV)	%atom.	BE (eV)	%atom.	BE (eV)	%atom.
NiMoAl-S	853.6	77.1	853.1	7.0	856.1	15.9
NiMoAl-S-spent	853.7	76.8	853.0	4.2	856.1	19.1
NiMoAl-SH	853.6	74.7	853.0	4.9	856.0	20.4
NiMoAl-SH-spent	853.5	73.3	853.1	4.4	856.3	22.3
NiMo-S	853.5	53.2	853.0	26.3	855.9	20.5
NiMo-S-spent	853.6	51.9	853.1	26.6	856.0	21.5
NiMo-SH	853.4	52.3	852.9	25.6	856.0	22.2
NiMo-SH-spent	853.5	53.7	852.9	24.6	855.8	21.7

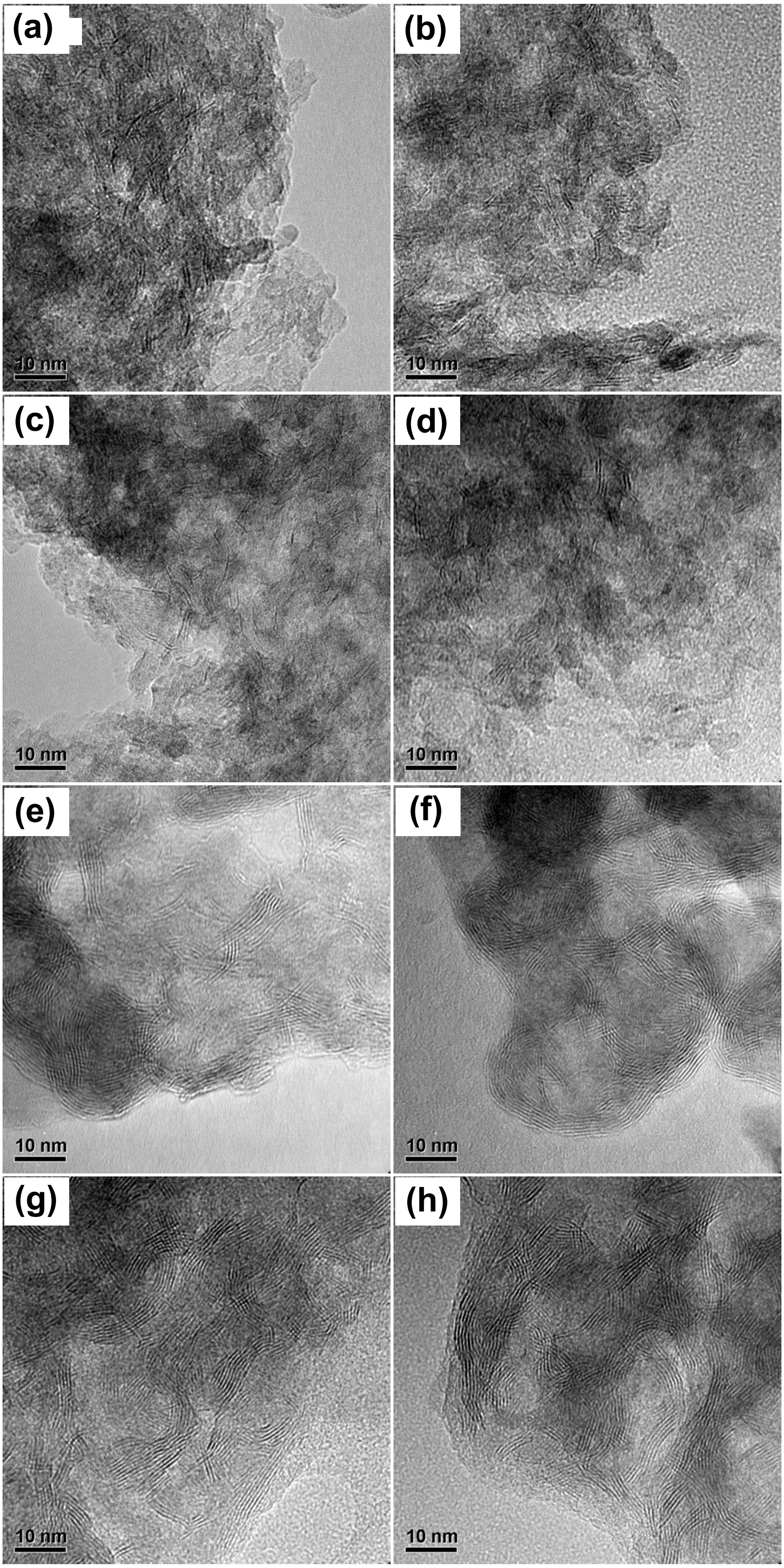
(a)
10 nm
(b)
10 nm
(c)
10 nm
(d)
10 nm
(e)
10 nm
(f)
10 nm
(g)
10 nm
(h)
10 nm

Fig. S4 HRTEM images of: (a) NiMoAl-S, (b) NiMoAl-S-spent, (c) NiMoAl-SH, (d) NiMoAl-SH-spent, (e) NiMo-S, (f) NiMo-S-spent, (g) NiMo-SH, (h) NiMo-SH-spent.

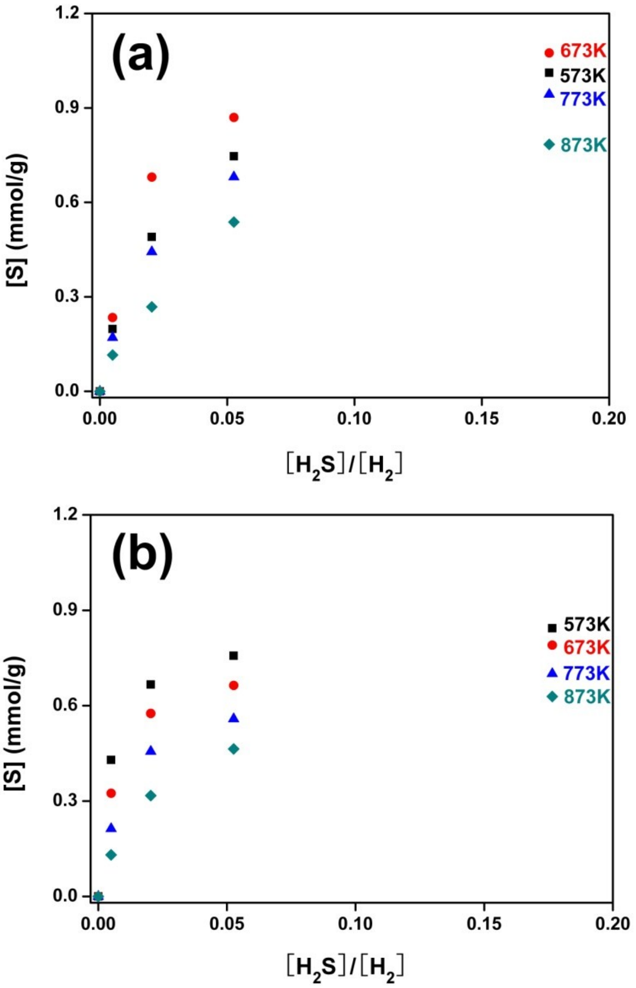

Fig. S5 Equilibrium labile sulfur content of NiMo/Al_2O_3 (a) and NiMo (b) samples measured at different H_2S partial pressure and different temperature.