Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: "Experimental and Computational and Studies of Sulfided NiMo/Al-PILC: Catalyst Activation and Guaiacol Adsorption Sites"

F. Oemry,*[a] I. B. Adilina,[b] W. T. Cahyanto,[c] N. Rinaldi,[b] F. Aulia,[b] A. Jackson,[d] S. F. Parker,[e] A. B. Kroner,[f] E. J. Shotton[f]

[a]Research Center for Quantum Physics, National Research and Innovation Agency, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten 15314, Indonesia
Email: fere001@brin.go.id
[b]Research Center for Advanced Chemistry, National Research and Innovation Agency, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten 15314, Indonesia
[c]Department of Physics, Universitas Jenderal Soedirman, Jl. dr. Soeparno 61, Purwokerto 53122, Indonesia
[d]Scientific Computing Department, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
[e]ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
[f]Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, United Kingdom

Table 1S: Mo K-edge EXAFS fitting parameters of NiMoPILC (*in situ*)

No.	Fitting model	Back scatterer	N	R(Å)	σ^2 (Å^2) x 10^{-3}	R-factor	Time-lapse	temp in ^{o}C
			Stage 4 (Δk= 3 - 11 Å^{-1}, H_2S/H_2/He gasses**)**					
1	$NiMoO_4$	O	2.4 ± 0.4	1.75 ± 0.04	0.31	0.0146	0:24:34	114.4 - 129.1
		O	3.6 ± 0.4	2.26 ± 0.04	18.85			
		Mo	2.0 ± 0.1	3.29 ± 0.01	11.8			
2	$NiMoO_4$	O	2.9 ± 0.4	1.75 ± 0.04	1.44	0.0123	0:27:38	147 - 164.6
		O	3.1 ± 0.4	2.25 ± 0.05	19.79			
		Mo	2.0 ± 0.1	3.28 ± 0.01	13.85			
3	$NiMoO_4$	O	2.8 ± 0.4	1.75 ± 0.04	1.27	0.0118	0:30:43	182.9 - 201.2
		O	3.2 ± 0.4	2.25 ± 0.05	19.69			
		Mo	2.0 ± 0.1	3.28 ± 0.01	14.09			
4	$NiMoO_4$	O	2.8 ± 0.4	1.75 ± 0.04	1.41	0.0111	0:33:47	219.6 - 237.8
		O	3.2 ± 0.4	2.24 ± 0.06	19.8			
		Mo	2.0 ± 0.1	3.28 ± 0.02	14.44			
5	$NiMoO_4$	O	2.7 ± 0.4	1.75 ± 0.04	1.56	0.0108	0:38:23	256.2 - 293.1
		O	3.3 ± 0.4	2.23 ± 0.07	19.54			
		Mo	2.0 ± 0.1	3.27 ± 0.02	15.1			
6	$NiMoO_4$	O	2.8 ± 0.4	1.75 ± 0.04	1.98	0.0105	0:39:55	308.8
		O	3.2 ± 0.4	2.22 ± 0.08	19.5			
		Mo	2.0 ± 0.1	3.27 ± 0.03	15.81			
7	$NiMoO_4$	O	2.9 ± 0.4	1.75 ± 0.04	2.27	0.0102	0:41:27	328.2
		O	3.2 ± 0.4	2.2 ± 0.09	19.21			
		Mo	2.0 ± 0.1	3.26 ± 0.03	16.2			
8	$NiMoO_4$	O	2.9 ± 0.3	1.75 ± 0.04	2.74	0.0115	0:43:00	345.9
		O	3.1 ± 0.3	2.18 ± 0.12	17.17			
		Mo	2.0 ± 0.1	3.25 ± 0.05	17.33			
9	$NiMoO_4$	O	2.9 ± 0.5	1.75 ± 0.04	3.65	0.0198	0:44:32	363.7
		O	3.2 ± 0.5	2.15 ± 0.15	14.29			
		Mo	2.0 ± 0.2	3.22 ± 0.07	17.85			
10	$NiMoO_4$	O	1.9 ± 0.2	1.76 ± 0.05	1.13	0.0057	0:46:04	379.7
		Mo	1.9 ± 0.2	3.27 ± 0.02	14.75			
	Mo_2S_9	S	**1.8**	2.47 ± 0.05	13.15			
		Mo	**0.6**	2.77 ± 0.11	11.32			
11	$NiMoO_4$	O	1.5 ± 0.1	1.76 ± 0.04	0.39	0.0060	0:47:36	396.3
		Mo	1.5 ± 0.1	3.25 ± 0.04	12.93			
	Mo_2S_9	S	**1.6**	2.45 ± 0.03	10.07			
		Mo	**0.5**	2.74 ± 0.08	10.77			
			Stage 5 (Δk= 3 - 11 Å^{-1}, H_2S/H_2/He gasses**)**					
12	$NiMoO_4$	O	0.9 ± 0.3	1.75 ± 0.04	1.81	0.0209	0:56:49	418.1
		Mo	0.9 ± 0.3	3.22 ± 0.07	9.74			
	Mo_2S_9	S	2.9 ± 0.7	2.44 ± 0.03	15.67			
13	$NiMoO_4$	O	0.6 ± 0.3	1.74 ± 0.03	0.87	0.0204	0:58:21	420
		Mo	0.6 ± 0.3	3.20 ± 0.09	7.10			
	Mo_2S_9	S	3.2 ± 0.9	2.43 ± 0.02	15.59			
			(Δk= 3.1 - 11 Å^{-1}, H_2S/H_2/He gasses**)**					
14	Mo-Oxy50	O	**0.4**	1.74 ± 0.05	0.07	0.0209	0:59:53	422.1
	Mo-Bare	S	3.7 ± 0.6	2.44 ± 0.08	15.90			
		Mo	3.7 ± 0.6	3.24 ± 0.09	20.08			
		S	1.9 ± 0.3	3.83 ± 0.07	13.20			

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15	Mo-Oxy50	O	**0.3**	1.72 ± 0.03	0.62	0.0180	1:01:25	423.7
	Mo-Bare	S	4.2 ± 0.6	2.43 ± 0.07	16.31			
		Mo	4.2 ± 0.6	3.23 ± 0.08	20.17			
		S	2.1 ± 0.3	3.90 ± 0.09	13.86			
		(Δk= 3 - 11 Å^{-1}, H_2S/H_2/He gasses**)**						
16	Mo-Oxy50	O	**0.4**	1.73 ± 0.04	1.78	0.0125	1:02:57	423.5
	Bulk MoS_2	S	5.7 ± 0.7	2.44 ± 0.03	20.04			
		Mo	5.7 ± 0.7	3.23 ± 0.08	21.46			
		S	5.7 ± 0.7	3.86 ± 0.11	25.10			
17	Mo-Oxy50	O	**0.4**	1.72 ± 0.02	2.98	0.0135	1:04:29	418.8
	Bulk MoS_2	S	6.0 ± 0.7	2.43 ± 0.01	19.92			
		Mo	6.0 ± 0.7	3.22 ± 0.06	21.93			
		S	6.0 ± 0.7	3.85 ± 0.12	25.83			
18	Mo-Oxy50	O	**0.5**	1.71 ± 0.02	6.47	0.0150	1:06:01	418.1
	Bulk MoS_2	S	6.6 ± 0.9	2.43 ± 0.02	20.46			
		Mo	6.6 ± 0.9	3.22 ± 0.07	21.95			
		S	6.6 ± 0.9	3.85 ± 0.12	26.59			
19	Mo-Oxy50	O	**0.5**	1.71 ± 0.01	7.72	0.0161	1:07:34	420
	Bulk MoS_2	S	6.6 ± 0.9	2.43 ± 0.02	20.08			
		Mo	6.6 ± 0.9	3.21 ± 0.06	21.83			
		S	6.6 ± 0.9	3.85 ± 0.12	26.69			
20	Mo-Oxy50	O	**0.4**	1.69 ± 0.0	5.97	0.0125	1:09:06	419.3
	Bulk MoS_2	S	6.4 ± 0.8	2.43 ± 0.01	19.16			
		Mo	6.4 ± 0.8	3.21 ± 0.06	21.48			
		S	6.4 ± 0.8	3.84 ± 0.12	26.34			
21	Mo-Oxy50	O	**0.4**	1.68 ± 0.02	6.32	0.0135	1:13:42	420.5 - 421.6
	Bulk MoS_2	S	6.3 ± 0.8	2.43 ± 0.02	18.85			
		Mo	6.3 ± 0.8	3.21 ± 0.06	20.80			
		S	6.3 ± 0.8	3.84 ± 0.13	25.66			
		(Δk= 3 – 10 Å^{-1}, H_2S/H_2/He gasses**)**						
22	Bulk MoS_2	S	5.4 ± 0.9	2.42 ± 0.0	15.78	0.0224	1:18:19	421.5 - 422.5
		Mo	5.4 ± 0.9	3.20 ± 0.05	18.91			
		S	5.4 ± 0.9	3.81 ± 0.15	24.53			
23	Bulk MoS_2	S	5.3 ± 0.8	2.42 ± 0.0	15.14	0.0201	1:21:23	420.4 - 421.9
		Mo	5.3 ± 0.8	3.19 ± 0.04	18.69			
		S	5.3 ± 0.8	3.82 ± 0.15	24.41			
24	Bulk MoS_2	S	5.5 ± 0.8	2.42 ± 0.0	15.15	0.0196	1:27:31	420.8 - 423.3
		Mo	5.5 ± 0.8	3.19 ± 0.04	18.28			
		S	5.5 ± 0.8	3.81 ± 0.16	24.54			
		(Δk= 3 – 10.2 Å^{-1}, H_2S/H_2/He gasses**)**						
25	Bulk MoS_2	S	5.3 ± 0.8	2.42 ± 0.0	14.34	0.0202	1:35:12	419.6 - 423.4
		Mo	5.3 ± 0.8	3.19 ± 0.04	17.81			
		S	5.3 ± 0.8	3.81 ± 0.16	24.20			
	Mo-S50	S	5.2 ± 0.7	2.42 ± 0.0	14.44	0.0192		
		Mo	3.5 ± 0.5	3.19 ± 0.04	14.74			
		S	1.7 ± 0.2	3.77 ± 0.28	12.26			
26	Bulk MoS_2	S	5.3 ± 0.7	2.42 ± 0.0	13.76	0.0197	1:45:57	419.9 - 423.7
		Mo	5.3 ± 0.7	3.19 ± 0.04	17.40			
		S	5.3 ± 0.7	3.81 ± 0.16	24.33			
	Mo-S50	S	5.2 ± 0.7	2.42 ± 0.0	13.86	0.0187		
		Mo	3.5 ± 0.5	3.19 ± 0.04	14.35			
		S	1.7 ± 0.2	3.78 ± 0.27	12.63			

27	Bulk MoS_2	S	5.3 ± 0.7	2.42 ± 0.0	13.61	0.0187	1:49:01	423.6 - 423.7
92		Mo	5.3 ± 0.7	3.19 ± 0.04	17.12			
93		S	5.3 ± 0.7	3.81 ± 0.16	24.21			
	Mo-S50	S	5.2 ± 0.7	2.42 ± 0.0	13.74	0.0175		
		Mo	3.5 ± 0.5	3.19 ± 0.04	14.05			
		S	1.7 ± 0.2	3.77 ± 0.28	12.29			
		Stage 6 (Δk= 3.2 - 11 $Å^{-1}$, He gas**)**						
28	Mo-Bare	S	4.5 ± 0.5	2.41 ± 0.05	11.71	0.0173	1:58:14	345.2 - 422
		Mo	4.5 ± 0.5	3.19 ± 0.04	15.53			
		S	2.5 ± 0.3	3.77 ± 0.13	13.17			
		S	2.5 ± 0.3	4.61 ± 0.02	16.40			
		S	10.0 ± 1.0	5.32 ± 0.29	28.50			
	Mo-S50	S	4.2 ± 0.5	2.41 ± 0.03	11.58	0.0178		
		Mo	2.8 ± 0.3	3.18 ± 0.03	12.53			
		S	1.4 ± 0.2	3.75 ± 0.30	11.54			
		S	1.4 ± 0.2	4.64 ± 0.01	12.82			
		S	7.0 ± 0.8	5.34 ± 0.27	26.78			
29	Mo-Bare	S	4.3 ± 0.5	2.41 ± 0.05	10.80	0.0182	2:07:27	238.4 - 325.4
		Mo	4.3 ± 0.5	3.17 ± 0.04	14.22			
		S	2.2 ± 0.2	3.77 ± 0.13	12.10			
		S	2.2 ± 0.2	4.63 ± 0.0	15.74			
		S	8.7 ± 0.9	5.32 ± 0.29	27.97			
	Mo-S50	S	4.1 ± 0.4	2.41 ± 0.03	10.70	0.0186		
		Mo	2.7 ± 0.3	3.18 ± 0.03	11.31			
		S	1.4 ± 0.1	3.75 ± 0.30	10.73			
		S	1.4 ± 0.1	4.66 ± 0.01	11.51			
		S	6.8 ± 0.7	5.33 ± 0.27	26.54			
30	Mo-Bare	S	4.3 ± 0.5	2.42 ± 0.05	9.85	0.0189	2:15:08	172.3 - 224
		Mo	4.3 ± 0.5	3.18 ± 0.12	12.96			
		S	2.1 ± 0.2	3.77 ± 0.13	11.65			
		S	2.1 ± 0.2	4.64 ± 0.01	14.49			
		S	8.5 ± 0.9	5.32 ± 0.29	27.47			
	Mo-S50	S	4.0 ± 0.4	2.41 ± 0.03	9.76	0.0194		
		Mo	2.7 ± 0.3	3.18 ± 0.03	10.11			
		S	1.3 ± 0.1	3.74 ± 0.31	10.22			
		S	1.3 ± 0.1	4.67 ± 0.02	10.28			
		S	6.7 ± 0.7	5.33 ± 0.26	25.99			
		(Δk= 3.3 - 11 $Å^{-1}$, He gas**)**						
31	Mo-Bare	S	4.3 ± 0.5	2.42 ± 0.05	9.53	0.0188	2:24:20	116.4 - 160.9
		Mo	4.3 ± 0.5	3.18 ± 0.11	12.30			
		S	2.2 ± 0.2	3.77 ± 0.13	11.56			
		S	2.2 ± 0.2	4.66 ± 0.03	14.63			
		S	8.6 ± 1.0	5.30 ± 0.27	26.80			
		(Δk= 3.2 - 11 $Å^{-1}$, He gas**)**						
	Mo-S50	S	4.0 ± 0.5	2.41 ± 0.03	9.25	0.0209		
		Mo	2.7 ± 0.3	3.18 ± 0.03	9.38			
		S	1.3 ± 0.1	3.74 ± 0.31	10.03			
		S	1.3 ± 0.1	4.68 ± 0.03	9.39			
		S	6.7 ± 0.8	5.32 ± 0.26	25.79			

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			(Δk= 3.3 - 11 Å^{-1}, He gas)					
32	Mo-Bare	S	4.3 ± 0.5	2.42 ± 0.05	9.21	0.0191	2:33:33	79 - 109.2
		Mo	4.3 ± 0.5	3.18 ± 0.11	11.77			
		S	2.2 ± 0.3	3.77 ± 0.13	11.37			
		S	2.2 ± 0.3	4.67 ± 0.03	13.45			
		S	8.7 ± 1.0	5.29 ± 0.26	26.20			
			(Δk= 3.4 – 11.5 Å^{-1}, He gas)					
	Mo-S50	S	4.1 ± 0.6	2.41 ± 0.04	8.88	0.0248		
		Mo	2.7 ± 0.4	3.18 ± 0.03	8.46			
		S	1.4 ± 0.2	3.73 ± 0.36	10.09			
		S	1.4 ± 0.2	4.70 ± 0.05	8.66			
		S	6.8 ± 0.9	5.29 ± 0.23	23.89			
			(Δk= 3.3 - 11 Å^{-1}, He gas)					
33	Mo-Bare	S	4.4 ± 0.5	2.42 ± 0.06	9.05	0.0192	2:41:14	58.7 - 74
		Mo	4.4 ± 0.5	3.18 ± 0.11	11.47			
		S	2.2 ± 0.3	3.77 ± 0.14	11.28			
		S	2.2 ± 0.3	4.67 ± 0.04	12.70			
		S	8.7 ± 1.0	5.29 ± 0.26	26.04			
			(Δk= 3.4 - 11 Å^{-1}, He gas)					
	Mo-S50	S	4.2 ± 0.5	2.42 ± 0.04	9.22	0.0176		
		Mo	2.8 ± 0.3	3.17 ± 0.03	8.85			
		S	1.4 ± 0.2	3.74 ± 0.31	10.51			
		S	1.4 ± 0.2	4.70 ± 0.05	9.03			
		S	4.1 ± 0.8	5.28 ± 0.22	24.02			
			(Δk= 3.3 - 11 Å^{-1}, He gas)					
34	Mo-Bare	S	4.4 ± 0.5	2.42 ± 0.06	8.89	0.0194	3:01:12	31.6 - 55.4
		Mo	4.4 ± 0.5	3.18 ± 0.11	11.17			
		S	2.2 ± 0.3	3.76 ± 0.13	11.18			
		S	2.2 ± 0.3	4.68 ± 0.05	12.52			
		S	8.7 ± 1.0	5.28 ± 0.25	25.49			
	Mo-S50	S	4.2 ± 0.5	2.42 ± 0.04	8.88	0.0191		
		Mo	2.8 ± 0.3	3.18 ± 0.03	8.46			
		S	1.4 ± 0.2	3.73 ± 0.36	10.09			
		S	1.4 ± 0.2	4.70 ± 0.05	8.66			
		S	7.0 ± 0.8	5.29 ± 0.23	23.89			

At stage 6, Hamilton test (ref. 58) was applied by imposing k- and R-ranges on the same values in order to test two different models on the same EXAFS data independently and both of them give almost similar results (same fitting parameters)

Table 2S: Ni K-edge EXAFS fitting parameters of NiMoPILC (*in situ*)

No.	Fitting model	Back scatterer	N	R(Å)	σ^2 (Å^2) x 10^{-3}	R-factor	Time-lapse	temp in ^{o}C
			Stage 4 (Δk= 3 - 11 Å^{-1}, H_2S/H_2/He gasses**)**					
1	$NiMoO_4$	O	5.2 ± 0.5	2.03 ± 0.02	7.56	0.008	1:13:11	127.8 - 159.5
		Ni	1.7 ± 0.2	3.02 ± 0.05	19.98			
		Mo	1.7 ± 0.2	3.19 ± 0.05	19.46			
		Mo	1.7 ± 0.2	3.78 ± 0.0	11.94			
2	$NiMoO_4$	O	5.2 ± 0.5	2.02 ± 0.02	7.95	0.0112	1:15:48	176.3 - 193.3
		Ni	1.7 ± 0.2	3.01 ± 0.04	20.55			
		Mo	1.7 ± 0.2	3.20 ± 0.06	19.61			
		Mo	1.7 ± 0.2	3.77 ± 0.07	11			

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3	$NiMoO_4$	O	5.1 ± 0.5	2.02 ± 0.02	8.43	0.0086	1:23:38	210.1 – 294.7
		Ni	1.7 ± 0.2	3.01 ± 0.05	19.01			
		Mo	1.7 ± 0.2	3.19 ± 0.05	19.65			
		Mo	1.7 ± 0.2	3.78 ± 0.07	14.52			
4	$NiMoO_4$	O	5.2 ± 0.6	2.01 ± 0.01	9.93	0.0118	1:26:14	311.6 – 328.3
		Ni	1.7 ± 0.2	3.02 ± 0.05	25.04			
		Mo	1.7 ± 0.2	3.21 ± 0.07	18.95			
		Mo	1.7 ± 0.2	3.71 ± 0.01	15.38			
			(Δk= 3 – 11.6 Å^{-1}, H_2S/H_2/He gasses**)**					
5	$NiMoO_4$	O	5.4 ± 0.7	2.01 ± 0.0	9.89	0.0169	1:27:33	345.1
		Ni	1.8 ± 0.3	3.02 ± 0.05	25.79			
		Mo	1.8 ± 0.3	3.18 ± 0.04	14.83			
		Mo	1.8 ± 0.3	3.74 ± 0.04	20.03			
6	$NiMoO_4$	O	5.6 ± 0.9	1.99 ± 0.01	11.34	0.02	1:28:51	362
		Ni	1.9 ± 0.3	3.05 ± 0.08	27.62			
		Mo	1.9 ± 0.3	3.20 ± 0.06	17.94			
		Mo	1.9 ± 0.3	3.69 ± 0.01	16.48			
			(Δk= 3 – 12 Å^{-1}, H_2S/H_2/He gasses**)**					
7	$NiMoO_4$	O	5.8 ± 0.5	2.01 ± 0.01	11.62	0.0096	1:30:09	378.9
		Ni	1.9 ± 0.2	3.01 ± 0.05	26.17			
		Mo	1.9 ± 0.2	3.18 ± 0.04	19.66			
		Mo	1.9 ± 0.2	3.77 ± 0.06	14.83			
8	$NiMoO_4$	O	3.5 ± 0.4	2.02 ± 0.02	6.26	0.0197	1:31:28	395.4
		Ni	1.2 ± 0.1	3.03 ± 0.06	21.3			
		Mo	1.2 ± 0.1	3.23 ± 0.09	11.33			
		Mo	1.2 ± 0.1	3.71 ± 0.01	15.12			
			Stage 5 (Δk= 2.8 – 10 Å^{-1}, H_2S/H_2/He gasses**)**					
9	$NiMoO_4$	O	**4.8**	1.99 ± 0.01	11.18	0.0199	1:34:51	414.2
		Ni	**1.6**	3.0 ± 0.03	16.69			
		Mo	**1.6**	3.16 ± 0.02	17.64			
			(Δk= 3 – 11 Å^{-1}, H_2S/H_2/He gasses**)**					
10	NiO	O	**2**	1.99 ± 0.1	3.79	0.0197	1:36:41	418.1
	Ni_3S_2	S	**1.2**	2.3 ± 0.05	23.06			
		Ni	**1.2**	2.51 ± 0.01	12.18			
			(Δk= 3 – 12 Å^{-1}, H_2S/H_2/He gasses**)**					
11	NiO	O	**4.5**	2.07 ± 0.02	12.58	0.0111	1:39:18	419.5
	Ni_3S_2	S	**1.6**	2.17 ± 0.08	10.50			
		Ni	**1.6**	2.55 ± 0.05	19.91			
		S	**1.6**	3.62 ± 0.06	12.72			
			(Δk= 3 – 10.8 Å^{-1}, H_2S/H_2/He gasses**)**					
12	NiO	O	**5.5**	2.05 ± 0.04	14.76	0.0183	1:41:15	421.9
	Ni_3S_2	S	**2**	2.16 ± 0.09	12.5			
		Ni	**2**	2.54 ± 0.04	22.65			
		S	**2**	3.58 ± 0.09	14.21			
			(Δk= 3 – 11 Å^{-1}, H_2S/H_2/He gasses**)**					
13	NiO	O	**5.5**	2.1 ± 0.01	19.99	0.0151	1:44:31	423.2
	Ni_3S_2	S	**2.3**	2.2 ± 0.05	11.28			
		Ni	**2.3**	2.55 ± 0.05	22.46			
		S	**2.3**	3.62 ± 0.06	13			
14	NiO	O	5.6 ± 0.4	2.04 ± 0.05	6	0.0133	1:47:08	424.1
	Ni_3S_2	S	**2.8**	2.07 ± 0.18	13.65			
		Ni	**2.8**	2.58 ± 0.08	20.99			
		S	**2.8**	3.66 ± 0.01	17.34			

… continued

			(Δk= 3.5 – 11 Å^{-1}, H_2S/H_2/He gasses**)**					
15	NiO	O	**2**	2.01 ± 0.08	15.58	0.0235	1:49:45	424.7
	Ni-Bare	S	**1.6**	2.22 ± 0.03	6.55			
		Mo	**0.8**	2.83 ± 0.08	12.92			
		S	**0.8**	3.55 ± 0.0	3.78			
			(Δk= 3 – 10 Å^{-1}, H_2S/H_2/He gasses**)**					
16	NiO	O	**1**	2.01 ± 0.08	7.91	0.0199	1:52:21	425 – 425.2
	Ni-Bare	S	**2.4**	2.21 ± 0.03	0.74			
		Mo	**1.2**	2.80 ± 0.05	11.96			
		S	**1.2**	3.53 ± 0.02	15.60			
			(Δk= 3.5 – 12 Å^{-1}, H_2S/H_2/He gasses**)**					
17	NiO	O	**1**	2.0 ± 0.09	19.30	0.0185	1:57:35	425.3
	Ni-Bare	S	**2.6**	2.20 ± 0.01	9.99			
		Mo	**1.3**	2.76 ± 0.01	11.12			
		S	**1.3**	3.48 ± 0.07	10.06			
			(Δk= 3.7 – 11 Å^{-1}, H_2S/H_2/He gasses**)**					
18	NiMoS	S	3.2 ± 0.4	2.19 ± 0.15	10.63	0.0094	2:00:12	425.4 - 426.3
	$(\bar{1}010)$	Mo	1.1 ± 0.1	2.74 ± 0.06	6.88			
		Mo	1.1 ± 0.1	2.93 ± 0.07	7.62			
		S	2.1 ± 0.3	3.53 ± 0.12	9.66			
			(Δk= 3.4 – 11 Å^{-1}, H_2S/H_2/He gasses**)**					
19	NiMoS	S	2.7 ± 0.4	2.19 ± 0.15	8.16	0.0163	2:12:18	426.1 - 426.6
	$(\bar{1}010)$	Mo	0.9 ± 0.1	2.76 ± 0.04	5.34			
		Mo	0.9 ± 0.1	2.94 ± 0.06	6.93			
		S	1.8 ± 0.2	3.52 ± 0.12	8.60			
			Stage 6 (Δk= 3 – 11 Å^{-1}, He gas**)**					
20	Ni-Bare	S	2.4 ± 0.3	2.2 ± 0.01	6.62	0.0129	2:38:04	199.6 - 427.2
		Mo	1.2 ± 0.1	2.76 ± 0.01	9.03			
		Ni	1.2 ± 0.1	3.14 ± 0.01	8.45			
		S	1.2 ± 0.1	3.52 ± 0.03	1.16			
	NiMoS	S	2.7 ± 0.3	2.2 ± 0.16	7.33	0.0102		
	$(\bar{1}010)$	Mo	0.9 ± 0.1	2.78 ± 0.02	4.30			
		Mo	0.9 ± 0.1	2.96 ± 0.04	4.43			
		S	1.8 ± 0.2	3.52 ± 0.12	5.91			
21	Ni-Bare	S	2.7 ± 0.3	2.2 ± 0.02	5.88	0.0146	2:57:39	86.2 - 188.7
		Mo	1.3 ± 0.2	2.76 ± 0.0	7.87			
		Ni	1.3 ± 0.2	3.12 ± 0.03	7.77			
		S	1.3 ± 0.2	3.51 ± 0.04	0.91			
	NiMoS	S	3.0 ± 0.3	2.21 ± 0.06	6.64	0.0153		
	$(\bar{1}010)$	Mo	1.0 ± 0.1	2.76 ± 0.04	3.07			
		Mo	1.0 ± 0.1	2.95 ± 0.06	3.35			
		S	2.0 ± 0.2	3.51 ± 0.13	5.51			
22	Ni-Bare	S	2.7 ± 0.4	2.21 ± 0.02	5.64	0.0175	3:17:14	42 - 81.2
		Mo	1.4 ± 0.2	2.75 ± 0.0	7.47			
		Ni	1.4 ± 0.2	3.12 ± 0.03	8.13			
		S	1.4 ± 0.2	3.51 ± 0.04	0.97			
	NiMoS	S	3.0 ± 0.4	2.21 ± 0.17	6.18	0.0185		
	$(\bar{1}010)$	Mo	1.0 ± 0.1	2.76 ± 0.04	2.87			
		Mo	1.0 ± 0.1	2.94 ± 0.06	3.61			
		S	2.0 ± 0.2	3.51 ± 0.13	5.08			

… continued

23	Ni-Bare	S	2.8 ± 0.4	2.21 ± 0.02	5.5	0.0177	3:43:13	29.6 - 40.4
		Mo	1.4 ± 0.2	2.75 ± 0.0	7.36			
		Ni	1.4 ± 0.2	3.12 ± 0.03	7.8			
		S	1.4 ± 0.2	3.51 ± 0.04	0.61			
	NiMoS ($\bar{1}010$)	S	3.0 ± 0.3	2.22 ± 0.17	5.79	0.0155		
		Mo	1.0 ± 0.1	2.76 ± 0.04	2.86			
		Ni	1.0 ± 0.1	2.94 ± 0.06	3.53			
		S	2.0 ± 0.2	3.52 ± 0.13	4.88			

At stage 6, Hamilton test (ref. 58) was applied by imposing k- and R-ranges on the same values in order to fit two different models on the same EXAFS data independently and both of them give almost similar results (same fitting parameters)

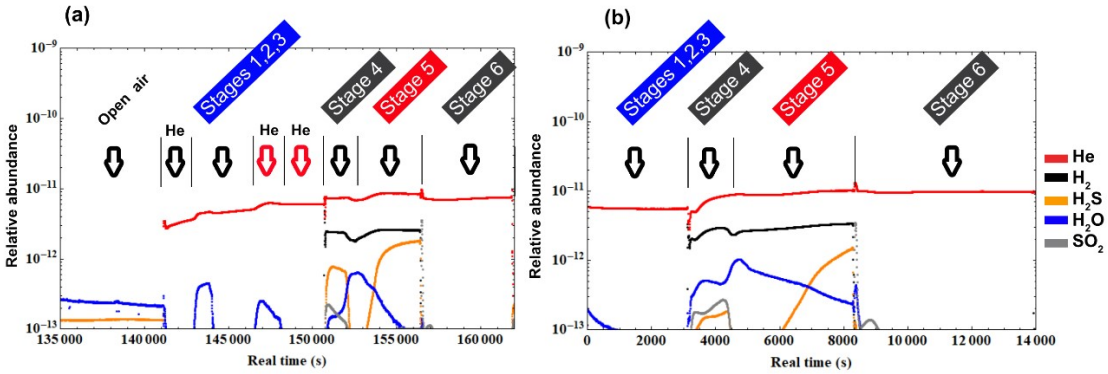

Figure 1S: Distribution profile of gas products (H_2O, SO_2) and inputs (He, H_2, H_2S) during *in situ* (a) Mo and (b) Ni K-edge XAS measurement using MS

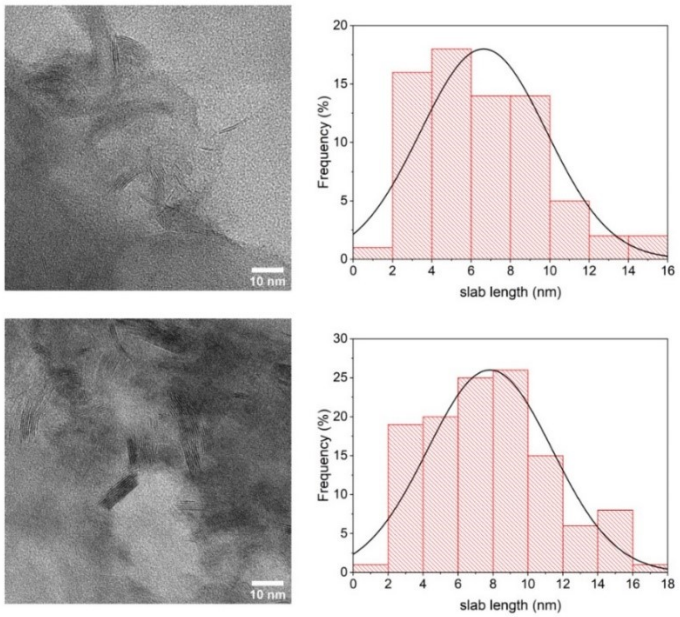

Figure 2S: HRTEM images (left) at two different locations and their respective slab length distributions (right) of sulfided $NiMoS_2$/Al-PILC catalyst.

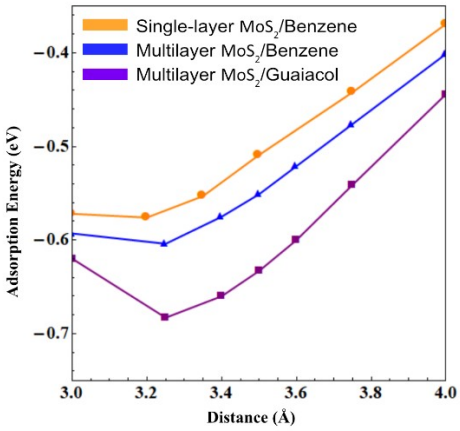

Figure 3S: Benzene and guaiacol adsorption on the basal plane of MoS_2 in planar configuration. The distance is from the center of mass of benzene and guaiacol to the z position of the top sulfur layer

Table 3S: Calculated vibrational frequencies (cm^{-1}) of guaiacol adsorbed on several $NiMoS_2$ sites

	Mo-Bare	Ni-Bare	Mo-S50	NiMoS ($\bar{1}010$)	Horiz-basal	Vert-basal	INS (ref. 25)
ν(C-C)	1512	1499, 1579, 1601	1499, 1578, 1620	1469, 1590, 1615	1512, 1593, 1608	1505, 1593, 1612	-
$\gamma(CH_3)$	1459	1451, 1458	1450, 1458	1455	-	1461	1463
ν(C-C) + $\gamma(CH_3)$	1443, 1450	1446	1449	1448	1446, 1459	1452	-
$\gamma(CH_3)$	-	-	-	-	1439	1447	-
$\delta(CH_3)$	-	1434	1436	1425, 1435	1429	1430	-
ν(C-C) + δ(COH)	1415, 1423	-	-	-	-	-	-
ν(C-C)	1335, 1366	1362	1368	1366	1397	1390	1378
δ(C-H)	1263	1290	1293	1296	1295	1297	-
ν(C-OH) + ν(C-OCH_3)	-	-	-	-	1272	1236, 1273	-
ν(C-OCH_3)	1205	1266	1270	-	1243		-
ν(C-OH)	1187	1221	1191	1251	-	-	-
ν(C-OCH_3)	-	-	-	1205	-	-	-
$\delta(CH_3)$	1174	1180	1180	1173	1179	1184	-
δ(C-H)	-	1169	1169	1168	1167	1164	1164
δ(CCC) ip	-	1156	1159	1157	1154	-	-
ν(C-OH)	-	-	1148	-	-	-	-
δ(O-CH_3)	1143	1142	1140	1142	1139	1142	1043
δ(CCC) ip	1140	-	-	1102	1101	1100	-
ν(C-OH)	1089	1096	1085	-	-	-	-
δ(CCC) ip	990, 1033	1055	1059	1050	1055	1069	-
δ(CCC) ip + ν(O-CH_3)	983	1028	1025	1009	1041	1042	-
τ(C-H)						953	
δ(CCC) oop	826, 898	833, 918,	827, 912,	830, 913,	895, 947	894	846,

		965	965	963			926, 963
δ(CCC) ip	-	891	-	824	832	830	-
δ(CCC) oop	-	-	-	-	821	816	-
δ(CCC) ip	787, 788	751	750, 814	771	764	765	752
δ(C-H)	-	748	741	742	745	746	-
δ(CCC) oop	747	713	-	-	721	718	-
δ(CCC) ip	728	-	-	-	-	-	-
δ(C-OH)	692	-	676	-	-	-	-
δ(CCC) oop	611	-	-	-	583	-	-
δ(CCC) ip	557	574	581	600	-	584	557
δ(CCC) oop	-	559	558	558	570	571	-
δ(C-OH)	-	548	-	-	-	-	-
ρ(C-O)	-	-	532	538	524	524	536
δ(CCC) ip	471, 476, 516	492	503	508	498	492	495
δ(CCC) oop	-	461	468	447	471	467	461
δ(C-OH)	-	-	-	437	-	-	-
γ(C-O)	-	-	-	412	-	-	-
δ(CCC) oop	403	-	-	-	-	-	-
δ(C-OH)	-	-	-	-	382	370	-
ν(Mo-O) + *ν*(Mo-C)	356	-	-	-	-	-	-
γ(C-O)	-	334	361		350	337	-
δ(CCC) oop	302, 333	323	344	314	317	319	314, 346
τ(O-CH_3)	-	271	268	-	-	266	-
γ(C-O)	-	-	258	268	-		
ν(Mo-O)	254	-	-	-	-	-	-
τ(O-CH_3)	234	-	-	243	249	-	252
γ(C-O)	227	231	-	-	233	227	-
τ(O-CH_3)	-	-	221	-	-	-	-
τ(C-O)	-	211	-	206	195	192	206
δ(O-CH_3)	173	-	-	190	169	126	-
δ (CCC) oop	137	138	149	-	-	-	147

ν---stretching, δ---bending, γ---scissoring, ω---wagging, τ---twisting, torsion, *ρ*---rocking, oop---out-of-plane, ip---in-plane. Vibrational mode descriptions obtained using animations in Chemcraft.