Supporting information for First-princples micro-kinetic study of CH_4 and H_2S catalytic conversion to methanethiol/dimethyl sulfide on Mo_6S_8 clusters: activity/selectivity of different promotors

Adam A. Arvidsson,† William Taifan,‡ Anders Hellman,† and Jonas Baltrusaitis*,‡

†*Department of Physics, Chalmers University of Technology, 412 96 Gothenburg, Sweden*

‡*Department of Chemical and BiomolecularEngineering, Lehigh University, B336 Iacocca Hall, 111 Research Drive, Bethlehem, PA 18015, USA*

E-mail: job314@lehigh.edu

Phone: +1-610-758-6836

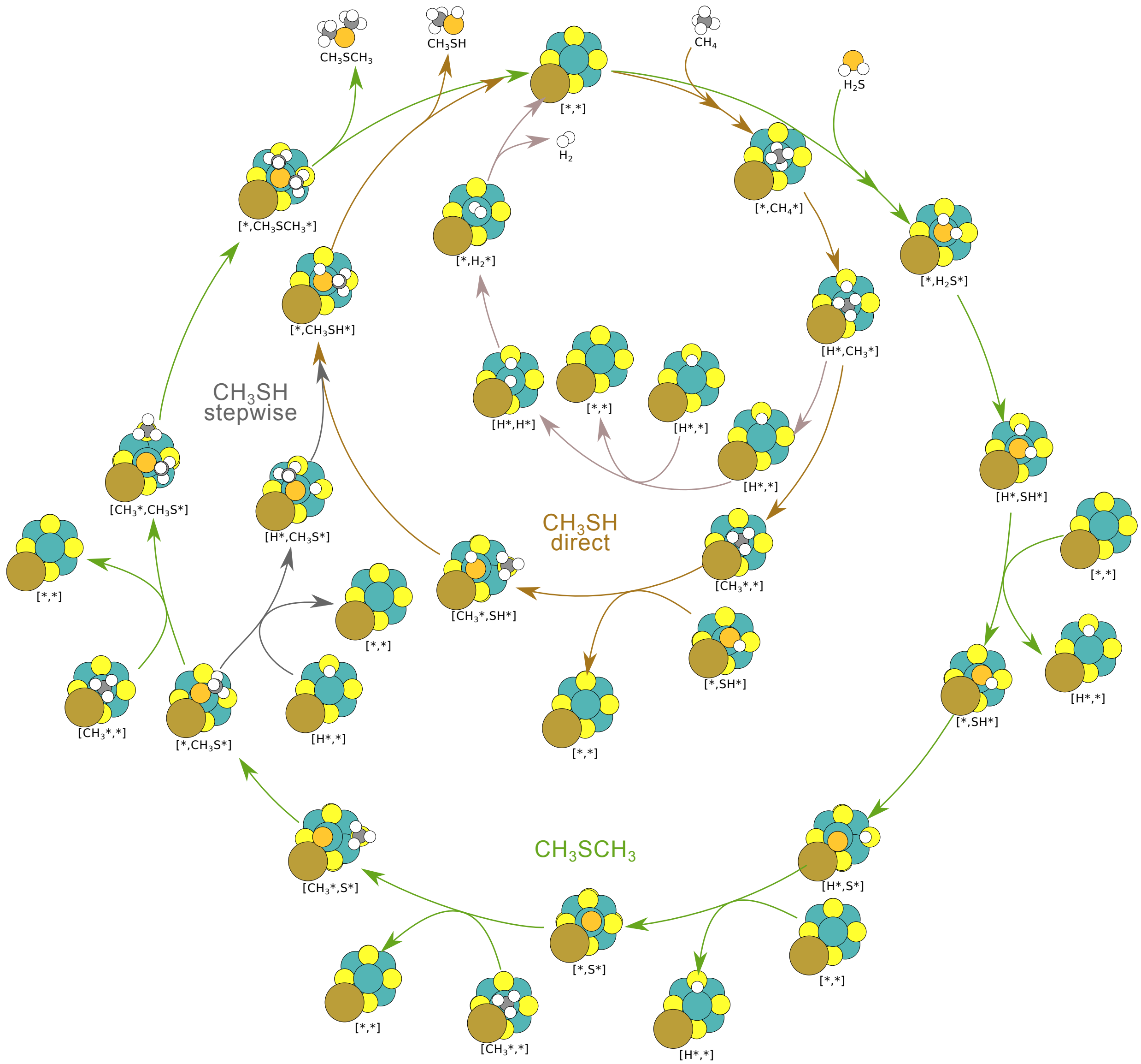

Figure S1: Reaction mechanism for the K-Mo_6S_8 cluster. Color code: hydrogen-white, carbon-black, sulfur-yellow, adsorbed sulfur (from H_2S)-orange, and molybdenum-green.

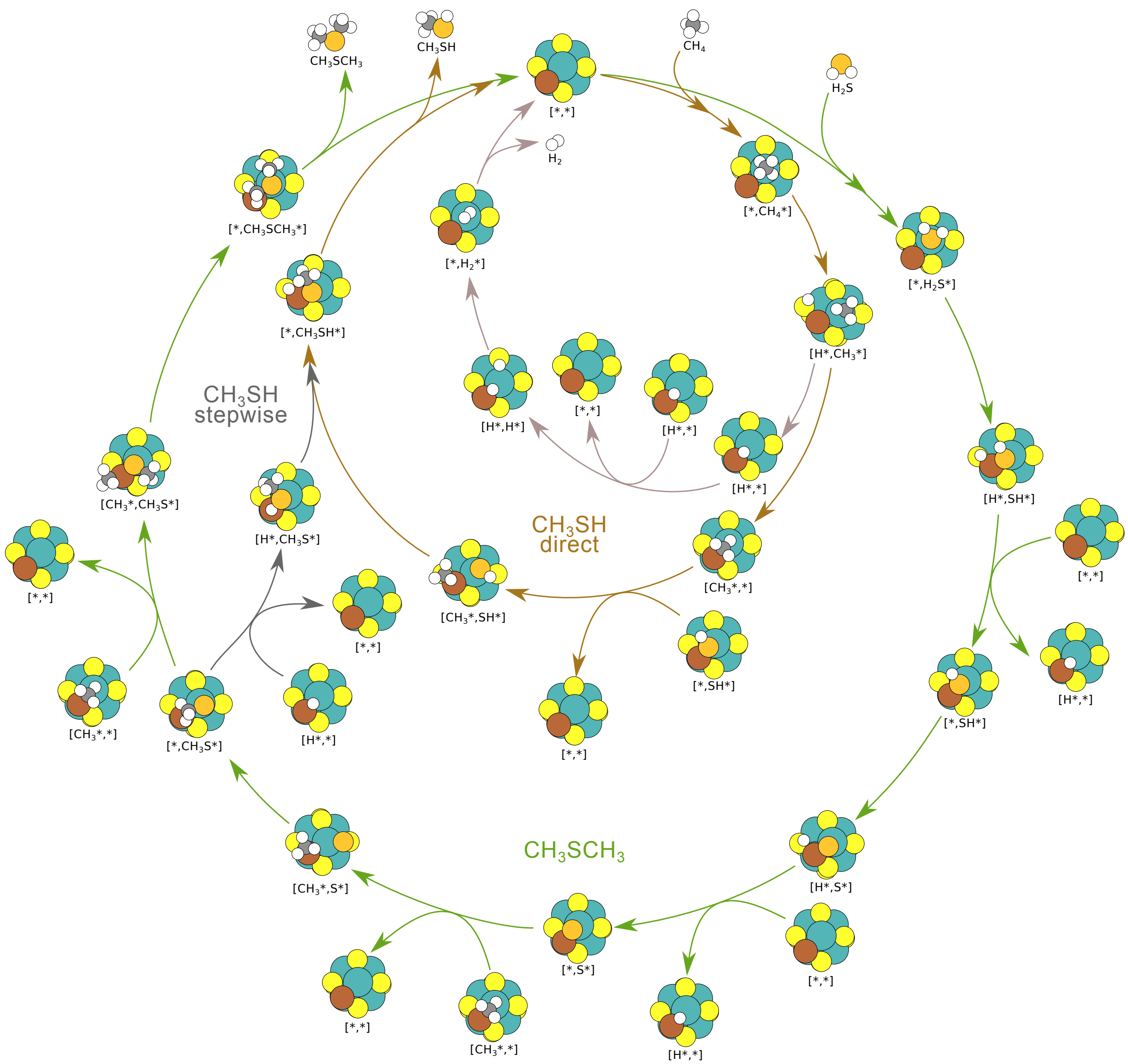

Figure S2: Reaction mechanism for the Ni-Mo_6S_8 cluster. Color code: hydrogen-white, carbon-black, sulfur-yellow, adsorbed sulfur (from H_2S)-orange, and molybdenum-green.

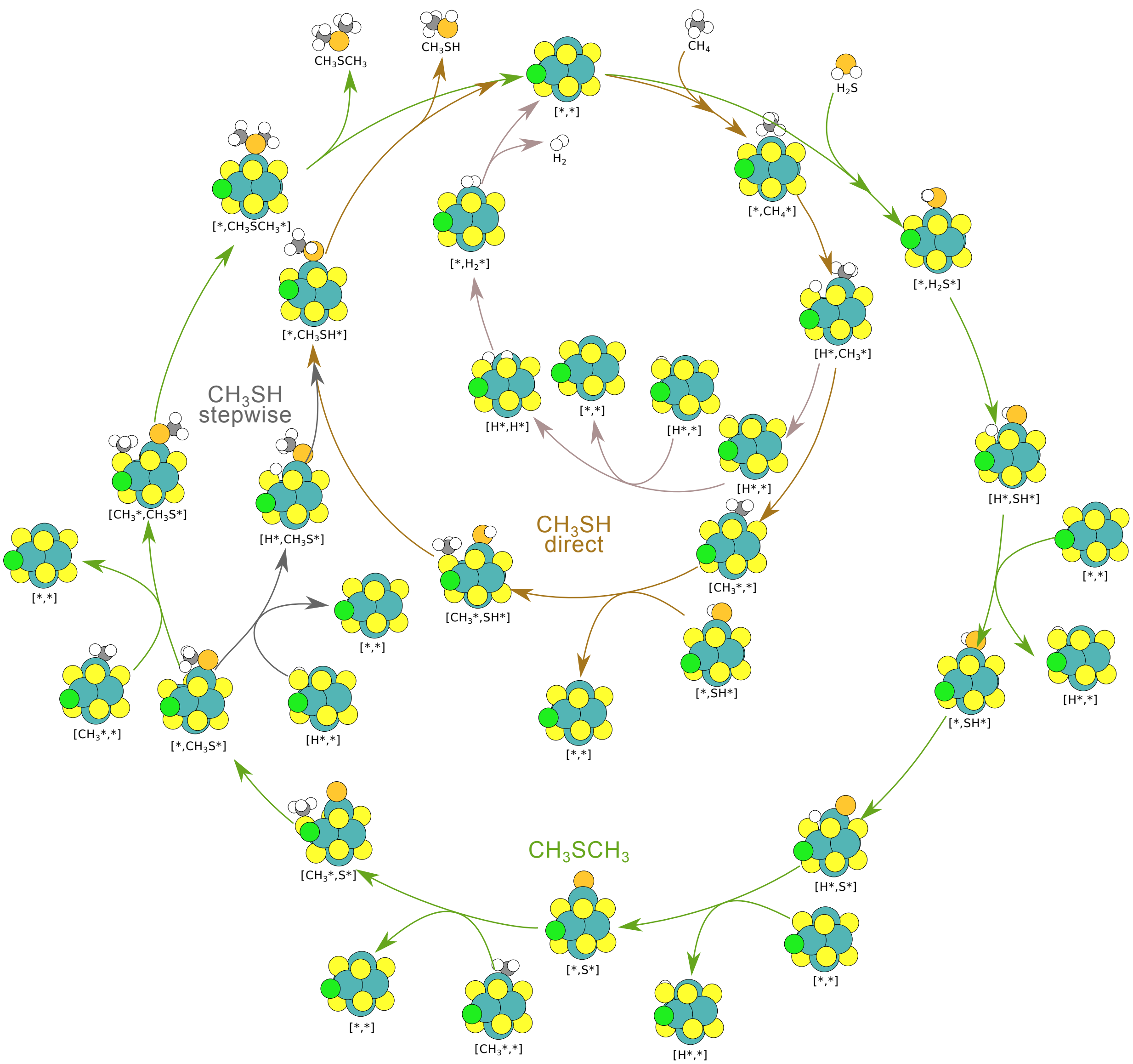

Figure S3: Reaction mechanism for the Cl-Mo_6S_8 cluster. Color code: hydrogen-white, carbon-black, sulfur-yellow, adsorbed sulfur (from H_2S)-orange, and molybdenum-green.

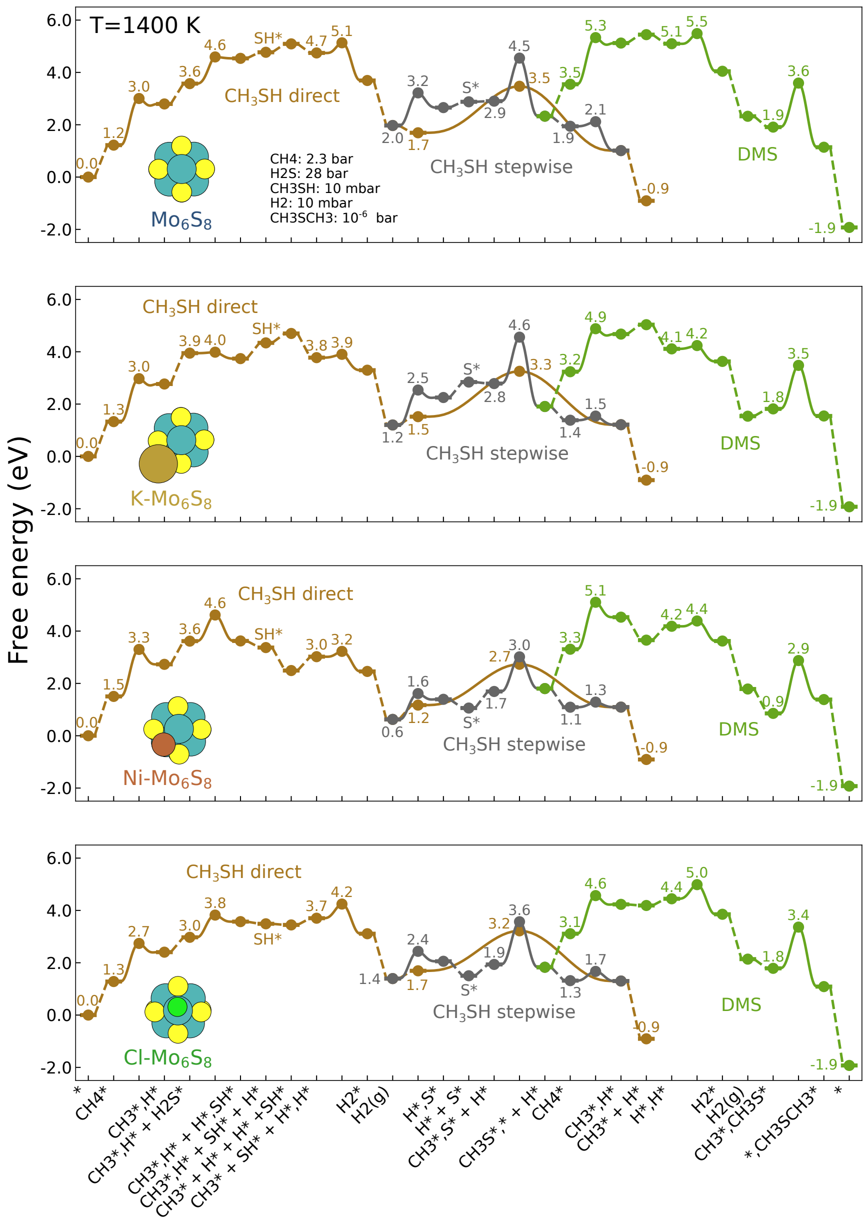

Figure S4: Free energy landscapes at 1400 K.

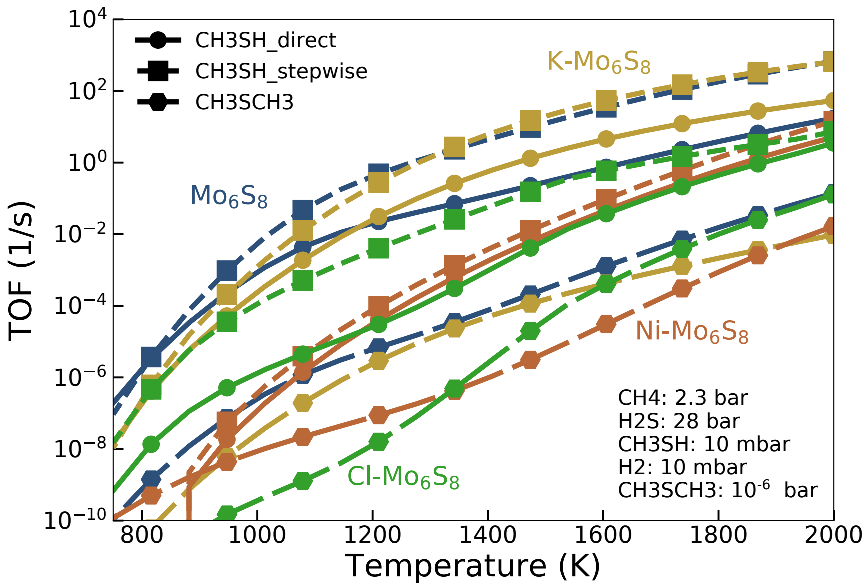

Figure S5: TOF with all clusters in the same plot.

Table S1: Rate constants and free energy barriers at 1400 K for the bare $\mathrm{Mo_6S_8}$ cluster.

Reaction	Type		Rate constant $[\mathrm{s}^{-1}]$	ΔG [eV]
$\mathrm{CH_4(g)} + [^*,^*] \rightleftarrows [^*, \mathrm{CH_4^*}]$	ads/des	$\rightarrow$	$4.97 \cdot 10^{8}$	1.22
		$\leftarrow$	$1.23 \cdot 10^{13}$	
$[^*, \mathrm{CH_4^*}] \rightleftarrows [\mathrm{H^*}, \mathrm{CH_3^*}]$	TS	$\rightarrow$	$1.11 \cdot 10^{7}$	1.78
		$\leftarrow$	$5.18 \cdot 10^{12}$	0.21
$\mathrm{H_2S(g)} + [^*,^*] \rightleftarrows [^*, \mathrm{H_2S^*}]$	ads/des	$\rightarrow$	$4.09 \cdot 10^{9}$	0.78
		$\leftarrow$	$2.56 \cdot 10^{12}$	
$[^*, \mathrm{H_2S^*}] \rightleftarrows [\mathrm{H^*}, \mathrm{SH^*}]$	TS	$\rightarrow$	$6.22 \cdot 10^{9}$	1.02
		$\leftarrow$	$1.86 \cdot 10^{13}$	0.05
$[\mathrm{H^*}, \mathrm{SH^*}] + [^*,^*] \rightleftarrows [\mathrm{H^*},^*] + [^*, \mathrm{SH^*}]$	diffusion	$\rightarrow$	$2.80 \cdot 10^{12}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[\mathrm{H^*}, \mathrm{CH_3^*}] + [^*,^*] \rightleftarrows [\mathrm{H^*},^*] + [\mathrm{CH_3^*},^*]$	diffusion	$\rightarrow$	$1.34 \cdot 10^{12}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[\mathrm{H^*},^*] + [\mathrm{H^*},^*] \rightleftarrows [\mathrm{H^*}, \mathrm{H^*}]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.09 \cdot 10^{12}$	
$[\mathrm{H^*}, \mathrm{H^*}] \rightleftarrows [^*, \mathrm{H_2^*}]$	TS	$\rightarrow$	$1.17 \cdot 10^{12}$	0.39
		$\leftarrow$	$1.90 \cdot 10^{8}$	1.44
$[^*, \mathrm{H_2^*}] \rightleftarrows [^*,^*] + \mathrm{H_2(g)}$	ads/des	$\rightarrow$	$9.47 \cdot 10^{12}$	
		$\leftarrow$	$6.08 \cdot 10^{6}$	1.72
$[\mathrm{CH_3^*},^*] + [^*, \mathrm{SH^*}] \rightleftarrows [\mathrm{CH_3^*}, \mathrm{SH^*}] + [^*,^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.92 \cdot 10^{12}$	
$[\mathrm{CH_3^*}, \mathrm{SH^*}] \rightleftarrows [^*, \mathrm{CH_3SH^*}]$	TS	$\rightarrow$	$1.16 \cdot 10^{7}$	1.78
		$\leftarrow$	$4.12 \cdot 10^{4}$	2.46
$[^*, \mathrm{SH^*}] \rightleftarrows [\mathrm{H^*}, \mathrm{S^*}]$	TS	$\rightarrow$	$9.50 \cdot 10^{8}$	1.25
		$\leftarrow$	$2.76 \cdot 10^{11}$	0.56
$[\mathrm{S^*}, \mathrm{H^*}] + [^*,^*] \rightleftarrows [^*, \mathrm{S^*}] + [\mathrm{H^*},^*]$	diffusion	$\rightarrow$	$3.07 \cdot 10^{12}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[\mathrm{CH_3^*},^*] + [^*, \mathrm{S^*}] \rightleftarrows [\mathrm{CH_3^*}, \mathrm{S^*}] + [^*,^*]$	diffusion	$\rightarrow$	$1.58 \cdot 10^{13}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[\mathrm{CH_3^*}, \mathrm{S^*}] \rightleftarrows [^*, \mathrm{CH_3S^*}]$	TS	$\rightarrow$	$3.47 \cdot 10^{7}$	1.65
		$\leftarrow$	$2.97 \cdot 10^{5}$	2.22
$[\mathrm{H^*},^*] + [\mathrm{CH_3S^*},^*] \rightleftarrows [\mathrm{H^*}, \mathrm{CH_3S^*}] + [^*,^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$7.88 \cdot 10^{11}$	
$[\mathrm{H^*}, \mathrm{CH_3S^*}] \rightleftarrows [^*, \mathrm{CH_3SH^*}]$	TS	$\rightarrow$	$6.80 \cdot 10^{12}$	0.18
		$\leftarrow$	$3.07 \cdot 10^{9}$	1.11
$[^*, \mathrm{CH_3SH^*}] \rightleftarrows [^*,^*] + \mathrm{CH_3SH(g)}$	ads/des	$\rightarrow$	$1.01 \cdot 10^{13}$	
		$\leftarrow$	$1.24 \cdot 10^{6}$	1.92
$[\mathrm{CH_3S^*},^*] + [\mathrm{CH_3^*},^*] \rightleftarrows [\mathrm{CH_3^*}, \mathrm{CH_3S^*}] + [^*,^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$6.23 \cdot 10^{11}$	
$[\mathrm{CH_3^*}, \mathrm{CH_3S^*}] \rightleftarrows [^*, \mathrm{CH_3SCH_3^*}]$	TS	$\rightarrow$	$2.56 \cdot 10^{7}$	1.68
		$\leftarrow$	$4.36 \cdot 10^{4}$	2.45
$[^*, \mathrm{CH_3SCH_3^*}] \rightleftarrows [^*,^*] + \mathrm{CH_3SCH_3(g)}$	ads/des	$\rightarrow$	$1.19 \cdot 10^{13}$	
		$\leftarrow$	$1.09 \cdot 10^{2}$	3.07

Table S2: Rate constants and free energy barriers at 1400 K for the K-Mo_6S_8 cluster.

Reaction	Type		Rate constant [s^{-1}]	ΔG [eV]
$CH_4(g) + [^*,^*] \rightleftarrows [^*, CH_4^*]$	ads/des	$\rightarrow$	$4.97 \cdot 10^{8}$	1.33
		$\leftarrow$	$3.03 \cdot 10^{13}$	
$[^*, CH_4^*] \rightleftarrows [H^*, CH_3^*]$	TS	$\rightarrow$	$3.54 \cdot 10^{7}$	1.64
		$\leftarrow$	$5.33 \cdot 10^{12}$	0.20
$H_2S(g) + [^*,^*] \rightleftarrows [^*, H_2S^*]$	ads/des	$\rightarrow$	$4.09 \cdot 10^{9}$	1.18
		$\leftarrow$	$7.16 \cdot 10^{13}$	
$[^*, H_2S^*] \rightleftarrows [H^*, SH^*]$	TS	$\rightarrow$	$2.14 \cdot 10^{13}$	0.04
		$\leftarrow$	$3.80 \cdot 10^{12}$	0.25
$[H^*, SH^*] + [^*,^*] \rightleftarrows [H^*,^*] + [^*, SH^*]$	diffusion	$\rightarrow$	$1.31 \cdot 10^{11}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[H^*, CH_3^*] + [^*,^*] \rightleftarrows [H^*,^*] + [CH_3^*,^*]$	diffusion	$\rightarrow$	$9.79 \cdot 10^{11}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[H^*,^*] + [H^*,^*] \rightleftarrows [H^*, H^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$9.09 \cdot 10^{9}$	
$[H^*, H^*] \rightleftarrows [^*, H_2^*]$	TS	$\rightarrow$	$1.02 \cdot 10^{13}$	0.13
		$\leftarrow$	$1.91 \cdot 10^{11}$	0.61
$[^*, H_2^*] \rightleftarrows [^*,^*] + H_2(g)$	ads/des	$\rightarrow$	$2.10 \cdot 10^{14}$	
		$\leftarrow$	$6.08 \cdot 10^{6}$	2.09
$[CH_3^*,^*] + [^*, SH^*] \rightleftarrows [CH_3^*, SH^*] + [^*,^*]$	diffusion	$\rightarrow$	$1.38 \cdot 10^{12}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[CH_3^*, SH^*] \rightleftarrows [^*, CH_3SH^*]$	TS	$\rightarrow$	$1.67 \cdot 10^{7}$	1.73
		$\leftarrow$	$1.32 \cdot 10^{6}$	2.04
$[^*, SH^*] \rightleftarrows [H^*, S^*]$	TS	$\rightarrow$	$4.54 \cdot 10^{8}$	1.34
		$\leftarrow$	$2.73 \cdot 10^{12}$	0.29
$[S^*, H^*] + [^*,^*] \rightleftarrows [^*, S^*] + [H^*,^*]$	diffusion	$\rightarrow$	$1.45 \cdot 10^{11}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[CH_3^*,^*] + [^*, S^*] \rightleftarrows [CH_3^*, S^*] + [^*,^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.19 \cdot 10^{13}$	
$[CH_3^*, S^*] \rightleftarrows [^*, CH_3S^*]$	TS	$\rightarrow$	$1.20 \cdot 10^{7}$	1.77
		$\leftarrow$	$8.40 \cdot 10^{3}$	2.65
$[H^*,^*] + [CH_3S^*,^*] \rightleftarrows [H^*, CH_3S^*] + [^*,^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$2.49 \cdot 10^{11}$	
$[H^*, CH_3S^*] \rightleftarrows [^*, CH_3SH^*]$	TS	$\rightarrow$	$7.81 \cdot 10^{12}$	0.16
		$\leftarrow$	$1.90 \cdot 10^{12}$	0.33
$[^*, CH_3SH^*] \rightleftarrows [^*,^*] + CH_3SH(g)$	ads/des	$\rightarrow$	$5.31 \cdot 10^{13}$	
		$\leftarrow$	$1.24 \cdot 10^{6}$	2.12
$[CH_3S^*,^*] + [CH_3^*,^*] \rightleftarrows [CH_3^*, CH_3S^*] + [^*,^*]$	diffusion	$\rightarrow$	$1.89 \cdot 10^{12}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[CH_3^*, CH_3S^*] \rightleftarrows [^*, CH_3SCH_3^*]$	TS	$\rightarrow$	$3.03 \cdot 10^{7}$	1.66
		$\leftarrow$	$3.19 \cdot 10^{6}$	1.93
$[^*, CH_3SCH_3^*] \rightleftarrows [^*,^*] + CH_3SCH_3(g)$	ads/des	$\rightarrow$	$3.41 \cdot 10^{14}$	
		$\leftarrow$	$1.09 \cdot 10^{2}$	3.47

Table S3: Rate constants and free energy barriers at 1400 K for the Ni-Mo_6S_8 cluster.

Reaction	Type		Rate constant [s^{-1}]	ΔG [eV]
$CH_4(g) + [*,*] \rightleftarrows [*, CH_4^*]$	ads/des	$\rightarrow$	$4.97 \cdot 10^{8}$	1.50
		$\leftarrow$	$1.28 \cdot 10^{14}$	
$[*, CH_4^*] \rightleftarrows [H^*, CH_3^*]$	TS	$\rightarrow$	$1.00 \cdot 10^{7}$	1.80
		$\leftarrow$	$2.59 \cdot 10^{11}$	0.57
$H_2S(g) + [*,*] \rightleftarrows [*, H_2S^*]$	ads/des	$\rightarrow$	$4.09 \cdot 10^{9}$	0.89
		$\leftarrow$	$6.38 \cdot 10^{12}$	
$[*, H_2S^*] \rightleftarrows [H^*, SH^*]$	TS	$\rightarrow$	$7.37 \cdot 10^{9}$	1.00
		$\leftarrow$	$7.84 \cdot 10^{9}$	0.99
$[H^*, SH^*] + [*,*] \rightleftarrows [H^*,*] + [*, SH^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$2.36 \cdot 10^{12}$	
$[H^*, CH_3^*] + [*,*] \rightleftarrows [H^*,*] + [CH_3^*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.33 \cdot 10^{10}$	
$[H^*,*] + [H^*,*] \rightleftarrows [H^*, H^*]$	diffusion	$\rightarrow$	$2.38 \cdot 10^{11}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[H^*, H^*] \rightleftarrows [*, H_2^*]$	TS	$\rightarrow$	$5.45 \cdot 10^{12}$	0.20
		$\leftarrow$	$5.07 \cdot 10^{10}$	0.77
$[*, H_2^*] \rightleftarrows [*,*] + H_2(g)$	ads/des	$\rightarrow$	$2.42 \cdot 10^{13}$	
		$\leftarrow$	$6.06 \cdot 10^{6}$	1.83
$[CH_3^*,*] + [*, SH^*] \rightleftarrows [CH_3^*, SH^*] + [*,*]$	diffusion	$\rightarrow$	$2.07 \cdot 10^{11}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[CH_3^*, SH^*] \rightleftarrows [*, CH_3SH^*]$	TS	$\rightarrow$	$7.09 \cdot 10^{7}$	1.56
		$\leftarrow$	$3.74 \cdot 10^{7}$	1.64
$[*, SH^*] \rightleftarrows [H^*, S^*]$	TS	$\rightarrow$	$8.08 \cdot 10^{9}$	0.99
		$\leftarrow$	$4.70 \cdot 10^{12}$	0.22
$[S^*, H^*] + [*,*] \rightleftarrows [*, S^*] + [H^*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.21 \cdot 10^{12}$	
$[CH_3^*,*] + [*, S^*] \rightleftarrows [CH_3^*, S^*] + [*,*]$	diffusion	$\rightarrow$	$1.01 \cdot 10^{11}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[CH_3^*, S^*] \rightleftarrows [*, CH_3S^*]$	TS	$\rightarrow$	$5.00 \cdot 10^{8}$	1.32
		$\leftarrow$	$1.26 \cdot 10^{9}$	1.21
$[H^*,*] + [CH_3S^*,*] \rightleftarrows [H^*, CH_3S^*] + [*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$5.24 \cdot 10^{10}$	
$[H^*, CH_3S^*] \rightleftarrows [*, CH_3SH^*]$	TS	$\rightarrow$	$5.81 \cdot 10^{12}$	0.19
		$\leftarrow$	$5.99 \cdot 10^{12}$	0.19
$[*, CH_3SH^*] \rightleftarrows [*,*] + CH_3SH(g)$	ads/des	$\rightarrow$	$1.99 \cdot 10^{13}$	
		$\leftarrow$	$1.24 \cdot 10^{6}$	2.00
$[CH_3S^*,*] + [CH_3^*,*] \rightleftarrows [CH_3^*, CH_3S^*] + [*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$8.53 \cdot 10^{9}$	
$[CH_3^*, CH_3S^*] \rightleftarrows [*, CH_3SCH_3^*]$	TS	$\rightarrow$	$1.56 \cdot 10^{6}$	2.02
		$\leftarrow$	$1.49 \cdot 10^{8}$	1.49
$[*, CH_3SCH_3^*] \rightleftarrows [*,*] + CH_3SCH_3(g)$	ads/des	$\rightarrow$	$8.93 \cdot 10^{13}$	
		$\leftarrow$	$1.09 \cdot 10^{2}$	3.31

Table S4: Rate constants and free energy barriers at 1400 K for the Cl-Mo_6S_8 cluster.

Reaction	Type		Rate constant [s^{-1}]	ΔG [eV]
$CH_4(g) + [*,*] \rightleftarrows [*, CH_4^*]$	ads/des	$\rightarrow$	$4.97 \cdot 10^{8}$	1.28
		$\leftarrow$	$2.05 \cdot 10^{13}$	
$[*, CH_4^*] \rightleftarrows [H^*, CH_3^*]$	TS	$\rightarrow$	$1.66 \cdot 10^{8}$	1.46
		$\leftarrow$	$1.82 \cdot 10^{12}$	0.33
$H_2S(g) + [*,*] \rightleftarrows [*, H_2S^*]$	ads/des	$\rightarrow$	$4.09 \cdot 10^{9}$	0.57
		$\leftarrow$	$4.54 \cdot 10^{11}$	
$[*, H_2S^*] \rightleftarrows [H^*, SH^*]$	TS	$\rightarrow$	$2.55 \cdot 10^{10}$	0.85
		$\leftarrow$	$3.68 \cdot 10^{12}$	0.25
$[H^*, SH^*] + [*,*] \rightleftarrows [H^*,*] + [*, SH^*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$9.67 \cdot 10^{12}$	
$[H^*, CH_3^*] + [*,*] \rightleftarrows [H^*,*] + [CH_3^*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.35 \cdot 10^{13}$	
$[H^*,*] + [H^*,*] \rightleftarrows [H^*, H^*]$	diffusion	$\rightarrow$	$2.30 \cdot 10^{12}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[H^*, H^*] \rightleftarrows [*, H_2^*]$	TS	$\rightarrow$	$3.31 \cdot 10^{11}$	0.54
		$\leftarrow$	$2.43 \cdot 10^{9}$	1.13
$[*, H_2^*] \rightleftarrows [*,*] + H_2(g)$	ads/des	$\rightarrow$	$9.03 \cdot 10^{12}$	
		$\leftarrow$	$6.08 \cdot 10^{6}$	1.71
$[CH_3^*,*] + [*, SH^*] \rightleftarrows [CH_3^*, SH^*] + [*,*]$	diffusion	$\rightarrow$	$1.64 \cdot 10^{12}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[CH_3^*, SH^*] \rightleftarrows [*, CH_3SH^*]$	TS	$\rightarrow$	$9.22 \cdot 10^{7}$	1.53
		$\leftarrow$	$3.62 \cdot 10^{6}$	1.92
$[*, SH^*] \rightleftarrows [H^*, S^*]$	TS	$\rightarrow$	$5.19 \cdot 10^{9}$	1.04
		$\leftarrow$	$1.25 \cdot 10^{12}$	0.38
$[S^*, H^*] + [*,*] \rightleftarrows [*, S^*] + [H^*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.95 \cdot 10^{11}$	
$[CH_3^*,*] + [*, S^*] \rightleftarrows [CH_3^*, S^*] + [*,*]$	diffusion	$\rightarrow$	$5.33 \cdot 10^{11}$	
		$\leftarrow$	$1.93 \cdot 10^{13}$	0.05
$[CH_3^*, S^*] \rightleftarrows [*, CH_3S^*]$	TS	$\rightarrow$	$3.89 \cdot 10^{7}$	1.63
		$\leftarrow$	$1.59 \cdot 10^{7}$	1.74
$[H^*,*] + [CH_3S^*,*] \rightleftarrows [H^*, CH_3S^*] + [*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$2.77 \cdot 10^{11}$	
$[H^*, CH_3S^*] \rightleftarrows [*, CH_3SH^*]$	TS	$\rightarrow$	$1.56 \cdot 10^{12}$	0.35
		$\leftarrow$	$1.39 \cdot 10^{12}$	0.37
$[*, CH_3SH^*] \rightleftarrows [*,*] + CH_3SH(g)$	ads/des	$\rightarrow$	$1.11 \cdot 10^{14}$	
		$\leftarrow$	$1.24 \cdot 10^{6}$	2.21
$[CH_3S^*,*] + [CH_3^*,*] \rightleftarrows [CH_3^*, CH_3S^*] + [*,*]$	diffusion	$\rightarrow$	$1.93 \cdot 10^{13}$	0.05
		$\leftarrow$	$1.05 \cdot 10^{12}$	
$[CH_3^*, CH_3S^*] \rightleftarrows [*, CH_3SCH_3^*]$	TS	$\rightarrow$	$6.18 \cdot 10^{7}$	1.58
		$\leftarrow$	$1.90 \cdot 10^{5}$	2.27
$[*, CH_3SCH_3^*] \rightleftarrows [*,*] + CH_3SCH_3(g)$	ads/des	$\rightarrow$	$7.74 \cdot 10^{12}$	
		$\leftarrow$	$1.09 \cdot 10^{2}$	3.01

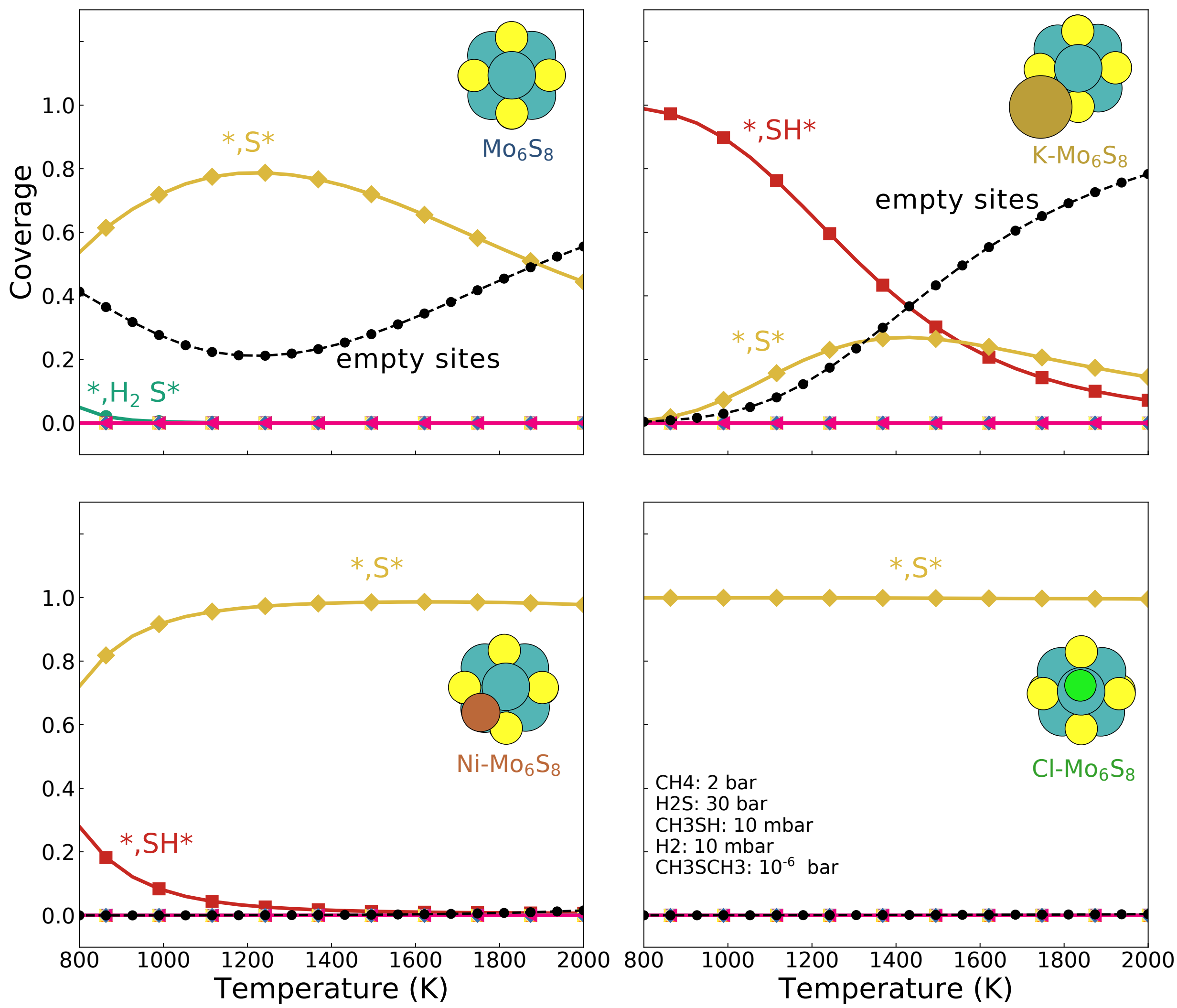

Figure S6: Coverages for the four different clusters.

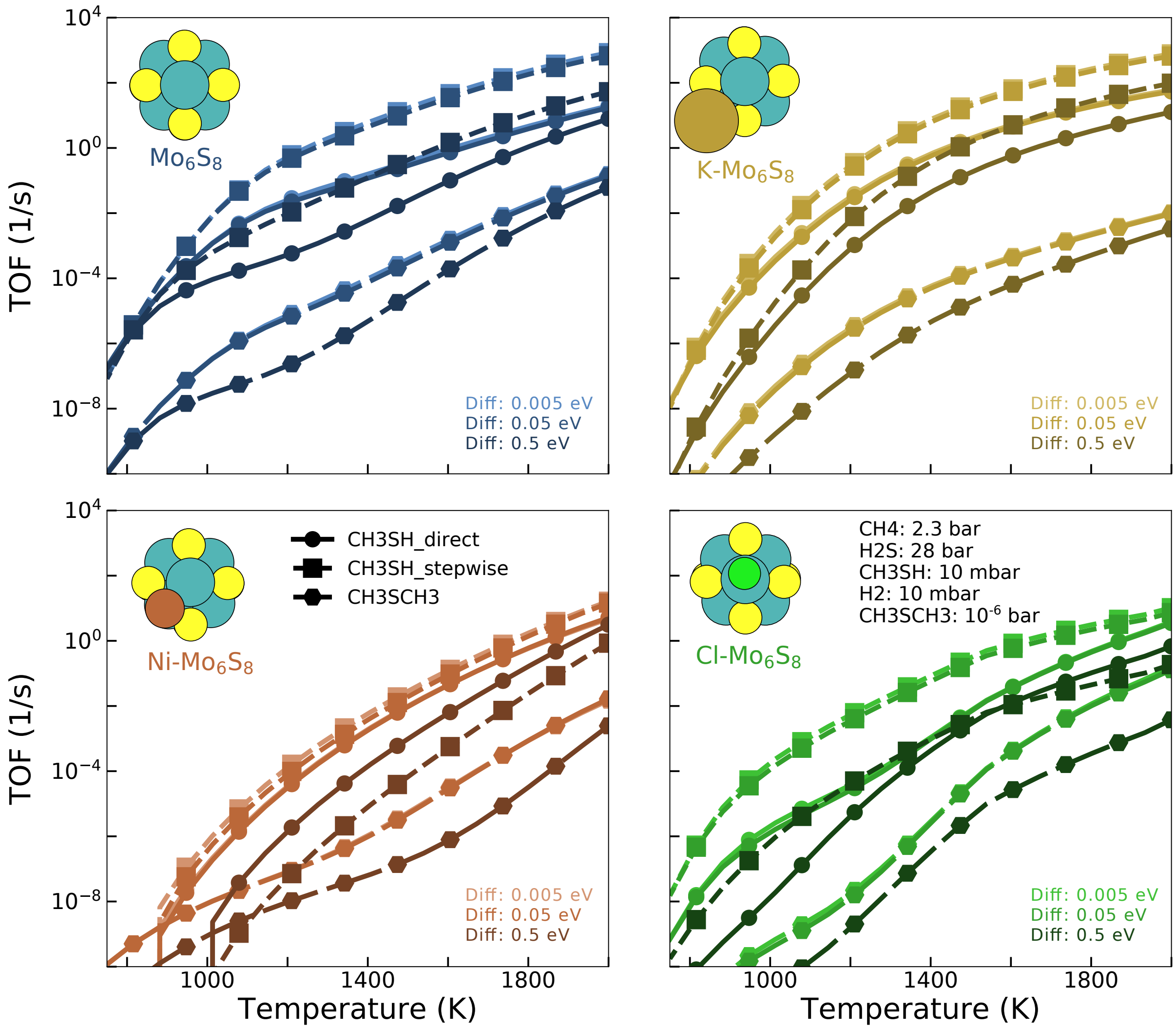

Figure S7: TOF comparing lowering and increasing the diffusion barriers by an order of magnitude.

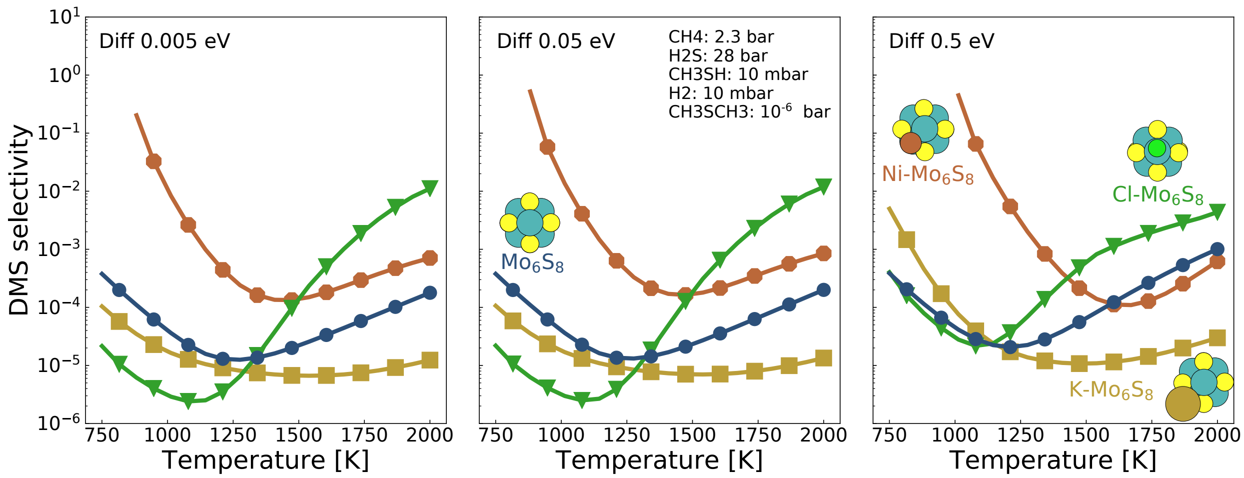

Figure S8: Selectivity towards DMS when lowering and increasing the diffusion barriers by an order of magnitude. Increasing the diffusion barrier by a factor of 10 affects the selectivity, but the trend remains the same.

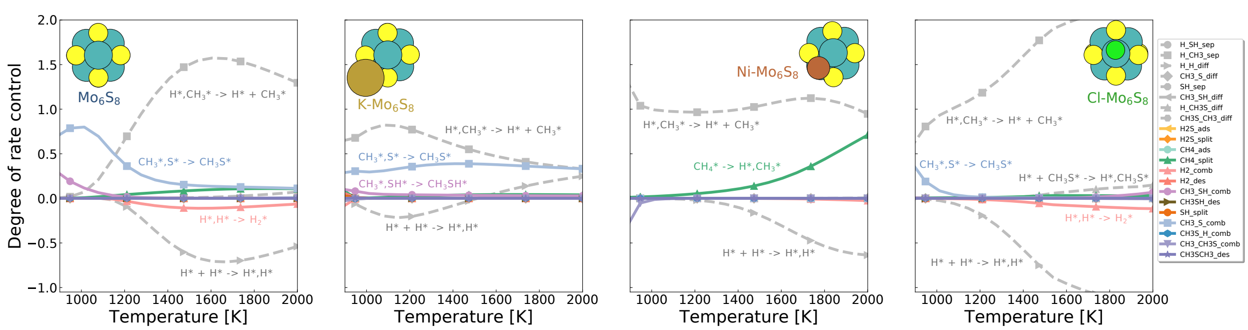

Figure S9: The degree of rate control as a function of temperature for the different clusters. The diffusion steps in gray, are important for the reactions to be possible. They also show the stochiometry, for instance the separation of H* and CH3* from the same cluster needs to happen two times before the H* + H* → H*,H* can happen one time.

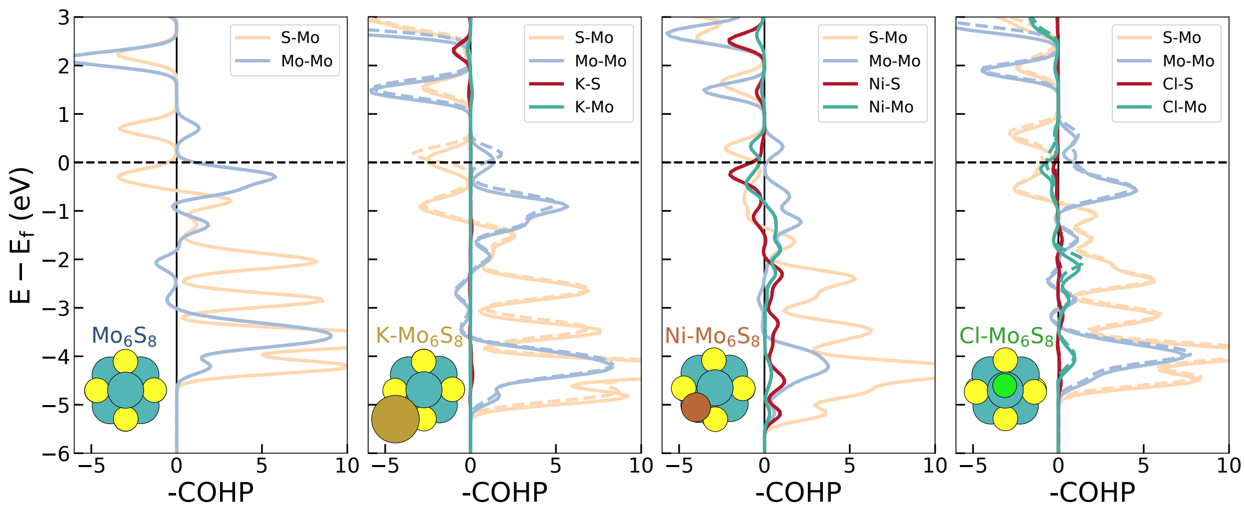

Figure S10: The projected COHP with the bonding orbitals with positive values to the right and antibonding character to the left. The solid and dashed lines are for the different spin channels. Promoting the cluster with K does not change the electronic structure that much, other than occupying some antibonding orbitals. Promoting the cluster with Ni and Cl changes more, where especially Ni introduces a lot of new features and weakens the Mo-Mo interaction.