Supporting Information

Atomic Perspective Elucidates Mixed Alcohol Synthesis from Syngas on Bilayered (K)/MoS_2 Catalysts

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For molybdenum sulfide based catalysts, we have constructed four-layer and two-layer stacking molybdenum sulfide models, drawing on the most widely accepted "Rim-Edge" model, and considered the effect of K doping on the adsorption of H_2 and CO on both models. The results show that the higher the Rim-Edge content, the more favorable the activation of H_2 molecules on the $MoS_2(100)$ surface, that is, the bilayer stacked $MoS_2(100)$ surface is more favorable for the activation of H_2 molecules. K can promote the dissociative adsorption of H_2 molecules, but at the same time occupy the sites for the dissociative adsorption of H_2 molecules and relatively inhibit their adsorption. Besides, K can provide more sites for the adsorption of CO. These also indicates that the doping of K not only has electronic effects, but also directly affects the process of CO hydrogenation from the structure of the active phase.

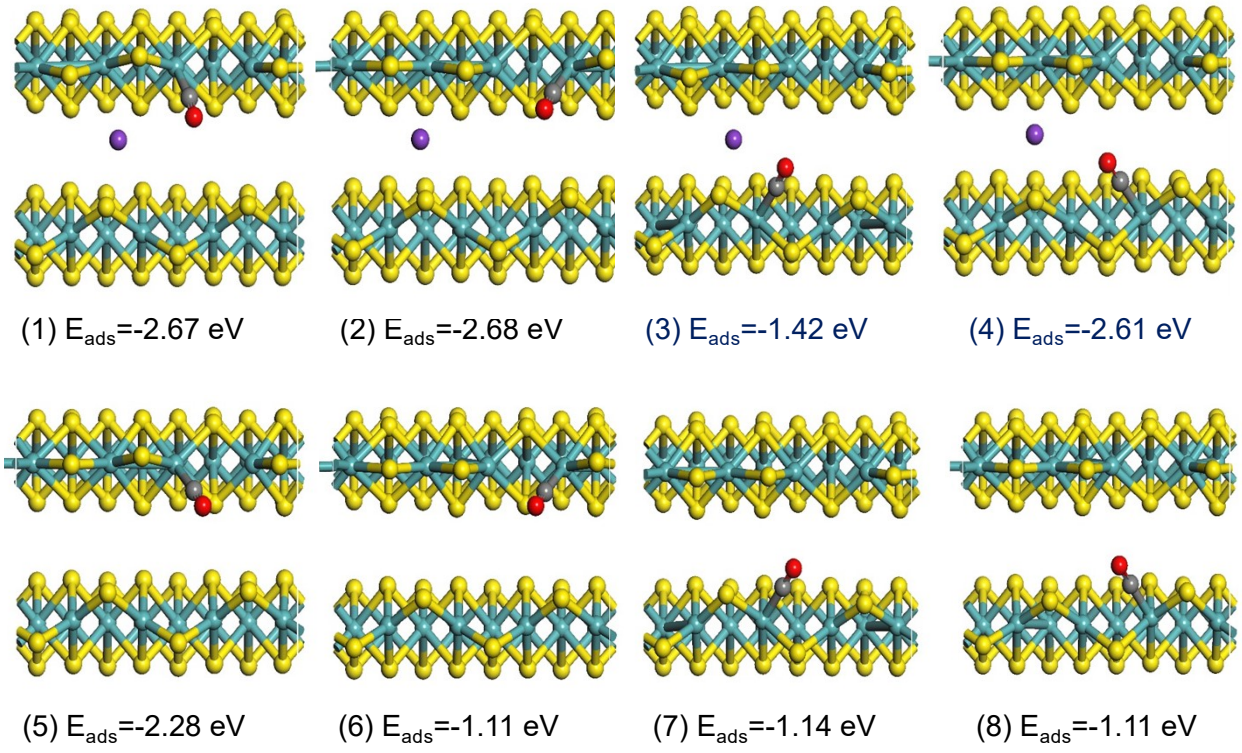


Figure S1 CO adsorption on the Mo and the S edges of the (Kdoped) $MoS_2(100)$ surfaces. The calculated CO adsorption energies are given for the undoped (below) and the K-doped (up) $MoS_2(100)$ surfaces. The light green, yellow, purple, gray, and red balls represent Mo, S, K, C, and O atoms, respectively.

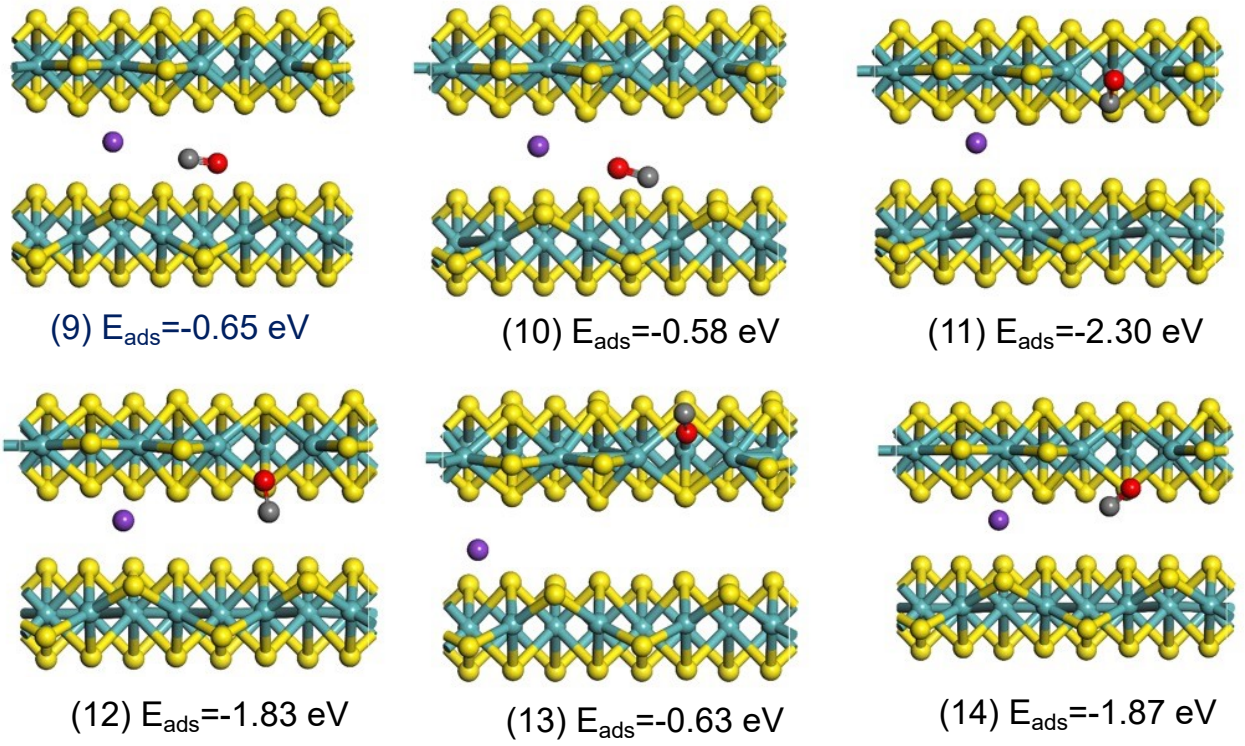


Figure S2 CO adsorption on the Mo and the S edges of the Kdoped MoS_2(100) surfaces. The calculated CO adsorption energies are given for t the K-doped (up) MoS_2(100) surfaces. The light green, yellow, purple, gray, and red balls represent Mo, S, K, C, and O atoms, respectively.

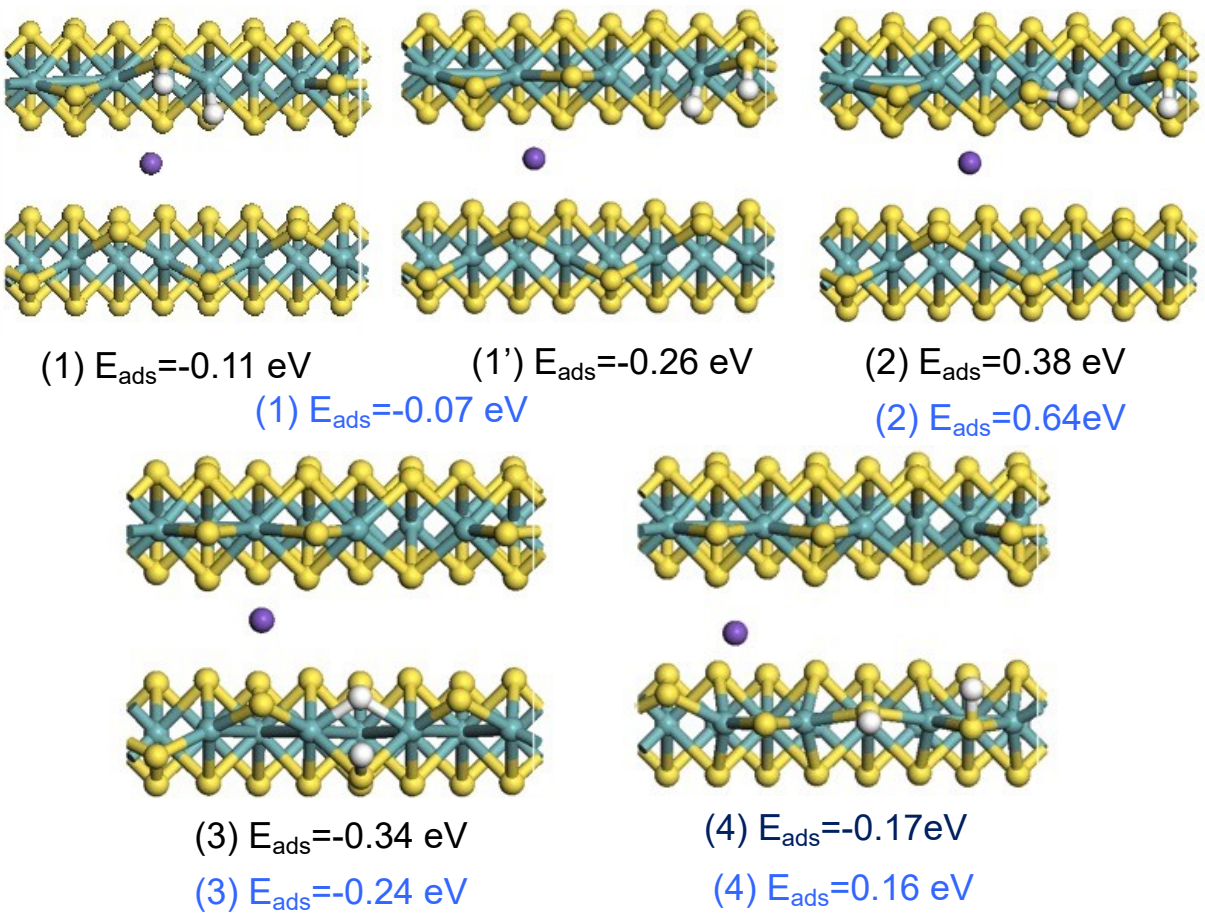


Figure S3 The dissociative H_2 adsorption on the Mo edge and the S edges of the (Kdoped) MoS_2(100) surfaces. The calculated adsorption energies relative to the gas phase molecular H_2 are given for the K-doped M (in dark) and the undoped MoS_2(100) surfaces. The color scheme in Fig. 1 is applied. White balls represent H atoms.

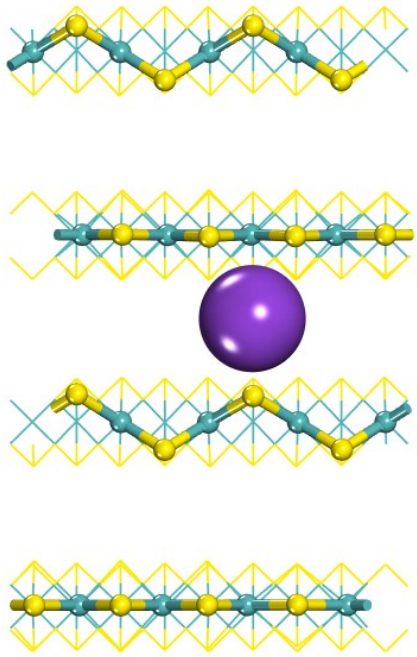


Figure S4 The optimized structure of 4 layered K/MoS_2(100).

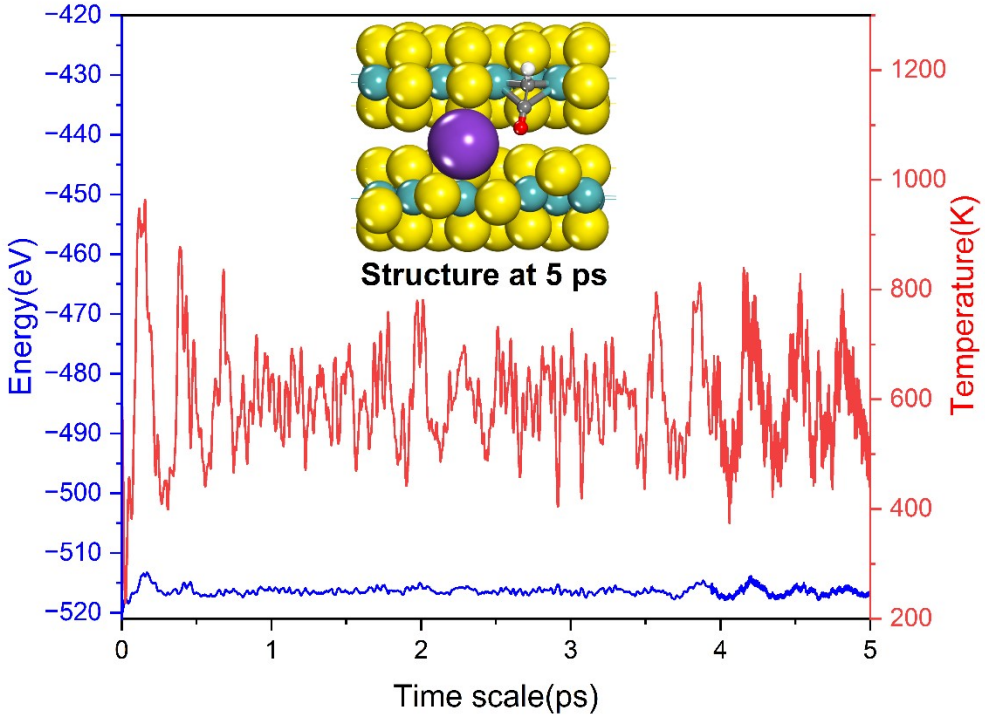


Figure S5 Energy and temperature fluctuations from AIMD simulations at 600 K for a duration of 5 ps.

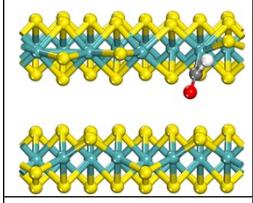
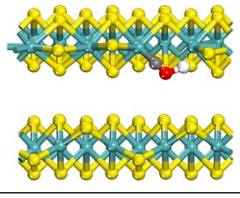
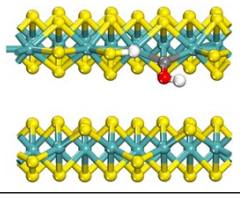
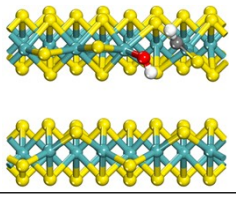
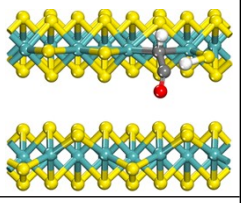
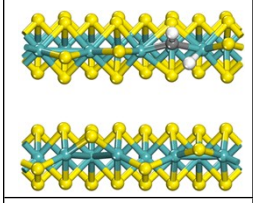
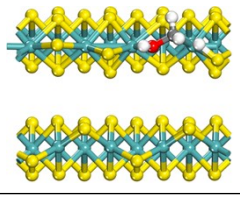
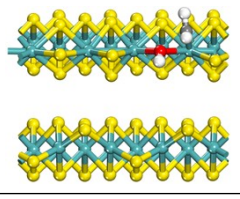
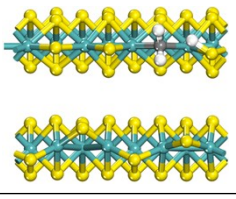
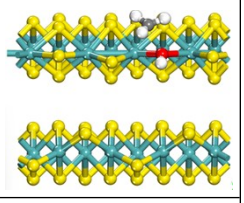
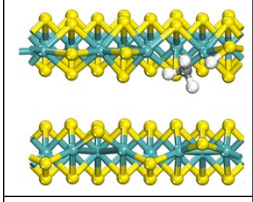
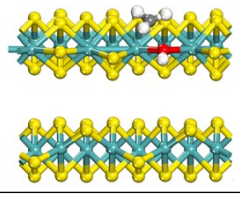
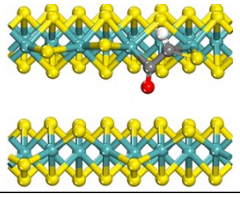
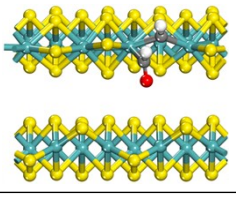
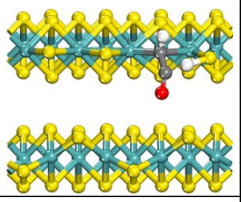
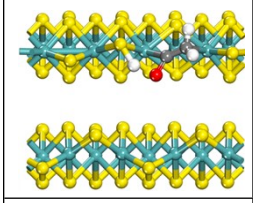
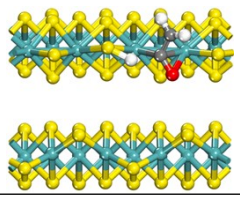
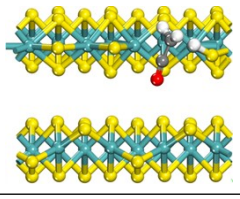
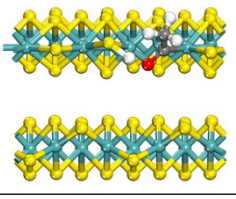
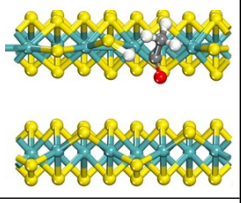
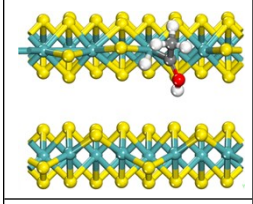
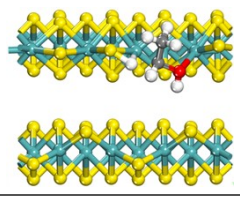
				
TS_{H-CO}	TS_{CO-H}	TS_{CHOH}	TS_{CH-OH}	TS_{CHOH-H}
f/i = 880.59 cm^{-1}	f/i = 556.40 cm^{-1}	f/i = 193.64 cm^{-1}	f/i = 245.02 cm^{-1}	f/i = 825.71 cm^{-1}
				
TS_{CH-H}	TS_{CH3OH}	TS_{CH2-OH}	TS_{CH2-H}	TS_{CH3-OH}
f/i = 924.59 cm^{-1}	f/i = 608.85 cm^{-1}	f/i = 485.54 cm^{-1}	f/i = 393.19 cm^{-1}	f/i = 558.83 cm^{-1}
				
TS_{CH3-H}	TS_{CH3-OH}	TS_{CH-CO}	TS_{CH-CHO}	TS_{CHCO-H}
f/i = 621.85 cm^{-1}	f/i = 558.83 cm^{-1}	f/i = 110.11 cm^{-1}	f/i = 191.48 cm^{-1}	f/i = 897.71 cm^{-1}
				
TSc_{H2COH}	$TS_{CH2CO-H}$	TS_{CH3CO}	TS_{CH3COH}	TS_{CH3CHO}
f/i = 634.66 cm^{-1}	f/i = 654.21 cm^{-1}	f/i = 400.49 cm^{-1}	f/i = 927.83 cm^{-1}	f/i = 501.93 cm^{-1}
				
TSc_{H3CHOH}	$TS_{CH3CH2OH}$			
f/i = 891.94 cm^{-1}	f/i = 544.88 cm^{-1}			

Figure S6 The structures of all transition state (TS) on Mo@$MoS_{2(}$100) site with the related frequency data.

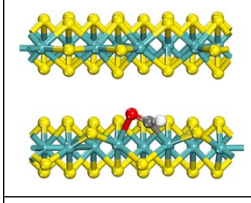
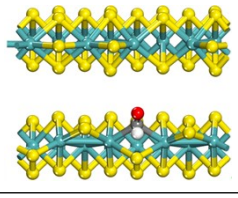
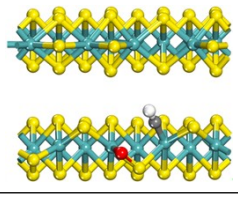
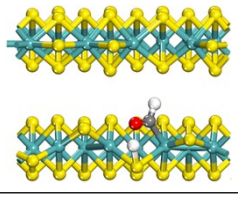
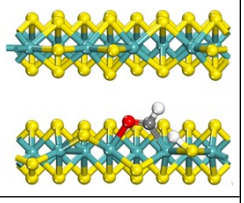
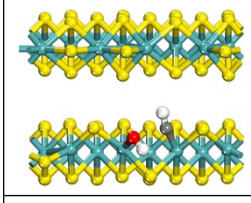
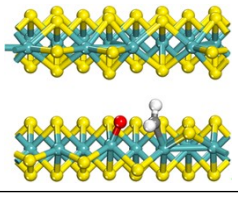
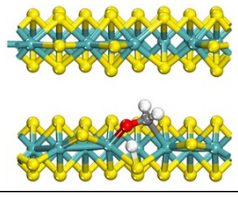
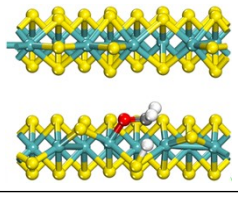
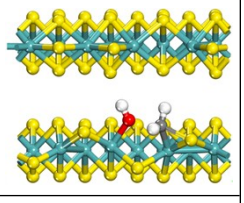
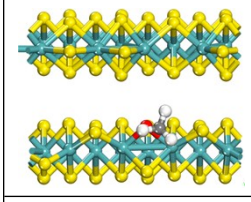
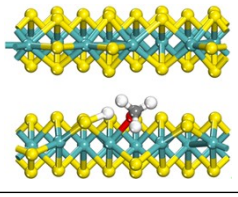
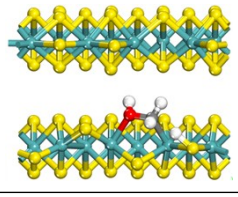
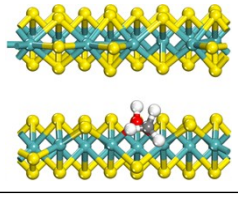
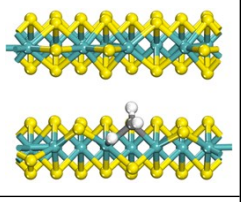
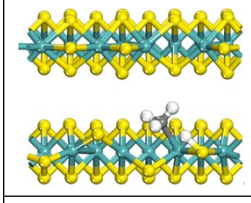
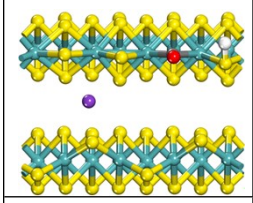
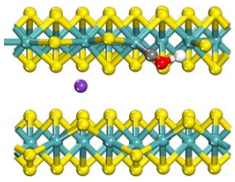
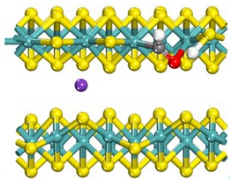
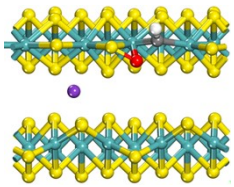
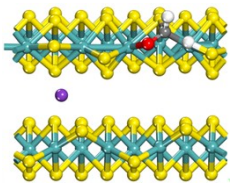
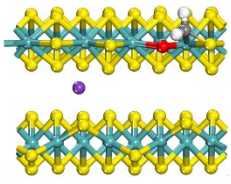
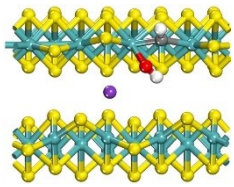
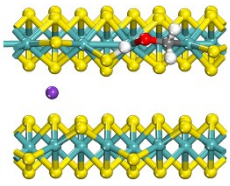
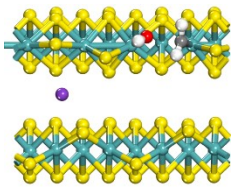
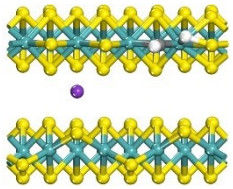
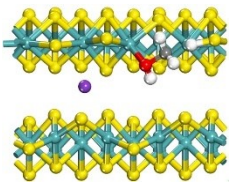
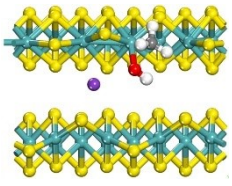
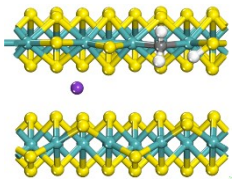
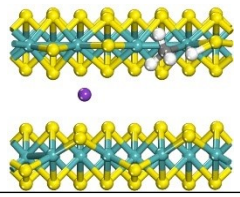
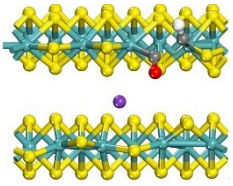
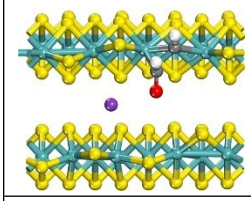
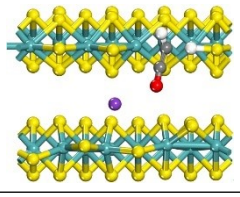
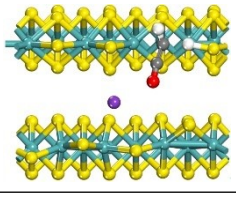
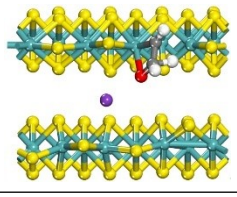
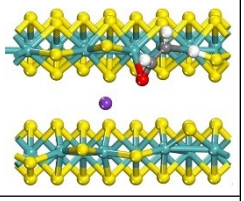
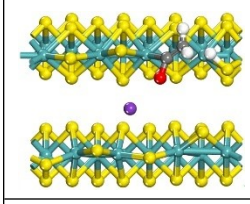
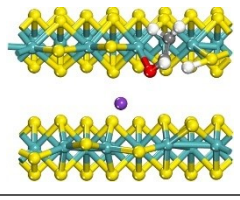
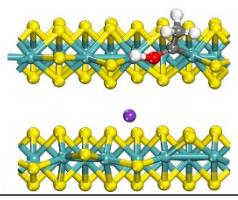
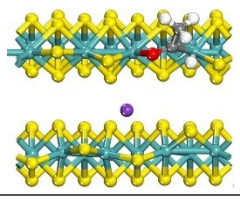
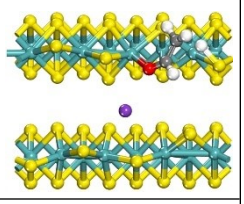
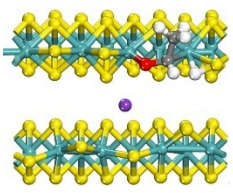
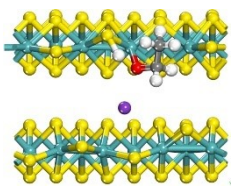
				
TS_{H-CO}	TS_{CO-H}	TS_{CH-O}	TS_{CHOH}	TS_{H2CO}
f/i = 621.85 cm^{-1}	f/i = 932.39 cm^{-1}	f/i = 189.21 cm^{-1}	f/i = 851.74 cm^{-1}	f/i = 459.99 cm^{-1}
				
TS_{CH-OH}	TS_{CH2-O}	TS_{CH2OH}	TS_{H3CO}	TS_{CH2-OH}
f/i = 346.02 cm^{-1}	f/i = 422.33 cm^{-1}	f/i = 1045.39 cm^{-1}	f/i = 774.71 cm^{-1}	f/i = 364.94 cm^{-1}
				
TSc_{H3-O}	TS_{H3CO-H}	TS_{CH3OH}	TS_{CH3-OH}	TS_{CH2-H}
f/i = 523.07 cm^{-1}	f/i = 967.74 cm^{-1}	f/i = 388.77 cm^{-1}	f/i = 335.54 cm^{-1}	f/i = 401.23 cm^{-1}
				
TSc_{H3-H}				
f/i = 341.84 cm^{-1}				

Figure S7 The structures of all transition state (TS) on S@MoS_2(100) site with the related frequency data.

				
TS_{H-CO}	TS_{CO-H}	TS_{CHOH}	TS_{CH-O}	TS_{H2CO}
f/i = 166.49 cm^{-1}	f/i = 860.75 cm^{-1}	f/i = 1009.69 cm^{-1}	f/i =407.92 cm^{-1}	f/i = 497.61 cm^{-1}
				
TS_{CH2-O}	TS_{CH-OH}	TS_{CH2OH}	TS_{CH2-OH}	TS_{CH-H}
f/i = 499.96cm^{-1}	f/i = 386.46 cm^{-1}	f/i = 895.12 cm^{-1}	f/i = 387.87 cm^{-1}	f/i = 837.45 cm^{-1}
				
TSc_{H2OH-H}	TS_{CH3-OH}	TS_{CH2-H}	TS_{CH3-H}	TS_{CH-CO}
f/i = 311.97 cm^{-1}	f/i = 513.03 cm^{-1}	f/i = 365.27 cm^{-1}	f/i = 882.88 cm^{-1}	f/i = 181.07 cm^{-1}
				
TSc_{H-CHO}	TS_{CHCO-H}	TS_{CH2CO}	TS_{CHCH2O}	TS_{CH2CHO}
f/i = 509.27 cm^{-1}	f/i = 535.72 cm^{-1}	f/i =602.68 cm^{-1}	f/i = 915.40 cm^{-1}	f/i = 329.23 cm^{-1}
				
TSc_{H3CO}	$TS_{CH2CH2O}$	TS_{CH3COH}	$TS_{CH3CO-H}$	TS_{CH3CHO}
f/i = 481.81 cm^{-1}	f/i = 1473.83 cm^{-1}	f/i = 1126.13 cm^{-1}	f/i = 865.04 cm^{-1}	f/i = 900.60 cm^{-1}
				

TSc_{H3CH2O}	$TSc_{H3CH2OH}$			
f/i = 124.08 cm^{-1}	f/i = 752.13 cm^{-1}			

Figure S8 The structures of all transition state (TS) on Mo@K/$MoS_{2(}$100) site with the related frequency data.

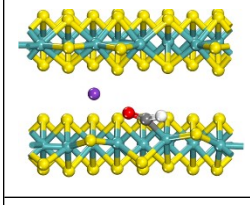
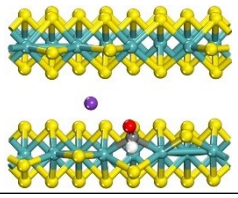
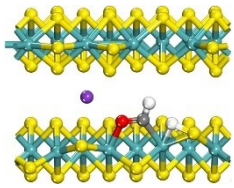
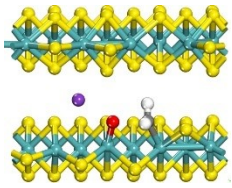
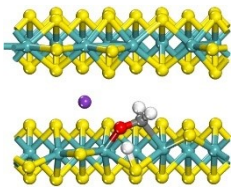
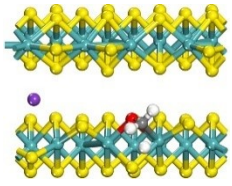
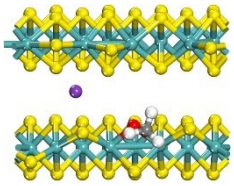
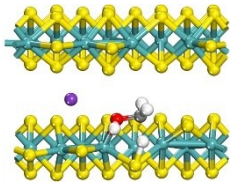
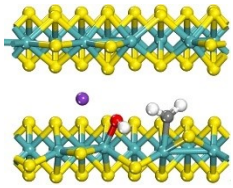
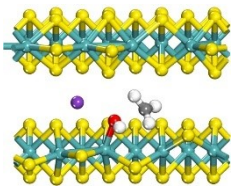
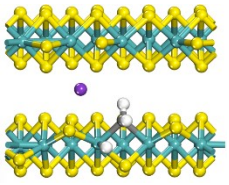
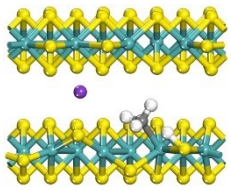
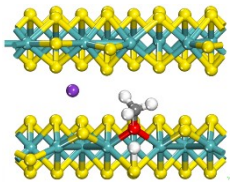
				
TS_{H-CO}	TS_{CO-H}	TS_{H2CO}	TS_{CH2-O}	TS_{CH2OH}
f/i = 439.84 cm^{-1}	f/i = 1855.12 cm^{-1}	f/i = 606.98 cm^{-1}	f/i = 370.13 cm^{-1}	f/i = 965.33 cm^{-1}
				
TS_{H3CO}	TS_{CH3-O}	TS_{CH3OH}	TS_{CH2-OH}	TS_{CH3-OH}
f/i = 1039.23 cm^{-1}	f/i = 542.90 cm^{-1}	f/i = 810.42 cm^{-1}	f/i = 418.53 cm^{-1}	f/i = 469.30 cm^{-1}
				
TS_{CH2-H}	TS_{CH3-H}	TS_{H3CO-H}		
f/i = 404.30 cm^{-1}	f/i = 342.43 cm^{-1}	f/i = 973.50 cm^{-1}		

Figure S9 The structures of all transition state (TS) on S@K/$MoS_{2(}$100) site with the related frequency data.