Electronic Supplementary Information for:

Synergetic Effect between Single Cu Site and S Vacancy on MoS_2 Basal Plane for Methanol Synthesis from Syngas

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Figure S1. Configurations (side view) for (a) CO (b) CHO (c) CH_2O (d) CHOH (e) CH_3O (f) CH_2OH (g) CH (h) CH_2 (i) CH_3 (j) H (k) O (l) OH adsorption on MoS_2(001) (I) and Cu/MoS_2(001) (II). The green, blue, yellow, grey, red and white balls represent Mo, Cu, S, C, O and H atoms, respectively. This notation is used throughout this paper.

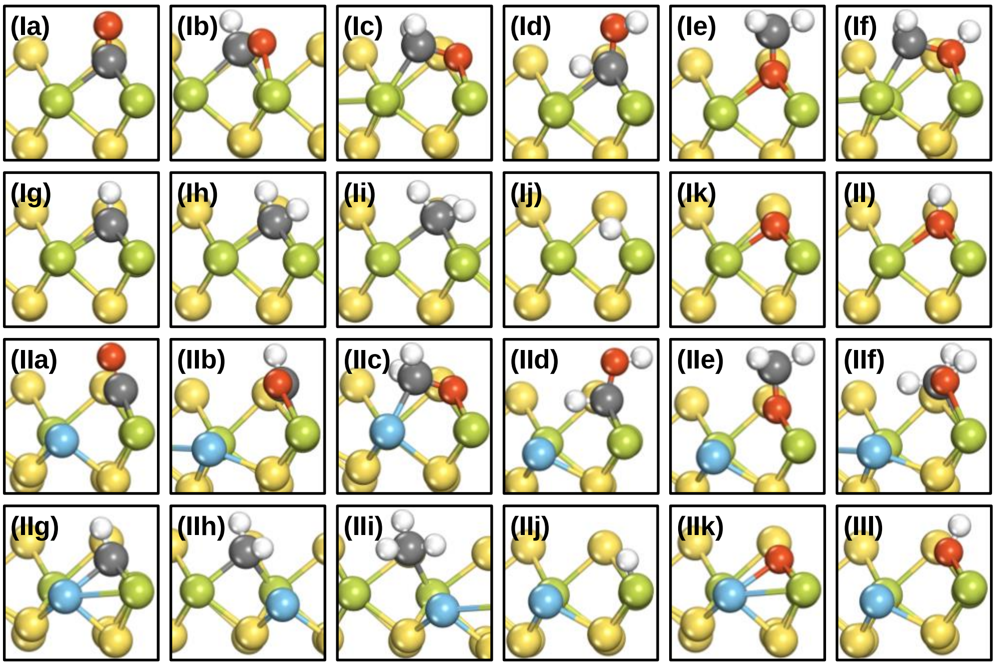

Figure S2. Top view (I) and side view (II) of configurations at the transition states of (a) $CH_2O \rightarrow CH_2+O$ (b) $CHOH \rightarrow CH+OH$ (c) $CH_3O \rightarrow CH_3+O$ (d) $CH_2OH \rightarrow CH_2+OH$ (e) $CO+O \rightarrow CO_2$ (f) $CHO+H \rightarrow CHOH$ (g) $CH_2O+H \rightarrow CH_2OH$ (h) $CHOH+H \rightarrow CH_2OH$ (i) $CH_2OH+H \rightarrow CH_3OH$ (j) $OH+H \rightarrow H_2O$ on MoS_2(001).

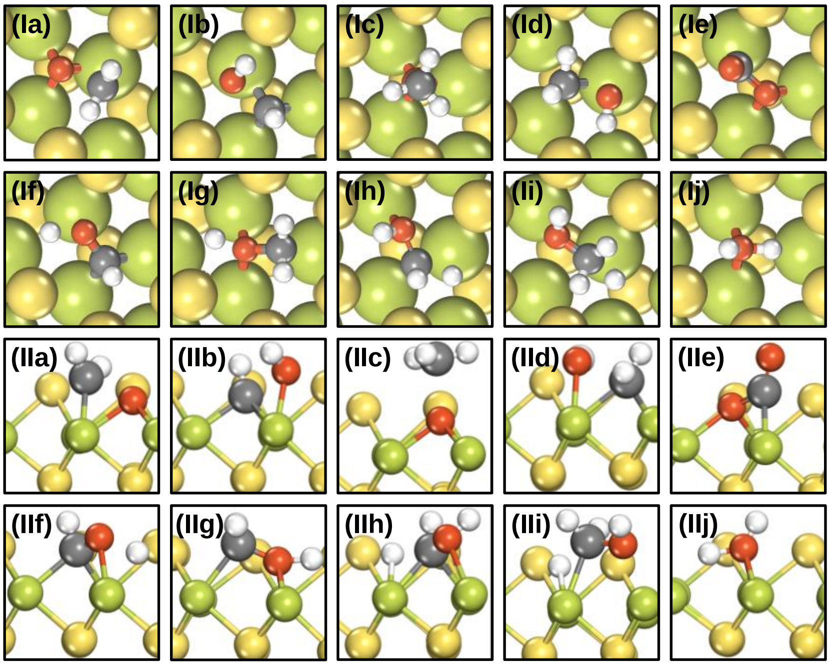

Figure S3. Configurations (side view) at the transition states of (a) CHO→CH+O (b) CO+H→CHO (c) CHO+H→CH_2O (d) CH_2O+H→CH_3O (e) CH_3O+H→CH_3OH (f) CH+H→CH_2 (g) CH_2+H→CH_3 (h) CH_3+H→CH_4 (i) O+H→OH (j) 2OH→H_2O+O/OH +H→H_2O on (I) MoS_2(001) and (II) Cu/MoS_2(001).

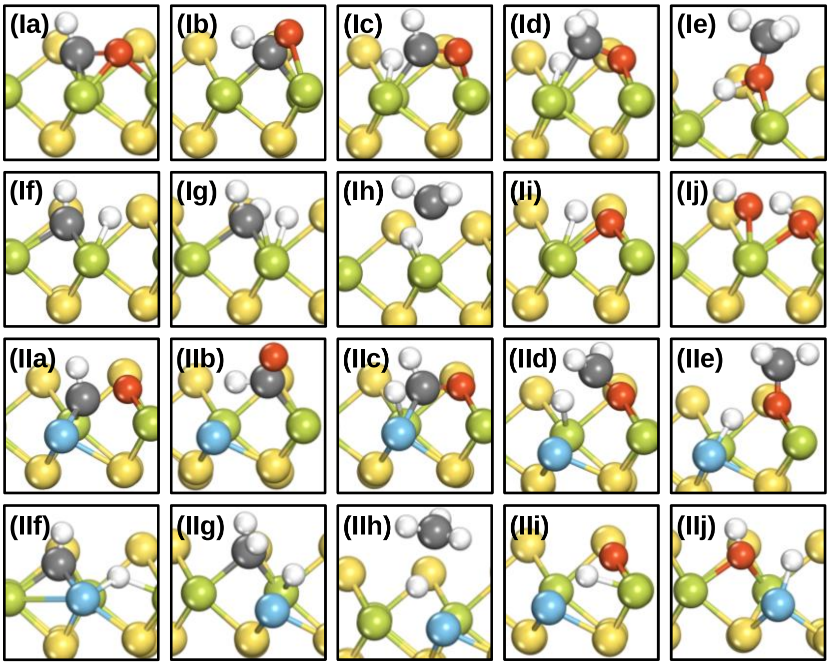

Figure S4. Top view (I) and side view (II) of configurations at the transition states of (a) $CH_2O \rightarrow CH_2+O$ (b) $CHOH \rightarrow CH+OH$ (c) $CH_3O \rightarrow CH_3+O$ (d) $CH_2OH \rightarrow CH_2+OH$ (e) $CO+O \rightarrow CO_2$ (f) $CHO+H \rightarrow CHOH$ (g) $CH_2O+H \rightarrow CH_2OH$ (h) $CHOH+H \rightarrow CH_2OH$ (i) $CH_2OH+H \rightarrow CH_3OH$ (j) $2OH \rightarrow H_2O+O$ on $Cu/MoS_2(001)$.

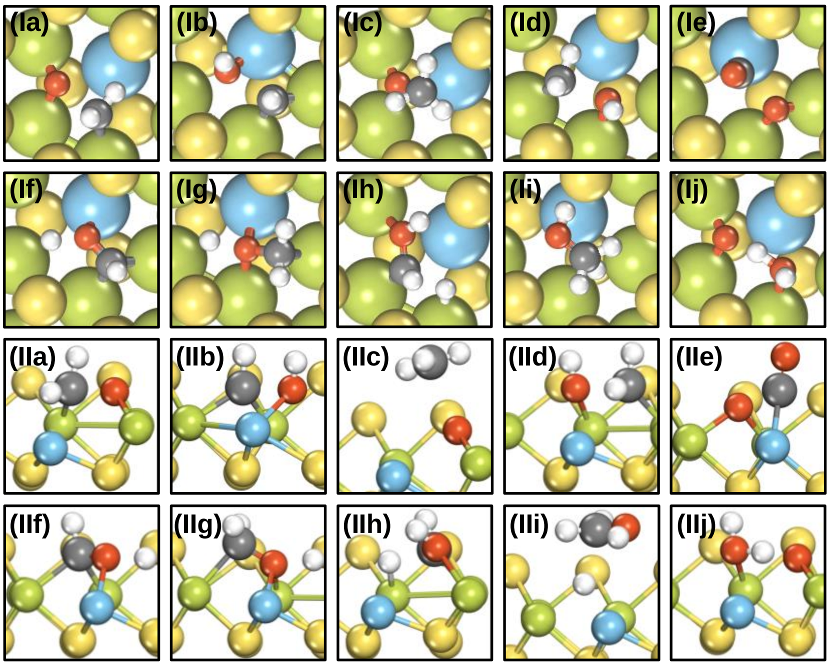

Table S1. Calculated adsorption energies (ΔE_{Ads}, in eV) of various species as a function of Maximum of Residual Forces (MRF, in eV/Å) on $MoS_2(001)$ and $Cu/MoS_2(001)$. No zero point energy corrections are included.

Species	MRF	$MoS_2(001)$	$Cu/MoS_2(001)$
		ΔE_{Ads}	ΔE_{Ads}
O	0.01	-7.29	-5.70
	0.03	-7.29	-5.70
	0.05	-7.29	-5.70
CO	0.01	-0.89	-0.80
	0.03	-0.89	-0.80
	0.05	-0.89	-0.80
CHO	0.01	-1.88	-1.70
	0.03	-1.88	-1.70
	0.05	-1.88	-1.70
CH_2	0.01	-4.58	-3.55
	0.03	-4.58	-3.54
	0.05	-4.58	-3.54
CHOH	0.01	-3.12	-2.35
	0.03	-3.12	-2.35
	0.05	-3.12	-2.35
CH_3O	0.01	-3.32	-3.01
	0.03	-3.32	-3.00
	0.05	-3.32	-3.00

Microkinetic Modeling

The reaction rate constant (k) is given by the Eying equation based on the transition-state theory:

$$k = \frac{k_B T}{h} e^{\frac{-\Delta E_{act}}{k_B T}} \text{ ....} \qquad (1)$$

where k_B, T, h and ΔE_{act} represent the Boltzmann constant, absolute temperature, Planck constant and activation energy, respectively. The rate constant of adsorption (k_{ads}) is calculated by the following:

$$k_{\mathrm{ads}} = \frac{S \cdot P \cdot A}{\sqrt{2\pi m k_B T}} \text{ ....} \qquad (2)$$

where S, P, A and m are the sticking coefficient, partial pressure of the adsorbed species, the area of the adsorption site and the molecular mass of adsorbed species, respectively. The value of S is assumed to be one for all the species.

We consider that the species have three rotational degrees of freedom, two translational degrees of freedom and 3N−6 vibrational degrees of freedom at the transition state. Furthermore, we assume that at the initial state (the absorbed state), the species only contains vibrational degrees of freedom. This gives us the following expression for the desorption rate:

$$k_{\mathrm{des}} = \frac{k_B T}{h} \frac{f_{trans}^{\neq(2)} f_{rot}^{\neq(3)} f_{vib}^{\neq(3N-6)}}{f_{vib}^{\neq(3N)}} e^{\frac{-E_{des}}{k_B T}} \text{ ....} (3)$$

We can work this out by plugging in the formulas for the partition functions and assuming that the vibrational partition functions approximate unity.

$$k_{\mathrm{des}} = \frac{k_B T^3}{h^3} \frac{A(2\pi m k_B)}{\sigma} \frac{8\pi^2 I k_B T}{h^2} e^{\frac{-E_{des}}{k_B T}} \text{ ....} (4)$$

After reduction of the above equation by noting that we can express the term $\frac{h^2}{8\pi^2 I k_B}$ as a temperature, known as the characteristic temperature for rotation. After plugging this value in and combining similar terms, this yields:

$$k_{\mathrm{des}} = \frac{k_B T^3}{h^3} \frac{A(2\pi m k_B)}{\sigma \theta_{rot}} e^{\frac{-E_{des}}{k_B T}} \qquad \text{..........................}(5)$$

where σ, θ_{rot} and E_{des} are the symmetry number, the characteristic temperature for rotation of adsorbed species and the activation energy of desorption.

Microkinetic simulations are performed by the MKMCXX program.[1] The reaction temperature ranges from 530 K to 710 K, and the total pressure is kept at 50 bar with H_2/CO ratio of 3. The degree of rate control $X_{RC,i}$ of step (*i*),[2] which can qualitatively determine the significance of single step *(i*) in the overall reaction, is defined as

$$X_{\mathrm{RC},i} = \frac{k_i}{r}\left(\frac{\partial r}{\partial k_i}\right)_{k_{j\neq i},K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i}\right)_{k_{j\neq i},K_i} \qquad \text{..................} \qquad (6)$$

where k_i, K_i and r are the forward rate constant, the equilibrium constant for elementary step *i* and the reaction rate, respectively.

The degree of selectivity control (DSC) is also performed,[3] which quantifies the particular elementary step that influences the selectivity to certain products. DSC for a particular key component is defined in the following manner

$$\varepsilon_{c,i} = \left(\frac{\partial \eta_c}{\partial k_i / k_i}\right)_{k_{j\neq i},K_i} = \left(\frac{\partial \eta_c}{\partial \ln(k_i)}\right)_{k_{j\neq i},K_i} \qquad \text{..................} \qquad (7)$$

where $\varepsilon_{c,i}$ is the DSC of product c because of a change in the kinetics of the elementary step *i* and η_c is the selectivity of product c. The products of CO hydrogenation considered in the present study are CH_4, CH_3OH, H_2O and CO_2.

References

[1] I. A. W. Filot, R. A. van Santen, E. J. M. Hensen, *Angew. Chem. Int. Ed.* **2014**, *53*, 12746-12750.

[2] C. Stegelmann, A. Andreasen, C. T. Campbell, *J. Am. Chem. Soc.* **2009**, *131*, 8077-8082.

[3] C. Stegelmann, N. C. Schiødt, C. T. Campbell, P. Stoltze, *J. Catal.* **2004**, *221*, 630–649.