

**Supporting Information for “Accuracy of Density Functional Theory for Predicting Kinetics of Methanol Synthesis from CO and CO<sub>2</sub> Hydrogenation on Copper”**

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## I. COMPUTATIONAL DETAILS FOR MICROKINETIC MODELING OF CO AND CO<sub>2</sub> HYDROGENATION ON Cu(211)

The details of microkinetic modeling are given in Table S.I and S.II. Table S.1 gives the reaction rates of the elementary steps in Table 1 in the paper, and the surface coverages of gas-phase molecules derived by assuming adsorption and desorption processes are at quasi-equilibrium.  $k_j$  and  $K_j$  are the rate constant and the equilibrium constant of the  $j^{th}$  reaction step in Table 1 in the paper, respectively. Table S.2 shows the equations for the time evolution of the coverages. Microkinetic modelings are performed for isolated CO, isolated CO<sub>2</sub>, and combined CO and CO<sub>2</sub> hydrogenations, respectively. Since the reaction steps have different time scales, the rate equations are stiff ordinary differential equations (ODEs) and are integrated with the “ode15s” function in MATLAB until the steady states are reached.

TABLE S.1. Rates and coverages of CO\*, H\*, CO<sub>2</sub>\*, H<sub>3</sub>COH\*, and H<sub>2</sub>O\*.

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$$\begin{aligned}
 r_3 &= k_3^+ \theta_{CO} \theta_H - k_3^- \theta_* \theta_{HCO} \\
 r_4 &= k_4^+ \theta_{HCO} \theta_H - k_4^- \theta_* \theta_{H_2CO} \\
 r_5 &= k_5^+ \theta_{H_2CO} \theta_H - k_5^- \theta_* \theta_{H_3CO} \\
 r_6 &= k_6^+ \theta_{H_3CO} \theta_H - k_6^- \theta_* \theta_{H_3COH} \\
 r_9 &= k_9^+ \theta_{CO_2} \theta_H - k_9^- \theta_* \theta_{HCOO} \\
 r_{10} &= k_{10}^+ \theta_{HCOO} \theta_H - k_{10}^- \theta_* \theta_{HCOOH} \\
 r_{11} &= k_{11}^+ \theta_{HCOOH} \theta_H - k_{11}^- \theta_* \theta_{H_2COOH} \\
 r_{12} &= k_{12}^+ \theta_{H_2COOH} \theta_* - k_{12}^- \theta_{OH} \theta_{H_2CO} \\
 r_{13} &= k_{13}^+ \theta_{OH} \theta_H - k_{13}^- \theta_* \theta_{H_2O} \\
 \\
 \theta_{CO} &= K_1 \theta_* \\
 \theta_H &= \sqrt{K_2} \theta_* \\
 \theta_{CO_2} &= K_8 \theta_* \\
 \theta_{H_3COH} &= K_7 \theta_* \\
 \theta_{H_2O} &= K_{14} \theta_*
 \end{aligned}$$


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TABLE S.2. Rate equations of the intermediates' coverages.

Isolated CO hydrogenation:

$$\begin{aligned}\frac{d\theta_{HCO}}{dt} &= k_3^+ \theta_{CO} \theta_H - k_3^- \theta_* \theta_{HCO} - k_4^+ \theta_{HCO} \theta_H + k_4^- \theta_* \theta_{H_2CO} \\ \frac{d\theta_{H_2CO}}{dt} &= k_4^+ \theta_{HCO} \theta_H - k_4^- \theta_{H_2CO} \theta_* - k_5^+ \theta_{H_2CO} \theta_H + k_5^- \theta_* \theta_{H_3CO} \\ \frac{d\theta_{H_3CO}}{dt} &= k_5^+ \theta_{H_2CO} \theta_H - k_5^- \theta_{H_3CO} \theta_* - k_6^+ \theta_{H_3CO} \theta_H + k_6^- \theta_* \theta_{H_3COH}\end{aligned}$$

Isolated CO<sub>2</sub> hydrogenation:

$$\begin{aligned}\frac{d\theta_{HCOO}}{dt} &= k_9^+ \theta_{CO_2} \theta_H - k_9^- \theta_{HCOO} \theta_* - k_{10}^+ \theta_{HCOO} \theta_H + k_{10}^- \theta_* \theta_{HCOOH} \\ \frac{d\theta_{H_2CO}}{dt} &= k_{12}^+ \theta_* \theta_{H_2COOH} - k_{12}^- \theta_{H_2CO} \theta_{OH} - k_5^+ \theta_{H_2CO} \theta_H + k_5^- \theta_* \theta_{H_3CO} \\ \frac{d\theta_{H_3CO}}{dt} &= k_5^+ \theta_{H_2CO} \theta_H - k_5^- \theta_* \theta_{H_3CO} - k_6^+ \theta_{H_3CO} \theta_H + k_6^- \theta_* \theta_{H_3COH} \\ \frac{d\theta_{HCOOH}}{dt} &= k_{10}^+ \theta_H \theta_{HCOO} - k_{10}^- \theta_* \theta_{HCOOH} - k_{11}^+ \theta_{HCOOH} \theta_H + k_{11}^- \theta_* \theta_{H_2COOH} \\ \frac{d\theta_{H_2COOH}}{dt} &= k_{11}^+ \theta_H \theta_{HCOOH} - k_{11}^- \theta_* \theta_{H_2COOH} - k_{12}^+ \theta_* \theta_{H_2COOH} + k_{12}^- \theta_{H_2CO} \theta_{OH} \\ \frac{d\theta_{OH}}{dt} &= k_{12}^+ \theta_* \theta_{H_2COOH} - k_{12}^- \theta_{H_2CO} \theta_{OH} - k_{13}^+ \theta_{OH} \theta_H + k_{13}^- \theta_* \theta_{H_2O}\end{aligned}$$

Combined CO and CO<sub>2</sub> hydrogenation:

$$\begin{aligned}\frac{d\theta_{HCO}}{dt} &= k_3^+ \theta_{CO} \theta_H - k_3^- \theta_* \theta_{HCO} - k_4^+ \theta_{HCO} \theta_H + k_4^- \theta_* \theta_{H_2CO} \\ \frac{d\theta_{H_2CO}}{dt} &= k_4^+ \theta_{HCO} \theta_H - k_4^- \theta_* \theta_{H_2CO} + k_{12}^+ \theta_* \theta_{H_2COOH} + k_{12}^- \theta_{H_2CO} \theta_{OH} - k_5^+ \theta_{H_2CO} \theta_H + k_5^- \theta_* \theta_{H_3CO} \\ \frac{d\theta_{H_3CO}}{dt} &= k_5^+ \theta_{H_2CO} \theta_H - k_5^- \theta_* \theta_{H_3CO} - k_6^+ \theta_{H_3CO} \theta_H + k_6^- \theta_* \theta_{H_3COH} \\ \frac{d\theta_{HCOO}}{dt} &= k_9^+ \theta_{CO_2} \theta_H - k_9^- \theta_* \theta_{HCOO} - k_{10}^+ \theta_{HCOO} \theta_H + k_{10}^- \theta_* \theta_{HCOOH} \\ \frac{d\theta_{HCOOH}}{dt} &= k_{10}^+ \theta_H \theta_{HCOO} - k_{10}^- \theta_* \theta_{HCOOH} - k_{11}^+ \theta_{HCOOH} \theta_H + k_{11}^- \theta_* \theta_{H_2COOH} \\ \frac{d\theta_{H_2COOH}}{dt} &= k_{11}^+ \theta_H \theta_{HCOOH} - k_{11}^- \theta_* \theta_{H_2COOH} - k_{12}^+ \theta_* \theta_{H_2COOH} + k_{12}^- \theta_{H_2CO} \theta_{OH} \\ \frac{d\theta_{OH}}{dt} &= k_{12}^+ \theta_* \theta_{H_2COOH} - k_{12}^- \theta_{H_2CO} \theta_{OH} - k_{13}^+ \theta_{OH} \theta_H + k_{13}^- \theta_* \theta_{H_2O}\end{aligned}$$

## II. CONVERGENCE ANALYSIS OF RPA CALCULATIONS

To reduce the high cost of RPA calculations, in this work we employ relatively low settings (kinetic energy cutoffs of 300 eV and  $k$ -point meshes of  $2 \times 2 \times 1$ ) in RPA calculations. It is known that RPA energy converges slowly with respect to kinetic energy cutoffs (i.e., the number of conduction bands) and the size of  $k$ -point mesh.<sup>1</sup> The challenge with using low kinetic energy cutoffs is partially alleviated in VASP by extrapolating the RPA results to infinite number of bands.<sup>2</sup> To further reduce the cost of clusters' RPA calculations, we reduce

the cell size,  $L_z$ , in the  $z$  direction, while still keeping the distance between images to be about 10 Å. In Table S.3, we perform the convergence tests of the kinetic energy cutoffs,  $k$ -point mesh, and  $L_z$ . Due to the high cost of RPA, we focus on the Gibbs energy difference,  $\Delta G_{\text{RLS}}$ , between H-HCO/Cu(211) and H-HCOOH/Cu(211), since they are the rate-limiting steps in CO and CO<sub>2</sub> hydrogenations.

To determine the cluster sizes, we test the convergence of  $\Delta G_{\text{RLS}}$  with one layer (1L), two layers (2L), and three layers (3L) of copper. The results are summarized in Table S.3. We find that  $\Delta G_{\text{RLS}}$  converges to 0.14 eV as we increase the number of top copper layers. Therefore, three layers of copper are used in the following tests. The reasons for the fast convergence can be attributed to that (a) we cut metallic bonds, (b) the charge transfers and the bonding between adsorbates and metal surfaces are local, and (c) the errors due to the cluster boundaries are canceled out between two systems.

By increasing the kinetic energy cutoff to 400 eV,  $\Delta G_{\text{RLS}}$  increases by 0.03 eV. By increasing  $L_z$  to 23 Å,  $\Delta G_{\text{RLS}}$  increases by 0.02 eV. By using a larger  $k$ -point mesh  $4 \times 4 \times 1$ ,  $\Delta G_{\text{RLS}}$  stays at 0.14 eV. In summary, low kinetic energy cutoffs, small  $k$ -point meshes, and a reduced  $L_z$  do not cause much error to  $\Delta G_{\text{RLS}}$ . The reason is that we compute the RPA correlation energy difference between two systems, and there is an effective error cancellation between the two systems.

## REFERENCES

- <sup>1</sup>J. Harl, L. Schimka, and G. Kresse, “Assessing the quality of the random phase approximation for lattice constants and atomization energies of solids,” *Phys. Rev. B* **81**, 115126 (2010).
- <sup>2</sup>J. Harl and G. Kresse, “Cohesive energy curves for noble gas solids calculated by adiabatic connection fluctuation-dissipation theory,” *Physical Review B* **77**, 045136 (2008).

TABLE S.3. Gibbs energies (in eV) of H-HCO\* and H-HCOOH\* calculated using RPA with different kinetic energy cutoffs,  $k$ -point meshes, and cell sizes in the  $z$  direction ( $L_z$ ). They are denoted by  $G_{\text{H-HCO}}$  and  $G_{\text{H-HCOOH}}$ , respectively. Relative energies are defined as  $\Delta G_{\text{RLS}} = G_{\text{H-HCOOH}} - G_{\text{H-HCO}}$ . Energies are in eV.

	$G_{\text{H-HCO}}$	$G_{\text{H-HCOOH}}$	$\Delta G_{\text{RLS}}$
$k$ -point: $2 \times 2 \times 1$			
300 eV, $L_z = 13 \text{ \AA}$ , 1L	1.92	2.02	0.10
300 eV, $L_z = 13 \text{ \AA}$ , 2L	1.82	1.96	0.14
300 eV, $L_z = 13 \text{ \AA}$ , 3L	1.80	1.94	0.14
400 eV, $L_z = 13 \text{ \AA}$ , 3L	1.82	1.99	0.17
300 eV, $L_z = 23 \text{ \AA}$ , 3L	1.87	2.04	0.16
$k$ -point: $4 \times 4 \times 1$			
300 eV, $L_z = 13 \text{ \AA}$ , 3L	1.84	1.98	0.14