

Supplementary Information

DFT and Microkinetic Investigation of Methanol Synthesis via CO₂ Hydrogenation on Ni(111)-based Surfaces

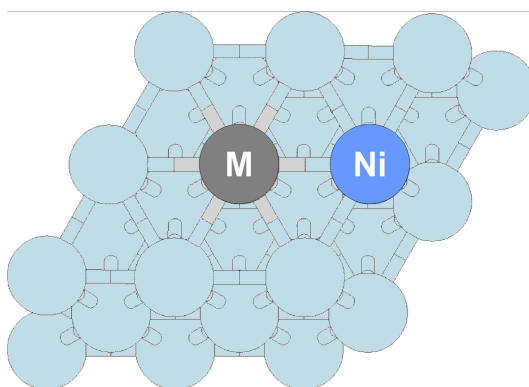
Arifin L. Maulana¹, Refaldi I. D. Putra¹, Adhitya G. Saputro^{1,2}, Mohammad K. Agusta^{1,2}, Nugraha^{1,2}, and Hermawan K. Dipojono^{1,2}

¹Advanced Functional Materials Research Group, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung 40132, Indonesia

²Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Bandung 40132, Indonesia

S.1 Rationale on Ni(111)-M Surfaces Structure

Several following subsections require visual assistance in locating important atoms. The following illustration will be used to refer the dopant M atom (symbolized with grey circle) and a near-to-dopant Ni atom (symbolized with blue circle). Both atoms are situated in the topmost layer of Ni(111)-M surface slab.



S.1.1 Convergence Test Result

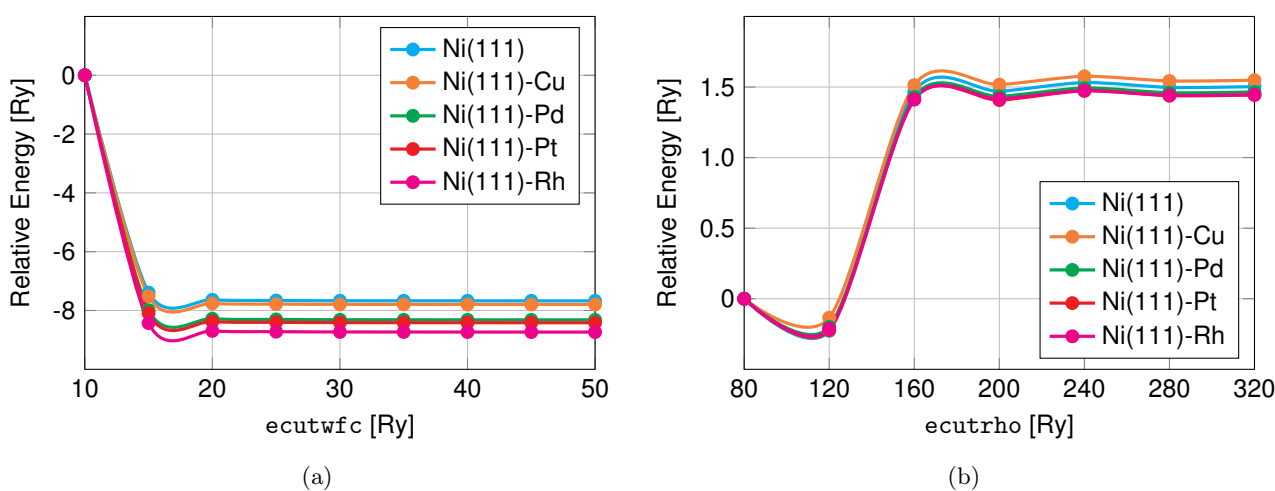


Figure S.1: Kinetic energy cutoff parameter optimization for (a) wavefunction (ecutwfc) and (b) charge density (ecutrho). The convergence test shows that 30 Ry for ecutwfc and 200 Ry for ecutrho are sufficient to obtain converged results.

S.1.2 Projected Density of States (PDOS) of Ni(111)-M Surfaces

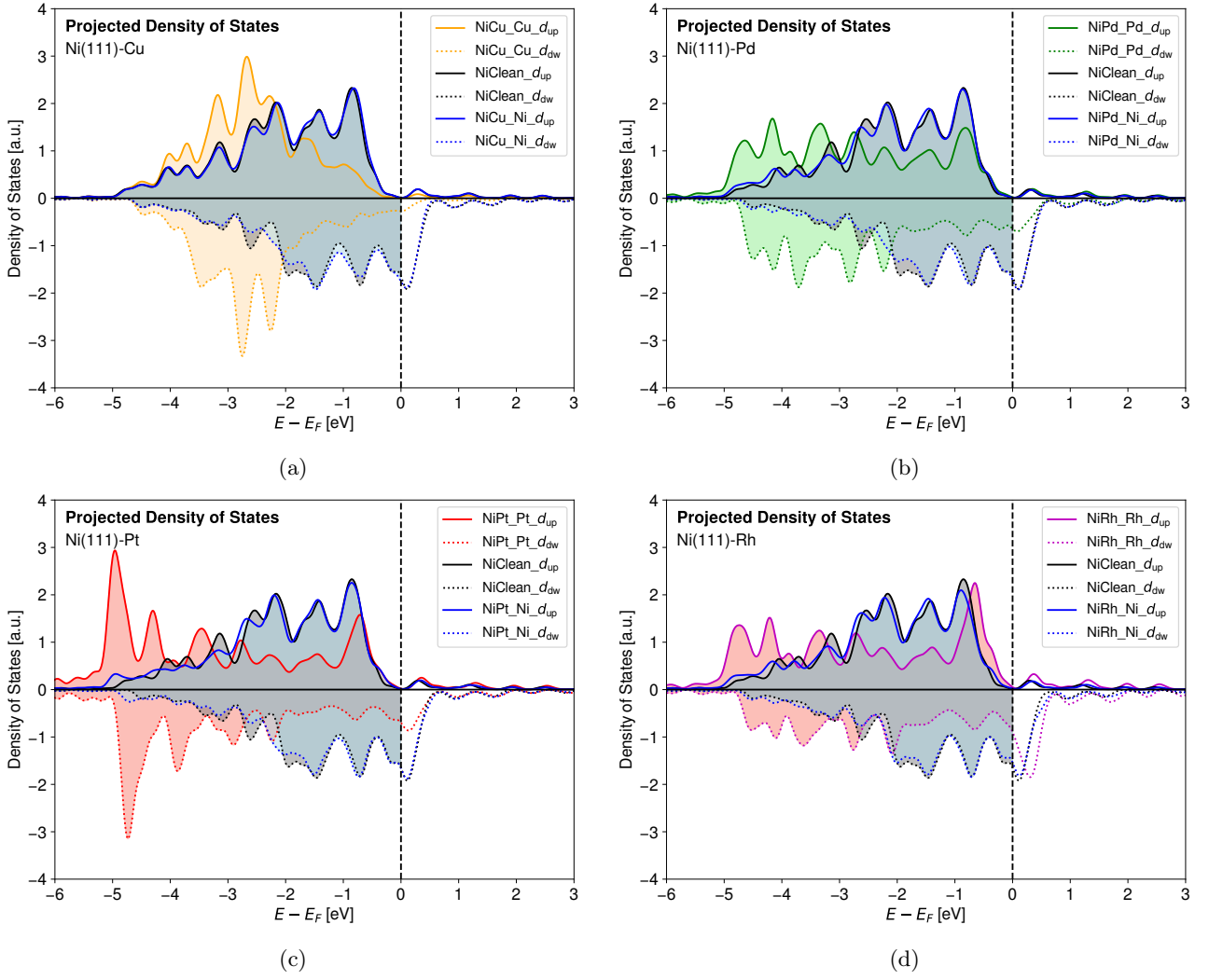


Figure S.2: PDOS of d -orbital of dopant M atom, near-to-dopant Ni atom, and Ni atom from Ni(111) surface for reference. The PDOS are calculated relative to each surface's Fermi energy (E_F).

Based on the projected d -orbital density of states, we calculated each surface's theoretical d -band center for spin-up, spin-down, and the average.

Table S.1: d -band center of each Ni(111)-M surface relative to its Fermi energy.

Surface	d -band center [eV]		
	Spin-up	Spin-down	Average
Ni(111)	-2.10	-1.63	-1.86
Ni(111)-Cu	-2.14	-1.75	-1.94
Ni(111)-Pd	-2.21	-1.80	-2.00
Ni(111)-Pt	-2.26	-1.88	-2.07
Ni(111)-Rh	-2.21	-1.77	-1.99

S.1.3 Magnetic Moment of Topmost Layer of Ni(111)-M

In this section, we provide magnetic moment value of dopant M atom and the near-to-dopant Ni atom.

Magnetic moment (in Bohr magneton)					
	Ni(111)	Ni(111)-Cu	Ni(111)-Pd	Ni(111)-Pt	Ni(111)-Rh
M	0.6950	0.0276	0.2096	0.2758	0.8343
Ni	0.6951	0.6687	0.7210	0.6953	0.7315

S.1.4 Adsorption Energy Comparison

Variation in Atomic Layers of Ni(111)-M

Table S.2: Adsorption energy of CO₂ and CH₃OH on Ni(111)-M of various number of atomic layers. Using 3 × 3 unit cell, three variations of layers were simulated: 3 layers (topmost layer is relaxed), 4 layers (2 topmost layers are relaxed), and 5 layers (2 topmost layers are relaxed).

Surface	$E_{\text{ads}} \text{ CO}_2$ [eV]			$E_{\text{ads}} \text{ CH}_3\text{OH}$ [eV]		
	3 Layers	4 Layers	5 Layers	3 Layers	4 Layers	5 Layers
Ni(111)	-0.24	-0.25	-0.26	-0.48	-0.77	-0.76
Ni(111)-Cu	-0.23	-0.23	-0.24	-0.71	-0.76	-0.76
Ni(111)-Pd	-0.23	-0.24	-0.25	-0.74	-0.78	-0.78
Ni(111)-Pt	-0.29	-0.29	-0.30	-0.78	-0.83	-0.83
Ni(111)-Rh	-0.23	-0.24	-0.25	-0.48	-0.51	-0.52

Variation in Pt Concentration

Table S.3: Adsorption energy of CO₂ and CH₃OH on Ni(111)-Pt of various dopant concentration. 1/9 ML coverage is represented with 3 × 3 unit cell size, 1/16 ML with 4 × 4, and 1/25 ML with 5 × 5. All surface slabs consist of 3 atomic layers where the topmost layer is relaxed and two beneath layers are fixed.

Surface	$E_{\text{ads}} \text{ CO}_2$ [eV]			$E_{\text{ads}} \text{ CH}_3\text{OH}$ [eV]		
	1/9 ML	1/16 ML	1/25 ML	1/9 ML	1/16 ML	1/25 ML
Ni(111)-Pt	-0.29	-0.28	-0.28	-0.78	-0.77	-0.77

S.1.5 Adsorbates Binding Energy on Ni(111)-M Surfaces

Table S.4: Binding energies (BE) of all adsorbed species involved in the reaction network. All of the BEs are calculated in respect to its molecular species. ZPE corrections are inadvertently neglected.

Species	Binding Energy [eV]				
	Ni(111)	Ni(111)-Cu	Ni(111)-Pd	Ni(111)-Pt	Ni(111)-Rh
H*	-3.83	-3.77	-3.74	-3.68	-3.82
OH*	-3.80	-3.69	-3.64	-3.59	-3.69
CO*	-2.05	-2.11	-2.02	-1.99	-2.05
H ₂ O*	-0.52	-0.52	-0.52	-0.57	-0.54
CO ₂ *	-0.24	-0.23	-0.23	-0.29	-0.23
HCOO*	-3.42	-3.45	-2.36	-2.60	-3.33
H ₂ COO*	-0.25	-0.34	-0.29	-0.14	-0.38
HCOOH*	-0.42	-0.42	-0.37	-0.37	-0.41
H ₂ COOH*	-3.00	-3.00	-2.93	-2.97	-2.91
COOH*	-2.89	-3.00	-2.92	-2.86	-2.90
HCO*	-2.80	-2.83	-2.77	-2.74	-2.86
COH*	-5.01	-5.05	-4.97	-4.95	-5.03
HCOH*	-3.30	-3.26	-3.20	-3.23	-3.42
H ₂ COH*	-2.35	-2.14	-2.35	-2.42	-2.24
H ₂ CO*	-1.02	-1.41	-1.30	-0.95	-1.04
H ₃ CO*	-3.15	-3.12	-3.04	-3.01	-3.04
CH ₃ OH*	-0.49	-0.71	-0.76	-0.78	-0.50

S.2 Microkinetic Modeling

S.2.1 Pre-exponential Factor Definition

The pre-exponential factor depends on the type of reactions: adsorption, surface, or desorption reaction [1]. For adsorption reaction [2],

$$A_0^{\text{ads}} = \frac{A\sigma}{\sqrt{2\pi mk_{\text{B}}T}} \quad (1)$$

where A is effective surface area of the catalyst, σ is sticking coefficient, and m is molecular mass. The pre-exponential factor has unit of $\text{Pa}^{-1} \text{s}^{-1}$. For all Ni(111)-M surfaces, the effective surface area has been calculated to be $2.71 \times 10^{-19} \text{ m}^2$. For surface reaction,

$$A_0^{\text{surf}} = \frac{k_{\text{B}}T}{h} \frac{Q^{\text{TS}}}{Q} \quad (2)$$

where h corresponds for Planck constant, Q^{TS} refers to partition function in transition state, and Q conforms to partition function in ground state (initial or final state). In most cases, the partition function ratios equal almost to 1 leaving the pre-exponential factor with order-of-magnitude estimates $k_{\text{B}}T/h \approx 10^{13} \text{ s}^{-1}$ [1]. For desorption reaction [2],

$$A_0^{\text{des}} = \frac{k_{\text{B}}T^3}{h^3} \frac{A(2\pi mk_{\text{B}})}{\varepsilon\Theta_{\text{rot}}} \quad (3)$$

where ε is molecular symmetry number and Θ_{rot} is the characteristic temperature for rotation.

S.2.2 Microkinetic Model Derivation

In this section, we demonstrate the derivation of microkinetic model for formate-mediated and carboxyl-mediated route taking place on Ni(111)-Cu surface as an example. For other surfaces, the derivation steps are identical. The elementary steps involved in formate-mediated route are arranged as:



Referring to the DFT result, we found that step S.R4 and S.R9 have the highest energy barrier. Therefore, we define step S.R4 and S.R9 as the rate-limiting steps for formate-mediated pathway taking place on Ni(111)-Cu. All other steps are then set to be quasi-equilibrated. The rate law for S.R4 and S.R9 are written as:

$$R_4 = k_4^+ \theta_{\text{HCOO}} \theta_{\text{H}} - k_4^- \theta_{\text{HCOOH}} \theta_* \quad (\text{S.1})$$

$$R_9 = k_9^+ \theta_{\text{H}_3\text{CO}} \theta_{\text{H}} - k_9^- \theta_{\text{CH}_3\text{OH}} \theta_* \quad (\text{S.2})$$

where k^+ corresponds to forward reaction rate constant, k^- for backward reaction rate constant, and θ_X is the coverage of species X. The equilibrium equation for other steps are defined as follow.

$$k_1^+ P_{\text{H}_2} \theta_*^2 = k_1^- \theta_{\text{H}}^2 \quad (\text{S.3})$$

$$k_2^+ P_{\text{CO}_2} \theta_* = k_2^- \theta_{\text{CO}_2} \quad (\text{S.4})$$

$$k_3^+ \theta_{\text{CO}_2} \theta_{\text{H}} = k_3^- \theta_{\text{HCOO}} \theta_* \quad (\text{S.5})$$

$$k_5^+ \theta_{\text{HCOOH}} \theta_{\text{H}} = k_5^- \theta_{\text{H}_2\text{COOH}} \theta_* \quad (\text{S.6})$$

$$k_6^+ \theta_{\text{H}_2\text{COOH}} \theta_* = k_6^- \theta_{\text{H}_2\text{CO}} \theta_{\text{OH}} \quad (\text{S.7})$$

$$k_7^+ \theta_{\text{OH}} \theta_{\text{H}} = k_7^- P_{\text{H}_2\text{O}} \theta_*^2 \quad (\text{S.8})$$

$$k_8^+ \theta_{\text{H}_2\text{CO}} \theta_{\text{H}} = k_8^- \theta_{\text{H}_3\text{CO}} \theta_* \quad (\text{S.9})$$

$$k_{10}^+ \theta_{\text{CH}_3\text{OH}} = k_{10}^- P_{\text{CH}_3\text{OH}} \theta_* \quad (\text{S.10})$$

P_X is standard pressure of species X ($P_X = p_X/p^\circ$ where $p^\circ = 1$ bar). The coverages are expressed as:

$$\theta_{\text{H}} = \sqrt{K_1 P_{\text{H}_2}} \theta_* = C_{\text{H}} \theta_* \quad (\text{S.11})$$

$$\theta_{\text{CO}_2} = K_2 P_{\text{CO}_2} \theta_* = C_{\text{CO}_2} \theta_* \quad (\text{S.12})$$

$$\theta_{\text{CH}_3\text{OH}} = \frac{P_{\text{CH}_3\text{OH}}}{K_{10}} \theta_* = C_{\text{CH}_3\text{OH}} \theta_* \quad (\text{S.13})$$

$$\theta_{\text{HCOO}} = K_3 C_{\text{CO}_2} C_{\text{H}} \theta_* = C_{\text{HCOO}} \theta_* \quad (\text{S.14})$$

$$\theta_{\text{OH}} = \frac{P_{\text{H}_2\text{O}}}{K_7 C_{\text{H}}} \theta_* = C_{\text{OH}} \theta_* \quad (\text{S.15})$$

$$\theta_{\text{H}_3\text{CO}} = \frac{k_4^+ C_{\text{HCOO}} C_{\text{H}} + k_9^- C_{\text{CH}_3\text{OH}}}{k_9^+ C_{\text{H}} + \frac{k_4^- C_{\text{CH}_3\text{OH}} P_{\text{H}_2\text{O}}}{K_5 K_6 K_7 K_8 C_{\text{H}}^3}} \theta_* = C_{\text{H}_3\text{CO}} \theta_* \quad (\text{S.16})$$

$$\theta_{\text{H}_2\text{CO}} = \frac{C_{\text{H}_3\text{CO}}}{K_8 C_{\text{H}}} \theta_* = C_{\text{H}_2\text{CO}} \theta_* \quad (\text{S.17})$$

$$\theta_{\text{H}_2\text{COOH}} = \frac{C_{\text{H}_2\text{CO}} C_{\text{OH}}}{K_6} \theta_* = C_{\text{H}_2\text{COOH}} \theta_* \quad (\text{S.18})$$

$$\theta_{\text{HCOOH}} = \frac{C_{\text{H}_2\text{COOH}}}{K_5 C_{\text{H}}} \theta_* = C_{\text{HCOOH}} \theta_* \quad (\text{S.19})$$

where K is equilibrium constant ($K = k^+/k^-$). These coverages have to suffice the conservation law of coverages:

$$\theta_{\text{H}} + \theta_{\text{CO}_2} + \theta_{\text{HCOO}} + \theta_{\text{HCOOH}} + \theta_{\text{H}_2\text{COOH}} + \theta_{\text{OH}} + \theta_{\text{H}_2\text{CO}} + \theta_{\text{H}_3\text{CO}} + \theta_{\text{CH}_3\text{OH}} + \theta_* = 1 \quad (\text{S.20})$$

Lastly, the turnover frequency of this mechanism can be expressed using either rate law of reaction S.R4 or S.R9. Using the rate law of S.R4,

$$R = [k_4^+ C_{\text{HCOO}} C_{\text{H}} - k_4^- C_{\text{HCOOH}}] \theta_*^2 \quad (\text{S.21})$$

The elementary steps involved in carboxyl-mediated route are arranged as:



On Ni(111)-Cu surface, reaction S.R16 and S.R19 are considered as the rate-limiting steps. Identical to what we have described before, all other steps are set to be quasi-equilibrated. The rate law for these rate-limiting steps are:

$$R_{16} = k_{16}^+ \theta_{\text{CO}} \theta_{\text{H}} - k_{16}^- \theta_{\text{HCO}} \theta_* \quad (\text{S.22})$$

$$R_{19} = k_{17}^+ \theta_{\text{H}_3\text{CO}} \theta_{\text{H}} - k_{19}^- \theta_{\text{CH}_3\text{OH}} \theta_* \quad (\text{S.23})$$

Equilibrium equation for other steps are listed as:

$$k_{11}^+ P_{\text{H}_2} \theta_*^2 = k_{11}^- \theta_{\text{H}}^2 \quad (\text{S.24})$$

$$k_{12}^+ P_{\text{CO}_2} \theta_* = k_{12}^- \theta_{\text{CO}_2} \quad (\text{S.25})$$

$$k_{13}^+ \theta_{\text{CO}_2} \theta_{\text{H}} = k_{13}^- \theta_{\text{COOH}} \theta_* \quad (\text{S.26})$$

$$k_{14}^+ \theta_{\text{COOH}} \theta_* = k_{14}^- \theta_{\text{CO}} \theta_{\text{OH}} \quad (\text{S.27})$$

$$k_{15}^+ \theta_{\text{OH}} \theta_{\text{H}} = k_{15}^- P_{\text{H}_2\text{O}} \theta_*^2 \quad (\text{S.28})$$

$$k_{17}^+ \theta_{\text{HCO}} \theta_{\text{H}} = k_{17}^- \theta_{\text{H}_2\text{CO}} \theta_* \quad (\text{S.29})$$

$$k_{18}^+ \theta_{\text{H}_2\text{CO}} \theta_{\text{H}} = k_{18}^- \theta_{\text{H}_3\text{CO}} \theta_* \quad (\text{S.30})$$

$$k_{20}^+ \theta_{\text{CH}_3\text{OH}} = k_{20}^- P_{\text{CH}_3\text{OH}} \theta_* \quad (\text{S.31})$$

The coverages are expressed as:

$$\theta_{\text{H}} = \sqrt{K_{11} P_{\text{H}_2}} \theta_* = C_{\text{H}} \theta_* \quad (\text{S.32})$$

$$\theta_{\text{CO}_2} = K_{12} P_{\text{CO}_2} \theta_* = C_{\text{CO}_2} \theta_* \quad (\text{S.33})$$

$$\theta_{\text{COOH}} = K_{13} C_{\text{CO}_2} C_{\text{H}} \theta_* = C_{\text{COOH}} \theta_* \quad (\text{S.34})$$

$$\theta_{\text{OH}} = \frac{P_{\text{H}_2\text{O}}}{K_{15} C_{\text{H}}} \theta_* = C_{\text{OH}} \theta_* \quad (\text{S.35})$$

$$\theta_{\text{CO}} = \frac{K_{14} C_{\text{COOH}}}{C_{\text{OH}}} \theta_* = C_{\text{CO}} \theta_* \quad (\text{S.36})$$

$$\theta_{\text{CH}_3\text{OH}} = \frac{P_{\text{CH}_3\text{OH}}}{K_{20}} \theta_* = C_{\text{CH}_3\text{OH}} \theta_* \quad (\text{S.37})$$

$$\theta_{\text{HCO}} = \frac{k_{16}^+ C_{\text{CO}} C_{\text{H}} + k_{19}^- C_{\text{CH}_3\text{OH}}}{k_{19}^+ K_{18} K_{17} C_{\text{H}}^3 + k_{16}^-} \theta_* = C_{\text{HCO}} \theta_* \quad (\text{S.38})$$

$$\theta_{\text{H}_2\text{CO}} = K_{17} C_{\text{HCO}} C_{\text{H}} \theta_* = C_{\text{H}_2\text{CO}} \theta_* \quad (\text{S.39})$$

$$\theta_{\text{H}_3\text{CO}} = K_{18} C_{\text{H}_2\text{CO}} C_{\text{H}} \theta_* = C_{\text{H}_3\text{CO}} \theta_* \quad (\text{S.40})$$

The conservation law of coverages can be written as:

$$\theta_{\text{H}} + \theta_{\text{CO}_2} + \theta_{\text{COOH}} + \theta_{\text{CO}} + \theta_{\text{OH}} + \theta_{\text{HCO}} + \theta_{\text{H}_2\text{CO}} + \theta_{\text{H}_3\text{CO}} + \theta_{\text{CH}_3\text{OH}} + \theta_* = 1 \quad (\text{S.41})$$

The turnover frequency for carboxyl-mediated route can be expressed using the rate law of S.R16.

$$R = [k_{16}^+ C_{\text{CO}} C_{\text{H}} - k_{16}^- C_{\text{HCO}}] \theta_*^2 \quad (\text{S.42})$$

S.2.3 Equilibrium Conversion

Using inlet gas (CO_2 and H_2) with pressure ratio of 1 : 3, respectively, we have calculated the equilibrium conversion for CO_2 at 473 – 573 K and 75 bar. The ratio choice is based on the stoichiometric coefficient of those species.

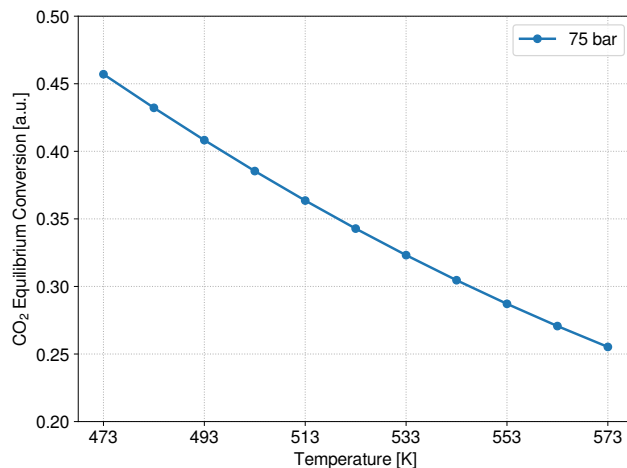


Figure S.3: Equilibrium conversion rate of CO_2 with initial pressure ratio of 1 : 3 in respect to H_2 at 473 – 573 K and 75 bar.

Result of this conversion rate is used to determine the partial pressure of all gaseous species involved in methanol synthesis process (CO_2 , H_2 , H_2O , and CH_3OH) at a total pressure of 75 bar.

S.2.4 Microkinetic Result

Using equations enlisted in our microkinetic model and each gaseous species' calculated partial pressure, we calculated TOF value of all pathways. In total, there are four pathways considered in this submission.

1. Formate-mediated route via H_2COO^* intermediate
2. Formate-mediated route via HCOOH^* intermediate
3. Carboxyl-mediated route via HCO^* intermediate
4. Carboxyl-mediated route via COH^* intermediate

TOF result as a function of temperature of these routes are depicted through Figure S.4.

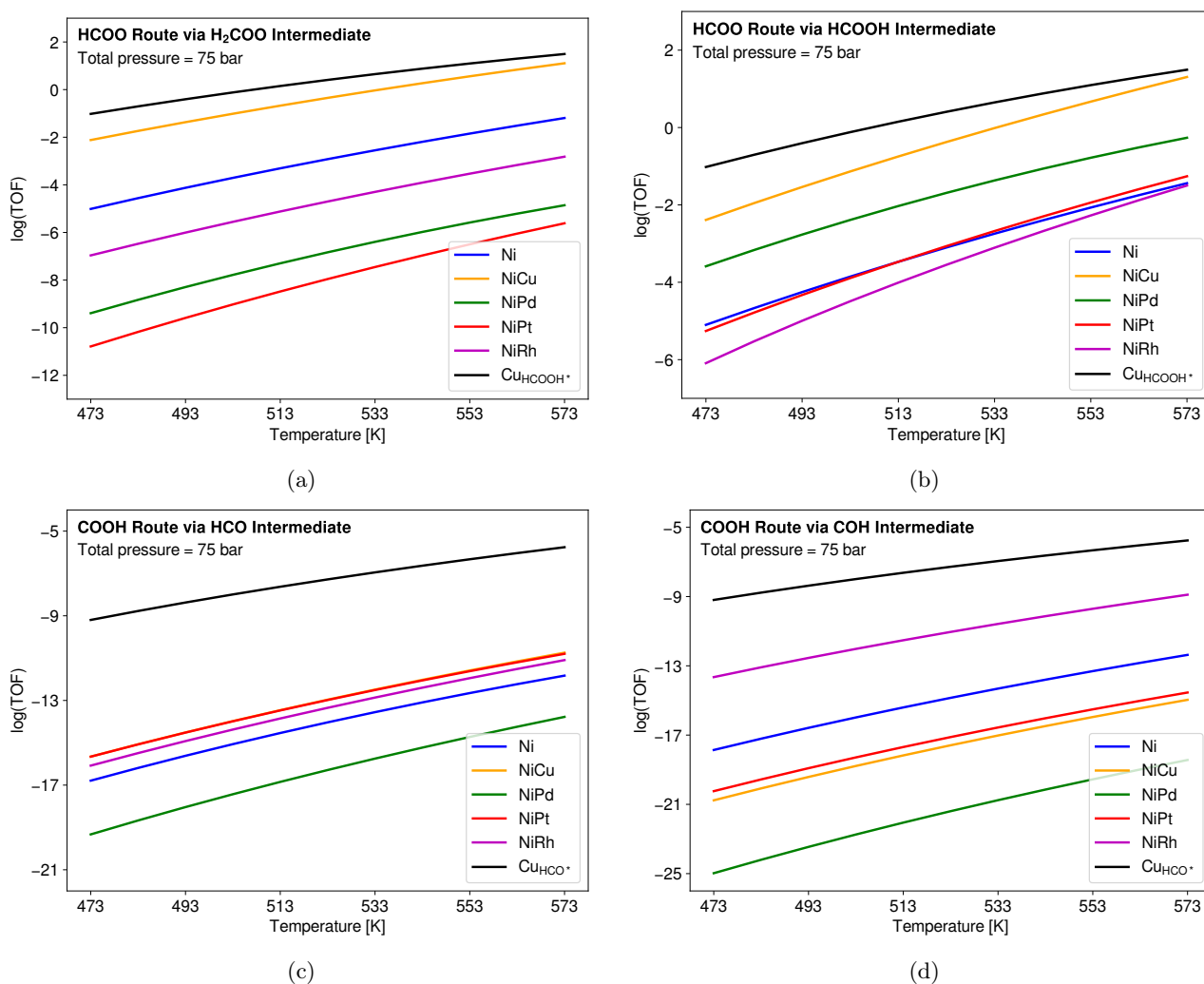


Figure S.4: TOF result as a function of temperature for (a) formate-mediated route via H_2COO^* intermediate, (b) formate-mediated route via HCOOH^* intermediate, (c) carboxyl-mediated route via HCO^* intermediate, and (d) carboxyl-mediated route via COH^* intermediate. The calculation was done using total pressure of 75 bar with temperature-dependent extent of reaction.

References

- [1] J. Dumesic, D. Rudd, L. Aparicio, J. Rekoske, and A. Trevino, *The Microkinetics of Heterogeneous Catalysis*. Washington, D.C., American Chemical Society, 1993.
- [2] A. Jansen, *An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions*, ser. Lecture Notes in Physics. Springer Berlin Heidelberg, 2012.