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Yao, Z., Guo, C., Mao, Y., & Hu, P. (2019). Quantitative Determination of C-C Coupling Mechanisms and Detailed Analyses on the Activity and Selectivity for Fischer-Tropsch Synthesis on Co(0001): Microkinetic Modeling with Coverage Effects. *ACS Catalysis*, 9, 5957-5973. <https://doi.org/10.1021/acscatal.9b01150>

Published in:
ACS Catalysis

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
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Quantitative Determination of C-C Coupling Mechanisms and Detailed Analyses on the Activity and Selectivity for Fischer-Tropsch Synthesis on Co(0001): Microkinetic Modelling with Coverage Effects

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ABSTRACT: The Fischer-Tropsch synthesis plays a significant role in reforming natural resources to meet global demand for commodities, whilst there is ongoing oil depletion and population growth. Mechanisms have been long investigated, but it is still a heavily debated issue. In this work, all the possible elementary reaction steps on a flat cobalt surface were calculated using density functional theory (DFT) with van der Waals's interactions. Kinetic simulations using standard DFT data (free energies and barriers at low coverages), the so-called non-coverage dependent kinetic model commonly used in the literature, are compared to those from a coverage dependent kinetic model for the system. We show that the coverage dependent kinetic model gives rise to a TOF which is approximately six orders of magnitude larger than the TOF calculated using the non-coverage dependent kinetic model. Furthermore, it is found that Co(0001) is highly selective to olefin production, and it is very likely to produce long chain hydrocarbons. Both models demonstrate that the CO insertion mechanism is the dominant mechanism on Co(0001). Our calculations also reveal that high coverage of CH_x leads to the carbide mechanism being significant and low coverage of CH_x results in the CO insertion mechanism being more favored. Direct CO dissociation is difficult on Co(0001), which leads to monomers CH_x being unable to occupy a certain amount of surface coverage making the carbide mechanism be inhibited. The reaction pathway through $\text{CO} + \text{H} \rightarrow \text{CHO}$, $\text{CHO} + \text{H} \rightarrow \text{CHOH}$, $\text{CHOH} \rightarrow \text{CH} + \text{OH}$ is the main channel to form monomer CH based on the coverage dependent kinetic model simulations. The temperature affects considerably the surface coverage and the total reaction rate, leading to the

selectivity being highly temperature dependent. Our coverage dependent kinetic model predicts that the selectivity of oxygenates is high in comparison to methane in the low-temperature region from 425 K and 475 K. From 475 K to 525 K, the selectivity towards CH₄ increases. From 525 K to 700 K, the selectivity of C₂ decreases significantly and the selectivity of CH₄ increases remarkably.

KEYWORDS: Fischer-Tropsch Synthesis, DFT, Micro-kinetic modelling, Adsorbate-adsorbate interaction.

1. INTRODUCTION

The Fischer-Tropsch (FT) process¹⁻⁷ utilizes the earth's resources, namely coal, natural gas, and biomass, which can be converted into synthesis gas (CO+H₂), to form hydrocarbons and oxygenated hydrocarbons. This process normally makes use of transition metal catalysts (mainly Fe and Co). Cobalt based catalysts attract great attention mainly due to the reason that they have both high activity and good selectivity to form long chain hydrocarbons.^{5, 8-13} The FT process involves the elementary steps of chain initiation, chain growth, and chain termination. The reaction systems include a large amount of possible elementary steps and reaction intermediates, leading to debates on the reaction mechanism.¹⁴⁻²⁵

Three general mechanisms have been proposed since the 1920s; the carbide mechanism proposed by Fischer and Tropsch,² the CO-insertion mechanism by Pichler and Schulz,²⁶ and the hydroxy-carbene mechanism by Anderson and Emmett.²⁷⁻²⁸ For the carbide mechanism, Fischer and Tropsch believed that the chain growth mechanism was achieved via repeating CH₂ couplings to form long chain hydrocarbons.² Pichler and Schulz suggested that the chain growth was achieved via the CO insertion into adsorbed alkyl groups, which is the CO insertion mechanism.²⁶ For the hydroxy-carbene mechanism,²⁷⁻²⁸ Anderson and Emmett proposed that the chain growth can be completed through dimerization between two CH₂OH species. The mainstream opinion²⁹⁻³⁰ is that the carbide mechanism^{2, 31-43} and the CO insertion mechanism^{26, 44-45} are the most probable pathways. Despite tremendous efforts devoted to F-T reaction for nearly a century, the unified theory is still on the way. With the extensive DFT calculations, the deeper understanding on the mechanisms can be investigated on the atomic level.

Outside the conventional three mechanisms, using DFT calculations Li and co-workers investigated CHO coupling to CO on Rh(111) and Co(0001), and found that the CHO insertion mechanism is competitive to the conventional carbide mechanism.⁴⁶ Chen et al.⁴⁷ investigated the mechanism of C₂ hydrocarbon formation on a fcc-Co(111) surface included carbide mechanism, CO insertion mechanism and CHO insertion mechanism, and it was believed that CHO insertion is more plausible for C–C chain formation compared with CO insertion and C-C coupling. It is clear that the fundamentals of forming long chain hydrocarbons on cobalt surfaces remain a contentious issue.

In the carbide mechanism, CO dissociates on the surface, and the carbon atoms are hydrogenated to yield CH_x monomers which act as the chain initiators. The present monomers on the surface are sequentially inserted into hydrocarbon chains, and the chain termination is achieved by the desorption process of the produced olefin or paraffin.

For the CO-insertion mechanism, CO inserts into a hydrocarbon first; then after forming oxygenates, the C-O bond breaks, and the process is repeated to form long chained hydrocarbons. Schweicher et al. provided some evidence to support CO insertion mechanism on Co/MgO catalysts.⁴⁸ The CO-insertion mechanism was investigated in the literature^{33, 44-45, 49} on the flat Co(0001) surface. From the PM-PAIR signal indicate that chain-growth is taking place on the defect sites, whereas the terrace sites act as a source for CO-monomers.⁵⁰ It was found experimentally that the TOF of FT synthesis is decreased if catalyst particle sizes are too small, and this was explained by the lack of terrace sites, and hydrocarbons strongly block the sites, leaving no room for the reservoir of CO-monomers, and consequently lowering the activity and selectivity.⁵⁰ Yang et al. carried out microkinetic studies on the activity of Rh(111) and Rh(211) and investigated the selectivity for the methane, acetaldehyde, and ethanol and their results showed that the (111) surface is selective towards C₂₊ oxygenates and the (211) surface is selective towards methane.⁵¹ It was suggested that the coupling of CO and CH was more favour on Rh(111) which is important to CO insertion mechanism.

The applications of microkinetic models combined with energy data calculated by DFT have achieved significant progress for the FT process.⁵¹⁻⁵⁷ A simple microkinetic model assumes that there are no interactions between adsorbates using the mean-field theory. However, for the high coverage system, the coverage effect becomes highly complex and cannot be ignored. Filot et al.⁵³ pointed out that their computed rates are lower than experimental values, and they proposed two

important reasons: (i) the chemisorption energies calculated by DFT are stronger (over-bonding); and (ii) their models did not include the coverage effect. The neglect of lateral interactions may cause large deviations between simulations and experiments. Understanding adsorbate–adsorbate interactions remains challenging for simulations.⁵⁸⁻⁵⁹ By investigating the reaction with the coverage effect, Nørskov and co-workers developed coverage dependent models for CO oxidation⁶⁰ and CO methanation⁶¹ on transition metal surfaces. A general method was used to describe the differential chemisorption energies which were reduced considerably after a threshold point.⁶⁰⁻⁶¹

In this work, we investigate the FT reaction mechanisms on the flat cobalt surface using DFT calculations that include van der Waals interactions combined with non-coverage dependent and our coverage-dependent kinetic modelling for two reasons. Firstly, cobalt is an active catalyst for the FT synthesis and the flat surface is the simplest model of catalysts. Secondly, although some elementary reactions may take place on cobalt defects, the reaction sites on the flat surface are the most abundant sites, connecting the defects. To obtain the activity and selectivity from the flat surface will provide insight into the cobalt system and give rise to the reference for other surfaces. It is, therefore, certainly the starting point to understand the cobalt system. The degree of rate control analysis⁶²⁻⁶⁵ is used to investigate elementary steps that control CO consumption rate and the product selectivity and to study how these steps change with reaction temperature from 425 K to 700 K. In this work, we only focused attention on hydrocarbon formation up to C₂ species. We aim to answer the following questions: (i) What is the chain growth mechanism on the flat cobalt? (ii) What influences the activity and selectivity on the cobalt surface if we consider the coverage effect? (iii) How temperature affects the activity and selectivity on the cobalt surface?

2. MODELS AND COMPUTATIONAL METHODS

2.1. Surface Model

To study FT reactions on the Co(0001) surface, a periodic four-layer surface (Figure 1) was utilized in the calculations. The bottom two layers of metal atoms were fixed, and the top two layers are relaxed with a 15 Å vacuum region. The thickness of the slab was verified to be sufficient. Due to the magnetic properties of cobalt, the spin polarized effect was considered in our calculations. Our calculation on Co(0001) yielded a moment of 1.64μ_B, being close to the value of 1.63μ_B on α-Co

in the literature.⁶⁶ The calculated lattice constant ratio b/a was 1.617, which was close to the experimental value 1.623.

Figure 1. The top view (left) and side view (right) of the flat cobalt surface. The red arrows are pointed at different adsorption sites, namely hcp, fcc, top and bridge.

2.2. Computational Methods

DFT calculations were carried out for the Fischer-Tropsch reaction within the framework of generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)⁶⁷ functional in the Vienna ab initio simulation program (VASP).⁶⁸⁻⁶⁹ The projector-augmented-wave (PAW)⁷⁰⁻⁷¹ pseudopotentials were used, and the cut-off energy of plane-wave basis expansion was set to 400 eV. The $p(3 \times 3)$ unit cell was utilized and $\mathbf{k}$ -point sampling parameters were tested using CO chemisorption energy with $1 \times 1 \times 1$, $2 \times 2 \times 1$, $3 \times 3 \times 1$ and $4 \times 4 \times 1$. The chemisorption energies were converged from $2 \times 2 \times 1$, and the errors were below 0.1 eV. Based on the tests, a $3 \times 3 \times 1$ Monkhorst pack $\mathbf{k}$ -point mesh sampling was used for all the calculations. Spin polarized calculations were included to account for the magnetic properties of cobalt. The effect of van der Waals's interactions is important for the hydrocarbon intermediates on the surface.⁷² Therefore, the DFT-D3 method⁷³⁻⁷⁴ was utilized to calculate all the intermediates and transition states. The ionic degrees of freedom were relaxed using the BFGS minimization scheme until the Hellman–Feynman forces on each ion were less than 0.05 eV/Å. The transition states (TSs) were searched using the method called a constrained optimization scheme.⁷⁵⁻⁷⁷ The transition states were confirmed by two rules: (i) all forces on atoms have been optimized to be less than 0.05 eV/Å; (ii) the total energy is a maximum along the reaction coordinate but a minimum with respect to all other degrees of freedom.

Vibrational frequency analyses were performed to confirm the integrity of initial states, transition states and final states. The zero-point energy (ZPE) correction was calculated as follows:

$$\text{ZPE} = \sum_i \frac{h\nu_i}{2} \quad (1)$$

where h is Planck's constant and the standard molar vibrational internal energy contribution is calculated as follows:

$$U_{\text{vib}}^0 = RT \sum_i \frac{h\nu_i/K_B}{e^{h\nu_i/K_B T} - 1} \quad (2)$$

where K_B is the Boltzmann constant and R is the gas constant. The standard molar vibrational entropy is given by:

$$S_{\text{vib}}^0 = R \sum_i \left[\frac{\frac{h\nu_i}{K_B T}}{e^{\frac{h\nu_i}{K_B T}} - 1} - \ln(1 - e^{-h\nu_i/K_B T}) \right] \quad (3)$$

Overall, adding the free energy corrections together, the standard molar Gibbs free energy change for the elementary reaction for the FT reaction can be written as follow:

$$\Delta G^0 = \Delta E + \Delta \text{ZPE} + \gamma RT \left(1 + \ln \frac{P}{P_0} \right) + \Delta U^0 - T \Delta S^0 \quad (4)$$

where ΔE represents the difference of the total energies from the VASP calculation. If it is gaseous molecule, then 1 is chosen as the value of γ and 0 is selected for γ for surface reactant and P is the partial pressure.

The free-energy corrections for molecules in the gas phase were calculated using the Gaussian 09 package,⁷⁸ and the basis set was B3LYP/6-311g.⁷⁹⁻⁸⁰

2.3. The Choice of Elementary Steps

To understand the FT synthesis, we investigated all the possible reaction pathways we can think of on Co(0001), corresponding to the formation of hydrocarbons (CH_4 , CH_2CH_2 , CH_3CH_3) and oxygenate (CH_3OH). The reaction pathways were classified as follows: (1) Direct CO dissociation and H-assisted CO dissociation; (2) water formation; (3) C_1 hydrogenation to methane; (4) $\text{C}_1 + \text{C}_1$ coupling reactions; (5) C_2 hydrogenation reactions; (6) CO and C_1 coupling reactions; (7) C_1 and OH coupling reactions; (8) $\text{CH}_x\text{CH}_y\text{O}$ hydrogenations; (9) $\text{CH}_x\text{CH}_y\text{O}$ dissociation; and (10) C_1 and CHO coupling reactions. The elementary steps are shown in Table 1. The geometry and energy data are presented in the Supporting Information.

Table 1. Elementary steps for FT reactions on Co(0001).

Elementary reaction steps	
(R1) $\text{CO}^+ \rightleftharpoons \text{CO}^*$	(R35) $\text{CH}_2\text{CO}^{*+} \rightleftharpoons \text{CCH}_2^* + \text{O}^*$
(R2) $\text{H}_2^{*+} \rightleftharpoons \text{H}^* + \text{H}^*$	(R36) $\text{CH}_3\text{CO}^{*+} \rightleftharpoons \text{CCH}_3^* + \text{O}^*$
(R3) $\text{CO}^{*+} \rightleftharpoons \text{C}^* + \text{O}^*$	(R37) $\text{CHCHO}^{*+} \rightleftharpoons \text{CHCH}^* + \text{O}^*$
(R4) $\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^{*+}$	(R38) $\text{CH}_2\text{CHO}^{*+} \rightleftharpoons \text{CHCH}_2^* + \text{O}^*$
(R5) $\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^{*+}$	(R39) $\text{CH}_2\text{OH}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^{*+}$
(R6) $\text{OH}^* + \text{OH}^* \rightleftharpoons \text{H}_2\text{O} + \text{O}^{*+}$	(R40) $\text{COH}^* + \text{H}^* \rightleftharpoons \text{CHOH}^{*+}$
(R7) $\text{H}^* + \text{C}^* \rightleftharpoons \text{CH}^{*+}$	(R41) $\text{CHOH}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{OH}^{*+}$
(R8) $\text{H}^* + \text{CH}^* \rightleftharpoons \text{CH}_2^{*+}$	(R42) $\text{CH}_3^* + \text{OH}^* \rightleftharpoons \text{CH}_3\text{OH}^{*+}$
(R9) $\text{H}^* + \text{CH}_2^* \rightleftharpoons \text{CH}_3^{*+}$	(R43) $\text{C}^* + \text{C}^* \rightleftharpoons \text{CC}^{*+}$
(R10) $\text{H}^* + \text{CH}_3^* \rightleftharpoons \text{CH}_4^{*+}$	(R44) $\text{C}^* + \text{CH}^* \rightleftharpoons \text{CCH}^{*+}$
(R11) $\text{CO}^* + \text{H}^* \rightleftharpoons \text{COH}^{*+}$	(R45) $\text{C}^* + \text{CH}_2^* \rightleftharpoons \text{CCH}_2^{*+}$
(R12) $\text{CO}^* + \text{H}^* \rightleftharpoons \text{CHO}^{*+}$	(R46) $\text{C}^* + \text{CH}_3^* \rightleftharpoons \text{CCH}_3^{*+}$
(R13) $\text{COH}^{*+} \rightleftharpoons \text{C}^* + \text{OH}^*$	(R47) $\text{CH}^* + \text{CH}^* \rightleftharpoons \text{CHCH}^{*+}$
(R14) $\text{CHO}^{*+} \rightleftharpoons \text{CH}^* + \text{O}^*$	(R48) $\text{CH}^* + \text{CH}_2^* \rightleftharpoons \text{CHCH}_2^{*+}$
(R15) $\text{CHO}^* + \text{H}^* \rightleftharpoons \text{CHOH}^{*+}$	(R49) $\text{CH}^* + \text{CH}_3^* \rightleftharpoons \text{CHCH}_3^{*+}$
(R16) $\text{CHOH}^{*+} \rightleftharpoons \text{CH}^* + \text{OH}^*$	(R50) $\text{CH}_2^* + \text{CH}_2^* \rightleftharpoons \text{CH}_2\text{CH}_2^{*+}$
(R17) $\text{CHO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{O}^{*+}$	(R51) $\text{CH}_2^* + \text{CH}_3^* \rightleftharpoons \text{CH}_2\text{CH}_3^{*+}$
(R18) $\text{CH}_2\text{O}^{*+} \rightleftharpoons \text{CH}_2^* + \text{O}^*$	(R52) $\text{CC}^* + \text{H}^* \rightleftharpoons \text{CCH}^{*+}$
(R19) $\text{CH}_2\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{OH}^{*+}$	(R53) $\text{CCH}^* + \text{H}^* \rightleftharpoons \text{CCH}_2^{*+}$
(R20) $\text{CH}_2\text{OH}^{*+} \rightleftharpoons \text{CH}_2^* + \text{OH}^*$	(R54) $\text{CCH}^* + \text{H}^* \rightleftharpoons \text{CHCH}^{*+}$
(R21) $\text{CH}_2\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{O}^{*+}$	(R55) $\text{CCH}_2^* + \text{H}^* \rightleftharpoons \text{CCH}_3^{*+}$
(R22) $\text{CH}_3\text{O}^{*+} \rightleftharpoons \text{CH}_3^* + \text{O}^*$	(R56) $\text{CCH}_2^* + \text{H}^* \rightleftharpoons \text{CHCH}_2^{*+}$
(R23) $\text{CH}_3\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^{*+}$	(R57) $\text{CCH}_3^* + \text{H}^* \rightleftharpoons \text{CHCH}_3^{*+}$
(R24) $\text{CH}^* + \text{CO}^* \rightleftharpoons \text{CHCO}^{*+}$	(R58) $\text{CH}_2\text{CH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_3^{*+}$
(R25) $\text{CH}_2^* + \text{CO}^* \rightleftharpoons \text{CH}_2\text{CO}^{*+}$	(R59) $\text{CH}_2\text{CH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{CH}_3^{*+}$
(R26) $\text{CH}_3^* + \text{CO}^* \rightleftharpoons \text{CH}_3\text{CO}^{*+}$	(R60) $\text{CHCH}^* + \text{H}^* \rightleftharpoons \text{CHCH}_2^{*+}$
(R27) $\text{CH}^* + \text{CHO}^* \rightleftharpoons \text{CHCHO}^{*+}$	(R61) $\text{CHCH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_2^{*+}$

(R28) $\text{CH}_2^* + \text{CHO}^* \rightleftharpoons \text{CH}_2\text{CHO}^{*+}$	(R62) $\text{CHCH}_2^* + \text{H}^* \rightleftharpoons \text{CHCH}_3^{*+}$
(R29) $\text{CHCO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CO}^{*+}$	(R63) $\text{CHCH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_3^{*+}$
(R30) $\text{CHCO}^* + \text{H}^* \rightleftharpoons \text{CHCHO}^{*+}$	(R64) $\text{CH}_2\text{CH}_2^* \rightleftharpoons \text{CH}_2\text{CH}_2^{*+}$
(R31) $\text{CH}_2\text{CO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CHO}^{*+}$	(R65) $\text{CH}_2\text{CHO}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{CHO}^{*+}$
(R32) $\text{CH}_2\text{CO}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{CO}^{*+}$	(R66) $\text{CH}_3\text{CHO}^{*+} \rightleftharpoons \text{CHCH}_3^* + \text{O}^*$
(R33) $\text{CHCHO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CHO}^{*+}$	(R67) $\text{CH}_3\text{CO}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{CHO}^{*+}$
(R34) $\text{CHCO}^{*+} \rightleftharpoons \text{CCH}^* + \text{O}^*$	

2.4. Microkinetic Model

2.4.1. Non-coverage Dependent Kinetic Model

To investigate mechanisms on Co(0001), the non-coverage dependent microkinetic model was used. The calculation flow diagram is displayed in Figure 2.

Figure 2. The calculated flow diagram for the basic settings of a microkinetic modelling.

The reaction elementary steps in Table 1 were chosen. r_i is the individual reaction rate of step i . $k_f(i)$ and $k_r(i)$ are the forward rate constant and reverse rate constant, respectively. The rate constants were calculated using the transition state theory, which can be expressed as:

$$k_i = \frac{k_B T}{h} e^{\frac{-\Delta G_i^{\neq 0}}{k_B T}} \quad (5)$$

where k_B is the Boltzmann constant, T is the temperature, h is the Planck's constant, $\Delta G_i^{\neq 0}$ is the change of standard molar Gibbs free energies between the transition state and the initial state for step i from the DFT calculations.

In the microkinetic model simulations, the set of ordinary differential equations (ODEs) were solved. The ODEs were integrated over time until a steady state solution was reached, in which all the coverage change of surface intermediates equates to zero. Namely, it is given by:

$$\frac{d\theta_i}{dt} = \sum_j v_{i,j} r_j = 0 \quad (6)$$

where θ_i is the coverage of the intermediate i and $v_{i,j}$ is the stoichiometric coefficient of intermediate at elementary step j .

2.4.2. Coverage-Dependent Kinetic Model

The traditional mean field microkinetic model ignored the effect of coverage, and it may fail to describe the coverage on the surface. Based on the coverage effect prevailing in the real system, we developed our model and the core concept is described as follows: The chemisorption energy is strongly affected by the coverage. The total coverage was assumed to be 1 monolayer (ML). Based on the strong chemisorption energy of CO, which was known to be the most abundant species on the surface, all the chemisorption energies of intermediates were calculated under a CO rich environment. The rationale is that because CO is abundant and the coverages of other species are low, it is likely that any surface species would be surrounded by CO and the chemisorption energy of a surface species would be considerably affected by CO rather than any other species. The differential chemisorption energy for an adsorbate as a function of CO coverage takes the form:

$$E_i(\theta_i) = a_1 \theta_i + b_1 \text{ when } \theta_i \leq \theta_0 \quad (7)$$

$$E_i(\theta_i) = a_2 \theta_i^2 + b_2 \theta_i + c_2 \text{ when } \theta_i > \theta_0 \quad (8)$$

where $E_i(\theta_i)$ is the differential chemisorption energy of adsorbate i at CO coverage θ_i .

On the cobalt surface, we set the threshold coverage as 1/3 ML. The differential chemisorption energy can be divided into two parts, namely the low coverage region and high coverage region.

The low coverage region can be fitted as a linear curve and the high coverage region can be fitted as a quadric curve.

For the other adsorbates, the differential chemisorption energies are expressed as:

$$E_i(\theta_i) = E_i^0 \quad \text{when } \theta_{CO} \leq \theta_0 \quad (9)$$

$$E_i(\theta_{CO}) = f_i(\theta_{CO}) \quad \text{when } \theta_{CO} > \theta_0 \quad (10)$$

where $E_i(\theta_{CO})$ is the differential chemisorption energy of adsorbate i under the CO environment at coverage θ_{CO} . The flow chart is showed in Figure 3.

Figure 3. Flow chart of fitting energy for the coverage dependent kinetic modelling.

The concept of iteration is displayed in Figure 4. All the chemisorption energies of each intermediate as a function of the CO coverage were obtained. All the barriers and reaction energies were also obtained by fitting the function $f_i(\theta_{CO})$ at different coverages of CO. We ignored other species affecting CO chemisorption. One has to use the approximation to describe complicated reactions such as the FT reaction involving a large number of elementary reaction steps and many intermediates in the coverage dependent model for practical use.⁵¹ Despite of the simplification, this work provides fundamental insight into the complex reactions such as the FT process.

Figure 4. Illustration of iterations of the coverage dependent microkinetic model.

3. RESULTS

3.1. Application of the Quasi-equilibrium Approximation

Cheng et al.⁸¹⁻⁸⁷ used the quasi-equilibrium approximation to investigate the FT mechanism on a cobalt surface based on the DFT calculations and the concept of effective barriers was derived. In this section, we will use this concept to characterize the mechanisms on the flat cobalt surface. Monomer coverages can be calculated as follows:⁸¹

$$\theta_{CH_i} = e^{\frac{-E_i}{RT}} \theta_C t^i \quad (11)$$

where t is the ratio of $\frac{\theta_H}{\theta_*}$, and E_i is relative energy between CH_i and C.

The details of the calculations can be found in the supporting information.

3.1.1. Comparison among the Mechanisms of Carbide, CO Insertion and CHO Insertion

We select the most probable coupling pathways among the carbide mechanism, the CO insertion mechanism and the CHO insertion mechanism and list them as follows:

$$r_{\text{CH}+\text{CH}} = 1.3 \times 10^7 t^2 \theta_{\text{C}}^2 \quad (12)$$

$$r_{\text{CH}+\text{CO}} = 7.8 \times 10^3 t \theta_{\text{C}} \theta_{\text{CO}} \quad (13)$$

$$r_{\text{CH}_2+\text{CHO}} = 5.7 \times 10^7 t^2 \theta_{\text{C}} \theta_{\text{CHO}} \quad (14)$$

First, comparing $r_{\text{CH}+\text{CH}}$ and $r_{\text{CH}+\text{CO}}$, we can obtain

$$\frac{r_{\text{CH}+\text{CH}}}{r_{\text{CH}+\text{CO}}} = 1.7 \times 10^3 t \frac{\theta_{\text{C}}}{\theta_{\text{CO}}} \quad (15)$$

$$r_{\text{CH}+\text{CH}} > r_{\text{CH}+\text{CO}} \text{ if } 1.7 \times 10^3 t \theta_{\text{C}} > \theta_{\text{CO}} \left(\frac{\theta_{\text{C}}}{\theta_{\text{CO}}} > \frac{1}{1.7 \times 10^3 t} \right) \quad (16)$$

$$r_{\text{CH}+\text{CH}} = r_{\text{CH}+\text{CO}} \text{ if } 1.7 \times 10^3 t \theta_{\text{C}} = \theta_{\text{CO}} \left(\frac{\theta_{\text{C}}}{\theta_{\text{CO}}} = \frac{1}{1.7 \times 10^3 t} \right) \quad (17)$$

$$r_{\text{CH}+\text{CH}} < r_{\text{CH}+\text{CO}} \text{ if } 1.7 \times 10^3 t \theta_{\text{C}} < \theta_{\text{CO}} \left(\frac{\theta_{\text{C}}}{\theta_{\text{CO}}} < \frac{1}{1.7 \times 10^3 t} \right) \quad (18)$$

Although this approximation is not very precise, it gives us some insight into the reaction kinetics.

If the ratio of $\frac{\theta_{\text{C}}}{\theta_{\text{CO}}}$ is increased, it is more likely to be carbide mechanism. Then, comparing $r_{\text{CH}+\text{CH}}$ and $r_{\text{CH}_2+\text{CHO}}$, we can obtain

$$\frac{r_{\text{CH}+\text{CH}}}{r_{\text{CH}_2+\text{CHO}}} = 0.23 \frac{\theta_{\text{C}}}{\theta_{\text{CHO}}} \quad (19)$$

$$r_{\text{CH}+\text{CH}} > r_{\text{CH}_2+\text{CHO}} \text{ if } 0.23 \theta_{\text{C}} > \theta_{\text{CHO}} \left(\frac{\theta_{\text{C}}}{\theta_{\text{CHO}}} > 4.3 \right) \quad (20)$$

$$r_{\text{CH}+\text{CH}} < r_{\text{CH}_2+\text{CHO}} \text{ if } 0.23 \theta_{\text{C}} = \theta_{\text{CHO}} \left(\frac{\theta_{\text{C}}}{\theta_{\text{CHO}}} = 4.3 \right) \quad (21)$$

$$r_{\text{CH}+\text{CH}} < r_{\text{CH}_2+\text{CHO}} \text{ if } 0.23 \theta_{\text{C}} < \theta_{\text{CHO}} \left(\frac{\theta_{\text{C}}}{\theta_{\text{CHO}}} < 4.3 \right) \quad (22)$$

Also, as the ratio of $\frac{\theta_{\text{C}}}{\theta_{\text{CHO}}}$ is increased, it is more likely to take the carbide pathway. Due to the short lifetime of CHO, its presence is very difficult to characterize.^{46, 88-90} Because of the very low

coverage of CHO on the surface, it is likely that the contribution of the CHO insertion mechanism is much smaller than that of the carbide mechanism (see below).

Overall, the most likely coupling mechanisms on Co(0001) are the carbide mechanism and the CO insertion mechanism. Compared with the flat Co(0001) surface, the carbide mechanism is more likely to occur at a cobalt surface with defects.⁹¹⁻⁹² The defective surface is more prone to activating CO dissociation: On the stepped cobalt surfaces, for example, C is the most stable species, and thus it is more likely to have high a surface coverage on the stepped surface.⁸¹

From the result of relative stabilities of monomers on the flat cobalt surface, we can find that the stabilities are in the following order: $\text{CH} > \text{C} > \text{CH}_3 > \text{CH}_2$; CH is the most stable species on the surface rather than C, which is consistent with the result of Cheng et al.⁸¹ There is still a possibility that the contribution of the CO-insertion mechanism is larger than the carbide mechanism on the flat cobalt surface if the coverage of monomers CH_x is low.

3.2. Comparison of the Intermediate Stabilities between the Non-coverage-dependent and Coverage-dependent Kinetic Modelling at 500 K

Thanks to the concept of relative stabilities of intermediates from Filot et al.,⁵³ we applied this concept to the analysis of intermediates on the surface with the van der Waals interactions which are significant, and cannot, therefore, be ignored in the simulations.^{51, 72, 93-96} The stabilities are with respect to the most stable adsorbates C, H, and O and can be calculated by the following equation:

$$E_{\text{stability}} = E_{\text{met+adsorbate}} - a(E_{\text{met+C}}) - b(E_{\text{met+H}}) - c(E_{\text{met+O}}) + (a + b + c - 1) * E_{\text{met}}$$

(23)

where $E_{\text{stability}}$ is the relative stability of an adsorbate on the metal surface, $E_{\text{met+adsorbate}}$ represents the energy of the metal surface with the adsorbate, $E_{\text{met+X}}$ is the energy of the metal surface with X where X is C or H or O, a, b and c are the numbers of atoms of C, H, O in the adsorbate individually, and E_{met} is the energy of the metal surface.

As shown in Figure 5, CHCH, CCH and CO are the most stable species from both models. As the monomers will significantly affect the rate, there should be a greater focus on the stabilities of the monomers. For the monomers of C, CH, CH_2 , CH_3 , the stabilities without lateral interactions are in the order of $\text{CH} > \text{C} > \text{CH}_3 > \text{CH}_2$, with the stability of CH_3 being only a little higher than CH_2 . The result of the low stability of CH_2 is consistent with the literature.⁹⁷⁻⁹⁸ However, this order

changes if we consider the coverage effect, and the stabilities with lateral interactions included are the following order: $\text{CH} > \text{C} > \text{CH}_2 > \text{CH}_3$: CH becomes much more stable than C, while the stability of CH_2 remains nearly the same and CH_3 becomes less stable. It illustrates the fact that different species possess different lateral interactions with co-adsorbed CO. In the coverage-dependent model, CO is the most stable species in our system, and it is consistent with the result of high CO coverage in Figure 5. We also find that COH and CH_3O are relatively more stable with the consideration of the coverage effect. Interestingly, CHCH is the second most stable species on the surface with the value of -0.77 eV, and it is less stable than $\text{CH} + \text{CH}$ (-0.84 eV). Based on this, CHCH may be very likely to dissociate into two CH monomers. For the other notable species like CCH_3 and CHCO, they all show high stability on the surface, and they are important species to form long chain hydrocarbons.

Figure 5. Stability bars of intermediates at 500 K. Negative stability means more stable and positive stability means less stable (equation 23). The unit of stability is in eV. For each intermediate, the left bar represents the stability without coverage effects, and the right bar represents the stability with the coverage effects.

3.3. Comparison of the Reaction Pathways between the Non-coverage-dependent Coverage-dependent Kinetic Modelling at 500 K

3.3.1. C_1 Reaction Pathways

If we compare the C_1 reaction pathways between the non-coverage-dependent model and the coverage-dependent model in Figure 6, we can find that the TOF on the coverage-dependent model

simulations is much higher. As the direct CO dissociation is difficult on the flat cobalt surface, H-assisted CO dissociation is the dominant pathway to break the C-O bond. The microkinetic results indicate that most C₁ oxygenates are likely to dissociate into monomers. This additional formation of monomers increases the likelihood of forming long chain hydrocarbons. Carefully comparing the monomer formation for the C₁ reaction pathways from both models, we can see that the reaction pathways are similar. There are three pathways to form monomer CH, namely $H^*+C^* \rightarrow CH^{*+*}$, $CHO^{*+*} \rightarrow CH^*+O^*$, $CHOH^{*+*} \rightarrow CH^*+OH^*$. The dominant reaction pathway is $CHO^{*+*} \rightarrow CH^*+O^*$ from non-coverage dependent model, but it is changed to $CHOH^{*+*} \rightarrow CH^*+OH^*$ from the coverage-dependent model. The reaction of CHOH dissociation is more likely to occur on the flat surface.⁹⁹⁻¹⁰¹

Regarding the monomer of CH₂, there are four pathways, namely $H^*+CH^* \rightarrow CH_2^{*+*}$, $CH_2O^{*+*} \rightarrow CH_2^*+O^*$, $CH_2OH^{*+*} \rightarrow CH_2^*+OH^*$, $CH_3^{*+*} \rightarrow CH_2^*+H^*$. The dominant reaction pathway is only $CH_2OH^{*+*} \rightarrow CH_2^*+OH^*$ for the non-coverage-dependent model, but it changes to $CH_3^{*+*} \rightarrow CH_2^*+H^*$ and $CH_2OH^{*+*} \rightarrow CH_2^*+OH^*$ if we consider the coverage effect. The increased stability of CH₂ on the surface promotes CH₃ dehydrogenation to form CH₂, which leads to the selectivity towards methane being suppressed on the flat cobalt surface. The formation of CH₂ is very important, as the CH₂ monomer is crucial for the chain formation during the FT process. Many DFT calculations and experiments have suggested that CH₂ is the most important species on the surface, regardless whether the carbide mechanism or the CO-insertion mechanism is the predominant pathway.^{33, 45, 81} As for the monomer formation of CH₃, both models show that $CH_3O^{*+*} \rightarrow CH_3^*+O^*$ is the dominant pathway.

Figure 6. (a) Non-coverage dependent pathways for C₁ species. Red arrow represents the important pathways according to the results of the microkinetic model simulations. The values represent the reaction rates for each elementary steps and unit is s⁻¹. (b) Coverage dependent pathways for C₁ species.

3.3.2. C₂ Reaction Pathways

C₂ reaction pathways for the non-coverage-dependent model and the coverage-dependent model are shown in Figure 7. Three possible chain growth mechanisms are included in our microkinetic model: the carbide mechanism; the CO insertion mechanism; and the CHO insertion mechanism. Both models indicate that the possibility of the contribution from the CO-insertion mechanism is larger than the carbide mechanism on the flat cobalt since the coverage of monomer C is not very high. The coupling of CO+CH₂ is the dominant chain growth pathway to form C₂ species. The CHO insertion is found to contribute very little to the reaction.

In section 3.1, we discussed that the elementary step of CH*+CH* → CHCH*+* would be the most likely reaction pathway if the carbide mechanism is the dominant chain growth mechanism. However, the CO dissociation is difficult on the flat cobalt surface, which is different from the stepped cobalt surface, and thus the monomers cannot achieve a certain coverage on the surface. From the non-coverage-dependent model, the coverage of CH is of the order of 10⁻¹², and from our

coverage-dependent model, the coverage of CH is of the order of 10^{-6} . In other words, the possibility of CH reacting with another CH is lower than that of CH reacting with CO. CO is likely to insert into CH or CH_2 , and then after forming CH_3CO , the C-O bond is broken, yielding the intermediate species CCH_3 . After several hydrogenation or dehydrogenation steps, olefin and paraffin are produced.

Figure 7. (a) Non-coverage dependent pathways for C_2 species. Red arrow represents the important pathways according the results of microkinetic model. The values represent the reaction rates for each elementary steps and unit is s^{-1} . (b) Coverage dependent pathways for C_2 species.

3.3.3 Chain Growth Mechanisms on the Flat $\text{Co}(0001)$ Surface

Based on the section 3.3.1 and section 3.3.2, we propose the generalized CO insertion mechanism, as shown in Figure 8. On the flat cobalt surface, the CH monomer is mainly provided by CHOH dissociation. The CH monomers may also be supplied by the dissociations of RCCH and dissociation of RCHCH , and RCH_2CH also contributes towards the formation of CH. Because of the dissociations, the carbide mechanism may be suppressed. CO probably inserts into CR or CHR first, and subsequently form RCH_2CO . Next, the C-O bond is broken, yielding the intermediate species RCH_2C . Then olefin and paraffin are produced through hydrogenation or dehydrogenation steps of RCH_2C .

Figure 8. Chain growth mechanism of FT synthesis based on our coverage dependent microkinetic model results

3.4 Comparison of the Activity/Selectivity between the Non-coverage-dependent and Coverage-dependent Kinetic Modelling at 500 K

Figure 9 shows the activity and selectivity for the FT process on the cobalt surface. Both models indicate the high selectivity towards ethylene. The selectivity for the non-coverage-dependent model follows the order: $C_2H_4 > CH_4 > CH_3OH > C_2H_6$. From the coverage-dependent model, it is the following: $C_2H_4 > CH_3OH > CH_4 > C_2H_6$. This causes an interesting question to arise: Why is the selectivity of CH_3OH greater than that of CH_4 on the coverage-dependent model? The question can be answered as follows: After considering the coverage effect, firstly the stability of CH_3O increases from 1.04 eV to 0.22 eV, and secondly the barrier for CH_3O dissociation is increased by 0.1 eV. These two reasons lead to the coverage of CH_3O being higher from the non-coverage-dependent model; the increased coverage of CH_3O promotes the formation of CH_3OH . The total consumption rate at 500 K is of the order of $10^{-5} s^{-1}$ from the coverage-dependent model, which is much higher than that of the non-coverage-dependent model that gives rise to the order of $10^{-11} s^{-1}$. This is consistent with the results in the literature: It was reported that the flat Rh(111) surface is not selective towards methane, and the existence of the Rh(211) surface (stepped) leads to the formation methane.⁵¹ Hence, our results suggest that the formation of the defect sites is one of the main reason for the increased selectivity of methane.

Figure 9. (a) Turnover frequencies (TOF) for methane, methanol, ethylene, ethane for non-coverage dependent model. (b) Turnover frequencies (TOF) for methane, methanol, ethylene, ethane for coverage dependent model. The reaction conditions are $T = 500$ K, $P_{\text{CO}} = 3.33$ bar, $P_{\text{H}_2} = 6.67$ bar.

3.5 Coverage Comparison between the Non-coverage-dependent and Coverage-dependent Kinetic Modelling at 500 K

The coverage is one of the most important factors that determine the final TOF. The coverages of surface species without the lateral interaction are shown in Table 2. It can be seen that because CO is the most abundant species in FT synthesis, from the non-coverage dependent model, CO considerably blocks all the sites on the surface which leads to other species having low coverages on the surface. This is clearly illustrated in Figure 10. The chemisorption energy without the lateral interaction is highly overestimated, leading to the unrealistic TOF. After we considered the coverage effect, CO is no longer the only species with high coverage on the surface, although it is still the most abundant species; the coverages of surface species are shown in the Table 3 and illustrated in Figure 10b.

Table 2. Coverages of intermediates from non-coverage dependent microkinetic model simulations.

species	coverage	species	coverage
CO	0.997	CH ₂ CO	1.1E-09
CH ₃ O	0.003	CCH ₃	2.1E-10
O	0.0001	v	1.5E-10
CH ₂ CHO	6.0E-05	CH ₂ OH	1.3E-10
CHCO	3.7E-06	CH ₂ CH ₂	7.3E-11
CH ₃ CO	3.4E-06	CHOH	2.7E-11
H	1.2E-06	CH ₂ CH ₃	7.0E-12
CH ₃ CHO	1.2E-06	CCH	4.4E-12
CHCH	3.3E-07	CH ₂	4.4E-12
OH	7.5E-08	CH	3.0E-12
CH ₃	6.6E-08	CHCH ₃	9.7E-13
COH	5.4E-08	CHCH ₂	1.1E-13
CH ₂ O	4.4E-08	CCH ₂	2.7E-14
CHCHO	3.0E-08	C	8.2E-17
CHO	4.3E-09	CC	5.3E-19

Table 3. Coverages of intermediates from the coverage-dependent microkinetic model simulations.

species	coverage	species	coverage
CO	0.60	CH ₃	7.1E-10
COH	0.21	CH ₃ CO	6.8E-10
CH ₃ O	0.11	CHOH	2.1E-10
H	0.08	CH ₂	1.3E-10
CCH ₃	0.002	CCH	8.2E-11
OH	0.0003	CHO	3.2E-11
v	5.2E-05	CHCH ₂	1.9E-11
O	2.7E-05	CHCHO	1.2E-11
CH ₃ CHO	6.4E-06	CH ₂ O	8.2E-12
CH	1.6E-06	CH ₂ CO	6.8E-12
CHCH	1.4E-06	CH ₂ CH ₃	5.8E-12
CHCH ₃	2.1E-09	CH ₂ OH	4.3E-12
CCH ₂	1.1E-09	C	5.9E-14
CH ₂ CHO	1.1E-09	CH ₂ CH ₂	6.7E-17
CHCO	8.2E-10	CC	5.7E-23

Figure 10. Coverage distributions from simulations of the non-coverage dependent model (a); the coverage dependent model (b).

Although the coverage of the monomer has been greatly increased after considering the influence of the adsorbate-adsorbate interaction, the flat cobalt surface lacks the B5 site, leading to the

carbon monoxide being unable to effectively dissociate. Furthermore, the formation of the monomer is suppressed, resulting to the CO insertion mechanism becoming dominant. On the other hand, the adsorbate-adsorbate interaction can lead to some surface areas originally blocked by CO being replaced by COH, CH₃O, H, CCH₃, OH and vacancy; the high-coverage COH changes the dominant dissociation mechanism from the original $\text{CHO}^{*+*} \rightarrow \text{CH}^{*}+\text{O}^{*}$ to the $\text{COH}^{*}+\text{H}^{*} \rightarrow \text{CHOH}^{*+*}$, $\text{CHOH}^{*+*} \rightarrow \text{CH}^{*}+\text{OH}^{*}$. The high coverages of CH₃O and CCH₃ greatly enhance the activity of forming CH₃OH and CH₂CH₂, respectively. More importantly, the increase in H coverage boosts the rates of hydrogenation reactions, and the increase in vacancy coverage contributes to dissociations and generating more monomers. In the discussion section below, we will reveal the coverage changes versus temperature to further understand the trends of the activity and selectivity.

4. DISCUSSIONS

4.1 Temperature Effects from 425 K to 700 K on the Activity and Selectivity from the Coverage-dependent Kinetic Modelling

We used the coverage-dependent microkinetic model to calculate the reaction rate and the selectivity as a function of temperature. The selected partial pressure of CO is 3.33 bar, and the partial pressure of H₂ is 6.67 bar. The activity and selectivity on the cobalt surface from 425 K and 700 K were investigated, and the results are shown in Figure 11. The kinetic results show that the total TOF increases with the temperature. With respect to the selectivity, we find that it changes dramatically as a function of temperature.

The selectivity towards C₂H₄ is dominant in the temperature range from 425 K to 675 K, and if the temperature is higher than 675 K, the dominant product changes to methane. It should be mentioned that the maximum selectivity of C₂H₄ appears at the temperature of 525 K. When we carefully examined the coverages of main species with temperature, which are displayed in Figure 12, we found that the coverage of CCH₃ reaches a peak at 525 K. Both the high coverages of CCH₃ and CO can lead to high selectivity of C₂H₄. Clearly, the increase of temperature will accelerate the overall reaction, and CH₃O will be consumed very quickly. Other species such as CO, CH₃C and COH will then occupy surface sites which were previously filled by CH₃O. When the

temperature is higher than 525 K, the coverages of CO, CH₃C, and COH begin to decrease very quickly and the coverages of H and vacant sites will increase.

CH₃OH is the second most dominant product from 425 K to 560 K. If the temperature is higher than 560 K, the selectivity of methane begins to exceed the selectivity of CH₃OH. The selectivity of CH₃OH is controlled by the coverage of CH₃O from 425 K to 525 K and in this temperature region, the selectivity of oxygenate formation is higher at 425 K and then decreases dramatically with increasing temperature. In the same temperature region from 425 K to 525 K, C₂ selectivity follows the reverse trend of the oxygenate. Our predicted selectivity on the flat cobalt surface is very similar to that of the experiment:¹⁰² Pendyala et al. used un-promoted and Pt promoted 25% Co/Al₂O₃ catalysts during aqueous-phase FTS at 438 K and found that the selectivity for hydrocarbons(C₂₊) is high at the value of 84.5% followed by oxygenates 9.2%, whilst methane is only 4% on the un-promoted 25 % Co/Al₂O₃ catalysts. It was proved that alkali metal-modified unsupported and supported cobalt worked efficiently for the production of oxygenates by Ishida and co-workers.¹⁰³ Product distributions were obtained by Co/SiO₂ and NaCo/SiO₂ catalysts at 518 K. It was found that methanol is the major products in the alcohol distributions by Co/SiO₂ and with the added sodium, the higher alcohol selectivity was exhibited.¹⁰³

The selectivity of CH₄ decreases from 425 K to 475 K as the selectivity of C₂H₄ is increased at 425 K to 525 K whilst the selectivity of CH₃OH still remains high at 475 K. From 475 K to 525 K, the selectivity of CH₄ increases slightly. From 525 K to 700 K, the selectivity of C₂H₄ decreases dramatically and the selectivity of CH₄ increases remarkably.

(a) —●— C₂H₄ —●— CH₃OH —●— CH₄ —●— C₂H₆

(c)

(b) —●— C₂H₄ —●— CH₃OH —●— CH₄ —●— C₂H₆

Figure 11. (a) Turnover frequencies and (b) selectivity for C₂H₄, CH₃OH, CH₄, C₂H₆ using coverage dependent model on flat Co(0001) from 425 K to 700 K. (c) Selectivity for CH₄ from 425 K to 575 K.

(a)

■ Q_CH3O ■ Q_CO ■ Q_COH ■ Q_H ■ Q_CCH3 ■ Q_v ■ Q_others

(b)

(c)

(d)

(e)

(f)

(g)

Figure 12. (a) Proportions of main species coverage from 425 K to 700 K. Blue is CH_3O , Red is CO, grey is COH, yellow is H, light blue is CCH_3 , and green is vacancy. (b) Coverage of CO from 425 K to 700 K. (c) Coverage of CCH_3 from 425 K to 700 K. (d) Coverage of CH_3O from 425 K to 700 K. (e) Coverage of COH from 425 K to 700 K. (f) Coverage of vacancy from 425 K to 700 K. (g) Coverage of H from 425 K to 700 K.

4.2 Temperature Effects on the Olefin/Paraffin Ratio from the Coverage-dependence Kinetic Modelling

FT reactions on cobalt-catalysts are typically carried out at the low temperatures (473 K to 513 K).¹⁰⁴ We used the ratio of olefin/paraffin ($\frac{\text{CH}_2\text{CH}_2}{\text{CH}_4 + \text{CH}_3\text{CH}_3}$) to characterize the selectivity towards olefin production. α -olefin can re-adsorb onto the surface and be hydrogenated to produce paraffin or reinsert into hydrocarbons. Improving the selectivity towards olefins will obtain great economic benefits from FT reactions and it is a hot topic of research on how to increase the ratio of olefin to paraffin.^{72, 105-111} Our results indicate that the peak of the ratio of olefin/paraffin ratio is around the temperature of 475 K, which is displayed in Figure 13. It is noticed that 475 K is very close to the typically used temperature range. When the temperature is in the range from 475 K to 513 K, it can still maintain a high ratio of olefin/paraffin. The higher temperature will, however, lead to a lower ratio of olefin/paraffin due to the higher selectivity of methane.

Figure 13. The ratio of olefin/paraffin from 425 K to 700 K.

4.3 Analysis of Degree of Rate Control from 425 K to 700 K

In this section, we will further discuss the complicated reaction pathways to elucidate the rate-determining step controlling the activity and selectivity of the FT process on the flat Co(0001) surface with respect to the temperature. Thanks to the concept of degree of rate control from

Campbell et al.,⁶²⁻⁶⁵ we used this approach to analyze the microkinetic modelling results. The application of degree of rate control can be used to evaluate the elementary reaction step affecting the net reaction rate as follows:

$$X_{\text{DRC},i} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{k_j \neq i, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_j \neq i, K_i} \quad (32)$$

where $X_{\text{DRC},i}$ is the relative derivative in the net rate per relative derivative in the rate constant for step i , k_i is the rate constant of elementary step i , r is the net reaction rate for the specific reactants or products we want to investigate and under the condition that fixes the values of other rate constants k_j and the equilibrium constant K_i . The larger the numeric value of $X_{\text{DRC},i}$ is for a given step, the bigger the influence of its rate constant on the overall reaction rate r is. If a DRC value of the elementary step is positive, decreasing the barrier at this step will increase the TOF of specific reactants or products. A negative value indicates the opposite; such steps are termed as the inhibition steps.⁶⁵ In Figure 14, we can see that for each set of DRC coefficients, the sum is equal to unity, which verifies that the microkinetic simulations were properly converged with a satisfactory numerical accuracy.

In the current work, the DRC analyses are carried out for the following key steps: (a) $\text{CO}^+ \rightarrow \text{CO}^*$, (b) $\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2\text{CH}_2^+*$, (c) $\text{H}^* + \text{CH}_3^* \rightarrow \text{CH}_4^{++*}$, (d) $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^{++*}$, and (e) $\text{CH}_2\text{OH}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^{++*}$, which are shown in the Figure 14.

	425 K	450 K	475 K	500 K	525 K	550 K	600 K	650 K	700 K
(a) $\text{CH}_3\text{O}^+ + ^* \rightleftharpoons \text{CH}_3^+ + \text{O}^*$	0.61	0.52	0.53	0.44	0.33	0.27	0.2	0.14	0.1
$\text{CHOH}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{OH}^*$	0.22	0.29	0.37	0.43	0.41	0.4	0.35	0.39	0.42
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{CHO}^+ + ^*$	0.14	0.1	0.06	0.03	0.01	0.02	0.04	0.05	0.08
$\text{CH}_3\text{CO}^+ + ^* \rightleftharpoons \text{CCH}_3^+ + \text{O}^*$	0	0	0	0	0.06	0.14	0.4	0.27	0.11
$\text{CH}_3\text{O}^+ + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^+ + ^*$	0.04	0.05	0.04	0.03	0.02	0.03	0.03	0.02	0.02
$\text{CH}^+ + \text{CH}^* \rightleftharpoons \text{CHCH}^+ + ^*$	0	0	0.02	0.1	0.82	0.44	0.05	-0.02	-0.01
$\text{H}^+ + \text{CH}_3^* \rightleftharpoons \text{CH}_4^{++} + ^*$	-0.01	0	0	0	-0.01	-0.03	-0.07	-0.06	-0.03
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{COH}^+ + ^*$	-0.01	0.01	-0.01	0	0.06	0.08	0.11	0.13	0.17
$\text{CHO}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{O}^*$	0	0.01	0.01	0.02	0.03	0.04	0.06	0.13	0.16
$\text{CHO}^+ + \text{H}^* \rightleftharpoons \text{CHOH}^+ + ^*$	-0.03	-0.01	-0.05	0	0.08	0.07	0.03	0.02	0
$\text{CH}_3\text{O}^+ + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^+ + ^*$	0.03	0.03	0.05	0.04	0.02	0.01	0	0	0
$\text{CHCH}_2^+ + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_2^+ + ^*$	0	0	-0.01	-0.06	-0.56	-0.39	-0.16	-0.07	-0.02
$\text{CHCH}_3^+ + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_3^+ + ^*$	0	0	-0.01	-0.01	-0.03	-0.03	-0.02	-0.01	0
(b) $\text{CH}_3\text{O}^+ + ^* \rightleftharpoons \text{CH}_3^+ + \text{O}^*$	0.69	0.59	0.59	0.48	0.35	0.29	0.22	0.16	0.12
$\text{CHOH}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{OH}^*$	0.23	0.30	0.38	0.44	0.41	0.41	0.37	0.44	0.52
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{CHO}^+ + ^*$	0.14	0.10	0.06	0.03	0.01	0.02	0.04	0.06	0.09
$\text{CH}^+ + \text{CH}^* \rightleftharpoons \text{CCH}^+ + ^*$	0.00	0.00	0.02	0.11	0.85	0.46	0.04	0.00	0.05
$\text{CH}_3\text{CO}^+ + ^* \rightleftharpoons \text{CCH}_3^+ + \text{O}^*$	0.00	0.00	0.00	0.01	0.06	0.16	0.49	0.38	0.17
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{COH}^+ + ^*$	-0.01	0.01	0.00	0.01	0.07	0.09	0.12	0.15	0.21
$\text{CHO}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{O}^*$	0.00	0.01	0.01	0.02	0.03	0.04	0.07	0.15	0.20
$\text{CH}_2\text{CH}_2^+ + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_3^+ + ^*$	0.00	0.00	-0.02	-0.07	-0.45	-0.19	-0.04	0.00	0.00
$\text{CHCH}_2^+ + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_2^+ + ^*$	0.00	0.00	-0.01	-0.06	-0.58	-0.40	-0.14	-0.01	0.08
(c) $\text{H}^+ + \text{CH}_3^* \rightleftharpoons \text{CH}_4^{++} + ^*$	0.98	0.99	0.99	0.99	0.98	0.95	0.84	0.78	0.74
$\text{CH}_3\text{O}^+ + ^* \rightleftharpoons \text{CH}_3^+ + \text{O}^*$	0.86	0.84	0.72	0.54	0.35	0.28	0.17	0.11	0.07
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{CHO}^+ + ^*$	0.19	0.14	0.07	0.03	0.01	0.02	0.03	0.03	0.05
$\text{CHOH}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{OH}^*$	0.17	0.22	0.34	0.42	0.41	0.40	0.31	0.30	0.30
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{COH}^+ + ^*$	-0.07	-0.04	-0.03	0.00	0.06	0.08	0.07	0.08	0.10
$\text{CH}_3^+ + \text{CO}^* \rightleftharpoons \text{CH}_3\text{CO}^+ + ^*$	-0.16	-0.05	-0.01	0.00	0.00	0.00	0.00	0.00	0.00
$\text{H}^+ + \text{CH}_2^* \rightleftharpoons \text{CH}_3^+ + ^*$	-0.77	-0.71	-0.35	-0.12	-0.01	-0.01	0.00	0.00	0.01
$\text{CH}^+ + \text{CH}^* \rightleftharpoons \text{CHCH}^+ + ^*$	0.00	0.00	0.03	0.17	1.10	0.66	0.09	-0.07	-0.12
$\text{CH}^+ + \text{CH}_2^* \rightleftharpoons \text{CHCH}_2^+ + ^*$	0.00	0.00	0.01	0.04	0.21	0.11	0.02	-0.01	-0.02
$\text{CHO}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{O}^*$	0.00	0.00	0.01	0.02	0.03	0.04	0.05	0.09	0.11
$\text{CH}_2\text{CH}_2^+ + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_3^+ + ^*$	0.00	0.00	-0.02	-0.11	-0.59	-0.27	-0.10	-0.03	-0.01
$\text{CHCH}_2^+ + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_2^+ + ^*$	0.00	0.00	-0.01	-0.10	-0.76	-0.58	-0.32	-0.25	-0.20
$\text{CH}_3\text{CO}^+ + ^* \rightleftharpoons \text{CCH}_3^+ + \text{O}^*$	-0.04	-0.18	-0.44	-0.61	-0.70	-0.66	-0.15	-0.02	0.00
(d) $\text{CH}_3\text{O}^+ + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^+ + ^*$	0.98	0.99	0.99	1	1	1	1	1	1
$\text{CHOH}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{OH}^*$	0.17	0.2	0.27	0.3	0.23	0.19	0.1	0.04	0.01
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{CHO}^+ + ^*$	0.2	0.15	0.08	0.04	0.02	0.04	0.09	0.12	0.19
$\text{CHO}^+ + \text{H}^* \rightleftharpoons \text{CHOH}^+ + ^*$	-0.12	-0.17	-0.22	-0.2	-0.15	-0.11	-0.05	-0.04	-0.02
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{COH}^+ + ^*$	-0.07	-0.06	-0.07	-0.12	-0.1	-0.1	-0.08	-0.04	-0.01
(e) $\text{CH}_3\text{O}^+ + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^+ + ^*$	0.98	0.98	0.99	0.98	0.96	0.96	0.96	0.95	0.93
$\text{CHO}^+ + \text{H}^* \rightleftharpoons \text{CHOH}^+ + ^*$	-0.12	-0.17	-0.22	-0.2	-0.14	-0.11	-0.05	-0.03	-0.02
$\text{CHOH}^+ + ^* \rightleftharpoons \text{CH}^+ + \text{OH}^*$	0.17	0.2	0.27	0.3	0.23	0.19	0.1	0.03	-0.01
$\text{CO}^+ + \text{H}^* \rightleftharpoons \text{CHO}^+ + ^*$	0.19	0.15	0.08	0.04	0.02	0.04	0.09	0.11	0.18

Negative DRC

Positive DRC

Figure 14. Degrees of rate control from the elementary steps on $\text{CO}^+ + ^* \rightarrow \text{CO}^*$ (a); those on $\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2\text{CH}_2 + ^*$ (b); those on $\text{H}^+ + \text{CH}_3^* \rightarrow \text{CH}_4^{++} + ^*$ (c); those on $\text{CH}_3\text{O}^+ + \text{H}^* \rightarrow \text{CH}_3\text{OH}^{++} + ^*$ (d); and those on $\text{CH}_2\text{OH}^+ + \text{H}^* \rightarrow \text{CH}_3\text{OH}^{++} + ^*$ (e) on Co(0001). Only elementary steps that are important are displayed and some values that are deemed to be too small to have a significant effect are not included. For example, only the steps that affect considerably $\text{CO}^+ + ^* \rightarrow \text{CO}^*$ are shown in (a).

Our results show that the whole temperature region can be divided into three specific regions: low temperature region ($425 \text{ K} \leq T < 500 \text{ K}$); medium temperature ($500 \text{ K} \leq T < 600 \text{ K}$); and high

temperature ($600 \text{ K} \leq T < 700 \text{ K}$). We first used our coverage-dependent model to analyse the reaction network for the elementary step of $\text{CO}^+ \rightarrow \text{CO}^*$ (Figure 14(a)) in low temperature region ($425 \text{ K} \leq T < 500 \text{ K}$). Three elementary reaction steps can considerably affect the step of $\text{CO}^+ \rightarrow \text{CO}^*$ (Figure 14(a)), and the order to their importance is as follows: $\text{CH}_3\text{O}^{*+} \rightarrow \text{CH}_3^* + \text{O}^* > \text{CHOH}^{*+} \rightarrow \text{CH}^* + \text{OH}^* > \text{CO}^* + \text{H}^* \rightarrow \text{CHO}^{*+}$. All the values for the DRC are positive, meaning that CO adsorption will increase if the barriers of these three reactions are decreased.

Overall, a low temperature leads to a low total TOF of CO consumption. When the temperature is increased to a medium temperature ($500 \text{ K} \leq T < 600 \text{ K}$), the DRC value of the elementary step of $\text{CHOH}^{*+} \rightarrow \text{CH}^* + \text{OH}^*$ slightly decreases from 0.43 to 0.33, while the DRC value of the elementary step $\text{CH}_3\text{O}^{*+} \rightarrow \text{CH}_3^* + \text{O}^*$ is dramatically decreased. Importantly, the DRC value of $\text{CHCH}^{*+} \rightarrow \text{CH}^* + \text{CH}^*$ increases dramatically to 0.82 at 525 K. It indicates that if the bond breaking barrier of CH-CH is decreased, it will result in more CH monomers, promoting the CO insertion mechanism. When the temperature is raised to high temperatures ($600 \text{ K} \leq T \leq 700 \text{ K}$), the DRC value of $\text{CHOH}^{*+} \rightarrow \text{CH}^* + \text{OH}^*$ still maintains a high level of approximately 0.38 compared other pathways. The DRC value of the elementary step of $\text{CH}_3\text{O}^{*+} \rightarrow \text{CH}_3^* + \text{O}^*$ is at a low level. Other elementary steps have a less significant effect on the CO consumption.

The DRC values of elementary steps of (b) $\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2\text{CH}_2^+ + *$ are similar with that of (a) $\text{CO}^+ \rightarrow \text{CO}^*$, illustrated in Figure 14. Interestingly, the DRC value of the elementary step $\text{CH}_3\text{CO}^{*+} \rightarrow \text{CCH}_3^* + \text{O}^*$ increases significantly from 525 K to 600 K. It can be understood as follows: Decreasing the barrier of $\text{CH}_3\text{CO}^{*+} \rightarrow \text{CCH}_3^* + \text{O}^*$ will increase the coverage of CCH_3 and the high coverage of CCH_3 means the high selectivity towards C_2 species, which has been discussed in section 4.1.

Regarding the selectivity of methane (Figure 14 (c)), when the temperature is in the low temperature region ($425 \text{ K} \leq T < 500 \text{ K}$), three elementary reaction steps, $\text{H}^* + \text{CH}_3^* \rightarrow \text{CH}_4^+ + *$, $\text{CH}_3\text{O}^{*+} \rightarrow \text{CH}_3^* + \text{O}^*$ and $\text{CH}_3^+ \rightarrow \text{H}^* + \text{CH}_2^*$, can considerably affect the methane formation. A barrier decreases of $\text{H}^* + \text{CH}_3^* \rightarrow \text{CH}_4^+ + *$ will facilitate the consumption of CH_3 , whilst reducing the barrier of $\text{CH}_3\text{O}^{*+} \rightarrow \text{CH}_3^* + \text{O}^*$ will increase the formation of CH_3 . It is worth mentioning that CH_3 can readily dissociate into CH_2 and H ; if equilibrium is reached under the reaction condition, increasing the barrier of $\text{CH}_2\text{-H}$ bond breaking will inhibit the formation of CH_2 , and the selectivity of C_2 formation will decrease. When the temperature rises to a medium temperature ($500 \text{ K} \leq T < 600 \text{ K}$), the selectivity of CH_4 is dramatically increased. The DRC value

of the elementary step $\text{H}^* + \text{CH}_3^* \rightarrow \text{CH}_4^{*+*}$ remains at a high value around 0.98. The DRC value of the elementary step of $\text{CH}_3\text{O}^{*+*} \rightarrow \text{CH}_3^* + \text{O}^*$ decreases quickly from the low temperature region to the medium temperature region as high temperatures lead to lower coverages of CH_3O on the surface and the rate of CH_3O dissociation increases at the higher temperatures. The DRC analyses also show that decreasing the barriers of the elementary steps $\text{CHOH}^{*+*} \rightarrow \text{CH}^* + \text{OH}^*$, and $\text{CHCH}^{*+*} \rightarrow \text{CH}^* + \text{CH}^*$ will facilitate the formation of CH . The negative DRC values associated with the elementary steps of $\text{CH}_2\text{CH}_3^{*+*} \rightarrow \text{CH}_2\text{CH}_2^* + \text{H}^*$, $\text{CHCH}_2^* + \text{H}^* \rightarrow \text{CH}_2\text{CH}_2^{*+*}$, and $\text{CH}_3\text{CO}^{*+*} \rightarrow \text{CCH}_3^* + \text{O}^*$, means that if we decrease their barriers, the selectivity of CH_2CH_2 will increase and the selectivity of CH_4 will decrease. When the temperature increases further ($600 \text{ K} \leq T \leq 700 \text{ K}$), the DRC value of the elementary step $\text{H}^* + \text{CH}_3^* \rightarrow \text{CH}_4^{*+*}$ remains high at approximately 0.78.

For elementary step (d), $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^{*+*}$ in Figure 14, its positive DRC value is nearly a constant regardless of the change of temperature. Similarly, for elementary step (e), $\text{CH}_2\text{OH}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^{*+*}$, the yield of CH_3OH is predominantly controlled by the barrier of CH_2O -H bond formation.

5. CONCLUSION

This work represents one of the first attempts to use the non-coverage dependent model and coverage dependent model with DFT-D3 functional energy data to investigate activity and selectivity of FT synthesis with respect to temperature on $\text{Co}(0001)$. The following conclusions have been reached:

(i) The total consumption of CO rate at 500 K was calculated to be in the order of 10^{-5} s^{-1} from the coverage dependent model. This was much higher than the result for the non-coverage dependent model which is in the order of 10^{-11} s^{-1} . Our results show that the formation of methane on $\text{Co}(0001)$ is low and the presence of defect sites is a major cause of increasing the selectivity towards methane and a higher total TOF.

(ii) Our kinetic simulations from the coverage dependent model show that the rapid CO dissociation is difficult on the flat $\text{Co}(0001)$ leading to monomers CH_x being unable to occupy enough surface sites and carbide mechanism being significantly inhibited. The reaction pathway through $\text{CO} + \text{H} \rightarrow \text{CHO}$, $\text{CHO} + \text{H} \rightarrow \text{CHOH}$, $\text{CHOH} \rightarrow \text{CH} + \text{OH}$ is the main pathway to form monomer CH .

(iii) The CO insertion mechanism is the dominant mechanism on the flat Co(0001) surface from both models. The chain growth mechanism is found to be as follows: CO is inserted into CR or CHR first, and then after forming RCH_2CO , the C-O bond is broken to form the intermediate species RCH_2C . After several hydrogenation or dehydrogenation steps, olefins and paraffins are produced.

(iv) Temperature can affect the surface coverage and the total reaction rate, leading to different selectivities. The kinetic simulations from the coverage dependent model show that the selectivity of oxygenate is high compared to that of methane at low temperatures. From 475 K to 525 K, the selectivity towards CH_4 increases. From 525 K to 700 K, the selectivity towards C_2 decreases significantly and the selectivity towards CH_4 increases remarkably.

(v) The simulations from the coverage dependent model show that the peak of the ratio of olefin/paraffin ratio is around the temperature of 475 K. This temperature is very close to typical optimal conditions of 473 K to 513 K. When the temperature shifts to 513 K, it can still maintain a high ratio of olefin/paraffin. When the temperature is higher than 525 K, our simulations predict that the selectivity towards CH_4 increases significantly. Our calculations also show that the temperature should not be too low or too high; low temperatures mean low activity and high selectivity towards long chain hydrocarbons and oxygenates, while high temperatures lead to high selectivity of methane.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests.

Supporting Information

Geometries, forward barriers, reaction energies of all elementary reaction steps on flat Co(0001) from the non-coverage dependent kinetic model and coverage dependent kinetic model.

ACKNOWLEDGMENT

The authors gratefully acknowledge Queen's University of Belfast and UKCP for providing high performance computing service. Z.Y thanks Queen's University of Belfast for a Ph.D. studentship and providing International PGR Scholarship.

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Graphical TOC Entry

Mechanism of FT Synthesis on Co(0001)

Supporting Information

Quantitative Determination of C-C Coupling Mechanisms and Detailed Analyses on the Activity and Selectivity for Fischer-Tropsch Synthesis on Co(0001): Microkinetic Modelling with Coverage Effects

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1.1 Adsorption Sites

Table S1. Generalized formation energies formulas and the corresponding energy of intermediates (unit is in eV). Parameterization of energy can avoid mistake and workload using generalized formation energy. This concept from Catmap¹ can be applied in our FT system. In our system $R_H = 0.5(U_{H_2})$, $R_C = U_{CH_4} - 4R_H$, $R_O = U_{H_2O} - 2R_H$. Herein E is generalized formation energy, U is the free energy calculated in the DFT, R is the reference atomic species. The formula to obtain the formation energies are also given. The geometries are the most stable sites from our calculations.

Species	Calculation Formula	Formation Energy	Geometry
CO(gas)	$E_{CO} = U_{CO} - R_C - R_O$	1.92	Gas phase
H ₂ (gas)	$E_{H_2} = U_{H_2} - R_H - R_H$	0.00	Gas phase
CH ₄ (gas)	$E_{CH_4} = U_{CH_4} - R_C - 4R_H$	0.00	Gas phase
CH ₂ CH ₂ (gas)	$E_{CH_2CH_2} = U_{CH_2CH_2} - 2R_C - 4R_H$	1.58	Gas phase
CH ₃ CH ₃ (gas)	$E_{CH_3CH_3} = U_{CH_3CH_3} - 2R_C - 6R_H$	0.71	Gas phase
H ₂ O(gas)	$E_{H_2O} = U_{H_2O} - 2R_H - R_O$	0.00	Gas phase
CH ₃ OH(gas)	$E_{CH_3OH} = U_{CH_3OH} - R_C - 4R_H - R_O$	1.28	Gas phase
CO(surface)	$E_{CO}(\text{surface}) = U(\text{CO}+\text{surface}) - U(\text{surface}) - R_C - R_O$	0.67	Threefold-hcp
H(surface)	$E_H(\text{surface}) = U(\text{H}+\text{surface}) - U(\text{surface}) - R_H$	-0.35	Threefold-fcc
C(surface)	$E_C(\text{surface}) = U(\text{C}+\text{surface}) - U(\text{surface}) - R_C$	1.17	Threefold-hcp
CH(surface)	$E_{CH}(\text{surface}) = U(\text{CH}+\text{surface}) - U(\text{surface}) - R_C - R_H$	0.76	Threefold-hcp
CH ₂ (surface)	$E_{CH_2}(\text{surface}) = U(\text{CH}_2+\text{surface}) - U(\text{surface}) - R_C - 2R_H$	0.78	Threefold-hcp
CH ₃ (surface)	$E_{CH_3}(\text{surface}) = U(\text{CH}_3+\text{surface}) - U(\text{surface}) - R_C - 3R_H$	0.41	Threefold-hcp
OH(surface)	$E_{OH}(\text{surface}) = U(\text{OH}+\text{surface}) - U(\text{surface}) - R_O - R_H$	-0.07	Threefold-hcp
O(surface)	$E_O(\text{surface}) = U(\text{O}+\text{metal}) - U(\text{surface}) - R_O$	-0.12	Threefold-hcp
COH(surface)	$E_{COH}(\text{surface}) = U(\text{COH}+\text{surface}) - U(\text{surface}) - R_C - R_H - R_O$	1.42	Threefold-hcp
CHO(surface)	$E_{CHO}(\text{surface}) = U(\text{CHO}+\text{surface}) - U(\text{surface}) - R_C - R_H - R_O$	1.54	Threefold-hcp
CH ₂ CHO(surface)	$E_{CH_2CHO}(\text{surface}) = U(\text{CH}_2\text{CHO}+\text{surface}) - U(\text{surface}) - 2R_C - 3R_H - R_O$	1.76	C1 top, C2 bridge
CH ₂ CO(surface)	$E_{CH_2CO}(\text{surface}) = U(\text{CH}_2\text{CO}+\text{surface}) - U(\text{surface}) - 2R_C - 2R_H - R_O$	2.19	C1 top, C2 bridge
CH ₂ O(surface)	$E_{CH_2O}(\text{surface}) = U(\text{CH}_2\text{O}+\text{surface}) - U(\text{surface}) - R_C - 2R_H - R_O$	1.48	Threefold-hcp
CH ₂ OH(surface)	$E_{CH_2OH}(\text{surface}) = U(\text{CH}_2\text{OH}+\text{surface}) - U(\text{surface}) - R_C - 3R_H - R_O$	1.76	Threefold-hcp
CH ₃ CO(surface)	$E_{CH_3CO}(\text{surface}) = U(\text{CH}_3\text{CO}+\text{surface}) - U(\text{surface}) - 2R_C - 3R_H - R_O$	1.89	Threefold-hcp
CH ₃ O(surface)	$E_{CH_3O}(\text{surface}) = U(\text{CH}_3\text{O}+\text{surface}) - U(\text{surface}) - R_C - 3R_H - R_O$	1.05	Threefold-hcp
CHCHO(surface)	$E_{CHCHO}(\text{surface}) = U(\text{CHCHO}+\text{surface}) - U(\text{surface}) - 2R_C - 2R_H - R_O$	2.05	C1 fcc, C2 top
CHCO(surface)	$E_{CHCO}(\text{surface}) = U(\text{CHCO}+\text{surface}) - U(\text{surface}) - 2R_C - R_H - R_O$	1.80	C1 fcc, C2 hcp
CHOH(surface)	$E_{CHOH}(\text{surface}) = U(\text{CHOH}+\text{surface}) - U(\text{surface}) - R_C - 2R_H - R_O$	1.79	Threefold-hcp
CC(surface)	$E_{CC}(\text{surface}) = U_{CC}(\text{surface}) - U(\text{surface}) - 2R_C$	2.07	C1 hcp, C2 fcc
CCH(surface)	$E_{CCH}(\text{surface}) = U_{CCH}(\text{surface}) - U(\text{surface}) - 2R_C - R_H$	1.42	C1 hcp, C2 fcc
CCH ₂ (surface)	$E_{CCH_2}(\text{surface}) = U_{CCH_2}(\text{surface}) - U(\text{surface}) - 2R_C - 2R_H$	1.53	C1 hcp, C2 top
CCH ₃ (surface)	$E_{CCH_3}(\text{surface}) = U_{CCH_3}(\text{surface}) - U(\text{surface}) - 2R_C - 3R_H$	1.19	Threefold-hcp
CH ₂ CH ₂ (surface)	$E_{CH_2CH_2}(\text{surface}) = U(\text{CH}_2\text{CH}_2+\text{surface}) - U(\text{surface}) - 2R_C - 4R_H$	1.22	C1 hcp, C2 top
CH ₂ CH ₃ (surface)	$E_{CH_2CH_3}(\text{surface}) = U(\text{CH}_2\text{CH}_3+\text{surface}) - U(\text{surface}) - 2R_C - 5R_H$	1.36	C1 hcp, C2 top
CHCH(surface)	$E_{CHCH}(\text{surface}) = U(\text{CHCH}+\text{surface}) - U(\text{surface}) - 2R_C - 2R_H$	0.98	C1 hcp, C2 fcc
CHCH ₂ (surface)	$E_{CHCH_2}(\text{surface}) = U(\text{CHCH}_2+\text{surface}) - U(\text{surface}) - 2R_C - 3R_H$	1.50	C1 hcp, C2 top
CHCH ₃ (surface)	$E_{CHCH_3}(\text{surface}) = U(\text{CHCH}_3+\text{surface}) - U(\text{surface}) - 2R_C - 4R_H$	1.46	Threefold-hcp
CH ₃ CHO(surface)	$E(\text{CH}_3\text{CHO}+\text{surface}) = U(\text{CH}_3\text{CHO}+\text{surface}) - U(\text{surface}) - 2R_C - 4R_H - R_O$	1.97	Threefold-hcp

Figure S1. Top views of all the optimized geometries of intermediates on Co(0001). (a) C; (b) CC; (c) CCH; (d) CCH₂; (e) CCH₃; (f) CH; (g) CH₂; (h) CH₂CH₂; (i) CH₃CH₂; (j) CH₂CHO; (k) CH₂CO; (l) CH₂O; (m) CH₂OH; (n) CH₃; (o) CH₃CHO; (p) CH₃CO; (q) CH₃O; (r) CHCH; (s) CHCH₂; (t) CHCH₃; (u) CHCHO; (v) CHCO; (w) CHO; (x) CHOH; (y) OH; (z) H; (aa) O; (ab) OH; and (ac) CO.

1.2 Direct CO dissociation and H-assisted CO Dissociation

The direct CO dissociation reaction was calculated on Co(0001).² The barrier of direct CO dissociation is as high as 2.12 eV (Table S2). Van Santen and his co-workers used DFT to investigate CO dissociation on Ru(0001) and their results showed that hydrogen assisted dissociation is easier than direct CO dissociation.³⁻⁴ Ojeda and co-workers⁵ studied both direct CO dissociation and H-assisted CO dissociation on the flat Co(0001) surface with 0.5 ML CO; their results indicated that H-assisted CO dissociation is dominated on the surface. Recently, Li and co-workers⁶ studied CH_x formation on a Co(10 $\bar{1}$ 1) surface and their results shown that CO hydrogenation to CHO is the most possible pathway to form monomers. Their findings were very similar to our calculated results which are listed in Table S2. The transition state structures are displayed in Figure S2, and corresponding energy data for the transition states are shown in Table S2. The barrier of CHO dissociation is much lower than direct CO dissociation. The calculated COH and CHO dissociation energies are 1.56 eV and 0.36 eV, respectively. Our energy profiles are shown in Figure S3 and the effective barriers are 2.12 eV, 2.32 eV, and 1.77 eV for direct CO dissociation, COH dissociation and CHO dissociation, respectively. In other words, H-assisted CHO dissociation is the most possible pathway to form the monomer from the non-coverage dependent kinetic simulations on Co(0001).

Table S2. The barriers and reaction energies of elementary reactions of direct CO dissociation and H-assisted CO dissociation.

Elementary reaction	Forward reaction barrier (eV)	Reaction energy (eV)
$\text{CO}^* + ^* \rightleftharpoons \text{C}^* + \text{O}^*$	2.12	0.38
$\text{CO}^* + \text{H}^* \rightleftharpoons \text{COH}^* + ^*$	1.76	1.09
$\text{CO}^* + \text{H}^* \rightleftharpoons \text{CHO}^* + ^*$	1.34	1.22
$\text{COH}^* + ^* \rightleftharpoons \text{C}^* + \text{OH}^*$	1.65	-0.31
$\text{CHO}^* + ^* \rightleftharpoons \text{CH}^* + \text{O}^*$	0.56	-0.91

Figure S2. Top views of calculated transition state geometries of direct CO dissociation and H-assisted CO dissociation reactions on Co(0001). (a) $\text{TS}_{\text{CO}+\text{H}}(\text{CHO})$; (b) $\text{TS}_{\text{CHO}}(\text{CH}+\text{O})$; (c) $\text{TS}_{\text{CO}+\text{H}}(\text{COH})$; (d) $\text{TS}_{\text{COH}}(\text{C}+\text{OH})$; and (e) $\text{TS}_{\text{CO}}(\text{C}+\text{O})$.

Table S3. Distances of transition states of direct CO dissociation and H-assisted CO dissociation reactions.

	Transition State	Distance (Å)
(a)	$\text{TS}_{\text{CO}+\text{H}}(\text{CHO})$	1.17
(b)	$\text{TS}_{\text{CHO}}(\text{CH}+\text{O})$	1.79
(c)	$\text{TS}_{\text{CO}+\text{H}}(\text{COH})$	1.3
(d)	$\text{TS}_{\text{COH}}(\text{C}+\text{OH})$	1.8
(e)	$\text{TS}_{\text{CO}}(\text{C}+\text{O})$	1.85

Figure S3. Energy profiles of direct CO dissociation and H-assisted CO dissociation reactions on Co(0001). The path in red is $\text{CO}(\text{gas}) + 0.5\text{H}_2(\text{gas}) \rightarrow \text{CO}(\text{ad}) + \text{H}(\text{ad}) \rightarrow \text{TS}_{\text{CO}}(\text{C}+\text{O})(\text{ad}) + \text{H}(\text{ad}) \rightarrow \text{C}(\text{ad}) + \text{O}(\text{ad}) + \text{H}(\text{ad})$. The path in blue is $\text{CO}(\text{gas}) + 0.5\text{H}_2(\text{gas}) \rightarrow \text{CO}(\text{ad}) + \text{H}(\text{ad}) \rightarrow \text{TS}_{\text{CO}+\text{H}}(\text{COH})(\text{ad}) \rightarrow \text{COH}(\text{ad}) \rightarrow \text{C}(\text{ad}) + \text{OH}(\text{ad})$. The path in black is $\text{CO}(\text{gas}) + 0.5\text{H}_2(\text{gas}) \rightarrow \text{CO}(\text{ad}) + \text{H}(\text{ad}) \rightarrow \text{TS}_{\text{CO}+\text{H}}(\text{CHO})(\text{ad}) \rightarrow \text{CHO}(\text{ad}) \rightarrow \text{CH}(\text{ad}) + \text{O}(\text{ad})$.

1.3 Water Formation

Gong et al.² investigated the O removal on both the flat and stepped cobalt surfaces. However, proton migration between two hydroxyl groups was not included in the calculation which was

highlighted by van Santen and his co-workers.⁷⁻⁸ Michaelides and Hu⁹ investigated water formation on Pt(111) and found that the barrier of $\text{OH}^* + \text{OH}^* \rightleftharpoons \text{H}_2\text{O} + \text{O}^{*+}$ was only 0.13 eV. The removal of oxygen is very important for the FT reaction to form long chain hydrocarbons. Two important pathways for water formation are summarized as follows: (i) $\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^{*+}$, $\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^{*+}$; (ii) $\text{OH}^* + \text{OH}^* \rightleftharpoons \text{H}_2\text{O} + \text{O}^{*+}$. Proton migration between two hydroxyl groups results in a lower barrier of 0.67 eV which is listed in Table S4, and the corresponding structures and distances of transition states are shown in Figure S4 and Table S4. Our energy profiles are illustrated in Figure S5, and the effective barrier of pathway (ii) is lower than pathway (i) by 0.18 eV.

Table S4. The barriers and reaction energies of elementary reactions of water formation.

Elementary reaction	Forward reaction barrier (eV)	Reaction energy (eV)
$\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^{*+}$	1.30	0.40
$\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^{*+}$	1.48	0.41
$\text{OH}^* + \text{OH}^* \rightleftharpoons \text{H}_2\text{O} + \text{O}^{*+}$	0.67	0.01

Figure S4. Top views of calculated transition state geometries of water formation on Co(0001). (a) $\text{TS}_{\text{O}+\text{H}}(\text{OH})$; (b) $\text{TS}_{\text{H}+\text{OH}}(\text{H}_2\text{O})$; and (c) $\text{TS}_{\text{OH}+\text{OH}}(\text{H}_2\text{O}+\text{O})$.

Table S5. Distances at the transition states of water formation.

	Transition State	Distance (Å)
(a)	$TS_{O+H(OH)}$	1.45
(b)	$TS_{H+OH(H_2O)}$	1.49
(c)	$TS_{OH+OH(H_2O+O)}$	1.73

Figure S5. Energy profiles of water formation on Co(0001). The path in red is $2O(ad)+2H(ad) \rightarrow TS_{O+H(OH)}(ad)+O(ad)+H(ad) \rightarrow OH(ad)+O(ad)+H(ad) \rightarrow OH(ad)$

+ $TS_{O+H(OH)}(ad) \rightarrow OH(ad)+OH(ad) \rightarrow TS_{OH+OH(H_2O+O)}(ad) \rightarrow H_2O(gas)+O(ad)$. The path in blue is $2O(ad)+2H(ad) \rightarrow TS_{O+H(OH)}(ad)+O(ad)+H(ad) \rightarrow OH(ad)+O(ad)+$

$H(ad) \rightarrow TS_{H+OH(H_2O)}(ad)+O(ad) \rightarrow H_2O(gas)+O(ad)$.

1.4 C₁ Hydrogenation to Methane

The calculated forward reaction barriers and reaction energies for C₁ hydrogenation to methane in this work are listed in Table S6, and the results are very similar to a previous finding using SIESTA code.¹⁰ Our results are consistent with previous findings that the last hydrogenation step is the highest step and also in agreement with experimental work.¹¹ The first hydrogenation of C to CH is little higher than those from CH to CH₂ and from CH₂ to CH₃. The transition state structures are displayed in Figure S6 and the distances of the transition states are listed in Table S7. The energy profile in Figure S7 is consistent with the relative stabilities of adsorbates on the metal surface in Figure 5, and their relative stabilities are in the following order: CH>C>CH₃>CH₂.

Table S6. The forward reaction barriers and reaction energies of elementary steps of C₁ hydrogenation to methane.

Elementary reaction	Forward barrier (eV)	Reaction energy (eV)
$\text{H}^* + \text{C}^* \rightleftharpoons \text{CH}^* + ^*$	0.71	-0.07
$\text{H}^* + \text{CH}^* \rightleftharpoons \text{CH}_2^* + ^*$	0.53	0.37
$\text{H}^* + \text{CH}_2^* \rightleftharpoons \text{CH}_3^* + ^*$	0.49	-0.03
$\text{H}^* + \text{CH}_3^* \rightleftharpoons \text{CH}_4^* + ^*$	1.11	-0.06

Figure S6. Top views of calculated transition state geometries of C₁ hydrogenation to methane on Co(0001). (a) TS_{C+H} (CH); (b) TS_{CH+H} (CH₂); (c) TS_{CH₂+H} (CH₃); and (d) TS_{CH₃+H} (CH₄).

Table S7. Distances at the transition states of C₁ hydrogenation to methane on Co(0001).

	Transition State	Distance (Å)
(a)	TS _{C+H (CH)}	1.68
(b)	TS _{CH+H (CH₂)}	1.61
(c)	TS _{CH₂+H (CH₃)}	1.75
(d)	TS _{CH₃+H (CH₄)}	1.61

Figure S7. Energy profile of C₁ hydrogenation to methane on Co(0001). The path is C(ad)+4H(ad) → TS_{C+H (CH)}(ad)+3H(ad) → CH(ad)+3H(ad) → TS_{CH+H (CH₂)}(ad)+2H(ad) → CH₂(ad)+2H(ad) → TS_{CH₂+H (CH₃)}(ad)+H(ad) → CH₃(ad)+H(ad) → TS_{CH₃+H (CH₄)}(ad).

1.5 C₁+C₁ Coupling Reactions

There are nine coupling pathways for C₁ and C₁ coupling and the calculated forward reaction barriers and reaction energies are listed in Table S8. The calculated barriers are consistent with the literature.¹⁰ Frequency analyses were applied to ensure that the correct transition states were found in the DFT calculations. The corresponding transition state structures are displayed in Figure S8 and the distances of transition states are listed in Table S9. Based on the stabilities of species and the corresponding barriers we converted data into the energy profile in Figure S9. We can clearly find that the most favoured coupling pathway is CH+CH and other coupling pathways are preferred. Although the coupling of CH₂+CH₂ is facile, the monomer of CH₂ is unstable on the surface which is shown in Figure S9.

Table S8. The forward reaction barriers and reaction energies of C_1+C_1 coupling steps.

Elementary reaction	Forward barrier (eV)	Reaction energy (eV)
$C^*+C^*\rightleftharpoons CC^*+^*$	1.38	-0.27
$C^*+CH^*\rightleftharpoons CCH^*+^*$	1.03	-0.51
$C^*+CH_2^*\rightleftharpoons CCH_2^*+^*$	1.02	-0.42
$C^*+CH_3^*\rightleftharpoons CCH_3^*+^*$	1.16	-0.39
$CH^*+CH^*\rightleftharpoons CHCH^*+^*$	0.70	-0.53
$CH^*+CH_2^*\rightleftharpoons CHCH_2^*+^*$	0.91	-0.04
$CH^*+CH_3^*\rightleftharpoons CHCH_3^*+^*$	1.18	0.30
$CH_2^*+CH_2^*\rightleftharpoons CH_2CH_2^*+^*$	0.51	-0.34
$CH_2^*+CH_3^*\rightleftharpoons CH_2CH_3^*+^*$	1.03	0.18

Figure S8. Top view of calculated transition state geometries of C_1+C_1 coupling reactions on the flat cobalt surface. (a) TS_{C+C} ; (b) TS_{C+CH} ; (c) TS_{C+CH_2} ; (d) TS_{C+CH_3} ; (e) TS_{CH+CH} ; (f) TS_{CH+CH_2} ; (g) TS_{CH+CH_3} ; (h) $TS_{CH_2+CH_2}$; (i) $TS_{CH_2+CH_3}$.

Table S9. Distances at the transition states of C_1+C_1 coupling reactions on Co(0001).

	Transition State	Distance(Å)
(a)	TS_{C+C} (CC)	2.12
(b)	TS_{C+CH} (CCH)	2.22
(c)	TS_{C+CH_2} (CCH ₂)	2.28
(d)	TS_{C+CH_3} (CCH ₃)	2.1
(e)	TS_{CH+CH} (CHCH)	1.97
(f)	TS_{CH+CH_2} (CHCH ₂)	1.93
(g)	TS_{CH+CH_3} (CHCH ₃)	1.98
(h)	$TS_{CH_2+CH_2}$ (CH ₂ CH ₂)	2.04
(i)	$TS_{CH_2+CH_3}$ (CH ₂ CH ₃)	2.05

Figure S9. Energy profiles of C_1+C_1 coupling reactions on Co(0001). The path is $CH_x(ad)+CH_y(ad)+(5-x-y)H(ad) \rightarrow TS_{CH_x+CH_y}(ad)+(5-x-y)H(ad) \rightarrow CH_xCH_y(ad)+(5-x-y)H(ad)$, where $x,y = 0, 1, 2, 3$. $x+y = 5$.

1.6 C₂ Hydrogenation Reactions

There are twelve hydrogenation reactions for C₂ species, which are listed in Table S10. Cheng et al.¹² only calculated three hydrogenations, namely CCH_3+H , $CHCH_3+H$, CH_2CH_3+H . In this work, all the twelve hydrogenation reactions were searched using the constrained optimization scheme. The structures of the transition states are shown in Figure S10 and the corresponding distances of the transition states are listed in Table S11. It should be mentioned that all the barriers of

hydrogenation reactions for C₂ are around 0.6 eV except for CHCH hydrogenation to CHCH₂ which has the barrier of 1.16 eV.

Table S10. The forward reaction barriers and reaction energies of C₂ hydrogenation reactions.

Elementary reaction	Forward reaction barrier (eV)	Reaction energy (eV)
$CC^*+H^* \rightleftharpoons CCH^*+^*$	0.66	-0.30
$CCH^*+H^* \rightleftharpoons CCH_2^*+^*$	0.78	0.46
$CCH^*+H^* \rightleftharpoons CHCH^*+^*$	0.62	-0.09
$CCH_2^*+H^* \rightleftharpoons CCH_3^*+^*$	0.48	0.003
$CCH_2^*+H^* \rightleftharpoons CHCH_2^*+^*$	0.51	0.31
$CCH_3^*+H^* \rightleftharpoons CHCH_3^*+^*$	0.67	0.62
$CH_2CH_2^*+H^* \rightleftharpoons CH_2CH_3^*+^*$	0.50	0.49
$CH_2CH_3^*+H^* \rightleftharpoons CH_3CH_3+^*+^*$	0.82	-0.30
$CHCH^*+H^* \rightleftharpoons CHCH_2^*+^*$	1.16	0.86
$CHCH_2^*+H^* \rightleftharpoons CH_2CH_2^*+^*$	0.46	0.07
$CHCH_2^*+H^* \rightleftharpoons CHCH_3^*+^*$	0.50	0.31
$CHCH_3^*+H^* \rightleftharpoons CH_2CH_3^*+^*$	0.56	0.25

Figure S10. Top views of the transition state geometries of C_2 hydrogenation reactions on $\text{Co}(0001)$. (a) $\text{TS}_{\text{CC}+\text{H}}(\text{CCH})$; (b) $\text{TS}_{\text{CCH}+\text{H}}(\text{CCH}_2)$; (c) $\text{TS}_{\text{CCH}+\text{H}}(\text{CHCH})$; (d) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CCH}_3)$; (e) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CHCH}_2)$; (f) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CH}_2\text{CH})$; (g) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$; (h) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$; (i) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$; (j) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$; (k) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$; (l) $\text{TS}_{\text{CCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$

(f) $\text{TS}_{\text{CCH}_3+\text{H}}(\text{CHCH}_3)$; (g) $\text{TS}_{\text{CH}_2\text{CH}_2+\text{H}}(\text{CH}_2\text{CH}_3)$; (h) $\text{TS}_{\text{CH}_2\text{CH}_3+\text{H}}(\text{CH}_3\text{CH}_3)$; (i) $\text{TS}_{\text{CHCH}+\text{H}}(\text{CHCH}_2)$; (j) $\text{TS}_{\text{CHCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$; (k) $\text{TS}_{\text{CHCH}_2+\text{H}}(\text{CHCH}_3)$; and (l) $\text{TS}_{\text{CHCH}_3+\text{H}}(\text{CH}_2\text{CH}_3)$.

Table S11. Distances at the transition states of C_2 hydrogenation reactions on $\text{Co}(0001)$.

	Transition State	Distance (Å)
(a)	$\text{TS}_{\text{CC}+\text{H}}(\text{CCH})$	1.7
(b)	$\text{TS}_{\text{CCH}+\text{H}}(\text{CCH}_2)$	1.35
(c)	$\text{TS}_{\text{CCH}+\text{H}}(\text{CHCH})$	1.71
(d)	$\text{TS}_{\text{CCH}_2+\text{H}}(\text{CCH}_3)$	1.58
(e)	$\text{TS}_{\text{CCH}_2+\text{H}}(\text{CHCH}_2)$	1.62
(f)	$\text{TS}_{\text{CCH}_3+\text{H}}(\text{CHCH}_3)$	1.5
(g)	$\text{TS}_{\text{CH}_2\text{CH}_2+\text{H}}(\text{CH}_2\text{CH}_3)$	1.47
(h)	$\text{TS}_{\text{CH}_2\text{CH}_3+\text{H}}(\text{CH}_3\text{CH}_3)$	1.62
(i)	$\text{TS}_{\text{CHCH}+\text{H}}(\text{CHCH}_2)$	1.57
(j)	$\text{TS}_{\text{CHCH}_2+\text{H}}(\text{CH}_2\text{CH}_2)$	1.7
(k)	$\text{TS}_{\text{CHCH}_2+\text{H}}(\text{CHCH}_3)$	1.54
(l)	$\text{TS}_{\text{CHCH}_3+\text{H}}(\text{CH}_2\text{CH}_3)$	1.71

1.7 CO and C_1 Coupling Reactions

Cheng et al.¹³ only calculated CH_3+CO for the CO insertion mechanism and the reported barrier to be quite high. Some groups proposed that $\text{CH}+\text{CO}$ and CH_2+CO may be possible pathways to form long chain hydrocarbons on $\text{Co}(0001)$.¹⁴⁻¹⁶ We listed three CO-insertion coupling pathways in Table S12 and the corresponding energy profiles are plotted in Figure S12. It is found that the coupling reactions of $\text{CH}+\text{CO}$ and CH_2+CO are much easier than the coupling of CH_3+CO , which are 0.96 eV and 0.79 eV, respectively. The calculated barrier of CH_3+CO is very similar to that of Cheng et al.¹³ The structures of the transition states are shown in Figure S11 and the corresponding distances of the transition states are listed in the Table S13.

Table S12. The forward reaction barriers and reaction energies of CO and C₁ coupling reactions.

Elementary reaction	Forward barrier (eV)	Reaction energy (eV)
$\text{CH}^* + \text{CO}^* \rightleftharpoons \text{CHCO}^* + ^*$	0.96	0.37
$\text{CH}_2^* + \text{CO}^* \rightleftharpoons \text{CH}_2\text{CO}^* + ^*$	0.79	0.73
$\text{CH}_3^* + \text{CO}^* \rightleftharpoons \text{CH}_3\text{CO}^* + ^*$	1.45	0.80

Figure S11. Top views of the calculated transition state geometries of CO and C₁ coupling reactions on Co(0001). (a) TS_{CH+CO} (CHCO); (b) TS_{CH₂+CO} (CH₂CO); and (c) TS_{CH₃+CO} (CH₃CO).**Table S13.** Distances at the transition states of CO and C₁ coupling reactions on Co(0001).

	Transition State	Distance (Å)
(a)	TS _{CH+CO} (CHCO)	1.8
(b)	TS _{CH₂+CO} (CH ₂ CO)	1.77
(c)	TS _{CH₃+CO} (CH ₃ CO)	1.88

Figure S12. Energy profiles of CO and C₁ coupling reactions on Co(0001). The path in red is CH(ad)+CO(ad)+2H(ad) → TS_{CH+CO}(ad)+2H(ad) → CHCO(ad)+2H(ad). The path in blue is CH₂(ad)+CO(ad)+H(ad) → TS_{CH₂+CO}(ad)+ H(ad) → CH₂CO(ad)+ H(ad). The path in black is CH₃(ad)+CO(ad) → TS_{CH₃+CO}(ad) → CH₃CO(ad).

1.8 C₁ and OH Coupling Reactions

Three C₁ and OH coupling reactions were calculated and the corresponding forward reaction barriers and reaction energies are listed in Table S14 and the energy profiles are plotted in Figure S14. Because of the repulsion effect of CH₃ on OH, which can be seen in the transition state in Figure S13, the coupling barrier of CH₃ and OH is much higher than the couplings of CH₂*+OH* and CH*+OH* and all the reactions are endothermic. The structures of the transition states are shown in Figure S13 and the corresponding distances of the transition states are listed in the Table S15.

Table S14. The forward reaction barriers and reaction energies of C₁ and OH coupling reactions.

Elementary reaction	Forward barrier (eV)	Reaction energy (eV)
CH ₃ *+OH* ⇌ CH ₃ OH+*+*	2.45	0.94
CH ₂ *+OH* ⇌ CH ₂ OH*+*	1.45	1.04
CH*+OH* ⇌ CHOH*+*	1.68	1.09

Figure S13. Top views of the calculated transition state geometries of C₁ and OH coupling reactions on Co(0001). (a) TS_{CH+OH} (CHOH); (b) TS_{CH_2+OH} (CH₂OH); and (c) TS_{CH_3+OH} (CH₃OH).

Table S15. Distances at the transition states of C₁ and OH coupling reactions on Co(0001).

	Transition State	Distance (Å)
(a)	TS_{CH+OH}	1.87
(b)	TS_{CH_2+OH}	2.01
(c)	TS_{CH_3+OH}	1.98

Figure S14. Energy profiles of C₁ and OH coupling reactions on Co(0001). The path in red is $CH(ad)+OH(ad)+2H(ad) \rightarrow TS_{CH+OH}(ad)+2H(ad) \rightarrow CHOH(ad)+2H(ad) \rightarrow TS_{CHOH+H}(CH_2OH)(ad)+H(ad) \rightarrow CH_2OH(ad)+H(ad) \rightarrow CH_3OH(gas)$. The path in blue is $CH_2(ad) +$

$\text{OH(ad)} + \text{H(ad)} \rightarrow \text{TS}_{\text{CH}_2 + \text{OH}(\text{CH}_2\text{OH})}(\text{ad}) + \text{H(ad)} \rightarrow \text{CH}_2\text{OH(ad)} + \text{H(ad)} \rightarrow \text{CH}_3\text{OH(gas)}$. The path in black is $\text{CH}_3(\text{ad}) + \text{OH(ad)} \rightarrow \text{CH}_3\text{OH(gas)}$.

1.9 $\text{CH}_x\text{CH}_y\text{O}$ Hydrogenations

In our work, we found 15 elementary steps of $\text{CH}_x\text{CH}_y\text{O}$ hydrogenation reactions, and the calculated reaction barriers and reaction energies are listed in Table S16. Most of $\text{CH}_x\text{CH}_y\text{O}$ hydrogenations are endothermic. It should be mentioned that $\text{CHO}^* + \text{H}^* \rightleftharpoons \text{CHOH}^* + ^*$, $\text{CH}_2\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{OH}^* + ^*$, $\text{CH}_3\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^* + ^*$, $\text{CHCO}^* + \text{H}^* \rightleftharpoons \text{CHCHO}^* + ^*$, $\text{CH}_2\text{CO}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{CHO}^* + ^*$ are much higher than other hydrogenations and the corresponding barriers are 1.11 eV, 1.02 eV, 1.66 eV, 1.27 eV, 1.26 eV, respectively. The rest of barriers are approximately 0.6 eV which are very similar to the C_xH_y hydrogenations.

Table S16. The forward reaction barriers and reaction energies of elementary steps of $\text{CH}_x\text{CH}_y\text{O}$ hydrogenation reactions.

Elementary reaction	Forward barrier (eV)	Reaction energy (eV)
$\text{CHO}^* + \text{H}^* \rightleftharpoons \text{CHOH}^* + ^*$	1.10	0.59
$\text{CHO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{O}^* + ^*$	0.60	0.29
$\text{CH}_2\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{OH}^* + ^*$	1.02	0.62
$\text{CH}_2\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{O}^* + ^*$	0.55	-0.09
$\text{CH}_3\text{O}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^* + ^*$	1.66	0.58
$\text{CHCO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CO}^* + ^*$	0.76	0.74
$\text{CHCO}^* + \text{H}^* \rightleftharpoons \text{CHCHO}^* + ^*$	1.27	0.59
$\text{CH}_2\text{CO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CHO}^* + ^*$	0.41	-0.08
$\text{CH}_2\text{CO}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{CO}^* + ^*$	0.52	0.04
$\text{CHCHO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CHO}^* + ^*$	0.45	0.06
$\text{CH}_2\text{OH}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^* + ^*$	0.88	-0.13
$\text{COH}^* + \text{H}^* \rightleftharpoons \text{CHOH}^* + ^*$	0.73	0.72
$\text{CHOH}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{OH}^* + ^*$	0.60	0.32
$\text{CH}_2\text{CHO}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{CHO}^* + ^*$	1.26	0.56

Table S17. Distances at the transition states of $\text{CH}_x\text{CH}_y\text{O}$ hydrogenations on Co(0001).

	Transition State	Distance (Å)
(a)	$\text{TS}_{\text{CHO}+\text{H}} (\text{CHOH})$	1.36
(b)	$\text{TS}_{\text{CHO}+\text{H}} (\text{CH}_2\text{O})$	1.64
(c)	$\text{TS}_{\text{CH}_2\text{O}+\text{H}} (\text{CH}_2\text{OH})$	1.37
(d)	$\text{TS}_{\text{CH}_2\text{O}+\text{H}} (\text{CH}_3\text{O})$	1.57
(e)	$\text{TS}_{\text{CH}_3\text{O}+\text{H}} (\text{CH}_3\text{OH})$	1.43
(f)	$\text{TS}_{\text{CHCO}+\text{H}} (\text{CH}_2\text{CO})$	1.41
(g)	$\text{TS}_{\text{CHCO}+\text{H}} (\text{CHCHO})$	1.4
(h)	$\text{TS}_{\text{CH}_2\text{CO}+\text{H}} (\text{CH}_2\text{CHO})$	1.62
(i)	$\text{TS}_{\text{CH}_2\text{CO}+\text{H}} (\text{CH}_3\text{CO})$	1.56
(j)	$\text{TS}_{\text{CHCHO}+\text{H}} (\text{CH}_2\text{CHO})$	1.7
(k)	$\text{TS}_{\text{CH}_2\text{OH}+\text{H}} (\text{CH}_3\text{OH})$	1.57
(l)	$\text{TS}_{\text{COH}+\text{H}} (\text{CHOH})$	1.43
(m)	$\text{TS}_{\text{CHOH}+\text{H}} (\text{CH}_2\text{OH})$	1.59
(n)	$\text{TS}_{\text{CH}_2\text{CHO}+\text{H}} (\text{CH}_3\text{CHO})$	1.46
(o)	$\text{TS}_{\text{CH}_3\text{CO}+\text{H}} (\text{CH}_3\text{CHO})$	1.44

Figure S15. Top views of the calculated transition state geometries of C_2 hydrogenation reactions on Co(0001). (a) $TS_{CHO+H} (CHOH)$; (b) $TS_{CHO+H} (CH_2O)$; (c) $TS_{CH_2O+H} (CH_2OH)$; (d) $TS_{CH_2O+H} (CH_3O)$; (e) $TS_{CH_3O+H} (CH_3OH)$; (f) $TS_{CHCO+H} (CH_2CO)$; (g) $TS_{CHCO+H} (CHCHO)$; (h) $TS_{CH_2CO+H} (CH_2CHO)$; (i) $TS_{CH_2CO+H} (CH_3CO)$; (j) $TS_{CHCO+H} (CH_2CO)$; (k) $TS_{CHCO+H} (CHCHO)$; (l) $TS_{CH_2CO+H} (CH_3CO)$; (m) $TS_{CHO+H} (CHOH)$; (n) $TS_{CHO+H} (CH_2O)$; (o) $TS_{CH_2O+H} (CH_2OH)$.

TS_{CHCHO+H (CH₂CHO)}; (k) TS_{CH₂OH+H (CH₃OH)}; (l) TS_{COH+H (CHOH)}; (m) TS_{CHOH+H (CH₂OH)}; (n) TS_{CH₂CHO+H (CH₃CHO)}; and (o) TS_{CH₃CO+H (CH₃CHO)}.

1.10 CH_xCH_yO Dissociation

CH_xCH_yO dissociations were considered in our simulation. The forward reaction barriers and reaction energies are given in Table S18. All the CH_xCH_yO dissociations are exothermic. It should be mentioned that CHCO*+* $\rightleftharpoons$ CCH*+O*, CH₂CHO*+* $\rightleftharpoons$ CHCH₂*+O*, CH₃CHO*+* $\rightleftharpoons$ CHCH₃*+O* are higher than other CH_xCH_yO dissociation and the corresponding barriers are 1.39 eV, 1.31 eV, 1.16 eV and 0.93 eV, respectively, and other barriers of CH_xCH_yO dissociation are around 0.8 eV. The structures of the transition states are shown in Figure S16 and the corresponding distances of the transition states are listed in Table S19.

Table S18. The forward reaction barriers and reaction energies of CH_xCH_yO dissociation.

Elementary reaction	Forward reaction barrier (eV)	Reaction energy (eV)
CH ₂ O*+* $\rightleftharpoons$ CH ₂ *+O*	0.83	-0.82
CHCO*+* $\rightleftharpoons$ CCH*+O*	1.39	-0.50
CH ₂ CO*+* $\rightleftharpoons$ CCH ₂ *+O*	0.83	-0.77
CH ₃ CO*+* $\rightleftharpoons$ CCH ₃ *+O*	0.83	-0.81
CHCHO*+* $\rightleftharpoons$ CHCH*+O*	0.67	-1.18
CH ₂ CHO*+* $\rightleftharpoons$ CHCH ₂ *+O*	1.31	-0.38
CH ₃ O*+* $\rightleftharpoons$ CH ₃ *+O*	1.16	-0.76
CH ₃ CHO*+* $\rightleftharpoons$ CHCH ₃ *+O*	0.93	-0.63

Figure S16. Top views of the calculated transition state geometries of $\text{CH}_x\text{CH}_y\text{O}$ dissociation reactions on Co(0001). (a) $\text{TS}_{\text{CH}_2\text{O}}$ (CH_2+O); (b) TS_{CHCO} ($\text{CHC}+\text{O}$); (c) $\text{TS}_{\text{CH}_2\text{CO}}$ ($\text{CH}_2\text{C}+\text{O}$); (d) $\text{TS}_{\text{CH}_3\text{CO}}$ ($\text{CH}_3\text{C}+\text{O}$); (e) TS_{CHCHO} ($\text{CHCH}+\text{O}$); (f) $\text{TS}_{\text{CH}_2\text{CHO}}$ ($\text{CH}_2\text{CH}+\text{O}$); (g) $\text{TS}_{\text{CH}_3\text{O}}$ (CH_3+O); and (h) $\text{TS}_{\text{CH}_3\text{CHO}}$ ($\text{CH}_3\text{CH}+\text{O}$).

Table S19. Distances at the transition states of $\text{CH}_x\text{CH}_y\text{O}$ dissociation on Co(0001).

	Transition State	Distance($\text{\AA}$)
(a)	$\text{TS}_{\text{CH}_2\text{O}}$ (CH_2+O)	1.88
(b)	TS_{CHCO} ($\text{CHC}+\text{O}$)	1.79
(c)	$\text{TS}_{\text{CH}_2\text{CO}}$ ($\text{CH}_2\text{C}+\text{O}$)	1.76
(d)	$\text{TS}_{\text{CH}_3\text{CO}}$ ($\text{CH}_3\text{C}+\text{O}$)	1.81
(e)	TS_{CHCHO} ($\text{CHCH}+\text{O}$)	1.76
(f)	$\text{TS}_{\text{CH}_2\text{CHO}}$ ($\text{CH}_2\text{CH}+\text{O}$)	1.85
(g)	$\text{TS}_{\text{CH}_3\text{O}}$ (CH_3+O)	1.88
(h)	$\text{TS}_{\text{CH}_3\text{CHO}}$ ($\text{CH}_3\text{CH}+\text{O}$)	1.84

1.11 C_1 and CHO Coupling Reactions

Formyl was regarded as an important intermediate by in situ spectroscopic experiments for CO methanation on a supported Ru catalyst.¹⁷ Zhao et al. used DFT calculations to investigate the coupling between CHO and CO on Rh(111) and Co(0001) and suggested that the CHO insertion mechanism is competitive with the traditional carbide mechanism.¹⁸ We considered the CHO insertion mechanism in our calculations and the corresponding forward reaction barriers and reaction energies are listed in Table S20 which are only 0.62 eV and 0.21 eV, respectively. All the C₁ and CHO coupling reactions are exothermic. The structures of transition states are shown in Figure S17 and the corresponding distances at the transition states are listed in Table S21.

Table S20. The forward reaction barriers and reaction energies of C₁ and CHO coupling reactions.

Elementary reaction	Forward barrier (eV)	Reaction energy (eV)
$\text{CH}^* + \text{CHO}^* \rightleftharpoons \text{CHCHO}^* + ^*$	0.62	-0.25
$\text{CH}_2^* + \text{CHO}^* \rightleftharpoons \text{CH}_2\text{CHO}^* + ^*$	0.21	-0.56

Figure S17. Top views of the calculated transition state geometries of C₁ and CHO coupling reactions on Co(0001). (a) TS_{CH+CHO} (CHCHO); and (b) TS_{CH₂+CHO} (CH₂CHO).

Table S21. Distances at the transition states of C₁ and CHO coupling reactions on Co(0001).

	Transition State	Distance (Å)
(a)	TS _{CH+CHO} (CHCHO)	1.91
(b)	TS _{CH₂+CHO} (CH ₂ CHO)	2.04

2.1.1. Carbide Mechanism

All the possible coupling reactions in the carbide mechanism on Co(0001) were calculated with van der Waals's interactions included. Based on the equation of Cheng et al., the reaction rates for C₁+C₁ can be expressed as follows:

$$r_{\text{CH}_i+\text{CH}_j} = \frac{k_b T}{h} e^{-\frac{E_a}{RT}} \theta_{\text{CH}_i} \theta_{\text{CH}_j} = \frac{k_b T}{h} e^{-\frac{E_a+E_i+E_j}{RT}} t^{i+j} \theta_C^2 \quad (1)$$

where $r_{\text{CH}_i+\text{CH}_j}$ is the rate of C_i+C_j coupling; k_b is the Boltzmann constant, T is the temperature, h is the Planck constant, E_a is the barrier of C_i+C_j coupling, and $E_a + E_i + E_j$ is defined as the effective barrier. The calculated barriers are listed in Table S8 and the effective barriers are listed in Table S22. Using the effective barriers in Table S22 and Eq. S1, the C_i+C_j coupling rates were calculated and the results are listed in Table 23. From the reaction rates in Table 23, we can see that the coupling of $\text{CH}+\text{CH}$ is the favored coupling pathway for C_2 species with the van der Waals interactions, which is consistent with the results of Cheng et al..¹⁰

Table S22. Effective barriers (eV) of all possible C_1 and C_1 coupling pathways on Co(0001).

Pathway	C+C	C+CH	C+CH ₂
Effective Barriers	1.38	0.97	1.33
Pathway	C+CH ₃	CH+CH	CH+CH ₂
Effective Barriers	1.44	0.58	1.16
Pathway	CH+CH ₃	CH ₂ +CH ₂	CH ₂ +CH ₃
Effective Barriers	1.40	1.13	1.62
Pathway	CH+CO	CH ₂ +CO	CH ₃ +CO
Effective Barriers	0.90	1.00	1.73

Table S23. Reaction rates (s⁻¹) of all possible C₁ and C₁ coupling reactions on Co(0001).

Pathway	C+C	C+CH	C+CH ₂
Reaction Rate	$0.12\theta_{\text{C}}^2$	$1.7 \times 10^3 t \theta_{\text{C}}^2$	$0.43 t^2 \theta_{\text{C}}^2$
Pathway	C+CH ₃	CH+CH	CH+CH ₂
Reaction Rate	$0.03 t^3 \theta_{\text{C}}^2$	$1.3 \times 10^7 t^2 \theta_{\text{C}}^2$	$20 t^3 \theta_{\text{C}}^2$
Pathway	CH+CH ₃	CH ₂ +CH ₂	CH ₂ +CH ₃
Reaction Rate	$0.08 t^4 \theta_{\text{C}}^2$	$41 t^4 \theta_{\text{C}}^2$	$10^{-4} t^5 \theta_{\text{C}}^2$

2.1.2. CO Insertion Mechanism

According to the transition state theory and Eq. 11, the CO insertion rate can be written as follows:

$$r_{\text{CH}_i+\text{CO}} = \frac{k_{\text{b}}T}{h} e^{\frac{-E_{\text{a}}}{RT}} \theta_{\text{CH}_i} \theta_{\text{CO}} = \frac{k_{\text{b}}T}{h} e^{\frac{-E_{\text{a}}}{RT}} e^{\frac{-E_{\text{i}}}{RT}} \theta_{\text{C}} t^i \theta_{\text{CO}} = \frac{k_{\text{b}}T}{h} e^{\frac{-(E_{\text{a}}+E_{\text{i}})}{RT}} t^i \theta_{\text{C}} \theta_{\text{CO}} \quad (2)$$

where $r_{\text{CH}_i+\text{CO}}$ is the rate of CO insertion, E_{a} is the barrier of C₁+CO coupling, and $E_{\text{a}} + E_{\text{i}}$ is the effective barrier. Using the calculated barriers in Table S22, the effective barriers are obtained, which are listed in Table S24. Using the effective barriers in the Table S24 and Eq. S2, the CO insertion rates can be computed and the results are listed in Table S25.

Table S24. Effective barriers (eV) of all the possible CO insertion reactions on Co(0001).

Pathway	CH+CO	CH ₂ +CO	CH ₃ +CO
Effect Barriers	0.90	1.00	1.73

Table S25. Reaction rates (s^{-1}) of all the possible CO insertion reactions on Co(0001).

Pathway	CH+CO	CH ₂ +CO	CH ₃ +CO
Reaction Rate	$7.8 \times 10^3 t \theta_C \theta_{CO}$	$832 t^2 \theta_C \theta_{CO}$	$4.0 \times 10^{-5} t^3 \theta_C \theta_{CO}$

From the reaction rates in Table S25, the coupling of CH₃+CO is the most difficult one compared with other CO insertion coupling reactions and the most likely couplings are CH+CO and CH₂+CO, from which we can obtain the following equation:

$$\frac{r_{CH+CO}}{r_{CH_2+CO}} = \frac{7.8 \times 10^3 t \theta_C \theta_{CO}}{832 t^2 \theta_C \theta_{CO}} = \frac{9.375}{t} \quad (3)$$

where the ratio of $\frac{\theta_H}{\theta_*}$ is typically about 1 to 10.

Hence, we can derive

$$\begin{aligned} r_{CH+CO} &> r_{CH_2+CO} \\ 0 < t < 9.375 \end{aligned} \quad (4)$$

$$\begin{aligned} r_{CH+CO} &< r_{CH_2+CO} \\ 9.375 < t < 10 \end{aligned} \quad (5)$$

$$\begin{aligned} r_{CH+CO} &= r_{CH_2+CO} \\ t &= 9.375 \end{aligned} \quad (6)$$

2.1.3. CHO Insertion Mechanism

Similarly, the CHO insertion rate can be written as:

$$r_{CH_i+CHO} = \frac{k_b T}{h} e^{\frac{-E_a}{RT}} \theta_{CH_i} \theta_{CHO} = \frac{k_b T}{h} e^{\frac{-E_a}{RT}} e^{\frac{-E_i}{RT}} \theta_C t^i \theta_{CHO} = \frac{k_b T}{h} e^{\frac{-(E_a+E_i)}{RT}} t^i \theta_C \theta_{CHO} \quad (7)$$

where r_{CH_i+CHO} is the rate of CHO insertion, E_a is the barrier of C₁+CHO coupling, and $E_a + E_i$ is the effective barrier. Based on the calculated barriers in Table S20, the effective barriers are determined and listed in Table S26. Using the effective barriers in Table S26 and Eq. S7, the CHO

insertion rates are obtained (Table S27), which show that the couplings of CH₂+CHO and CH+CHO are similar with CH+CHO being slightly favored.

Table S26. Effective barriers (eV) of all the possible CHO insertion reactions on Co(0001).

Pathway	CH+CHO	CH ₂ +CHO
Effect Barriers	0.56	0.52

Table S27. Reaction rates (s⁻¹) of all the possible CHO insertion reactions on Co(0001).

Pathway	CH+CHO	CH ₂ +CHO
Reaction Rate	$2.3 \times 10^7 t \theta_C \theta_{CHO}$	$5.7 \times 10^7 t^2 \theta_C \theta_{CHO}$

3.1 Choice of Partial Pressure and Temperature

The kinetic simulations were carried out at pressure at 10 bars, and the ratio of H₂ to CO is 2. The partial pressures were estimated from experimental data.¹⁹⁻²⁰

Table S28. Partial pressures of gases on Co(0001) at 500 K. All the values are in bar.

Partial pressure on Cobalt Surface (bar) at 500 K						
CO	H ₂	CH ₄	H ₂ O	C ₂ H ₄	C ₂ H ₆	CH ₃ OH
3.33	6.67	0.457	0.01	0.0087	0.0261	0.01

4.1 Differential Chemisorption Energies

Based on strong CO adsorption on the cobalt surface, it is expected that CO will be the most abundant surface intermediate, and thus our model includes all interactions of surface intermediates with CO.

The differential chemisorption energy is used in our kinetic modeling and is calculated as follows:

$$E_{\text{differential}}(\frac{1}{2}(\frac{n-1}{N} + \frac{n}{N})) = E_{n.\text{adsorbate}} - E_{(n-1).\text{adsorbate}} - E_{\text{gas}} \quad (7)$$

where n is the number of the adsorbate, N is the number of surface sites in the unit cell, $E_{\text{differential}}(\frac{1}{2}(\frac{n-1}{N} + \frac{n}{N}))$ represents the differential chemisorption energy at the middle point coverage at $(\frac{n-1}{N} + \frac{n}{N})$, $E_{n.\text{adsorbate}}$ represents the total energy of metal with n adsorbates, $E_{(n-1).\text{adsorbate}}$ represents the total energy of metal with $n-1$ adsorbates and E_{gas} is the total energy of the adsorbate in the gas phase.

The threshold coverage is usually located at 0.33 ML on Co(0001), and this point is also consistent with experimental work.²¹ If the coverage of CO is in the low coverage region, the differential chemisorption of CO can be regarded as a constant. However, if the coverage of CO is located in the high coverage region, CO-CO interactions will weaken the differential chemisorption energy.

Figure S18. The calculated structures of CO adsorption with varying amounts of coverage on Co(0001) in the p(3x3) unit cell. The red, grey and blue balls represent O, C, Co atoms, respectively. (a) 1/9 ML; (b) 2/9 ML; (c) 3/9 ML; (d) 4/9 ML; (e) 5/9 ML; (f) 6/9 ML; (g) 7/9 ML; (h) 8/9 ML; and (i) 1 ML.

4.2 High CO Coverage Intermediates and Transition States

The key issue of the coverage dependent kinetic model is to find the most stable geometry at a particular coverage. For the transition states, we firstly obtained the structure at a low coverage and then the transition state was fixed and the lowest energy configuration at a certain CO coverage was searched. Finally, we located the final geometry of the transition state using constrained optimization scheme.²²⁻²⁴

4.2.1 Intermediates under CO Environment

4.2.1.1 4CO+intermediates

Figure S19. Top views of all the optimized geometries of intermediates in the presence of 4CO on Co(0001). (a) C; (b) CC; (c) CCH; (d) CCH₂; (e) CCH₃; (f) CH; (g) CH₂; (h) CH₂CH₂; (i) CH₃CH₂; (j) CH₂CHO; (k) CH₂CO; (l) CH₂O; (m) CH₂OH; (n) CH₃; (o) CH₃CHO; (p) CH₃CO; (q) CH₃O; (r) CHCH; (s) CHCH₂; (t) CHCH₃; (u) CHCHO; (v) CHCO; (w) CHO; (x) CHOH; (y) COH; (z) H; (aa) O; and (ab) OH.

4.2.1.2 5CO+intermediates

Figure S20. Top views of all the optimized geometries of intermediates in the presence of 5CO on Co(0001). (a) C; (b) CC; (c) CCH; (d) CCH₂; (e) CCH₃; (f) CH; (g) CH₂; (h) CH₂CH₂; (i) CH₃CH₂; (j) CH₂CHO; (k) CH₂CO; (l) CH₂O; (m) CH₂OH; (n) CH₃; (o) CH₃CHO; (p) CH₃CO; (q) CH₃O; (r) CHCH; (s) CHCH₂; (t) CHCH₃; (u) CHCHO; (v) CHCO; (w) CHO; (x) CHOH; (y) COH; (z) H; (aa) O; and (ab) OH.

4.2.1.3 6CO+intermediates

Figure S21. Top views of all the optimized geometries of intermediates in the presence of 6CO on Co(0001). (a) C; (b) CC; (c) CCH; (d) CCH₂; (e) CCH₃; (f) CH; (g) CH₂; (h) CH₂CH₂; (i) CH₃CH₂; (j) CH₂CHO; (k) CH₂CO; (l) CH₂O; (m) CH₂OH; (n) CH₃; (o) CH₃CHO; (p) CH₃CO; (q) CH₃O; (r) CHCH; (s) CHCH₂; (t) CHCH₃; (u) CHCHO; (v) CHCO; (w) CHO; (x) CHOH; (y) COH; (z) H; (aa) O; and (ab) OH.

4.2.2 Transition States under CO Environment

4.2.2.1 The transition states in the presence of 4CO

4.2.2.1.1 Direct CO dissociation and H-assisted CO dissociation with 4CO

Figure S22. Top views of the calculated transition state geometries of direct CO dissociation and H-assisted CO dissociation reactions on Co(0001) in the presence of 4CO. (a) $\text{TS}_{\text{CO}+\text{H}}(\text{CHO})$; (b) $\text{TS}_{\text{CHO}}(\text{CH}+\text{O})$; (c) $\text{TS}_{\text{CO}+\text{H}}(\text{COH})$; (d) $\text{TS}_{\text{COH}}(\text{C}+\text{OH})$; and (e) $\text{TS}_{\text{CO}}(\text{C}+\text{O})$.

4.2.2.1.2 Water formation in the presence of 4CO

Figure S23. Top views of the calculated transition state geometries of water formation on Co(0001) in the presence of 4CO. (a) $\text{TS}_{\text{O}+\text{H}}(\text{OH})$; (b) $\text{TS}_{\text{H}+\text{OH}}(\text{H}_2\text{O})$; and (c) $\text{TS}_{\text{OH}+\text{OH}}(\text{H}_2\text{O}+\text{O})$.

4.2.2.1.3 C_1 hydrogenation to methane in the presence of 4CO

Figure S24. Top views of the calculated transition state geometries of C_1 hydrogenation to methane on Co(0001) in the presence of 4CO. (a) $\text{TS}_{\text{C}+\text{H}}(\text{CH})$; (b) $\text{TS}_{\text{CH}+\text{H}}(\text{CH}_2)$; (c) $\text{TS}_{\text{CH}_2+\text{H}}(\text{CH}_3)$; and (d) $\text{TS}_{\text{CH}_3+\text{H}}(\text{CH}_4)$.

4.2.2.1.4 C₁+C₁ coupling reactions in the presence of 4CO

Figure S25. Top views of the calculated transition state geometries of C₁+C₁ coupling reactions on Co(0001) in the presence of 4CO. (a) TS_{C+C}; (b) TS_{C+CH}; (c) TS_{C+CH₂}; (d) TS_{C+CH₃}; (e) TS_{CH₂+CH₃}; (f) TS_{CH₂+CH₂}; (g) TS_{CH+CH}; (h) TS_{CH+CH₂}; and (i) TS_{CH+CH₃}.

4.2.2.1.5 C₂ hydrogenation reactions in the presence of 4CO

Figure S26. Top views of the calculated transition state geometries of C₂ hydrogenations on Co(0001) in the presence of 4CO. (a) TS_{CC+H (CCH)}; (b) TS_{CCH₂+H (CCH₃)}; (c) TS_{CCH₂+H (CHCH₂)}; (d) TS_{CCH₃+H (CHCH₃)}; (e) TS_{CCH+H (CCH₂)}; (f) TS_{CCH+H (CHCH)}; (g) TS_{CH₂CH₂+H (CH₂CH₃)}; (h) TS_{CH₂CH₃+H (CH₃CH₃)}; (i) TS_{CHCH₂+H (CH₂CH₂)}; (j) TS_{CHCH₂+H (CHCH₃)}; (k) TS_{CHCH₃+H (CH₂CH₃)}; (l) TS_{CHCH+H (CHCH₂)}.

4.2.2.1.6 CO and C₁ coupling reactions in the presence of 4CO

Figure S27. Top views of the calculated transition state geometries of CO and C₁ coupling reactions in the presence of 4CO on Co(0001). (a) TS_{CH+CO} (CHCO); (b) TS_{CH₂+CO} (CH₂CO); and (c) TS_{CH₃+CO} (CH₃CO).

4.2.2.1.7 C₁ and OH coupling reactions in the presence of 4CO

Figure S28. Top views of the calculated transition state geometries of C₁ and OH coupling reactions in the presence of 4CO on Co(0001). (a) TS_{CH+OH} (CHOH); (b) TS_{CH₂+OH} (CH₂OH); and (c) TS_{CH₃+OH} (CH₃OH).

4.2.2.1.8 CH_xCH_yO hydrogenations in the presence of 4CO

Figure S29. Top views of the calculated transition state geometries of CH_xCH_yO hydrogenations on Co(0001) in the presence of 4CO. (a) TS_{CH₂CHO+H} (CH₃CHO); (b) TS_{CH₂CO+H} (CH₂CHO); (c) TS_{CH₂CO+H} (CH₃CO); (d) TS_{CH₂O+H} (CH₂OH); (e) TS_{CH₂O+H} (CH₃O); (f) TS_{CH₂OH+H} (CH₃OH); (g) TS_{CH₃CO+H} (CH₃CHO); (h) TS_{CH₃O+H} (CH₃OH); (i) TS_{CHCO+H} (CH₂CO); (j) TS_{CHCO+H} (CHCHO); (k) TS_{CHO+H} (CH₂O); (l) TS_{CHO+H} (CHOH); (m) TS_{CHOH+H} (CH₂OH); and (n) TS_{COH+H} (CHOH).

4.2.2.1.9 CH_xCH_yO dissociation in the presence of 4CO

Figure S30. Top views of the calculated transition state geometries of CH_xCH_yO dissociation reactions on Co(0001) in the presence of 4CO. (a) TS_{CH₂CHO} (CH₂CH+O); (b) TS_{CH₂CO} (CH₂C+O); (c) TS_{CH₂O}

(CH₂+O); (d) TS_{CH₃CHO (CH₃CH+O)}; (e) TS_{CH₃CO (CH₃C+O)}; (f) TS_{CH₃O (CH₃+O)}; (g) TS_{CHCHO (CHCH+O)}; and (h) TS_{CHCO (CHC+O)}.

4.2.2.1.10 C₁ and CHO coupling reactions in the presence of 4CO

Figure S31: Top views of the calculated transition state geometries of C₁ and CHO coupling reactions in the presence of 4CO on Co(0001). (a) TS_{CH+CHO (CHCHO)}; and (b) TS_{CH₂+CHO (CH₂CHO)}.

4.2.2.2 Transition state geometries in the presence of 5CO

4.2.2.2.1 Direct CO dissociation and H-assisted CO dissociation in the presence of 5CO

Figure S32. Top views of the calculated transition state geometries of direct CO dissociation and H-assisted CO dissociation reactions on Co(0001) in the presence of 5CO. (a) TS_{CO+H (CHO)}; (b) TS_{CHO (CH+O)}; (c) TS_{CO+H (COH)}; (d) TS_{COH (C+OH)}; and (e) TS_{CO (C+O)}.

4.2.2.2.2 Water formation in the presence of 5CO

Figure S33. Top views of the calculated transition state geometries of water formation on the flat cobalt surface with 5CO. (a) TS_{O+H (OH)}; (b) TS_{H+OH (H₂O)}; and (c) TS_{OH+OH (H₂O+O)}.

4.2.2.2.3 C₁ Hydrogenation to Methane in the presence of 5CO

Figure S34. Top views of the calculated transition state geometries of C₁ hydrogenation to methane on Co(0001) in the presence of 5CO. (a) TS_{C+H (CH)}; (b) TS_{CH+H (CH₂)}; (c) TS_{CH₂+H (CH₃)}; and (d) TS_{CH₃+H (CH₄)}.

4.2.2.2.4 C₁+C₁ coupling reactions in the presence of 5CO

Figure S35. Top views of the calculated transition state geometries of C₁+C₁ coupling reactions on Co(0001) in the presence of 4CO. (a) TS_{C+C}; (b) TS_{C+CH}; (c) TS_{C+CH₂}; (d) TS_{C+CH₃}; (e) TS_{CH+CH}; (f) TS_{CH+CH₂}; (g) TS_{CH+CH₃}; (h) TS_{CH₂+CH₂}; (i) TS_{CH₂+CH₃}.

4.2.2.2.5 C₂ hydrogenation reactions in the presence of 5CO

Figure S36: Top views of the calculated transition state geometries of C₂ hydrogenations on Co(0001) in the presence of 5CO. (a) TS_{CC+H} (CCH); (b) TS_{CCH+H} (CCH₂); (c) TS_{CCH+H} (CHCH); (d) TS_{CCH₂+H} (CCH₃); (e) TS_{CCH₂+H} (CHCH₂); (f) TS_{CCH₃+H} (CHCH₃); (g) TS_{CH₂CH₂+H} (CH₂CH₃); (h) TS_{CH₂CH₃+H} (CH₃CH₃); (i) TS_{CHCH+H} (CHCH₂); (j) TS_{CHCH₂+H} (CH₂CH₂); (k) TS_{CHCH₂+H} (CHCH₃); and (l) TS_{CHCH₃+H} (CH₂CH₃).

4.2.2.2.6 CO and C₁ coupling reactions in the presence of 5CO

Figure S37. Top views of the calculated transition state geometries of CO and C₁ coupling reactions in the presence of 5CO on Co(0001). (a) TS_{CH+CO} (CHCO); (b) TS_{CH₂+CO} (CH₂CO); and (c) TS_{CH₃+CO} (CH₃CO).

4.2.2.2.7 C₁ and OH coupling reactions in the presence of 5CO

Figure S38: Top views of the calculated transition state geometries of C₁ and OH coupling reactions in the presence of 5CO on Co(0001). (a) TS_{CH+OH} (CH+OH); (b) TS_{CH₂+OH} (CH₂+OH); and (c) TS_{CH₃+OH} (CH₃OH).

4.2.2.2.8 CH_xCH_yO hydrogenations in the presence of 5CO

Figure S39. Top views of the calculated transition state geometries of CH_xCH_yO hydrogenations on Co(0001) in the presence of 5CO. (a) TS_{CH₂CHO+H} (CH₃CHO); (b) TS_{CH₂CO+H} (CH₂CHO); (c) TS_{CH₂CO+H} (CH₃CO); (d) TS_{CH₂O+H} (CH₂OH); (e) TS_{CH₂O+H} (CH₃O); (f) TS_{CH₂OH+H} (CH₃OH); (g) TS_{CH₃CO+H} (CH₃CHO); (h) TS_{CH₃O+H} (CH₃OH); (i) TS_{CHCO+H}(CH₂CO); (j) TS_{CHCO+H} (CHCHO); (k) TS_{CHO+H} (CH₂O); (l) TS_{CHO+H} (CHOH); (m) TS_{CHOH+H} (CH₂OH); and (n) TS_{COH+H} (CHOH).

4.2.2.2.9 CH_xCH_yO dissociation in the presence of 5CO

Figure S40. Top views of the calculated transition state geometries of CH_xCH_yO dissociation reactions on Co(0001) in the presence of 5CO. (a) TS_{CH₂CHO} (CH₂CH+O); (b) TS_{CH₂CO} (CH₂C+O); (c) TS_{CH₂O}

(CH₂+O); (d) TS_{CH₃CHO (CH₃CH+O)}; (e) TS_{CH₃CO (CH₃C+O)}; (f) TS_{CH₃O (CH₃+O)}; (g) TS_{CHCHO (CHCH+O)}; and (h) TS_{CHCO (CHC+O)}.

4.2.2.2.10 C₁ and CHO coupling reactions in the presence of 5CO

Figure S41. Top views of the calculated transition state geometries of C₁ and CHO coupling reactions in the presence of 5CO on Co(0001). (a) TS_{CH+CHO (CHCHO)}; and (b) TS_{CH₂+CHO (CH₂CHO)}.

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