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Mechanistic Insights into the Selectivity of Catalytic CO₂ Hydrogenation to High-value Chemicals over Fe-Co Bimetallic Catalysts

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Abstract:

Carbon dioxide hydrogenation has captured significant attention as a key reaction in CO₂ valorization. This reaction has proved valuable as it is considered as both a mitigating solution to harmful greenhouse gas emissions and a production method of high-value chemicals and fuels. Due to the thermal stability of CO₂, an intermediate C1 building block is required to initiate the formation of valuable C₂+ hydrocarbon products. As such, considerable previous research has sought to identify possible precursor-mediated pathways for the formation of C₂+ products, revealing two as the most prominent: 1) methanol-synthesis route, where methanol is the C1 precursor, and 2) Fischer-Tropsch synthesis (FTS) route, which utilizes CO as the C1 precursor. For the FTS route, Fe and Co catalysts have proven to be the most promising. However, the wide range of products formed with such catalysts imposes a challenge on understanding the underlying mechanism of FTS, and thus selectivity control limitations. Here, we explore the active surface of an Fe-Co bimetallic catalyst under experimentally optimized reaction conditions using a theoretical approach. We model the catalyst in CO₂ hydrogenation conditions as Co doped χ -Fe₅C₂ carbide. We show that the mechanism initiated by the C-O bond cleavage in CO₂ is preferred and we identify two main chain-lengthening schemes involving carbon coupling of: 1) CH_x* species,

and 2) active oxygen-containing species (HCO^*). The energetic span approximation shows that both schemes are comparatively active for CO_2 -FTS under the experimental conditions, however, we establish that through the CH_x^* species coupling route, more undesired side reactions producing light products, such as methane and methanol, arise. In contrast, the active oxygen-containing intermediate route (via HCO^*) shows a more direct pathway to desired C_2+ and C_5+ products (including higher alcohols) with minimal undesired side reactions.

Introduction:

The global continuous rise in greenhouse gas (GHG) emissions poses significant challenges to our environment and atmosphere, making sustainability a critical concern that requires serious interventions. According to the IPCC Climate Change 2023 report¹, the global surface temperature in 2011-2020 has increased by 1.1 °C compared to the temperature in 1850-1900. Despite seeming modest, this increase has already caused substantial damages including an increase in the global mean sea level, global retreat of glaciers, decrease in Arctic Sea ice area, acidification of the global surface ocean, and other widespread disruptions to ecosystems¹. As the majority of GHG emissions originate from human-driven activities within the energy sector and the largest portion of such anthropogenic GHG emissions is CO_2 , mitigation solutions for CO_2 have been a central focus of research efforts in the last few decades². As such, along with CO_2 capture and storage (CCS), CO_2 chemical conversion and utilization (CCU), and CO_2 emissions control efforts, the transition to cleaner and more sustainable energy sources has been of great interest³⁻⁶. Most notably, hydrogen, has emerged as an exceptional sustainable energy carrier with low to no GHG emissions when produced from renewable energy, such as wind and solar energies^{7,8}. Thus, hydrogen demand and production are projected to continue to increase to over

600 million tonnes in 2050⁹. Additionally, several giga-scale green hydrogen production projects, such as HyDeal Ambition (67GW) in Western Europe and Western Green Energy Hub (28GW) in Australia have been announced⁹. By integrating sustainable hydrogen production with CO₂ reduction efforts, an alternative approach of producing high-value chemicals and fuels (C₂+ products) is introduced.

Herein, CO₂ hydrogenation is explored as a key process for valorizing CO₂, specifically, CO₂ hydrogenation towards liquid hydrocarbon products via thermal heterogeneous catalysis. Although many reviews have been published on this topic and multiple catalyst systems have been experimentally discussed for their unique CO₂ hydrogenation capabilities, it is important to further investigate the underlying mechanisms to enhance the production of high-value chemicals. Substantial research done on this topic established that the hydrogenation of CO₂ to produce liquid hydrocarbons mainly proceeds through two possible mechanisms. The first is the methanol-synthesis route, where methanol is used as a bridging intermediate to produce a wide range of long-chain compounds such as dimethyl ether (DME), olefins, aromatics, and gasoline-range hydrocarbons^{10–12}. The second mechanism is the Fischer-Tropsch Synthesis (FTS) based CO₂ hydrogenation, which involves an endothermic reverse water-gas shift reaction (RWGS) followed by an exothermic FTS, where CO serves as the C1 building block for converting CO₂ to C₂+ products. Consequently, the conditions required for each of the reactions are different^{6,13–15}. The need for the RWGS reaction prior to the FTS reaction arises from the high thermal stability of CO₂. Although it is more technically convenient to use two reactors for these systems, the direct single-reactor system has sparked considerable attention. This is because a one-reactor system would simplify the process, potentially reducing costs and improving efficiency. Additionally, the Anderson-Schulz-Flory (ASF) distribution imposes inherent limitations on the selectivity of

typical FTS catalysts towards C_2+ hydrocarbons^{16–19}. As a result, modified catalyst systems are required to overcome these restrictions and enhance hydrocarbon production efficiency.

Widely used RWGS catalysts include Pt, Pd, Rh, and Cu-based catalysts. On the other hand, FTS reported catalysts are typically Fe, Co, and Ru-based catalysts. To successfully integrate the two reactions into one system, a catalyst that is efficient for both of RWGS and FTS under the same conditions is required¹³. Moreover, the catalyst needs to exhibit limited water-gas shift (WGS) activity, low methane selectivity, and high selectivity to C_2+ hydrocarbons. To achieve limitation on the selectivity of methane, alkali metals promoters (e.g. Na, Cs, and K) are reported to have a suppressing effect on the formation of methane and an enhancement effect on the selectivity to C_2+ products^{20–22}. Between the different alkali metals, potassium gained most attention as it showed drastic improvements in the selectivity towards long-chain hydrocarbons^{20–23}. Metals such as Ni, Cu, Zn, and Zr are also proven to provide significant improvement on the selectivity of catalysts. These metals can be incorporated into catalysts either as the support, or a metal modification. Wang et al.²⁴ reported that K-Fe/ZrO₂ exhibited a high selectivity to C_2 - C_4 olefins in comparison to K-Fe catalysts with carbon support materials. Bimetallic catalysts, such as K-promoted Fe-Cu/Al₂O₃, Fe-Zn-K, and Fe-Co-K also received significant attention as they are highly active and selective^{25–27}.

In this work, light is shed from first principles simulations on Fe-Co-K catalysts. Specifically, we relate to a highly dispersed K-promoted Fe-Co bimetallic catalyst (Fe₉CoK₆) that was reported by Wang et al.²⁶ to have a C_5+ (mostly linear α -olefins in the $C_{10} - C_{20}$ range) selectivity of 51% at a CO₂ conversion of 35% under 300 °C and 20 bar reaction conditions. High dispersion of K and Co is achieved using a sol gel synthesis method²⁶. Potassium's significance as a promoter for FTS catalysts has been an area of extensive investigation, especially in iron-based

catalysts. It is attributed to the weakening of H₂ adsorption and the enhancement of CO adsorption and activation, due to its electron donating nature, where it is able to alter the basicity of the metal surface by increasing the electron density^{26,28–30}. Potassium is also recognized to enhance the carburization of metallic catalysts by complete decomposition of CO₂, forming metal carbide phases, which are suggested to be the active phases in FTS^{26,31–37}. While the impact of potassium promoters on FTS catalysts and thus C₂⁺ product selectivity is thoroughly explored, a comprehensive understanding of the synergetic role of bimetallic catalysts, Fe-Co in this case, on the underlying mechanisms for C₂⁺ hydrocarbon formation remains to be fully developed.

The main component of the catalyst is iron, and the catalyst nature in FTS reaction conditions is a carbide. Iron carbide is a highly versatile material that has integrated its way into various fields due to its unique and distinctive characteristics. Its high thermal stability, catalytic activity, reasonable abundance and cost of production have rendered it a highly desirable and effective material for various applications, especially catalysis. Iron carbides have been widely studied as efficient catalysts for Fischer-Tropsch synthesis^{33,38,39}, hydrocarbon hydrogenation reactions such as the conversion of dimethyl oxalate to ethanol⁴⁰, CO₂/CO hydrogenation to hydrocarbons^{41,42}, and catalytic methane decomposition for the formation of carbons and hydrogen^{43–47}. It exists in different phases, each phase with distinct properties due to its unique crystal structure and location of carbon atoms within the structure^{33,48,49}. Some of the main phases that are observed under FTS conditions are stoichiometric and nonstoichiometric epsilon carbide (ϵ – Fe₂C and ϵ' – Fe_{2.2}C), Cementite (θ – Fe₃C), Hägg carbide (χ -Fe₅C₂), and Fe₇C₃^{33,38}. Among these phases, θ – Fe₃C, (χ -Fe₅C₂), and Fe₇C₃ are the most experientially reported to exist under FTS conditions³³. Moreover, leveraging ab initio atomistic thermodynamics, de Smit et al. reported low deformation energies, carbon diffusion limitations, and vibrational entropy for the

same experimentally observed phases compared to $\varepsilon - \text{Fe}_2\text{C}$ and $\varepsilon' - \text{Fe}_{2.2}\text{C}^{33}$. Here, we present and investigate two different C-C coupling schemes on the active carbide surface of a Fe-Co bimetallic catalyst during CO_2 hydrogenation. The first is C-C coupling via CH_x^* intermediates, which is suggested by literature to be the main coupling pathway on Fe-based FTS catalysts. The other is a coupling route that utilizes active HCO^* intermediate species at the catalyst surface as the building block for carbon chain growth.

Models:

We modelled the catalyst active phase under FTS conditions as Co doped $\chi\text{-Fe}_5\text{C}_2$ carbide. This is justified by experimental XRD characterization of the spent catalyst that showed a mixture of Fe_2O_3 and iron carbide phases, with no Co bulk phase, while TEM shows a dispersion of the Co on the Fe particles.²⁶ Although $\chi\text{-Fe}_5\text{C}_2$ and Fe_3C iron carbide species were found by XRD on the spent catalyst, we selected $\chi\text{-Fe}_5\text{C}_2$ since it is supposed to be more active for long chain growth in FTS^{50,51}. Although Fe_2O_3 has been proposed as a catalyst for RWGS, it was not considered here and we focused on the catalytic activity of the Co doped iron carbide^{51–53}. The parameters used for the $\chi - \text{Fe}_5\text{C}_2$ Hägg carbide unit cell are $a = 11.589 \text{ \AA}$, $b = 4.500 \text{ \AA}$, $c = 4.988 \text{ \AA}$, and $\beta = 97.605^\circ$. Using the optimized bulk, four surfaces: (001), (100), (510), and (021) were built, and multiple unique surface terminations were constructed by cutting the bulk unit cell at different distances in the perpendicular direction to the Miller plane (**Figure S1**). If a surface cut creates two different surface terminations, a numerical label is added as (1) or (2); for example, the cut S2 shown in **Figure S1b** creates the two unique surfaces S2(1) and S2(2). After the influence of slab thickness on surface energy (γ) of each of the different four surfaces was analyzed (**Figure S2, Table S2**),

symmetric slabs of the different terminations were built. Although the (010) surface is reported to have a comparable stability to (100) and low CO dissociation barriers^{34,54}, in this work we focus on surfaces that are not only reported to be thermodynamically stable (more exposed for the reacting species), but are also widely recognized for their role in facilitating C-C coupling and hydrocarbon chain growth, namely (001), (100), (510), and (021)^{55–57}. Using the optimized constructed slabs, surface stabilities (E_{surf}) were evaluated to determine the most stable surface and termination, which correlates with its contribution to the overall equilibrium surface area of the $\chi - \text{Fe}_5\text{C}_2$ crystal structure^{34,58–60}. The surface energies of the stoichiometric slabs, which are intrinsic to their nature and are already in a balanced state, are determined using **Eq. 1**. On the other hand, the surface energies of the nonstoichiometric surfaces, which have different atomic ratios of elements compared to the balanced state bulk material, are determined using **Eq. 2**^{60–62}. A detailed explanation of the surface energy calculations can be found in **SI**.

$$E_{surf} = (E_{slab} - N E_{bulk})/A \quad \text{Eq. 1}$$

$$E_{surf}(T, p) = (G_{slab} - \frac{N_{Fe} g_{Fe_5C_2}^{bulk}}{5} + \frac{2 \mu_C(T, p) N_{Fe}}{5} - N_C \mu_C(T, p))/2A \quad \text{Eq. 2}$$

Where E_{slab} is the total energy of the slab, E_{bulk} is the total energy of the bulk unit cell, N is the number of bulk units in the slab, A is the surface area of the slab, G_{slab} is the Gibbs free energy of the slab, N_{Fe} and N_C are the numbers of Fe and C atoms, μ_C is the chemical potential of C, and $g_{Fe_5C_2}^{bulk}$ is the Gibbs free energy per formula unit of the Fe_5C_2 bulk. To determine a reasonable chemical potential range, it is taken into consideration that at low μ_C conditions, the formation of iron carbides is less favorable as metallic Fe is more favorable and surface/subsurface carbon are more stable^{58,60,63}. Thus, a calculated minimum μ_C boundary is used with reference to the total energy of an isolated carbon atom to obtain a reasonable $\Delta\mu_C$ value, which is found to be

-7.76 eV. Therefore, $\chi - \text{Fe}_5\text{C}_2$ exists at $\Delta\mu_C > -7.76$ eV. After determining the minimum $\Delta\mu_C$, the surface energies of the different terminations of each of the four surfaces are plotted against $\Delta\mu_C$, as shown in **Figure S3** (taking into consideration that the vibrational contribution to the surface Gibbs free energy is neglected and the total energy derived from DFT is used). From the surface stability assessment done on each of the four surfaces, the most stable terminations are shortlisted as shown in **Figure 1**. The most stable terminations are S1(100), S3(2) (100) followed by S1(510), S3(1) (510) then, S1(021), S2(1) (021), S3(2) (021) and finally, S2(001), S3(2) (001), agreeing with the literature⁵⁸.

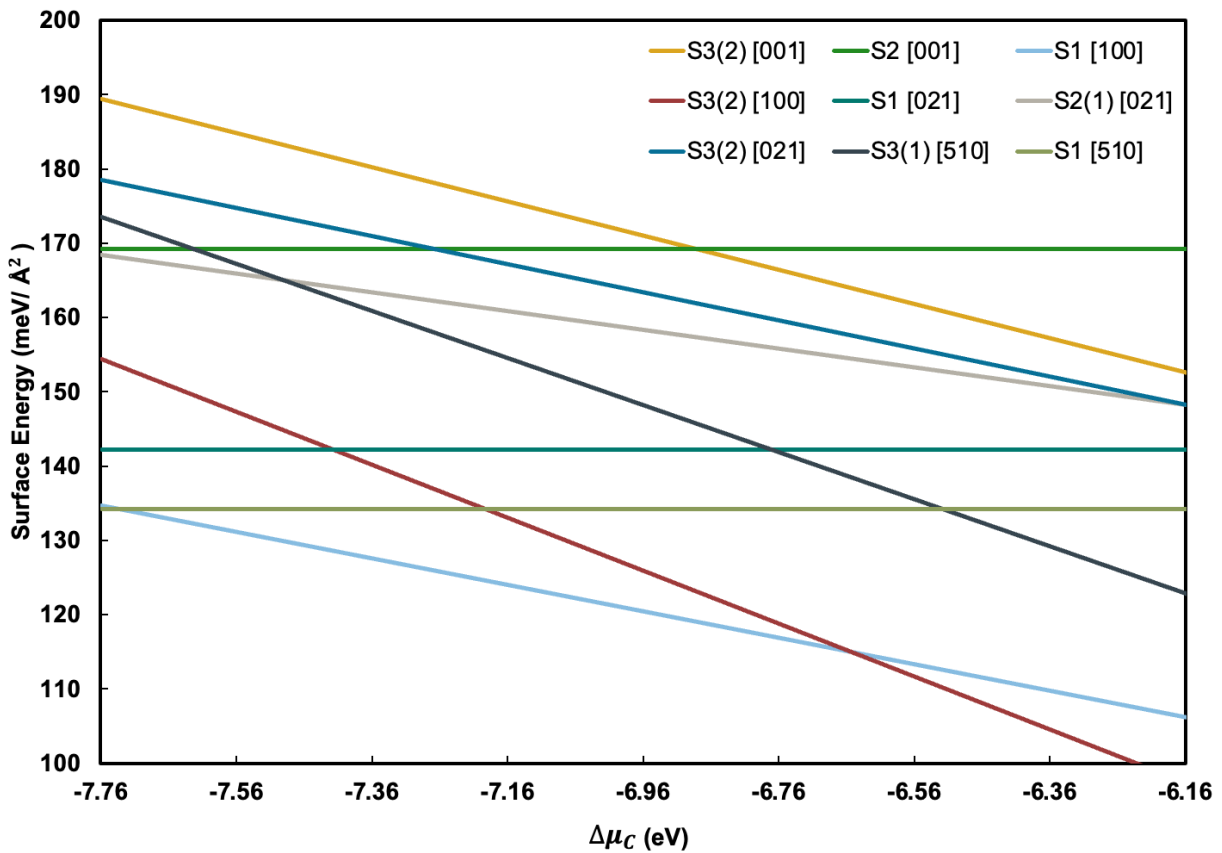


Figure 1: Relationship between surface free energy and carbon chemical potential ($\Delta\mu_C$) for the most stable terminations of each of the four facets (100), (001), (021), and (510) of $\chi - \text{Fe}_5\text{C}_2$.

Looking at **Figure 1**, we see that the S1 and S3(2) terminations of the (100) surface show the most stable energies for our Fe_5C_2 active surface. S1 is the most stable at $\Delta\mu_{\text{C}} < -6.66$ eV, and S3(2) is more stable at higher $\Delta\mu_{\text{C}}$. Due to our reaction being operated at low CO selectivity conditions (low temperatures) with a relatively high H_2/CO_2 volumetric ratio reaction feed, it is expected that the $\Delta\mu_{\text{C}}$ value will be low, but not lower than the iron carbide phase stability limit (-7.76 eV). As the H_2/CO ratio is the dominant factor influencing $\Delta\mu_{\text{C}}$, with increasing ratios leading to its decrease, $\Delta\mu_{\text{C}}$ typically falls below -6.7 eV under standard FTS conditions (CO pretreatment)^{33,58,63,64}. The carbon chemical potential reference is defined from the gas equilibrium ($\text{CO}_2 + 2\text{H}_2 \rightarrow \text{C} + 2\text{H}_2\text{O}$), evaluated at 573.15 K using ideal-gas thermochemistry and outlet partial pressures from 35% CO_2 conversion at 20 bar ($\text{H}_2:\text{CO}_2 = 2:1$, $p_{\text{H}_2\text{O}} = 5.964$ bar, $p_{\text{H}_2} = 6.504$ bar, and $p_{\text{CO}_2} = 5.574$ bar), yielding $\mu_{\text{C}} = -8.807$ eV per C ($\Delta\mu_{\text{C}} = -7.522$ eV)⁶⁵. Thus, this work is done on the S1 surface. A closer look at the clean $\text{Fe}_5\text{C}_2(100)$ S1 surfaces is shown in **Figure S4 (a, b)**. Fe atoms exist in two distinctive positions on the carbide surface forming a two parallel zigzag chain pattern, F1 and F2. The F2 located Fe atoms form a chain that occupies a slightly higher plane than the F1 chain. Since the Co dopant level is relatively low, we assumed that the most stable termination is not affected by the Co doping. As the Co doping into the catalyst is intentionally highly dispersed within Fe experimentally with no bulk phases observed, it is doped in the form of single atoms in this model. The Co-doped S1 $\text{Fe}_5\text{C}_2(100)$ surface is built by substituting surface Fe atoms with Co to achieve the desired Fe:Co ratio. An analysis of the placement of Co on the S1 $\text{Fe}_5\text{C}_2(100)$ surface was carried (as shown in **SI, Figure S5, and Table S3**) to ensure optimal interaction ability of Co with the reaction species. Due to the two unique Fe atom positions on the topmost layer of the surface, Co can be doped into the surface in two

positions, which are both have similar stabilities with only a 0.05 eV difference. However, after probing the surface with key reactants and intermediates of our reaction, as shown in **Table S3**, it is observed that Co doped in the F1 position restricted its interaction with the reactant molecules and thus, Co had negligible effect on the adsorption behavior of the reactants. On the other hand, when Co is doped at the F2 position, its interaction with the reactant species becomes more pronounced. Therefore, the Co-doped $\text{Fe}_5\text{C}_2(100)$ surface used in this work includes Co doped at the F2 position, as shown in **Fig S4 (c)**.

Methods:

This work utilized Density Functional Theory (DFT) for all energy calculations in the framework of the Vienna Ab initio Simulation Package (VASP) program^{66,67}. Electron-ion interactions were described using the projected augmented wave (PAW) method⁶⁸. The exchange and correlation energies were computed using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)⁶⁹. To account for the Van Der Waals interactions, the DFT-D3 method of Grimme with zero-damping function correction was applied⁷⁰. A plane wave-basis set with a cutoff energy of 450 eV for surface calculations was used. Electronic smearing was employed using the Methfessel-Paxton technique, with a smearing width of 0.2 eV. The electronic convergence criterion for all calculations is set at 10^{-6} eV and the force convergence at 0.02 eV/Å. Considering the ferromagnetic nature of Fe and Co, spin-polarized calculations were used throughout this work. The magnetic moment of the Co atom doping on the surface is found to be 1.06 μB . On the Co-doped surface, the average magnetic moment of surface Fe atoms is 2.23

μB , whereas Fe atoms in the subsurface layers exhibit an average moment of approximately 1.78 μB . The (100) iron carbide surface was modeled using a nine-Fe layer slab ($\sim 9 \text{ \AA}$) with 25 $\text{\AA}$ of vacuum. A 2 x 1 supercell was used for the iron carbide (100) surface for all calculations unless otherwise specified. For the Co-alloyed Fe_5C_2 system, the desired Fe:Co ratio of 9:1 is modeled by alloying a Co atom into the 2 x 1 supercell surface to mimic experimental ratio of the catalyst Fe_9CoK_6 ²⁶. All reported adsorption, reaction, and transition-state energies are evaluated at low surface coverage, where lateral interactions between ad-species and periodic images are negligible. During structural optimization, the bottom three Fe layers of the slab were constrained to simulate the bulk. A 2x5x5 Γ -centered k-point mesh scheme to sample the Brillouin zones for bulk optimization ($\chi - \text{Fe}_5\text{C}_2$ Hägg carbide unit cell parameters: $a = 11.589 \text{ \AA}$, $b = 4.500 \text{ \AA}$, $c = 4.988 \text{ \AA}$) and 3 x 5 k-space mesh within the Monkhorst-Pack scheme was used for each of the surface unit cells unless otherwise specified. The Atomic Simulation Environment (ASE) was utilized throughout this work for the calculation of the free energies and the zero point energies⁷¹.

Transition state searches between intermediates were performed using the Climbing Image Nudged Elastic Band (CI-NEB) method with 4-8 images⁷². The force convergence criterion was set to be 0.2 eV/ $\text{\AA}$ for each image. To further refine the transition state and the activation energy calculation, dimer and Quasi-Newton (RMM-DIIS) methods were subsequently implemented with a tighter force convergence criterion. Furthermore, vibrational frequencies were analyzed to confirm minimum and transition states. All imaginary vibrational frequencies corresponding to each transition state can be found in **Table S1**.

Results and Discussion:

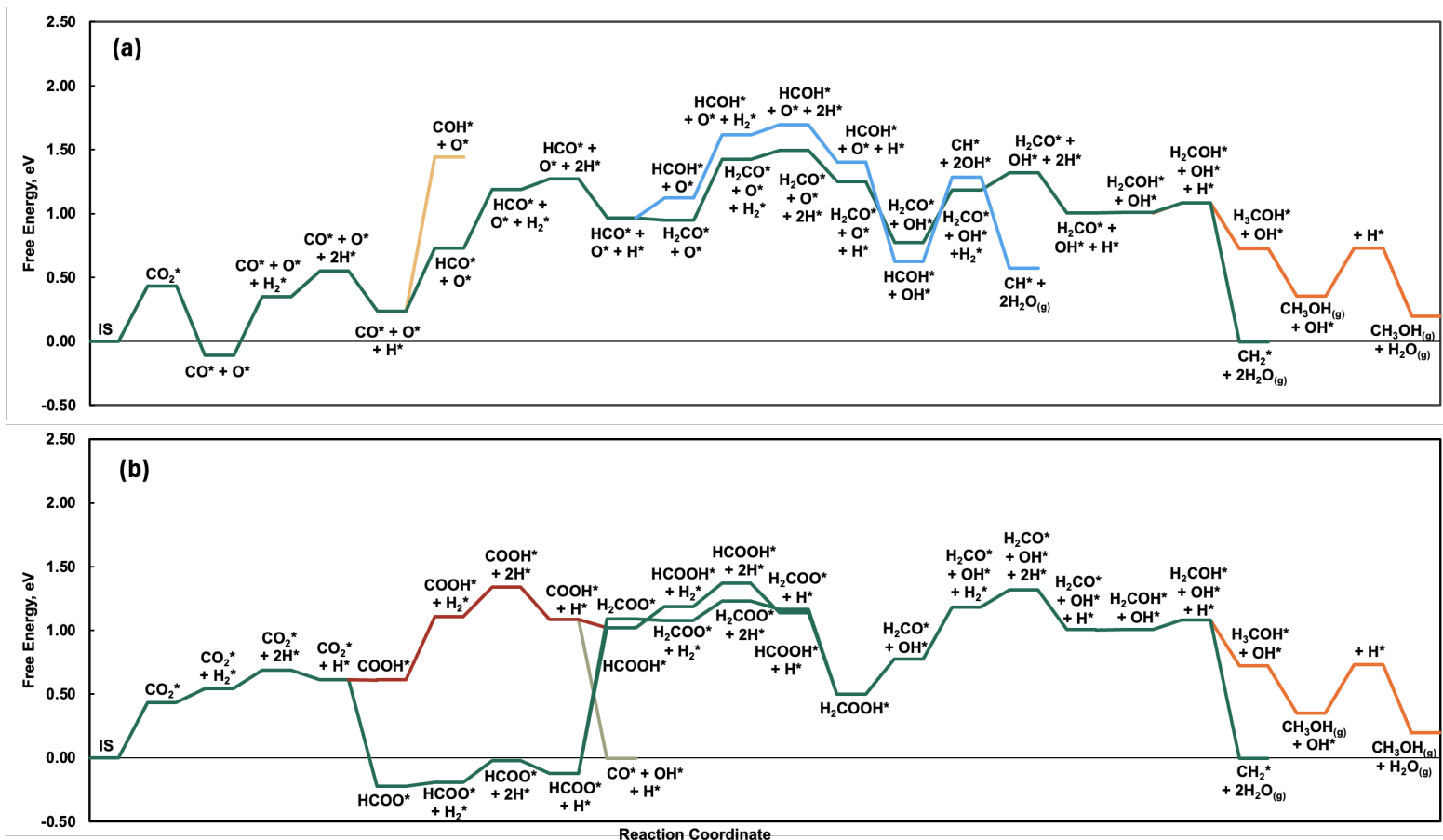


Figure 2: Thermodynamic reaction profile for CO_2 hydrogenation to CH_x species on the Co-doped $\text{Fe}_5\text{C}_2(100)$ surface following two classes of mechanisms a) initial direct C-O dissociation for CO_2 , and b) formate or carboxyl pathways. (dark green paths = formation of CH_2^* species, blue path = formation of CH^* species, orange path = formation of $\text{CH}_3\text{OH}_{(g)}$, red path = carboxyl pathway of CH_2^* species formation). Initial state (IS) is Co-doped $\text{Fe}_5\text{C}_2(100)$ bare surface with $\text{H}_{2(g)}$ and $\text{CO}_{2(g)}$. Reaction conditions are: $T = 573.15 \text{ K}$, $P(\text{CO}_2) = 1.0 \text{ bar}$, $P(\text{H}_2) = 20.0 \text{ bar}$, $P(\text{H}_2\text{O}) = 2.67 \text{ bar}$, and $P(\text{methanol}) = 1.0 \text{ bar}$.

Mechanism for CH_x* species formation:

While previous work focused on the reaction mechanism of CO₂-FTS on Fe-based catalysts have been controversial (both experimental and theoretical), they generally indicate a tendency towards CH_x* species (where * indicates an adsorbed species) being the building block of C₂+ carbon chains¹³, where both the CH_x* formation pathway and overall product distribution depend on the nature of the active site¹³. For example, Nie et al. reported that CH* is the most stable CH_x* species and is the building block for both CH₄ and C₂ products⁷³. Nie et al. also reported that those CH* species are formed either through a CO₂* → CO* → HCO* → HCOH* → CH* mechanism on a pure metallic Fe(100) surface or CO₂* → HCOO* → HCOOH* → HCO* → HCOH* → CH* on a bimetallic Cu-Fe(100) surface⁷³. In contrast, our interpretation of the active site highlights the formation of iron-carbides on the Fe-based catalysts, facilitated by the potassium promoter modification, and the highly dispersed addition of Co metal, which have been recognized to enhance the overall C₂+ selectivity on Fe-catalysts. Thus, on our system, we trace the possible paths for the formation of CH_x* species starting from the initial activation of CO₂.

When CO₂ adsorbs onto the active surface, the reaction can proceed along two primary pathways to activate the C–O bonds. CO₂ can either directly dissociate, producing CO* and O* species (* indicates an adsorbed species), or it can go through initial hydrogenation, leading to the formation of intermediates such as formate (HCOO*) or carboxyl (COOH*). Looking at the full reaction diagram on the Co-doped Fe₅C₂(100) S1 surface, shown in **Figure 2**, we see that among those initiating steps, the direct hydrogenation of CO₂* to formate HCOO* is the most thermodynamically favored, with a reaction free energy of -0.83 eV from CO₂* and H* and -0.22

eV from gas phase CO_2 and $1/2 \text{H}_2$. The second most favorable initiating step is direct C-O dissociation yielding CO^* and O^* , with a reaction free energy of -0.54 eV from CO_2^* and -0.11 eV from gas phase CO_2 . In contrast, the hydrogenation towards COOH^* is the least favored. Although the direct hydrogenation to form HCOO^* is the most thermodynamically favored, the following hydrogenation steps are endothermic, specifically the second hydrogenation forming either HCOOH^* or H_2COO^* .

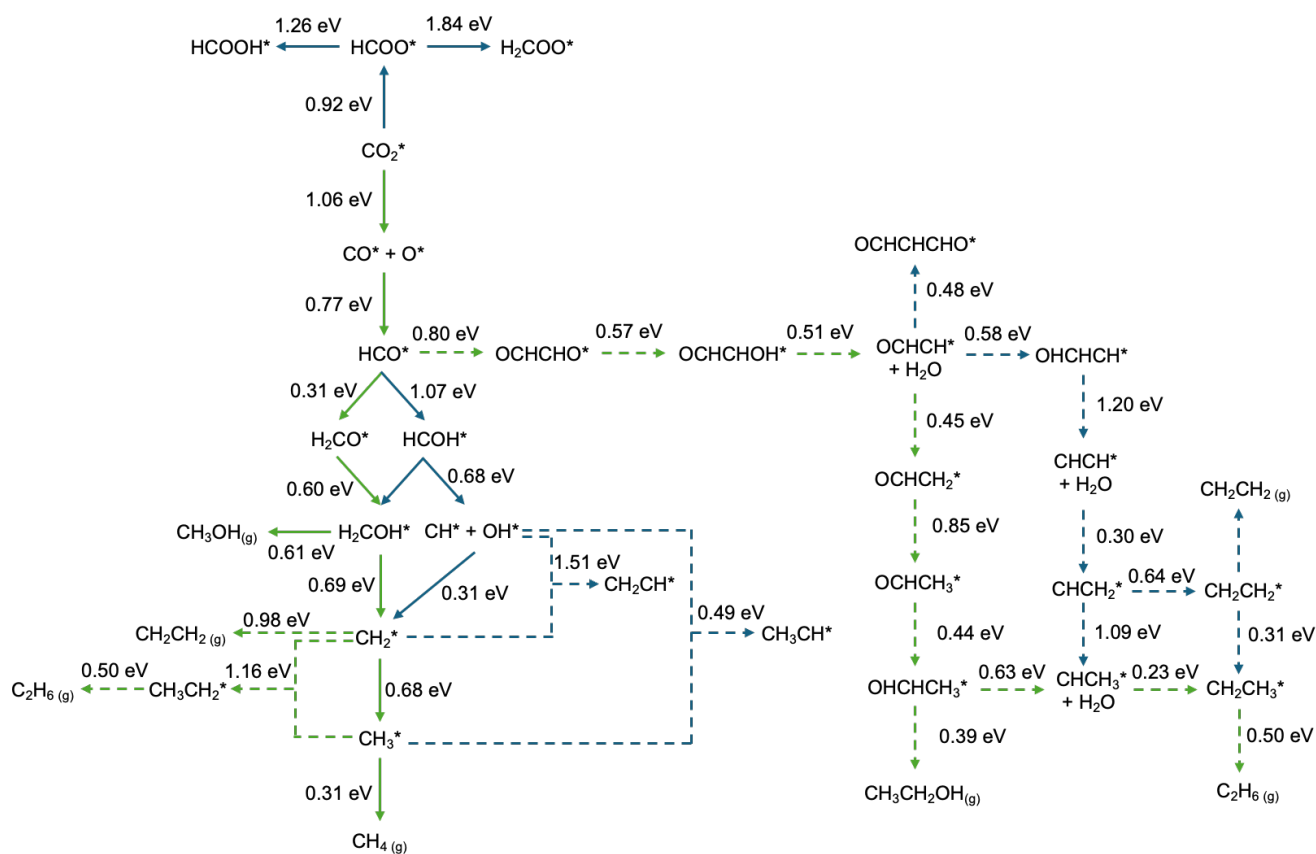


Figure 3: Reaction network, with forward energy barriers, investigated including most favorable CH_x^* and HCO^* species coupling schemes. (green path = preferred CH_x^* and HCO^* formation and coupling paths, dashed lines = considered coupling pathways). Reaction energies have been provided in Figure 2.

While the direct hydrogenation of CO_2^* to HCOO^* is the most thermodynamically favorable pathway, as shown in **Figure 2b**, and has a reasonably activation energy barrier of 0.92 eV (**Figure 3**) it is worth noting that the next hydrogenation steps are extremely thermodynamically and kinetically demanding. The reaction energy and energy barrier of HCOO^* hydrogenation to H_2COO^* are 1.21 eV and 1.84 eV, respectively, while for HCOOH^* formation, they are 1.14 eV and 1.26 eV. On the other hand, the direct CO_2^* dissociation path to CO^* and O^* species is found to have a reasonable barrier of 1.06 eV (as shown in **Figure 3**), considering the reaction temperature of 300 °C and an exothermic reaction energy of -0.54 eV (**Figure 2a**). We have therefore explored the following elementary step barriers for that direct CO_2 dissociation path. The first hydrogenation of CO^* to COH^* has a high reaction energy of 1.20 eV and was not considered further. However, the hydrogenation to HCO^* has a less uphill reaction energy of 0.49 eV accompanied with a low energy barrier of 0.77 eV. After the HCO^* intermediate is formed, a C-H bond can either be formed to create H_2CO^* or a O-H bond to form HCOH^* . Due to the orientation of the most stable HCO^* intermediate on the surface, the hydrogenation to form H_2CO^* is found to be more active with a thermoneutral reaction energy and an energy barrier of 0.31 eV. In contrast, the formation of HCOH^* is thermodynamically endothermic and has a barrier more than twice as high as that of H_2CO^* . Although the path through H_2CO^* is more favorable, the path through HCOH^* is also active since the barrier remains small for a reaction at 300 °C. Therefore, both pathways were considered as active for the formation of CH_x^* species. On one hand, CH^* is formed as the C-O bond in HCOH^* is cleaved, which is an endothermic step with a barrier of 0.68 eV. On the other hand, H_2CO^* goes through further hydrogenation to form H_2COH^* , in a step that has a barrier of 0.60 eV. This is followed by a second hydrogenation step that cleaves the C-O bond by hydrogenating the oxygen atom, resulting in H_2O desorption and the formation of CH_2^* ,

with a barrier of 0.69 eV. The competing pathway of H₂COH* hydrogenation to methanol is found here to have an energy barrier of 0.61 eV, which is comparable to that of CH₂* formation.

Despite the fact that hydrogen diffusion barriers are low on both Fe₅C₂ and Co-doped surfaces (0.34 eV and 0.28 eV, respectively), as shown in **Figure S6**, it is important to note that H₂* adsorption and dissociation are thermally uphill steps, with overall endothermic reaction energies ranging from 0.14 to 0.73 eV, as shown in **Figures 2a and b**, where the activation barrier of the dissociation elementary step for adsorbed molecular hydrogen is 0.14 eV. Thus, in addition to the similar energy barriers for H₂COH* dissociation (0.69 eV) and hydrogenation to methanol (0.61 eV), both steps also require the same thermally uphill H₂* adsorption and dissociation. As a result, they are comparably competitive.

While the formation of both CH* and CH₂* is possible, it is important to assess the stability of these species on the surface to better understand the behavior of C-C coupling through CH_x* intermediates. CH* is found to be most stable in 4-fold hollow sites, CH₂* in 3-fold hollow sites, and CH₃* a C top site. The relative energies of these CH_x* intermediates with respect to C* are listed in **Table 1**. These relative energies (E_{r, x}) are calculated as shown in **Eq. 3** in reference to the work reported by Nie et al.⁷³

$$E_{r, x} = [\text{CH}_x^* + (3 - x)\text{H}^*] - [\text{C}^* + 3\text{H}^*] \quad \text{Eq. 3}$$

Where x = 1-3, [CH_x* + (3 - x)H*] is the total adsorption energy of CH_x* intermediate and (3 - x)H*, and [C* + 3H*] is the total adsorption energy of C* and 3H* atoms. The more negative the value is, the more stable the CH_x* intermediate is compared to the C* reference. CH₃* is found to be the most stable, followed by CH₂* and then CH*, which has around the same stability as C*. Moreover, reaction and activation energies of the competing hydrogenation steps of CH*, CH₂*, and CH₃* are reported in **Table 2**. Looking at the pathway and activation barrier of CH*

hydrogenation to CH_2^* , shown in **Figure 4**, we see that this step is almost instantaneous with a low barrier of 0.31 eV from the coadsorbed state (0.55 eV from the CH^* state). This shows that CH^* species will rarely exist on the surface as its hydrogenation is both thermodynamically favorable and kinetically unhindered. A similar low barrier hydrogenation can be seen for the hydrogenation of CH_3^* to CH_4^* (0.31 eV), however in this case, CH_3^* has a higher stability on the surface, as opposed to CH^* . On the other hand, the hydrogenation of CH_2^* to CH_3^* is observed to have a larger energetic barrier of 0.68 eV (TS2). This larger energetic barrier compared to the two other hydrogenations barriers, TS1 and TS3, could indicate the possibility of CH_2^* species accumulation on the surface, resulting in the possibility of the species to proceed to coupling reactions. While Mars–van Krevelen-like mechanisms involving lattice carbon have been proposed for iron carbides under certain conditions^{74–76}, their contribution is expected to be minor over time under reaction conditions, when a steady yield of C_2^+ products is achieved. Since our study focuses on conditions where a steady C_2^+ yield is maintained, we assume a static Fe_5C_2 surface without lattice carbon turnover.

Table 1: Relative stabilities of adsorbed CH_x^* species (CH , CH_2 , and CH_3) on Co-doped $\text{Fe}_5\text{C}_2(100)$ surface with respect to adsorbed C.

Species	Relative stability
C (reference)	0.00
CH	0.00
CH_2	-0.80
CH_3	-1.30

Table2: CH_x^* species hydrogenation reaction energies and activation barriers on Co-doped $\text{Fe}_5\text{C}_2(100)$ surface at 1/9 ML Co coverage.

Hydrogenation reaction	E_{rxn} (eV)	E_{act} (eV)
$\text{CH}^* + \text{H}^* \rightarrow \text{CH}_2^*$	-0.81	0.31
$\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^*$	-0.55	0.68
$\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4(\text{g})$	-0.91	0.31

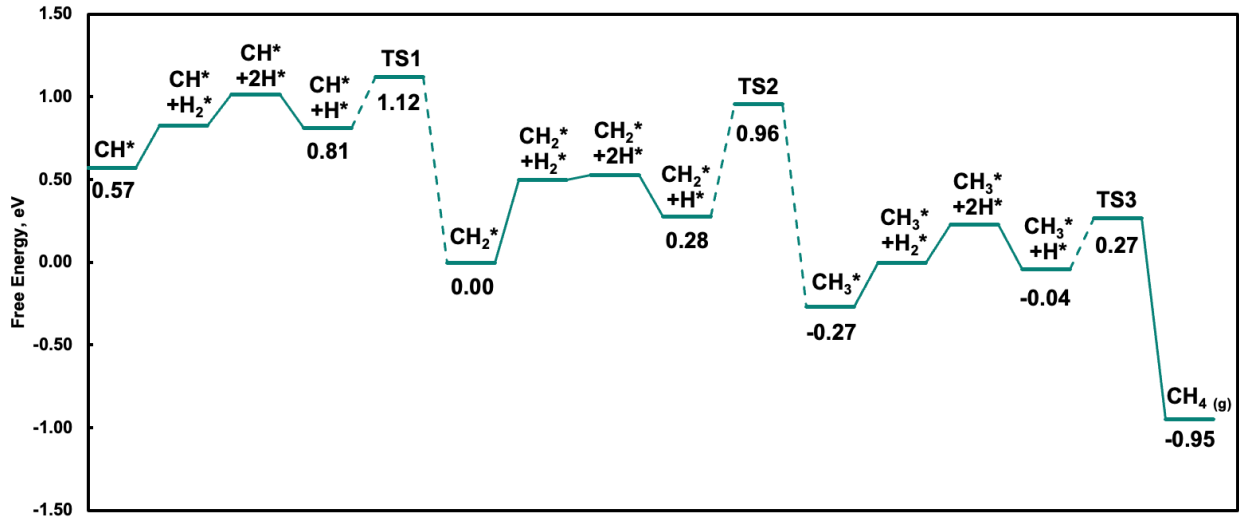


Figure 4: Gibbs free energy profile for molecular H_2 adsorption, dissociation and CH_x^* hydrogenation on the Co-doped $\text{Fe}_5\text{C}_2(100)$ surface. Reference initial state is Co-doped $\text{Fe}_5\text{C}_2(100)$ bare surface with $\text{H}_{2(\text{g})}$ and $\text{CO}_{2(\text{g})}$. Step label $+\text{H}_2^*$: molecular hydrogen adsorption, $+2\text{H}^*$: molecular hydrogenation dissociation, and $+\text{H}^*$: one atomic H on the surface and the other desorbed. Since H_2 adsorption and dissociation is endergonic, the H^* coverage should be small, so the second H^* in the unit cell was desorbed, assuming it can recombine with a H^* from another unit cell. Reaction conditions are: $T = 573.15 \text{ K}$, $P(\text{H}_2) = 20.0 \text{ bar}$, and $P(\text{methane}) = 10.13 \text{ bar}$.

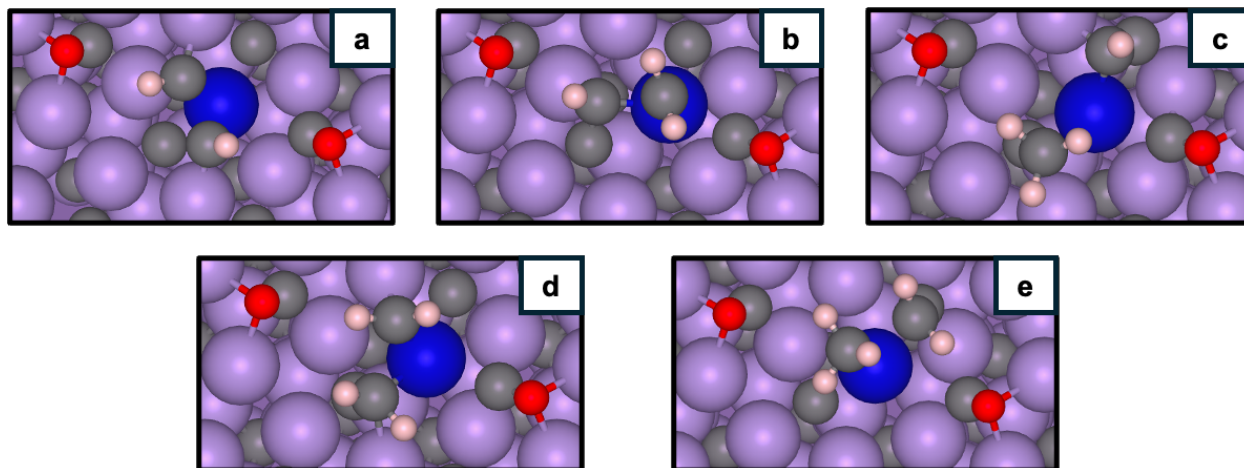


Figure 5: Top view of optimized transition state structures associated with various C-C coupling reactions; a) $\text{CH}^* + \text{CH}^*$, b) $\text{CH}_2^* + \text{CH}^*$, c) $\text{CH}_3^* + \text{CH}^*$, d) $\text{CH}_2^* + \text{CH}_2^*$, and e) $\text{CH}_2^* + \text{CH}_3^*$ on Co-doped $\text{Fe}_5\text{C}_2(100)$ surfaces at 1/9 ML Co coverage (purple = iron, blue = cobalt, gray = carbon, red = oxygen, and pink = hydrogen).

Table 3: C-C coupling reaction energies and activation barriers of the formation of C_2 species on Co-doped $\text{Fe}_5\text{C}_2(100)$ surfaces at 1/9 ML Co coverage.

C-C Coupling reaction through CH_x^*	$E_{rxn}(\text{eV})$	$E_{act}(\text{eV})$
$\text{CH}^* + \text{CH}^*$	-0.48	2.07
$\text{CH}_2^* + \text{CH}^*$	-0.31	1.51
$\text{CH}_2^* + \text{CH}_2^*$	-0.49	0.98
$\text{CH}_3^* + \text{CH}^*$	-1.13	0.49
$\text{CH}_3^* + \text{CH}_2^*$	-0.44	1.16

C-C coupling through CH_x^* species:

We systematically examined all theoretically possible coupling reactions between the CH_x^* species (CH^* , CH_2^* , and CH_3^*) to assess their feasibility and identify the most favorable pathways for C_2^+ formation. For the initial states of each of the coupling steps analyzed, each of the CH_x^* species is optimized in its most stable adsorption site. Thus, CH^* is always in a 4-fold hollow site, CH_2^* is in 3-fold hollow site, and CH_3^* is in a C top site. All optimized transition states are shown in **Figure 5**. All C-C coupling reaction energies and energy barriers are listed in **Table 3**. First, the reaction of two CH^* species has an extremely large barrier of 2.07 eV. This shows that further hydrogenation of the CH^* species is expected before coupling, as also suggested by the significantly small hydrogenation barrier of 0.31 eV. On the other hand, the barrier of $\text{CH}_2^* + \text{CH}^*$ is smaller at 1.51 eV. This pathway passes through an intermediate adsorption mode as CH_2^* moves from its most stable 3-fold hollow site to a Co top site closer to the CH^* , which is adsorbed in a stable neighboring hollow site. This intermediate adsorption mode allows for a reasonable energetic barrier. For the $\text{CH}_2^* + \text{CH}_2^*$ coupling, the barrier is at 0.98 eV. Although this coupling pathway does not pass through an intermediate adsorption mode, the barrier is lower than that of $\text{CH}_2^* + \text{CH}^*$ by a significant 0.53 eV. Additionally, due to the higher CH_2^* hydrogenation barrier, CH_2^* species are expected to be present at significant coverage on the surface, increasing the likelihood of coupling. The $\text{CH}_3^* + \text{CH}^*$ barrier is even lower at 0.49 eV. In this coupling pathway, CH^* first migrates to a neighboring 3-fold stable adsorption mode producing a stable intermediate configuration. The CH_3^* then migrates towards the CH^* with simultaneous rotation of the two species. Lastly, the $\text{CH}_3^* + \text{CH}_2^*$ coupling has a barrier of 1.16 eV. In this coupling reaction, the pathway involves a fairly stable intermediate where CH_3^* is adsorbed at a Co on-top site and CH_2^* at a 2-fold site. After the intermediate is formed, CH_3^* continues its migration on top of Co until the $\text{CH}_3^*-\text{CH}_2^*$ bond is formed. The coupling of $\text{CH}_3^* + \text{CH}_3^*$ is not considered as CH_3^* exhibits

a strong tendency for immediate hydrogenation to CH_4 when compared to its formation from CH_2^* . We find that $\text{CH}_3^* + \text{CH}^*$ has the lowest barrier, followed by $\text{CH}_2^* + \text{CH}_2^*$ and $\text{CH}_3^* + \text{CH}_2^*$, and finally $\text{CH}_2^* + \text{CH}^*$. Although the $\text{CH}_3^* + \text{CH}^*$ coupling has the lowest energy barrier, there is no thermodynamic or kinetic indication that these species would accumulate sufficiently on the surface to enable coupling. Thus, we consider $\text{CH}_2^* + \text{CH}_2^*$ and $\text{CH}_3^* + \text{CH}_2^*$ couplings as the more significant pathways contributing to C_2 product formation. After these possible active coupling steps, the C_2 species (CH_2CH_2^* and CH_3CH_2^*) can lead to the formation and release of either ethylene or ethane, with further hydrogenation steps if required. To introduce another CH_2 species on the surface for the C-C coupling reactions in **Figure 6**, we included a second CH_2^* production from adsorbed CO_2 , along with the formation and desorption of two H_2O molecules. After the coupling of 2CH_2^* species to form chemisorbed ethylene, and since the desorption of CH_2CH_2 is not strongly thermodynamically downhill, CH_2CH_2^* can either desorb from the surface or further hydrogenate to ethane via kinetically feasible steps. The energy barrier for the hydrogenation of CH_2CH_2^* to CH_3CH_2^* is 0.31 eV, whereas the barrier for the subsequent hydrogenation of CH_3CH_2^* to form ethane is 0.50 eV. These results suggest that coupling via CH_x^* species is possible; however, the system needs to overcome its kinetic propensity to form methanol and methane. Indeed, this pathway is observed to facilitate the formation of methane, methanol, and C_2 hydrocarbons.

Using the energetic span model, the reactivity of a pathway is approximated by the energetic span, which is the largest difference between a transition state on the said pathway (TOF-determining transition state, TDTS) and an intermediate on any pathway (TOF-determining intermediate, TDI)⁷⁷. The energetic span for methane formation is 1.71 eV, where the TDTS is the dissociative hydrogenation of H_2COH^* to form CH_2^* (1.60 eV, TS5 as shown in **Figure 6**), and

the TDI is the ($\text{CO}^* + \text{O}^*$) intermediate state at -0.11 eV. Similarly, we observe that the TDTS and TDI for both ethane and ethylene formations are the same as for methane formation, with an energetic span of 1.71 eV for both. On the other hand, the energetic span for methanol formation is found to be 1.63 eV, where the TDTS is the TS for the hydrogenation of H_2COH^* to CH_3OH^* (**Figure S11**, TS5b), which is 1.52 eV from IS, and the TDI is $\text{CO}^* + \text{O}^*$ at -0.11 eV. For methane, ethane, and ethylene, the TOF determining process is the same and it occurs before the separation of pathways leading to the different products. The energetic span therefore controls the rate, but not the selectivity. Effective barriers on the pathways after the last common intermediate, which is CH_2^* , control the selectivity. For methane formation, the effective barrier after the branching point (CH_2^*) and referenced to CH_2^* is 0.96 eV (**Figure 4**). For ethane formation, the effective barrier referenced to CH_3^* though the coupling between CH_3^* and CH_2^* is 1.35 eV (**Figure 6**). Finally, the effective barrier for ethylene formation through 2CH_2^* coupling is 1.12 eV, referenced to CH_2^* . Most competitive paths are therefore forming methane or chemisorbed ethylene. For ethylene, a final question is whether it will desorb or be further hydrogenated. Although the desorption process of CH_2CH_2 is thermoneutral ($\Delta G \approx 0$), as shown in **Figure 6**, it has a free energy barrier. The activation Gibbs free energy for ethylene desorption is estimated from the kinetic theory of gases at a sticking coefficient of 0.1 (see SI, **Table S7**) to be 0.58 eV, giving the position of the corresponding TS_d (0.39 eV, **Figure 6**)^{77,78}. Alternatively, CH_2CH_2^* is further hydrogenated to CH_3CH_2^* through TS_c (0.27 eV, **Figure 6**), followed by TS_9 (0.49 eV) to form ethane. We observe a close competition between the transition state energy for ethylene desorption (0.39 eV) and ethane formation (0.49 eV), given the limited accuracy of DFT exchange correlation functionals. Experiments show a zero olefin/ paraffin (C2-C4) product ratio with Fe-Co catalysts, suggesting that the hydrogenation of chemisorbed ethylene to ethane prevails over ethylene desorption.

Overall, for the reaction selectivity aspects, we observe that the formation of ethane through CH_2CH_2^* is more viable than through $\text{CH}_3 + \text{CH}_2$ coupling, and that it occurs with an effective barrier of 1.12 eV, referenced to CH_2^* . On the other hand, the effective barrier of methane formation is 0.96 eV, again referenced to CH_2^* . Both products are therefore expected from the considered pathway going through $^*\text{CH}_2$.

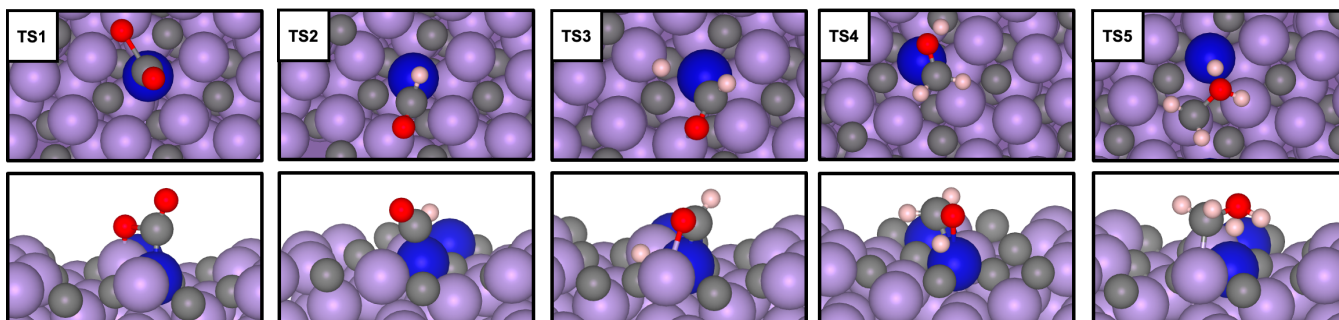
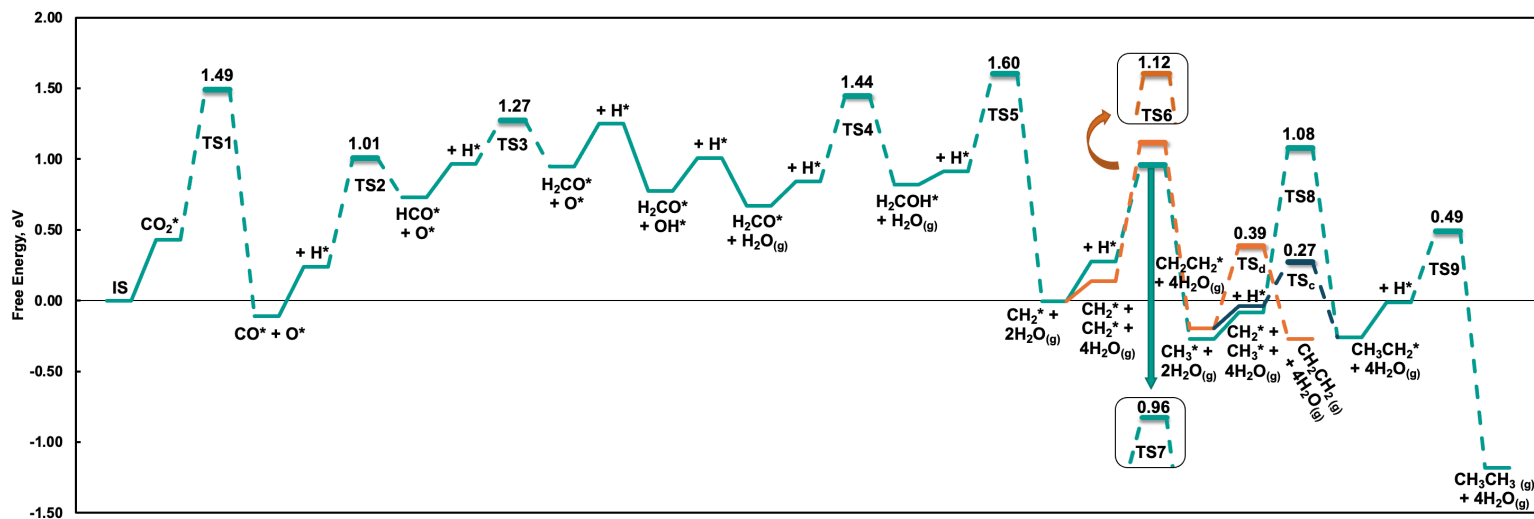


Figure 6: Gibbs free energy pathway involving the most favorable CH_x^* species coupling and top and side views of optimized transition state structures. (green path = formation of ethane (C_2H_6) from CH_2^* and CH_3^* coupling, orange path = formation of ethylene (C_2H_4) from 2CH_2^* coupling). Initial state (IS) is Co-doped $\text{Fe}_5\text{C}_2(100)$ bare surface with $\text{H}_{2(\text{g})}$ and $\text{CO}_{2(\text{g})}$. Reaction conditions are: $T = 573.15 \text{ K}$, $P(\text{CO}_2) = 1.0 \text{ bar}$, $P(\text{H}_2) = 20.0 \text{ bar}$, $P(\text{H}_2\text{O}) = 2.67 \text{ bar}$, $P(\text{ethylene}) = 4.56 \text{ bar}$, and $P(\text{ethane}) = 3.55 \text{ bar}$.

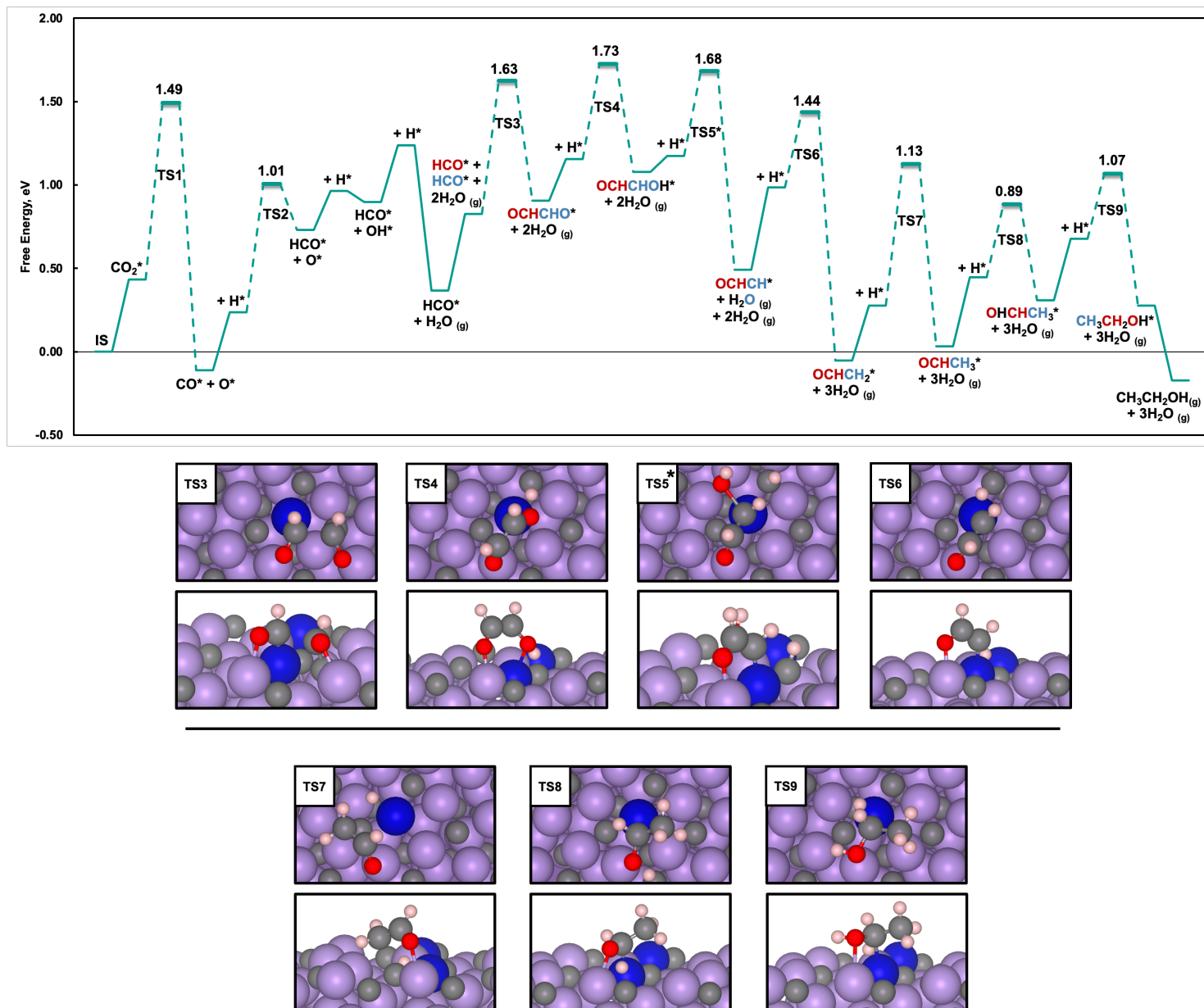


Figure 7: Gibbs free energy pathway and top and side views of optimized transition state structures for most favorable HCO* species coupling. Initial state (IS) is the Co-doped Fe₅C₂(100) surface with H_{2(g)} and CO_{2(g)}. TS5* is a transition state calculated on a 2 x 2 supercell instead on 2 x 1 to avoid lateral interactions between ad-species and periodic images. Reaction conditions are: T = 573.15 K, P(CO₂) = 1.0 bar, P(H₂) = 20.0 bar, P(H₂O) = 2.67 bar, and P(ethanol) = 1.0 bar.

C-C coupling through active oxygen containing intermediates:

Here we discuss an alternative route for C-C coupling on our CO₂-FTS system. Although CH_x* species are often discussed to be the active C-C coupling intermediates in CO₂-FTS, we show that oxygen containing species HCO* are active intermediates for the formation of C₂+ and possibly even C₅+ products. This provides another reaction channel in addition to the CH_x intermediate pathway usually discussed in the literature. This C-C coupling pathway shows reasonably active steps for the formation of desired long-chain hydrocarbons/ high alcohols and presents less undesired side reactions. This route starts with two HCO* intermediates coupling to form a stable OCHCHO* intermediate with a strong C-C bond. The energetic barrier for this step is 0.80 eV, as shown in **Figure 7** (TS3), which is slightly lower than the barrier for the CH₂-CH₂ coupling but higher than the effective one for HCO* hydrogenation to H₂CO* (that combines H₂ adsorption, dissociation, and C-H bond formation). The formation of the second HCO* species, which participates in the mentioned coupling reaction, comes from another adsorbed CO₂, along with the formation and desorption of two H₂O molecules. The OCHCHO* intermediate then goes through hydrolysis of one of the C-O bonds, where the first O-H bond formation has a barrier of 0.57 eV. This first hydrogenation, forming OCHCHOH*, weakens the C-O bond, where the bond lengthens by around 0.1 Å. The second hydrogenation step of the C-O bond hydrolysis has a barrier of 0.51 eV. This step desorbs H₂O from the surface and leaves OCHCH*. For this specific transition state, the lateral interactions observed between the periodic images on the 2 x 1 cell were tested using the 2 x 2 supercell, and the difference was found to be ~0.1 eV, which is within DFT error and thus was neglected for this transition state. Following the formation of OCHCH*, two possible hydrogenation steps can occur due to the adsorption configuration where only the oxygen atom and the terminal carbon are in contact with the surface, as shown in **Figure S7(a)**. The first is the hydrogenation of the end carbon to form OCHCH₂*, which is highly favored

thermodynamically, with a reaction energy of -1.0 eV, and kinetically with a low activation energy of 0.45 eV (TS6). The second is the hydrogenation of the oxygen atom forming OHCHCH*, which is less thermodynamically favored however, kinetically active with an energetic barrier of 0.58 eV, as shown in **Figure 3**. Additionally, we find that a further C-C coupling reaction to form C₃ is also possible at this stage as the end carbon of the OCHCH* chain is close enough to the surface to interact with another HCO species. We find that the formation of OCHCHCHO* is exothermic by 0.52 eV and has an activation energy of 0.48 eV. This coupling barrier is low and comparable to the first HCO* + HCO* coupling step, giving a strong indication that this pathway could be fully active for the formation of C₅+ products.

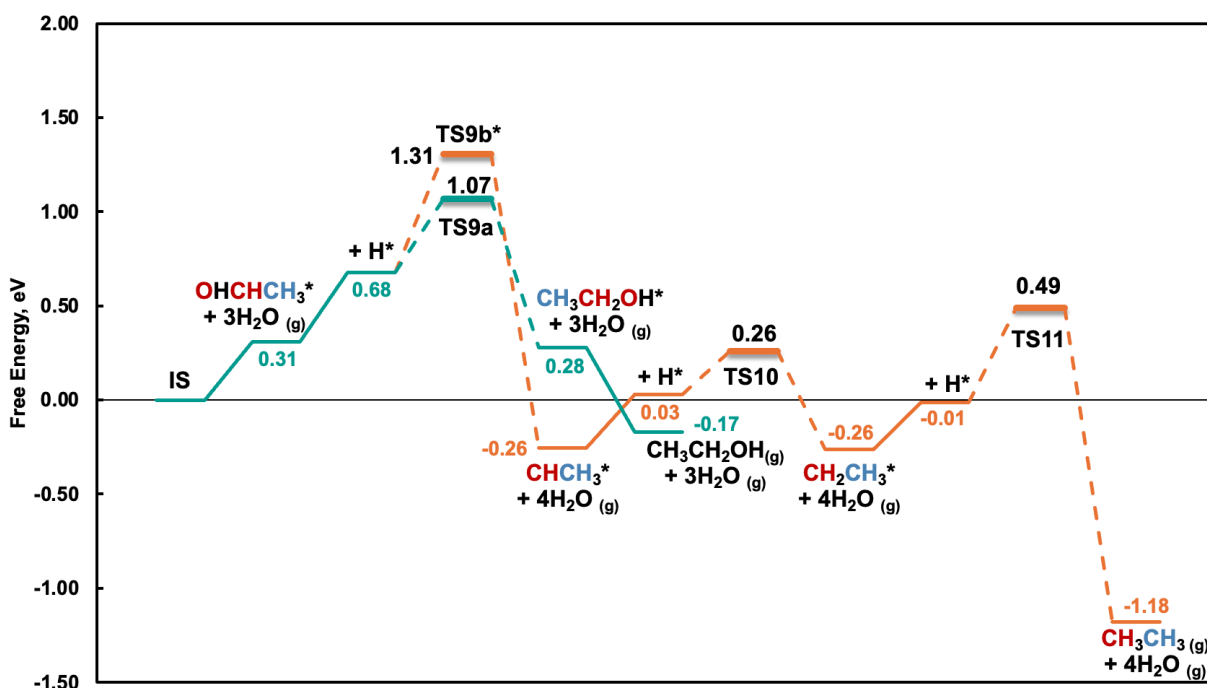


Figure 8: Gibbs free energy profile of the two possible hydrogenation steps of OHCHCH_3^* . Initial state (IS) is Co-doped $\text{Fe}_5\text{C}_2(100)$ bare surface with $\text{H}_{2(\text{g})}$ and $\text{CO}_{2(\text{g})}$. TS9b^* is a transition state performed on a 2×2 supercell instead on 2×1 . TS9a is the same transition state as TS9 in Figure 7. (green path = formation of ethanol, orange path = formation of ethane). Top and side views of optimized transition state structures of the orange path are shown in **Figure S8**. Reaction conditions are: $T = 573.15 \text{ K}$, $P(\text{CO}_2) = 1.0 \text{ bar}$, $P(\text{H}_2) = 20.0 \text{ bar}$, $P(\text{H}_2\text{O}) = 2.67 \text{ bar}$, $P(\text{ethanol}) = 1.0 \text{ bar}$, and $P(\text{ethane}) = 3.55 \text{ bar}$.

Following the first discussed OCHCH^* hydrogenation path, forming OCHCH_2^* , we find that the hydrogenation of the end carbon to form OCHCH_3^* is thermodynamically exothermic with a slightly higher activation barrier of 0.85 eV (**Figure 7**, TS7), in contrast to the other hydrogenation steps in this coupling pathway, however still active. The next hydrogenation is found to be thermally favorable on the oxygen atom, which has a barrier of 0.44 eV to form OHCHCH_3^* . Lastly, due to the adsorption configuration of OHCHCH_3^* , shown in **Figure S7(b)**, where both the single hydrogenated C and O are in close proximity to the surface, both the C and O have the possibility of being hydrogenated. Looking at both hydrogenation possibilities of either full hydrolysis of the C-O bond, releasing H_2O from the surface and forming CH_3CH^* species on the surface, or hydrogenating the bridging C (single hydrogenated C) to release ethanol, the formation of ethanol is found to have a slightly lower activation barrier of 0.39 eV , as shown in **Figure 8**. Alternatively, the hydrogenation step to release H_2O and form CH_3CH^* species is observed to have a slightly higher energetic barrier of 0.63 eV . After the formation of CH_3CH^* , hydrogenation to form and release ethane is found thermodynamically favorable with significantly small energetic barriers. Where the hydrogenation of CH_3CH^* forming CH_3CH_2^* is found to have an energetic barrier of 0.23 eV , and the following hydrogenation of CH_3CH_2^* desorbing ethane has an energetic barrier of 0.50 eV . Thus, this pathway is observed to facilitate the formation of

both C₂ hydrocarbons and alcohols. In this pathway, the energetic span for both ethane and ethanol formations through HCO* is found to be 1.84 eV, where the TDTS is TS4 at 1.73 eV (**Figure 7**) and the TDI is CO* + O* at -0.11 eV (**Figure 7**). Similarly to the reaction pathways through CH_x* species coupling, the selectivity is not determined by the energetic span. Therefore, looking into each pathway after the last common intermediate, which is the OHCHCH₃* intermediate shown in **Figures 7 and 8**, we see that the largest effective barrier for ethanol formation is 0.76 eV (TS9a, **Figure 8**, referenced to OHCHCH₃*). On the other hand, the effective barrier for ethane formation is 1.0 eV (TS9b, **Figure 8**, referenced to OHCHCH₃*).

On the other hand, when the reaction proceeds with hydrogenation of the oxygen on the OCHCH* species forming OHCHCH*, it leads to another pathway for the formation of C₂ hydrocarbons. After the formation of OHCHCH*, the pathway goes through another hydrogenation of the oxygen atom cleaving the C-O bond, forming the CHCH* species and desorbing water. This step is found significantly uphill activated with an energy barrier of 1.20 eV. The first hydrogenation of CHCH* to CHCH₂* is found to have an exothermic reaction energy of -0.39 eV, and an energy barrier of 0.30 eV. The next hydrogenation step can either form CH₂CH₂*, which has reaction energy of around -0.30 eV and a kinetic barrier of 0.64 eV, or form CHCH₃*, which has around the same reaction energy but a larger kinetic barrier of around 1.09 eV. The CH₂CH₂* species can either desorb from the surface as ethylene or further hydrogenate to desorb as ethane, as similarly discussed in the previous section (C-C coupling through CH_x* species). CHCH₃* is also observed to lead to the formation of ethane via a series of hydrogenation steps as shown in **Figure 3** and previously discussed. In this pathway, the energetic span for ethylene

formation is significantly large due to the high TDTS, which is the hydrogenation of OHCHCH* releasing H₂O and forming CHCH* (TS7, **Figure S10**).

All in all, when comparing the energetic span of each of the different reactions and pathways, we observe that the energetic spans of methanol formation (1.63 eV), methane formation through CH_x* (1.71 eV), ethane formation through CH_x* (1.71 eV), and ethane and ethanol formations through HCO* (1.84 eV) are all comparable, taking into account the limited accuracy of DFT exchange correlation functionals. Selectivity is determined by steps which occur after the TOF limiting process and further inspection of the different reactions branching after the initial TDTS is required. Through inspecting the branched pathways, we observe that the largest barriers for methane and ethane formations through the CH_x* species route are 0.96 and 1.12 eV, respectively. Through the HCO* species route, the largest barriers for ethane and ethanol formations are 1.0 and 0.76, respectively. Although we see a small reactivity difference between C₂ product formation through CH_x* and HCO* species pathways (1.71 and 1.84 eV, respectively), we observe that through the CH_x* pathway, more undesired side reactions and thus short-chain products, such as methanol and methane, arise. In contrast, on the HCO* pathway, we observe only desirable reactions of either further C-C coupling, ethanol formation, or C₂ hydrocarbon production.

In this work, we observe a strong involvement of the Co doping into both the hydrogenation and coupling steps. As the addition of Co into the Fe₅C₂ surface is shown to stabilize both molecular and atomic hydrogen adsorptions, it is also observed to increase the stability of CO₂, CO and other C intermediates important to our analyzed pathways including CH_x and HCO species (**Table S6**), decreasing their mobility on the surface. The higher stability of hydrocarbon fragments (CH_x) and oxygen-containing intermediates, such as CH_xO*-like species, on Co-containing Fe

catalysts compared to Fe catalysts, is also observed in the work of Guo et al⁷⁹. In their in situ DRIFT spectra analysis of K-Fe-Co and K-Fe catalysts, a higher abundance of these species was observed on the Co-containing catalyst. Therefore, it is necessary to leverage promoters, such as alkali metals, to control the increase in hydrogen affinity, allowing higher selectivity to coupling reactions and minimizing termination by full hydrogenation. We observe that many formations of C-H, O-H, and C-C bonds, as well as the dissociation of C-OH bonds, occur with the lowest barrier on or adjacent to the Co site, therefore underlining the key role of Co doping on the catalytic activity. While this work captures the effect of Co single atom doping, we recognize that the relatively low abundance of Co sites under realistic conditions may limit their overall contribution to the proposed reaction mechanisms. However, due to the low stability of almost all species involved in formations occurring with low energy barriers on or adjacent to the Co sites, we consider this limitation to be negligible.

Conclusions:

In this work, we presented new mechanistic insights to elucidate the synergetic effect found in iron-based bimetallic catalysts demonstrating high selectivity for long-chain/ olefinic hydrocarbon production under mild reaction conditions. Based on established experimental data, we leveraged DFT calculations to unravel the full mechanisms for the formation of the reaction products methane, methanol, ethane, ethylene, and ethanol on an active Co-doped Fe₅C₂(100) surface site. We show that there are two active mechanisms for the formation of C₂⁺ products: through the CH_x^{*}, and the HCO^{*} species. In both mechanisms, the carbon in CO₂^{*} is firstly activated via direct C-O dissociation to produce CO^{*}, which is less thermodynamically stable than

CO₂*, then it's hydrogenated to form HCO*. For the CH_x* species C-C coupling pathway, the mechanism follows HCO* → H₂CO* → H₂COH* → CH₂* → CH₃*, forming the CH_x* that couple forming longer chains. Whereas the HCO* species route follows the direct coupling of HCO* species to form OCHCHO*. We found that both mechanisms are comparatively active for the formation of C₂ hydrocarbons with almost identical energy spans.

Although both mechanisms are active, our investigation predicts that the CH_x* species pathway presents more undesired side reactions that are in strong competition with the desired C-C coupling path. These side reactions include the formation of short-chain hydrocarbons, i.e. methanol and methane. In contrast, the HCO* species route has no identified competing undesired side reactions, where the pathway only leads to the production of long chain alcohols (C_xH_(2x+1)OH) and C₂+ hydrocarbons.

The species most responsible for C-C coupling through the CH_x* path are shown to be CH₂* and CH₃*. This coupling path has strongly favored competing pathways that produce C1 products including CH₄ and CH₃OH due to the low energetic barriers of hydrogenation steps. This pathway also has to go through multiple hydrogenation steps prior to the formation of C1 coupling species, which is governed by the slightly thermodynamically uphill H₂* adsorption and activation. On the other hand, the coupling species in the HCO* path is directly HCO*, where C-C coupling can occur with no extra steps required to form the coupling species. This HCO* coupling path is identified to either produce CH₃CH₂OH, when terminated with the last hydrogenation step of the middle C, form C₂ hydrocarbons including ethylene and ethane, or carry on the coupling reactions to produce higher-chain alcohols. With the considered model Co-doped Fe₅C₂(100) catalyst, although both hydrogenation of CO₂ to C1 products and coupling to C₂+ species are possible, the hydrogenation steps generally show lower barriers and the selectivity to C₂+ products is expected

to be low. This is in agreement with experiment where additional doping with K alkali metal is needed to reach a high C₂⁺ selectivity.

Overall, this work establishes a comprehensive view of the mechanistic aspects of CO₂ conversion to long-chain hydrocarbons and alcohols on iron-based catalyst systems. Most importantly, it identifies the active C-C coupling intermediates and their involvement in the highly selective formation of the desired products. These insights ultimately contribute to the fine-tuning of single-step catalyst systems for the selective production of high-value C₅⁺ hydrocarbons and alcohols.

Supplementary Information:

Details of all surface terminations and their corresponding surface energies, additional computational details, all transition state structures and their corresponding imaginary frequencies, additional adsorption and atomic hydrogen diffusion data, overall Gibbs free energies and formation enthalpies of products (methane, methanol, ethane, ethylene, and ethanol), and Gibbs free energy pathways for methanol and ethylene formations.

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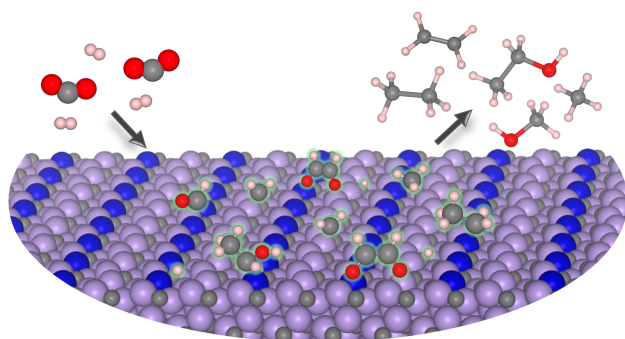
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