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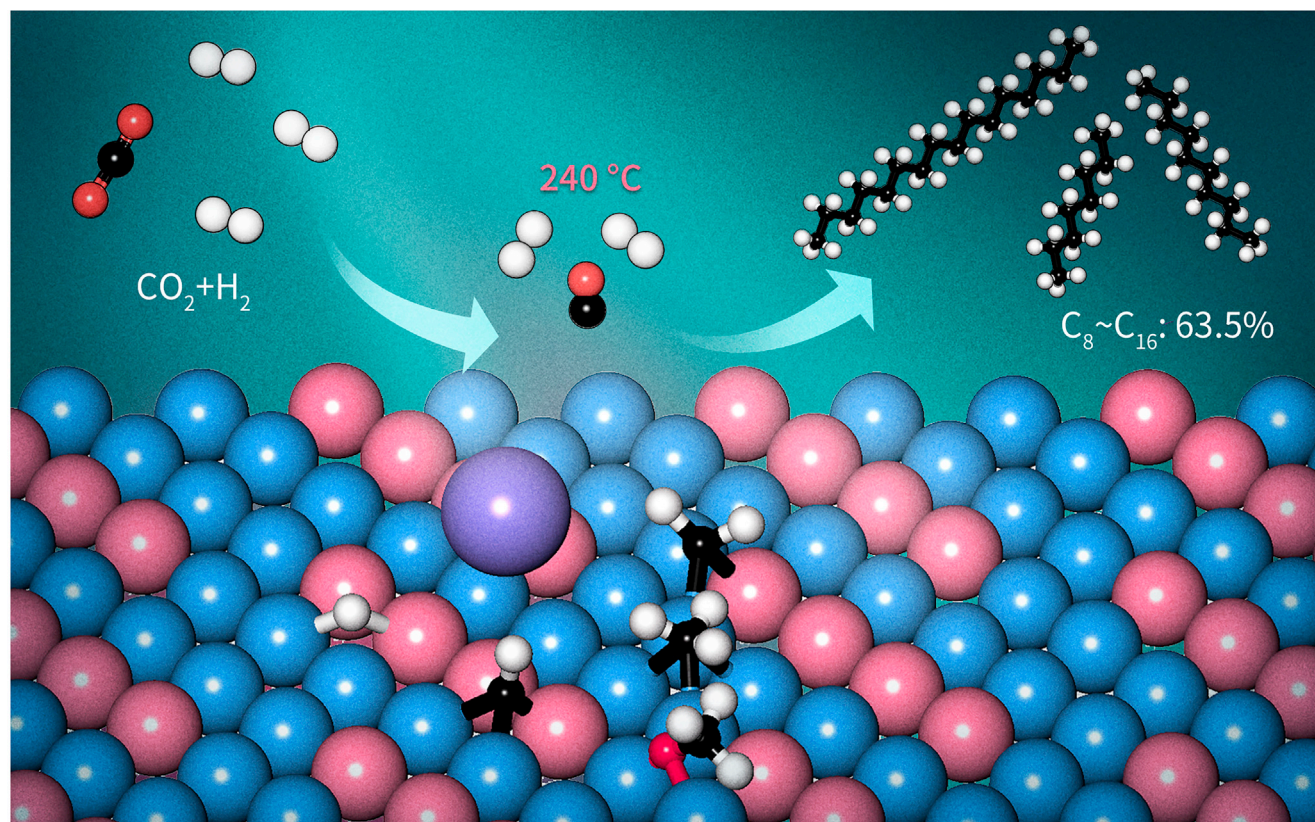
Lei Zhang,^{1,5,7} Yaru Dang,^{1,2,7} Xiaohong Zhou,^{2,4,7} Peng Gao,^{1,2,*} Alexander Petrus van Bavel,³ Hao Wang,¹ Shenggang Li,^{1,2,4,*} Lei Shi,¹ Yong Yang,^{1,4} Evgeny I. Vovk,⁴ Yihao Gao,¹ and Yuhan Sun^{1,4,6,*}

*Correspondence: gaopeng@sari.ac.cn (P.G.); lisg@sari.ac.cn (S.L.); sunyh@sari.ac.cn (Y.S.)

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Graphical abstract



Public summary

- An alloy is developed for the direct CO₂ hydrogenation to jet-fuel-range hydrocarbons
- The selectivity of the hydrocarbons (63.5%) exceeds the theoretical maximum value
- The CoFe alloy is the active phase in the coupling reaction between surface carbons
- The CoFe alloy is a highly efficient catalyst in the presence of a sodium promoter



Direct conversion of CO₂ to a jet fuel over CoFe alloy catalysts

Lei Zhang,^{1,5,7} Yaru Dang,^{1,2,7} Xiaohong Zhou,^{2,4,7} Peng Gao,^{1,2,*} Alexander Petrus van Bavel,³ Hao Wang,¹ Shenggang Li,^{1,2,4,*} Lei Shi,¹ Yong Yang,^{1,4} Evgeny I. Vovk,⁴ Yihao Gao,¹ and Yuhan Sun^{1,4,6,*}

¹CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

²University of Chinese Academy of Sciences, Beijing 100049, China

³Shell Global Solutions International B.V., 1031HW Amsterdam, the Netherlands

⁴School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

⁵China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China

⁶Shanghai Institute of Clean Technology, Shanghai 201620, China

⁷These authors contributed equally

*Correspondence: gaopeng@sari.ac.cn (P.G.); lising@sari.ac.cn (S.L.); sunyh@sari.ac.cn (Y.S.)

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The direct conversion of carbon dioxide (CO₂) using green hydrogen is a sustainable approach to jet fuel production. However, achieving a high level of performance remains a formidable challenge due to the inertness of CO₂ and its low activity for subsequent C–C bond formation. In this study, we prepared a Na-modified CoFe alloy catalyst using layered double-hydroxide precursors that directly transforms CO₂ to a jet fuel composed of C₈–C₁₆ jet-fuel-range hydrocarbons with very high selectivity. At a temperature of 240°C and pressure of 3 MPa, the catalyst achieves an unprecedentedly high C₈–C₁₆ selectivity of 63.5% with 10.2% CO₂ conversion and a low combined selectivity of less than 22% toward undesired CO and CH₄. Spectroscopic and computational studies show that the promotion of the coupling reaction between the carbon species and inhibition of the undesired CO₂ methanation occur mainly due to the utilization of the CoFe alloy structure and addition of the Na promoter. This study provides a viable technique for the highly selective synthesis of eco-friendly and carbon-neutral jet fuel from CO₂.

Keywords: carbon dioxide hydrogenation; C–C coupling; heterogeneous catalysis; jet fuel; CoFe alloys

INTRODUCTION

The increased consumption of fossil resources is responsible for the emission of large amounts of anthropogenic CO₂, which results in climate change and ocean acidification. The recent popularization of electric cars has helped reduce gasoline consumption. Nonetheless, in the near future, liquid fuels consisting of long-chain hydrocarbons will remain a necessity for the transportation sector, especially the aviation, nautical, and land-based automotive industries.¹ Therefore, it is imperative to develop processes and technologies for the effective hydrogenation of CO₂ to liquid fuels using renewable hydrogen (H₂). Despite some breakthroughs in the synthesis of gasoline (C₅–C₁₁-range hydrocarbons) directly via CO₂ hydrogenation,^{2–6} there have been few reports on the selective synthesis of jet fuel (C₈–C₁₆-range hydrocarbons).^{7,8} The traditional approach to the direct synthesis of products with more than two carbons (C₂₊) through CO₂ hydrogenation involves the carbon monoxide (CO) intermediate formed by cascading the reverse water-gas shift (RWGS) and Fischer-Tropsch synthesis (FTS) reactions. However, methanation of CO₂ or CO can also occur, which diminishes the economic value of this process.^{9–11}

Of the industrially relevant FTS catalysts, Fe and Co, the Fe-based catalysts are preferred, using CO₂ as a carbon source, owing to their high RWGS activities.^{9,12–14} Typically, alkenes are the main products, but large quantities of undesired CO are also formed. The alkenes are upgraded to hydrocarbon fuels over zeolites.^{2,15–21} According to some recent reports, high C₅₊ selectivity (58%–65%) can be achieved using modified Fe catalysts. However,

the hydrocarbon products obtained have a very broad distribution.^{13,22} When following the FTS mechanism, the hydrocarbon selectivity toward a specific fraction is mainly determined by the Anderson–Schulz–Flory (ASF) distribution, which predicts that the C₈–C₁₆ selectivity cannot exceed 41%.^{9,23} Therefore, it is extremely challenging to achieve a higher product selectivity during jet fuel synthesis via a “one-pot” FTS process. In traditional FTS, Co-based catalysts featuring metallic Co active sites are known to have much higher chain growth capabilities and improved catalytic stability compared with Fe-based catalysts with iron carbide active sites.^{24,25} However, for FTS starting from CO₂, short-chain hydrocarbons are predominantly formed, with a CH₄ selectivity of up to 70%.^{12,26–29} An intuitive approach is to tune the product distribution using FeCo bimetallic catalysts. Recently, carburized CoFe catalysts have been reported to perform CO₂ hydrogenation, generating lower olefins as the main products.^{18,30–33} Since, at high temperature (>280°C), CoFe catalysts can be easily carburized by CO/syngas pre-treatment or under high CO partial pressure, as in syngas conversion or the RWGS reaction,^{18,30,34–36} there are few studies of C–C coupling reactions on the CoFe bimetallic alloy phase.^{35–37} Therefore, it is necessary to obtain CoFe bimetallic alloy catalysts with superior performance in the selective production of jet fuel via direct CO₂ hydrogenation.

Herein, we report a Na-modified CoFe alloy catalyst for the direct hydrogenation of CO₂ to jet-fuel-range hydrocarbons. This catalyst exhibits an outstanding selectivity toward C₈–C₁₆ hydrocarbons (up to 63.5%), which exceeds the maximum value predicted by the ASF model by a significant margin. In addition, it has a low combined selectivity of ~22% toward CO and CH₄. We also demonstrate that the CoFe bimetallic alloy phase is responsible for the chain propagation reaction and ensures a very high product selectivity.

RESULTS AND DISCUSSION

Composition and catalytic performance

As can be seen from Table S1, the Co/Fe atomic ratio is approximately 1.9 for the CoFe catalysts obtained by the calcination of CoFe-layered double hydroxides (LDHs), denoted as CoFe-xNa, where x represents the Na concentration in wt % (x = 0.23, 0.81, 3.54), and the catalyst without Na is labeled as CoFe. For comparison, catalysts without Fe (Co and Co-0.63Na with 0.63 wt % Na and 70.5 wt % Co) or Co (Fe and Fe-0.67Na with 0.67 wt % Na and 69.7 wt % Fe) were also prepared.

We assessed the CO₂ hydrogenation performance of the various catalysts, and the results are listed in Table 1. CoFe exhibits high catalytic activity, with a conversion of 19.6%, and high CH₄ selectivity of 77.3%. With increasing Na concentration, the extent of CO₂ conversion decreases gradually, with a concomitant increase in CO selectivity. The CH₄ selectivity drops significantly, while the C₈₊ selectivity increases remarkably, reaching a maximum of 64.2%

Table 1. Catalytic hydrogenation of CO₂ over various catalysts

| Entry | Catalyst | Conv. (%) | CO sel. (%) | Hydrocarbon distribution (C mol %) | | | |
|-------|-------------|-----------|-------------|------------------------------------|--------------------------------|--------------------------------|-----------------|
| | | | | CH ₄ | C ₂ -C ₄ | C ₅ -C ₇ | C ₈₊ |
| 1 | CoFe-3.54Na | 7.0 | 8.8 | 12.7 | 14.9 | 9.2 | 63.1 |
| 2 | CoFe-0.81Na | 10.2 | 5.2 | 17.8 | 9.4 | 8.7 | 64.2 |
| 3 | CoFe-0.23Na | 12.6 | 5.0 | 55.1 | 5.4 | 0.5 | 39.0 |
| 4 | CoFe | 19.6 | 2.9 | 70.3 | 2.3 | 0.3 | 27.1 |
| 5 | Co-0.63Na | 8.3 | 7.2 | 76.5 | 3.6 | 2.3 | 17.5 |
| 6 | Co | 49.3 | 0.3 | 89.9 | 6.3 | 1.4 | 2.4 |

Standard reaction conditions: H₂/CO₂/N₂ ratio 73/24/3, temperature (T) 240°C, gas hourly space velocity (GHSV) 5,500 mL·g⁻¹·h⁻¹, pressure (P) 3 MPa. The data were collected after 48 h on stream.

at a Na concentration of 0.81 wt %. Compared with CoFe, CoFe-0.81Na achieves a 2.4-fold increase in C₈₊ selectivity, with a 4-fold lower CH₄ selectivity, suggesting that the effect of Na in decreasing CH₄ production is more pronounced than that in promoting C₈₊ formation. In addition, according to Figure 1A, with increasing space velocity of the feed gas, the C₈₊ fraction corresponding to CoFe-0.81Na increases substantially from 52.5% to 73.1%, along with a notable reduction in the CH₄ selectivity and CO₂ conversion, and CO formation is promoted. This indicates the suppression of CO₂ methanation at a lower conversion level. Moreover, with decreasing reaction temperature, the CH₄ selectivity declines remarkably from 26.5% to 5.8%, while the C₈₊ selectivity increases significantly from 42.2% to 81.7%, with a slight increase in CO selectivity. The catalytic activity is also decreased significantly (Figure 1B). Notably, most of the CoFe, Fe, or oxide/zeolite bifunctional catalysts developed for the hydrogenation of CO₂ to higher hydrocarbons tend to produce large amounts of the by-product, CO, partly because the RWGS reaction is favored at high reaction temperatures (>300°C).^{9,38} The CO selectivity of the CoFe catalysts in previous reports exceeded 30% even at lower reaction temperatures.¹⁸ In this study, the CO selectivity is well below 10% for all the CoFe-xNa catalysts at 240°C. Most of the CO₂ input is transformed to hydrocarbons on the CoFe-0.81Na catalyst. However, the CO selectivity is as high as 59.2% over Fe-0.67Na, indicating that the RWGS reaction is more likely to occur at the Fe sites modified by Na.

In addition to the low selectivity toward the undesired CH₄ and CO, the formation of light hydrocarbons (C₂-C₄) is also suppressed. A C₅₊ selectivity of up to 71.7% is observed, with the dominant products being liquid paraffins and hydrocarbon products in accordance with a double ASF model (Figure S1A).^{39,40} The chain growth probability is 0.76 for C₂-C₇ (α₁) and 0.6 for heavier C₈₊ hydrocarbons (α₂). The catalyst exhibits a selectivity of 63.5% for C₈-C₁₆ hydrocarbons (Figure 1C), outperforming the Fe-Mn-K catalyst reported previously for the synthesis of C₈-C₁₆ hydrocarbons (47.8% of all hydrocarbons) from CO₂⁷ and exceeding the maximum fraction (41%) obtained via the ASF mechanism. This differs significantly from the catalytic performance of Fe-based^{13,22,41,42} or CoFe catalysts^{30,34,43} with carbides as the active sites for the hydrogenation of CO₂ to higher hydrocarbons, producing olefins as the main products with very broad distributions (the highest carbon number typically exceeds 20) at higher temperatures (~300°C). In addition, we tested the performance of CoFe-0.81Na for CO hydrogenation, which afforded liquid fuels with a narrow hydrocarbon distribution (Figure S1B).

The product selectivity of the Na-modified Co catalysts changes significantly upon alloying with Fe. Comparing CoFe-0.81Na with Co-0.63Na, an increase in CO₂ conversion from 8.3% to 10.2% was observed. A more significant difference was found in the hydrocarbon distribution. For Co-0.63Na, the CH₄ selectivity is remarkably high (76.5%), while the C₈₊ selectivity is only 17.5%. The C₈₊ selectivity over CoFe-0.81Na is 64.2%, which is approximately 4-fold that of Co-0.63Na. The catalytic activity is significantly

enhanced upon introducing Co. The CO₂ conversion over CoFe-0.81Na is more than twice that over Fe-0.67Na, which has a similar Na content (Table S3). Although the CH₄ selectivity over Fe-0.67Na is as low as 17.2%, the C₈₊ selectivity of 44.1% is considerably lower than that over CoFe-0.81Na. A similar trend was observed for catalysts without Na. Compared with the pure Co catalyst, the CoFe catalyst exhibits significantly higher C₈₊ selectivity and lower CH₄ selectivity. A C₈₊ selectivity of 6.8% is achieved over the pure Fe catalyst, with a reduced CH₄ selectivity of 50.9% (Table S3), while the CO₂ conversion (9.1%) is much lower than that over the Co (49.3%) or CoFe (19.6%) catalysts. The stability of the CoFe-0.81Na catalyst was also investigated. The catalyst required less than 48 h to reach a steady-state operation (Figure 1D). However, the C₈-C₁₆ selectivity increased and a similar amount of time was required for the process to stabilize on stream. The CO selectivity increased continuously and stabilized at 8.5% after approximately 110–120 h. In the stability test, the extent of CO₂ conversion decreased from 14.8% to 10.6% during the initial 28 h and was maintained at 10.5% after 120 h. Similar trends were observed for CoFe-3.54Na with respect to time when the process was conducted on stream (Figure S2A). For the CoFe catalyst without Na and catalysts without Fe, the incubation time was shortened to 8 h (Figures S2B–S2D).

Structural characterization

Uncalcined CoFe-LDH precursors have lamellar structures (Figures 2A, S3, and S4). X-ray diffraction (XRD) analysis showed that the typical (001) basal reflection peaks of LDH materials were absent from the calcined samples (Figures S5A and 2C). A new phase of Fe^{III}-substituted Co₃O₄ (Co^{II}Co^{III}Fe^{III}O₄), hereafter denoted as Co₂FeO₄, was detected for the CoFe-xNa catalysts. The LDH-derived catalysts maintain the layered structure (Figures S3 and S6A), which promotes metal dispersion.⁴⁴ In addition, compared with other samples, CoFe-0.23Na and CoFe-0.81Na exhibited much higher specific surface areas (Table S1). Further reduction of CoFe-xNa in a pure H₂ atmosphere at 400°C for 6 h yielded cubic Co₇Fe₃ alloy nanoparticles, and no other phases were detected (Figures S5B and S6D). The CoFe alloy nanoparticle sizes of CoFe-0.81Na increased after reduction (Figures S6B and S6C). The influence of Na ions on the formation of the CoFe alloy phase was investigated using *in situ* XRD and H₂ temperature-programmed reduction (TPR) measurements, the results of which are illustrated in Figures S7 and S8, respectively. Initially, Co₂FeO₄ was reduced to CoO and FeO as the reduction temperature increased from 200°C to 350°C, and this process had negligible effect on the Na content. The Co₇Fe₃ alloy phase was formed when the reduction temperature exceeded 400°C. The introduction of excess Na inhibited the reduction of CoO and FeO to metallic Co and Fe, respectively. The addition of Na also suppressed the reduction of CoO to Co over Co-0.63Na.

On examination of the XRD patterns of the spent catalysts (Figures S5C and S5D), highly crystallized Co and poorly crystallized CoO phases were detected for Co and Co-0.63Na after 48 h of reaction. The occurrence of solely the Co₇Fe₃ alloy phase for the spent CoFe-xNa catalysts indicated that the formation of the CoFe alloy structure inhibited the oxidation of metallic Co during CO₂ hydrogenation. We also performed transmission electron microscopy (TEM) and scanning TEM (STEM)-energy dispersive X-ray spectrometry (EDX) characterizations to investigate the morphology and elemental distribution of the reduced and spent CoFe-xNa catalysts. No phase segregation was observed, and only the Co₇Fe₃ alloy phase was found after the CO₂ hydrogenation reaction (Figures 2A, 2B, S9, and S10). In addition, the oxygen was primarily distributed in the outer shell region of the spent CoFe alloy nanoparticles, whereas Na was homogeneously distributed in the CoFe alloy particles of the reduced and spent catalysts (Figures 2B and S10).

To determine the fine structure of CoFe-0.81Na, we performed X-ray adsorption near-edge structure (XANES) and extended X-ray adsorption fine structure (EXAFS) experiments (Figures 2E, 2F, and S11). The Co and Fe K-edge XANES spectra of the reduced and spent CoFe-0.81Na catalysts were similar, and the peaks at 7,111 and 7,712 eV corresponded to the 1s to 3d transitions in Fe⁰ and Co⁰, respectively, indicating that the Co and Fe species were mainly present in the metallic form. The Co-O and Fe-O

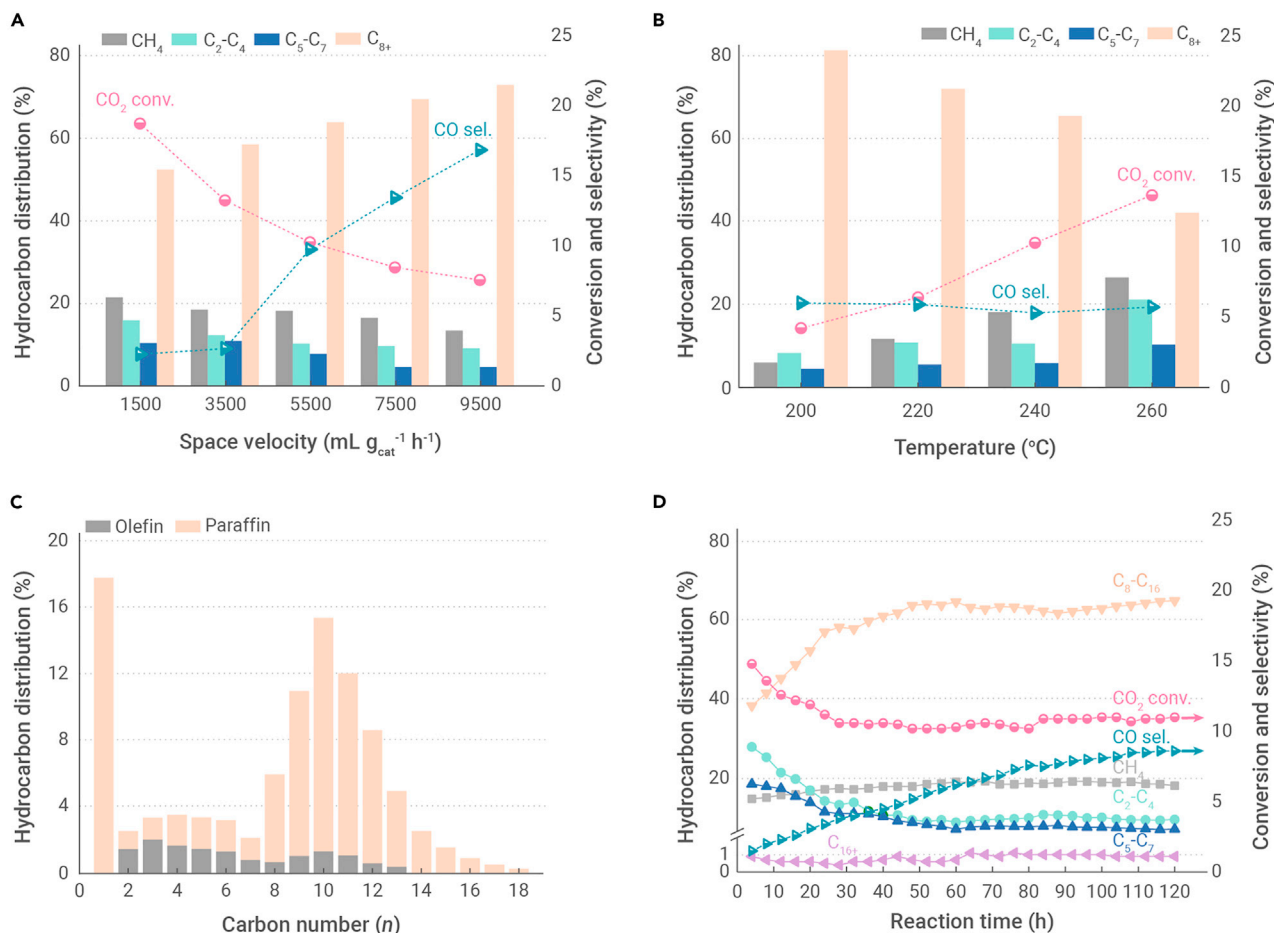


Figure 1. The evaluation data of CO₂ hydrogenation (A and B) Effects of (A) space velocity and (B) reaction temperature on conversion of CO₂, selectivity of CO, and hydrocarbon distribution. (C) Detailed distribution of hydrocarbons without CO obtained over CoFe-0.81Na under reaction conditions shown in Table 1. (D) Catalytic stability of CO₂ hydrogenation over the CoFe-0.81Na catalyst under standard reaction conditions.

coordination shells were absent from both the reduced and the spent samples, while new Co-Fe (Fe-Co) coordination shells were observed in both (Figures 2E and 2F), which indicates that the CoFe alloy structure is formed after the reduction and remains stable during the reaction. Fitting of the Co and Fe edge EXAFS data also reveals the formation of new Co-Fe bonds after the reduction (Tables S4 and S5). In addition, the Co-Fe (Co) and Fe-Co (Fe) coordination numbers increase slightly after the reaction.

To investigate the CO₂ adsorption properties of the Co, Co-0.63Na, and CoFe-xNa catalysts, their surface basicity was measured using CO₂ temperature-programmed desorption (TPD). With increasing Na content, the CO₂ desorption peaks were shifted to higher temperatures and the total number of basic sites increased significantly (Figure 2D). Compared with Co and Co-0.63Na, the peaks associated with weakly (50°C–200°C) and strongly (>200°C) basic sites were observed at much higher temperatures for the CoFe and CoFe-0.81Na samples, indicating that the formation of the Co₇Fe₃ alloy structure strengthened the chemisorption of CO₂. As can be seen from the H₂-TPD profiles (Figure S12A), the desorption peaks at 150°C–400°C, which are related to the hydrogenation ability of the samples and spillover or subsurface hydrogen adsorption,^{42,45} were shifted to higher temperatures with increasing Na content, indicating that the hydrogenation ability is weakened upon addition of Na. H₂ desorption from CoFe and CoFe-0.81Na occurs at higher temperatures than from the corresponding samples without Fe, which indicates the lower reactivity of the hydrogen species adsorbed on the CoFe and CoFe-0.81Na surfaces. The enhanced CO₂ adsorption and weakened hydrogenation ability inhibit CH₄ production and increase the chain growth probability owing to the lower ratio of

hydrogen to carbon species on the sample surface.^{14,46} As shown in Figure S12B, CO adsorption on CoFe in the high-temperature desorption regions (200°C–400°C) is remarkably enhanced compared with that on Co, particularly in the presence of Na, which favors the transformation of the CO intermediates in the tandem process.¹⁹ However, the degree of transformation decreases with increasing Na concentration. Therefore, the Co₇Fe₃ alloy structure inhibits CH₄ formation and plays a crucial role in the selective hydrogenation of CO₂ to the higher hydrocarbons that constitute jet fuel.

In situ DRIFTS study

The CO₂ activation and hydrogenation reactions over the Co and CoFe catalysts were studied using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). As shown in Figure S13, compared with the CO₂-DRIFTS results of CoFe, the infrared (IR) peak intensities corresponding to the surface carbonate, bicarbonate, and formate species, which are important intermediates formed during the RWGS reaction,⁴² for the Co catalyst are markedly weakened, which is consistent with the results of the CO₂-TPD analysis. This leads to a lower activity of the Co catalyst toward RWGS.

Switching from CO₂ to pure H₂ over the CoFe catalyst at 240°C led to the immediate formation of gaseous CO (2,178 and 2,117 cm⁻¹), the concentration of which decreased sharply after a few minutes (Figure S14). As shown in Figures 3A and S14, along with the consumption of CO, CH₄, and C₂₊, paraffins and olefins were detected after only 3 min. The band intensities of the higher olefins were very weak, while those of the higher paraffins increased remarkably during the initial 30 min and stabilized in the following 60 min,

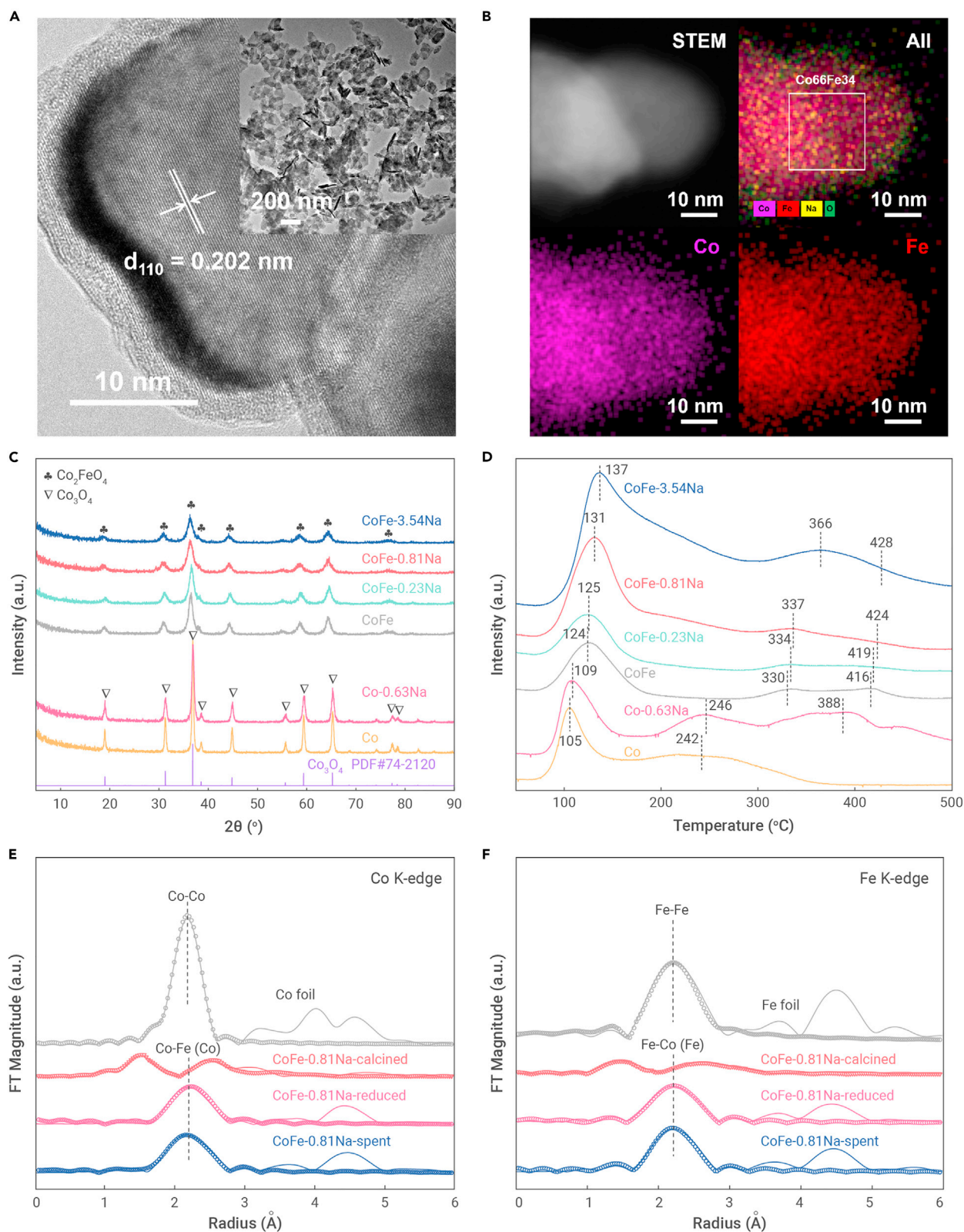


Figure 2. Catalyst characterization (A) High-resolution TEM image of spent CoFe-0.81Na and TEM image (inset) of the corresponding uncalcined precursors. (B) STEM image with the corresponding elemental mapping of spent CoFe-0.81Na. (C) XRD patterns of the samples after calcination. (D) CO_2 -TPD profiles of various calcined samples. (E and F) Fourier transforms of the k^3 -weighted EXAFS spectra (solid lines) and fitted curves (circles) of the calcined, reduced, and spent CoFe-0.81Na (after reaction for 48 h) and reference samples at the (E) Co K-edge and (F) Fe K-edge.

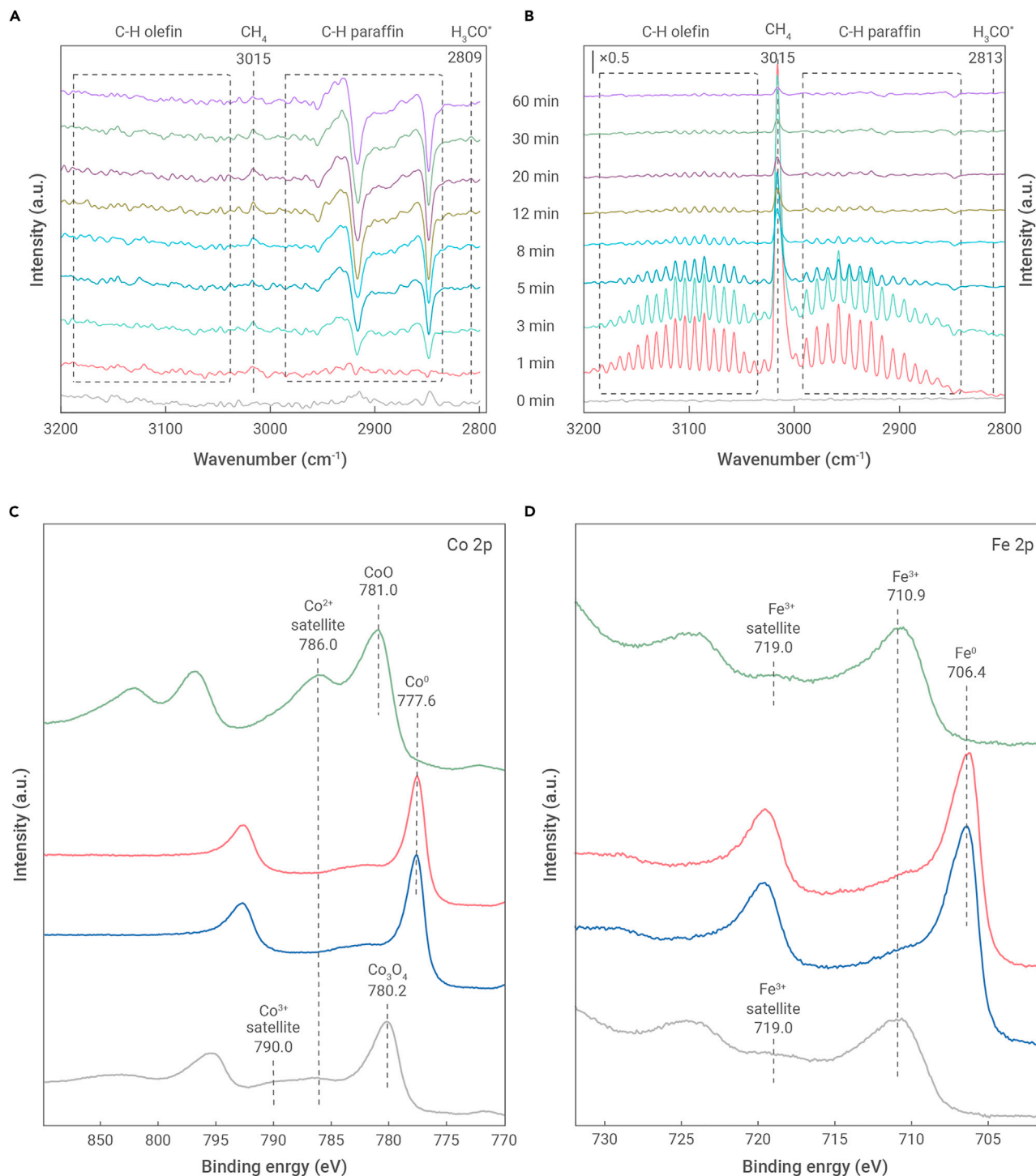


Figure 3. *In situ* characterization (A and B) DRIFTS spectra were recorded for CO₂ hydrocarbon reaction over (A) CoFe and (B) Co at 240°C. (C and D) XPS (C) Co 2p and (D) Fe 2p core level spectra of fresh CoFe-0.81Na catalyst (gray curves), after reduction in pure hydrogen (blue curves), and after CO₂ hydrogenation reaction at 200°C (red curves) or 240°C (green curves).

indicating that the C₂₊ paraffins were the principal hydrocarbons formed over CoFe. After 8 min of H₂ flow, methoxy species (CH₃O*, 1,036 and 2,809 cm⁻¹) were also detected, and the intensity of the band corresponding to CH₄ increased. Compared with the IR bands over CoFe, the band intensity of the methoxy species was enhanced and that of CH₄ was significantly lowered over CoFe-0.81Na. For the pure Co catalyst, the bands corresponding to CH₄ and the higher hydrocarbons were observed after only 1 min of H₂ flow (Figure 3B), and the band intensity of CH₄ was much stronger than those of

the higher hydrocarbons, indicating that the methanation activity of the Co catalyst was considerably higher. The intensities of these bands over Co decreased significantly upon exposure to H₂ flow. In addition, the band assigned to the methoxy species disappeared after 3 min. These results indicate that the formation of CH₄ may be related to the methoxy species. Compared with the pure Co catalyst, the band intensities for CH₄ are much weaker over CoFe, suggesting that the CoFe catalyst has a lower activity toward CO₂ methanation.

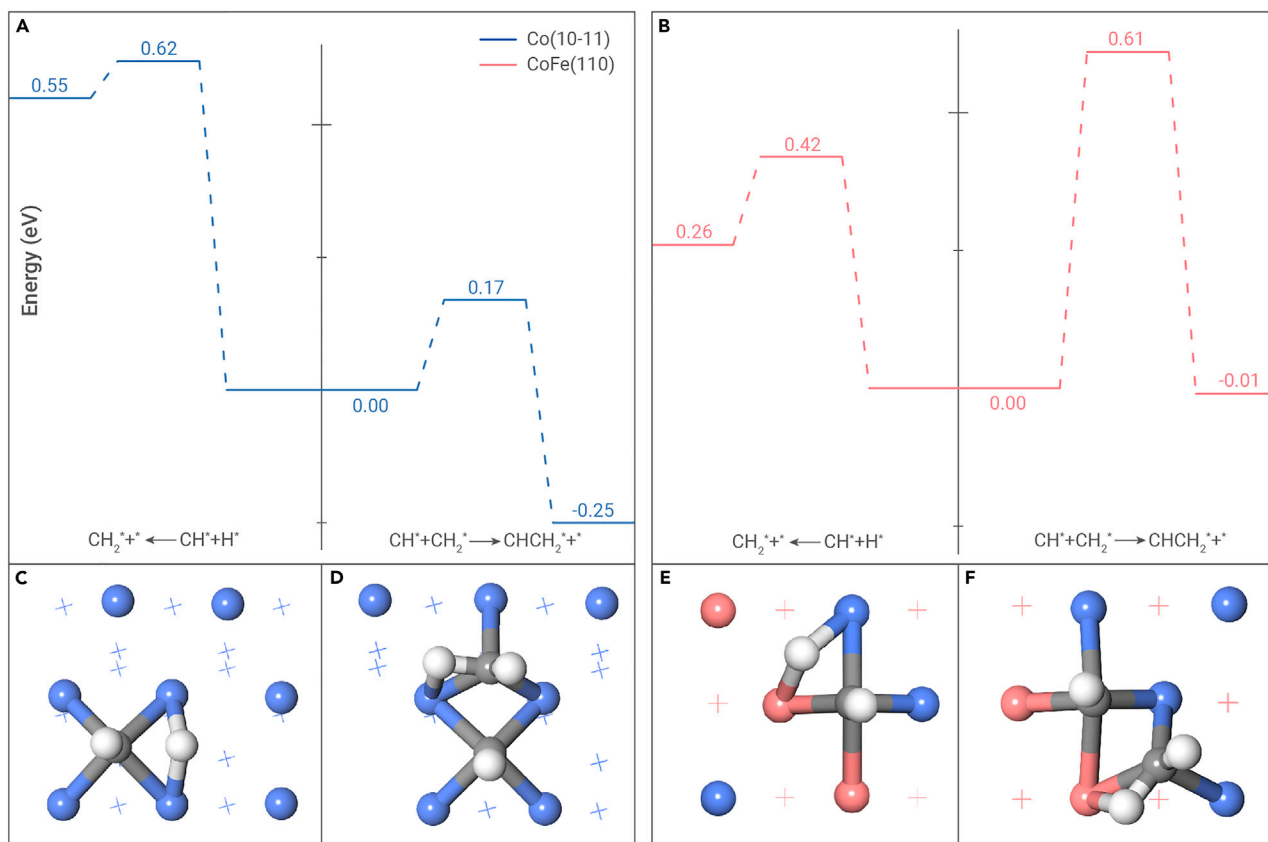


Figure 4. DFT prediction of the relative reactivities of hydrogenation and C–C coupling reactions (A and B) Potential energy profiles for CH* hydrogenation versus CH* + CH₂* coupling on the Co and CoFe alloy phases modeled by the (A) Co(10-11) and (B) CoFe(110) slabs. (C–F) Structures of the optimized transition states for (C and E) CH* hydrogenation and (D and F) CH* + CH₂* coupling on the (C and D) Co(10-11) and (E and F) CoFe(110) slabs, respectively (colors of surface atoms: Co, blue; Fe, magenta; C, gray; H, white).

Active sites

The XRD, STEM-EDX, and XAFS results confirm that the CoFe alloy species are the active phases participating in CO₂-based FTS. However, Co²⁺ and Fe³⁺ species were detected on the spent CoFe-xNa surface through *ex situ* X-ray photoelectron spectroscopy (XPS) analysis (Figure S15). To reveal the sites responsible for CO₂ activation and the formation of hydrocarbon products, we investigated the evolution of the surface electronic structure of CoFe-0.81Na during the CO₂ activation/hydrogenation process using XPS in an ultra-high-vacuum chamber directly connected to the high-pressure reaction cell. The Co 2p spectrum of the as-prepared sample has a profile similar to that of Co₃O₄, with a peak at 780.2 eV for Co 2p_{3/2} and two shoulder peaks at 787 and 790 eV (Figure 3C).⁴⁷ The Fe 2p spectrum of the as-prepared sample is consistent with that of Fe₂O₃ reported elsewhere (Figure 3D).⁴⁸ After reduction, both the Co 2p_{3/2} and the Fe 2p_{3/2} peaks became much sharper and were shifted toward the lower binding energies of 777.6 and 706.4 eV, confirming their nearly complete reduction (Figures 3C, 3D, and S16), and demonstrating the presence of the CoFe alloy.

After the subsequent reaction at 200°C for 5 h, no noticeable changes were observed in the Co 2p and Fe 2p spectra, which confirms the metallic states of the elements under the above reaction conditions. However, significant changes were observed in the spectra when CO₂ hydrogenation was performed at 240°C over the reduced sample. The Co 2p spectrum exhibits a Co 2p_{3/2} peak at 781 eV and a prominent Co²⁺ satellite peak, indicating the transformation of the surface metallic Co to CoO (Figure 3C). The Fe 2p spectrum after reaction at 240°C is similar to that of the fresh catalyst containing Fe³⁺ species (Figure 3D). These results are consistent with the STEM-EDX results

of the spent CoFe-based catalysts (Figures 2B and S10). The oxidation of the metal is attributed to its exposure to oxidative products, such as water, at higher concentrations and temperatures. Previous studies suggest that the formation of iron oxide on the CoFe alloy surface due to oxidation promotes the formation of surface CO intermediates via RWGS,⁴⁹ which facilitates the formation of long carbon chains during the subsequent FTS process. Thus, the C₈₊ selectivity over the CoFe catalysts is much higher than that over Co catalysts. Moreover, it can be seen from Figures 3C, 3D, S15, and S16 that no iron or cobalt carbides were observed when the reaction was performed at 240°C.

Reaction mechanism

To elucidate the influence of the catalyst structure on the selectivity toward long-chain hydrocarbons, density functional theory (DFT) calculations were performed to predict the energetics of hydrogenation and self- and cross-coupling of the CH_x (x = 1, 2) species formed via CO activation (Table S6), which have been suggested to influence the chain growth probability during the FTS reactions.^{35,50,51} Although CoO species may exist on the CoFe catalyst surface, chain growth typically occurs over metallic Co surfaces. We postulate that as long as the intermediate species has a CH or CH₂ moiety, it can couple with another unsaturated hydrocarbon species such as CH or CH₂, leading to continued carbon chain growth until the CH or CH₂ moiety is hydrogenated, which results in chain termination. Therefore, we first compared the differences in the energy barriers for the hydrogenation of the CH adsorbate (denoted as CH*) and its coupling with the CH₂ adsorbate (denoted as CH₂*) on the Co(10-11) and CoFe(110) slab models. As shown in Figure 4A, over the Co(10-11) surface, CH* + CH₂* coupling involves a much lower energy barrier (0.17 eV) than CH* hydrogenation (0.62 eV). The

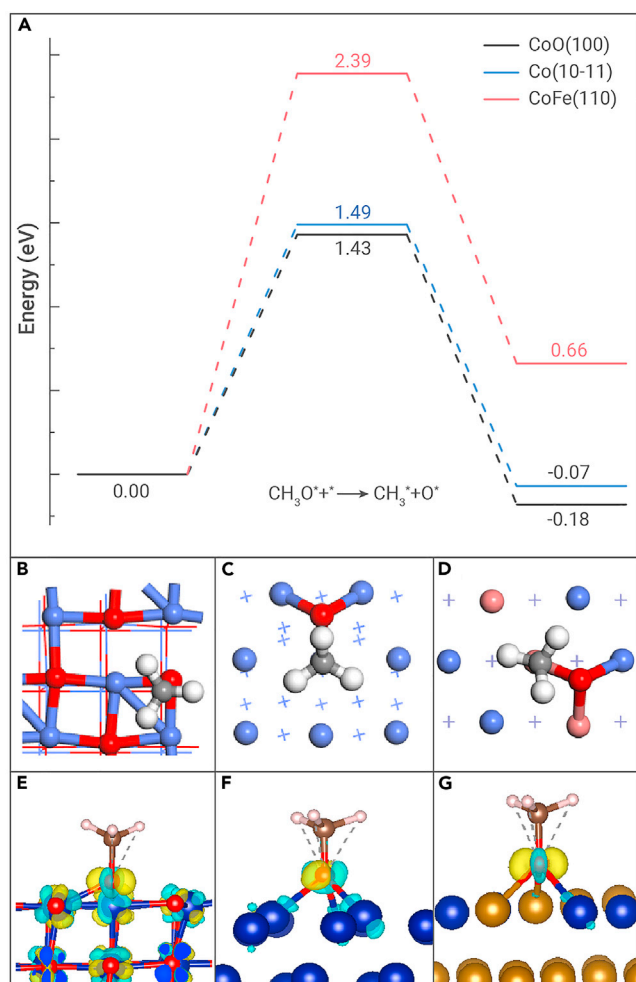


Figure 5. DFT calculations on the rate-determining step of the CO₂ methanation reaction (A) Potential energy profiles for CH₃O* dissociation on the CoO, Co, and CoFe alloy phases modeled by the CoO(100), Co(10-11), and CoFe(110) slab models. (B–D) Structures of the transition states on (B) CoO(100), (C) Co(10-11), and (D) CoFe(110) (additional surface atomic color: O, red). (E–G) Charge density difference plots upon CH₃O* adsorption on (E) CoO(100), (F) Co(10-11), and (G) CoFe(110), where the light blue and light yellow regions represent charge depletion and charge accumulation.

coupling reaction on the CoFe(110) surface also involves a relatively low energy barrier and is thermodynamically more favorable than hydrogenation, as shown in Figure 4B, although the energy barrier of CH* hydrogenation (0.42 eV) is somewhat lower than that of CH* + CH₂* coupling (0.61 eV). These results suggest that the Co catalyst favors chain growth over chain termination, which is important for the generation of long-chain hydrocarbons. However, Co has negligible activity toward RWGS, which restricts the formation of long-chain hydrocarbons during CO₂ hydrogenation owing to the scarcity of CH*/CH₂* species on the Co surface. In contrast, the CoFe alloy catalyst is less efficient at promoting chain growth. The transition states for CH* hydrogenation and CH* + CH₂* coupling reactions are shown in Figures 4C–4F. As shown in Figure S17A, CH₂* self-coupling on the Co(10-11) surface involves a much lower energy barrier (0.38 eV) compared with that on the CoFe(110) surface (0.51 eV), and it is also lower than that of CH₂* hydrogenation on the Co(10-11) surface (0.53 eV). These computational results suggest that the CoFe alloy phase is less favorable for the carbon chain propagation than the Co phase. Structures of the transition states involved in CH₂* hydrogenation and self-coupling on the above two surfaces are shown in Figures S17B–S17E, whereas those of the initial and final states are presented in Figures S18 and S19. The active site identified by these studies is consistent with that obtained via charge density analysis, as shown in Figure S20.

Considering that the Na promoter significantly affects both the activity and the selectivity of the Co and CoFe alloy catalysts, we further calculated the energy barriers to hydrogenation and self- and cross-coupling of CH_x over the Na-promoted Co(10-11) and CoFe(110) catalyst models. As illustrated in Figure S21 (with the additional data listed in Table S6 in parentheses), the computational results, which indicate that the addition of the Na promoter to the Co catalyst leads to a lower catalytic activity, are consistent with the experimentally observed reduced CO₂ reactivity and increased CO selectivity over the Co catalyst upon Na addition. However, for the CoFe alloy catalyst, the Na promoter favors the coupling over hydrogenation, as evidenced by the significantly higher C₈₊ selectivity and lower CH₄ selectivity.

It can be concluded from the above theoretical analysis that Co is a stronger promoter of chain growth, with a significantly higher energy barrier to CH* hydrogenation, while the main product formed during CO₂ hydrogenation over both the Co and the Co-0.63Na catalysts is CH₄. Therefore, we suggest two pathways for CO₂ hydrogenation, namely CO₂ methanation and RWGS + FTS, with the latter pathway facilitating the formation of both CH₄ and long-chain hydrocarbons. For an improved understanding of the significantly lower CH₄ selectivity over the CoFe and CoFe-0.81Na catalysts compared with the corresponding Co-based catalysts, we performed additional DFT calculations to study the methanation activity. Previous studies suggest that the dissociation of the CH₃O* species into CH₃* + O* is rate limiting during CO₂ methanation.⁵² For the catalysts used in this study, three possible phases can be relevant, namely the Co, CoFe, and CoO phases. Moreover, the CoFe alloy was found to suppress CH₄ formation via CO₂ methanation. The structures of the Co(10-11), CoFe(110), and CoO(100) slab models and the corresponding structures of the CH₃O* adsorbates on these surfaces are presented in Figures S22 and S23, respectively. As can be seen in Figure 5A, the energy barrier to CH₃O* dissociation on the CoO(100) surface with a surface O vacancy is the lowest at 1.43 eV, whereas it is slightly higher at 1.49 eV on the Co(10-11) surface, and much higher at 2.39 eV on the CoFe(110) surface. The corresponding transition states are shown in Figures 5B–5D. Therefore, according to our calculations, both the Co and the CoO phases are more favorable for CO₂ methanation than the CoFe phase, which is in agreement with our experimental findings. Moreover, the gradual increase in CO₂ methanation activity over CoFe-0.81Na with increasing reaction temperatures may also be attributed to the CoO phase formed *in situ* during the reaction. Notably, the reaction energies corresponding to CH₃O* dissociation also follow the same trend, which is consistent with the correlation between the energy barriers and the corresponding reaction energies in accordance with the Brønsted-Evans-Polanyi (BEP) relationship.⁵³ Furthermore, as shown in Figures 5E–5G, the differences in reactivity of the above three surfaces toward CH₃O* dissociation were rationalized by performing charge density difference ($\Delta\rho$) analyses. Therefore, our DFT calculations and theoretical analyses suggest that the CoFe alloy surface has a remarkable inhibitory effect on CH₄ production via CO₂ methanation.

Conclusions

Herein, we report on a Na-modified CoFe alloy catalyst that enables the efficient production of jet-fuel-range hydrocarbons via direct CO₂ hydrogenation. The selectivity toward C₈–C₁₆ hydrocarbons is as high as 63.5% at 10.2% CO₂ conversion. The catalyst demonstrates a high carbon efficiency, with a combined selectivity of approximately 22% toward undesired CH₄ and CO. The combined spectroscopic and computational studies suggest that the metallic CoFe alloy is the active phase responsible for producing C₂₊ hydrocarbons from the CO intermediate, whose formation is facilitated by the iron oxide surface sites generated *in situ* during the CO₂ hydrogenation reaction. The Na-modified CoFe alloy phase has an intermediate chain propagation activity, which promotes the C–C coupling reaction and enables high C₈–C₁₆ selectivity. In addition, the introduction of Na and formation of the CoFe alloy structure effectively suppress CO₂ methanation. Therefore, our knowledge of the intricate reaction network involved in CO₂-based FTS is improved by these experimental and theoretical findings, which can

potentially facilitate the rational development of efficient materials for the direct hydrogenation of CO₂ to advanced liquid fuels.

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AUTHOR CONTRIBUTIONS

P.G. and Y.S. conceived the project. P.G. and S.L. analyzed the data and wrote the paper. P.G., L.Z., Y.D., X.Z., A.B., and H.W. drafted the manuscript. L.Z. prepared various materials. L.Z. and H.W. performed sample characterization and catalytic evaluation. X.Z., E.V., and Y.Y. did the *in situ* XPS experiments and analysis. Y.D., L.S., Y.G., and S.L. performed the DFT calculations. All authors discussed the experimental and theoretical results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

LEAD CONTACT WEBSITE

<https://www.researchgate.net/profile/Peng-Gao-15>.

SUPPLEMENTAL INFORMATION

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