Direct conversion of CO$_2$ to a jet fuel over CoFe alloy catalysts

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Graphical abstract

Public summary

- An alloy is developed for the direct CO$_2$ 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
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 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. 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.³-¹¹

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.⁵,¹²-¹⁴ Typically, alkenes are the main products, but large quantities of undesired CO are also formed. The alkenes are upgraded to hydrocarbon fuels over zeolites.¹⁵-²¹ According to some recent reports, high C₈+ selectivity (58%-65%) can be achieved using modified Fe catalysts. However, the hydrocarbon products obtained have a very broad distribution.¹⁵,²²

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 C₄-C₁₆ selectivity cannot exceed 41%.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%.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.²⁴,²⁶-³³ 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.²⁴,²⁶,³⁴-³⁵ there are few studies of C-C coupling reactions on the CoFe bimetallic alloy phase.²⁶-³⁷ 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 CH₂. 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 CH₂ selectivity drops significantly, while the C₄ selectivity increases remarkably, reaching a maximum of 64.2%
at a Na concentration of 0.81 wt %. Compared with CoFe, CoFe-0.81Na achieves a 2.4-fold increase in \( \text{C}_8^{+} \) selectivity, with a 4-fold lower CH\(_4\) selectivity, suggesting that the effect of Na in decreasing CH\(_4\) production is more pronounced than that in promoting \( \text{C}_8^{+} \) formation. In addition, according to Figure 1A, with increasing space velocity of the feed gas, the \( \text{C}_8^{+} \) fraction corresponding to CoFe-0.81Na increases substantially from 52.5% to 73.1%, along with a notable reduction in the CH\(_4\) selectivity and CO\(_2\) conversion, and CO formation is promoted. This indicates the suppression of CO\(_2\) methanation at a lower conversion level. Moreover, with decreasing reaction temperature, the CH\(_4\) selectivity declines remarkably from 26.5% to 5.8%, while the \( \text{C}_8^{+} \) 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 CO\(_2\) 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 CO\(_2\) 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 CH\(_4\) and CO, the formation of light hydrocarbons (C\(_2\)–C\(_4\)) is also suppressed. A C\(_{6}\) 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 \( \text{C}_6^{–}\text{C}_7 \) (\( \alpha_1 \)) and 0.6 for heavier \( \text{C}_3 \) hydrocarbons (\( \alpha_2 \)). The catalyst exhibits a selectivity of 63.5% for \( \text{C}_6^{–}\text{C}_6 \) hydrocarbons (Figure 1C), outperforming the FeMn-K catalyst reported previously for the synthesis of \( \text{C}_6^{–}\text{C}_6 \) hydrocarbons (47.8% of all hydrocarbons) from CO\(_2\), and exceeding the maximum fraction (41%) obtained via the ASF mechanism. This differs significantly from the catalytic performance of Fe-based\(^{32,22,41,42}\) or Co catalysts\(^{10,34,43}\) with carbides as the active sites for the hydrogenation of CO\(_2\) 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 CO\(_2\) conversion from 8.3% to 10.2% was observed. A more significant difference was found in the hydrocarbon distribution. For Co-0.63Na, the CH\(_4\) selectivity is remarkably high (76.5%), while the \( \text{C}_8^{+} \) selectivity is only 17.5%. The \( \text{C}_8^{+} \) 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 CO\(_2\) conversion over CoFe-0.81Na is more than twice that over Fe-0.67Na, which has a similar Na content (Table S3). Although the CH\(_4\) selectivity over Fe-0.67Na is as low as 17.2%, the \( \text{C}_8^{+} \) 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 \( \text{C}_8^{+} \) selectivity and lower CH\(_4\) selectivity. A \( \text{C}_8^{+} \) selectivity of 6.8% is achieved over the pure Fe catalyst, with a reduced CH\(_4\) selectivity of 50.9% (Table S3), while the CO\(_2\) conversion (9.1%) is much lower than that of 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 \( \text{C}_8^{–}\text{C}_6 \) 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 CO\(_2\) 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-3.5Na 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 S2C). A new phase of Fe\(_{1.23}\) substituted Co\(_{0.77}\)O\(_2\) (Co\(_{0.77}\)Fe\(_{0.23}\)O\(_2\)) hereafter denoted as CoFe\(_{0.77}\)O\(_2\) 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 H\(_2\) atmosphere at 400°C for 6 h yielded cubic CoFe\(_{1.23}\) alloy nanoparticles, and no other phases were detected (Figures S5B and S6D). The CoFe alloy nanoparticle sizes of CoFe\(_{0.81}\)Na 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 H\(_2\) temperature-programmed reduction (TPR) measurements, the results of which are illustrated in Figures S7 and S8, respectively. Initially, Co\(_2\)Fe\(_{0.67}\)O\(_4\) 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 Co\(_2\)Fe\(_3\) 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 and CoO to Co\(_2\)O\(_3\)Na.

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 CoO-0.63Na after 48 h of reaction. The occurrence of the solely the Co\(_2\)Fe\(_3\) alloy phase for the spent CoFe-xNa catalysts indicated that the formation of the CoFe alloy structure inhibited the oxidation of metallic Co during CO\(_2\) hydrogenation. We also performed transmission electron microscopy (TEM) and scanning TEM (STEM)-energy dispersive X-ray spectrometry (EDX) characterization to investigate the morphology and elemental distribution of the reduced and spent CoFe-xNa catalysts. No phase segregation was observed, and only the Co\(_2\)Fe\(_3\) alloy phase was found after the CO\(_2\) 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 Fe\(_2\) and Co\(_2\), respectively, indicating that the Co and Fe species were mainly present in the metallic form. The Co-O and Fe-O
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 CoFe alloy structure strengthened the chemisorption of CO2. A similar trend 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 CoFe 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 C2H6, 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.
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 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).
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-₀.₈₁Na 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 2p₃/₂ and two shoulder peaks at 787 and 790 eV (Figure 3C). The Fe 2p spectrum of the as-prepared sample is consistent with that of Fe₂O₃ reported elsewhere (Figure 3D). After reduction, both the Co 2p₃/₂ and the Fe 2p₃/₂ 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 2p₃/₂ 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, 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 CHₓ (x = 1, 2) species formed via CO activation (Table S6), which have been suggested to influence the chain growth probability during the FTS reactions. 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).
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: 0, red). (E–G) Charge density analyses for CH3O dissociation on the CoO(100), Co(10-11), and CoFe(110) surfaces. The light blue and yellow regions represent charge depletions and charge accumulations.

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 CH2 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 CH2 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 CH2 hydrogenation, while the main product formed during CO2 hydrogenation over both the Co and the Co0.63Na 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 CoFe0.81Na 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* + OH* is rate limiting during CO2 methanation.6 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 S5, the energy barrier to CH3O* dissociation on the CoO(100) surface with a surface 0 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 SB–SD. 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.66 Furthermore, as shown in Figures SE–SG, the differences in reactivity of the above three surfaces toward CH3O* dissociation were rationalized by performing charge density difference (Δρ) 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–C15 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 CH2 hydrocarbons from the CO intermediate, whose formation is facilitated by the iron oxide surface sites generated during the CO2 hydrogenation reaction. The Na-modified CoFe alloy phase has an intermediate phase propagation activity, which promotes the C–C coupling reaction and enables high CH2 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

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potentially facilitate the rational development of efficient materials for the direct hydrogenation of CO\(_2\) 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.

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