



Article A Core-Shell Structured Na/Fe@Co Bimetallic Catalyst for Light-Hydrocarbon Synthesis from CO₂ Hydrogenation

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Abstract: The direct CO₂ Fischer–Tropsch synthesis (CO₂-FTS) process has been proven as one of the indispensable and effective routes in CO₂ utilization and transformation. Herein, we present a core-shell structured Na/Fe@Co bimetallic catalyst to boost CO₂ conversion and light hydrocarbon (C₂ to C₄) selectivity, as well as inhibit the selectivity of CO. Compared to the Na/Fe catalyst, our Na/Fe@CoCo-3 catalyst enabled 50.3% CO₂ conversion, 40.1% selectivity of light hydrocarbons (C₂-C₄) in all hydrocarbon products and a high olefin-to-paraffin ratio (O/P) of 7.5 at 330 °C and 3.0 MPa. Through the characterization analyses, the introduction of CoCo Prussian Blue Analog (CoCo PBA) not only increased the reducibility of iron oxide (Fe₂O₃ to Fe₃O₄), accelerated the formation of iron carbide (Fe_xC_y), but also adjusted the surface basic properties of catalysts. Moreover, the trace Co atoms acted as a second active center in the CO₂-FTS process for heightening light hydrocarbon synthesis from CO hydrogenation. This work provides a novel core-shell structured bimetallistic catalyst system for light hydrocarbons, especially light olefin production from CO₂ hydrogenation.

Keywords: CO₂ hydrogenation; bimetallic catalyst; iron and cobalt; light hydrocarbons; Fischer– Tropsch synthesis

1. Introduction

The massive carbon dioxide (CO₂) emissions are the main cause of global warming, sea-level rising, and extreme weather events nowadays. Thus, the development of CO₂ capture, usage and storage (CCUS) technologies has become an important research direction. Recently, the conversion of CO₂ into high-value-added chemicals (such as methanol, ethanol, light hydrocarbons, gasoline range hydrocarbons, and aromatics) has attracted widespread attention [1–3]. To produce C₂₊ chemical products from CO₂ hydrogenation, the direct CO₂ Fischer–Tropsch synthesis (CO₂-FTS) process and the methanol intermediate route have been proven as two indispensable and effective routes [4–9]. The methanol intermediate route involves methanol synthesis from CO₂ and H₂ by single or multiple metal-oxide catalysts and follows by using zeolites to catalyze methanol into dimethyl ether, light olefins, gasoline range hydrocarbons, light aromatics, etc. [5,10–16]. In comparison, the CO₂-FTS would be a more promising strategy to achieve high CO₂ conversion and low CO selectivity at more moderate reaction conditions [17–19].

Iron-based catalysts have been verified as efficient catalysts and are used widely in the CO_2 -FTS process [17,19–21]. During the reaction, two iron components have been reported as key roles in CO_2 hydrogenation to hydrocarbons. Firstly, CO formed from CO_2 and H_2 via the reverse water gas shift (RWGS) reaction on the Fe_3O_4 sites, then, CO and H_2 convert into hydrocarbon products on the Fe_xC_y sites by the FTS reaction. However, because of the Anderson–Schulz–Flory (ASF) distribution law and the thermodynamic conversion



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equilibrium of CO₂, there is still a big challenge for the highly selective production of the target range hydrocarbon with high CO₂ conversion [22,23]. Various studies have been adopted to regulate the activity and product selectivity over iron catalysts, such as introducing alkali promoters (such as Na, K), combining with acidic zeolites (including ZSM-5, MCM-22, Y, Beta), and co-feeding with other metal or metal-oxide components (Mn, Cu, Co, ZnO, MgO, Al₂O₃, etc.) [2,19,20,24–26] for production of light olefins, gasoline-range liquid fuel, and aromatics.

Light hydrocarbons (C_2 - C_4) are very important and well-used intermediate materials and energy sources in the chemical industry and our daily life. Light olefins, including ethylene, propylene, and butene, are widely used in the production of various plastics, solvents, drugs, cosmetics, etc. Propane and butane are the main components of liquefied petroleum gas (LPG). However, light hydrocarbons are mainly produced in the process of petroleum refining [27,28]. A green and new light hydrocarbon formation route starting from sustainable raw materials such as CO₂ is becoming particularly important. In our previous works, we prepared a series of metal-oxide and zeolite bifunctional catalysts for CO and CO₂ hydrogenation to light hydrocarbons through both FTS and methanol intermediate routes [29,30]. Moreover, a series of hybrid catalysts with unique core-shell structures were developed for highly selective synthesis of target hydrocarbons from CO and CO₂ hydrogenation [11,31–36].

Herein, we report a series of novel Na promoted Fe@Co bimetallic catalysts with different ratios of Co/Fe, named Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3, for light hydrocarbon production via the CO₂-FTS reaction process. Compared to the normal Na/Fe catalyst, the Na/Fe@CoCo-3 catalyst enabled a high C₂-C₄ selectivity of 40.1% (CO free) and a high olefin-to-paraffin ratio (O/P) of 7.5, with CO₂ conversion as high as 50.3% at 330 °C, 3.0 Mpa. The characterization analyses indicated that with the introduction of CoCo Prussian Blue Analog (CoCo PBA), the reducibility of iron oxide (Fe₂O₃ to Fe₃O₄) was increased, the formation of iron carbide (Fe_xC_y) was accelerated, and the strong basic sites on the catalyst surface were weakened. Moreover, the Co nanoparticles also acted as a second active center for heightening light hydrocarbon synthesis in the FTS reaction.

2. Results and Discussion

2.1. Structural Characterization

The XRD analysis was utilized to investigate the crystalline structure of the Na/Fe@Co catalysts. The normal Na/Fe catalyst was employed as a reference catalyst in this study. As shown in Figure 1, the typical diffraction peaks of hematite (Fe₂O₃) at 24.3°, 33.2°, 25.4°, 40.7°, 49.5°, 53.9°, 57.5°, 62.3°, and 64.2°, correspond to (012), (104), (110), (113), (024), (116), (122), (214), and (300) planes. The prepared Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3 exhibited weaker diffraction patterns of Fe₂O₃ than that of the Na/Fe [37,38]. We can see from Figure 1, the diffraction peak of (104) plane of Fe₂O₃ almost disappeared, and the other Fe₂O₃ peak shifted gradually into FeCo bimetallic-oxide species when the Co content increased. These results indicating that the existence of interaction between Fe and Co atoms, which significantly affected the iron oxide nanoparticle size and exposed crystal planes. Moreover, we did not observe the characteristic peaks of CoO or CoCo PBA (see Figure 3a) on these Na/Fe@Co catalysts. This suggests that these Na/Fe@Co samples had good Co dispersion and made the Fe₂O₃ species highly dispersed on the CoCo PBA core.



Figure 1. X-ray diffraction (XRD) patterns of the fresh Fe-based catalysts.

We also utilized XRD to analyze the catalysts after the CO₂-FTS reaction, as shown in Figure 2. After the reduction and reaction process, all Fe₂O₃ crystal diffraction patterns were eliminated. Although four catalysts obtained inferior diffraction patterns of Fe₃O₄, it can be found that more Fe_xC_y species (group peaks between 42 and 47°) were formed on these Na/Fe@Co catalysts after CO₂-FTS reaction, compared to that of Na/Fe. In addition, the Fe_xC_y species peaks intensities were followed as Na/Fe@CoCo-3 > Na/Fe@CoCo-2 > Na/Fe@CoCo-1 > Na@Fe, indicating more Co species boosted the in situ production of Fe_xC_y species during the CO₂-FTS reaction process. The Fe_xC_y species are considered as an active center of the FTS reaction, and high Fe_xC_y species content would be an important effect for the CO₂-FTS reaction.



Figure 2. XRD patterns of the spent Fe-based catalysts.

Scanning electron microscopy (SEM) analysis was utilized to observe surface morphology for the pure CoCo PBA, Na/Fe, Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3 catalysts. The result revealed that the pure CoCo PBA samples contained a regular cubic geometrical structure with a mean size of 120 nm, as seen in Figure 3b [39,40]. Figure 3c shows the Na/Fe sample exhibited random spherical nanoparticle geometry, and the particles are much smaller than that of CoCo PBA. The SEM images of the Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3 were listed in Figure 3d-f, respectively. Uniformly attached iron oxide nanoparticles can be seen on the surface of these Na/Fe@Co samples, and no cubic geometrical structure CoCo PBA particles could be found. Interestingly, the CoCo PBA core was not based on one crystal, but a CoCo PBA cluster. As seen in Figure 3b, a number of CoCo PBA crystals were assembled as a cluster, and iron oxide nanoparticles were further attached to this cluster evenly and transformed into a core-shell such as Na/Fe@Co catalysts in size of a few microns. There was no significant difference in morphology between the Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3 catalysts. Furthermore, we further conducted the SEM element mapping analysis of the Na/Fe@CoCo-3 catalyst as indicated in Figure 3g. Only Fe, O, and Na atoms signals appeared and were distributed on the catalyst surface evenly. These results indicating a core-shell structured catalyst with CoCo PBA crystal core covered with iron oxide nanoparticles shell was successfully designed and prepared.



Figure 3. XRD pattern of CoCo PBA (**a**); Scanning electron microscopy (SEM) image of CoCo PBA (**b**), Na/Fe (**c**), Na/Fe@CoCo-1 (**d**), Na/Fe@CoCo-2 (**e**), and Na/Fe@CoCo-3 (**f**); and SEM element mapping analysis image of Na/Fe@CoCo-3 (**g**), the element mapping images of Fe, O, Co, Na, and C listed as (**g**₁) to (**g**₅), respectively.

In addition, we employed N₂ physisorption to investigate the textural properties of the Na/Fe, Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3 catalysts. As indicated in Figure 4 and Table 1, all four catalysts exhibit similar hysteresis loops for N₂ adsorption-desorption isotherms. The normal Na/Fe sample showed higher BET surface area (S_{BET}), total pore volume, and average pore diameter of 40 m²/g, 0.59 cm³/g, and 67 nm, respectively. Moreover, the S_{BET} of the Na/Fe@Co catalysts decreases gradually from 30 m²/g to 28 m²/g to 16 m²/g, with increasing the CoCo PBA amount, demonstrating because of the existence of CoCo PBA, iron oxide nanoparticles became tighter during precipitation. Three

Na/Fe@Co catalysts display similar total pore volume of approximately 0.22–0.24 cm³/g, while the Na/Fe@CoCo-3 manifests a higher average pore diameter of over 51 nm than that of Na/Fe@CoCo-1 (32 nm) and Na/Fe@CoCo-2 (33 nm). The different N₂ physisorption behavior may have some unpredictable effects on the chemical properties and reactivity of the catalysts.



Figure 4. N₂ adsorption-desorption isotherms for the Fe-based catalysts.

Catalysts	$S_{BET}/(m^2/g)^{a}$	Total Pore Volume/(cm ³ /g) ^b	Average Pore Diameter/(nm) ^b
Na/Fe	40	0.59	67
Na/Fe@CoCo-1	30	0.24	32
Na/Fe@CoCo-2	28	0.24	33
Na/Fe@CoCo-3	16	0.22	51

Table 1. The S_{BET}, total pore volume, and average pore diameter of the fresh catalysts.

^a The specific surface area was determined by Brunauer–Emmett–Teller (BET) method. ^b The total pore volume was determined by Barrett–Joyner–Halenda (BJH) method.

The H₂-TPR results are utilized to compare the reducing properties of pure CoCo PBA and four catalysts, as shown in Figure 5. The Na/Fe sample exhibits three main peaks for its TPR profile under pure H_2 atmosphere. The three peaks at around 370 °C, 460 °C, and 605 °C are assigned to the reduction of Fe₂O₃ to Fe₃O₄, Fe₃O₄ to FeO, and FeO to Fe, respectively [2,17]. Compared to the Na/Fe, after the introduction of CoCo BPA, the reduction peaks of Fe_2O_3 to Fe_3O_4 , and Fe_3O_4 to FeO shifted to a lower temperature (lower than 400 °C). Importantly, the reduction peak area of Fe_2O_3 to Fe_3O_4 also increased with the increase in CoCo BPA amount, certifying more Fe_2O_3 species reduced under the first reduction temperature and easier for further reduction. These observations suggest that the introduction of CoCo BPA not only demonstrated the existence of interaction between Fe and Co species but also significantly improved the reducibility of the Fe₂O₃ species. The reduced ability of the Fe₂O₃ species could be a key factor affecting the CO₂-FTS reaction performance. Furthermore, as seen in Figure 5, the reduction peaks of pure CoCo PBA and those marked with blue dash of Na/Fe@Co catalysts were considered to be the thermal decomposition of CoCo PBA at high temperatures, indicating it possesses good thermal stability at the reduction and reaction temperatures in this study, that of 400 °C and 330 °C, respectively [40,41].



Figure 5. H₂-TPR profiles for the Fe-based catalysts.

To elucidate the CO₂ adsorption properties, also known as the basic nature of the catalysts, we performed CO₂-TPD analysis for the Na/Fe, Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3 samples as in Figure 6. Before CO₂-TPD analysis, all catalysts were reduced at 400 °C under pure H₂ atmosphere for 2 h. The Na/Fe sample observed a large high-temperature broad desorption peak from 530 °C to 640 °C, which was mainly caused by the strong basic properties of the Na component impregnated on the catalyst [26,42]. On these Na/Fe@Co samples, besides a high-temperature desorption peak at approximately 570 °C, a supernumerary low-temperature desorption peak, at approximately 400 °C, appeared. Compared to the Na/Fe catalyst, the high-temperature CO₂ adsorption peaks (>500 °C) of the Na/Fe@Co samples were significantly inhibited. In addition, both low-temperature and high-temperature desorption peaks were strengthened because of the introduction of CoCo PBA. This demonstrated that the Na/Fe@CoCo-3 sample generated the highest CO₂ adsorption properties among these Na/Fe@Co catalysts. The unequal CO₂ adsorption properties further indicate that they may have different performances for CO₂ hydrogenation to light hydrocarbons in the CO₂-FTS process.



Figure 6. CO₂-TPD profiles for the Fe-based catalysts.

2.2. CO₂ Hydrogenation Performance

The CO₂-FTS reaction performance of four catalysts were tested in a continuous fixedbed reactor. The conversions of CO_2 and the product distributions are summarized in Figure 7. In the comparison of the Na/Fe, these Na/Fe@Co catalysts enabled both high CO2 conversion and light hydrocarbon selectivity. In particular, the CO₂ conversion of the Na/Fe@CoCo-3 increased from 39.3% to 50.3%, and the C_2 - C_4 selectivity was enhanced from 28.2% to 40.1% in all hydrocarbon products. Moreover, the Na/Fe@CoCo-3 catalyst exhibited a lower CO selectivity (4.6%) than the other catalysts, especially that of the Na/Fe (8.5%). The CO by-product selectivity was inversely correlated with the amount of CoCo PBA added. Moreover, in these four samples, CO_2 conversion and C_2 - C_4 selectivity grew linearly, while higher hydrocarbon (C_{5+}) selectivity decreased linearly from the Na/Fe to Na/Fe@CoCo-1 to Na/Fe@CoCo-2. With the further increasing CoCo PBA amount of the Na/Fe@CoCo-2 to Na/Fe@CoCo-3, the CO2-FTS performance of the catalyst further improved, but the growth slowed down. The reaction performance results strongly indicated that the Na/Fe@Co catalyst not only boosted CO₂ conversion conspicuously but also largely increased the C_2 - C_4 selectivity and inhibited the formation of the unwanted by-product, CO.



Figure 7. CO₂ hydrogenation performance of the Fe–based catalysts. Reaction conditions: 330 °C, 3.0 MPa, feed gas (H₂ (71.96 v%), CO₂ (24.03 v%), and Ar (4.01 v%)), W/F = 5 g h/mol, catalyst 0.25 g, reaction time 6 h.

According to the characterization results, we demonstrated that the order of the formed Fe_xC_y amounts in the spent catalysts was followed as Na/Fe@CoCo-3 > Na/Fe@CoCo-2 > Na/Fe@CoCo-1 > Na/Fe. From the H₂-TPR analysis results, the Fe₂O₃ reducibility proved that there should be more Fe₃O₄ species in the Na/Fe@Co catalysts than that in Na/Fe after the reduction and reaction process. The more active Fe₃O₄ species increased CO₂ activation capacity in the RWGS reaction naturally. Moreover, as an active center of the FTS reaction, the Fe_xC_y species play a key role in converting CO to hydrocarbons. As a tandem reaction process, there is a delicate balance and interplay between the RWGS reaction and FTS reaction in the CO₂-FTS reaction process. That is, the reaction rate of the second step reaction (FTS reaction) has a great influence on the reaction rate of the fTS reaction) [17,20,21,25]. Therefore, more Fe_xC_y species would enhance the FTS reactivity and can further promote the reaction rate of the first step RGWS reaction in the CO₂-FTS reaction from 39.3% to 44.7% to 49.6% to 50.3% for the Na/Fe@CoCo-3 catalyst achieved higher CO₂ conversion and lower CO

selectivity at the same time than all the other Na/Fe@Co catalysts, including the Na/Fe catalyst [18,22,43,44].

In contrast, the Na/Fe@Co catalysts generated high selectivity of C_2 - C_4 products and low selectivity of C_{5+} hydrocarbons in the CO₂-FTS process. It has been proved that Fe-based catalysts modified by alkali metals such as Na or K are beneficial to improving the selectivity toward long-chain hydrocarbon products since alkali metals, as highly efficient electron donors, favor the adsorption and activation of CO₂ [25,26,42,45,46]. In the CO_2 -TPD analysis results, the introduction of CoCo PBA decreased the strength of basic properties, with the same Na amount (1% wt. in all catalysts) as that of Na/Fe. The low basic properties of these Na/Fe@Co suppressed their C-C chain growth ability to produce long-chain (C_{5+}) hydrocarbons. As seen in Figure 7, the C_{5+} hydrocarbon selectivity of the Na/Fe, Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3 decreased from 59.7% to 46.2% to 44.8% to 43.5%. The olefin-to-paraffin ratio (O/P) of C_2 - C_4 hydrocarbon products was also enhanced from 5.7 to 6.7 to 7.5 with the increased introduction of CoCo PBA. Nevertheless, Co species can also improve the hydrogenation ability in the CO₂-FTS reaction, rising the C_2 - C_4 selectivity [23]. Simultaneously, the existence of Co species maybe also the reason for the slightly increased methane production (13.5%) at such a high reaction temperature, compared to that of Na/Fe (7.1%). These results unveiled that the suitable basic properties and additional Co species of the Na/Fe@Co catalysts achieved their high C_2 - C_4 products selectivity.

3. Materials and Methods

3.1. Catalyst Synthesis

All reagents used in this study were of A.R. grade and used as received without any additional purification. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99.9%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan), urea (assay NH₂CONH₂, 99.0%, FUJI-FILM Wako Pure Chemical Corporation), potassium hexacyanocobaltate (III) (K₃[Co(CN)₆], 98.0%, FUJIFILM Wako Pure Chemical Corporation), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99.5%, FUJIFILM Wako Pure Chemical Corporation), and sodium nitrate (NaNO₃, 99.0%, FUJIFILM Wako Pure Chemical Corporation), and sodium nitrate (NaNO₃, 99.0%, FUJIFILM Wako Pure Chemical Corporation).

Synthesis of CoCo PBA. The CoCo PAB particles were prepared by a facile solutionbased ion-exchange/precipitation strategy. Typically, 3.6 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 5.4 mmol of sodium citrate were added into 120 mL of deionized (DI) water and magnetically stirred to form transparent solution A. Another solution B was obtained by dissolving 2.4 mmol of potassium hexacyanocobaltate (III) (0.7975 g) into 120 mL of DI water. Next, solution B was added slowly into solution A with magnetic stirring, followed by stirring for 10 min and then aging for 48 h at ambient temperature. The resultant precipitate was collected by centrifugation and finally dried at 60 °C for 12 h.

Synthesis of Fe_2O_3 nanoparticles (Fe NPs). Typically, 45 mmol of $Fe(NO_3)_3$ ·9H₂O and 450 mmol of urea were dissolved into 400 mL of DI water with vigorously stirring. Next, the mixture solution was heated from ambient temperature to 90 °C using a water bath and kept for 4 h. The resulting product was collected by suction filtration and dried at 60 °C. Then, the dried product was calcined at 400 °C for 4 h after being ground and denoted as Fe NPs.

Synthesis of Fe@CoCo PBA catalysts. Initially, CoCo PBA of x g (x = 1, 2, 3, each gram of CoCo PBA contains approximately 4.5 mmol of Co), 45 mmol of Fe(NO₃)₃·9H₂O and 450 mmol of urea were fully dispersed in 400 mL of DI water with violent ultrasonication. Following the same preparation process of Fe NPs, the Fe@CoCo PBA samples were synthesized. The obtained Fe@CoCo PBA samples with different CoCo PBA content were named as Fe@CoCo-1, Fe@CoCo-2, and Fe@CoCo-3, respectively. Finally, Na (1% wt.) was introduced by a wet-impregnation method. An amount of 0.0739 g of NaNO₃ was dissolved in 1 g of DI water and dipped then in 2 g of Fe-based catalyst. The resulting samples were named as Na/Fe, Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3,

respectively. Before the CO_2 hydrogenation reaction, all the as-prepared samples were pressed into a 40–60 mesh particle size.

3.2. Catalyst Characterization

The crystal phase of both the fresh and spent catalysts was determined by conducting powder X-ray diffraction (XRD) analysis using a Rigaku Ultima IV-NS diffractometer. The X-ray source employed was Cu-K α (λ = 0.15406 nm). The scanning range was set from 5 to 80 °C at a scanning speed of 2 °C per minute. To examine the morphologies and structures of the catalysts, a Field Emission Scanning Electron Microscope (FE-SEM) with Energy Dispersive Spectroscopy (EDS) capability was employed. The specific surface area and pore size distribution were calculated using an AUTOSORB-1 instrument at a temperature of liquid nitrogen. Prior to conducting N₂ adsorption measurements, the samples were subjected to vacuum degassing at a temperature of 160 °C for a duration of 10 h.

To assess the fundamental characteristics of the catalysts, we conducted temperatureprogrammed desorption of carbon dioxide (CO₂-TPD) experiments using a BELCAT II-T-SP instrument manufactured by Microtrac MRB, USA. The experimental procedure involved introducing 50 mg of catalyst into a quartz tube. Initially, the catalyst was purged with a flow of 5.0% H₂ gas at a rate of 30 mL/min, while maintaining a temperature of 150 °C. Following that, the catalyst was subjected to reduction at 400 °C for 120 min in a pure H₂ flow rate of 30 mL/min. Subsequently, the temperature was lowered to 80 °C, and the catalyst was flushed with a flow of helium gas for 120 min to eliminate any remaining gaseous H₂. To perform the CO₂-TPD, a constant flow of 5.0% CO₂ mixed with argon (20 mL/min) was passed over the catalyst. The temperature was increased from 80 to 800 degrees Celsius at a heating rate of 10 °C per minute. The concentration of CO₂ in the gas exiting the system was monitored using a thermal conductivity detector (TCD). The obtained peak area was then quantitatively calibrated using CO₂ pulses.

To assess the reducibility of the catalysts, we employed the H₂ temperature-programmed reduction (H₂-TPR) technique. Initially, 50 mg of the catalyst was subjected to a pretreatment step, where it was heated at 400 °C for 1 h in a pure helium (He) atmosphere at a flow rate of 30 mL/min. Following this, the temperature was gradually lowered to 50 °C. Subsequently, the catalyst was subjected to a temperature ramp-up, starting from 50 °C and reaching 900 °C at a heating rate of 10 °C per minute. This ramp-up was performed under a flow of 5.0% H₂ mixed with Ar at a flow rate of 30 mL/min. The consumption of H₂ during the process was monitored and recorded using a TCD.

3.3. Catalytic Performance Tests

The CO₂ hydrogenation reactions were performed in a fixed-bed reactor made of SUS316. The reactor was loaded with 0.25 g of catalyst, which was diluted with 1 g of quartz granules. Prior to the reaction, the catalyst underwent a reduction step. It was first subjected to a temperature of 400 $^{\circ}$ C for 6 h in a pure H₂ flow with a flow rate of 60 mL/min, at atmospheric pressure. After the completion of the reduction reaction, the reactor was allowed to naturally cool down to 330 °C. Subsequently, a gas mixture containing H₂, CO₂, and Ar was introduced into the reactor. The composition of the gas mixture was as follows: H₂ (71.96% v), CO₂ (24.03% v), and Ar (4.01% v). The pressure of the system was set to 3 MPa. The gaseous products produced in the reactor were continuously monitored using two online gas chromatographs (GC). The first GC, equipped with a thermal conductivity detector (TCD), was used to detect Ar, CH₄, CO, and CO₂. The second GC, equipped with a flame ionization detector (FID), was employed to analyze the gaseous hydrocarbons. Furthermore, the liquid hydrocarbon products and oxygenates were collected using an ice trap containing tridecane as a solvent. These collected samples were subsequently analyzed using two offline GC equipped with FID for the liquid hydrocarbon products and oxygenates, respectively. If not indicated otherwise, the CO_2 hydrogenation reactions were conducted under the conditions of $H_2/CO_2 = 3$ (with 4% Ar), 330 °C, 3 MPa and

 CO_2 conversion (CO_2 conv.) was calculated by Equation (1):

$$CO_2 \text{ conv.} (C-mol\%) = \frac{CO_{2 \text{ in}} - CO_{2 \text{ out}}}{CO_{2 \text{ in}}} \times 100\%$$
(1)

where $CO_{2 \text{ in}}$ and $CO_{2 \text{ out}}$ represent the molar fraction of CO_2 at the inlet and outlet, respectively.

CO selectivity (CO sel.) was calculated using Equation (2):

$$S_{CO} (C-mol\%) = \frac{CO_{out}}{CO_{2 in} - CO_{2out}} \times 100\%$$
⁽²⁾

where CO_{out} represents the molar fraction of CO at the outlet.

The hydrocarbon selectivity (C_i sel.) was given according to Equation (3):

$$C_{i} \text{ sel. } (C-mol\%) = \frac{M_{C_{i}}}{\sum_{i=1}^{n} M_{C_{i}} + \sum_{i=1}^{n} M_{C_{i} \text{ oxy.}}} \times 100\%$$
(3)

where M_{Ci} and $M_{Ci \text{ oxy.}}$ represent the carbon mole fractions of hydrocarbon i and oxygenate i at the outlet, respectively.

4. Conclusions

In conclusion, a series of Na/Fe@Co bimetallic catalysts with a core-shell structure, named Na/Fe@CoCo-1, Na/Fe@CoCo-2, and Na/Fe@CoCo-3, were successfully designed and prepared for the CO₂-FTS reaction process. The CoCo PBA was introduced as a core catalyst to improve CO₂ conversion and light hydrocarbon production. The characterization results demonstrated that these Na/Fe@Co catalysts possessed better reduction ability of iron oxide (Fe₂O₃ to Fe₃O₄), suitable surface basic properties, and CO₂ adsorption properties. More importantly, the Na/Fe@Co catalysts significantly increased the in situ Fe_xC_y formation during the CO₂-FTS reaction, largely boosting CO₂ conversion and light hydrocarbon production. As a result, the Na/Fe@CoCo-3 catalyst achieved an improved selectivity of C₂-C₄ as high as 40.1% in all hydrocarbon products and a high olefin-to-paraffin ratio (O/P) of 7.5 with a high CO₂ conversion of 50.3%. These results and observations confirmed that a well-designed core-shell Fe@Co bimetallic structure with a suitable basic property can enhance CO₂ conversion capacity, light hydrocarbon formation, and inhibit CO selectivity in the CO₂-FTS reaction process.

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