



Article Sr_{1-x}K_xFeO₃ Perovskite Catalysts with Enhanced RWGS Reactivity for CO₂ Hydrogenation to Light Olefins

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Abstract: The catalytic hydrogenation of CO_2 to light olefins (C_2 – C_4) is among the most practical approaches to CO₂ utilization as an essential industrial feedstock. To achieve a highly dispersed active site and enhance the reactivity of the reverse water-gas shift (RWGS) reaction, ABO₃-type perovskite catalysts $Sr_{1-x}K_xFeO_3$ with favorable thermal stability and redox activity are reported in this work. The role of K-substitution in the structure–performance relationship of the catalysts was investigated. It indicated that K-substitution expedited the oxygen-releasing process of the SrFeO₃ and facilitated the synchronous formation of active-phase Fe₃O₄ for the reverse water-gas shift (RWGS) reaction and Fe_5C_2 for the Fischer–Tropsch synthesis (FTS). At the optimal substitution amount, the conversion of CO₂ and the selectivity of light olefins achieved 30.82% and 29.61%, respectively. Moreover, the selectivity of CO was up to 45.57% even when $H_2/CO_2=4$ due to CO_2 -splitting reactions over the reduced Sr₂Fe₂O₅. In addition, the reversibility of perovskite catalysts ensured the high dispersion of the active-phase Fe_3O_4 and Fe_5C_2 in the SrCO₃ phase. As the rate-determining step of the CO₂ hydrogenation reaction to light olefins over Sr_{1-x}K_xFeO₃ perovskite catalysts, FTS should be further tailored by partial substitution of the B site. In sum, the perovskite-derived catalyst investigated in this work provided a new idea for the rational design of a catalyst for CO_2 hydrogenation to produce light olefins.

Keywords: olefins; carbon dioxide hydrogenation; perovskite-type oxides; K-substituting

1. Introduction

As a major greenhouse gas, atmospheric carbon dioxide has been increasing in concentration in the last two decades, causing severe global warming and extreme climates [1]. Efficient utilization of carbon dioxide to obtain high-value-added chemicals can alleviate both the environmental problems and the overdependence on other carbon resources [2]. The hydrogenation of carbon dioxide to C_2 – C_4 light olefins, which are basic building blocks in chemical industries, has attracted extensive attention [3–5]. The main limitation of CO₂ conversion is its high thermodynamic stability, thus requiring catalysts and energy input to drive the transformation.

 CO_2 hydrogenation to olefins mainly follows a CO_2 -modified Fischer–Tropsch synthesis (CO_2 -FTS) route or a methanol-mediated (MeOH) route, but is often limited by low selectivity and catalyst deactivation [4–6]. The CO_2 -FTS synthesis route usually consists of two consecutive catalytic reactions using Fe-based catalysts. Firstly, a reverse water–gas shift (RWGS) reaction converts CO_2 to CO with a Fe₃O₄ phase. Subsequently, an FTS reaction causes CO hydrogenation to hydrocarbons, catalyzed by active iron carbide phase of Fe₅C₂ [7,8]. Because RWGS is related to the formation of the CO intermediate, while FTS determines the yield and distribution of the olefin products, both reactions should be controlled carefully.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). To overcome low CO₂ conversion and Anderson–Schulz–Flory (ASF) distribution caused by bulk Fe-based catalysts, various modification strategies [4] were adopted by adding electron promotors (e.g., alkali metals) and structure promotors (e.g., copper, zinc, and cobalt), as well as supports (e.g., Al_2O_3 , SiO_2 , or MOFs). As efficient electron donors, the alkali metals Na and K favor the adsorption of CO₂ onto Fe oxides, and facilitate the generation of the Fe₅C₂ phase [9–11]; however, excessive additions likely reduce the activity of CO₂ hydrogenation by decreasing the total surface area and creating a hydrogen-lean environment [12]. The formed metallic Cu nanoparticles with CuO-doping benefits Febased catalyst activity for the RWGS [13,14], while ZnO addition suppresses the sintering of Fe oxides by generating ZnFe₂O₄ spinel [15], improving the catalyst's stability [16]. Inert support such as Al_2O_3 and SiO₂ can promote the dispersion of Fe species and suppress the aggregation of active iron particles due to the strong interactions between active phases and the support [17,18]. However, the active particles' aggregation of the supported catalysts is still inevitable due to a lack of confinement [19].

Complicated metal oxides with superstructures, such as ABO₃-type perovskites and AB₂O₄-type spinel, could confine transition metal ions' A sites and B sites in the specific crystallite, therefore leading to a higher dispersion of the related metal ions at the atomic level over the supported metals [20,21]. Meanwhile, their activity can be adjusted flexibly using the substituted A site and B site with a transition metal [21]. On the one hand, these complicated metal oxides are well-known heterogeneous catalysts for redox reactions. As oxygen carriers, perovskite materials are applied widely in chemical-looping processes due to their excellent redox performances [22,23]. Perovskite materials including CaMnO₃, SrFeO₃, and LaFeO₃ exhibited outstanding properties in CO_2/H_2O splitting to generate CO/H₂ during chemical-looping dry/steam reforming [24–27]. On the other hand, these complicated metal oxides are prominent precursors in the preparation of metal nanoparticles for RWGS and FTS, thanks to the merits of the highly dispersed metal active site and its interaction with supports [28–32]. As for RWGS, a perovskite-derived catalyst provides oxygen vacancies for efficient CO_2 adsorption and activation [28,29]. As for FTS, Ao et al. [30] achieved higher alcohol synthesis from syngas with a perovskite-derived trimetallic Co-Ni-Cu catalyst. Liu et al. [31] employed spinel ZnAl₂O₄-supported iron– catalyst for FTS, and gained an admirable light olefin selectivity of 64.4%. Ma et al. [32] reported a K/LaFeMnO₃ perovskite-derived catalyst for FTS with a light olefin fraction of 54%. As for CO_2 hydrogenation, Utsis et al. [33] adopted an Fe–Al–O spinel and an Fe–Ba–hexaaluminate as the catalyst precursor for CO_2 hydrogenation, and yielded a high productivity of C^{5+} hydrocarbons. Recently, Xu et al. [34] fabricated a ternary spinel-type ZnCo_xFe_{2-x}O₄ catalyst for an unprecedentedly high iron time yield for CO₂ conversion of 29.1 μ mol CO₂·gFe⁻¹·s⁻¹. However, to the best of our knowledge, a perovskite-derived iron catalyst for CO₂ hydrogenation to light olefins has been seldom reported.

To this end, a perovskite-type complicated metal oxide, SrFeO₃, was firstly chosen as the precursor for CO₂ hydrogenation to light olefins. SrFeO₃ possesses the virtues of a relatively low cost without expressive elements, a high stability, and easily tunable chemical properties [35–37]. According to a report by Marek et al. [36], SrFeO₃ could be reversibly reduced to SrO and Fe, resulting in the release of oxygen at a chemical potential suitable for splitting CO₂/H₂O. Its deep reduction in a CO₂ atmosphere was susceptible to generating SrCO₃; however, it could be reserved by increasing the temperature or lowering the CO₂ partial pressure. These results highlighted the redox performance and structural stability of the SrFeO₃ in a wide temperature range. Considering that potassium is a vital promoter that improves the reaction rate and increases the selectivity of olefins [38], the substitution of the A-site with potassium is a potential strategy to tailor the catalytic activity of SrFeO₃ for both RWGS and FTS.

In the current work, a series of catalysts with perovskite-type $Sr_{1-x}K_xFeO_3(x = 0-0.6)$ as a precursor were prepared by using the sol-gel method. Characterizations including H₂-TPR, XRD, XPS, and SEM demonstrated that K-substitution could lead to the formation of active-phase Fe₃O₄ for RWGS and Fe₅C₂ for FTS. The reversible ABO₃-type perovskite

structure ensured the high dispersion and stability of the active sites. Furthermore, the redox reaction of intermediate $Sr_2Fe_2O_5$ gave rise to the dynamic regulation of CO_2 by either splitting CO_2 or forming $SrCO_3$, thereby markedly promoting CO generation for FTS. The results shed light on the application of perovskite-type $Sr_{1-x}K_xFeO_3$ in CO_2 hydrogenation to light olefins.

2. Materials and Methods

2.1. Perovskite Preparation

The Sr_{1-x}K_xFeO₃ perovskites (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) were prepared by using the sol-gel method. The detailed procedures were as follows. Firstly, analytical reagents Sr(NO₃)₂, KNO₃, and Fe(NO₃)₃.9H₂O at the desired stoichiometric ratios; i.e., (1-x):x:1 (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6), were dissolved in deionized water and continuously stirred at 80 °C. Subsequently, citric acid and ethylene glycol with a molar ratio to metal ions of 1.5 was added into the solution to form a viscous gel. Then, the gel was dried at 100 °C for 24 h in an oven, followed by calcination at 400 °C for 2 h and 800 °C in air. The obtained particles were ground and sieved into 40~80 meshes for use. The perovskite samples of Sr_{1-x}K_xFeO₃ with different K contents were respectively designated as SKFx.

2.2. Catalyst Characterization

The as-prepared and used catalysts were characterized by an X-ray diffractometer (XRD, Rigaku D-MAX 2500/PC) equipped with a Cu K α radiation source (λ = 0.15406 nm). The 2 θ range was from 10° to 80° at a scan rate of 5°/min in ambient conditions. The operation current and voltage were 150 mA and 40 kV, respectively. X-ray photoelectron spectra (XPS) were collected using a Thermo Fisher (Waltham, MA, USA) 250XI XPS spectrometer at the monochromatic Al Ka radiation and calibrated using the C peak at 284.6 eV. The deconvolution of the XPS spectra was carried out through the XPS PEAK 41 program with Gaussian functions by subtracting a Shirley background. The microscopic morphology of the catalyst particles was examined by TESCAN MIRA4 (Brno, Czech Republic) scanning electron microscopy (SEM) operated at an accelerating voltage of 0.2-30 keV. Energy-dispersive X-ray spectroscopy (EDS) mapping was examined using an Xplore facility with an operation voltage of 200 eV. H₂ temperature-programmed reduction (H2-TPR) experiments were carried out on AutoChemiII 2920 chemical adsorption instrument (Micromeritics Instrument Corporation, GA, USA), with a flow of 10 vol % H₂ in argon (30 mL/min) from 100 to 900 °C at a constant heating rate of 10 °C/min. The CO₂ temperature-programmed desorption (CO₂-TPD) experiments were implemented on a Chembet Pulsar (Billing, MT, USA) chemical adsorption instrument. The sample (0.1 g) was first degassed at 400 °C for 1 h under an argon flow. After cooling to ambient temperature, CO_2 -TPD curves were obtained by heating up to 900 °C. Thermogravimetric analysis (TGA) was conducted by using NETZSCH STA (Selb, Germany) 409PC equipment under a 100 mL/min N₂ or O₂ (20%)/N₂ atmosphere at a heating rate of 20 k/min. The specific surface area was obtained through the BET method.

2.3. Catalytic Performance Testing

The evaluation setup for the CO₂ hydrogenation to olefins is shown in Figure 1. An appropriate amount of catalyst (2.0 g, 40–80 mesh) was loaded in the middle of the fixedbed reactor with an inner diameter of 20 mm, and a small amount of quartz wool was filled at both ends to prevent the catalyst from being blown out. Before the activity test, the reactor was purged with argon for 30 min to remove the residual air, and then reduced to a flow of 10% H₂/Argon at 450 °C for 2 h. At 350 °C, the reactant gas of H₂/CO₂ was fed into the reactor at 1 MPa and a GHSV of 7200 mL·g_{cat}⁻¹·h⁻¹. The gaseous products with N₂ as the internal standard were analyzed offline by using gas chromatography (PANNA A91 PLUS). CO, CH₄, CO₂, and N₂ were detected with a TCD detector with a TDX-01 packed column, while the C₁–C₄ hydrocarbons were analyzed with an FID detector with a CP–Al₂O₃/KCl capillary column.



Figure 1. Schematic diagram of reactor for carbon dioxide hydrogenation to prepare light olefins: (a) pressure gauge; (b) mass flowmeter; (c) preheater; (d) temperature controller; (e) thermocouple and temperature display; (f) silica wool; (g) catalyst; (h) gas–liquid separator; (i) gas chromatograph; (j) computer; (k) fixed-bed reactor.

When the reaction was maintained continuously at least 4 h of time on stream, the CO_2 conversion and product selectivities were determined using the following Equations (1)–(4):

$$X(CO_2) = \frac{(CO_2)_{in} - (CO_2)_{out}}{(CO_2)_{in}} \times 100\%$$
(1)

$$S(CO) = \frac{(CO)_{out}}{(CO_2)_{in} - (CO_2)_{out}} \times 100\%$$
(2)

$$S(C_2^{=}-C_4^{=}) = \frac{(C_2^{=}-C_4^{=})_{out}}{(CO_2)_{in} - (CO_2)_{out}} \times 100\%$$
(3)

$$S(C_5^+) = 1 - S(CH_4) - S(CO) - S(C_2 - C_4)$$
 (4)

3. Results and Discussion

3.1. Characterization of As-Prepared Catalysts

The XRD patterns of the as-prepared SKFx (x = 0–0.6) catalysts are presented in Figure 2. All the SKFx (x = 0–0.6) catalysts displayed a typical diffraction peak of a cubic perovskite structure at $2\theta = 32-34^{\circ}$, which was consistent with the literature reports [22,39]. There were no any other crystalline phases for the potassium-promoted catalysts, indicating that potassium successfully entered the lattice of the perovskite. Nevertheless, with an increasing K/Sr molar ratio, characteristic diffractions of the perovskite phase of all the K-substituting catalysts shifted gradually toward higher diffraction angles. This indicated that the entry of K into the A-site of the perovskites led to the changes in the lattice parameters. Since the valence of the K ion was lower and the ionic radius of K was larger than that of Sr, the intensities of the characteristic diffraction peaks over the modified perovskite decreased with an increase in the K substitution. In addition, the diffraction peak at $2\theta = 46-48^{\circ}$ was gradually divided into two peaks, and the degree of lattice distortion gradually increased. Moreover, SEM and EDS-mapping characterizations showed a high dispersion of all ions (Figure S1).



Figure 2. XRD patterns of the as-prepared SKFx (x = 0–0.6) catalysts: (**A**) full pattern; (**B**) at $2\theta = 46-48^{\circ}$.

SrFeO₃ is generally regarded as an oxygen-storage material due to its splendid redox performance. The O_2 -deficient state exhibits potential CO_2/H_2O splitting to generate CO/H_2 . Therefore, the O₂-releasing behaviors of the as-prepared SKFx (x = 0–0.6) catalysts were investigated by thermogravimetric analysis. As shown in Figure 3, all as-prepared SKFx (x = 0–0.6) catalysts could release O_2 at the evaluated temperature under an inert atmosphere. As for SKF0.0; i.e., SrFeO₃, three O_2 -releasing phases were observed with an increase in the temperature that corresponded to three crystal structures. The calculated mass loss meant that the three crystal structures included $Sr_8Fe_8O_{23}$ (SrFeO_{2.875}) below 300 °C, Sr₄Fe₄O₁₁ (SrFeO_{2.75}) at 300–600 °C, and Sr₂Fe₂O₅ (SrFeO_{2.5}) above 600 °C, which agreed with the experimental results in the literature [40]. However, further decomposition of the brownmillerite structure Sr₂Fe₂O₅ into SrO and Fe was not observed. According to the reported literature [22,36], only under a reducing atmosphere could the deep reduction of SrO and Fe occur. As for SKFx (x = 0.2, 0.4 and 0.6), the substitution of Sr with K significantly enhanced the release of O₂, thereby promoting the generation of SrO and Fe. At 300–600 $^{\circ}$ C, the O₂-releasing molar ratio approached 30 %, while this value was just 8.3 % for SrFeO₃. The oxygen vacancy resulted from O_2 releasing was conductive to the adsorption and conversion of CO_2 into CO_2 ; i.e., RWGS. At the temperature of CO_2 hydrogenation to light olefins, the SKF0.4 catalyst displayed the highest oxygen vacancy. In addition, the final mass loss increased gradually with the increase in the substitution amount of K. The O₂-releasing molar ratio was close to 60% for the SKF0.6 catalyst, which suggested the total release of oxygen, and that the ultimate products were SrO, K₂O, and Fe.

To reveal the redox behaviors of the SKFx catalysts in depth, H₂-TPR experiments were carried out. As depicted in Figure 4, there were three distinct reduction peaks for all samples, in the vicinity of 450 °C, 600 °C, and 800 °C, respectively. They represented the reduction of SrFeO₃ to Sr₂Fe₂O₅, the further reduction of Sr₂Fe₂O₅, and the formation of SrO and Fe, which were in line with the reported literature [22,36]. Combined with the aforementioned TG results, the reducing gas H₂ accelerated the release behavior of oxygen, and achieves the deep reduction to SrO and Fe, even at 800 °C. According to [9], alkali metals act as electron promoters to inhibit the chemisorption of H₂ on the catalyst surface, restricting the reduction of metal oxide ions. Thus, the first reduction peak of the SKFx (x = 0.2, 0.4, 0.6) catalysts was extended to a higher temperature. Meanwhile, the consumption of H₂ decreased when is the temperature was lower than 450 °C. Nevertheless, among the three K-substituting catalysts, the SKF0.4 exhibited the maximum consumption of H₂ in the temperature range to conduct CO₂ hydrogenation (200–450 °C).



Figure 3. Thermogravimetric analysis of the SKFx (x = 0, 0.2, 0.4, 0.6) catalysts from ambient temperature to 900 °C under the inert atmosphere.



Figure 4. H₂-TPR profiles of SKFx (x = 0, 0.2, 0.4, 0.6) perovskite catalysts.

To obtain insights into the basic site distribution of the SKFx (x = 0, 0.2, 0.4) catalysts, CO_2 -TPD experiments were conducted. As shown in Figure 5, there were two basic sites on the surface of the SrFeO₃ at 450 °C and 600 °C. However, the K-substituting SKF0.2 catalyst had a sharp desorption peak at 665 °C, while the SKF0.4 catalyst had two distinct sharp desorption peaks at 697 °C and 855 °C. Generally, the desorption peaks below 600 °C reflected the basic site distribution. The desorption peaks of the K-substituting catalysts at higher temperatures showed that the reactions between the K-substituting catalysts and CO_2 took place. According to the following experiments and those in [22,41], we know that the reaction 5 between the generated $Sr_2Fe_2O_5$ and CO_2 occurred. The CO_2 desorption

peak at 665 °C for SKF0.2 and 697 °C for SKF0.4 were attributed to the reverse reaction 5, while the CO₂ desorption peak at 855 °C was ascribed to the decomposition of SrCO₃ to generate SrO and CO₂. It should be pointed out that the K-substituting catalysts still possessed certain basic sites.



$$Sr_2Fe_2O_5 + 2CO_2 = 2SrCO_3 + Fe_2O_3$$
 (5)

Figure 5. CO₂-TPD profiles of SKFx (x = 0, 0.2, 0.4, 0.6) perovskite catalysts.

3.2. Catalytic Performance of SKFx Catalysts

To investigate the effect of K-substituting content on the catalytic performances, CO2 catalytic hydrogenation experiments using SKFx catalysts were carried out in a fixed-bed reactor. The CO₂ conversion and product distribution using the SKFx catalysts are indicated in Figure 6. When $SrFeO_3$ was used as the catalyst, the CO selectivity was up to 83.92%; however, few FTS products were generated. The main reason was a lack of the active iron carbide phase of Fe_5C_2 due to the confinement of the perovskite structure to B-site Fe ions. In addition, the high CO selectivity was ascribed to the outstanding redox performance of reduced SrFeO₃; i.e., Sr₂Fe₂O₅, which promoted the dissociation of CO₂ into CO. With the substitution of Sr with K at the A-site, the distortion of the lattice gradually increased, and the confinement of the perovskite structure to Fe was weakened. Consequently, the active phases, such as Fe_3O_4 and Fe_2C_5 , were prone to generation, followed by the increases in the CO₂ conversion and FTS products. On the other hand, the alkalinity of the catalyst surface increased with the increasing substitution of K, which could promote CO₂ adsorption and inhibit H_2 adsorption indirectly [42], thereby promoting the accession of light-olefin selectivity. However, lower K substitution reduced the amount of active phases generated. More K substitution took the edge off both the CO₂ conversion and the selectivity of light olefins, which could be attributed to the covering of the active site [12]. The optimal substitution amount was 0.4. As for the SKF0.4 catalyst, the highest light-olefin selectivity of 29.61% and CO₂ conversion of 30.82% were achieved.



Figure 6. CO₂ conversion and product distribution over SKFx catalysts (reaction conditions: $H_2/CO_2 = 3/1, 350 \text{ °C}, 1.0 \text{ MPa}, \text{GHSV} = 7200 \text{ mL} \cdot \text{gcat} \cdot ^{-1} \cdot \text{h}^{-1}$).

The composition of the SKFx catalysts after 4 h of reaction was detected using XRD analysis. As depicted in Figure 7, the SrFeO3 catalyst comprised an oxygen-deficient brownmillerite structure, Sr₂Fe₂O₅, without any other phases. However, after the substitution of Sr with K at the A-site, the brownmillerite structure Sr₂Fe₂O₅ disappeared. Instead, the Sr-containing phase became $SrCO_3$, while the Fe-containing phase was composed of Fe_3O_4 , Fe_5C_2 , and Fe_2O_3 , among which Fe_3O_4 and Fe_5C_2 were acknowledged as the active phases for RWGS and FTS, respectively. According to Marek's research [36], only under a reduction atmosphere and an elevated CO₂ pressure could SrFeO₃ carbonate to SrCO₃. Furthermore, they argued that SrCO₃ could be removed by oxidation or avoided entirely at higher temperatures (>850 °C). Obviously, the XRD analysis indicated that K substitution made $SrFeO_3$ more susceptible to carbonation. The Fe_2O_3 phase was accompanied by a carbonation process, referring to reaction (5). The generated carbonate weakened the confinement of the perovskite structure to iron ions, thereby promoting the generation of Fe₃O₄ and Fe₅C₂. As for the SKF0.6 catalyst, the other iron phase, Fe₃C, was detected, which was attributed to the deep carbonization. This result could explain the excellent catalytic performance of the SKF0.4 over the SKF0.6 in CO₂ hydrogenation. Despite the SrFeO₃ being converted to SrCO₃ and an iron-containing phase, a high dispersion of the active phase still could be achieved. First, the SKFx catalysts could regenerate under a high-temperature and oxidation atmosphere according to the reversible reaction (5), which will be further elaborated in the following section. Second, the elements were confined within the specific structure, thereby retaining its high dispersion. The surface topographies of the SrFO₃ and SKF0.4 catalysts and their element distributions are shown in Figure 8. It is clear that the surface of both fresh SrFO₃ and SKF0.4 catalysts were smooth and porous, and without any agglomeration. Compared with the SrFO₃, the porosity of the fresh SKF0.4 catalyst decreased; however, it increased after the catalytic reaction. This could be attributed to their specific surface areas. This value was $6.9932 \text{ m}^2 \cdot \text{g}^{-1}$ for the fresh SrFO₃ and 3.8366 $m^2 \cdot g^{-1}$ for the fresh SKF0.4, respectively; while it was 5.849 $m^2 \cdot g^{-1}$ for the reacted SKF0.4. Furthermore, elements including Fe, Sr, K, and O were dispersed evenly on the perovskite structure, as shown in their EDS mappings in Figure 8D–H. Meanwhile, the uniform distribution of the C element, which existed in the form of FeCx, was also observed.



Figure 7. XRD patterns for the SKFx catalysts after reaction ($H_2/CO_2 = 3/1$, 350 °C, 1.0 MPa, GHSV = 7200 mL·gcat·⁻¹·h⁻¹).



Figure 8. SEM patterns of perovskite catalysts: (**A**) SKF0.0 (fresh); (**B**) SKF0.4 (fresh); (**C**) SKF0.4 (after reaction). (**D**–**H**) EDS mapping.

3.3. Redox Performance of Catalysts

Aside from the catalytic effect of the active phase Fe_3O_4 and Fe_5C_2 on RWGS and FTS, the inherent redox properties of the SrFO₃ and Sr₂Fe₂O₅ played significant roles in the CO₂-splitting reaction and the H₂-oxidation reaction. Thus, the change in valence states and the oxidation behavior of the reacted SKFx were investigated.

As illustrated in Figure 9, the Fe2p spectra of both the fresh SrFeO₃ and SKF0.4 had double peaks and two small satellite peaks, indicating the different chemical valence states of Fe [43]. The binding energies of 709.2 eV, 710.4 eV, and 711 eV corresponded to Fe²⁺, Fe³⁺, and Fe⁴⁺, respectively. The deconvolution of the O 1s spectra involved three peaks: lattice oxygen (O_{lat}) at 528 eV, chemisorbed oxygen (O_{car}) at 529 eV, and physisorbed oxygen (O_{ads}) at 530.5 eV [44]. The component contents calculated from the integrated area of the subpeaks are tabulated in Table 1. As for the fresh catalysts, in light of the electroneutrality

principle, the substitution of Sr with K increased the content of Fe⁴⁺, which had a stronger reducibility. The increase in Fe⁴⁺ might have been responsible for the formation of iron carbide. The decreases in O_{lat} and O_{car} and the increase in O_{ads} represented the rising oxygen vacancies and oxygen mobility, which benefited the redox performance and the formation of iron carbide during the CO₂ hydrogenation reaction.



Figure 9. O 1s and Fe 2p XPS spectra and deconvolution of fresh samples: (a,c) SKF0.0; (b,d) SKF0.4.

Table 1. Percentage of O1s and Fe2p3/2 of fresh perovskites.

Sample		Fe2p _{3/2}		O1s			
	Fe ²⁺ /%	Fe ³⁺ /%	Fe ⁴⁺ /%	O _{lat} /%	O _{car} /%	O _{ads} /%	
SKF0.0 (fresh)	20.41	53.85	25.74	20.81	21.63	57.56	
SKF0.4 (fresh)	22.24	44.6	33.16	15.36	14.74	69.9	
SKF0.0 (used)	28.02	49.23	22.75	15.31	32.64	41.35	

The XPS spectra of both the SrFeO₃ and SKF0.4 after the reaction were analyzed (Figure 10). As for the SrFeO₃ catalyst, the increasing peak area of the Fe²⁺ and hydroxyl oxygen O_{car} indicated that partial Fe⁴⁺ conversion into Fe³⁺ and Fe²⁺ occurred under the reductive atmosphere, which corresponded to the generation of Sr₂Fe₂O₅ (Figure 7). As for the reacted SKF0.4, three types of oxygen existed on its surface, among which the peaks at 529.1, 530.9, and 532.6 eV corresponded to the binding energies of the Fe₃O₄, Fe₂O₃, and SrCO₃ respectively. Within the binding-energy region of the Fe $2p_{3/2}$ core level, the peaks located at 720.15 eV (Fe $2p_{1/2}$) and 707.3 eV (Fe $2p_{3/2}$) were attributed to the Fe_xC_y species. The dominance of the broad peak centered around 710 eV was caused by the overlapping signals of Fe³⁺ and Fe²⁺, which suggested that the Fe₃O₄ species was present as the main component on the surface of these Fe catalysts.

Intensity, au

526

Intensity, au

526

528

530

Binding Energy, eV



Figure 10. O 1s and Fe 2p XPS spectra and deconvolution of spend samples: (**a**,**c**) SKF0.0; (**b**,**d**) SKF0.4 ($H_2/CO_2 = 3/1, 350 \degree C, 1.0 \text{ MPa}, \text{GHSV} = 7200 \text{ mL} \cdot \text{gcat} \cdot ^{-1} \cdot \text{h}^{-1}$).

710

720

Binding Energy, eV

730

740

To conduct the regeneration of the perovskite structure, the oxidation behaviors of the SKFx (x = 0-0.6) catalysts after reaction were investigated using thermogravimetric analysis under an O_2 atmosphere. As shown in Figure 11, all the used SKFx (x = 0–0.6) catalysts underwent three stages: a mass-loss stage I at around 300 $^\circ$ C, followed by a mass-gain stage II, and then a sharp mass-loss stage III above 600 °C. Compared with the constant mass of the SrFeO₃, stage I was attributed to the oxidation of FeC_x . The maximum mass loss of SKF0.4 manifested the highest amount of FeC_x forms in the catalytic process. The following mass-gain stage II resulted from the oxygen-obtaining process of the oxygen-deficient perovskite. This suggested the excellent regeneration of the used catalyst to its perovskite structure. It was surprising to observe the occurrence of O_2 release, even under the O_2 atmosphere. As distinguished from the mass-loss behavior of the fresh catalysts under an inert atmosphere, the sharp mass loss herein was caused by the reaction (5) between the SrCO₃ and Fe_2O_3 to generate $Sr_2Fe_2O_5$ and CO_2 . Meanwhile, the decomposition of Sr₂Fe₂O₅ occurred due to K-substituting promotions. This highlighted that the gain of oxygen and loss of K-substituting catalysts verified the remarkable stability of the perovskite structure.



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536 700

Figure 11. Thermogravimetric analysis of the used SKFx (x = 0, 0.2, 0.4, 0.6) catalysts when heated to 900 °C under 20% O₂ atmosphere.

3.4. Probable Reaction Mechanism over K-Substituting Catalysts

To determine the influence factor and probable reaction mechanism of the SKF0.4 catalyst, different reaction conditions, including the reaction atmosphere and the H/C molar ratio, were examined. The CO₂/CO conversion and product distributions using SKF0.4 are tabulated in Table 2. When using CO₂ (25%) as the reaction gas, the CO₂ conversion was 6.54%, with a CO selectivity of 86.22%. On the one hand, the CO₂-splitting reaction to generate CO occurred when using the reduced catalyst existing in the form of Sr₂Fe₂O₅ (Figure 12). On the other hand, CO₂ was deeply reduced to form FeCx, accompanied by the production of SrCO₃. The absence of the H₂ reduction gas gave rise to the deep carbonization of iron, resulting in the formation of Fe₇C₃. The XRD patterns (Figure 12) of the catalysts after the reaction confirmed this inference.

Table 2. CO_2/CO conversion and product distribution using SKF0.4 under different conditions (350 °C, 1.0 MPa).

Conditions	H/C -	Convers	Conversion (%)		Selectivity (%)					
		CO ₂	СО	CO	CO ₂	CH ₄	$C_{2}^{0}-C_{4}^{0}$	$C_2^{=}-C_4^{=}$	S/C ₅ +	
CO ₂ +N ₂	-	6.54	-	86.22	-	-	-	-	-	
CO ₂ +H ₂	1	16.89	-	68.56	-	10.39	2.19	17.14	1.72	
	2	28.74	-	61.52	-	11.21	4.04	15.25	7.98	
	3	30.82	-	46.68	-	13.96	5.40	29.61	4.35	
	4	31.54	-	45.57	-	19.30	7.34	25.91	1.88	
CO+H ₂	2	-	86.36	-	35.02	22.57	2.96	22.10	17.35	
	3	-	89.57	-	41.42	21.75	3.82	24.69	8.32	



Figure 12. XRD patterns for SKF0.4 catalysts after reduction under different conditions (350 °C, 1.0 MPa).

To unveil the catalytic properties in FTS, the reactions using the SKF0.4 catalyst with H_2 and CO as the reaction gas were separately investigated. We obtained 86.36% CO conversion, but only 22.57% CH₄ and 22.1% light olefins. The selectivity of CO₂ up to 35.02% indicated the intense WGS reaction. Furthermore, the selectivity of light olefins had a limited increase with the increase in H_2/CO . As the XRD showed, the active phases of Fe₅C₂ and Fe₃O₄ were still generated with H_2 and CO as the reaction gas, the same as that under the CO₂ atmosphere. Obviously, the K-substituted SrFeO₃ enhanced the generation

of the active phase for both the RWGS and FTS in the presence of CO or CO₂. With H₂ and CO₂ as the reaction gas, a high CO₂ partial pressure restricted the WGS, resulting in higher light olefins (up to 29.61%). It should be pointed out that the CO selectivity was as high as 45.57%, even when the H₂/CO₂ molar ratio was equal to 4. Except for the catalysis of Fe₃O₄ on the RWGS, the redox properties of the SKFx catalysts elevated the conversion of CO₂ to CO. In addition, the FTS was the rate-determining step of the CO₂ hydrogenation reaction to light olefins with the SKFx perovskite catalysts, which should be enhanced in the future.

An ABO3-type perovskite SrFeO3 could be stepwise reduced to Sr2Fe2O5, and further to SrO and Fe, on the premise of being completely reversible, and oxidized to its perovskite structure. The H_2O/CO_2 splitting over SrO and Fe could produce H_2/CO via the reversible reaction (6) and (7). However, the realization of a deep reduction required a high temperature. The A-site substitution of Sr with K increased the lattice distortion, thereby decreasing the confinement of ions within the crystal structure. The increasing oxygen vacancy improved the adsorption of CO_2 on catalysts, furthering the generation of $SrCO_3$ and Fe_2O_3 via reaction (5). Generally, the formation of CO in the RWGS reaction has two controversial paths; i.e., a redox mechanism with the dissociation of adsorbed CO_2 as the rate-determining step, and the intermediates mechanism of carbonate and formate species [44]. In this work, apart from the catalytic properties of the acknowledged Fe_3O_4 , both the redox effect of Sr₂Fe₂O₅ on the CO₂ splitting and the formation of SrCO₃ carbonates were responsible for the enhanced RWGS. In addition, the reversible reaction (5) could regulate the CO₂ equilibrium to accommodate the FTS. The probable reaction mechanism of CO₂ hydrogenation to light olefins using K-substituting SKF0.4 catalysts is displayed in Figure 13. After being reduced by H_2 , the O_2 -deficient crystal structure $Sr_2Fe_2O_5$ was formed. Under the impact of K-substitution, Sr₂Fe₂O₅ reacted with CO₂ to generate SrCO₃ and Fe_2O_3 , and then produced the active-phase Fe_3O_4 and Fe_5C_2 . Furthermore, the redox properties of $Sr_2Fe_2O_5$ and the carbonate $SrCO_3$ promoted the RWGS. In addition, the reversible reaction (5) ensured the structural stability and high dispersion of the active phase. In sum, the SKFx perovskites exhibited immense potential for CO₂ hydrogenation to light olefins.

$$2SrO + 2Fe + 3CO_2 = Sr_2Fe_2O_5 + 3CO$$
(6)

$$2SrO + 2Fe + 3H_2O = Sr_2Fe_2O_5 + 3H_2$$
(7)



Figure 13. Mechanism of CO₂ hydrogenation on SKFx perovskite to generate products.

4. Conclusions

In light of their favorable thermal stabilities and redox activities, ABO₃-type perovskitederived catalysts of $Sr_{1-x}K_xFeO_3$ with a highly dispersed active site and enhanced RWGS reactivities were reported in this work. The following conclusions were drawn.

- (1) K-substitution using SKFx perovskite catalysts could promote the production of activephase Fe_3O_4 for the RWGS and Fe_5C_2 for the FTS. SKF0.4 displayed the optimal CO₂ conversion of 30.82% and light olefin selectivity of 29.61%.
- (2) Apart from the catalytic properties of the acknowledged Fe₃O₄, both the redox effect of the Sr₂Fe₂O₅ on the CO₂ splitting and the formation of SrCO₃ carbonates were responsible for the enhanced RWGS.
- (3) The reversible reaction $Sr_2Fe_2O_5 + 2CO_2 = 2SrCO_3 + Fe_2O_3$ ensured the structural stability and high dispersion of the active phase. As the rate-determining step of the CO_2 hydrogenation reaction to light olefins using SKFx perovskite catalysts, the FTS should be enhanced in the future by partially substituting the B-site of perovskite-type catalysts.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/atmos13050760/s1, Figure S1: SEM and EDS mapping of fresh SKF0.0 and SKF0.4.

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