Hydrogenation of carbon dioxide to light olefins over non-supported iron catalyst

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ABSTRACT

The hydrogenation of CO_2 to light olefins was investigated over non-supported Fe catalysts. It was found that the addition of alkali metal ions to the Fe catalyst led to significant increases in both the CO_2 conversion and the selectivity for olefins. Over K- or Rb-modified catalysts, about 40% CO_2 conversion and more than 50% olefin selectivity were obtained. The yield of C_2–C_4 olefins exceeded 10% over these modified catalysts. Catalyst characterization suggested that the formation of iron carbide species was accelerated by the modification of the Fe catalyst with alkali metal ions, and this enhancement may be one of the key reasons for the enhanced catalytic performance. For the K-modified Fe catalysts, K content has a major influence on the catalyst behavior. An increase in the K content from 1 to 5 wt% increased both CO_2 conversion and olefin selectivity. However, too high a K content led to a decrease in the activity, probably because of decreases in the surface area and CO_2 chemisorption capacity of the catalyst. The presence of an appropriate amount of B in the K-modified Fe catalyst was found to be beneficial to the olefin selectivity, without significantly decreasing the conversion of CO_2.

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1. Introduction

The use of CO_2 as a carbon resource for the production of fuels and chemicals not only contributes to the alleviation of global climate changes caused by growing CO_2 emissions, but also provides an attractive approach to reducing dependence on fossil fuel resources. Recently, many studies have been devoted to the catalytic conversion of CO_2 to hydrocarbons and oxygenates [1–8]. One promising route for the use of CO_2 is the selective production of light olefins by the hydrogenation of CO_2 with H_2 [9]. Generally, the hydrogenation of CO_2 by H_2 to hydrocarbons proceeds via two steps, i.e., the reduction of CO_2 to CO via the reverse water-gas shift (RWGS) reaction and subsequent CO hydrogenation, which is known as Fischer-Tropsch (FT) synthesis [10–12]. As efficient catalysts for both the RWGS reaction and FT synthesis [13,14], Fe-based catalysts have received much attention for the hydrogenation of CO_2 [15–20]. However, Fe catalysts alone are not suitable for FT synthesis as they produce undesired CH_4 as the main product, and rapid deactivation of the catalysts also occurs easily [13,14]. Many studies have therefore focused on supported Fe catalysts modified with electronic and/or structural promoters to enhance the catalytic activity and product selectivity. For example, a K-modified Fe/Al_2O_3 catalyst has been reported to provide CO_2 conversion of 69% and a C_2–C_4 olefin selectivity of 40%, with CH_4 selectivity of less than 20%, at 673 K [15]. Other additives,

e.g., Ce, Mn, and Cu, could also be used as promoters for Fe/Al_2O_3 or Fe/silicate-2 catalysts, which enhanced both CO_2 conversion and C_{2+} olefin selectivity [16–20].

To date, studies of non-supported Fe catalysts are scarce [21]. Fe is a relatively cheap metal, and it can be used as an industrial catalyst without a support. To simplify the catalytic system and to gain more straightforward information on the effects of promoters without the complication of the "support effect", we performed the hydrogenation of CO_2 to olefins over non-supported Fe catalysts. In the present paper, we report the effects of the modification of Fe catalysts with alkali metal ions on the catalyst structure and catalytic performance.

2. Experimental

2.1. Catalyst preparation

The non-supported Fe catalyst was prepared by calcining ammonium ferric citrate, i.e., $Fe(NH_4)_3(C_6H_5O_7)_2$, at 773 K for 5 h. The alkali-metal-ion-promoted Fe catalysts were prepared using ammonium ferric citrate and alkali metal nitrates as precursors. In brief, the required amounts of ammonium ferric citrate and alkali metal nitrate were dissolved in deionized water and stirred vigorously at room temperature for 6 h. Water was then evaporated from the mixed aqueous solution at 353 K with continuous stirring. The dried sample was calcined at 773 K in air for 5 h. B-modified catalysts were prepared using the same procedure, except for the addition of boric acid (H_3BO_3) to the mixed aqueous solution of alkali metal nitrate and ammonium ferric citrate.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Altima IV diffractometer with Cu K_α radiation (35 kV, 15 mA). The specific surface area of catalysts was measured by N_2 adsorption using a Micromeritics Tristar II 3020 instrument. Transmission electron microscopy (TEM) measurements were performed using a Tecnai F30 microscope at a voltage of 200 kV for all catalysts. The mean size of Fe (or iron oxide) particles was estimated from the TEM micrographs by counting ca. 100–200 particles. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Quantum 2000 Scanning ESCA Microprobe instrument using Al K_α radiation. The binding energy was calibrated using the C 1s photoelectron

peak at 284.8 eV as a reference.

CO_2 chemisorption measurements were performed at 323 K using a Micromeritics ASAP 2020 instrument. The sample (0.10 g) used for the chemisorption study was reduced at 673 K in an H_2 gas flow, followed by evacuation at the reduction temperature and then cooling to 323 K. The difference between the adsorption isotherms obtained by repeated use of a gas dosing and degassing system provided the amount of CO_2 chemisorbed on the catalyst.

2.3. Catalytic reaction

The hydrogenation of CO_2 was performed on a fixed-bed high-pressure stainless-steel reactor. The catalyst loaded in the reactor was first pretreated in an H_2 gas flow (50 ml/min) at 673 K for 5 h prior to reaction. After the reactor was cooled to 353 K, a mixture of $H_2/CO_2/Ar$ with a molar ratio composition of 69/23/8 was introduced into the reactor. The pressure was typically regulated to 2.0 MPa. The reaction was started by raising the temperature to the desired reaction temperature (typically 613 K). The products were analyzed using gas chromatography, and the results after 10 h of reaction were typically used for discussion.

3. Results and discussion

3.1. Catalytic performance of non-supported Fe catalysts

Table 1 shows the catalytic performance of Fe and alkali-metal-ion-modified Fe catalysts for the hydrogenation of CO_2. The Fe catalyst without modification exhibited very low activity and gave a CO_2 conversion of only 5.6% at 613 K. CH_4 and light (C_2–C_4) paraffins were the predominant products and no olefins were formed over the unmodified Fe catalyst. The modification of the Fe catalyst with an alkali metal ion significantly enhanced the catalytic performance for CO_2 hydrogenation. For example, the CO_2 conversion using an Li^+-modified Fe catalyst was four times higher than that achieved using the unmodified catalyst. The selectivity for CH_4 decreased significantly from 62% to 29%, and olefins were formed with a selectivity of about 35% in the hydrocarbon products. Over K^+- or Rb^+-modified Fe catalysts, the conversion of CO_2 and the olefin selectivity further increased to about 40% and 50%, respectively. The yield of light (C_2–C_4) olefins reached 10%–12%. The alkali metal ion therefore not only greatly promoted the con-

Table 1
Effects of various alkali metal ion modifiers on catalytic performance of Fe catalysts for hydrogenation of CO_2.

Modifier	CO_2 conversion (%)	Selectivity [a] (%)			Hydrocarbon distribution [b] (%)					C_{2-4}= yield (%)
		CO	HC	C-oxy	CH_4	C_{2-4}=	C_{2-4}^0	C_{5+}=	C_{5+}^0	
None	5.6	12	89	0.0	62	0.0	38	0.0	0.9	0.0
Li^+	27	17	73	10	29	30	30	4.8	5.5	5.8
Na^+	24	21	68	11	30	36	24	5.6	4.0	5.9
K^+	38	7.3	78	15	21	34	14	19	11	10
Rb^+	42	5.9	77	17	27	37	17	12	6.1	12
Cs^+	39	6.6	90	3.9	28	24	31	8.6	7.4	8.6

Reaction conditions: catalyst (alkali metal content = 5 wt%), 1.0 g; F = 20 ml/min; H_2/CO_2 = 3; p = 2 MPa; T = 613 K; t = 10 h.
[a] HC and C-oxy denote hydrocarbons and organic oxygenates, respectively.
[b] C_{2-4}= and C_{2-4}^0 denote C_2–C_4 olefins and paraffins, respectively, while C_{5+}= and C_{5+}^0 denote C_{5+} olefins and paraffins, respectively.

version of CO_2 but also significantly changed the product distributions in the hydrogenation of CO_2. The selectivities for CH_4 and C_2–C_4 paraffins were suppressed, whereas olefin selectivity, particularly C_2–C_4 olefins, was significantly enhanced. The yield of C_2–C_4 olefins increased in the following order: Fe < Li^+-modified Fe < Na^+-modified Fe < Cs^+-modified Fe < K^+-modified Fe < Rb^+-modified Fe. In other words, a catalyst modified with an alkali metal ion with a stronger basicity exhibits a more significant promoting effect for the hydrogenation of CO_2 to light olefins, except for the Cs^+-modified catalyst. To the best of our knowledge, this is the first report to demonstrate that considerable C_2–C_4 olefin yields can be achieved by simply modifying an Fe catalyst with an alkali metal ion.

Although the Rb^+-modified catalyst gave the best yield of C_2–C_4 olefins, the K^+-modified Fe catalyst was also efficient and was much cheaper than the Rb^+-modified catalyst. We therefore further investigated the effect of the K content on the catalytic performance of the K^+-modified Fe catalysts for the hydrogenation of CO_2. Table 2 shows that, with increasing K content up to 5 wt%, the conversion of CO_2 and the olefin selectivity increased rapidly, and the CH_4 selectivity decreased sharply. The highest C_2–C_4 olefin yield was achieved over the catalyst with a K content of 5–10 wt%. Further increases in the K content led to decreases in the conversion of CO_2 and yield of C_2–C_4 olefins. An appropriate K/Fe ratio was required to obtain high olefin yields from CO_2 hydrogenation.

We found that the catalytic performance, particularly the C_2–C_4 olefin selectivity, could be further promoted to some extent by B-doping of the Fe catalyst modified with 5 wt% K^+. As shown in Table 3, the addition of a small amount of B (≤1.0 wt%) to the 5-wt%-K^+-modified Fe catalyst did not change, or slightly increased, the conversion of CO_2. However, as the content of B increased to ≥3 wt%, significant decreases in CO_2 conversion were observed. The interesting point is that modi-

fication with B can modify the product distribution. In particular, with increasing B content from 0.5 wt% to 5.0 wt%, the selectivity for C_2–C_4 olefins increased from 34% to 52%. The C_2–C_4 olefin selectivity and yield were 40% and 12%, respectively, over the 1.0 wt% B–5.0 wt% K^+–Fe catalyst. However, when the content of B rose to ≥3.0%, the CO selectivity increased from <10% to 19%–28%, and that for hydrocarbons decreased to 65%–75%. Because of this and the decrease in CO_2 conversion, catalysts with higher B contents (>1 wt%) did not give higher yields of C_2–C_4 olefins. In spite of this, modification with an appropriate amount of B (1.0–5.0 wt%) decreased the selectivity for C_{5+} hydrocarbons and increased that for C_2–C_4 olefins, without increasing that for CH_4.

3.2. Characterization of non-supported Fe catalysts

Figure 1 shows the XRD patterns of the Fe catalysts with and without alkali metal ion modifications. Analyses of the diffraction patterns in Fig. 1(a) reveal that magnetite (Fe_3O_4) and hematite (Fe_2O_3) co-exist in all of the fresh catalysts. The relatively strong intensities of the XRD peaks ascribed to Fe_3O_4 suggest that Fe_3O_4 is the main crystalline phase in all the alkali-metal-ion-modified Fe catalysts. The diffraction peaks of Fe_3O_4 and Fe_2O_3 for the unmodified Fe catalyst were narrower and sharper than those for the Fe catalysts modified with alkali metal ions (Fig. 1(a)). This indicates decreases in the sizes of the Fe_3O_4 and Fe_2O_3 crystallites after modification with alkali metal ions. We calculated the size of the Fe_3O_4 crystallites from the Scherrer equation using the (311) facet of Fe_3O_4. The results showed that the size of the Fe_3O_4 crystallites in the 5-wt%-K^+-modified Fe catalyst was about 17 nm, smaller than that (27 nm) in the unmodified Fe catalyst. No diffraction peaks corresponding to alkali metal compounds were detected in the XRD patterns. It is probable that the alkali metal ions are highly

Table 2

Catalytic performance of K^+-modified Fe catalysts with different K contents for hydrogenation of CO_2.

K content (wt%)	CO_2 conversion (%)	Selectivity (%)			Hydrocarbon distribution (%)					$C_{2-4}^=$ yield (%)
		CO	HC	C-oxy	CH_4	$C_{2-4}^=$	C_{2-4}^0	$C_{5+}^=$	C_{5+}^0	
0	5.6	12	88	0.0	62	0.0	38	0.0	0.9	0.0
1.0	5.0	10	89	1.3	45	2.1	48	0.1	5.2	0.1
2.0	37	5.8	86	7.8	28	25	34	6.8	3.4	7.9
5.0	38	7.3	78	15	21	34	14	19	11	10
10	27	7.2	89	4.3	22	39	13	18	7.2	9.3
16	25	8.3	79	13	23	37	18	21	6.7	7.3
32	25	20	71	9.6	24	36	11	22	6.5	6.3

Reaction conditions: catalyst, 1.0 g; F = 20 ml/min; H_2/CO_2 = 3; p = 2 MPa; T = 613 K; t = 10 h.

Table 3

Effect of B modification on catalytic performance of 5-wt%-K^+-modified Fe catalysts.

B content (wt%)	CO_2 conversion (%)	Selectivity (%)			Hydrocarbon distribution (%)					$C_{2-4}^=$ yield (%)
		CO	HC	C-oxy	CH_4	$C_{2-4}^=$	C_{2-4}^0	$C_{5+}^=$	C_{5+}^0	
0	38	7.3	78	15	21	34	14	19	11	10
0.5	43	6.4	81	13	22	34	18	13	12	12
1.0	38	7.6	79	13	23	40	18	10	8.6	12
3.0	25	26	68	6.8	19	52	17	8.1	3.9	8.8
5.0	23	29	65	5.8	19	52	20	6.9	3.0	7.6
6.0	22	19	74	6.9	36	33	25	3.4	3.0	5.3
8.0	21	21	75	4.7	51	19	27	1.2	1.9	3.0

Reaction conditions: catalyst (B- and K^+-modified Fe), 1.0 g; F = 20 ml/min; H_2/CO_2 = 3; p = 2 MPa; T = 613 K; t = 10 h.
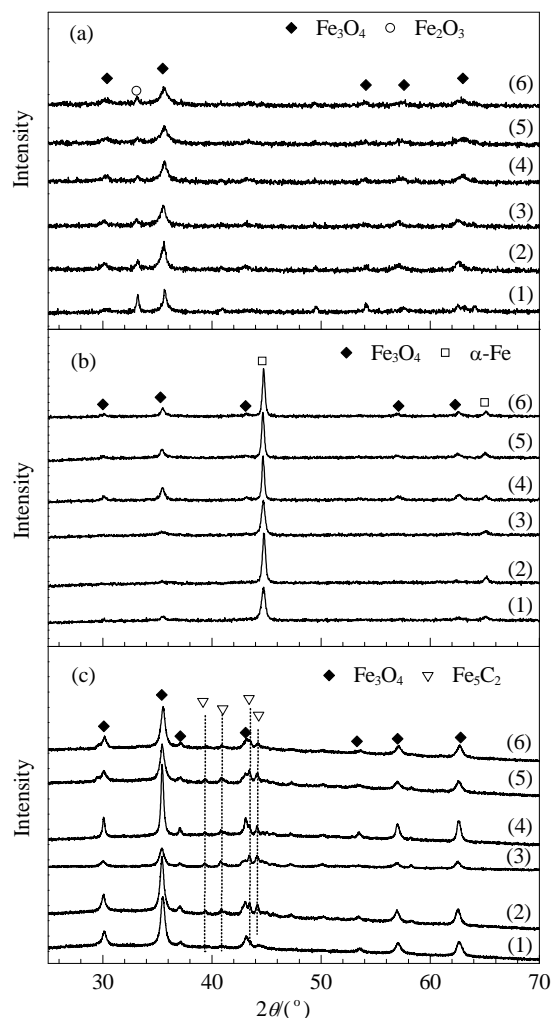
Fig. 1. XRD patterns of Fe catalysts with and without alkali metal ion modifications. (a) Before reaction; (b) After reductive treatment in H_2 at 673 K; (c) After 10 h of reaction under the following conditions: $H_2/CO_2/Ar$ = 69/23/8, p = 2 MPa, T = 613 K. (1) Fe; (2) 5 wt% Li-Fe; (3) 5 wt% Na-Fe; (4) 5 wt% K-Fe; (5) 5 wt% Rb-Fe; (6) 5 wt% Cs-Fe.

dispersed in the modified catalysts and may interact with iron oxide particles, preventing the growth of iron oxide particles during calcination.

After reductive treatment in H_2 at 673 K, a key step for catalyst activation, all of the samples displayed diffraction peaks at 2θ values of 44.7° and 65.0°, which could be ascribed to crystalline α-Fe. The stronger intensity of the XRD peak at a 2θ value of 44.7° suggests that α-Fe is the major phase in all the catalysts (Fig. 1(b)). This indicates that a large part of the Fe_3O_4 and Fe_2O_3 in the fresh catalysts has been reduced to α-Fe after reduction in H_2 at 673 K. However, some Fe_3O_4 was still detectable in the reductively treated catalysts.

After catalytic reaction for 10 h, Fe_3O_4 became the major crystalline phase in all the catalysts (Fig. 1(c)). Moreover, new diffraction peaks at 2θ values of 44.2° and 43.4° were observed in the alkali-metal-ion-modified Fe catalysts. However, these peaks were not clearly observed in the used unmodified Fe catalyst. These peaks could be assigned to the (021) and (510) reflections of crystalline χ-Fe_5C_2 [22]. This observation suggests

that the alkali metal ions accelerate generation of the χ-Fe_5C_2 phase in the catalysts after reaction.

The XRD patterns of K^+-modified Fe catalysts with different K contents are displayed in Fig. 2. Only iron oxide (i.e., Fe_3O_4 and Fe_2O_3) phases were observed for all the fresh catalysts (Fig. 2(a)). No diffraction peaks of K-related compounds were detected using XRD, even for the catalyst with a very high K content (32 wt%). Figure 2(b) shows that the content of K exerts little influence on the reduction of iron oxides to α-Fe. After the catalytic reaction at 613 K, the diffraction peaks attributed to the χ-Fe_5C_2 phase appeared in all the K-modified Fe catalysts with different K contents (Fig. 2(c)). This is further evidence that K promotes formation of iron carbide species. A weak diffraction peak attributable to K_2O was observed for the catalyst with a K content of 32 wt% (Fig. 2(c), curve (7)), and the intensities of the diffraction peaks of Fe_3O_4 decreased when the content of K increased to 32 wt%.

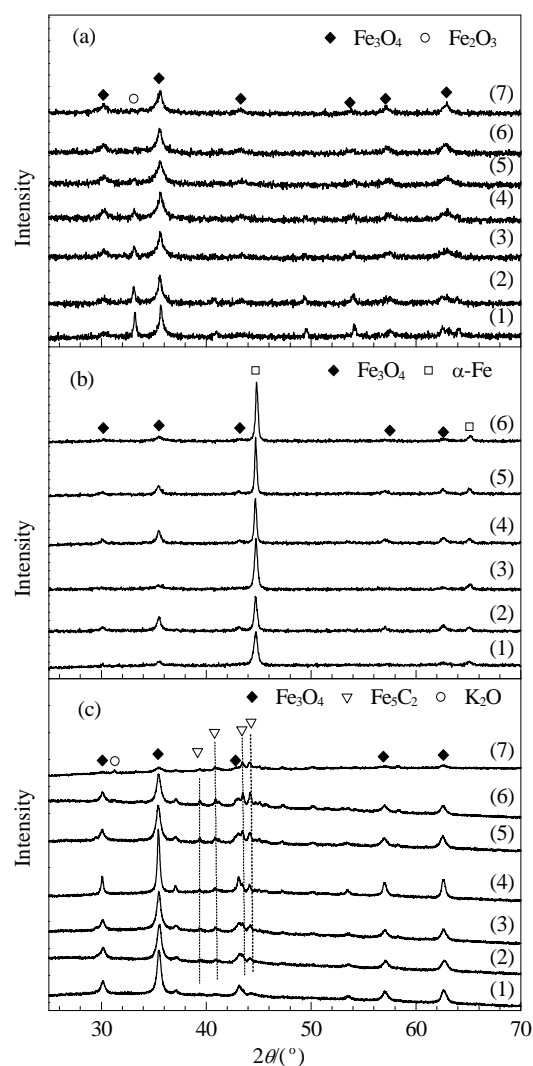The addition of B to the 5-wt%-K-modified Fe catalyst

Fig. 2. XRD patterns of K^+-modified Fe catalysts with different K^+ contents. (a) Before reaction; (b) After reductive treatment in H_2 at 673 K; (c) After 10 h of reaction under the following conditions: $H_2/CO_2/Ar$ = 69/23/8, p = 2 MPa; T = 613 K. (1) Fe; (2) 1 wt% K-Fe; (3) 2 wt% K-Fe; (4) 5 wt% K-Fe; (5) 10 wt% K-Fe; (6) 16 wt% K-Fe; (7) 32 wt% K-Fe.

changed the XRD pattern. As shown in Fig. 3, all of the diffraction peaks ascribed to iron oxides were broadened by the presence of B in the K⁺-modified Fe catalyst. Moreover, the hematite (Fe_2O_3) phase in the fresh catalyst disappeared immediately after the introduction of B into the K⁺-modified Fe catalyst, and only the magnetite (Fe_3O_4) phase was detectable by XRD (Fig. 3(a)). Figure 3(b) shows that the ratio of the intensity of the strongest diffraction peak of α-Fe to that of Fe_3O_4 decreases with increasing B content, implying that the reduction of Fe_3O_4 in a H_2 flow at 673 K becomes more difficult in the presence of a B modifier. After the catalytic reactions, the formation of the χ-Fe_5C_2 phase in the B-modified samples was still clearly observed although the intensities of all the diffraction peaks were weaker (Fig. 3(c)).

Further investigations revealed that the surface area and the amount of CO_2 chemisorption changed after modification of the Fe catalyst with K⁺ and/or B. As shown in Table 4, although no
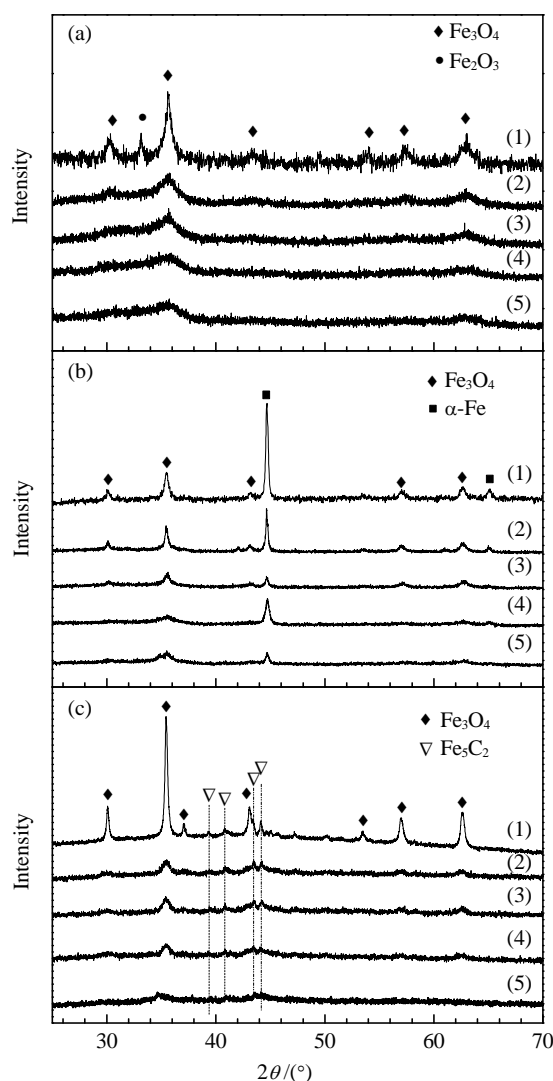
Table 4
Surface areas and amounts of CO_2 chemisorption for fresh Fe catalysts modified with different amounts of K and B.

Catalyst	Surface area (m²/g)	Amount of CO_2 chemisorption (μmol/g)
Fe	54	116
1 wt% K-Fe	67	116
5 wt% K-Fe	63	218
10 wt% K-Fe	54	126
16 wt% K-Fe	21	52
1 wt% B-5 wt% K-Fe	95	220
3 wt% B-5 wt% K-Fe	122	184
5 wt% B-5 wt% K-Fe	117	133
8 wt% B-5 wt% K-Fe	120	99

support was used in our study, a specific surface area of 54 m²/g was attained for the non-modified Fe catalyst prepared by calcination of ammonium ferric citrate. Compared with the conventional precipitation method or the microemulsion technique for the preparation of Fe catalysts [21], this simple procedure is an effective way of obtaining non-supported Fe materials with relatively high surface area. After the addition of a low amount of K⁺ (1–5 wt%), the surface area of the catalyst is larger than that of the unmodified Fe catalyst. We speculate that a lower content of alkali metal ions may help to disperse iron oxides, thus avoiding the growth of iron oxide particles during calcination. This was supported by calculation of the crystallite size of Fe_3O_4 from the XRD patterns in Fig. 1(a). Furthermore, the TEM images shown in Fig. 4 confirm that the mean size of iron oxide particles decreased from 30.9 nm to 11.1 nm as a result of modification with K⁺. However, too high a K content led to a decrease in the surface area (Table 4). Recently, Dorner et al. [23] reported that K species could form a monomer layer on Fe surfaces when 8 wt% K was loaded on a 17 wt% Fe-Mn/Al_2O_3 catalyst. Although Al_2O_3 was used as the support in their case, the K⁺ was still found to cover the Fe surface preferentially. It is also interesting that the addition of B to the 5-wt%-K-modified Fe catalyst significantly increased the surface area. The surface area rose to about 120 m²/g with increasing B content to 3 wt%. A further increase in the B content did not change the surface area significantly. The mean size of the iron oxide particles in the 1 wt% B-5 wt% K-modified Fe catalyst was 11.0 nm (Fig. 4).

Table 4 also shows that the amount of CO_2 chemisorption is significantly enhanced by the addition of 5–10 wt% K⁺ to the Fe catalyst. The degree of increase in the amount of CO_2 chemisorption for the 5 wt% K⁺-modified catalyst was larger than that in the surface area. This is believed to be caused by increased surface basicity as a result of the introduction of K⁺ in the catalyst. With further increases in the K⁺ content, the amount of CO_2 chemisorption decreased, probably because of a decrease in the surface area. For the B-K-Fe series of catalysts, the amount of CO_2 chemisorption decreased with increasing B content. Generally, B has an acidic character, and thus the basicity of the 5-wt%-K⁺-modified catalyst decreased on addition of acidic B.

Figure 5 shows the XPS spectra of the Fe catalysts modified with different amounts of K and B. For all the catalysts modified with K⁺, the binding energies of K $2p_{3/2}$ and K $2p_{1/2}$ were locat-
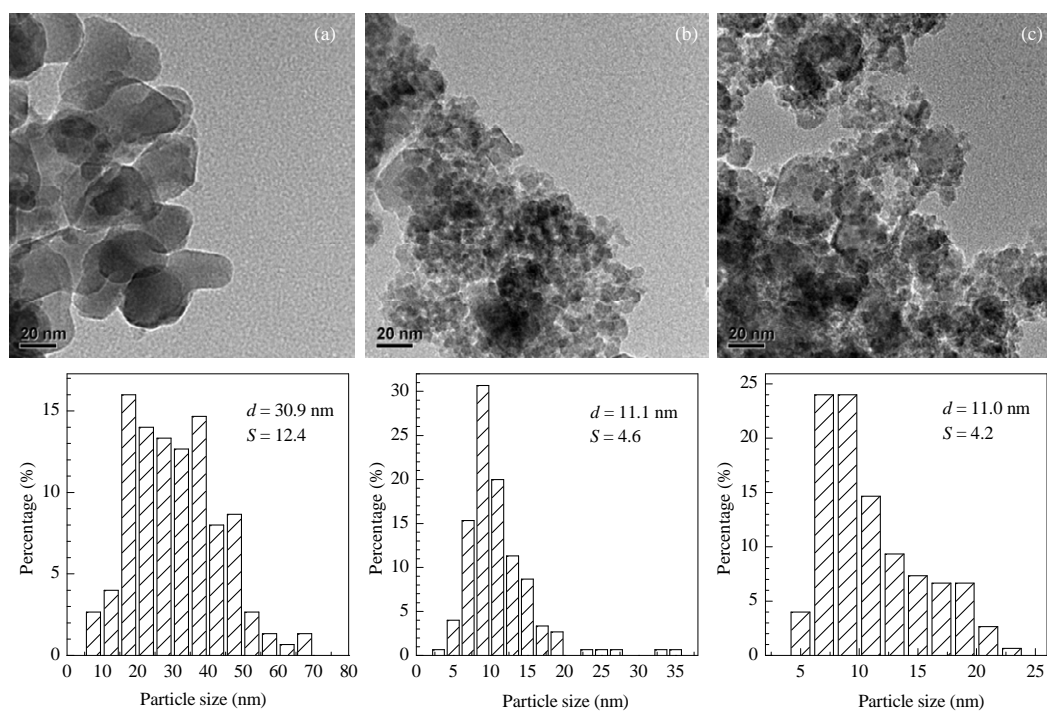
Fig. 3. XRD patterns of B-doped 5 wt% K-Fe catalysts with different B contents. (a) Fresh catalyst; (b) After reductive treatment in H_2 at 673 K; (c) After 10 h of reaction under the following conditions: $H_2/CO_2/Ar$ = 69/23/8, p = 2 MPa; T = 613 K. (1) 5 wt% K-Fe; (2) 1 wt% B-5 wt% K-Fe; (3) 3 wt% B-5 wt% K-Fe; (4) 5 wt% B-5 wt% K-Fe; (5) 8 wt% B-5 wt% K-Fe.

Fig. 4. TEM images and particle size distribution of Fe (a), 5 wt% K-Fe (b), and 1 wt% B-5 wt% K-Fe (c). *d* and *S* denote mean size and standard deviation, respectively.
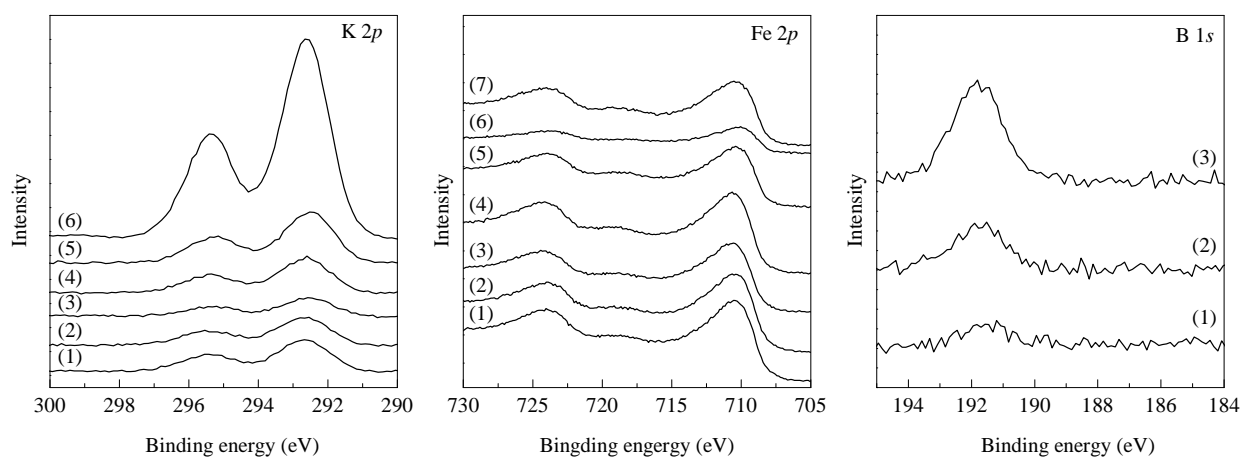

Fig. 5. XPS spectra of fresh Fe catalysts modified with different amounts of K+ and B. (1) 1 wt% B-5 wt% K-Fe; (2) 3 wt% B-5 wt% K-Fe; (3) 8 wt% B-5 wt% K-Fe; (4) 5 wt% K-Fe; (5) 16 wt% K-Fe; (6) 32 wt% K-Fe; (7) Fe.

ed at 292.6 eV and 295.4 eV, respectively, suggesting that K_2O was the dominant K species on the catalyst surfaces. We calculated the K/Fe atomic ratios for the K-Fe catalysts using the XPS results (Table 5). Over the catalysts with 5–16 wt% K, the surface and bulk K/Fe ratios were very close. However, as the K content increased to 32 wt%, the K/Fe ratio on the surface reached 2.0 and became significantly larger than that in the bulk (0.67). This indicates that the catalyst surface is covered by excess K_2O; this is in agreement with the XRD observations (Fig. 2).

It is also clear that the introduction of B into the K-Fe catalyst does not change the oxidation states of K and Fe (Fig. 5). The peak at a binding energy of 191.8 eV, for B 1*s*, which is assignable to B_2O_3 [24], can be detected for all the B-doped catalysts. Comparison of the B/Fe and K/Fe ratios for the B-K-Fe

catalysts clearly suggests that the B species are preferentially located in the bulk of the catalyst, irrespective of the amount of

Table 5

Atomic ratios of K/Fe and B/Fe for fresh Fe catalysts modified with different amounts of K and B.

Catalyst	K/Fe atomic ratio		B/Fe atomic ratio	
	Calculated[a]	Measured[b]	Calculated[a]	Measured[b]
5 wt% K-Fe	0.075	0.090	—	—
16 wt% K-Fe	0.27	0.24	—	—
32 wt% K-Fe	0.67	2.0	—	—
1 wt% B-5 wt% K-Fe	0.076	0.072	0.055	0.041
3wt% B-5 wt% K-Fe	0.078	0.083	0.17	0.13
8 wt% B-5 wt% K-Fe	0.082	0.067	0.48	0.34

[a] Calculated from the amounts of materials used for preparation.
[b] Measured by XPS.

B, whereas the K species are probably well dispersed throughout the catalyst (Table 5).

3.3. Roles of K and B modifications

The modification of the Fe catalyst with an appropriate amount of K^+ significantly enhanced the conversion of CO_2 (Tables 1 and 2). The selectivity for CO decreased, and that for hydrocarbons and organic oxygenates increased. This implies that not only the activation and conversion of CO_2 but also the subsequent conversion of CO to hydrocarbons and organic oxygenates was accelerated by the modification with K^+ and other alkali metal ions because the hydrogenation of CO_2 to hydrocarbons is believed to involve two steps, i.e., the RWGS reaction and subsequent CO hydrogenation. The enhanced CO_2 chemisorption as a result of the presence of K^+ may be one of the reasons for the increase in the conversion of CO_2. It is also possible that the adsorption of CO_2 on K-, Rb-, or Cs-modified Fe catalysts with stronger basicities is easier than that on Li- or Na-modified Fe catalysts, and thus the first set of catalysts gave higher CO_2 conversions.

However, it is well known that K^+ promotes activity in CO hydrogenation, i.e., FT synthesis [13]. Many studies have proposed an electronic promoting effect of K^+ [13]. The K may weaken the bonds of CO adsorbed on Fe by increasing the electronic density of Fe particles, which can then be back-donated to the anti-bonding orbital of CO, leading to increased dissociation of CO. Strongly basic alkali metal ions, including K^+, Rb^+ and Cs^+, may therefore function as electronic promoters for the enhancement of CO conversion; this is supported by the lower selectivity for CO over these modified catalysts (Table 1).

Our XRD results suggest that modification with K^+ enhances generation of the χ-Fe_5C_2 phase during the reaction (Figs. 1 and 2). Many studies have proposed that the χ-Fe_5C_2 phase is the active phase for FT synthesis over Fe-based catalysts [22,25,26]. Although the magnetite (Fe_3O_4) phase, which was previously suggested to be the active phase in FT synthesis [14], was observed in all the catalysts, the low activity of the non-modified Fe catalyst in CO_2 hydrogenation (Table 1) allowed us to exclude the possibility of Fe_3O_4 as the active phase. We therefore speculate that K^+ and other alkali metals accelerate CO conversion by accelerating formation of the χ-Fe_5C_2 phase.

Furthermore, the product distribution in the hydrocarbon products was changed significantly by modification with K^+ or other alkali metal ions (Tables 1 and 2). The significant decreases in the selectivities for CH_4 and C_2–C_4 paraffins, and the increases in those for C_2–C_4 olefins and C_{5+} hydrocarbons (particularly C_{5+} olefins), clearly indicate that the hydrogenation ability decreases and the chain-growth ability increases in the presence of K^+ or other alkali metal ion modifiers. We speculate that the enhanced CO adsorption and dissociation ability in the presence of K^+ may lower the adsorption of H_2 on the catalyst surface and thus decrease the hydrogenation ability.

Concerning the role of B, the addition of a small amount of B to the 5-wt%-K^+-modified Fe catalyst slightly increased the conversion of CO_2, possibly because of the increased specific surface area. However, when the content of B became ≥3 wt%, decreases in CO_2 conversion were observed (Table 3). We speculate that this is caused by a decrease in the amount of CO_2 chemisorption (Table 4) as a result of the acidic character of B. It is interesting that modification of the 5-wt%-K^+-modified Fe catalyst with B significantly suppressed the formation of C_{5+} hydrocarbons, but the selectivity for CH_4 was not enhanced (Table 3). For example, the selectivity for C_{5+} hydrocarbons decreased from 30% to 19%, whereas that for C_2–C_4 olefins increased from 34% to 40% after the addition of 1.0 wt% B to the 5 wt% K-Fe catalyst. The selectivity for C_2–C_4 olefins further increased to 52% when the B content was increased to 3 wt%, but the CO_2 conversion decreased. In an early work, Li et al. [27] observed that the products shifted to lower-molecular-weight hydrocarbons, particularly C_2–C_4, on B-doping of a Co-based catalyst during FT synthesis. The increased fraction of cobalt oxide to metallic Co or the decreased reducibilities of the Co catalysts in the presence of B were suggested to be responsible for the change in product selectivity. In our case, we still do not have a satisfactory explanation for the role of B in regulating the product selectivity. Future studies are needed to clarify the role of B.

4. Conclusions

The hydrogenation of CO_2 to light (C_2–C_4) olefins was studied over non-supported Fe catalysts. We found that modification of the Fe catalyst, which was prepared by calcining ammonium ferric citrate, with alkali metal ions significantly enhanced the conversion of CO_2 and the selectivity for C_2–C_4 olefins. The selectivity for C_{5+} hydrocarbons, particularly C_{5+} olefins, was also enhanced by the addition of an alkali metal ion. The formation of CH_4 and C_2–C_4 paraffins was largely suppressed. The fresh catalyst without modification contained iron oxide (Fe_3O_4 and Fe_2O_3) phases, which were transformed into α-Fe together with a small amount of Fe_3O_4 after reduction in H_2 at 673 K. This was also the case for the catalyst modified with an alkali metal ion, but the size of the iron oxide particles in the fresh catalyst was smaller after modification. After reaction under the specified reaction conditions, the formation of χ-Fe_5C_2 occurred over the alkali-metal-ion-modified Fe catalysts, but iron carbide species were not observed in the unmodified catalyst after the reaction. The generation of iron carbide species in the presence of an alkali metal ion was proposed to be one reason for the enhanced catalytic performance. The increase in the amount of CO_2 chemisorption as a result of the presence of K^+ may also contribute to the increased CO_2 conversion. The content of K^+ also affected the catalytic performance. If the K content was too high, this led to a decrease in the surface area and the amount of CO_2 chemisorption and thus decreased the conversion of CO_2. We found that the addition of a small amount of B to the K-modified Fe catalyst could suppress the formation of C_{5+} hydrocarbons and increase the selectivity for C_2–C_4 hydrocarbons, without significantly increasing the selectivity for CH_4. With an appropriate B content, the selectivity for C_2–C_4 olefins reached 52%. This provided another possibility for regulating the product distribution.

Graphical Abstract

Hydrogenation of carbon dioxide to light olefins over non-supported iron catalyst

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The modification of a non-supported Fe catalyst by alkali metal ions, particularly K+, in combination with a small amount of B, significantly enhanced the hydrogenation of CO2 to light olefins.

CO2 /H2 — Fe modified by K and B — K-B-Fe — C2-C4 olefins Select.: 40%-52% — methane Select.: 62% — Non-supported Fe
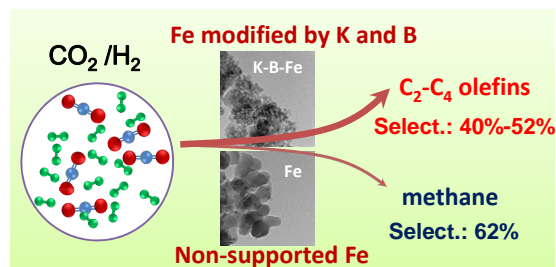
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非负载型铁催化剂上二氧化碳加氢制低碳烯烃

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摘要：研究了非负载型铁催化剂上CO2加氢制低碳烯烃反应. 结果显示, 添加碱金属可显著提高铁催化剂上的CO2转化率和烯烃选择性. 在经K和Rb修饰的Fe催化剂上, CO2转化率可达约40%, 烯烃选择性达到50%以上, 其中C2~C4烯烃收率超过10%. 催化剂表征结果表明, 碱金属促进了催化剂中碳化铁的生成, 这可能是催化剂性能提高的一个关键原因. 随着K含量由1 wt%增加至5 wt%, CO2转化率及烯烃选择性均升高. 但K含量过高时, 催化剂活性降低. 这可能是由于催化剂比表面积和CO2化学吸附量降低所致. 当K含量为5%~10%时, K-Fe催化剂上烯烃收率较高; 进一步添加适量的硼可进一步提高烯烃选择性, 且CO2转化率下降不大.

关键词：二氧化碳; 加氢反应; 低碳烯烃; 铁催化剂