

# Hydrogenation of Carbon Dioxide over K-Promoted FeCo Bimetallic Catalysts Prepared from Mixed Metal Oxalates

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The hydrogenation of carbon dioxide over K-promoted FeCo bimetallic catalysts prepared by sequential oxalate decomposition and carburization of FeCo with CO was studied in a fixedbed reactor at 240 °C and 1.2 MPa. The initial CO<sub>2</sub> conversion was found to be dependent on K loading, whereas both unpromoted and K-promoted FeCo catalysts (except 90Fe10Co3.0K) exhibited similar levels of CO<sub>2</sub> conversion after a few hours of time on stream. A decarburization study on freshly activated and used FeCo suggests that potassium in-

Introduction

The increase in CO<sub>2</sub> emissions with industrialization and the resulting greenhouse effect have given rise to ever-increasing concerns about the disposal of CO<sub>2</sub>. The chemical transformation of CO<sub>2</sub> into fuels and chemicals is a topic of interest for many.<sup>[1-5]</sup> Hydrogenation of carbon dioxide to form higher hydrocarbons is one way of utilizing CO2.<sup>[6-8]</sup> Various catalysts based on Fe,<sup>[9]</sup> Co,<sup>[10]</sup> Ni,<sup>[11]</sup> and Ru<sup>[12]</sup> metals were tested for this reaction, and all catalysts, except for those based on iron, produced solely methane.<sup>[13]</sup> It seems likely that the transformation of carbon dioxide into higher hydrocarbons proceeds mainly by reverse water-gas shift (RWGS), which makes CO from CO<sub>2</sub>, with the carbon monoxide that is produced reacting subsequently by Fischer-Tropsch (FT) synthesis to produce mostly hydrocarbons. Fe-based FT catalysts possess WGS/ RGWS activity under typical FT-synthesis conditions, which makes iron a suitable candidate for CO<sub>2</sub> conversion.<sup>[14]</sup>

Iron FT catalysts are often promoted by alkali metals such as potassium<sup>[15,16]</sup> and structural promoters, for example, SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>,<sup>[17]</sup> as well as reduction promoters such as copper;<sup>[18]</sup> promotion effects include higher conversion and C<sub>5</sub>+ selectivity for CO hydrogenation. Similarly, a promoter effect of potassium for CO<sub>2</sub> hydrogenation has also been reported.<sup>[19-21]</sup> An early work from Küster<sup>[22]</sup> showed that alkali-promoted Fe and Co

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creases the stability of iron carbides and graphitic carbon under a reducing atmosphere. Also, K addition tends to decrease the hydrogenation function of FeCo bimetallic catalysts and, thus, controls product selectivity. Under similar CO<sub>2</sub> conversions, potassium enhanced acetic acid formation while suppressing ethanol production, which indicates that a common intermediate might be responsible for the changes observed with C<sub>2</sub> oxygenates.

catalysts yielded a small amount of oil from CO<sub>2</sub> hydrogenation; however, the authors found only methane from an alkalipromoted, Kieselguhr-supported FT catalyst. In another study, Cubeiro et al.<sup>[23]</sup> obtained higher olefin selectivity for C<sub>2</sub>-C<sub>4</sub> hydrocarbons with K-promoted Fe catalysts obtained by thermal decomposition of iron citrate. Fierro and co-workers<sup>[24]</sup> have shown that alkali addition promotes long-chain hydrocarbon products for both CO and  $\text{CO}_2$  hydrogenation processes. The authors concluded that CO<sub>2</sub> conversion was favored by alkali addition, especially addition of potassium, as a result of the promotion of the water-gas shift reaction.

In an early study, Stowe and Russell<sup>[25]</sup> used cobalt, iron, and some of their alloys as catalysts for the hydrogenation of carbon dioxide. Satthawong et al.<sup>[26]</sup> performed CO<sub>2</sub> hydrogenation over K-promoted alumina-supported FeCo bimetallic catalysts, and these authors found that the selectivity for light olefins increased with K addition. They correlated this with weaker adsorption of hydrogen on the metal surfaces. In a recent study, we showed that FeCo bimetallic catalysts offer advantages for CO<sub>2</sub> hydrogenation over monometallic catalysts (Fe or Co) for the production of higher  $C_2$  + hydrocarbons.<sup>[27]</sup> In a continuation of this vein of research, in this work, the effect of potassium on FeCo-catalyzed CO<sub>2</sub> hydrogenation was explored. The FeCo bimetallic catalyst was prepared by decomposition of metal oxalates and carburization with CO. The effects of K content on the carburization rate of FeCo and catalyst performance parameters (that is, stability, activity, and selectivity) for CO<sub>2</sub> hydrogenation were investigated.

# **Results and Discussion**

The detailed elemental analyses of K-promoted FeCo bimetallic oxalates are shown in Table 1. The ratios of Co/Fe and K/(Fe+

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| Table 1. Elemental analysis by ICP-OES.      |  |      |                           |                   |               |  |  |  |  |  |  |
|--|--|------|---------------------------|-------------------|---------------|--|--|--|--|--|--|
| Catalyst                                     | Elemental composition [wt%]<br>Fe Co K |      | ${\sf Co}/{\sf Fe}^{[a]}$ | $K/(Fe+Co)^{[a]}$ |               |  |  |  |  |  |  |
| 90Fe10Co0K                                   | 86.2                                   | 10.3 | 0.0                       | 0.11 (0.11)       | 0.0 (0)       |  |  |  |  |  |  |
| 90Fe10Co0.5K                                 | 81.4                                   | 9.7  | 0.3                       | 0.11 (0.11)       | 0.005 (0.005) |  |  |  |  |  |  |
| 90Fe10Co1.0K                                 | 74.6                                   | 10.0 | 0.7                       | 0.13 (0.11)       | 0.012 (0.01)  |  |  |  |  |  |  |
| 90Fe10Co2.0K                                 | 77.9                                   | 9.8  | 1.2                       | 0.12 (0.11)       | 0.020 (0.02)  |  |  |  |  |  |  |
| 90Fe10Co3.0K                                 | 79.5                                   | 8.7  | 1.6                       | 0.10 (0.11)       | 0.026 (0.03)  |  |  |  |  |  |  |
| [a] Theoretical ratios given in parenthesis. |  |      |                           |                   |               |  |  |  |  |  |  |

Co) for various catalysts obtained by ICP-OES match very well with those of the theoretical values according to the formula of  $Fe_{0.9}Co_{0.1}(C_2O_4)\cdot 2H_2O$ .

Reference [28] provides details about the Mössbauer fitting procedure. Mössbauer spectroscopy results (Table 2 and Figure 1) for the unpromoted catalyst (90Fe10Co0K) indicate that 56% of iron is present as Hägg carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>) and 22%

Table 2. Phase compositions of Fe for freshly carburized and used catalysts. Results obtained by using Mössbauer spectroscopy measured at T=-253 °C. Fresh [% Fe]<sup>[a]</sup> Used [% Fe]<sup>[a]</sup> Catalyst χ-Fe₅C<sub>2</sub> Fe<sub>3</sub>O<sub>4</sub> Fe<sub>3</sub>O₄ χ-Fe₅C<sub>2</sub>  $\epsilon'$ -Fe<sub>2.2</sub>C  $\varepsilon'$ -Fe<sub>22</sub>C 90Fe10Co0K 56 22 39 45 22 16 90Fe10Co0.5K 22 51 27 36 39 25 90Fe10Co1K 30 24 44 26 44 32 90Fe10Co2K 28 46 26 28 42 30 90Fe10Co3K 31 44 25 32 34 34

[a] Uncertainty in these numbers varies by 3-5%



**Figure 1.** Mössbauer spectra of fresh (left), and used (right) 90Fe10Co(*x*)K catalysts (*x*=0.0, 0.5, 1.0, 2.0, and 3.0) performed at *T*=-253 °C after catalyst pretreatment in a CO flow at *T*=250 °C and *P*=1.2 MPa The fitted curves are shown as solid lines: black, total spectra; red, Fe<sub>3</sub>O<sub>4</sub>; blue,  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>; green,  $\epsilon$ '-Fe<sub>22</sub>C.

is epsilon carbide ( $\epsilon$ -Fe<sub>2.2</sub>C), with the remaining 22% of iron in the magnetite form. The concentration of Hägg carbide was found to decrease with the increase in K content in the catalyst, whereas the epsilon carbide content increased slightly. The magnetite phase slightly increased with increasing K content. Cubeiro et al.<sup>[23]</sup> obtained a similar trend over thermally decomposed iron citrate promoted with potassium. The authors observed a slight decrease in iron carbide content with an increase in K loading.

The X-ray diffraction patterns for the freshly carburized catalysts are shown in Figure 2. Diffraction patterns corresponding to iron carbide and magnetite phases were observed for all catalysts. The presence of the magnetite phase is slightly dominant with higher K contents. The XRD pattern corresponding to the low-temperature iron carbide is usually either composed of very small crystallites or is very distorted, which results in the XRD patterns looking broader in nature. Similarly, in this case, FeCo bimetallic oxalates decomposed to ferrites, which



**Figure 2.** XRD patterns of freshly activated samples of 90Fe10Co(*x*)K in CO at T=250 °C and 0.10 MPa pressure (top) and of used catalysts (bottom).

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then carburized in CO at T=250 °C; notably, this temperature is approximately 20 °C less than the typical carburization temperature of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is 270 °C. The peaks corresponding to the iron carbide phase appear very broad and are not very intense.

The carbon deposits and carbides formed under our activation conditions were investigated by temperature-programmed decarburization. This method gives information about the relative amount and stability of various surface carbon species formed after carburization and during the reaction. Figure 3 shows the decarburization profiles of the unpromoted and K-promoted 90Fe10Co catalysts after activation (top) and after the reaction (bottom). The decarburization profile for the unpromoted carburized catalyst has two peaks; one is centered at  $T = 415 \,^{\circ}\text{C}$  and another at  $T = 475 \,^{\circ}\text{C}$ . K addition was found to shift the peak maxima toward higher temperature, and the intensities corresponding to the low-temperature peaks decreased. This indicates that potassium increases the stability of surface carbides formed on the catalyst. Eliason and Bartholomew<sup>[29]</sup> investigated various carbonaceous surface species and bulk iron carbides formed under FT-synthesis conditions by using temperature-programmed hydrogenation. The authors classified mainly four different carbon species (carbidic



Figure 3. Temperature-programmed decarburization profiles of various freshly carburized (top) and used (bottom) catalysts.

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( $\alpha$ ), amorphous ( $\beta$ ), iron carbides ( $\gamma$ ), and graphitic ( $\delta$ )) based on the temperature at which the species becomes hydrogenated. The authors suggested that the atomic carbon species exhibited higher FT activity, whereas amorphous carbon species showed only moderate activity; finally, semiordered graphitic carbon exhibited low reactivity. In our case, potassium shifts the low-temperature peak from T=415 to 529 °C, along with a significant drop in the intensities. At the same time, multiple peaks appear in the higher temperature region, which indicates that the strength of these carbides could vary depending upon the nature of the carbides and graphitic carbon present, as well as their interaction with potassium.

HRTEM images of the freshly carburized/passivated samples of unpromoted and K-promoted FeCo bimetallic catalysts are shown in Figure 4. TEM images at lower magnification (Figure 4A–C) shows iron particles uniformly distributed for all three catalysts (90Fe10Co0K, 90Fe10Co1K, and 90Fe10Co3K) with the particle diameter of iron varying from 20 to 30 nm. At higher magnification, all three catalysts displayed Hägg carbide surrounded by carbon fringes. The thickness of the carbon fringes increased with increasing K content in 90Fe10Co. At the same time, metallic Co or FeCo bimetallic compounds were observed to have imperfect crystalline structures (that is, short-range order). This shows that potassium increases additional carbon deposition over Fe FT catalysts in the form of semicrystalline carbon, which could control the stability of the Fe catalysts during the reaction.

The conversions of CO<sub>2</sub> and H<sub>2</sub> over unpromoted and various K-promoted FeCo bimetallic catalysts are shown in Figure 5. The initial CO<sub>2</sub> conversions were higher in the case of 90Fe10Co0K and 90Fe10Co0.5K catalysts and then dropped with further increases in K content (1.0, 2.0, and 3.0). The variations in CO<sub>2</sub> conversion diminished with time on stream, except in the case of 90Fe10Co3.0K. Regarding H<sub>2</sub> conversions, both 90Fe10Co0K and 90Fe10Co0.5K catalysts showed similar activity, and the conversions of H<sub>2</sub> for these two catalysts were higher than those with the other K-containing FeCo bimetallic catalysts. The H<sub>2</sub> conversions of the various catalysts followed in the order: 90Fe10Co0K = 90Fe10Co0.5K > 90Fe10Co1.0K >90Fe10Co2.0K > 90Fe10Co3.0K. The trend indicates that potassium improves CO<sub>2</sub> conversion of FeCo bimetallic catalysts only to a certain extent and, at the same time, potassium diminishes the hydrogenation activity of the catalyst.

The FT product distributions (CO free) obtained from the CO<sub>2</sub> hydrogenation reaction over unpromoted and various Kpromoted FeCo bimetallic catalysts are shown in Figure 6. The selectivity to methane decreased with addition of potassium to the FeCo bimetallic catalyst. For 90Fe10Co0K, methane selectivity remained at approximately 62%, whereas with 90Fe10Co0.5K, the selectivity decreased to 50%, with further decreases to approximately 38% for 90Fe10Co1.0K, 25% for 90Fe10Co2.0K, and 22% for 90Fe10Co3.0K. Furthermore, C<sub>2</sub>+ hydrocarbon selectivity was found to increase with increasing K content. The selectivity to oxygenates increased proportionally with the K content in the catalyst. Interestingly, the selectivity to oxygenates for the highly K-loaded catalyst (90Fe10Co3.0K) was three times higher ( $\approx$ 15–17 C%, CO free)

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Figure 4. HRTEM images of the carburized sample of A) 90Fe10Co0K, B) 90Fe10Co1K, and C) 90Fe10Co3K. Images of the respective catalyst particles (D, E, F) taken at a higher magnification.

than that for the unpromoted catalyst ( $\approx$  5 C%, CO free). The alkene/(alkene+alkane) fractions for  $\mathsf{C}_3$  and  $\mathsf{C}_4$  hydrocarbon products plotted against time on stream for various catalysts are shown in Figure 7. The promoting effect of potassium in the 90Fe10Co0.5K catalyst is manifested in the  $C_3$  and  $C_4$ alkene ratios, which are twice the value of those with the unpromoted catalyst. In the case of the  $C_3$  and  $C_4$  hydrocarbon fraction, the alkene ratios for 90Fe10Co1.0K were double those of 90Fe10Co0.5K. However, further increases in K loading did not result in any further changes to the alkene selectivity. Some authors have reported that olefins are formed as a primary product over paraffins and undergo hydrogenation in a secondary step. In our system, the hydrogenation activity of the catalysts decreased with increasing K content in the catalyst and, therefore, olefins formed in the reaction did not undergo further hydrogenation to form higher olefins. Similar conclusions were drawn by others.<sup>[30]</sup>

Hydrogenation of  $CO_2$  involves two different pathways: direct hydrogenation [Eq. (1)] and reverse water–gas shift [Eq. (2)], whereby CO produced is hydrogenated through the FT reaction.

$$n\operatorname{CO}_2 + 3n\operatorname{H}_2 \to (\operatorname{CH}_2)_n + 2n\operatorname{H}_2\operatorname{O}$$
(1)

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$
 (2a)

$$CO + 2H_2 \rightarrow (CH_2)_n + H_2O \tag{2b}$$

In the present work, hydrogenation of CO<sub>2</sub> on Fe may proceed by reverse water-gas shift. The presence of cobalt also influences the product selectivity of the FeCo bimetallic catalyst to some extent, especially in terms of light hydrocarbon formation. The product selectivity was compared for unpromoted and K-promoted FeCo bimetallic catalysts at a similar level of  $CO_2$  conversion, as indicated in Table 3. The selectivity to  $C_1$  decreased from 54.3 to 11.5 (C, mol%) upon an increase in the K/ (Fe+Co) ratio from 0 to 0.03. On the other hand, the lower hydrocarbon ( $C_2-C_4$ ) selectivity for the 90Fe10Co0.5K catalyst was higher than that with 90Fe10Co0K; however, further increases in potassium caused a drop in the selectivity to  $C_2-C_4$  hydrocarbons. We could only manage to quantify C<sub>5</sub> + hydrocarbons for 90Fe10Co3.0K; however, their presence with other catalysts tested in this series cannot be ruled out because they may be present but below the detection limit. Surprisingly, CO selectivity for the catalysts increased from 15.1 to 55.7 (C, mol%) with increasing K/(Fe+Co) mole ratios from 0 to 0.03. Some authors reported that the selectivity for CO decreases with increasing K content for CO<sub>2</sub> hydrogenation over alumina-supported Fe catalysts.<sup>[31]</sup> However, Martinelli et al.<sup>[32]</sup> obtained higher selectivity for CO with increasing K loading for the hydrogenation of CO<sub>2</sub> over traditional Fe-Zn-Cu-K catalysts. Riedel et al.[33] indicated that potassium yields higher CO selectivity for CO<sub>2</sub> hydrogenation over Fe/Al<sub>2</sub>O<sub>3</sub> catalysts because of an enhancement in CO shift activity. In the present work, though the conversion of CO<sub>2</sub> obtained remains more or less the same (except with 90Fe10Co3.0K) for catalysts with different K content, the hydro-





**Figure 5.** Conversions of CO<sub>2</sub> and H<sub>2</sub> over carburized samples of 90Fe10Co(*x*)K with varying K content (*x*=0, 0.5, 1.0, 2.0, and 3.0). Reaction conditions:  $T = 240 \,^{\circ}$ C,  $P = 1.2 \text{ MPa H}_2/\text{CO}_2 = 3.0$ , space velocity (SV) = 1.5 nL h<sup>-1</sup> g<sup>-1</sup> of metal oxalates.

genation activities varied from 17.6 to 9.6% with increasing K/ (Fe+Co) ratios from 0 to 0.02. This suggests that potassium suppresses the hydrogenation function of the catalyst, probably by depositing more carbon on the surface of the iron, as evidenced from H<sub>2</sub> temperature-programmed decarburization. Also, if hydrogen tends to donate electrons to iron on adsorption, the presence of potassium would be expected to weaken the iron-hydrogen bond and this could contribute to suppression of the dissociation of the H<sub>2</sub> molecule. Therefore, potassium can function in two ways on iron with regard to CO and CO<sub>2</sub> activation. It could facilitate the dissociative adsorption of the other hand, the basic nature of potassium may decrease the adsorption strength of H<sub>2</sub> on the surface of the iron.

The rates of formation of  $C_2$  oxygenates (ethanol, acetaldehyde, and acetic acid) plotted against conversion rate of  $H_2$  for FeCo bimetallic catalysts at three different K loadings are shown in Figure 8. The rate of formation of acetic acid decreased with increasing hydrogen conversion, and acetaldehyde formation followed a similar trend. The rate of ethanol formed from  $CO_2$  initially increased with an increase in hydro-



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**Figure 6.** Product distributions obtained for the hydrogenation of carbon dioxide over carburized samples of 90Fe10Co(*x*)K with varying K content (*x*=0, 0.5, 1.0, 2.0, and 3.0). Reaction conditions: T=240 °C, P=1.2 MPa, H<sub>2</sub>/ CO<sub>2</sub>=3.0, SV=1.5 nL h<sup>-1</sup>g<sup>-1</sup> of metal oxalates.

gen conversion but then leveled off with further increases in hydrogen conversion. These findings suggest that acetic acid, acetaldehyde, and ethanol may originate from the same intermediate (Scheme 1). Davis<sup>[34]</sup> documented the formation of surface acetate species over an Fe catalyst, in which CO insertion onto M–OCH<sub>3</sub> species may be responsible for the acetate formation. In that perspective, CO<sub>2</sub> can only initiate chain growth and does not take part in chain propagation, as shown in Scheme 2.<sup>[35]</sup>



**Figure 7.** Olefin-to-paraffin ratios of C<sub>3</sub> and C<sub>4</sub> hydrocarbons obtained with time on stream for the hydrogenation of carbon dioxide over carburized samples of 90Fe10Co(*x*)K with varying K content (x=0, 0.5, 1.0, 2.0, and 3.0). Reaction conditions: T=240 °C, P=1.2 MPa, H<sub>2</sub>/CO<sub>2</sub>=3.0, SV=1.5 nLh<sup>-1</sup>g<sup>-1</sup> metal oxalates.

|   |                       |       | <u></u> |      |      |  |  |  |  |
|---|-----------------------|-------|---------|------|------|--|--|--|--|
|   | K/(Fe+Co) Molar ratio |       |         |      |      |  |  |  |  |
|   | 0                     | 0.005 | 0.01    | 0.02 | 0.03 |  |  |  |  |
| TOS [h]   | 68.6                  | 118.7 | 139.5   | 95.0 | 77.0 |  |  |  |  |
| conversions [%]:                                  |                       |       |         |      |      |  |  |  |  |
| carbon dioxide                                    | 14.5                  | 14.2  | 14.5    | 14.0 | 8.0  |  |  |  |  |
| hydrogen  | 17.6                  | 16.0  | 12.4    | 9.6  | 10.5 |  |  |  |  |
| Product distribution [C, mol%]:                   |                       |       |         |      |      |  |  |  |  |
| C <sub>1</sub>                                    | 54.3                  | 36.5  | 20.3    | 13.0 | 11.5 |  |  |  |  |
| C <sub>2</sub> -C <sub>4</sub>                    | 26.7                  | 32.6  | 26.9    | 22.7 | 19.1 |  |  |  |  |
| C <sub>5</sub> +                                  | -                     | -     | -       | -    | 7.6  |  |  |  |  |
| CO  | 15.1                  | 26.2  | 45.5    | 57.9 | 55.7 |  |  |  |  |
| CH₃OH   | 2.7                   | 1.0   | 0.7     | 0.1  | 0.2  |  |  |  |  |
| C₂H₅OH  | 1.1                   | 3.7   | 5.9     | 2.9  | 2.6  |  |  |  |  |
| CH₃CHO  | -                     | -     | 0.3     | 0.6  | 0.7  |  |  |  |  |
| CH <sub>3</sub> CO <sub>2</sub> H                 | -                     | -     | 0.4     | 2.4  | 2.2  |  |  |  |  |
| C <sub>3</sub> H <sub>7</sub> OH                  | -                     | -     | -       | -    | -    |  |  |  |  |
| CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H | -                     | -     | -       | 0.4  | 0.4  |  |  |  |  |

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**Figure 8.** Rates of C<sub>2</sub> oxygenates (ethanol, acetic acid, and acetaldehyde) formed from CO<sub>2</sub> as a function of hydrogenation rates of CO<sub>2</sub> for carburized K-promoted FeCo bimetallic catalysts. Reaction conditions:  $T = 240 \degree$ C, P = 1.2 MPa, H<sub>2</sub>/CO<sub>2</sub> = 3.0, SV = 1.5 nL h<sup>-1</sup> g<sup>-1</sup> metal oxalates. The values in parentheses indicate the K/(Fe + Co) ratio.

On the other hand,  $Dry^{[36]}$  proposed two pathways for acetic acid formation from CO or CO<sub>2</sub>. In the first, CO<sub>2</sub> terminates FT chain growth, as shown in Scheme 3 A. In another pathway, aldehyde, alcohol, or acid formation depends on whether H<sub>2</sub> or H<sub>2</sub>O is involved in chain termination (Scheme 3 B).

The hydrogenation activity of the Fe catalyst likely plays an important role in controlling the formation of oxygenates, particularly acids from CO or CO<sub>2</sub>. In the current context, a significant drop in the conversion of hydrogen was observed with K addition. This is consistent with our earlier proposed mechanism on FeCo bimetallic catalysts,<sup>[27]</sup> in which potassium may take part in the catalytic cycle for the formation of acetic acid from CO<sub>2</sub>.

Many have agreed that the deactivation of iron occurs under Fischer-Tropsch synthesis conditions, mainly as a result of the loss of active catalyst surface area because of accumulation of carbonaceous species on iron carbide surfaces and/or the loss of iron carbides ( $\epsilon$ -Fe<sub>2.2</sub>C,  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>,  $\theta$ -Fe<sub>3</sub>C) through oxidation. It has been reported that losses in the catalytic activity of Fe catalysts for CO<sub>2</sub> hydrogenation occur mainly by oxidation of the active iron carbide phase to magnetite.<sup>[37]</sup> In the current work, we examined the used Fe catalysts (after passivation under flowing  $1 \% O_2$  in  $N_2$  at room temperature for a few hours) by XRD, Mössbauer spectroscopy, and decarburization techniques. The XRD patterns of the used catalysts are shown in Figure 2 (bottom). Diffraction lines corresponding to the magnetite phase were observed very clearly for the unpromoted catalyst. On the other hand, the diffraction lines for K-promoted FeCo catalysts were less pronounced.

The Mössbauer spectrum of the used unpromoted and K-promoted FeCo catalysts are shown in Figure 1 (right). The corresponding quantitative estimation of the various Fe carbide phases present in each sample is shown in Table 2. After reaction, the percentage of magnetite formed had increased from 22 to 39% for the unpromoted FeCo catalyst and the  $\chi$  and  $\varepsilon$ -iron carbides had decreased from 56 to 45% and 22 to 16%,

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Scheme 1. A plausible pathway for the formation of acetic acid, acetaldehyde, and ethanol from acetate intermediate on Fe catalysts.



Scheme 2. Formation of surface acetate species over Fe catalyst through CO insertion onto  $M-OCH_3$  species.<sup>[34]</sup>

respectively. Similar results were observed with 90Fe10Co0.5K. On the other hand, all other catalysts (90Fe10Co1.0K, 90Fe10Co2.0K, and 90Fe10Co3.0K) showed that either the percentage of magnetite remains the same or decreases slightly before and after reaction. Another noticeable difference found

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between the fresh and used catalyst was the  $\varepsilon$ -Fe carbide (Fe<sub>2.2</sub>C) content. In the used catalyst, the amount of  $\varepsilon$ -Fe carbide increased with increasing K content, whereas the  $\varepsilon$ -Fe<sub>2.2</sub>C content for the freshly activated catalysts remained more or less the same; this indicates that potassium enhanced the transformation of highly active  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> carbide into less active  $\varepsilon$ -Fe<sub>2.2</sub>C carbide. A similar result was reported by our group with CO hydrogenation over precipitated Fe catalysts.<sup>[38]</sup> The origin of this transformation is not well understood.

The decarburization of used Fe catalysts was performed to know what kinds of carbon species remained in the used catalyst and to make an attempt to elucidate their individual roles in the reaction. Bartholomew and co-workers<sup>[29,39]</sup> made a detailed study of the temperature-programmed hydrogenation of carbonaceous species on Fe FT catalysts during steady-state synthesis. The authors suggested that the deactivation of Fe catalysts in FT synthesis under the conditions of their study could be explained by two factors: first, the transformation of high-activity Hägg carbide to less active epsilon carbide, and second, the formation of highly ordered graphite on the surface of the catalyst. As shown in Figure 3, in the current work, most of the low-temperature carbon species ( $T=325-500^{\circ}C$ ) were consumed by the reaction and only those catalysts with moderate to higher levels of potassium had significant levels of amorphous and atomic carbon species. Moreover, the used unpromoted FeCo catalyst exhibited carbon species for which the reduction temperature was greater than 550°C, which indicates

either that atomic carbon or Hägg carbide was stabilized in the presence of hydrocarbon products or that amorphous moderately ordered graphitic carbon formed during the course of the reaction.

The present data reveal that potassium protects iron carbides (active form of iron for CO and CO<sub>2</sub> hydrogenation) from oxidation to magnetite (not a significantly active phase for the reaction) during the hydrogenation of carbon dioxide. However, there is an optimum K loading for the Fe catalysts, in this case, 1.0 K, to achieve an optimal balance between activity and stability for the conversion of CO<sub>2</sub> to higher hydrocarbons. For instance, the 90Fe10Co3.0K catalyst displayed greater stability in preserving the active Hägg carbide phase of iron during the reaction and, at the same time, the content of the less active epsilon iron carbide (E-Fe2.2C) increases as well. Therefore, the catalyst activity declined over time, as shown in Figure 5. It seems that the unpromoted FeCo bimetallic catalyst suffers from deactivation, likely as a result of the loss of the active Hägg carbide phase to magnetite during the reaction, whereas highly loaded K-promoted FeCo catalysts (such as 90Fe10C03.0K) exhibit lower initial activity and experience more rapid deactivation, probably because of the lower hydrogenation activity caused by the deposition of highly ordered graphite on the Fe surface.



Scheme 3. A) Acetic acid formation from CO or CO<sub>2</sub> over Fe catalyst proposed by Dry.<sup>[35]</sup>

# Conclusions

The hydrogenation of carbon dioxide over K-promoted FeCo bimetallic catalysts was investigated by using a fixed-bed reactor at moderate temperature and pressure. The carburized form of the Fe catalyst was obtained from an oxalate precursor after decomposition and carburization with CO. The decarburization of the freshly activated FeCo catalysts suggests that potassium decreases the low-temperature surface carbon species and increases bulk iron carbides and graphitic carbon formed on the Fe surface during activation. The addition of potassium to FeCo up to 1.0 K was found to enhance the activity and stability of iron carbide for the hydrogenation of carbon dioxide. At the same time, the hydrogenation function of the catalyst is suppressed with increasing K levels in the catalyst, which results in a higher selectivity to CO (that is, the product of the RWGS reaction) and oxygenates. Mössbauer spectroscopy analysis of the freshly carburized FeCo bimetallic catalysts suggests that the unpromoted FeCo bimetallic catalyst oxidizes to a greater extent than the K-promoted catalyst. The selectivity to  $C_2-C_4$  hydrocarbons increases from 26.7 to 32.6% with an increase in the K level from 0 to 0.05 [90Fe10Co(x)K], whereas further increases in potassium were found to decrease the selectivity to 26.9, 22.7, and 19.1% for 0.1 K, 0.2 K, and 0.3 K, respectively. As expected, the olefin ratios for C<sub>3</sub> and C<sub>4</sub> hydrocarbons increased monotonically with increases in K level in the catalyst. The selectivity to oxygenates for FeCo bimetallic catalysts increases (to a maximum of 18 C%, CO free) with increases in the K content. Potassium shifts the product distribution of C<sub>2</sub> oxygenates from CO<sub>2</sub> towards acetic acid. A synergistic effect by potassium (that is, possible involvement in the catalytic cycle, as proposed in our previous work<sup>[27]</sup>), along with a decrease in the hydrogenation function of the Fe catalyst, likely prevents ethanol formation from the intermediate.

# OOH Experimental Section

### **Catalyst preparation**

Iron(II) sulfate heptahydrate 98%, cobalt(II) nitrate hexahydrate 98%, potassium nitrate (99.9%), and oxalic acid dihydrate 99% were purchased from Sigma-Aldrich Co. and used without further purification. The preparation iron bimetallic of cobalt-containing oxalates (90Fe:10Co) is described elsewhere.<sup>[27]</sup> Typically, oxalic acid (37.821 g, 0.3 mol) was dissolved in deionized water (250 mL) with constant stirring at T = 35 °C. In a separate flask, iron sulfate (50.549 g, 0.18 mol) and cobalt nitrate (5.939 g, 0.02 mol) were dissolved in deionized water (750 mL) at T = 35 °C. The metal-containing solution was added dropwise to the aqueous oxalic acid. Precipitation was virtually instantaneous, and the mixture was vigorously stirred at T=35 °C for 1 h. The solution was then allowed to cool to room temperature with continued stirring. After removal of the supernatant, the precipitated metal oxalate complexes were filtered and washed three times with deionized water (1 L). The resulting solid was dried at  $T = 100 \degree$ C in air in an oven for 24 h. Potassium was added to obtain K/

((Fe+Co) atomic ratios of 0.005, 0.01, 0.02, and 0.03 by using a slurry-phase impregnation technique. The catalyst was then dried overnight at T=100 °C.

## **Catalyst activation**

The FeCo bimetallic oxalates (2.5 g) with and without K were decomposed in flowing nitrogen (100 sccm) at T=400 °C for 2 h and subsequently treated with CO (10%CO in N<sub>2</sub>) at T=250 °C for 24 h. The resulting FeCo bimetallic carbides were tested for CO<sub>2</sub> hydrogenation or passivated under a flow of 1% O<sub>2</sub>/N<sub>2</sub> at T=25 °C for 4 h for the purpose of characterization.

## Characterization

#### Elemental analysis

The compositions of FeCo bimetallic oxalate complexes were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Varian 720-ES analyzer. The materials were dissolved in a perchloric/nitric acid mixture, and the emission spectra of dissolved species (Fe, Co, and K) were compared to those of a series of standard solutions of known concentrations.

## X-Ray diffraction (XRD)

Powder X-ray diffractograms of the freshly CO-activated and used catalyst samples were recorded after passivation in 1% O<sub>2</sub> in He at room temperature by using a Philips X'Pert diffractometer with monochromatic Cu<sub>ka</sub> radiation ( $\lambda = 1.5418$ ). XRD scans were taken over a 2 $\theta$  range of 10–90°. The scanning step was 0.01, the scan speed was 0.0025 s<sup>-1</sup>, and the scan time was 4 s.

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![](_page_8_Picture_0.jpeg)

#### Temperature-programmed decarburization

The carburized/passivated catalyst (about 0.2 g) was positioned between a bed of quartz wool, and an H<sub>2</sub>:He (1:3) gas mixture was introduced at 100 cc min<sup>-1</sup>. The temperature of the catalyst bed was increased to 850 °C with a ramp of 2.3 °C min<sup>-1</sup>. The evolved product was methane, and it was continuously detected by a flame ionization detector (SRI-GC), which gave the temperature-programmed decarburization profile. A similar procedure was followed to that described above to study the decarburization of the used catalysts for the purpose of comparison.

### High-resolution transmission electron microscopy (HRTEM)

In-depth analysis of individual particles of unpromoted and K-promoted FeCo bimetallic catalysts in carburized form was obtained with a field-emission analytical transmission electron microscope (JEOL JEM-2010F) operated at an accelerating voltage of 200 kV. HRTEM images were recorded under optimal focus conditions at typical magnifications of 100–500 K. The electron beam had a point-to-point resolution of 0.5 nm. Gatan Digital Micrograph software was used for image processing. Samples were prepared on lacey-carbon copper grids and dispersed as powders.

### <sup>55</sup>Fe Mössbauer spectroscopy

<sup>55</sup>Fe Mössbauer spectra were collected in transmission mode with a standard constant-acceleration spectrometer (MS-1200, Ranger Scientific). A radiation source of 50 mCi <sup>57</sup>Co in Rh matrix was used, and the spectra were obtained with a gas detector. To transport each sample for Mössbauer spectroscopy, each sample was carefully fixed into wax inside a glove box after activation. All samples were investigated at low temperature (-253 °C) by using a closedcycle refrigerator, typically over a velocity range of  $\pm 10$  mms<sup>-1</sup>. Structure analysis of each sample was preformed by least-squares fitting of the Mössbauer spectra to a summation of hyperfine sextets. Details about the least-squares fitting procedures are described elsewhere.<sup>[28]</sup>

# CO<sub>2</sub> hydrogenation reaction

The CO<sub>2</sub> hydrogenation reaction was performed by using a fixedbed reactor (stainless steel with a length of 17 cm and an inside diameter of 1.6 cm). The reaction was performed with no internal or external heat and mass-transfer limitations.<sup>[27]</sup> Typically, the dried metal oxalate (2.5 g; after activation, the weight of the catalyst sample was 1.2 g; 60–100  $\mu$ m) was diluted with powdered glass beads (2.5 g) in the size range 40–100  $\mu$ m and loaded on to a quartz wool plug in the reactor. The temperature of the catalyst bed was monitored by placing a K-type thermocouple in the middle of the catalyst bed. After activation, a gas mixture, containing 71.5 %  $H_2$  and 28.5 %  $CO_2$  at 2.0 nL  $h^{-1}g^{-1}$  catalyst, was fed into the reactor, which was maintained at a temperature of 240  $^\circ\text{C}$  and a pressure of 0.92 MPa. Brooks mass-flow controllers were used to control the flow rates of H<sub>2</sub> and CO<sub>2</sub>. The conversions of CO<sub>2</sub> and H<sub>2</sub> were obtained by gas chromatography (GC) analysis (micro-GC equipment with a thermal conductivity detector) of the exit-gas mixture from the reactor. The reaction products were collected in two traps maintained at different temperatures: a hot trap (T =150 °C) and a cold trap (T = 5 °C). The products were separated into different fractions for quantification. The liquid products condensed in the hot trap were analyzed by using an HP 7890 GC instrument with DB-5 capillary column, whereas the aqueous phase

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was analyzed by using an SRI (Torrance, CA) GC-TCD-8610C apparatus with a 6' Poropak-Q stainless steel packed column. A 5973N MSD instrument coupled to a 6890 gas chromatograph from Agilent was employed for qualitative analysis of various oxygenated compounds. The conversion and selectivity reaction parameters are defined as in Equations (3) and 4, in which  $n_{CO_{2m}}$  and  $n_{CO_{2m}}$  are the numbers of moles of CO<sub>2</sub> fed and not-consumed, respectively. The selectivity is defined as the percentage of moles of CO<sub>2</sub> consumed to form a particular C<sub>n</sub> product (hydrocarbon, CO, or oxygenate), normalized by the amount of CO<sub>2</sub> consumed.

conversion = 
$$100 \times \frac{n_{CO_2 \text{ in}} - n_{CO_2 \text{ out}}}{n_{CO_2 \text{ in}}}$$
 (3)

selectivity = 
$$100 \times \frac{n_{\text{product out}} \text{ carbon number}}{n_{\text{CO}_2 \text{ in}} - n_{\text{CO}_2 \text{ out}}}$$
 (4)

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**Keywords:** bimetallic catalysts · carbon dioxide · hydrogenation · cobalt · iron · potassium

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![](_page_9_Picture_0.jpeg)

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# **FULL PAPERS**

**Promoting effect of potassium**: In the hydrogenation of CO<sub>2</sub> over K-promoted FeCo bimetallic catalysts, initial CO<sub>2</sub> conversion was dependent on K loading, whereas most catalysts exhibited similar conversion levels after a few hours. Decarburization suggests that potassium stabilizes iron carbides and decreases the hydrogenation function of the catalysts; thus, it controls product selectivity. Potassium enhanced acetic acid formation and suppressed ethanol production.

![](_page_10_Figure_2.jpeg)

M. K. Gnanamani, H. H. Hamdeh, G. Jacobs, W. D. Shafer, S. D. Hopps, G. A. Thomas, B. H. Davis\*

![](_page_10_Figure_4.jpeg)

Hydrogenation of Carbon Dioxide over K-Promoted FeCo Bimetallic Catalysts Prepared from Mixed Metal Oxalates