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Tandem conversion of CO₂ to valuable hydrocarbons in highly concentrated potassium iron catalysts

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Abstract: The alarming atmospheric concentration and continuous emissions of carbon dioxide (CO₂) require immediate action. As a result of advances in CO₂ capture and sequestration technologies (generally involving point sources such as energy generation plants), large amounts of pure CO₂ will soon be available. In addition to geological storage and other applications of the captured CO₂, the development of technologies able to convert this carbon feedstock into commodity chemicals may pave the way towards a more sustainable economy. Here, we present a novel multifunctional catalyst consisting of Fe₂O₃ encapsulated in K₂CO₃ that can transform CO₂ into olefins via a tandem mechanism. In contrast to traditional systems in Fischer-Tropsch reactions, we demonstrate that when dealing with CO₂ conversion (in contrast to CO), very high K loadings are key to activate CO₂ via the well-known 'potassium carbonate mechanism'. The proposed catalytic process is demonstrated to be as productive as existing commercial processes based on synthesis gas while relying on economically and environmentally advantageous CO₂ feedstock.

Introduction

Carbon dioxide capture and utilization is the only viable short-to medium-term option for moving towards a more sustainable society. Despite the rapid increase in the implementation of nonemitting energy generation technologies, 35 Gtons of CO₂ are emitted into the atmosphere every year^[1, 2]. Therefore, methods to convert this greenhouse gas into valuable commodities are urgently needed^[3]. Given that our society is greatly dependent on carbon materials that are traditionally manufactured from oil (e.g.,

polymers), the development of techniques for directly transforming CO₂ into such chemicals, making use of renewable energy, could substantially impact our society^[4, 5]. Among all possible chemicals, olefins are especially attractive owing to their large demand^[6].

The transformation of CO₂ into olefins generally proceeds through a modified Fischer-Tropsch (FTS) process using synthesis gas over an iron catalyst^[7-9]. Here, CO₂ is first transformed into CO via a reverse water-gas shift (RWGS) reaction and further converted to olefins via a conventional FTS process. The main drawback of this route lies in the first hydrogenation of CO₂ to CO. Although Fe in its different oxidation states is a good RWGS catalyst, achieving an appropriate balance between the amount of oxides (responsible for RWGS) and carbides (responsible for FTS) is not straightforward. As a consequence, CO₂ hydrogenation catalysts need to be doped with potassium^[10, 11]. The addition of small amounts of K (circa 0.5 to 1 wt. %) forges an appropriate balance between the different Fe active phases and enhances the selectivity of the reaction for low-molecular-weight olefins^[12]. However, high K loadings usually lead to catalyst sintering and deactivation^[11].

Notably, K is also well known for CO₂ capture purposes via the 'potassium carbonate mechanism', which has already been applied for CO₂ removal in more than 700 plants worldwide^[13, 14]. In this system, the carbonate reacts with CO₂ and water, yielding potassium bicarbonate, KHCO₃ (equation S1). Furthermore, early reports^[15] also discussed RWGS reactions catalyzed by potassium carbonate in a H₂-rich atmosphere via a formate intermediate (equations S2 to S4). However, there is no testimony of these reactions taking place at typical CO₂ hydrogenation conditions.

With this information in hand, we speculated that, with the proper catalyst, these reactions could be combined into a single catalytic cycle that involves the activation of CO₂ and release of CO on the K phase under FTS conditions, enhancing the overall RWGS activity and therefore the productivity of the catalyst.

In this spirit, here we report a highly K concentrated Fe catalyst that is able to activate CO₂ in the K while simultaneously transform it into olefins on the Fe via a tandem mechanism. Catalytic results demonstrate that similar productivity as commercial FTS processes based on synthesis gas can be achieved, with the obvious advantage of using CO₂ as carbon source.

Results and Discussion

First, in order to explore the feasibility of the proposed dual mechanism under hydrogenative conditions, we computed the thermodynamics of all possible K RWGS reactions (see Figure

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1.A) using density functional theory (DFT) (see Experimental Section and Figures S1, S2). Our results show that, in the range of 0–300 °C, all three phases have similar stabilities (within 0.2 eV, see Figure 1.B). Moreover, the computed Gibbs free energies for the different reactions suggest that the interconversion between KHCO_3 and KOOCH during the catalysis is possible at all the considered temperatures (Figure 1.C).

Figure 1. RWGS reaction on carbonaceous potassium. (A) Catalytic cycle. (B) Calculated Gibbs free energies of KHCO_3 and KOOCH relative to that of K_2CO_3 at 1 bar pressure of all reactants and products. The brown area marks the range that is readily accessible thermodynamically (within 5 kT of the most stable phase). A continuous line is used to denote the thermodynamically most stable phase, and dashed lines are used to denote less stable phases. (C) Gibbs energies for the indicated reactions, $\Delta_r G$, as function of temperature.

Therefore, we prepared a catalyst with a high K concentration by grinding commercial iron oxide and potassium superoxide together in a mortar; a molar Fe/K ratio of 2 was maintained. Despite its simplicity, pronounced changes take place in the

catalyst during synthesis and reaction, leading to a particular structure that results in high selectivity for olefins. Figure 2.A shows the X-ray diffraction (XRD) patterns of the starting $\gamma\text{-Fe}_2\text{O}_3$ precursor, the fresh catalyst and used catalysts after 50 h on the stream. The basic structure of $\gamma\text{-Fe}_2\text{O}_3$ is closely related to the inverse spinel Fe_3O_4 , but it differs by the presence of disordered iron vacancies. When the vacancies become ordered, the symmetry decreases from cubic to tetragonal, and consequently, additional weak superstructure reflections appear^[16]. This is the case for the commercial maghemite used in this study as superlattice reflections of a primitive tetragonal unit cell ($a = 8.344$ Å, $c = 25.033$ Å) are observed at $2\theta = 11.17^\circ$ and 12.74° , which correspond to Miller indices of (1 0 1) and (1 0 2), respectively. Because potassium superoxide is air sensitive, the catalyst was initially prepared in a glove box. Once exposed to the air, the sample was indeed found to be extremely reactive to carbon dioxide and water over time, as indicated by powder XRD (Figure S3).

To allow better control over the catalyst mass before the catalytic experiments, maghemite and potassium superoxide were mechanically mixed in the air and then dried at 100 °C. This process slowed the uptake of water and the resulting fresh catalyst was a mixture of maghemite and potassium carbonate (i.e., $\text{Fe}_2\text{O}_3 @ \text{K}_2\text{CO}_3$, Figure 2.A). The instability of the potassium superoxide under ambient conditions may be the driving force behind the redistribution of potassium around $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, as shown by elemental mappings performed by scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray (EDX) spectrometry (Figure S4). Once submitted to the reaction conditions no evidence of the crystalline potassium carbonate is observed by powder XRD, and the Fe_2O_3 precursor is partially transformed into Fe_2C_5 , the carbide-selective phase in FTS^[17].

High-angle annular dark-field (HAADF) STEM imaging coupled to X-ray fluorescence spectroscopy was used to further investigate the morphological properties of the $\text{Fe}_2\text{O}_3 @ \text{K}_2\text{CO}_3$ catalyst after the reaction. The low magnification micrograph and the elemental mapping presented in Figure 2.B are representative of the whole sample. There are two main components in the spent catalyst: i) iron-based nanoparticles (200–350 nm) surrounded by a thick layer of carbonaceous potassium and ii) iron atoms redistributed on the surface of the carbonaceous potassium. The latter is better observed with elemental mapping at higher magnification (Figure 2.C).

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Figure 2. Characterization of the Fe₂O₃@K₂CO₃ material. (A) X-ray diffraction patterns of the fresh and spent catalyst. (B) HAADF-STEM imaging and elemental mapping of the spent catalyst. (C) High magnification mapping of the spent catalyst.

The activation under a H₂ atmosphere and the evolution of the iron phases during the CO₂ hydrogenation reaction (30 bar, CO₂:H₂ = 1:3, 350 °C) were monitored by High energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) at the Fe K-edge (Figure 3.A). The spectra were acquired ex situ with samples retrieved inside a glove box and loaded into an X-ray absorption spectroscopy (XAS) cell dedicated to air-sensitive solids. The spectrum of the fresh catalyst was almost identical to that of the γ-Fe₂O₃ reference. Upon hydrogenation at 3 bar at a temperature of 350 °C, the pre-edge peak (1s→3d-4p transitions) disappeared from the XANES spectrum, the white line intensity decreased, and the main absorption edge shifted to lower energy. These changes are typical of a reduction to the metallic state, which is further

supported by comparison with the spectrum of the metallic foil. Upon 1 h of exposure to the CO₂/H₂ mixture at 30 bar, the spectrum of the catalyst further evolves with a shift in the postedge oscillations and subtle changes in the main edge. Linear combination fitting was attempted with several iron references (Figure 3.B and Figure S5), and the best match was obtained with a mixture of γ-Fe₅C₂ and metallic Fe^[17]. After 50 h of reaction, the white line and the pre-edge intensity both increase, suggesting a reoxidation of the iron under the reaction conditions, in agreement with previous reports^[18]. The composition of the spent catalyst was further refined by air protected capillary single crystal X-ray diffraction, and it was determined to be mostly a mixture of γ-Fe₅C₂, Fe₂O₃ and metallic Fe (Figure S6), consistent with the XANES results.

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Figure 3. Evolution of the $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ material during the reaction. (A) HERFD-XANES spectrum of the $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ catalyst at different stages of the reaction. (B) Linear combination fitting of the HERFD-XANES spectrum of the $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ catalyst at different stages of the reaction. (C) Thermal conductivity detector signal (TCD) for the CO_2 temperature-programmed oxidation of the iron oxide precursor and the $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ catalyst. (D) X-ray photoelectron spectroscopy of the fresh and spent $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ catalyst at the K2p level. (E) X-ray photoelectron spectroscopy at the C1s and K2p level of the K carbonates and formate precursors. (F) ^{39}K magic angle spinning (unless stated otherwise) solid-state NMR spectra (acquired at 21.1 T and 298 K) of the spent $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ catalyst and different K precursors.

CO_2 temperature-programmed oxidation (TPO) after a reduction pretreatment of the iron oxide precursor and $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ catalyst reveals a 100 °C shift to lower temperatures when the carbonate is involved (Figure 3.C). After incorporation of the carbonate, the CO_2 peak is precisely centered in the hydrogenation temperature range (350 to 400 °C). Furthermore, the CO_2 uptake is increased by 86.5% upon K promotion, affording a final uptake of 2.13 mmol of CO_2 per gram of $K_2\text{CO}_3$, which is close to the theoretical maximum of potassium carbonate^[14]. Analysis of the surface by air-protected X-ray photoelectron spectroscopy (XPS) of the fresh and spent catalysts at the K2p level revealed a shift to higher binding energies (Figure 3.D). This shift can be attributed to the transformation of the $K_2\text{CO}_3$ phase^[19] and suggests that the proposed mechanism (see Figure 1.A) is occurring during the reaction. To confirm this hypothesis, the C1s and K2p spectra of all possible K precursors ($K_2\text{CO}_3$, $KHCO_3$ and $KOOCH$) were measured and individually compared with the spectra of the fresh and spent catalyst (see Figure 3.E and S7). The presence of $K_2\text{CO}_3$ in the fresh catalyst was confirmed, and the spectrum of the spent catalyst showed the presence of $KOOCH$. In particular, the $K2p_{3/2}$ band of fresh catalyst at 292.25 eV matches the one of

$K_2\text{CO}_3$ while the $K2p_{3/2}$ band at 292.52 eV of the spent catalyst matches the presence of $KOOCH$. The formation of carbon-iron bonds in the spent catalyst is confirmed by the XPS data via the appearance of a new peak at 283.4 eV (see Figure S7.D), which can be attributed to iron carbide species^[20]. Analysis of the O1s signals revealed a decrease in the O atoms bound as metal oxides^[21] (Figure S8), which is consistent with the transformation of Fe_2O_3 to Fe_2C_5 indicated by XRD and XANES.

To clarify the transformations of potassium during the reaction, the spent $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ was analyzed by high-field ^{39}K solid-state nuclear magnetic resonance (ssNMR) spectroscopy, and the spectrum was compared with those of $K_2\text{CO}_3$, $KHCO_3$, $KOOCH$ and the hydrated KO_2 precursor (Figure 3.F). Among these species, the spectra of $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ and $KOOCH$ show identical sharp peaks at 4.5 ppm, similar to that of hydrated KO_2 . These results suggest the K^+ ions have very high mobility in the solid state, presumably in their formate form. In addition, the secondary peak of $\text{Fe}_2\text{O}_3@K_2\text{CO}_3$ at approximately -2.6 ppm is similar to those of both $KHCO_3$ and $K_2\text{CO}_3$, which indicates that a portion of the potassium is converted to the corresponding carbonated salt under the reaction conditions. Altogether, these

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results confirm that the reaction pathway shown in Figure 1.A indeed takes place under these hydrogenation conditions.

Figure 4. Catalytic performance of the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ material. (A) Effect of reaction temperature after a time-on-stream (TOS) of 50 h. (B) CO_2 conversion and total olefin selectivity at 350 °C as functions of TOS. (C) Hydrocarbon distribution and ASF plot after a TOS of 150 h at 350 °C. Reaction conditions: 30 bar, $\text{H}_2/\text{CO}_2 = 3$, and $10000 \text{ mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$.

The performance of the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ catalysts in the hydrogenation of CO_2 after 50 h on stream at different reaction temperatures is shown in Figure 4.A. Raising the temperature by 50 °C increases the conversion from 39.7% to 48.3% and leads to the formation of greater amounts of methane. The optimum performance can be achieved at 350 °C. At this temperature, the reaction shows a CO_2 conversion of 44.2% with a total olefin ($\text{C}_2\text{-C}_{10}$) selectivity of 62.6%, a CH_4 selectivity of 13.3% and a CO selectivity of only 12.7%. This catalytic performance is stable for at least 150 h on stream (Figure 4.B). The details of the hydrocarbon distribution are reported in Figure 4.C. The light olefins ($\text{C}_2\text{-C}_4$) fraction accounts for 53.3% of the total olefins with a total olefin/paraffin ratio of 7.5. The value of α , derived from the Anderson-Schulz-Flory (ASF) plot, is 0.41, which is in the optimum range for olefin production^[7].

The iron-time yield (FTY; mmol of CO_2 converted to hydrocarbons per gram of Fe per hour) obtained for the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ material reached a maximum of $265.4 \text{ mmol}_{\text{CO}_2} \cdot \text{g}_{\text{Fe}}^{-1} \cdot \text{h}^{-1}$ at 375 °C. These activities are on the same order of magnitude as those of typical Fe catalysts for olefin production via existing commercial Fischer-

Tropsch processes^[22-25] (Table 1). In addition, the production of light olefins ($\text{C}_2\text{-C}_4$), expressed as iron based space-time yield (STY; mmol of light olefins produced per gram of Fe per hour) reported here is twice than the ones achieved by FTS catalysts. Furthermore, the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ catalyst here reported also outperforms conventional CO_2 hydrogenation materials^[26-41], yielding the highest productivity of light olefins per gram of catalyst (see Table S1).

Table 1. Comparison of the catalyst performance measured as light olefin selectivity ($\text{C}_2\text{-C}_4$), iron-time yield (FTY) and light olefins space-time yield (STY) of the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ catalyst and different Fe Fischer-Tropsch catalysts.

Catalyst	Sel $\text{C}_2\text{-C}_4$ (%)	FTY	STY $\text{C}_2\text{-C}_4$	Ref.
Fe/CNF	30	107.3	32.4	22
Fe/ $\alpha\text{-Al}_2\text{O}_3$ (6% Fe)	19	305.3	57.7	22
Fe/ $\alpha\text{-Al}_2\text{O}_3$ (12% Fe)	23	95.8	22.0	22
Fe/ $\alpha\text{-Al}_2\text{O}_3$ (25% Fe)	32	48.6	15.5	22
Fe/ $\beta\text{-SiC}$	11	229.7	25.3	22
Fe/ $\gamma\text{-Al}_2\text{O}_3$	26	9.0	2.4	22
Fe-Ti-Zn-K	17	17.6	2.9	22
Fe-Cu-K-SiO ₂	23	40.3	9.1	22
Rurchemie	16	106.4	17.1	23
Sasol	[b]	140.7	[b]	24
Mobil	17	52.5	8.4	25
$\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ ^[a]	31	265.4	82.6	This work

[a] Fe loading determined by Inductively coupled plasma (ICP).

[b] Data not available.

This outstanding performance can be attributed to the optimal composition of the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ material, which enables the tandem conversion of CO_2 (Figure 5.A). In our proposed reaction mechanism, two well differentiated steps take place: (i) CO_2 initially reacts on the K_2CO_3 phase that undergoes several transformations, yielding KCOOH and releasing CO, which is (ii) subsequently hydrogenated to olefins via conventional FTS. The high potassium loading in the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ catalyst is key for the CO_2 transformation to CO, while the optimal ratio of the iron oxide and iron carbide phases accounts for the high olefin/paraffin ratio via a conventional FTS chemistry^[10, 15]. To further confirm this reaction pathway, CO_2 hydrogenation tests were carried out with stand-alone potassium carbonates and formate precursors (in the absence of Fe). All the potassium precursors were able to convert CO_2 and release CO via RGWS with selectivities close to 100% with no sign of deactivation after 150 h (Figure 5.B).

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Figure 5. (A) Proposed reaction scheme of the CO₂ capture and transformation on the Fe₂O₃@K₂CO₃ catalyst. The process takes place in two steps: (i) the CO₂ is initially activated on the K₂CO₃ that undergoes several transformation yielding KCOOH and CO, which is subsequently hydrogenated (ii) to olefins via FTS. (B) Catalytic performance of the K carbonates and formate precursors. Reaction conditions: 30 bar, H₂/CO₂ = 3, 350 °C and 10000 mL·g⁻¹·h⁻¹.

Conclusions

In conclusion, we have developed a novel catalyst that dramatically surpasses traditional CO₂ conversion technologies by simultaneously capturing and converting CO₂ into valuable chemicals. The Fe₂O₃@K₂CO₃ material presented here can produce olefins from CO₂ with high selectivity and productivity, rivaling existing commercial Fisher-Tropsch catalysts. In contrast to traditional iron-based systems, we demonstrate that very high K loadings are key to activate CO₂ via the well-known 'potassium carbonate mechanism' and converting it to CO via potassium bicarbonate/formate interconversion. Given their high activity, stability, productivity and their low price, if combined with green H₂ sources, these catalysts may facilitate the mass adoption of nonfossil fuel-based technologies for the production of hydrocarbons in the near future.

Experimental Section

Chemicals

Iron oxide (Fe₂O₃, Aldrich), Potassium superoxide (KO₂, Aldrich), Potassium carbonate (K₂CO₃, Aldrich), Potassium bicarbonate (KHCO₃, Aldrich) and Potassium formate (KOOCH, Aldrich) were used as received.

Catalyst preparation

The Fe₂O₃@K₂CO₃ catalyst was obtained by mortar mixing of Fe₂O₃ and KO₂ keeping a molar ratio of Fe/K=2. The resultant mixture was left overnight at room temperature to react with ambient CO₂ and H₂O. Afterwards, the mixture was heated up to 100 °C for 12 h.

CO₂ hydrogenation tests

Catalytic tests were executed in a 16 channel Flowrence® of Avantium. 50 mg of the Fe₂O₃@K₂CO₃ catalyst were typically used. The mixed feed has 25vol% of CO₂ and 75vol% of H₂. In addition, 8 ml/min of He is mixed with the feed as internal standard. We aimed to have 10000 mL·g⁻¹·h⁻¹ per channel. The channels are 300 mm long stainless steel tubes inserted in furnace. Outside diameter is 3 mm and inside diameter of tubes is 2 mm. One of the 16th channels was always used without catalyst as blank. The reaction temperature is typically set at 350°C. Prior to feeding the reaction mixture all samples are pretreated in-situ with a pure H₂ atmosphere for 4 hours at 350°C at 3 bars. Afterwards, the reaction mixture is fed and the tubes are pressurized to 30 bar using a membrane based pressure controller.

A 16 position selector valve sends reactor effluents to the gas chromatograph (GC), allowing for sequential monitoring of one reactor after the other. Switching of the valve is based on the time needed for the GC method. GC is an Agilent 7890B with two sample loops. After flushing the loops for 24 min, the content is injected. One sample loop goes to TCD channel with 2 Haysep pre-column and MS5A, where He, H₂, CH₄ and CO are separated. Gases that have longer retention times than CO₂ on the Haysep column (Column 4 Haysep Q 0.5 M G3591-80023) are back-flushed. Further separation of permanent gases is done on another Haysep column (Column 5 Haysep Q 6 Ft G3591-80013) to separate CO₂ before going to MS5A. CO₂ is sent to a channel with restrictor avoiding CO₂ on MS5A. Another sample loop goes to an Innowax pre-column (5m, 0.20MM OD, 0.4 uM film), first 0.5 min of the method the gases coming from pre-column are sent to Gaspro column (Gaspro 30M, 0.32 MM OD) followed by FID. After 0.5 min, valve is switched and gases are sent to Innowax column (45 m, 0.2 MM OD, 0.4 uM) followed by FID. Gaspro column separates C1-C8, paraffins and olefins. Innowax separates larger paraffins and olefins (>C9) and aromatics BTX and C9+ aromatics. The conversions (X, %), space time yields (STY, mmol·gcat⁻¹·h⁻¹), and selectivities (S, %) are defined as follow:

$$X_{CO_2} = \left(1 - \frac{C_{He,blk} \cdot C_{CO_2,R}}{C_{He,R} \cdot C_{CO_2,blk}}\right) \cdot 100$$

$$S_{Cn} = \frac{n \cdot \left(\frac{C_{Cn,R}}{C_{He,R}}\right)}{\left(\frac{C_{CO_2,blk}}{C_{He,blk}} - \frac{C_{CO_2,R}}{C_{He,R}}\right)} \cdot 100$$

$$STY_{C2-C4} = \frac{X_{CO_2}/100 \cdot S_{C2-C4}/100 \cdot GHSV_{CO_2}}{22.4}$$

where C_{He,blk}, C_{He,R}, C_{CO₂,blk}, C_{CO₂,R} are the concentrations determined by GC analysis of He in the blank, He in the reactor effluent, CO₂ in the blank, and CO₂ in the reactor effluent, respectively, C_{Cn,R} is the concentration the reactor effluent determined by GC analysis of a product with n carbon atoms, and GHSV is the space time velocity in mL·gcat⁻¹·h⁻¹. The error in carbon balance was better than 2.5% in all cases.

X-ray diffraction measurements (XRD)

X-ray diffraction patterns for air stable materials were collected using a Bruker D8 Advanced A25 diffractometer in Bragg-Brentano geometry fitted with a copper tube operating at 40 kV and 40 mA and a linear position sensitive detector (opening 2.9 °). The diffractometer was configured with a 0.14 ° diverging slit, 3.2 ° anti-scattering slit, 2.5 ° Soller slits, and a Ni filter. The data sets were acquired in continuous scanning mode over the

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2 θ range 5–90, using a step interval of 0.028 and a counting time of 17 s per step.

Powder X-ray diffraction measurements for air sensitive catalyst were conducted using a Bruker D8 Venture single crystal diffractometer equipped with a PHOTON II area detector and an I μ S microfocus source (set to 50 kV, 1 mA) providing an Mo K α radiation (λ_{K1} = 0.70930 Å, λ_{K2} = 0.71359 Å). The detector was positioned at a swing angle θ = 0° and a sample-to-detector distance of 40 mm to collect an extended 2 θ range of 2.7–107.2°. Capillaries of 1 mm diameter were filled with powders using standard procedure to handle air sensitive compound (e.g. the spent catalyst), then air-sealed and finally mounted on the goniometer for transmission measurement. A single frame per sample was recorded with an exposure time of 10 min using a phi-360 scan. Integration over the 5–63° 2 θ range was performed by DIFFRAC.EVA software from Bruker.

Temperature programmed oxidation (TPO) measurements.

The temperature programmed oxidation (TPO) experiments were carried out in a Micromeritics Asap 2020. The samples were first heated up in an helium flow at 350°C followed by a reduction in 10% H₂ for 4 hours. After cooling, a flow with 10% of CO₂ was fed and the temperature of the samples was increased linearly at a rate of 10 K/min. The CO₂ consumption was continuously monitored by a thermal conductivity detector (TCD).

Inductively coupled plasma (ICP) measurements.

The analyses were carried out using a PerkinElmer Model Optima 8300 instrument. Prior to the measurement, 40 mg of a sample were digested in 8 ml of aqua regia. Microwave-assisted heating program was implemented using 15 min ramp time and 20 min hold time at 1000W applied power and 220°C.

Electron Microscopy and Elemental Mapping.

Transmission electron microscopy (TEM) of the samples was performed with a Titan Themis-Z microscope from Thermo Fisher Scientific by operating it at the accelerating voltage of 200 or 300 kV and with a beam current of 0.3 up to 0.8 nA. Dark field imaging was performed by scanning TEM (STEM) coupled to a high-angle annular dark-field (HAADF) detector. The STEM-HAADF data were acquired with a convergence angle of 20.9 mrad and a HAADF inner angle of 77 mrad. Furthermore, a X-ray energy dispersive spectrometer (FEI SuperX, $\approx$ 0.7 sr collection angle) was also utilized in conjunction with DF-STEM imaging to acquire STEM-EDS spectrum-imaging datasets. During the acquisition of these datasets, at every image-pixel, a corresponding EDS spectrum was also acquired for generating simultaneously the elemental maps of Fe, O, C, and K atoms. It is also pertinent to note herein that spectrum-imaging datasets were acquired in so-called frame mode in which electron beam was allowed to dwell at each pixel for only a time of few microseconds in order to keep a total frame time to 6 seconds or less. Both imaging and spectroscopy datasets for each sample were both acquired as well as analyzed with a newly developed software package called Velox from Thermo Fisher Scientific. The elemental maps for Fe, O, C and K atoms were computed using the extracted intensity of their respective K α lines after background subtraction.

X-ray photoelectron spectroscopy (XPS) measurements.

The XPS experiments were performed on a Kratos Axis Ultra DLD instrument equipped with a monochromatic Al K α x-ray source ($h\nu$ = 1486.6 eV) operated at a power of 75 W and under UHV conditions in the range of $\sim$ 10–9 mbar. All spectra were recorded in hybrid mode using electrostatic and magnetic lenses and an aperture slot of 300 μ m $\times$ 700 μ m. The survey and high-resolution spectra were acquired at fixed analyzer pass energies of 160 eV and 20 eV, respectively. The samples were mounted in floating mode in order to avoid differential charging. Therefore, XPS spectra were acquired using charge neutralization. Due to the possible formation of a passivation layer hindering the detection of carbide bonds, the sample subjected to reaction was transferred to the XPS instrument and analyzed without exposing it to the ambient air. For this purpose, the sample was first prepared inside the glovebox always kept under argon atmosphere and was subsequently transferred to the XPS instrument using a special transfer chamber filled with argon prior to be sealed. The sample was promptly analyzed after being loaded into the instrument.

Potassium nuclear magnetic resonance (NMR) measurements.

The ³⁹K magic angle spinning (MAS) solid-state nuclear magnetic resonance (ssNMR) spectroscopic experiments were performed on 900 MHz Bruker AVANCE IV 21.1 T spectrometers equipped with 4 mm CPMAS probes. ³⁹K shifts were referenced to KBr and typically recycle delays of 1 s was used.

Density functional theory (DFT) calculations.

We performed density functional theory (DFT) calculations using the Vienna Ab initio Simulation Package (VASP)^[42–35]. Core electrons were described using projector augmented wave (PAW) pseudopotentials^[46,47], whereas valence electrons were described using the plane wave basis set with 400 eV energy cut-off and 0.1 eV Methfessel-Paxton smearing of electron density^[48]. For K₂CO₃, KHCO₃, and KOOCH single crystals 5 $\times$ 3 $\times$ 5, 5 $\times$ 3 $\times$ 7, and 7 $\times$ 5 $\times$ 5 k-points grids were used to sample the reciprocal space.

Gaseous species were placed in a simulation cell of dimensions 12 Å $\times$ 13 Å $\times$ 14 Å to minimize interaction between adjacent molecules. Geometry optimization was performed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional until all forces were less than 0.005 eV/Å. Optimized unit cells are shown in Figure S1. Gibbs free energies of gas phase species were calculated using the ideal gas approximation. Free energies of solids were obtained using phonopy^[49] package for 2 $\times$ 2 $\times$ 2 supercells with the 8 $\times$ 8 $\times$ 8 q-point grid. Vibrational frequencies were obtained from VASP using 0.03 Å displacements.

In order to choose a suitable exchange-correlation functional, we calculated the standard Gibbs reaction energies of two reactions that involve species whose standard formation enthalpies and entropies were available in NIST database: (i) the reverse water gas shift (RWGS) and (ii) the addition of carbon dioxide to potassium oxide to produce potassium carbonate:

	Chemical equation	$\Delta_r G^\circ$ (eV) ^[50]
(i)	$CO_2(g) + H_2(g) = CO(g) + H_2O(g)$	0.30
(ii)	$K_2O(s) + CO_2(g) = K_2CO_3(s)$	-3.62

Geometries were optimized with the PBE functional, and single-point energy calculations were also performed with the rPBE, PBE0, HSE and TPSS functionals. In addition, we also tested the PBE-D3 functional, which includes Grimme's dispersive D3 correction^[51]. In the latter case we also reoptimized the geometries. Differences between the calculated Gibbs reaction energies and the NIST data are summarized in Figure S3. Although the hybrid functionals (PBE0 and HSE) perform better than the other considered functionals, they still overestimate the RWGS reaction energy by more than 0.2 eV.

The deviation of the RWGS reaction energy calculated using DFT methods, relative to experimental data, was discussed by Peterson et al.^[10]. Following suggestions in ref. 7, we added to the DFT energies 0.10 eV for every H–H bond, and 0.15 eV for every C=O double bond. These corrections improved the accuracy of all methods for the energies of the two considered reactions. The lowest inaccuracy of 0.15 eV is achieved for the corrected PBE-D3 method, which is used to obtain results discussed in the main text.

For the reactions listed in Figure 1.C the Gibbs reaction energies, $\Delta_r G$, were calculated for temperatures between 250 K and 650 K assuming 1 bar partial pressures of all reactants and products. Relative stability of the three solids at different temperatures were calculated using the following formulas:

Species	Stability formula relative to K ₂ CO ₃
KHCO ₃	$\Delta_f G^\circ(KHCO_3) = (2 G^\circ(KHCO_3) - G^\circ(K_2CO_3) - G^\circ(H_2O) - G^\circ(CO_2))/2$
KOOCH	$\Delta_f G^\circ(KOOCH) = (2 G^\circ(KOOCH) - G^\circ(K_2CO_3) - G^\circ(H_2) - G^\circ(CO))/2$

High energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES).

HERFD-XANES spectra at the Fe K-edge were obtained at the European Synchrotron Radiation Facility (Grenoble, France) on the CRG-FAME-UHD beamline (BM16). The ring was operated at 6 GeV with a nominal current of 200 mA in 7/8+1 mode. The beamline was equipped with a liquid-nitrogen-cooled double-crystal Si (220) monochromator surrounded by two Rh-coated mirrors for harmonic rejection. The beam size on the sample was 220 $\times$ 100 μ m (H $\times$ V, FWHM). The monochromator was energy-calibrated by measuring the iron K absorption edge using a metallic iron foil (7112 eV).

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Acquisition of spectra was performed ex-situ with samples retrieved inside a glove box and loaded into a XAS cell dedicated for air-sensitive solids. The Fe HERFD-XANES spectra were recorded with a crystal analyzer spectrometer (CAS) using five spherically bent Ge (620) crystals in a Rowland geometry. The spectra were recorded at the iron K β emission line using a 2D XPAD detector. The total energy resolution of the HERFD-XANES data was estimated to be approximately 2.4 eV.

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**Tandem conversion of CO_2 to
valuable hydrocarbons in highly
concentrated potassium iron
catalysts**

Potassium carbonate-iron catalyst for tandem conversion of CO_2 : The potassium carbonate activates the CO_2 while undergoing several transformation, yielding KOOCH and releasing CO . This CO is subsequently hydrogenated to olefins on the iron nanoparticles via Fisher-Tropsch.