Metal Organic Framework derived iron catalysts for the direct hydrogenation of CO₂ to short chain olefins

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ABSTRACT: We report the synthesis of a highly active, selective and stable catalyst for the hydrogenation of CO₂ to short chain olefins in one single step by using a Metal Organic Framework as catalyst precursor. By studying the promotion of the resulting Fe(41 wt %)-carbon composites with different elements (Cu, Mo, Li, Na, K, Mg, Ca, Zn, Ni, Co, Mn, Fe, Pt and Rh) we have found that only K is able to enhance olefin selectivity. Further catalyst optimization in terms of promoter loading results in catalysts displaying unprecedented C₂-C₄ olefin space time yields: 33.6 mmol·gcat⁻¹·h⁻¹ at X_{CO_2} = 40%, 320 ° C, 30 bar, H₂/CO₂ = 3, and 24000 mL·g⁻¹·h⁻¹. Extensive characterization demonstrates that K promotion affects catalytic performance by: (i) promoting a good balance between the different Fe active phases playing a role in CO₂ hydrogenation, namely

iron oxide and iron carbides and by (ii) increasing CO₂ and CO uptake while decreasing H₂ affinity, interactions responsible for boosting olefin selectivity.

INTRODUCTION

Carbon dioxide levels today are higher than at any point in the past 800,000 years, exceeding 400 ppm in 2016 [1] and leading to a dangerous temperature increase of the Earth's surface [2, 3]. Along with the necessity to develop efficient capture technologies, advances in the catalytic transformation of CO₂ to base chemicals would add an additional economic incentive to empower initiatives into CO₂ capture [4-9]. In a potential (and feasible) scenario of cheap hydrogen produced via electrolysis, the formation of light olefins, the most demanded base chemicals, from CO₂ may become a very attractive technology. However, efficient catalysts for this process are still to be developed [8].

The conversion of CO₂ to olefins and other hydrocarbons generally proceeds through a direct route [7] where CO₂ is first transformed into CO via reverse water gas shift (RWGS) followed by the subsequent conversion of CO to hydrocarbons following a classical Fischer-Tropsch synthesis (FTS) mechanism. In another approach, the conversions of CO₂ to olefins can also proceed via methanol as intermediate using a bifunctional zeolite catalyst [10, 11]. The main advantage of this route is that is possible to break the limitation of the Anderson-Schulz-Flory (ASF) distribution, being able to obtain selectivities to olefins in the hydrocarbon fraction higher than 80% [12]. However, the high selectivity to carbon monoxide during methanol synthesis makes this process unattractive (50 to 90% of the total product is CO). On the other hand, using the FTS route, CO selectivity can be kept below 20% [10-14] (see table S1 for a complete overview of the state of the art, via the direct or the indirect Methanol To Olefins (MTO) route). When it comes to the direct hydrogenation of CO₂ to olefins, most of the catalysts reported are Fe based materials [15-35]. The

main reason behind the exceled behavior of iron lies in the fact that Fe can successfully catalyze both the RWGS and the FTS reaction [36], being Fe_3O_4 and Fe_5C_2 the active phases, respectively [37, 38]. Iron catalyst are often promoted to increase olefin selectivity, usually with K and Na. The highest CO_2 activity has been reported by Choi et al. with a K promoted alumina supported iron catalyst [26]. At a low space velocity of $1900 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ conversion levels of 70% could be achieved with a $\text{C}_2\text{-C}_4$ olefin selectivity of 23%. On the other hand, the highest $\text{C}_2\text{-C}_4$ olefin space time yield (STY) reported to date are $49.9 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for a Fe-Co/K- Al_2O_3 catalyst (see entry 16, table S1) [25].

Recently, some of us reported the use of Fe based Metal Organic Frameworks as precursors for the production of highly dispersed Fe nanoparticles in a porous carbon matrix for application in FTS [39-41]. Here we demonstrate that similar base catalysts can be tuned to display an unprecedented catalytic performance in the more challenging direct hydrogenation of CO_2 .

MATERIALS AND METHODS

All chemicals were purchased from Sigma Aldrich and used as received.

Catalyst preparation. The Fe/C catalysts were obtained by carbonization of the Basolite F300 MOF precursor. The heating was carried out on a tubular oven at 600°C for 8 h with a heating rate of $2^\circ\text{C}/\text{min}$, under nitrogen atmosphere. Prior to opening to the atmosphere the samples were passivated under 2% O_2 in N_2 for 4 h at room temperature. The promoted catalysts were prepared by incipient wetness impregnation. A certain amount of the precursor to achieve the desired 0.75 wt. % promotion level was dissolved in a mixture of water and methanol (50:50) and impregnated inside the pores of the Fe/C catalyst. The resultant material was heated up to 75°C for 12 h and to 350°C for 2h under N_2 atmosphere.

The Fe/cellulose catalyst was obtained by wetness impregnation of commercial cellulose with iron nitrate, followed by flash pyrolysis. First, a certain amount of the iron precursor enough to achieve 35 wt. % iron content was dissolved in deionized water and further impregnated inside the pores of the cellulose support. The resultant material was heated up to 75 °C for 12 h. Then, the dry material was heated up on a tubular oven at 800 °C for 60 min with a heating rate of 30°C/min under nitrogen atmosphere. Prior to opening to the atmosphere the samples were passivated under 2% O₂ in N₂ for 4 h at room temperature. The promotion with K was carried out in the same way as the MOF mediated catalyst.

CO₂ hydrogenation tests. Catalytic tests were executed in 16 channel Flowrence® of Avantium. One mixed feed gas flow is distributed over 16 channels with Relative Standard Deviation of 2%. The mixed feed has 25vol% of CO₂ and 75vol% of H₂. In addition, 0.5 ml/min of He is mixed with the feed as internal standard. It was aimed to have 24000 mL·g⁻¹·h⁻¹ per channel. The channels are stainless steel tubes inserted in furnace. Outside diameter is 3mm and inside diameter of tubes is 2 mm and they have 300mm length. To make sure that the bed is in the isothermal zone of the furnace, the tubes are first filled with coarse SiC (corundum) particle, grit 46. 300μl results in 9.5 cm bed length, which is the position in the tube where isothermal zone begins. Then, after pressing and crushing, the catalyst samples are sieved to obtain a fraction between 150 μm and 250 μm and 50 mg of the sieved sample is loaded on top of SiC bed. One of the 16th channels was always used without catalyst as blank. Prior to feeding the reaction mixture all samples are pretreated *in-situ* with a pure H₂ atmosphere for 5 hours at 350°C. The tubes are pressurized to 30 bar using a membrane based pressure controller working with N₂ pressure.

The conversions (X , %), space time yields (STY , mmol·gcat⁻¹·h⁻¹), and selectivities (S , %) are defined as follows:

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

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

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

where $C_{He,blk}$, $C_{He,R}$, $C_{CO_2,blk}$, $C_{CO_2,R}$ are the concentrations determined by GC analysis of He in the blank, The error in carbon balance was better than 2% in all cases with the exception of the Fe/C+Rh catalyst that gave an error of 3.5%. Traces (below 1%) of oxygenated compounds (Methanol and iso-Propanol) were detected for the Cu, Mn, Mg, Co, Zn, Rh and Pt promoted catalysts.

Catalyst characterization. *Nitrogen adsorption measurements.* Nitrogen adsorption and desorption isotherms were recorded on a Micromeritics Asap 2040 at 77 K. Samples were previously evacuated at 373 K for 16 h. The BET method was used to calculate the surface area.

X-ray diffraction measurements (XRD). X-ray diffraction patterns were obtained in a Bruker D8 equipment in Bragg Brentano configuration using CuK radiation. The spectra were scanned with step size of 0.02° in the 2θ range of 20–80°. The crystalline phase was identified by comparison data from the inorganic crystal structure database, ICSD.

Temperature programmed reduction (TPR) measurements. The temperature programmed reduction (TPR) experiments were carried out in a Micromeritics Asap 2020. The catalyst samples were first activated in an argon flow at 350 °C for 4 h, followed by cooling to 50 °C. A gas mixture of 10% H₂/Ar was passed over the samples at a flow rate of 50 mL/min. The temperature of the

samples was increased linearly at a rate of 10 K/min. The hydrogen consumption was continuously monitored by a thermal conductivity detector.

X-ray fluorescence (XRF) measurements. X-ray fluorescence measurements were obtained in a HORIBA XGT-700. For every measurement 5 different spots were analyzed for each sample with a total analysis time of 1500 seconds per sample.

CO₂, CO and H₂ chemisorption measurements. Chemisorption measurements were performed at 50 °C using a Micromeritics ASAP 2020 instrument. The samples (100 mg) used for the chemisorption study were first reduced at 350 °C in a H₂ gas flow for 5 hours, similarly to the reaction pretreatment, followed by evacuation at the reduction temperature and then cooling to 50°C. Then, a known volume of CO₂, CO or H₂ was injected in the system. The gas consumption was continuously monitored by a thermal conductivity detector.

X-ray photoelectron spectroscopy (XPS) measurements. The X-ray photoelectron analysis (XPS) was performed with an Axis Ultra DLD (Kratos Tech.) equipment. The spectra were excited by a monochromatized Al K α source (1486.6 eV) run at 15 kV and 10 mA. For the calibration measurement, C1s peak at 284.8 eV was used as reference standard to calibrate the binding energy and the XPS data were processed and analyzed in CasaXPS software.

Inductively coupled plasma (ICP) measurements. The analyses were carried out on an ICP-OES after digestion of the solid samples. Complete digestion of the powder samples was achieved using aqua regia in a ratio 1 mg catalyst: 1 mL aqua regia, during 24 h at room temperature.

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 300 kV and with a beam current of 0.5 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 29.9 mrad and a HAADF inner angle of 30 mrad. Furthermore, a X-ray energy dispersive spectrometer (FEI SuperX, ≈ 0.7 sR collection angle) was also utilized in conjunction with DF-STEM imaging to acquire STEM-EDS spectrum-imaging datasets (image size: 1024 x 1024 pixels, dwell time 5 μ s).

RESULTS AND DISCUSSION

In our approach (Figure 1.a), the Fe-based MOF Basolite F300® was used as a template for the preparation of the Fe/C catalysts through a carbonization at 600 °C for 8 h under N₂ atmosphere. Based on a literature review, we selected 14 potential promoters and designed a high throughput campaign to identify the most promising doping elements. The Fe/C material was further loaded with the promoter (0.75% wt.) by incipient wetness impregnation in order to obtain the final promoted Fe/C+M catalyst (M = Fe, Cu, Mo, Li, Na, K, Mg, Ca, Zn, Ni, Co, Mn, Pt or Rh). These 14 elements were selected as promoters as it has been reported that they can either improve RWGS activity (Fe, Cu, Mo, Rh, Pt, Ni) [42-47] or olefins selectivity (Li, Na, K, Mg, Mn, Ca, Zn, Co) [25, 34, 48-50].

Figure 1. Morphological characterization of the Fe MOF-mediated catalyst. a) Synthesis strategy for the Fe-based catalyst. b) Bright field TEM imaging of a spent Fe/C catalyst. The inset is a particle size histogram of the smallest and also major population of nanoparticles.

In good agreement with our previous works, transmission electron microscopy (TEM) of the base catalyst (see figure 1) shows Fe nanoparticles confined within the porous carbon matrix with

an average particle size of 4.4 nm. Despite the high Fe loading (41.2% wt., measured by Inductively coupled plasma mass spectrometry, ICP) only a small fraction of the Fe particles have sizes bigger than 20 nm. Carbonization also reduces the material porosity from 924 m²/g to 243 m²/g (see figure S1). X-ray fluorescence (XRF) was employed in all samples to confirm the promoter loading, showing a good agreement between theoretical and experimental values (see table S2). Furthermore, impurities of Cl and S from the original Basolite F300 MOF are revealed, also in line with previous studies [40].

The performance of the different catalysts in the hydrogenation of CO₂ after 50 hours under relevant reaction conditions is showed in figure 2.a. The unpromoted material gives a conversion of 24% with a CO selectivity of 39%, a CH₄ selectivity of 40%, and a very low selectivity of 0.7% for C₂-C₆ olefins. In contrast to most other promoters, addition of K has a dramatic effect on product distribution: C₂-C₆ olefin selectivity increases from 0.7% to 36% while improving catalyst activity.

Figure 2. Catalytic performance of promoted and unpromoted Fe catalysts. a) CO₂ conversion and product distribution after 50 h T.O.S. b) Hydrocarbon distribution and ASF plot on the Fe/C+K(0.75) catalyst. c) Hydrocarbon distribution and ASF plot on the Fe/C catalyst. Reaction conditions: 320 °C, 30 bar, H₂/CO₂ = 3, and 24000 mL·g⁻¹·h⁻¹, T.O.S. = 50h.

The effect of K can be further evaluated when comparing the detailed hydrocarbon distribution of the bare catalyst and the K promoted sample (see figures 2.b and 2.c.) Regarding the other promoters, Na also increases olefin formation, but to a much lower extent than K. Neither of the other 12 promoters were able to enhance olefin formation in a significant manner, but some interesting effects were observed: (i) Cu and Pt increase the CO₂ conversion and the CH₄ and C₂-C₆ paraffin selectivities, (ii) Mn, Mg and Mo enhance CO selectivity and (iii) Ni, Co, and Rh mostly promote methanation. To better understand the effect of these groups of promoters, we selected Fe/C+K, Fe/C+Mo, Fe/C+Pt as representative samples of the three effects described above together with the starting material, Fe/C, for in depth characterization.

Figure 3.a shows the X-Ray diffraction patterns of the different catalysts after 50 hours on stream. In all samples a complex mixture of magnetite, metallic iron, and iron carbide phases can be observed. The potassium promoted catalyst is peculiar since it includes the Fe₅C₂, Fe₇C₃ carbides, while the unpromoted and Pt/Mo promoted catalyst only display the Fe₃C phase (see table S2 and figures S2 and S3), which has been reported as less active than the Fe₅C₂ and Fe₇C₃ phases in FTS [38, 41]. Particularly, the Fe₇C₃ phase has the highest intrinsic activity among the carbides [51]. Another key difference is related to the Fe₃O₄ phase which has undergone a larger sintering with Fe/C+K catalyst, as derived from the higher intensities of the reflections belonging to the Fe₃O₄ phase within this sample, in agreement with the hypothesis that addition of K favors Fe reoxidation [52]. On the other hand, the TPR profiles of the fresh catalysts confirms the presence of only one oxidized species (Fe₃O₄, [53]) that can be reduced at around 600 °C (see figure S4).

Figure 3. Characterization of the selected Fe catalysts. a) XRD after 50 h on stream under standard reaction conditions. b) XPS spectra of Fe 2p core after 50 h on stream under standard reaction conditions. HAADF-STEM imaging and elemental mapping of the Fe/C + K catalyst: c) low magnification image, superposition of d) Fe and O maps, e) Fe and C maps, f) Fe and K maps.

Analysis of the surface of the different catalysts after 50 h on stream by X-ray photoelectron spectroscopy (XPS) at the Fe2p level reveals in most cases the following contributions: a first peak of the spectra at 706.9 eV corresponding to metallic iron [54], a second peak at 707.9 eV characteristic of iron carbides [55], two subsequent peaks at 710.6 and 712.6 eV corresponding to Fe(II) and Fe(III) 2p_{3/2} respectively, a group of satellite peaks around 719 eV, two additional peaks at 723.9 and 725.6 eV arising from Fe(II) and Fe (III) 2p_{1/2} [25, 56] and, finally, the Fe 2p_{1/2} shake-up around 733.4 eV(see figure 3.b). To address the evolution of iron species, additional XPS measurements at the Fe2p level were carried out in the fresh Fe/C+K sample (see figure S5). The absence of a second peak at 707.9 eV, characteristic of iron carbides, suggest that these species are formed on the surface of the catalyst in situ during reaction, in accordance with previous publications and supporting a classical FTS mechanism [18, 38]. The chemical state of K was also investigated by XPS measurement at the C1s level. The two characteristic peaks of K₂CO₃ [57] around 295.9 and 292.9 eV were observed in the fresh and the used samples (see figure S6). Therefore, we conclude that K remains in the carbonate form.

HAADF-STEM was used to further investigate the properties of the Fe/C+K catalyst after reaction. The micro-graph presented in figure 3.c and figure S7.a shows typical example of agglomerates containing small nanoparticles in the 10-20 nm range with few larger particles (>100 nm). This evidenced a partial sintering of the initial 4 nm nanoparticles along the catalytic reaction. Elemental mapping of selected areas confirmed the partial oxidation of the Fe/C+K catalyst as observed on figure 3.d, 3.e, 3.f and figure S7.b. More precisely, some of the largest metallic iron nanoparticles had only their surface oxidized (figure S8.a) while other medium sized nanoparticles were fully oxidized (figure S8.b), most probably as Fe₃O₄. Unfortunately, it was not possible to pinpoint the iron carbide nanoparticles since the catalyst is embedded in a carbon matrix (figure

3.e). However, the potassium distribution was highlighted successfully in figure 3.f and was found homogenous through the sample.

According to the proposed mechanism for this process, CO₂ is initially reduced to CO via RWGS on Fe₃O₄, followed by a subsequent hydrogenation of CO via FTS on Fe₅C₂ sites [7, 38]. Olefin selectivity on the Fe₅C₂ sites depends mainly on reactions involving secondary olefins. Re-adsorption of these species results in further chain growth, leading to higher α values and to a decrease in the O/P ratio (paraffins, once formed do not re-adsorb) [58, 59]. Olefin re-adsorption depends strongly on the relative strength of the Fe-C bond compared to the Fe-H bond. Stronger Fe-C bonds will entail an increase in the surface CO/H₂ ratio on the catalyst surface inhibiting olefin re-adsorption, hindering the formation of paraffins through H insertion, and finally leading to higher olefin selectivities [9, 60-62]. CO₂ and H₂ chemisorption measured on selected samples (table 1) shows that CO₂ uptake increases considerably upon K promotion (+258.2%). At the same time, H₂ chemisorption decreases by more than half (-60.8%). K is a very strong base and efficient electron donor. We speculate that, as CO₂ tends to accept electrons from iron upon adsorption, the presence of K on the surface favors the adsorption of this reactant and strengthens Fe-C interactions [60]. The reverse argument can be used to rationalize the decreased hydrogen affinity: hydrogen donates electrons to iron upon adsorption and, consequently, the presence of the electron-donating alkali makes Fe less electrophilic and less prone to chemisorb hydrogen. Based on these arguments, we propose that the enhanced olefin selectivity of the Fe/C+K is due to the observed differences in CO₂ and H₂ affinities. The results of the Pt promoted sample show an increase of the H₂ chemisorbed in comparison with CO₂, implying a weakening of the Fe-C interactions. Such enhanced H₂ coverage is responsible for the observed high selectivities to both CH₄ and paraffins (see figure 2.a). Finally, promotion with Mo weakens both CO₂ and H₂ affinities.

This implies that, most likely, once formed, CO would quickly desorb rather than engage in FTS, in accordance with the observed high selectivity to CO on the Mo sample. Since CO is an important reaction intermediate, CO adsorption measurements were also carried out (see table S4) on the selected catalyst. The CO uptake increases considerably upon K promotion (+271.5%), similarly to the CO₂ chemisorption. Supporting the hypothesis of a higher CO coverage and lower H₂ coverage, responsible for a higher selectivity to olefins.

Table 1. CO₂ and H₂ chemisorption on selected catalysts at 50 °C and 1 bar.

Sample	H ₂ uptake (cm ³ /g)	CO ₂ uptake (cm ³ /g)	ΔH ₂ (%)	ΔCO ₂ (%)
<i>Fe/C</i>	0,0046	0,470	-	-
<i>Fe/C+K</i>	0,0018	1,683	-60,87	258,09
<i>Fe/C+Pt</i>	0,0090	0,538	95,65	14,55
<i>Fe/C+Mo</i>	0,0010	0,084	-78,26	-82,13

In order to better understand the effect of temperature and K loading, we performed additional catalytic tests. Increasing the temperature leads to the formation of higher amounts of CO and methane (see figure 4.a) at the expenses of C₇₊ hydrocarbons, as would be expected from a reaction mechanism involving Fischer–Tropsch [57]. An optimum in performance can be found at 350 °C, yielding a CO₂ conversion of 38.5% with a C₂–C₆ olefin selectivity of 38.8%. Regarding the effect of K loading, surprisingly all the catalyst are stable regardless of the amount of alkali (see figure 4.b), in contrast with the conventional CO FTS catalysts [39]. In terms of hydrocarbon distribution, increasing the K content decreases the formation of methane while increasing the amount of olefins (se figure 4.c). Nevertheless, loadings higher than 0.75% lead to an increase in the formation of longer hydrocarbons. When it comes to CO selectivity, a volcano correlation with an optimum

(low) selectivity at a 0.75 wt.% loading of K is found. This intermediate loading seems to offer the best compromise in terms of product selectivity when short chain olefins are targeted as primary product.

Figure 4. Catalytic performance of the K promoted catalyst. a) Effect of reaction temperature on the Fe/C + K(0.75) catalyst. b) Time-on-stream evolution of CO₂ conversion for the K promoted Fe/C catalysts at 350 °C. c) Effect of K loading on CO₂ conversion and product distribution after 50 h T.O.S. at 350 °C. Reaction conditions: 30 bar, H₂/CO₂ = 3, and 24000 mL·g⁻¹·h⁻¹.

The possibility of cross interactions between the different promoters was checked by preparing different bimetallic catalysts with different K, Pt and Mo concentrations. The results are summarized in figure S9. No specific interactions were observed, being the amount of olefins formed highly dependent upon the K loading. Furthermore, in order to compare the performance of our MOF-mediated catalyst with a conventional iron-carbon catalyst, we synthesized a Fe/cellulose derived material [63] promoted with K. This Fe/cellulose catalyst consists of well dispersed iron nanoparticles in a carbonaceous matrix, similarly to our MOF-mediated catalyst (see figure S10). However, the performance in the CO₂ hydrogenation is not comparable, as the Cellulose material yields mainly CO, even when promoted with K (see figure S11), highlighting the unique nature of catalysts obtained through the MOF-mediated approach.

Figure 5. Effect of the operational conditions in the catalytic performance of the Fe/C + K(0.75) catalyst. a) Effect of pressure. a) Effect of space time. a) Effect of H₂/CO₂ ratio. a) Effect of CO co-feeding. Standard reaction conditions: 350 °C, 30 bar, H₂/(CO+CO₂) = 3, and 24000 mL·g⁻¹·h⁻¹, T.O.S. = 24h.

The effect of the operational conditions in the catalytic performance of the Fe/C + K(0.75) catalyst was thoroughly investigated for three different temperatures: 325, 350 and 375 °C. Higher pressures lead to an increase of the conversion, while the selectivity to olefins is slightly reduced. On the other hand, lowering the pressure to 20 bar reduces both the conversion and the selectivity

to olefins, but increases the olefin/paraffin ratio. The effect of pressure on the conversion is clear, as the hydrogenation of CO₂ to hydrocarbons is followed by a volume decrease and is thermodynamically favored by the pressure increase. However, the effect of pressure in the olefin selectivity is very complex due to the many reactions involved [57].

Increasing the GHSV to 36000 mL·g⁻¹·h⁻¹ reduces the CO₂ conversion, while lowering the GHSV to 12000 mL·g⁻¹·h⁻¹ increases the CO₂ converted. Surprisingly, the effect on the olefins selectivity depends on the reaction temperature. At 325 °C the selectivity decreases with the space time, at 350 °C the selectivity remains invariable and at 375 °C the selectivity increases with the space time. Also, highest o/p ratios are obtained with the highest GHSV, suggesting that the formation of olefins is a competitive intermediate step. This behavior is consistent with the mechanism of the secondary reactions of olefins, such as hydrogenation or hydrogen transfer [58], that decrease the olefin selectivity yielding paraffins.

Varying the H₂/CO₂ ratio leads to a decrease of the selectivity to olefins. However, lower H₂ concentration in the feed leads to an increase of the o/p ratio, achieving a remarkable o/p ratio of 6.95 at 325 °C. This is evidently caused by the decreased hydrogenation ability of the catalyst in an atmosphere with lower H/C ratio that, consequently, slows secondary hydrogenation of olefins. Also, higher H₂/CO₂ ratios lead to higher conversions and vice versa. According to the RWGS equilibrium [8, 9], higher H₂ pressures will displace the equilibrium towards CO, which is further converted to olefins and paraffins on the carbide [7], while lower H₂ pressures will have the opposite effect.

Finally, CO co-feeding was also studied since from an industrial point of view the recycling of the CO plus the uncovered CO₂ is highly desirable. The addition of CO to the feed decreases the conversion, in accordance with the low CO adsorption values in our MOF mediated catalyst (see

table S4). Furthermore, addition of CO to the feed will displace the RWGS equilibrium towards the formation of CO₂, decreasing the conversion. On the other hand, higher CO in the feed leads to higher olefin selectivity and higher o/p ratios. Similar selectivity trends were reported by Prasad et al. for a Fe-Cu-Si-K catalyst [18]. Altogether, CO₂ hydrogenation is very sensitive to the reaction conditions.

Last but not least, the obtained C₂-C₄ olefin STY of the here reported Fe/C+K(0.75) catalyst, when put in perspective with the state of the art (see table S1), turns out to be at least one order of magnitude higher than in the bulk of the existing literature [10-34] and 3 times higher than the best catalyst published to date [25] (see figure 6). Our material even vastly outperforms another MOF mediated catalyst (last entry of table S1), showing a C₂-C₄ olefins space time yield 6 times higher than the Fe-MIL-88B catalyst reported by Guo et al. [35].

Figure 6. C₂-C₄ olefin STY (mmol·g_{cat}⁻¹·h⁻¹) obtained in this work for the Fe/C+K(0.75) catalyst at 350 °C compared to the best catalysts available for CO₂ hydrogenation (refs 10-35).

CONCLUSIONS

In summary, our work further demonstrates that the use of metal organic frameworks as precursors for the preparation of heterogeneous catalysts offers very interesting opportunities. In the specific case here considered, the challenging direct hydrogenation of CO₂ to olefins, key factors dominating catalyst performance are: (i) the high Fe content with an optimal dispersion of the active iron phases responsible for RWGS and FTS chemistries and (ii) fine tuning of H₂ and CO₂ interactions with the catalyst by K promotion.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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