Transforming carbon dioxide into jet fuel using an organic combustion-synthesized Fe-Mn-K catalyst

Benzhen Yao, Tiancun Xiao, Ofentse A. Makgae, Xiangyu Jie, Sergio Gonzalez-Cortes, Shaoliang Guan, Angus I. Kirkland, Jonathan R. Dilworth, Hamid A. Al-Megren, Saeed M. Alshihri, Peter J. Dobson, Gari P. Owen, John M. Thomas & Peter P. Edwards

With mounting concerns over climate change, the utilisation or conversion of carbon dioxide into sustainable, synthetic hydrocarbons fuels, most notably for transportation purposes, continues to attract worldwide interest. This is particularly true in the search for sustainable or renewable aviation fuels. These offer considerable potential since, instead of consuming fossil crude oil, the fuels are produced from carbon dioxide using sustainable renewable hydrogen and energy. We report here a synthetic protocol to the fixation of carbon dioxide by converting it directly into aviation jet fuel using novel, inexpensive iron-based catalysts. We prepare the Fe-Mn-K catalyst by the so-called Organic Combustion Method, and the catalyst shows a carbon dioxide conversion through hydrogenation to hydrocarbons in the aviation jet fuel range of 38.2%, with a yield of 17.2%, and a selectivity of 47.8%, and with an attendant low carbon monoxide (5.6%) and methane selectivity (10.4%). The conversion reaction also produces light olefins ethylene, propylene, and butenes, totalling a yield of 8.7%, which are important raw materials for the petrochemical industry and are presently also only obtained from fossil crude oil. As this carbon dioxide is extracted from air, and re-emitted from jet fuels when combusted in flight, the overall effect is a carbon-neutral fuel. This contrasts with jet fuels produced from hydrocarbon fossil sources where the combustion process unlocks the fossil carbon and places it into the atmosphere, in longevity, as aerial carbon - carbon dioxide.
For more than a century our industrial society and human-kind’s prosperity, wealth and well-being, have been based on the combustion of hydrocarbon fossil fuels. However, it is abundantly clear this has disturbed the natural environment by the emission of greenhouse gases, most notably carbon dioxide (CO$_2$), nitrous oxide, and methane. Nevertheless, the use of fossil fuels continues to grow with an expected annual increase of 1.3% to 2030, continually exacerbating this problem in the form of climate change. Air transport, playing a significant role in the modern world in worldwide social contact, business and marketing, is a recognized source of high CO$_2$ emissions.

Jet fuel, the generic name for the aviation fuels used in gas-turbine powered aircraft has as its main components linear and branched alkanes and cycloalkanes with a typical carbon chain-length distribution of C$_n$ to C$_{18}$, and where the ideal carbon chain length is C$_{8}$ to C$_{16}$.

Given these recognized environmental concerns, it is now imperative to develop clean, energy-efficient technologies for producing sustainable or renewable aviation fuels. Converting CO$_2$ into fuels and high value-added chemicals has attracted significant worldwide interest in the past few years, as it not only contributes to mitigating greenhouse gas emissions but also produces valuable chemical commodities. As such, CO$_2$ conversion and utilization should be taken both an integral and important part of greenhouse gas control and sustainable development.

Nevertheless, the activation of CO$_2$ is extremely challenging; CO$_2$ is a fully oxidized, thermodynamically stable and chemically inert molecule. Furthermore, hydrocarbon synthesis via the hydrogenation of CO$_2$ usually favours the formation of short-chain, rather than desirable long-chain, hydrocarbons. Hence most of the research in this area have focused on the selective hydrogenation of CO$_2$ to CH$_4$, the oxygenates, CH$_3$OH, HCOOH, and light olefin (C$_2$–C$_4$ olefin)22–41. There have been limited studies on producing liquid hydrocarbons of molecularity C$_5$–C$_8$42–44.

There are two ways to convert CO$_2$ to liquid hydrocarbons; an indirect route, which converts CO$_2$ to CO or methanol and subsequently into liquid hydrocarbons, or the direct CO$_2$ hydrogenation route, which is usually described as a combination of the reduction of CO$_2$ to CO via the reverse water gas shift (RWGS) reaction and the subsequent hydrogenation of CO to long-chain hydrocarbons via Fischer-Tropsch synthesis (FTS)45. Jet fuel can then be obtained from the products after industrially recognized treatments such as distillation or hydro-isomerization. The second, direct route is generally recognized as being more economical and environmentally acceptable as it involves fewer chemical process steps, and the overall energy consumption for the entire process is lower.

The relevant chemical reactions for hydrocarbon fuel production are:

Hydrogenation of CO$_2$:

$$\text{CO}_2 + 3\text{H}_2 \rightleftharpoons (\text{CH}_3)_2 + 2\text{H}_2\text{O} (\Delta H_{298}^0 = -125 \text{ kJ mol}^{-1})$$

The RWGS reaction:

$$\text{CO} + \text{H}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} (\Delta H_{298}^0 = +41 \text{ kJ mol}^{-1})$$

And the FTS reaction:

$$\text{CO} + 2\text{H}_2 \rightleftharpoons (\text{CH}_3)_2 + \text{H}_2\text{O} (\Delta H_{298}^0 = -166 \text{ kJ mol}^{-1})$$

The direct conversion of CO$_2$ into fuels through these various reactions has attracted great interest in recent years, and a compilation of some of these investigations is highlighted in Table 1. However, there are few reports of the direct catalytic conversion of CO$_2$ to jet fuel range hydrocarbons20,47. The key to advancing this process is to search for a highly efficient inexpensive catalyst, that can preferentially synthesise the target hydrocarbon range of interest. Iron-based catalysts, widely used in both the RWGS and FTS reactions, are typically prepared by chemical co-precipitation routes, which unfortunately consumes significant amounts of water19–52.

In this investigation, we report the preparation of iron-based catalysts using the Organic Combustion Method (OCM) and determined their catalytic performance for the direct and efficient conversion of CO$_2$ to jet fuel range hydrocarbons. In brief, the Fe–Mn–K catalyst shows a CO$_2$ conversion of 38.2% and selectivity to C$_8$–C$_{16}$ hydrocarbons of 47.8% with a correspondingly BHETA
low selectivity for CH₄ and CO. In addition, the process also shows a high molar production ratio of olefin-paraffin for C₂–C₄ hydrocarbons.

Results

The rising concerns over climate change and the stringent environmental regulations to deplete the utilization of fossil-derived fuels have generated great opportunities—and major scientific challenges—on the transformation of CO₂ into sustainable, synthetic hydrocarbons fuels, particularly in the synthesis of renewable aviation fuels. At the heart of any progress in this area, the all-important conversion process is closely related to the development of advanced catalysts of high performance for the CO₂ hydrogenation reaction. Therefore, the utilization of novel methods of catalyst preparation represents an important strategy to produce advanced catalytic formulations having high-performance levels. Among the catalyst synthesis methods, the so-called OCM is recognized as an energy-efficient and economically viable approach for the one-pot synthesis of a variety of nanostructured solid catalysts. In this method, the utilization of an organic fuel, having also a cation-complexation character, to yield a homogenous redox solution of the different metal precursors is highly advantageous. In addition, a relatively moderate self-sustaining exothermic reaction of the redox gel may be beneficial to produce the necessary nanostructured catalysts with an efficient promoter effect due to the well-controlled aqueous chemistry of the preparation route and ensuing combustion conditions.

The performance of Fe–Mn–K catalysts for the hydrogenation of CO₂. In terms of the conversion of CO₂ and H₂ to hydrocarbons and CO, the product selectivities, the Anderson–Schulz–Flory (ASF) product distribution, together with the molar ratio of olefin-to-paraffin ratio for C₂–C₄ from the hydrogenation of CO₂ using a Fe–Mn–K catalyst, is shown in Fig. 1; specifically, both the conversions and selectivities for CO₂ hydrogenation are shown for a reaction time of 20 h over a variety of Fe-based catalysts. The GC-MS spectrum of the collected liquid products from the hydrogenation of CO₂ on a Fe–Mn–K catalyst. The jet fuel range hydrocarbons (C₈–C₁₆) are shown.

Fig. 1 Catalyst performance for the hydrogenation of CO₂ using a Fe–Mn–K catalyst. a % conversion of CO₂ and H₂ as a function of reaction time for the hydrogenation of CO₂. b Selectivity of various hydrocarbon products with reaction time for the hydrogenation of CO₂. c Molar ratio of olefin-to-paraffin for the C₂–C₄ range with reaction time for the hydrogenation of CO₂. d ASF plot and α values at reaction time of 20 h. e Conversion and CO selectivity of CO₂ hydrogenation for a reaction time of 20 h over different catalysts. f Products selectivities of CO₂ hydrogenation for a reaction time of 20 h over different catalysts. g GC-MS total ion chromatogram (TIC) of the hydrocarbon fuel from the hydrogenation of CO₂ on a Fe–Mn–K catalyst. The jet fuel range hydrocarbons (C₈ to C₁₆) are shown.


from CO₂ hydrogenation for a reaction time of 20 h, using an example Fe–Mn–K catalyst, is presented in Supplementary Fig. 1.

The data in Fig. 1 illustrate that the Fe–Mn–K catalyst showed high activity for the CO₂ hydrogenation. The CO₂ and H₂ conversion increased rapidly with onset of reaction time in the first 5 h, reaching a stable value of around 40%. The methane selectivity decreased from 30% to 10% from the beginning of the reaction until 20 h, and decreased by a small amount after a further 20 h. In contrast, the light olefin selectivity (C₂–C₄ olefins) increased to an apparent limiting value of 25% at a reaction time of 10 h and above. The liquid product (C₅) selectivity was stable at around 60% and showed a small increase with reaction time. Similarly with FTS, the hydrocarbon products from CO₂ hydrogenation on Fe–Mn–K generally follow the ASF distribution. Figure 1d shows the double ASF product distribution, whose chain growth probabilities (α) are 0.79 for α₁ within the C₁–C₁₂ carbon range and α₂ is 0.57 for C₁₂+ (i.e., heavy hydrocarbons). A high chain growth probability (α) means a low methane selectivity whilst the chain growth decreases when the carbon number increases above 12, indicating lower selectivity for higher (heavier) hydrocarbons.

Compared with the literature results in Table 1, the prepared Fe–Mn–K catalyst showed higher liquid products (C₅+) yield, with the catalyst presenting both high CO₂ conversion and high C₅+ selectivity.

Interestingly, the methane selectivity decreased dramatically at the beginning of the reaction due to the main reaction being CO₂ methanation over the catalyst active sites (Fe₂Fe₃). They produced a high pressure of water and unconverted CO₂ which, importantly, can then oxidize Fe₂Fe₃ to Fe₂O₄. The CO production via the RWGS reaction on Fe₂O₄ active site reacts with H₂ (Fisher-Tropsch synthesis (FTS)), and the CO₂ conversion increased rapidly (Fig. 1a). The product selectivity was then stable after a reaction time of 10 h.

The catalyst also showed a high selectivity for the production of light olefins versus alkanes, with molar ratios of ethylene -to-ethane, propylene-to-propane, and butane-to-butane of 5.8, 2.6, and 7, respectively (Fig. 1c). The GC-FID chromatograms (Supplementary Fig. 1) also show that olefins are the dominant products in the C₂–C₄ hydrocarbon fractions. Overall, the Fe–Mn–K catalyst showed high activity for CO₂ hydrogenation reactions and high liquid hydrocarbons, and light olefin product selectivity.

The GC-MS spectrum of the collected liquid products clearly demonstrate that the Fe–Mn–K catalyst has high selectivity for jet fuel range hydrocarbons as liquid products; the total jet fuel range hydrocarbon selectivity is up to 47.8% among all hydrocarbons. The corresponding yield of jet fuel range hydrocarbons was 17.2% with a CO₂ conversion of 38.2%.

Catalyst characterisation. The catalyst precursor was firstly activated in situ with syngas (H₂:CO = 2:1) prior to catalytic performance evaluation, with a GHSV (gas hourly space velocity) conditions of 1000 mL·g⁻¹·h⁻¹ at atmospheric pressure, a temperature of 320 °C and for 24 h duration. The powder X-ray diffraction (XRD) spectra of the catalyst precursor, together with the activated and used Fe–Mn–K catalysts are shown in Fig. 2 (a).

It can be seen from Fig. 2a, that all the reflections from the catalyst precursor can be assigned to Fe₂O₄ but in contrast, and importantly, all reflections from the activated catalyst can be assigned to Fe₂O₄, which indicated that the Fe₂O₄ is fully carburized to Fe₂O₄ under the treatment with syngas (CO/H₂ ratio of 1:2). The reflections in the powder diffractogram from the activated catalyst phase were considerably more complex, consisting of mixtures of Fe₂O₄, Fe₂O₃, and Fe₂O₅. Interestingly, Fe₂O₅ is widely acknowledged to be the active catalytic species in the in situ hydrogenation of CO and/or CO₂ and this iron carbide phase plays a crucial role in the subsequent C–C chain growth reactions.

We have observed that the catalyst precursor is almost fully converted to Fe₂O₄ during the in situ activation process, whilst Fe₂O₄ is partially regenerated during the first hours of the
catalytic reaction, hence explaining the increases in H2 and CO2 conversion during this period. This finding is perfectly consistent with the recognized “Tandem mechanism” in which these two catalytically active phases (\(\chi-Fe_5C_2\) and Fe3O4) are responsible for the conversion of CO2 and H2 to syngas and for the subsequent C–C chain growth step to produce jet fuel\(^{44,58-60}\).

The formation of Fe3O4 in the used catalyst probably arises from the oxidation of Fe2O3 by CO2 and/or water during the reaction, while the Fe2O3 was reduced to Fe3O4 in the presence of H2 (showed in Supplementary Fig. 24).

Crystallite sizes were calculated using the Scherrer equation for the Fe-based catalysts precursor and these are listed in Table 2. The crystallite size for the Fe–Mn–K catalyst is typically around 14 nm, which is reflected in the observed broad reflections in the XRD spectrum of the catalyst precursor (as shown in Fig. 2).

Surface elemental compositions and the oxidation states of the metals were analyzed using XPS in the region 0–800 eV. The survey spectrum (Fig. 2b) clearly indicates that the sample contains Fe, Mn, K, and O. Figure 2c shows the XPS spectrum of the Fe 2p region, which can be fitted with two spin-orbit doublets corresponding to the Fe 2p3/2 and Fe 2p1/2 peaks with a binding energy gap of 13.7 eV and a shakeup satellite which is assigned to Fe3\(^+\), consistent with those for Fe3O4.\(^{61}\) The measured molar ratio of Fe2\(^+\) : Fe3\(^+\) is 1:2.38, which approximates to the stoichiometry of Fe3O4 (the ratio of Fe2\(^+\):Fe3\(^+\) for Fe3O4 is 1:2). In Fig. 2d we show the Mn 2p XPS spectra, which displayed a spin-orbit doublet of Mn 2p3/2 and Mn 2p1/2 peaks with a binding energy gap of 11.6 eV can be assigned to Mn2O3. In addition, in Fig. 2e we show the O 1s, XPS spectra with a main peak at 529.4 eV, clearly originating from the presence of metal–O bonds.

Table 2 Crystallite sizes of prepared catalysts (with different transition metal promoters) with the citric acid method.

| Catalyst   | 20 | FWHM | d-spacing (nm) | Crystallite size (nm) |
|------------|----|------|----------------|-----------------------|
| Fe–Zn–K   | 35.73 | 0.13 | 0.25          | 64                     |
| Fe–Cu–K   | 35.91 | 0.11 | 0.25          | 74                     |
| Fe–Mn–K   | 35.75 | 0.60 | 0.25          | 14                     |

The effects of transition metal promoters. Manganese compounds are widely utilised as promoters in iron-based catalysts for FTS where the addition of Mn typically improves activity, increases the surface basicity and enhances the carburization of the catalyst\(^{64,65}\). In addition to Mn, Zn\(^{66,67}\) and Cu\(^{43,68}\) have also been used as promoters for Fe-based catalysts for FTS. Thus, Fe–Zn–K and Fe–Cu–K catalysts were also prepared by the same method as the Fe–Mn–K catalyst. The catalytic performance for CO2 hydrogenation using these different catalysts are shown in Fig. 1e, f.

The data in Fig. 1e show that even the iron-catalyst without promoter showed high activity for CO2 hydrogenation, as reflected in the high conversion values. However, from Fig. 1f we can see the methane selectivity was very high, and reached 32.2% while the liquid product selectivity was very low.

In contrast, the promoter-added catalysts, Fe–Zn–K, Fe–Cu–K, and Fe–Mn–K showed high CO2 conversion and high jet fuel range hydrocarbon selectivity. There was no significant difference between the performances of these three catalysts, but the Fe–Mn–K catalyst showed slightly better selectivity for jet fuels synthesis (47.8%) than catalysts of Fe–Cu–K (40.8%) and Fe–Zn–K (45.1%).

Temperature-programmed oxidation (TPO) results of Fe–Mn–K catalyst precursor prepared with citric acid combustion method shown in Supplementary Fig. 24 revealed a small amount (about 3.5 wt%) of carbon residue in the after calcination at 350 °C. The presence of this small amount of carbon in the catalyst is reported to be beneficial for a higher olefin product selectivity. Thus, previous work\(^{2,63}\) reported that the surrounding carbonaceous matter could indeed facilitate the formation of iron carbides during activation, hence improving the higher liquid products selectivity.

Scanning electron microscopy (SEM) images of both the catalyst precursor and the used catalysts are shown in Fig. 3. The precursor consists of closely packed, regular particles (Fig. 3a). Obvious changes take place in the morphology of the catalyst after reaction (Fig. 3b). STEM-BF images of the catalyst precursor and used catalyst were also recorded as shown in Fig. 4.

From Fig. 4a–c it is evident that the catalyst precursor consists of nanoparticles with sizes of ~15 nm. Interestingly, there was no obvious change in catalyst particle size following the hydrogenation reaction (Fig. 4d). In the catalyst precursor (Fig. 4b, c), the measured lattice spacings of 0.25 and 0.3 nm correspond to the (311) and (220) planes of Fe2O3, respectively. In addition to the Fe2O3 phase (Fig. 4e), a \(\chi-Fe_5C_2\) phase was also observed in the used catalysts (Fig. 4f). This has been proposed as the source of the catalytically active sites for CO and/or CO2 hydrogenation to hydrocarbons, as previously reported\(^{44-57}\).
Table 3 Crystalite size of the various prepared catalysts (different base metal) with citric acid method.

| Catalyst   | 2θ  | FWHM | d-spacing (nm) | Crystallite size (nm) |
|------------|-----|------|----------------|-----------------------|
| Fe-Mn-Li   | 36.07 | 0.45 | 0.25           | 19                    |
| Fe-Mn-Na   | 35.98 | 0.26 | 0.25           | 32                    |
| Fe-Mn-Cs   | 36.03 | 0.30 | 0.25           | 28                    |

Effects of base-metal promoters. The impact of potassium (K) compounds on the performance of Fe-based catalysts for FTS has been studied extensively. K is known to promote the formation of longer-chain hydrocarbons, the carburization of surface Fe, and the suppression of CH₄ formation. Therefore, these base metals have also been tested as promoters for the catalytic hydrogenation of CO₂ and their various catalytic performance are summarised in Table 3. The catalysts Fe-Mn-K and Fe-Mn-Cs showed lower catalytic activity (CO₂ conversion of 28.6%) compared with the catalyst prepared with citric acid (CO₂ conversion of 38.2%). In addition to using citric acid as a fuel in the OCM catalyst preparation, we have also investigated other organic chemicals as potential fuel sources. A series of catalysts of the Fe–Mn–K type were therefore prepared with different organic compounds in the catalyst preparation by the combustion route and their catalytic performances for the hydrogenation of CO₂ are listed in Table 4.

It is clear, therefore, that compared to the catalyst prepared without an organic fuel, all the Fe–Mn–K catalysts prepared with organic compounds generally showed both higher CO₂ conversion and higher jet fuel range hydrocarbon selectivity. The catalysts prepared with EDTA, citric acid, oxalic acid, NTA, DTPA, Tartaric acid, HEDTA, and salicylic acid also exhibited good catalytic performance for both CO₂ conversion and jet fuel selectivity. In general, all these organic fuels could also act as chelating agents and hence facilitating the formation of nanostructured catalysts.

The XRD spectra of various catalysts are shown in Supplementary Fig. 4. The catalyst prepared without fuel showed characteristic reflections assigned to Fe₂O₃. However, most of the catalysts prepared with organic fuel compounds showed Fe₃O₄ as the dominant crystalline phase which clearly indicates that part of Fe³⁺ present in Fe₂O₃ was partially reduced to Fe²⁺ in Fe₃O₄ during the catalyst preparation stage. The catalyst prepared with oxalic acid showed XRD reflections corresponding to Fe₃O₄ instead of Fe₂O₃. This implies that under the conditions applied in this investigation, oxalic acid did not reduce the Fe₂O₃ to Fe₃O₄ consistent with its low reducing power compared to other organic fuels.

The crystallite sizes of catalysts calculated from the Scherrer equation for the different base metal promoted catalysts precursor are listed in Table 3. The catalysts have different crystallite sizes ranging from 19 to 32 nm.

Effects of organic fuel compounds. Recently, the Organic-Combustion Method (OCM), also known as the Solution Combustion Method, has been developed to prepare highly active metal catalysts for a variety of processes. In order to investigate the fundamental, underlying efforts of organic fuel compounds, the catalyst prepared without fuel also been synthetised. It is clear that the catalyst prepared without fuel showed lower catalytic activity (CO₂ conversion of 28.6%) compared with the catalyst prepared with citric acid (CO₂ conversion of 38.2%). In addition to using citric acid as a fuel in the OCM catalyst preparation, we have also investigated other organic chemicals as potential fuel sources. A series of catalysts of the Fe–Mn–K type were therefore prepared with different organic compounds in the catalyst preparation by the combustion route and their catalytic performances for the hydrogenation of CO₂ are listed in Table 4.

The XRD spectra of various catalysts are shown in Supplementary Fig. 4. The catalyst prepared without fuel showed characteristic reflections assigned to Fe₂O₃. However, most of the catalysts prepared with organic fuel compounds showed Fe₃O₄ as the dominant crystalline phase which clearly indicates that part of Fe³⁺ present in Fe₂O₃ was partially reduced to Fe²⁺ in Fe₃O₄ during the catalyst preparation stage. The catalyst prepared with oxalic acid showed XRD reflections corresponding to Fe₃O₄ instead of Fe₂O₃. This implies that under the conditions applied in this investigation, oxalic acid did not reduce the Fe₂O₃ to Fe₃O₄ consistent with its low reducing power compared to other organic fuels.

The crystallite sizes of catalysts calculated from the Scherrer equation for the different base metal promoted catalysts precursor are listed in Table 3. Importantly, catalysts prepared with a range of different organic compounds showed smaller crystallite sizes than the catalyst prepared without fuel. We attribute these differences in crystallite sizes as the possible origins of the higher activity of catalysts prepared with organic fuels.

Compared to the co-precipitation method, widely applied in the preparation of Fe-based catalysts, we show that the OCM is a particularly facile production process where, in addition to

Fig. 4 STEM-BF images of the Fe–Mn–K at different nanoscales. a–c The Fe–Mn–K catalyst precursor; d–f the used Fe–Mn–K catalyst.
The combustion reactions are highly exothermic and lead to a rapid evolution of a large volume of gaseous products during the catalysts preparation process. This release of gas depletes the fuel combustion heat and hence limits the rapid temperature rise, thereby advantageously reducing any premature local partial sintering of the primary metal oxides particles. The gas evolution also results in limiting any extended crystal growth or inter particle contact, thereby contributing to smaller particle size catalysts.76.

Although combustion was nominally carried out at 350 °C, the in situ flame temperature during combustion can be very high due to the combustion of gases produced during the decomposition of metal nitrates and the organic compounds. This high-temperature persists for a few minutes and disappears, producing a rapid quenching effect76, which is known to enhance the interaction between Fe3O4 and the promoter, further improving catalytic performance. It is interesting that most of redox gel when combusted at a calcining temperature of 350 °C, produces Fe2O3 without any apparent O2 participation from the atmosphere. However, the main products are Fe3O4 when the calcination temperature increased to 500 °C, one presumes clearly as a consequence of the participation of atmospheric oxygen and/or the associated oxygens from the complexing ligands. In general, the Fe–Mn–K catalysts synthesised with carboxylic acids and polycarboxylic acids as fuels showed superior catalytic performances than those prepared using urea and sugar (glucose) and the catalyst prepared without fuel. Our assertion is that this trend probably derives from two crucial roles (i.e., both a first role can enhance the interaction between Fe3O4 and the promoter, further improving catalytic performance. The first role can enhance the interaction between Fe3O4 and the promoter, further improving catalytic performance. The second (fuel) function can closely control the severity of the precipitation or aggregation during the gel formation, whilst the second role (i.e., both a chelating agent and fuel) that these organic molecules play in the formation of uniform, highly dispersed metal oxide catalysts via the combustion method.

The gaseous products from the organic compound and nitrate combustion reactions are N2, CO2, and H2O. Using citric acid as an example, the stoichiometric reactions can be described as follows, according to the principle of propellant chemistry:

\[
54 \text{Fe(NO}_3\text{)}_3 + 9\text{H}_2\text{O} + 46 \text{C}_x\text{H}_y\text{O}_z = 18 \text{Fe}_3\text{O}_4 + 81 \text{N}_2 + 276 \text{CO}_2 + 716 \text{H}_2\text{O}
\]

These combustion reactions are highly exothermic and lead to a rapid evolution of a large volume of gaseous products during the catalysts preparation process. This release of gas depletes the fuel combustion heat and hence limits the rapid temperature rise, thereby advantageously reducing any premature local partial sintering of the primary metal oxides particles. The gas evolution also results in limiting any extended crystal growth or inter particle contact, thereby contributing to smaller particle size catalysts.

Although combustion was nominally carried out at 350 °C, the in situ flame temperature during combustion can be very high due to the combustion of gases produced during the decomposition of metal nitrates and the organic compounds. This high-temperature persists for a few minutes and disappears, producing a rapid quenching effect, which is known to enhance the interaction between Fe3O4 and the promoter, further improving catalytic performance. It is interesting that most of redox gel when combusted at a calcining temperature of 350 °C, produces Fe2O3 without any apparent O2 participation from the atmosphere. However, the main products are Fe3O4 when the calcination temperature increased to 500 °C, one presumes clearly as a consequence of the participation of atmospheric oxygen and/or the associated oxygens from the complexing ligands.

In general, the Fe–Mn–K catalysts synthesised with carboxylic acids and polycarboxylic acids as fuels showed superior catalytic performances than those prepared using urea and sugar (glucose) and the catalyst prepared without fuel. Our assertion is that this trend probably derives from two crucial roles (i.e., both a chelating agent and fuel) that these organic molecules play in the formation of uniform, highly dispersed metal oxide catalysts via the combustion method.

The gaseous products from the organic compound and nitrate combustion reactions are N2, CO2, and H2O. Using citric acid as an example, the stoichiometric reactions can be described as follows, according to the principle of propellant chemistry:

\[
54 \text{Fe(NO}_3\text{)}_3 + 9\text{H}_2\text{O} + 46 \text{C}_x\text{H}_y\text{O}_z = 18 \text{Fe}_3\text{O}_4 + 81 \text{N}_2 + 276 \text{CO}_2 + 716 \text{H}_2\text{O}
\]

Although combustion was nominally carried out at 350 °C, the in situ flame temperature during combustion can be very high due to the combustion of gases produced during the decomposition of metal nitrates and the organic compounds. This high-temperature persists for a few minutes and disappears, producing a rapid quenching effect, which is known to enhance the interaction between Fe3O4 and the promoter, further improving catalytic performance. It is interesting that most of redox gel when combusted at a calcining temperature of 350 °C, produces Fe3O4 without any apparent O2 participation from the atmosphere. However, the main products are Fe2O3 when the calcination temperature increased to 500 °C, one presumes clearly as a consequence of the participation of atmospheric oxygen and/or the associated oxygens from the complexing ligands.

The gaseous products from the organic compound and nitrate combustion reactions are N2, CO2, and H2O. Using citric acid as an example, the stoichiometric reactions can be described as follows, according to the principle of propellant chemistry:

\[
54 \text{Fe(NO}_3\text{)}_3 + 9\text{H}_2\text{O} + 46 \text{C}_x\text{H}_y\text{O}_z = 18 \text{Fe}_3\text{O}_4 + 81 \text{N}_2 + 276 \text{CO}_2 + 716 \text{H}_2\text{O}
\]
Finally, we have also examined commercial sugar and flour powders as possible fuels in the catalyst preparation process. Catalysts prepared with these fuels also showed high CO₂ hydrogenation activity and jet fuel range hydrocarbon selectivity. The catalytic performance for CO₂ hydrogenation of catalysts prepared with different fuels are shown in Supplementary Figs. 10–22.

The reaction scheme. Hägg carbide (χ–Fe₅C₂) is widely accepted to be the active catalytic species in the FTS and this iron carbide phase plays a crucial role in the C–C chain growth reactions. The χ–Fe₅C₂ usually prepared by activation of hematite under syngas atmosphere at temperature of 200–450 °C, the whole activation process contains a three-step reduction process of Fe₃O₄ to iron (Fe₂O₃ → Fe₃O₄ → FeO → Fe) and then followed by carburisation of Fe to χ–Fe₅C₂. In our experiments, the χ–Fe₅C₂ was reduced and carburised from Fe₃O₄ in the process of magnetite (Fe₃O₄) → wüstite (FeO) → iron metal (Fe) → Hägg carbide (χ–Fe₅C₂). Wei et al. have proposed a comprehensive reaction scheme where χFe₅C₂ is involved in the hydrogenation of CO₂ to gasoline fuel range hydrocarbons, using a Na–Fe₂O₃/Zeolite multifunctional catalyst. We believe that a related, but slightly different, reaction scheme is operating here for the hydrogenation of CO₂ to aviation jet fuel and this is illustrated schematically in Fig. 5.

In contrast to the report by Wei et al., who described catalysts prepared by a one-pot synthesised Na–Fe₂O₃ catalyst with zeolite, we have prepared catalysts using the direct OCM route which showed higher liquid products yield on CO₂ hydrogenation. Thus the Fe₂O₃ catalyst precursor is fully carburised to χ–Fe₅C₂ during our catalyst activation (reduction) process, whilst Fe₃O₄ is partially regenerated from the oxidation of χ–Fe₅C₂ by CO₂ /water in the first hours of the catalytic reaction. Jet fuel synthesis via CO₂ hydrogenation initially takes place by the RWGS reaction (CO₂ + H₂ → CO + H₂) on the catalytically active sites of Fe₃O₄, and subsequently by the FTS reactions (CO + H₂ → CₓHₘ + H₂O) on catalytically active sites on χ–Fe₅C₂.

Using iron-based catalysts for FTS synthesis a fast and reversible exchange of Fe₂O₃ to Fe₅C₂ carbides and vice versa can occur under appropriate reaction conditions. This relatively facile and reversible phase transformation makes possible the incorporation of carbon atoms from the carbide surface into the reaction products via Mars–van Krevelen mechanism as was determined by Gracia et al. through a computational study of the CO hydrogenation on an iron carbide surface. Remarkably, this Mars–van Krevelen-like mechanism on supported Fe catalysts rationalised the enhanced reactivity of highly dispersed iron carbide particles in the initiation of chain growth in F–T synthesis.

As far as we know, there is not a single report in the scientific literature of the Mars–van Krevelen mechanism operating in the CO₂ hydrogenation reaction on Fe catalysts. Obviously, this reaction is more challenging than conventional FT synthesis since the catalyst must have an excellent balance of active sites (phases) to catalyse—in tandem mode—the reverse-water gas shift reaction (or CO₂ partial hydrogenation) and also the CO hydrogenation via the FT reaction to produce Jet Fuel. Our tandem mechanism through the participation of Fe₅O₄ and χ–Fe₅C₂ can easily rationalise the jet fuel formation and give a wider picture of the evolution of the gas, liquid and solid phases during the catalytic reaction. Further work is needed to gain further insight into the possible occurrence of Mars-van Krevelen-like mechanism in the FT stage through carbon isotopic labelling studies. In a flowing gas system these will clearly be experimentally—and financially (!)—challenging.

The carbide phase detected by powder-XRD diffraction was χ–Fe₅C₂, which plays a principal role in the formation of hydrocarbons via FT reaction. According to the literature and our own results, the carburisation process of Fe nanoparticles during the catalytic reaction forms the Fe carbide phase, which through a FT pathway favours the C–C condensation reactions to produce large hydrocarbons within the range of aviation fuel. In our experiments, the χ–Fe₅C₂ was formed during the catalyst activation/reduction process, in the beginning of the reaction what it is happening is mainly CO₂ methanation reaction on χ–Fe₅C₂, the relatively high pressure of water can then oxidise χ–Fe₅C₂ to Fe₂O₃, and the Fe₂O₃ was simultaneously carburised by CO₆₀. In model experiments, Fe₃O₄ was produced from the oxidation of Fe₂O₃ by CO₂/H₂O, and Fe₂O₃ was steadily reduced to Fe₂O₃ by H₂ in the reaction system (Supplementary Fig. 23). Thus Fe₂O₃, χ–Fe₅C₂, and Fe₂O₃ co-exist during the reaction. Using Mn compounds as a promoter noticeably improved the catalyst FTS activity, increased the catalyst surface basicity and enhanced the carburisation of the catalyst. The addition of K compounds promoted the formation of longer-chain hydrocarbon molecules, the carburisation of surface Fe, and the suppression of CH₄ formation, which strongly favours liquid hydrocarbon synthesis. We also find that the addition of both Mn and K as promoters improved the Fe-catalyst performance, directly converting CO₂ into jet fuel range hydrocarbons with high efficiency.

Renewable jet fuels and the circular economy. The Circular Economy (CE) is an attractive, holistic concept gradually and steadily positioning itself as an alternative and reliable alternative to the present, “Business-as-Usual”, unsustainable Linear Economy (LE) based on the “Take, make and dispose” paradigm. Nowadays, researchers have risen to the challenge of climate change and advanced the concept of the so-called “CO₂ Circular Economy”, which directly integrates CO₂ capture from the air (Direct Air Capture, DAC) and converts CO₂ into value-added products. This CO₂ Circular Economy is a valid and highly powerful alternative route to simply burying huge volumes of captured CO₂ underground and one in which future generations will surely expect us to have formed a major aspect of sustainable CO₂ management.

Renewable jet fuels offer considerable potential in the worldwide drive for a future Sustainable Circular Economy Future for the aviation industry. The vision centres on CO₂ conversion as an integral part of carbon recycling. The advances reported here offer a route out of the current, worldwide LE for jet fuels, based...
on the (present) Production-Consumption-Disposal/Emission structure, where the valuable natural resource, crude oil, is extracted, shipped across oceans, transformed into jet fuel and then combusted, with the combustion product either emitted into the atmosphere, or trapped and buried underground (through Carbon Capture and Storage). On the other hand, the CE approach is based on fundamentally—different Production—Consumption—Recycling/Recovery structure or Carbon Capture and Utilization, where, in this case, CO₂ is indeed recognized as a powerful “Resource” to be recirculated using renewable energy to yield carbon-neutral jet aviation fuel.

Obviously, our advance can contribute significantly to more sustainable fuel production process if we input renewable energy into the chain for transforming CO₂ into aviation jet fuel as an additional driving force for the inevitable and urgently required transition toward a circular fuel economy centred on renewable CO₂ utilization.

Within a Jet Fuel CO₂ Circular Economy, the “Goods” (here the Jet Fuel) are continually reprocessed in a closed environment, which saves the natural fossil resources and preserves the environment, whilst also, of course, creating significant numbers of new jobs, new economies and new markets.

In Fig. 6, we attempt to show a comparison of the Aviation Jet Fuel Linear Economy and the Aviation Jet Fuel Circular Economy. For the latter, Green H₂ is derived from renewable energy, and CO₂ is directly converted to Aviation Jet Fuel using our novel catalysts with CO₂ captured from the atmosphere (“Air Capture”). Note the fundamental difference between the Jet Fuel Linear Economy, as compared to the CO₂ to Jet Fuel Circular Economy, where the entire latter process is a closed loop and hence a CO₂ neutral process. This CO₂ Circular Economy for aviation can surely empower worldwide momentum toward not only major economic development for countries but also achieving the UN’s sustainable development goals.

**Methods**

**Catalyst preparation.** Catalysts were prepared by the OCM method; citric acid was used as the organic compound. Typically, a Fe–Mn–K catalyst was prepared from citric acid monohydrate (99%, Sigma-Aldrich), Iron (III) Nitrate nonahydrate (98%, Sigma-Aldrich), Manganese(II) nitrate tetrahydrate (97%, Sigma-Aldrich) and potassium nitrate (99%, Sigma-Aldrich), in a molar ratio of citric acid:Fe (or Co) : Mn : K = 2, and a weight ratio of (Fe- and Mn- and K-precursors + citric acid)/water = 2:1. This initial mixture was stirred to form a homogeneous aequous solution and heated at 50 °C for 1–2 h to obtain a citric acid-based slurry. This paste was then ignited at 350 °C in the air for 4 h to produce a carbon-free powder.

Catalyst samples with different first-row transition metal (Mn, Cu, Zn) promoters were also prepared using the same method: Fe–Cu–K and Fe–Zn–K catalysts were prepared using copper (II) nitrate trihydrate (99–104%, Sigma-Aldrich), and zinc nitrate hexahydrate (98%, Sigma-Alrdrich) as transition metal precursors respectively. Similarly, catalysts with different Fe–Mn–Li, Fe–Mn–Na, and Fe–Mn–Cs base metal promoters were prepared using lithium carbonate (99%, Sigma-Aldrich), sodium carbonate (99.6%, Acros Organics) and cesium carbonate (99%, Sigma-Aldrich), respectively. Typically, the molar ratio of Fe: transition metal base metal used was 10:1:1.

Fe–Mn–K catalysts were also prepared using other organic compounds other than citric acid, specifically: urea (Bio-Reagent, Sigma-Aldrich), tannic acid (ACS reagent, Sigma-Aldrich), Ethylenediamine Tetracetic Acid (EDTA, 99.5%, Fisher Scientific), oxalic acid (99.0%, Sigma-Aldrich), Nitritriacetic acid (NTA, 99%, Sigma-Aldrich), Diethylenetriaminepentaacetic acid (DTPA, 98%, Sigma-Aldrich), tartaric acid (99.5%, Sigma-Aldrich), Na-(2-Hydroxyl) ethylenediamine-N,N’, N’-triacetic acid (HEDTA,98%, Sigma-Aldrich), salicylic acid (99.0%, Sigma-Aldrich). In all discussions catalysts were prepared with citric acid as the organic compound unless otherwise stated.

**Catalysts performance evaluation.** CO₂ hydrogenation experiments were carried out in a stainless steel fixed bed reactor with an inner diameter of 1.0 cm (Zhixiang Blue Evaluation Equipment Technology) with a typical 2.0 g catalyst load. Prior to the reaction, the catalyst was in situ reduced with syngas (H₂:CO = 2:1) at atmospheric pressure, with a GHSV (gaz hourly space velocity) of 1000 mL g⁻¹ h⁻¹, at 320 °C for 24 h. Following reactor cooling to below 50 °C, a mixture of gas with an H₂/CO₂ ratio of 3 and N₂ (as an internal standard gas) was introduced at a gas flow of 40 mL min⁻¹ (GHSV = 2400 mL g⁻¹ h⁻¹). The reactor was then heated at a rate of 2 °C/min to 300 °C. The reaction pressure was fixed at 10 bar (1 MPa) using a back pressure regulator. The effluent gaseous products were analysed using an online Gas Chromatograph (Perkin Elmer Clarus 580 GC) with flame ionization (FID) and thermal conductivity detectors (TCD), and the collected liquid products were analysed by Gas Chromatograph Mass Spectrometry (SHIMADZU GCMS-QP2010 SE).

The CO₂ and H₂ conversion and product selectivity’s were calculated from the following relationships:

\[
\text{CO}_2 \text{ conversion} = \frac{\text{CO}_2 \text{ inlet} - \nu \text{ CO}_2 \text{ outlet}}{\text{CO}_2 \text{ inlet}} \times 100\%
\]

\[
\text{H}_2 \text{ conversion} = \frac{\text{H}_2 \text{ outlet}}{\nu \text{ H}_2 \text{ outlet}} \times 100\%
\]

**Discussion**

A series of Fe-based catalysts were prepared by the OCM for the conversion of carbon dioxide into jet fuel range hydrocarbons. This synthetic process can be used to produce homogeneous, ultrafine and high-purity crystalline metal oxide powder catalysts. The as-prepared catalysts, following activation, showed high carbon dioxide hydrogenation activity and high jet fuel range selectivity as a consequence of the small (ca. 15 nm) nanoparticle size and the presence of two catalytically active Fe phases that operate in tandem. The first phase corresponds to FeO₄ which catalyses the conversion of carbon dioxide to CO via the RWGS reaction whilst the second active Fe phase (Fe₅C₂) catalyses the hydrogenation of CO through the Fischer-Tropsch process.

This catalytic process provides an attractive route not only to mitigate carbon dioxide emissions but also to produce renewable and sustainable jet fuel. The recycling of carbon dioxide as a carbon source for both fuels and high-value chemicals offers considerable potential for both the aviation and petrochemical industries. It also represents a significant social advance; thus, instead of consuming fossil crude oil, jet aviation fuels and petrochemical starting compounds are produced from a valuable and renewable raw material, namely, carbon dioxide. These advances highlight carbon dioxide recycling and resource conservation as an important, pivotal aspect of greenhouse gas management and sustainable development. This, then, is the vision for the route to achieving net-zero carbon emissions from aviation; a fulcrum of a future global zero-carbon aviation sector.
1. Tian, H. et al. The terrestrial biosphere as a net source of greenhouse gases to the atmosphere. Nature 531, 225 (2016).

2. Bello, B. Captured CO2 to grow microalgae for bio-jet fuel production. (UKCCSC Winter School, University of Cambridge, Cambridge, UK, 2012).

3. Hari, T. K., Yaakob, Z. & Binitha, N. N. Aviation biofuel from renewable resources: routes, opportunities and challenges. Renew. Sust. Energy. Rev. 42, 1234–1245 (2015).

4. Kallio, P., Päätser, A., Ahkhtar, M. K. & Jones, P. R. Renewable jet fuel.Curr. Opin. Biotechnol. 26, 50–55 (2014).

5. Liu, G., Yan, B. & Chen, G. Technical review on jet fuel production. Renew. Sust. Energ. Rev. 25, 59–70 (2013).

6. Gnanamani, M. K. et al. Hydrogenation of carbon dioxide over Co–Fe bimetallic catalysts. ACS Catal. 6, 913–927 (2016).

7. Jiang, Z., Xiao, T., Kuznetsov, V. & Edwards, P. P. Turning carbon dioxide into fuel. Phil. Trans. R. Soc. A 368, 3343–3364 (2010).

8. Li, S. et al. Tuning the selectivity of catalytic carbon dioxide hydrogenation over iridium/cerium oxide catalysts with a strong metal–support interaction. Angew. Chem. Int. Ed. 56, 10761–10765 (2017).

9. Schneidewind, J., Adam, R., Baumann, W., Jackstell, R. & Beller, M. Low-temperature hydrogenation of carbon dioxide to methanol with a homogeneous cobalt catalyst. Angew. Chem. Int. Ed. 56, 1890–1893 (2017).

10. Song, Q.-W., Zhou, Z.-H. & He, L.-N. Efficient, selective and sustainable catalysis of carbon dioxide. Green Chem. 19, 3707–3728 (2017).

11. Wang, W., Wang, S., Ma, X. & Gong, J. Recent advances in catalytic hydrogenation of carbon dioxide. Chem. Soc. Rev. 40, 3703–3727 (2011).

12. Yang, H. et al. A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons. Catal. Sci. Technol. 7, 4580–4598 (2017).

13. Zhang, X. et al. Product selectivity in plasmonic photocatalysis for carbon dioxide hydrogenation. Nat. Commun. 8, 15442 (2017).

14. Asadi, M. et al. Nanostructured transition metal dichalcogenide electrocatalysts for CO2 reduction in ionic liquid. Science 353, 467–470 (2016).

15. Buclens, L. C., Galvita, V. V., Poelmans, H., Detavernier, C. & Marin, G. B. Super dry reforming of methane intensifies CO2 utilization via Le Chatelier's principle. Science 354, 449–452 (2016).

16. Choi, Y. H. et al. Carbon dioxide Fischer–Tropsch synthesis: A new path to carbon–neutral fuels. Appl. Catal. B 202, 605–610 (2017).

17. Kattel, S., Ramírez, P. J., Chen, J. G., Rodriguez, J. A. & Liu, P. Active sites for CO2 hydrogenation to methanol on Cu/ZnO catalysts. Science 355, 1296–1299 (2017).

18. Klankermayer, J. & Leitner, W. Love at second sight for CO2 and H2 in organic synthesis. Science 350, 629–630 (2015).

19. Mariano, R. G., McKelvey, K., White, H. S. & Kanan, M. W. Selective increase in CO2 electroreduction activity at grain-boundary surface terminations. Science 358, 1187–1192 (2017).

20. Satthawong, R., Koizumi, N., Song, C. & Prasassarakhitch, P. Bimetallic Fe–Co catalysts for CO2 hydrogenation to higher hydrocarbons. J. CO2 Util. 3, 102–106 (2013).

21. Dowson, G. R. & Stirling, P. Demonstration of CO2 conversion to synthetic transport fuel at flue gas concentrations. Front. Energy Res. 5, 26 (2017).

22. Michallos, S., McCord, S., Sick, V., Stokes, G. & Stirling, P. Dimethyl ether synthesis via captured CO2 hydrogenation within the power to liquids process: a techno-economic assessment. Energy Convers. Manage. 184, 262–276 (2019).

23. Vogt, C. et al. Understanding carbon dioxide activation and carbon–copper coupling over nickel. Nat. Commun. 10, 5330 (2019).

24. Wang, L. et al. Silica accelerates the selective hydrogenation of CO2 to methanol on cobalt catalysts. Nat. Commun. 11, 1033 (2020).

25. Chen, L., Zhang, L., Xia, S. & Sun, F. Entropy generation minimization for CO2 hydrogenation to light olefins. Energy 147, 187–196 (2018).

26. Hu, B. et al. Selective hydrogenation of CO2 and CO to useful light olefins over octahedral molecular sieve manganese oxide supported iron catalysts. Appl. Catal. B 132, 54–61 (2013).

27. Hu, S. et al. Hydrothermally stable MOFs for CO2 hydrogenation over iron-based catalyst to light olefins. J. CO2 Util. 15, 89–95 (2016).

28. Liang, B. et al. Mn decorated NaFe catalysts for CO2 hydrogenation to light olefins. Catal. Sci. Technol. 9, 456–464 (2019).

29. Zhang, J. et al. Selective formation of light olefins from CO2 hydrogenation over Fe–Zn–K catalysts. J. CO2 Util. 12, 95–100 (2013).

30. Bourin, E. et al. Aquous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine. Angew. Chem. Int. Ed. (2019).

31. Guset, R., Kumar, P., Sharma, O. P., Jain, S. L. & Khatri, O. P. Reduced graphene oxide–CuO nanocomposites for photocatalytic conversion of CO2 into methanol under visible light irradiation. Appl. Catal. B 181, 352–362 (2016).

32. Kothandaraman, J., Goepert, A., Czaun, M., M., G. A. & Prakash, G. S. Conversion of CO2 from air into methanol using a polyaniline and a homogeneous ruthenium catalyst. J. Am. Chem. Soc. 138, 778–781 (2016).

33. Frontera, P., Macario, A., Ferraro, M. & Antonucci, P. Supported catalysts for CO2 methanation: a review. Catalysts 7, 59 (2017).

34. Wang, F. et al. Active site dependent reaction mechanism over Ru/Co2O4 catalyst toward CO2 methanation. J. Am. Chem. Soc. 138, 6298–6305 (2016).

35. Xu, J. et al. Influence of pretreatment temperature on catalytic performance of rutile TiO2-supported ruthenium catalyst in CO2 methanation. J. Catal. 333, 227–237 (2016).

36. Liu, B. et al. Novel sour water gas shift catalyst (SWGS) for lean steam to gas ratio applications. Fuel Process. Technol. 134, 65–72 (2015).

37. Upadhye, A. A. et al. Plasma-enhanced reverse water gas shift reaction over supported Au catalysts. Catal. Sci. Technol. 5, 2590–2601 (2015).

38. Bahruji, H. et al. Hydrogenation of CO2 to dimethyl ether over Brønsted acidic PdZn catalysts. Ind. Eng. Chem. Res. 57, 6821–6829 (2018).

Data availability
The authors declare that the main data supporting the findings of this study are contained within the paper and its associated Supplementary Information. All other relevant data are available from the corresponding author upon reasonable request.

Received: 6 July 2020; Accepted: 20 November 2020;
Published online: 22 December 2020
performed the TEM, S. G. performed the XPS. B.Y., T.X., O.A.M., X.J., S. G-C., S. G., A.I.K., J.R.D., H.A.A., S.M.A., P.J.D., G.P.O., J.M.T. and P.P.E. contributed to analysis and discussion on the data, revising the article for intellectual content. T.X. and P.P.E. supervised the research. We dedicate this contribution to the memory of Sir John Meurig Thomas, FRS.

Competing interests
The authors (B.Y., T.X., and P.P.E.) have a patent application: Iron-manganese based catalyst, catalyst precursor and catalytic process, WO 2020/201749, B.Y., P.P.E., and T.X., related to this research. All other authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-20214-z.

Correspondence and requests for materials should be addressed to T.X. or P.P.E.

Peer review information Nature communications thanks Vitaly Ordomsky, and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.