Integrated CO₂ capture and conversion into valuable hydrocarbons

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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 capture and simultaneously transform CO₂ into olefins. In contrast to traditional systems in Fischer-Tropsch reactions, we demonstrate that when dealing with CO₂ activation (in contrast to CO), very high K loadings are key to capturing the 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.

Main Text: 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. Generally, both classic FTS and CO₂ hydrogenation catalysts need to be doped with potassium (10, 11). The addition of small amounts of K (circa 0.5 to 1 wt. %) generates 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 captures CO₂ and water, yielding potassium bicarbonate, KHCO₃ (equation S1). Furthermore, early reports (15) discussed RWGS reactions catalyzed by potassium carbonate in a H₂-rich atmosphere *via* a formate intermediate (equations S2 to S4). With this information in hand, we speculated that, with the proper catalyst, both reactions could be combined into a single catalytic cycle that also involves the capture of CO₂ and release of CO under FTS conditions (Figure 1.A). To explore the feasibility of this mechanism under hydrogenative conditions, we computed the thermodynamics of these reactions using density functional theory (DFT) (see supplementary text and Figures S1 to S3). In the range of 0-300 °C, all three phases have similar stabilities (within 0.2 eV, Figure 1.B). Moreover, the computed Gibbs free energies for the different reactions suggest that interconversion between KHCO₃ and KOOCH during catalysis is possible at all the considered temperatures (Figure S2).

Fig. 1. RWGS reaction on carbonaceous potassium. (A) Catalytic cycle. (B) Calculated Gibbs free energies of KHCO₃ and KOOCH relative to that of K₂CO₃ 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.

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 γ -Fe₂O₃ precursor, the fresh catalyst and used catalysts after 50 h on the stream. The basic structure of γ -Fe₂O₃ is closely related to the inverse spinel Fe₃O₄, 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 S4). 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 and Figure S5). 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 S6). Once submitted to the reaction conditions (30 bar, $\text{CO}_2:\text{H}_2 = 1:3$, 350°C), 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).

Fig. 2. Characterization of the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ 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.

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).

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

The activation under a H_2 atmosphere and the evolution of the iron phases during the CO_2 hydrogenation reaction (30 bar, $\text{CO}_2:\text{H}_2 = 1:3$, 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 $\gamma\text{-Fe}_2\text{O}_3$ 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 CO_2/H_2 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 S7), and the best match was obtained with a mixture of χ -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 powder X-ray diffraction, and it was determined to be a mixture of χ -Fe₅C₂ and Fe₂O₃ (Figure S5), consistent with the XANES results.

CO₂ temperature-programmed oxidation (TPO) of the iron oxide precursor and Fe₂O₃@K₂CO₃ catalyst reveals a 100 °C shift to lower temperatures when the carbonate is involved (Figure 3.B). After incorporation of the carbonate, the CO₂ peak is precisely centered in the hydrogenation temperature range (350 to 400 °C). Furthermore, the CO₂ uptake is increased by 86.5% upon K promotion, affording a final uptake of 2.13 mmol of CO₂ per gram of K₂CO₃, 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.C). This shift can be attributed to the transformation of the K₂CO₃ phase (19) and suggests that the proposed CO₂ capture mechanism is occurring during the reaction. To confirm this hypothesis, the C1s and K2p spectra of all possible K precursors (K₂CO₃, KHCO₃ and KOOCH) were measured and individually compared with the spectra of the fresh and spent catalyst (see Figure S8 and S9). The presence of K₂CO₃ in the fresh catalyst was confirmed, and the spectrum of the spent catalyst showed 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, 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 S10), which is consistent with the transformation of Fe₂O₃ to Fe₂C₅ indicated by XRD and XANES. To clarify the transformations of potassium during the reaction, the spent Fe₂O₃@K₂CO₃ was analyzed by high-field ³⁹K solid-state nuclear magnetic resonance (ssNMR) spectroscopy, and the spectrum was compared with those of K₂CO₃, KHCO₃, KOOCH and the hydrated KO₂ precursor (Figure 3.D). Among these species, the spectra of Fe₂O₃@K₂CO₃ and KOOCH show identical sharp peaks at 4.5 ppm, similar to that of hydrated KO₂. 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 Fe₂O₃@K₂CO₃ at approximately -2.6 ppm is similar to those of both KHCO₃ and K₂CO₃, which indicates that a portion of the potassium is converted to the corresponding carbonated salt under the reaction conditions. Altogether, these results confirm that the reaction pathway shown in Figure 1.A indeed takes place under these hydrogenation conditions.

The performances of the Fe₂O₃@K₂CO₃ catalysts in the hydrogenation of CO₂ after 50 h on stream at different reaction temperatures are 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 CO₂ conversion of 44.2% with a total olefin selectivity of 62.6%, a CH₄ 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 low-molecular-weight olefins 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).

Fig. 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 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 low-molecular-weight olefins, expressed as space-time yield (STY) reported here, is twice that achieved by FTS catalysts. 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 simultaneous capture and conversion of CO_2 (Figure S11). The high potassium loading in the $\text{Fe}_2\text{O}_3@\text{K}_2\text{CO}_3$ catalyst allows CO_2 capture (11) and release of CO, while the optimal ratio of the iron oxide and iron carbide phases accounts for the high olefin/paraffin ratio *via* a conventional FTS process (10, 15). To further elucidate this reaction pathway, CO_2 hydrogenation tests were

carried out with stand-alone potassium carbonates and formate precursors. All the potassium precursors were able to convert CO₂ and release CO with selectivities close to 100% with no sign of deactivation after 150 h (Figure S12).

Table 1. Comparison of the catalyst performance measured as iron-time yield (FTY) and space-time yield (STY) of the Fe₂O₃@K₂CO₃ catalyst and different Fe Fischer-Tropsch catalysts.

Catalyst	Sel C ₂ -C ₄ = (%) ^b	FTY (mmol _{COx} /g _{Fe} /h)	STY C ₂ -C ₄ = (mmol _{COx} /g _{Fe} /h)	Ref.
Fe/CNF	30	107.3	32.4	22
Fe/ α -Al ₂ O ₃ (6% Fe)	19	305.3	57.7	22
Fe/ α -Al ₂ O ₃ (12% Fe)	23	95.8	22.0	22
Fe/ α -Al ₂ O ₃ (25% Fe)	32	48.6	15.5	22
Fe/ β -SiC	11	229.7	25.3	22
Fe/ γ -Al ₂ 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	- ^c	140.7	- ^c	24
Mobil	17	52.5	8.4	25
Fe ₂ O ₃ @K ₂ CO ₃	31	265.4	82.6	This work

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

^b Total low-molecular-weight olefin selectivity.

^c Data not available.

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 capturing 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.

References:

1. “WMO Greenhouse Gas Bulletin (GHG Bulletin) - No. 13. The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2016”, World Meteorological Organization (2017).

2. “Energy Technology Perspectives 2014 - Harnessing Electricity's Potential”, International Energy Agency (2014).
3. E. Alper, O. Y. Orhan, CO₂ utilization: Developments in conversion processes. *Petroleum* **3**, 109-126 (2017).
- 5 4. G. Centi, A. Elsje Quadrelli, S. Perathoner, Catalysis for CO₂ conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environmental Science* **6**, 1711-1731 (2013).
5. A. Álvarez, A. Bansode, A. Urakawa, A. V. Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO₂ Hydrogenation Processes. *Chemical Reviews* **117**, 9804-9838 (2017).
- 10 6. K. Weissrnel, H. J. Arpe, *Industrial Organic Chemistry* (John Wiley & Sons, 2017).
7. G. P. Van der Laan, A. A. C. M. Beenackers, Kinetics and Selectivity of the Fischer–Tropsch Synthesis; A Literature Review. *Catalysis Reviews: Science and Engineering* **41**, 255-318
- 15 (2011).
8. S. Saeidi, S. Najari, F. Fazlollahi, M. K. Nikoo, F. Sefidkon, J. J. Klemes, L. L. Baxter, Mechanisms and kinetics of CO₂ hydrogenation to value-added products; A detailed review on current status and future trends. *Renewable and Sustainable Energy Reviews* **80**, 1292-1311 (2017).
- 20 9. A. Dokania, A. Ramirez, A. Bavykina, J. Gascon, Heterogeneous Catalysis for the Valorization of CO₂: Role of Bifunctional Processes in the Production of Chemicals. *ACS Energy Letters* **4**, 167-176(2019).
10. R. Satthawong, N. Koizumi, C. Song, P. Prasassarakich, Light olefin synthesis from CO₂ hydrogenation over K-promoted Fe–Co bimetallic catalysts. *Catalysis Today* **251**, 34-40
- 25 (2015).
11. V. P. Santos, T. A. Wezendonk, J. J. D. Jaén, A. I. Dugulan, M. A. Nasalevich, H. Islam, A. Chojecki, S. Sartipi, X. Sun, A. A. Hakeem, A. C. J. Koeken, M. Ruitenbeek, T. Davidian, G. R. Meima, G. Sankar, F. Kapteijn, M. Makkee, J. Gascon, Metal organic framework-mediated synthesis of highly active and stable Fischer-Tropsch catalysts. *Nature Communications* **6**, 6451 (2015).
- 30 12. A. Ramirez, L. Gevers, A. Bavykina, S. Ould-Chikh, J. Gascon, Metal Organic Framework-Derived Iron Catalysts for the Direct Hydrogenation of CO₂ to Short Chain Olefins. *ACS Catalysis* **8**, 9174–9182 (2018).
13. Tohid Nejad Ghaffar Borhani, Abbas Azarpour, Vahid Akbari, Sharifah Rafidah Wan Alwi, Zainuddin Abdul Manan, CO₂ capture with potassium carbonate solutions: A state-of-the-art review. *International Journal of Greenhouse Gas Control* **41**, 142-162 (2015).
- 35 14. S. C. Lee, H. J. Chae, S. J. Lee, B. Y. Choi, C. K. Yi, J. B. Lee, C. K. Ryu, J. C. Kim, Development of Regenerable MgO-Based Sorbent Promoted with K₂CO₃ for CO₂ Capture at Low Temperatures. *Environmental Science & Technology* **42**, 2736-2741 (2008).

15. C. W. Zielke, W. A. Rosenhoover, E. Gorin, "Production of hydrogen via catalytic decomposition of aqueous alkali formats" (Research Division Conoco Coal Development Company Library, Pennsylvania).
- 5 16. J. E. Jørgensen, L. Mosegaard, L. E. Thomsen, T. R. Jensen, J. C. Hanson, Formation of g-Fe₂O₃ nanoparticles and vacancy ordering: An in situ X-ray powder diffraction study. *Journal of Solid State Chemistry* **180**, 180-185 (2007).
- 10 17. T. A. Wezendonk, V. P. Santos, M. A. Nasalevich, Q. S. E. Warringa, A. I. Dugulan, A. Chojecki, A. C. J. Koeken, M. Ruitenbeek, G. Meima, H. Islam, G. Sankar, M. Makkee, F. Kapteijn, J. Gascon. Elucidating the Nature of Fe Species during Pyrolysis of the Fe-BTC MOF into Highly Active and Stable Fischer-Tropsch Catalysts. *ACS Catalysis* **6**, 3236–3247 (2016).
- 15 18. T. Riedel, H. Schulz, G. Schaub, K.W. Jun, J.S. Hwang, K.W. Lee, Fischer-Tropsch on Iron with H₂/CO and H₂/CO₂ as Synthesis Gases; The Episodes of Formation of the Fischer-Tropsch Regime and Construction of the Catalyst. *Top Catalysis* **26**, 41-54 (2003).
- 20 19. A. V. Shchukarev, D. V. Korolkov, XPS Study of Group IA Carbonates. *Central European Journal of Chemistry* **347**, 362 (2004).
- 25 20. A. Furlan, U. Jansson, J. Lu, L. Hultman, M. Magnuson, Structure and Bonding in Amorphous Iron Carbide Thin Films. *Journal of Physics: Condensed Matter* **27**, 045002 (2015).
- 30 21. A.R. Gonzalez-Elipe, J.P. Espinos, A. Fernandez, G. Munuera, XPS study of the surface carbonation/hydroxylation state of metal oxides. *Applied Surface Science* **45**, 103-108 (1990).
22. T. Galvis, H. M. Bitter, J. H. Khare, C. B. Ruitenbeek, M. Dugulan, A. Iulian, K. P. de Jong, Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins. *Science* **335**, 835-838 (2012).
23. D. B. Bukur, S. A. Patel, X. Lang, Fixed bed and slurry reactor studies of Fischer-Tropsch synthesis on precipitated iron catalyst. *Applied Catalysis* **61**, 329-349 (1990).
24. "Method for the preparation of a hydrocarbon synthesis catalyst material and the use thereof in a hydrocarbon synthesis process" (Sasol Technology (Pty) Limited, WO2010070541A2, 2008).
25. "Method for preparing a promoted iron catalyst and catalyst prepared by the method for conversion of synthesis gas to liquid hydrocarbons" (ExxonMobil Oil Corp, US4994428, 1985).
26. G. Kresse, J. Hafner, Ab Initio Molecular Dynamics for Liquid Metals. *Physical Review B* **47** 558-561 (1993).
27. G. Kresse, J. Furthmüller, Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Computational Material Science* **6**, 15-50 (1996).
28. G. Kresse, J. Furthmüller, Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Physical Review B* **54**, 11169-11186 (1996).
29. P. E. Blöchl, Projector Augmented-Wave Method. *Physical Review B* **50**, 17953-17979 (1994).

30. G. Kresse, D. Joubert, From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Physical Review B* **59**, 1758-1775 (1999).
31. M. Methfessel, A. T. Paxton, High-Precision Sampling for Brillouin-Zone Integration in Metals. *Physical Review B* **40**, 3616-3621 (1989).
- 5 32. A. Togo, I. Tanaka, First Principles Phonon Calculations in Materials Science. *Scripta Materialia* **108**, 1-5 (2015).
33. P. J. Linstrom, W. Mallard, "NIST Standard Reference Database Number 69" in *G.NIST Chemistry WebBook* (Eds. National Institute of Standards and Technology: Gaithersburg MD, 20899).
- 10 34. S. Grimme, J. Antony, S. Ehrlich, H. A Krieg, Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *Journal of Chemical Physics* **132** (2010).
35. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Nørskov, How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels. *Energy Environmental Science* **3**, 1311 (2010).
- 15

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Supplementary Materials:

Materials and Methods

Equations S1-S4

Figures S1-S12

List of Calculated Structures

References (26-35)