Unraveling Mechanistic Reaction Pathways of the Electrochemical CO$_2$ Reduction on Fe–N–C Single-Site Catalysts

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Supporting Information

ABSTRACT: We report a joint experimental—computational mechanistic study of electrochemical reduction of CO$_2$ to CH$_4$, catalyzed by solid-state Fe–N–C catalysts, which feature atomically dispersed, catalytically active Fe–N$_4$ sites and represent one of the very rare examples of solid, non-Cu-based electrocatalysts that yield hydrocarbon products. Work reported here focuses on the identification of plausible mechanistic pathways from CO$_2$ to various C$_1$ products including methane. It is found that Fe–N$_4$ sites convert only CO$_2$, CO, and CH$_2$O into methane, whereas CH$_2$OH appears to be an end product. Distinctly different pH dependence of the catalytic CH$_4$ evolution from CH$_2$O in comparison with that of CO$_2$ and CO reduction indicates differences in the proton participation of rate-determining steps. By comparing the experimental observations with density functional theory derived free energy diagrams of reactive intermediates along the CO$_2$ reduction reaction coordinates, we unravel the dominant mechanistic pathways and roles of CO and CH$_2$O during the catalytic CO$_2$-to-CH$_4$ cascades and their rate-determining steps. We close with a comprehensive reaction network of CO$_2$RR on single-site Fe–N–C catalysts, which may prove useful in developing efficient, non-Cu-based catalysts for hydrocarbon production.

The direct electrochemical CO$_2$ reduction reaction (CO$_2$RR) is a potentially attractive technology to close the energetic carbon cycle by converting CO$_2$ into useful carbon-based chemicals. Renewable electricity, generated from solar or wind, could provide the energy needed for this conversion in a sustainable manner.

Since the 1980s, when Hori and his co-workers pioneered the field and extensively tested the process on metallic electrodes, the CO$_2$RR has been continuously studied. It is well-known that the product distribution of the CO$_2$RR strongly depends on the nature of the catalytic metals. Copper has always been unique in its capability of producing higher-value hydrocarbons and oxygenates. This is why whenever “beyond CO” reaction products were concerned, that is, molecules resulting from the protonation of CO, it was Cu and its derivatives that were at the center of attention in mechanistic studies or optimization developments.

Non-Cu-based families of (molecular) catalysts with the capability to electrochemically reduce CO$_2$ are metal-coordinated macrocycles, cyclams, bipyridines, as well as various metalated porphyrins. Density functional theory (DFT) analyses have suggested that a metal (M)-porphyrin-inspired M–N$_4$ motif acts likely as the catalytically active site. More importantly, our recent studies have shown that the coordinative-isolated metal (ion) sites hold the key structural advantage to kinetically suppress the competitive hydrogen evolution reaction (HER), further benefiting the selectivity to CO$_2$RR. However, these molecular catalysts, when immobilized on a solid substrate, have notoriously suffered from poor electron transfer and low active-site densities, restricting their practical technological usefulness.

Pyrolyzed, solid-state M–N–C catalysts with their M–N$_4$ motifs structurally embedded in a solid-state graphene matrix could overcome the shortcomings of the molecular catal-

Received: May 15, 2019
Accepted: June 17, 2019
Published: June 17, 2019
the in building on some previous works, we established the results and computational reaction pathway predictions and detailed reaction network of the CO2RR toward CH4 over a products. The details of these mechanistic catalytic vital intermediate for the "beyond CO" hydrocarbon products. The details of these mechanistic catalytic pathways, however, have remained elusive yet are critical for a thorough understanding of the processes. This contribution will change that.

In a previous study, we reported how the chemisorption of CO and H on metals controls the experimental product and its selectivity. Balanced CO binding at moderate H binding, present for only Cu surfaces, favored the protonation of adsorbed CO associated with beyond CO products. However, Fe–N4 moieties of Fe–N–C catalysts were predicted to generate beyond CO products, as well. Indeed, Fe–N–C catalysts showed measurable, though moderate, selectivity for methane. To increase the faradaic hydrocarbon production, the mechanistic obstacles causing finite but low CH4 selectivity must be addressed.

We carried out a combined computational–experimental study of the CO2RR to CH4 on single-site Fe–N–C catalysts. To learn more about the molecular mechanism, we considered the electrochemical reduction of a range of possible reactive intermediates, such as CO (CORR), CH2O (CH2ORR), CH3OH, and formate. We monitored the selectivity of each reactant for CH4 and focusing on the CH2ORR, we studied the influence of the reactant concentrations and pH and arrived at new conclusions as to the involvement of protons in the rate-determining step (RDS). Linking our experimental results and computational reaction pathway predictions and building on some previous works, we established the first detailed reaction network of the CO2RR toward CH4 over a member of the family of M–N–C single-site electrocatalysts.

Fe–N–C Catalyst Preparation and Characterization. The polyaniline-derived single-site Fe–N–C catalysts with atomically dispersed Fe–N4 moieties employed here are identical to those described and characterized in our previous work. To ensure the role of the atomically dispersed Fe–N4 motifs, an iron-free yet otherwise identical N–C catalyst was prepared as used as a control. Conventional ex situ characterization of physiochemical properties of the Fe–N–C material is shown in the Supporting Information (Table S1, Figures S1–S3). X-ray diffraction patterns (XRD, Figure S1) and transmission electron microscopy (TEM, Figure S2) indicated that the Fe–N–C catalyst had a similar amorphous carbon structure as the metal-free N–C one. N2-specific adsorption and double-layer capacity measurements were carried out, which suggested comparable surface areas (Figure S3) of Fe–N–C and N–C. Elemental analysis revealed the same or similar nitrogen content in the two catalysts and absence of Fe in the control (ICP). CO adsorption confirmed the absence of CO adsorbing centers in the control (Table S1). Moreover, the dispersed single-site Fe–N4 motifs were identified and confirmed using N 1s X-ray photoelectron emission spectroscopy, Mossbauer spectroscopy, and also X-ray absorption spectroscopy in our previous approaches. All of these confirm the dominant character of the coordinative Fe–N4 motifs in our Fe–N–C model catalyst, whereas the inorganic iron species remain in trace portion, catalytically not responsible for methane evolution. Catalytic Products and Their Efficiencies during CO2RR on Fe–N–C Catalysts. Upon electrochemical reduction of CO2 using CO2-saturated electrolytes in an H cell, CO, H2, and CH4 were identified as the main CO2RR products over the Fe–N–C catalyst. The overall faradaic efficiency reached 95% during bulk electrolysis tests at constant electrode potentials. Liquid products such as alcohols, aldehydes, and formate were below the detection limit for the typical present electrolysis time of 75 min. However, we also performed a few longer-term, 1000 min CO2RR experiments (see Table S2). Similarly, prolonged CO reduction reaction (CORR) was carried out in buffered potassium phosphate solution for 480 min at the same pH. Now, very small yet clearly detectable amounts of both methanol and formaldehyde were found during these longer-term electrolysis tests (see Figures S4 and S5), demonstrating that these two compounds are apparently involved in the mechanistic network of the CO2RR as well as of the CORR over the Fe–N–C catalyst. Electrochemical Reduction of a Set of Different COxHy Molecules. To get insight into the electrochemical CO2-to-
CH$_4$ reaction pathways, CO$_2$, CO, CH$_2$O, CH$_3$OH, and formate were used separately as feed reactants in order to investigate their relative reaction rates and resulting product spectra. The choice of these feeds was based on the fact that all of them may constitute reactive intermediates of the CO$_2$RR process. In particular, we were interested in whether and to what degree these potential reactive intermediates can be electrochemically reduced to CH$_4$ on the Fe−N=C catalysts, which carries useful insight in the catalytic CO$_2$-to-CH$_4$ reaction cascade. Table S2 lists the reaction parameters used in the experiments.

The formal chemical transformations and their standard potentials read

$$\text{CO}_2 + 8(\text{H}^+ + e^-) \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$$

$$E_0 = 0.17 \text{ V}_\text{RHE}$$

(1)
HCOOH + 6(H⁺ + e⁻) → CH₄ + 2H₂O

\[ E_0 = 0.28 \text{ V}_{\text{RHE}} \] (2)

CO + 6(H⁺ + e⁻) → CH₄ + H₂O

\[ E_0 = 0.26 \text{ V}_{\text{RHE}} \] (3)

CH₃O + 4(H⁺ + e⁻) → CH₄ + H₂O

\[ E_0 = 0.45 \text{ V}_{\text{RHE}} \] (4)

CH₃OH + 2(H⁺ + e⁻) → CH₄ + H₂O

\[ E_0 = 0.63 \text{ V}_{\text{RHE}} \] (5)

The overall electrocatalytic polarization behavior comprising all cathodic processes was studied for each individual feed molecule using transient linear sweep voltammetry (LSV) (Figure 1a) and stationary bulk electrolysis (Figure 1b). Reactivity trends of transient and stationary measurements matched well. CO₂ outperformed the HER control activity (N₂ as feed in Figure 1a), largely thanks to significant CO evolution (Figure S6) below -0.4 V_{RHE}. CO₂ was followed by formic acid, while the other reactants exhibited faradic currents comparable to the HER background. CO feeds, likely due to its site blocking nature, displayed lower currents than the background (Figure 1a). Liquid products remained below the detection limit. Methane formation, however, was observed for CO₂, CO, and CH₂O feeds (Figure 2) and became the primary focus of subsequent kinetic studies.

First, we analyzed how the CH₄ formation rate changed with applied potential. Figure 2 shows the potential-dependent electrocatalytic methane production rate and the faradaic efficiency for each feed on Fe–N–C catalysts (solid symbols) and Fe-free “N–C” control (open symbols) catalysts. The Fe-free catalysts displayed little to no CH₄ yield, evidencing the catalytic role of the Fe–N₄ single sites in the CO protonation process. Closer inspection of Figure 2 reveals more anodic CH₄ onset potentials under CH₃OH feeds compared to CO or CO₂ feeds. This suggests that CH₂O activation and subsequent protonation to methane is fast, while activation barriers in the catalytic cascade from CO₂ or CO to CH₂O appeared to delay their reduction kinetics. Indeed, the fact that the CH₄ yields under CO₂ and CO feeds track each other so closely is an indication that they are kinetically limited by a shared elementary process, more specifically the protonation of adsorbed CO, *CO. Note that we will abbreviate surface-adsorbed species with an asterisk on the left to symbolize a surface site that binds to the element adjacent to it. All three feeds showed steadily increasing catalytic CH₄ formation rates with increasing applied overpotential up to -0.65 V_{RHE}. Beyond -0.65 V_{RHE}, catalytic CH₄ rate hikes with potential slowed down for CO₂ yet increased sharply for CH₃OH. For CO feeds, the CH₄ formation rates actually peaked and subsequently dropped slightly at more cathodic potentials. We attribute this distinct kinetic behavior to the poisoning effect of adsorbed *CO on the Fe–N₄ sites due to their strong binding, which will be supported later by computational analysis. For CO₂, even though its saturated bulk concentration is about 30 times that of CO, local depletion in CO₂ concentration at the double layer will limit sustained CH₄ formation rates at sufficiently cathodic potentials. With the cathode at -0.65 V_{RHE}, the CH₄ formation rate from CH₂O displayed a sudden growth, suggesting a shift in the rate-determining reaction step. We want to point out that previous kinetic studies invariably showed that the electroreduction of aldehydes on metallic electrocatalysts exclusively generated the respective primary alcohols. Here, however, the solid nonmetallic, single-site Fe–N–C catalysts with graphene-embedded molecular sites generated selectively the respective hydrocarbon (CH₄). This is consistent with results on molecular catalysts and suggests mechanistic analogies between molecular and solid-state catalysts.

Next, we investigated the CH₄ formation rate and its faradaic efficiency as a function of the initial CH₂O concentration in Figure 3a. Results in Figure 3a indicated the Nernstian behavior of the CH₄ generation rate. *CH₂O/*CH₃OH/*CH₂OH/*CH₄ reached the Nernstian behavior of the CH₄ rate law at a given applied potential, with the slope varying with the applied potential. This suggests that the CH₄ rate law is approximately first order with respect to CH₂O, which was confirmed in kinetic log–log analysis (see Figure S8).

Proton-Coupled and -Decoupled Catalytic Reaction Steps. The generation of CH₄ during the electrochemical reduction of CO₂ on Fe–N–C (and similarly on molecular cobalt protoporphyrin) is known to show a Nernstian dependence on pH, suggesting that the rate-determining protonation of adsorbed *CO does involve a concerted proton-coupled electron transfer (PCET). To verify this, we studied the pH dependence of the CORR on the single-site catalysts. Results in Figure S9 confirmed the Nernstian behavior of the CH₄ onset potentials and CH₄ formation rates, evidenced by the 59 mV shift per pH unit on the NHE scale. Thus, on the present Fe–N–C single-site catalysts, experiments suggest the protonation of *CO at the carbon atom to *CHO to be the slowest and thus RDS in the CORR pathway to methane. This will be compared to computational predictions further below.

Similar pH tests were then conducted using CH₃OH as the reactant feed (see Figure 3b). Now, the CH₄ onset potentials exhibited close to no pH dependence on the NHE scale (Figure 3b) yet did so on the RHE scale (Figure 3b). We conclude that the catalytic pathway from CH₃OH to CH₄ is limited by a proton-decoupled electron transfer (PDET) step resulting in an experimental rate law following

\[ \text{Rate}_{CH_4} \approx k e^{-a[CH_2O]}[H^+]^{-b} \] (6)
where \( k \) is a heterogeneous rate constant, the exponential term describes the rate dependence on the applied cathodic overpotential \( \eta [V] \), and \( \alpha [V^{-1}] \) denotes a parameter related to the inverse Tafel slope.

To summarize our experimental findings on Fe–N–C catalysts, the CO\(_2\)RR as well as the CORR generally exhibit a wider range of products, primarily CO, methane, as well as some formaldehyde and methanol. The CH\(_2\)ORR exclusively yields CH\(_4\). Both the CO\(_2\)-to-CO and CH\(_2\)O-to-CH\(_4\) reactions appear to be rate-limited by a slow PDET, while the CO-to-CH\(_4\) reaction features a concerted PCET as its slowest step.

Mechanistic DFT calculations are now needed to rationalize the experimental findings and to establish a full mechanistic network.

Density Function Theory Calculations of Reaction Pathways to CH\(_4\). DFT predictions of possible mechanistic pathways from CO\(_2\) to CH\(_4\) were carried out by calculating the free energy of possible intermediates on single-site Fe–N\(_4\)–C motifs at 0 V\(_{\text{RHE}}\). This particular metal coordination was chosen because iron sites generally prefer four coordinative nitrogens.\(^4^3\) Calculation details are presented in the Supporting Information (Experimental Section, Tables S3–S5, and Figure S9).

Figure 4 presents the free energy network diagram of the individual reaction pathways from the different reactants to methane. The calculations are assuming concerted proton electron transfer and are evaluated at 0 V\(_{\text{RHE}}\) and with reference made to CH\(_4\)(g) as this reference is common for the reactions investigated. It shows that Fe–N\(_4\)–C binds *CO relatively strongly and the most difficult step from CO\(_2\)/CO to CH\(_4\) is the protonating *CO to *CHO (V\(_2\): \( \Delta G_{\text{CO}} \) to...
Indeed, the *COH has also been proposed as the first reduced intermediate following *CO on metallic Cu facets.\textsuperscript{32,33} However, considering that the M–N–C type catalysts contribute isolated active sites, the free energy of the *COH intermediate is about 1.5 eV higher than that of *CHO, possibly accommodating an unfavorable triple bond between Fe–N and the *COH intermediate.

In comparison, the reduction of CO\textsubscript{2} to CO (\(V_{1}: \Delta G_{\text{CO}} \rightarrow \Delta G_{\text{CHO}}\)) and that of CH\textsubscript{2}O to CH\textsubscript{4} (\(V_{3}: \Delta G_{\text{CHO}} \rightarrow \Delta G_{\text{CH}_2\text{OH}/\text{OCH}_3}\)) exhibit lower energetic pathways, leading to less potential requirement to drive these two conversions, which is in line with the experiment observations (see Figures 2 and S6).

We first focus on a discussion of the selectivity of the reduction of CH\textsubscript{2}O. Notably, no methanol was observed over Fe–N–C catalysts, which is distinctly different from metals (Cu, Ag, and Au), which majorly produces methanol. Previously, for metal catalyst, we tried to classify the two types of products from aldehyde reductions to be a matter of choice: oxygen bonding (*OCH\textsubscript{3}) gives alcohols, while the carbon bonding (*CH\textsubscript{2}OH) leads to fully reduced hydrocarbons.\textsuperscript{13} Nevertheless, we do observe that the calculated *CH\textsubscript{2}OH and *OCH\textsubscript{3} for the Fe–N–C on the free energy scale are similar (see Figure 4). Given the fact that CH\textsubscript{2}O reduction on Fe–N–C produces only CH\textsubscript{4}, we thus propose that uniquely this catalyst offers a special reaction path or has very different water stabilization as compared to the metal catalyst. Water indeed highly influences the stabilization of CO\textsubscript{2}RR intermediates for Cu facets,\textsuperscript{28,29} and for ORR/ORE intermediates, static water solvation has been shown on M–N–C systems.\textsuperscript{44} Investigating water dynamics on the M–N–C for this analysis was found to be challenging due to the spin-polarized nature of the calculations. This issue could be addressed with ab initio molecular dynamics (AIMD) of water on the M–N–C system, which is out of scope of the present study.

Second, we turn to the pH dependence of these reactions, where the CO\textsubscript{2}RR into CO (performed in our early work,\textsuperscript{35} data is presented in Figure S10) and CH\textsubscript{2}OH into CH\textsubscript{4} showed a non-Nernstian behavior while the CO-to-CH\textsubscript{4} process followed a Nernstian one. We hypothesize that a PDET is the key to rationalize this pH dependence. A PDET was reported to be more likely if the interaction of the intermediates with the catalyst is weak.\textsuperscript{36} On the basis of this, for weakly bound species, the adsorption becomes a slow RDS, and the reaction is limited by a PDET, as shown in the equations below

\[
\text{CO}_2 + * + e^- \rightarrow *\text{CO}_2^- \quad (7)
\]

\[
\text{CH}_2\text{O} + * + e^- \rightarrow *\text{CH}_3\text{O}^- \quad (8)
\]

accounting for the experimentally observed pH-independent catalytic rates on the NHE scale. Our DFT calculations using the computational hydrogen electrode (CHE) assume a concerted proton–electron transfer (equivalent to PCET) and thus could not capture the feature of the PDET. Previous investigations have indeed shown the simulation of stable [M–N–C–CO\textsubscript{2}]\textsuperscript{+} transition states,\textsuperscript{32,36} however, without clearly pointing to the reference potential for such PDET. This implies that both models have their limitations to clearly describe the electrocatalytic process. The experiments, however, provide important information about the reaction mechanism.

We now turn to the discussion of the relatively low (yet finite compared to methanol) methane selectivity on the Fe–Ni–C catalyst. The Fe–Ni motifs show similar “binding” properties as copper (the well-known excellent hydrocarbon producer), holding the ability to bind *CO without having *H under the potential deposited. Upon this, to better understand the performance difference in CH\textsubscript{4} selectivity of these two types of candidates, we compared the proton transfer details of the *CO-to-*CHO steps on the single-site Fe–Ni motif and the extended metal Cu(111) facet.\textsuperscript{27} Illustrated in Figure 5, comparable PCET barriers (marked as \(V_{3}\) in Figure S5a,b, \(\Delta G_{\text{CO}} \rightarrow \Delta G_{\text{CHO}} \sim 1\) eV) could be observed on these two candidates. For the Cu(111) facet, a pre-*H/CO coadsorption (the schematic is displayed in Figure 5a) is energetically favored, leaving \(V_{2}(\sim 1\) eV) as the major limiting step. This is in agreement with a recent work focusing on CH\textsubscript{4} evolution via CORR on a Cu-based catalyst,\textsuperscript{58} suggesting that the protonation of adsorbed *CO into *CHO (RDS of CH\textsubscript{4} formation) is preferentially via the Langmuir–Hinshelwood reaction channel (*CO + *H \rightarrow *CHO). On the contrary, on the Fe–Ni–C motif, the coadsorption of *CO/*H step (V marked in Figure 5b) sets the main dynamic barrier, emerging as the limiting step, resulting in low hydrocarbon activity, and forcing an Eley–Rideal-type protonation step (*CO + H\textsubscript{ads} + e\textsuperscript{−} \rightarrow *CHO).

In principle, the single-site Fe–Ni–C catalyst constitutes an excellent catalytic CO producer and thus could contribute sufficient reactive *CO intermediates for higher hydrocarbon yields. Unfortunately, indicated by our simulations, the isolated active site structure on the other hand causes difficulty in *CO and *H coadsorption, precluding dominant formation of hydrocarbons. This finding suggests that the highly active CH\textsubscript{4}(g) product formation may require an extended surface or a nearby proton source to lower the barrier of protonation. Strategies to circumvent this would be to increase the number of active sites and thus reduce their mutual distance, or else, the introduction of suitable hydrogen adsorption/CO\textsubscript{2} reactive twin sites may be a way toward enhanced hydrocarbon yields.

As a summary, the present combined experimental and theoretical mechanistic study has addressed the kinetics of the electroreduction of various small molecules that may constitute reactive intermediates on the way to methane, in particular, CO\textsubscript{2}, CO, and CH\textsubscript{2}O. The study aimed at (i) identifying the role of these reducible reactants during the overall CO\textsubscript{2}-toward-CH\textsubscript{4} pathway; (ii) understanding the rate-limiting factor of these key reactions; and (iii) reasoning the obstructed hydrocarbon selectivity of the Fe–Ni–C catalyst. This knowledge will be crucial in the design of novel catalysts to reduce CO\textsubscript{2} into hydrocarbons.

To achieve the first two goals, unfortunately, neither our experiments nor computation delivers direct evidence to address the CH\textsubscript{2}O reduction details. By tracking the methanol reduction (see Figure 6), which is produced in terms of CO\textsubscript{2}/CORR electrolysis (Figure S5) while denied in CH\textsubscript{2}OH reduction (Figures S7 and S8), we could speculate that methanol more likely originated via a non-CH\textsubscript{2}O channel, and the *CH\textsubscript{2}OH is the key intermediate (*CO \rightarrow *CHO \rightarrow *CHOH \rightarrow *CH\textsubscript{2}OH \rightarrow CH\textsubscript{4}OH). Upon this hypothesis, the *CH\textsubscript{2}OH—relevant for methanol formation—could be filtered out from the pure CH\textsubscript{2}OHRR, making methane as the only end-product (CH\textsubscript{2}O \rightarrow *OCH\textsubscript{3} \rightarrow *OCH\textsubscript{3} \rightarrow CH\textsubscript{4}, shown in Figure 6). This shows that the Fe–Ni–C catalyst provides different CH\textsubscript{2}OHRR paths than the metals,\textsuperscript{31,37} and better
understanding requires more systematical investigation upon a broader catalyst benchmark.

On the basis of the preceding discussions, we establish an overall reaction network of electrochemical CO₂ reduction into CH₄ clearly addressing the contribution of CO₂, CO, and CH₂O. Here, CO plays as the key intermediate toward methane, formaldehyde, and methanol. Moreover, the produced CH₂O in this reaction network could be further reduced and open up an extra reaction channel toward methane. On the contrary, methanol is more likely yielded from the non-CH₂O reaction channel and poses as a byproduct aside the methane. More interestingly, our experimental studies have shown that some of the reduction steps involve PCET (namely, CO-to-CH₄) steps, whereas others, in particular, such that involved rather weakly bounded catalysts. Alternatively, “trident catalyst” schemes (also referred to as “double tandem” or “hybrid cascade catalyst”) are conceivable, consisting of Fe–N–C motifs acting as local CO producers and ii) dispersed Cu nanoparticles, where the protonation of adsorbed CO occurs generating hydrocarbons or oxygenates. One such scheme would consist of i) high surface area Fe–N–C catalysts with atomically dispersed Fe–Nₓ moieties acting as local CO producers and ii) dispersed Cu nanoparticles, where the protonation of readsorbed CO occurs generating hydrocarbons or oxygenates. In a next step, more sophisticated “Tridem catalyst” schemes (also referred to as “double tandem” or “hybrid cascade catalyst”) are conceivable, consisting of Fe–N–C catalysts with supported and diffusively coupled Cu and Ni nanoparticles, where the Ni particles take care of reducing aldehydes into their respective alcohols, thereby maximizing the effective alcohol yields.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b01049.

Description of the material, electrochemical characterization, and theoretical calculation (PDF)

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Notes

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■ ACKNOWLEDGMENTS

The authors acknowledge Climate-KIC under the EnCO2re project. P.S., W.J., and X.L.W are grateful for partial support by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) under Grant #03SF0523A-C—“CO2EKAT” and FCH Joint Undertaking 2 (CRESCENDO Project, Grant Agreement No. 779366). A.B. and J.R. thank the Carlsberg Foundation (Grant CF15-0165) and the Innovation Fund Denmark (Grand Solution ProActive 5124-00003A). A.S.V. acknowledges funding from CONACyT (Project No. 282552). P.S. and W.J. acknowledge financial support by the Cluster of Excellence (“UniSysCat”) funded by the Deutsche Forschungsgemeinschaft and managed by the TU Berlin.

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