

# Methanol formation from CO<sub>2</sub> catalyzed by Fe<sub>3</sub>S<sub>4</sub>{111}: formate *versus* hydrocarboxyl pathways†

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Carbon capture and utilisation is one of the most promising techniques to minimize the impact of the increasing amount of carbon dioxide in the atmosphere. Recently, the mineral greigite was shown to be capable of catalysing CO<sub>2</sub> conversion, leading to useful small organic molecules. Here, we have carried out a systematic study of the adsorption and selective reduction of CO<sub>2</sub> on the Fe<sub>3</sub>S<sub>4</sub>{111} surface. We have considered both formate and hydrocarboxyl key intermediates, leading to different reaction pathways *via* Eley–Rideal and Langmuir–Hinshelwood mechanisms, and we have built a kinetic model considering the wide range of intermediates in the reaction network. Our results show that the mechanism to produce formic acid takes place *via* formate intermediate mostly on Fe<sub>A</sub> sites, while methanol is formed *via* hydrocarboxyl intermediates on Fe<sub>B</sub> sites. From the kinetic model, we have derived a reaction constant comparison and determined the limiting step rates. The overall process takes place under very mild conditions, requiring only a small energy input that might come from a chemiosmotic potential.

## Introduction

Our present dependence on fossil fuels means that, as our demand for energy inevitably increases, so do emissions of greenhouse gases, most notably carbon dioxide (CO<sub>2</sub>). To avoid the obvious consequence of severe climate change,<sup>1</sup> the concentration of such greenhouse gases in the atmosphere must be stabilized.<sup>2–5</sup> Integrated carbon capture and subsequent sequestration is generally recognized as the most promising option to tackle CO<sub>2</sub> gases in the short to medium term. A long-term solution is its reduction and conversion to suitable compounds: CO<sub>2</sub> is a source of carbon and may be used as a feedstock for conversion to useful chemicals.<sup>6</sup> Reductive reactions involving CO<sub>2</sub> are a grand challenge because they require energy to generate reduced forms of CO<sub>2</sub>, such as formate or CO.<sup>7</sup> In particular, production of CO is considered an important objective in the context

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of production of renewable carbon feedstock chemicals.<sup>8</sup> The main challenge in CO<sub>2</sub> reduction is increasing the energy efficiency of the activation process of the molecule, which is hindered primarily by high CO<sub>2</sub> reduction over-potentials,<sup>9</sup> which is also suggested to be the rate limiting step in the conversion process. In most cases, mild temperatures but high CO<sub>2</sub> pressures (>10 bar) and long reaction times are required.<sup>10,11</sup> Nevertheless, experiments on iron sulfide have shown that electroreduction under room conditions and small overpotentials is achievable.<sup>12</sup>

Reactions of interest for CO<sub>2</sub> conversion are classified into two types: reductive and non-reductive reactions, both requiring the activation of the C=O double bond, which is accompanied by charge transfer to the lowest unoccupied molecular orbital.<sup>13</sup> Solid state catalysts may act as a redox center, transferring electrons from its valence band to the molecular orbital while decreasing the O–C–O bond angle.<sup>9,14</sup> In this process, two problems are encountered: (i) the large thermodynamic stability of the molecule<sup>15</sup> and (ii) the appreciable kinetic energy barrier to activate CO<sub>2</sub>.<sup>16</sup> Several possible reaction pathways have been proposed to transform CO<sub>2</sub> into one-carbon organic molecules, such as CH<sub>4</sub> or CH<sub>3</sub>OH. These involve the reverse water gas-shift (rev-WGS) reaction, yielding CO followed by the subsequent hydrogenation *via* formyl intermediate (HCO) to methanol<sup>17</sup> or to a variety of long chain hydrocarbons *via* the Fischer–Tropsch process.<sup>18</sup> This reaction mechanism on Cu showed that, under ambient conditions, the reaction takes place through carboxyl intermediate.<sup>19</sup> Other possible pathways have shown formate intermediate (HCOO) with subsequent O–CO bond scission, yielding similar products.<sup>11,12</sup> Recent studies have claimed that CH<sub>3</sub>OH is produced by the subsequent hydrogenation of HCOOH to H<sub>3</sub>CO *via* C–O bond scission,<sup>20</sup> although formic acid might dissociate back to formate with a low energy barrier.<sup>17</sup> It has also been proposed that the hydrogenation of CO<sub>2</sub> towards CH<sub>3</sub>OH takes place through dihydroxycarbene (COHOH), hydroxymethyldyne (COH) and hydroxymethylene (HCOH) intermediates.<sup>20</sup>

Based on such mechanistic information, we have analyzed, in detail, the CO<sub>2</sub> interaction and conversion on greigite (Fe<sub>3</sub>S<sub>4</sub>) surfaces. This magnetite (Fe<sub>3</sub>O<sub>4</sub>) isomorphic mineral is formed as an intermediate in the solid-state transformation of mackinawite into pyrite, playing a crucial role in the pyrite formation pathway.<sup>21–26</sup> Fe<sub>3</sub>S<sub>4</sub> has been widely identified in marine soils and sedimentary rocks of up to a few million years old.<sup>27,28</sup> Greigite has also been associated as a catalyst in a number of key biochemical reactions associated with the “iron–sulfur world” hypothesis for the origin of life.<sup>12,29–37</sup> Inspired by the CO<sub>2</sub> conversion in this hypothesis and recent experimental results, we have explored the entire reaction network on the Fe<sub>3</sub>S<sub>4</sub>{111} surface, mapping out the complete energy profile, and implemented it into a comprehensive kinetic model under particular initial conditions. This model is based on unrestricted elementary reaction steps derived rigorously from density functional theory (DFT) calculations, which have been shown to be instrumental in unravelling multiple aspects of heterogeneous catalysis.<sup>17,20,38,39</sup>

## Computational details

### Electronic structure calculations

Periodic plane-wave DFT calculations were carried out to study the CO<sub>2</sub> adsorption and its reactivity with adsorbed hydrogen on the greigite surface Fe<sub>3</sub>S<sub>4</sub>{111}.



All calculations were performed using the VASP software.<sup>40,41</sup> Ion–electron interactions were represented by the projector-augmented wave (PAW) method<sup>42</sup> and the generalized gradient approximation (GGA) with the Perdew–Wang 91 functional<sup>43</sup> within the spin interpolation formula of Vosko *et al.*<sup>44</sup> We also considered non-spherical contributions from the gradient corrections to the PAW spheres. All the calculations include the long-range dispersion correction approach by Grimme,<sup>45</sup> which is an improvement on pure DFT when considering large polarizable atoms.<sup>46–51</sup> We have used the global scaling factor parameter optimized for PBE ( $s_6 = 0.75$ ). The Kohn–Sham valence states were expanded in a plane-waves basis set with a cut-off of 600 eV for the kinetic energy.<sup>52</sup> This high value for the cut-off energy ensured that no Pulay stresses occurred within the cell during relaxations.

The initial magnetic moment was described by high spin distributions in both types of Fe, octahedral and tetrahedral, with antiparallel orientation as reported previously.<sup>53,54</sup> For an accurate treatment of the electron correlation in the localized d-Fe orbital, we have used the  $U$  approximation<sup>55,56</sup> ( $U_{\text{eff}} = 1$  eV),<sup>57–59</sup> which improves the description of localized states in this type of system where standard LDA and GGA functionals fail.<sup>60</sup> The choice of the  $U$  parameter is rather empirical, a feature that also appears when using computationally expensive hybrid functionals since the amount of Fock exchange is system-dependent.<sup>60–63</sup> Calculations were described by a Monkhorst–Pack grid of  $5 \times 5 \times 1$   $K$ -points, which ensures electronic and ionic convergence.<sup>64</sup> The geometry of all stationary points was found with the conjugate-gradient algorithm and was considered converged when the force on each ion dropped below  $0.03 \text{ eV } \text{\AA}^{-1}$ . The energy threshold defining self-consistency of the electron density was set to  $10^{-5}$  eV. In order to improve the convergence of the Brillouin-zone integrations, the partial occupancies were determined using the tetrahedron method with Blöch corrections smearing, with a set width for all calculations of 0.02 eV. All total energies have been extrapolated to  $K_{\text{B}}T = 0$  eV.

## Computational model

The greigite unit cell consists of eight  $\text{Fe}_3\text{S}_4$  subunits with a cubic lattice parameter of  $\sim 9.8 \text{ \AA}$ ,<sup>65,66</sup> which is close to the calculated parameter resulting from the cell optimization ( $9.671 \text{ \AA}$ ). The inverse thio-spinel arrangement is reflected by the formula  $\text{AB}_2\text{S}_4$ , where there are two possible locations for the Fe ions: the tetrahedral sites (A), filled by  $\text{Fe}^{3+}$  ions, and the octahedral sites (B), where both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions co-exist.<sup>24,25,58,67–70</sup> In agreement with experiments, the electronic structure shows a high-spin configuration for both Fe sites in antiparallel alignments, resulting in a ferromagnetic material.<sup>24,25,59,67,68,70–72</sup> The orbital spin-splitting in the valence region results in localized outermost 3d-electrons and in ordered magnetism.<sup>69,73,74</sup> Good agreement with experimental evidence has been obtained by using the same computational details as listed above.<sup>53,54</sup>

We prepared the  $\text{Fe}_3\text{S}_4\{111\}$  surface as a slab model by cutting the bulk structure with the METADISE code,<sup>75</sup> which considers periodicity in the plane direction and provides atomic layer stacking, resulting in non-dipolar reconstructions.<sup>76</sup> The slab contains 56 atoms (24 Fe and 32 S) per unit cell, where the atoms are positioned in four layers of two  $\text{Fe}_3\text{S}_4$  units each, exposing an area of  $81.0 \text{ \AA}^2$  and a thickness of sufficient size to relax the two uppermost layers



(four  $\text{Fe}_3\text{S}_4$  units) until energy convergence, keeping the bulk structure frozen at the bottom. We added a vacuum width of 12 Å between periodic slabs, big enough to avoid the interaction between images. Isolated molecules were placed in the center of a  $15 \times 16 \times 17$  Å<sup>3</sup> cell and optimized with the same criteria.

Every intermediate is linked to the next minimum along the reaction mechanism by a saddle point in the pathway of minimum energy across the potential surface. These saddle points are the reaction transition states (TS), which determine the kinetics of the process. We have determined the TS by means of either the dimer method<sup>77,78</sup> or Climbing Image Nudge Elastic Band (CI-NEB),<sup>79,80</sup> depending on how far the starting structure is from the products. For instance, CI-NEB was used when in the initial structure hydrogen is further than 2.5 Å from the hydrogenated centre. The identified TS were further confirmed by a vibrational frequency calculation, in which only one imaginary frequency is obtained, corresponding to the reaction coordinate. The dimer image is relaxed to both local minima, leading to the initial state and the final state.

All binding energies ( $E_B$ ) are given with respect to the naked slab and the reactants in the gas phase, see eqn (1). In the discussion of the DFT results, we have referred to energy values where the zero point energy (ZPE) correction is neglected unless noted otherwise.

$$E_B = E_{\text{Mol}+\text{Fe}_3\text{S}_4\{111\}} - \left( E_{\text{Fe}_3\text{S}_4\{111\}} + \sum_i E_{\text{Mol}}^i \right) \quad (1)$$

$E_{\text{Mol}+\text{Fe}_3\text{S}_4\{111\}}$  corresponds to the total energy of the adsorbate(s) on the  $\text{Fe}_3\text{S}_4\{111\}$  slab,  $E_{\text{Fe}_3\text{S}_4\{111\}}$  is the energy of the  $\text{Fe}_3\text{S}_4\{111\}$  slab and  $E_{\text{Mol}}$  is the energy of the isolated molecule(s) in vacuum. The activation energy ( $E_A$ ) of a certain step is the energy required to surmount the potential barrier characteristic of the transition state. We have defined this energy barrier as the difference between the initial state and transition state energy for the forward process. The reaction energy ( $E_R$ ) of each step is calculated as the total energy difference between the final state (product(s)) and the initial state (reactant(s)). We have discussed the feasibility of particular steps and the overall reaction trends ( $\Delta E$ ) as a function of the reference energy, *i.e.* clean surface and gas phase molecules,  $\text{H}_2$  and  $\text{CO}_2$ .

## Kinetic model

We have presented an extensive kinetic model<sup>81–83</sup> for the reduction of  $\text{CO}_2$  on  $\text{Fe}_3\text{S}_4\{111\}$  surfaces on the basis of 140 elementary steps, with the migration of the CO intermediate between the two different active sites,  $\text{Fe}_A$  and  $\text{Fe}_B$ . No assumptions regarding the mechanism or the rate-limiting step are made, all the processes are bi-directional, and all model parameters are rigorously derived from DFT calculations, which we have compared with experimental data collected under realistic conditions, see Fig. S1 in ESI.† In the frame of transition state theory,<sup>84,85</sup> this kinetic model may poorly describe the surface kinetics when local ordering is important and diffusion of adsorbents as H ad-atoms is slow. In these cases, computationally expensive approximations can be used, for instance kinetic Monte Carlo (kMC) is capable of accounting for the correct local structure.<sup>86</sup> Unfortunately, such an analysis remains completely impractical for reaction networks as complicated as the one described here. Lateral adsorbate–adsorbate interactions can also influence the stability of intermediates.<sup>87</sup>



Although we have included in the reaction network the effect of H ad-atoms near the catalytic center and the diffusion of CO<sub>2</sub> and CO molecules among Fe-sites, we have nevertheless considered the total surface H coverage ( $\theta_{\text{H}}$ ) to be low under typical conditions, and we have also included the H<sub>2</sub> evolution reaction as a function of  $\theta_{\text{H}}$ . The maximum surface coverage was restricted to 1 ML, and multilayer adsorption was not considered. We have considered three different adsorption sites, a surface sulfur for the H ad-atom adsorption (eight per unit cell) and the metal centers, Fe<sub>A</sub> or Fe<sub>B</sub> (one site per cell).

## Results and discussion

In order to develop a comprehensive model, firstly we have systematically studied the adsorption–desorption processes for the different reactants, followed by their co-adsorption and reaction leading to an extensive reaction network. Secondly, we have implemented these results in a micro-kinetics model to obtain a description of the process dynamics. Given the large amount of data, we have not described all the results in detail; the interested reader can find more relevant data in the ESI.<sup>†</sup> Finally, we have discussed the overall reaction trends and their implications in the CO<sub>2</sub> conversion process.

### Density functional theory results

Greigite (Fe<sub>3</sub>S<sub>4</sub>) is an inverse spinel-structured material whose particles in hydrothermal synthesis expose {001} and {111} surfaces.<sup>88</sup> We have focused our attention on the Fe<sub>3</sub>S<sub>4</sub>{111} surface as this surface has shown conversion of carbonate species.<sup>37</sup> The Fe<sub>3</sub>S<sub>4</sub>{111} surface contains eight S atoms and three Fe atoms at the top layer of a unit cell, two from a tetrahedral bulk position (Fe<sub>A</sub>) and one from an octahedral bulk position (Fe<sub>B</sub>).

**CO<sub>2</sub> adsorption and activation.** Carbon dioxide interacts with the Fe centers as well as with a surface depleted in S through the oxygen lone pair electrons. The most stable configurations led to practically undisturbed molecules, see Table 1. The weak interactions with the surface, and the lack of charge transfer and molecule distortion, indicate physical adsorption on the naked surface, see Fig. 1.

**Table 1** Summary of binding energies ( $E_{\text{B}}$ ) and optimized geometry parameters for the different adsorbents as well as for the activated CO<sub>2</sub> on Fe<sub>3</sub>S<sub>4</sub>{111} (# denotes the activated state). The sorption sites are described as Fe<sub>B</sub>, Fe<sub>A</sub> and S vacancy ( $v_{\text{S}}$ ). The distances ( $d$ ), angles ( $\angle$ ), and asymmetric stretching frequencies ( $\nu_{\text{C-O}}$ ) are given. The transferred charge ( $q$ ) refers to the number of electrons transferred from the surface. Adsorbed structures are represented in the ESI, Fig. S3.1<sup>†</sup>

System	Site	$E_{\text{B}}$ (eV)	$d_{\text{O-C}}$ (Å)	$\angle_{\text{O-C-O}}$ (°)	$\nu_{\text{C-O}}$ (cm <sup>-1</sup> )	$q$ (e <sup>-</sup> )
CO <sub>2</sub>	Fe <sub>A</sub>	−0.02	1.176	178.3	2359	0.0
CO <sub>2</sub>	Fe <sub>B</sub>	−0.19	1.175	179.4	2363	0.0
CO <sub>2</sub>	$v_{\text{S}}$	−0.20	1.175	179.4	2366	0.0
CO <sub>2</sub> <sup>#</sup>	Fe <sub>A</sub>	0.40	1.233	138.1	1879	0.4
CO <sub>2</sub> <sup>#</sup>	Fe <sub>B</sub>	0.19	1.207	157.4	2103	0.2
CO <sub>2</sub> <sup>#</sup> + 2H	Fe <sub>A</sub>	−0.33	1.250	131.9	1700	0.8
CO <sub>2</sub> <sup>#</sup> + 2H	Fe <sub>B</sub>	−0.31	1.213	153.9	2050	0.8



The activation of CO<sub>2</sub> from the physisorbed state is an endothermic process, but it is more likely to take place on Fe<sub>B</sub> than on Fe<sub>A</sub>, by 0.2 eV, perhaps due to the different ability of Fe<sub>A</sub> and Fe<sub>B</sub> to exchange electron density. The atomic charge analysis indicates that the transferred charge by Fe<sub>A</sub> is twice that of Fe<sub>B</sub>. We have noticed that, although most of the charge is transferred directly through the Fe site, its spin density remains unchanged. Fig. S3† represents the electron density depletion on the sulfur and appearance on both S-C and O lone pairs; rearrangement around the Fe atoms displays changes in the atomic orbital hybridization. Thus, the transferred charge is originally from the sulfur atoms near the metal centers. We have also considered the presence of atomic hydrogens on the CO<sub>2</sub> activation process. Accordingly to the adsorption energies, the presence of H ad-atoms on the surface stabilizes the activated species (CO<sub>2</sub><sup>#</sup>) on both metal centers owing to the hydrogen providing labile electrons on the sulfur, which transfers them to the CO<sub>2</sub> antibonding orbital. CO<sub>2</sub> activation produces notable changes in the molecular structure: the O-C distance elongates by 0.07 Å, the O-C-O angle bends (~130–160°), and the  $\nu(\text{C-O})$  shifts by 300 cm<sup>-1</sup> on Fe<sub>B</sub> and up to 660 cm<sup>-1</sup> on Fe<sub>A</sub>.

The positive  $E_B$  values of the activated CO<sub>2</sub> with respect to the energy reference indicate the preference of the molecule to desorb without modification before being activated. However, the presence of co-adsorbed hydrogens stabilizes CO<sub>2</sub><sup>#</sup> and its transition state, as shown by the reaction energies in Table 2. The lack of H ad-atoms on the surface makes the activation of CO<sub>2</sub> thermodynamically unfavourable and high pressures are required to increase the CO<sub>2</sub> activity. On the other hand, the presence of electron-donating species, *i.e.* H ad-atoms, enhances the CO<sub>2</sub> activation by decreasing the energy barrier, especially on electron deficient centers such as Fe<sub>B</sub>.

**Formate and hydrocarboxyl intermediates.** From CO<sub>2</sub> adsorption and activation in the presence of H ad-atoms, we have systematically studied its hydrogenation on both Fe<sub>A</sub> and Fe<sub>B</sub>, leading to formate and hydrocarboxyl intermediates *via* Langmuir–Hinshelwood (LH) reaction mechanism, where both reactants lie on the surface. The hydrogenation with the lowest activation energy is on the oxygen (3c from Table 3), leading to COOH, which binds to S and Fe<sub>A</sub> by C and O, respectively, see Fig. 2. The product is practically in thermodynamic equilibrium with the reactants by an energy difference of only 0.02 eV. The most favourable process on Fe<sub>B</sub> is reaction 3d, which proceeds through the hydrogenation of the

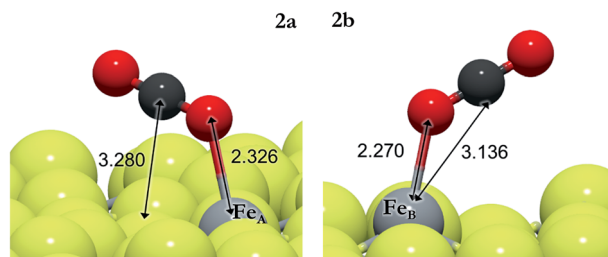


Fig. 1 Schematic representation of non-activated CO<sub>2</sub> on Fe<sub>A</sub> (left) and on Fe<sub>B</sub> (right). The light grey and yellow balls represent Fe and S, respectively, and the red and dark grey balls represent O and C, respectively.



**Table 2** Elementary reaction energies for CO<sub>2</sub><sup>\*</sup> activation on Fe<sub>3</sub>S<sub>4</sub>{111} (\* denotes the adsorbed state and # denotes the activated state). E<sub>A</sub> is the activation energy, E<sub>R</sub> is the product reaction energy and ΔE indicates the product energy with respect to isolated molecules and the Fe<sub>3</sub>S<sub>4</sub>{111} slab. The structures are represented in the ESI, Fig. S3.1†

Label	Reaction	Site	E <sub>A</sub> (eV)	E <sub>R</sub> (eV)	ΔE (eV)
<b>2a</b>	CO <sub>2</sub> <sup>*</sup> → CO <sub>2</sub> <sup>#</sup>	Fe <sub>A</sub>	0.43	0.39	0.36
<b>2b</b>	CO <sub>2</sub> <sup>*</sup> → CO <sub>2</sub> <sup>#</sup>	Fe <sub>B</sub>	0.41	0.38	0.20
<b>2c</b>	CO <sub>2</sub> <sup>*</sup> + 2H <sup>*</sup> → CO <sub>2</sub> <sup>#</sup> + 2H <sup>*</sup>	Fe <sub>A</sub>	0.62	0.06	−0.33
<b>2d</b>	CO <sub>2</sub> <sup>*</sup> + 2H <sup>*</sup> → CO <sub>2</sub> <sup>#</sup> + 2H <sup>*</sup>	Fe <sub>B</sub>	0.36	0.32	−0.30

oxygen coordinated to Fe, at −0.16 eV below co-adsorbed CO<sub>2</sub><sup>#</sup> and two H ad-atoms.

We have also investigated the Eley–Rideal (ER) mechanism, describing the interaction between gas phase CO<sub>2</sub> molecules and pre-adsorbed H on Fe<sub>3</sub>S<sub>4</sub>{111}. We have brought the molecule from a vacuum to the Fe center, exposing independently carbon or oxygen to the H ad-atom, which produces formate or hydrocarboxyl intermediates on the surface. The reaction energies are summarized in Table 3 (**3e–3h**). HCOO is derived from reaction **3e** on Fe<sub>A</sub>, which is the most suitable pathway for the formation of formic acid after surmounting a barrier of 0.3 eV above the energy reference. The generation of HCOO on Fe<sub>B</sub> has an energy barrier of over 1 eV. Optimized HCOO binds to both Fe<sub>A</sub> and Fe<sub>B</sub> with an Fe–O distance of ∼1.8 Å, see Fig. 2. The formate intermediate was also identified experimentally on metallic Cu upon exposure to CO<sub>2</sub> and H<sub>2</sub> gases (ref. 89 and references therein).

The barrier energies for COOH formation *via* the ER mechanism are 0.1 (**3g**) and 0.6 eV (**3h**) lower than those for **3e** and **3f** on Fe<sub>A</sub> and Fe<sub>B</sub>, respectively. The formation of COOH as an intermediate is not surprising as it has been identified as the key reaction intermediate in the water gas shift reaction.<sup>19</sup> Hydrocarboxyl has two distinguishable configurations depending on the direction of the hydroxyl group: *trans*-COOH and *cis*-COOH. The energy difference makes the *trans*-configuration the most stable by 0.4 eV.

Considering both mechanisms, *i.e.* LH and ER, the most favorable paths leading to HCOO intermediates are **3e** *via* ER and **3b** *via* LH on Fe<sub>A</sub> and Fe<sub>B</sub>,

**Table 3** Elementary reaction energies for the CO<sub>2</sub><sup>#</sup> hydrogenation *via* Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms on the Fe<sub>3</sub>S<sub>4</sub>{111} surface. The structures are represented in the ESI, Fig. S3.2†

Label	Mechanism	Reaction	Site	E <sub>A</sub> (eV)	E <sub>R</sub> (eV)	ΔE (eV)
<b>3a</b>	LH	CO <sub>2</sub> <sup>#</sup> + 2H <sup>*</sup> → HCOO <sup>*</sup> + H <sup>*</sup>	Fe <sub>A</sub>	1.21	−0.28	−0.60
<b>3b</b>		CO <sub>2</sub> <sup>#</sup> + 2H <sup>*</sup> → HCOO <sup>*</sup> + H <sup>*</sup>	Fe <sub>B</sub>	1.15	−1.25	−1.56
<b>3c</b>		CO <sub>2</sub> <sup>#</sup> + 2H <sup>*</sup> → COOH <sup>*</sup> + H <sup>*</sup>	Fe <sub>A</sub>	0.10	0.02	−0.31
<b>3d</b>		CO <sub>2</sub> <sup>#</sup> + 2H <sup>*</sup> → COOH <sup>*</sup> + H <sup>*</sup>	Fe <sub>B</sub>	0.71	−0.16	−0.46
<b>3e</b>	ER	CO <sub>2</sub> + 2H <sup>*</sup> → HCOO <sup>*</sup> + H <sup>*</sup>	Fe <sub>A</sub>	0.94	0.03	−0.60
<b>3f</b>		CO <sub>2</sub> + 2H <sup>*</sup> → HCOO <sup>*</sup> + H <sup>*</sup>	Fe <sub>B</sub>	1.86	−0.92	−1.56
<b>3g</b>		CO <sub>2</sub> + 2H <sup>*</sup> → COOH <sup>*</sup> + H <sup>*</sup>	Fe <sub>A</sub>	0.84	−0.17	−0.81
<b>3h</b>		CO <sub>2</sub> + 2H <sup>*</sup> → COOH <sup>*</sup> + H <sup>*</sup>	Fe <sub>B</sub>	1.28	0.19	0.65





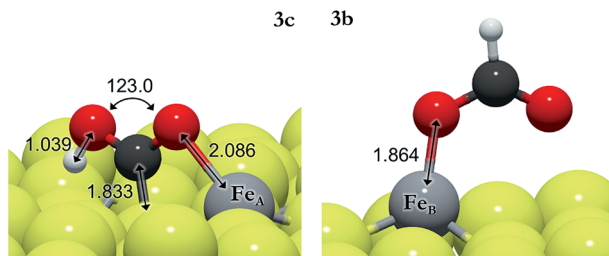


Fig. 2 Schematic representation of hydrocarboxyl (from **3c**) on  $\text{Fe}_A$  (left) and formate (from **3b**) on  $\text{Fe}_B$  (right). The light grey and yellow balls represent Fe and S, respectively, and the red and dark grey balls represent O and C, respectively.

respectively. In the transition state structure for the **3e** process, almost linear  $\text{CO}_2$  hovers close to the H ad-atom at a distance (C–H) of 1.526 Å and the molecule starts bending with an angle of  $145^\circ$ . The activation energy for the process **3b** is 1.15 eV above that of the reactants and the C–H distance (1.692 Å) indicates an early transition state. The lowest activation energy for the formation of COOH is reaction **3c**, although the energy required for the adsorption of the reactants and products on  $\text{Fe}_A$  is higher than that for the ER reaction **3g**. The early saddle point for the hydrogenation of  $\text{CO}_2$  via **3c** places the H at 1.300 Å from the oxygen on  $\text{Fe}_A$ , while on  $\text{Fe}_B$ , the  $\text{CO}_2$  in the **3d** transition state lies at a distance of 1.374 Å from the H. Upon COOH formation, the HO–C bond becomes weaker and elongates by 0.1 Å compared with  $\text{CO}_2$ . We have further investigated the COOH dissociation to CO and OH, and found that it is thermodynamically and kinetically likely ( $E_A = 0.60$  eV;  $E_R = -0.11$  eV), proceeding to the formation of  $\text{H}_2\text{O} + \text{CO}$ .

The small difference between the energy barriers (**2c** and **3e** < 0.05 eV) to HCOO and COOH intermediates indicates the low selectivity of the process on  $\text{Fe}_A$ , while a difference of 0.44 eV between the activation barriers of **3b** and **3d** indicates the selectivity for COOH intermediates on  $\text{Fe}_B$ . However, external conditions and the presence of dopants and promoters may influence the stability of intermediates, increasing the energy difference and therefore the selectivity.

**Formic acid, formaldehyde and carbon monoxide.** Formate intermediates remain adsorbed on the surface, allowing further changes such as C–O bond scission or additional hydrogenation. We have studied the breaking of the C–O bond but the process is thermodynamically and kinetically unfavourable ( $E_R > 1.5$  eV;  $E_A > 1.8$  eV). We have also studied the H migration process from formate to hydrocarboxyl but the process is kinetically unaffordable ( $E_A \sim 3$  eV). A consecutive hydrogenation of the formate intermediate leads to compounds such as formic acid ( $\text{HCOOH}$ ) and formaldehyde ( $\text{H}_2\text{CO}$ ), see Table 4.

We have explored the energy profile for HCOOH formation, see Fig. 3, and found that, from HCOO, the transition states leading to hydrogenation of the uncoordinated oxygen (**4a,b**) are more favourable than those leading to hydrogenation of the oxygen coordinated to Fe (**4c,d**). We have also noticed that the process is thermodynamically and kinetically more likely on  $\text{Fe}_B$  than on  $\text{Fe}_A$ . Between the two sites, pathway **4a** is more feasible, leaving the HCOOH molecule adsorbed on  $\text{Fe}_A$  with a binding energy of  $-0.86$  eV. The formation of HCOOH is



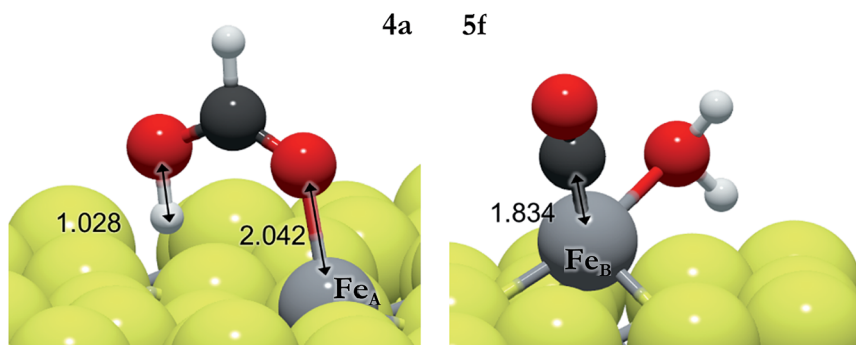


**Table 4** Elementary reaction energies for the HCOO hydrogenation on the Fe<sub>3</sub>S<sub>4</sub>{111} surface. Notice that we have differentiated O<sup>1</sup> and O<sup>2</sup> from the same CO<sub>2</sub> molecule. The structures are represented in the ESI, Fig. S3.3†

Label	Reaction	Site	E <sub>A</sub> (eV)	E <sub>R</sub> (eV)	ΔE (eV)
4a	HCOO* + H* → HCOO <sup>1</sup> H*	Fe <sub>A</sub>	0.08	−0.45	−1.05
4b	HCOO* + H* → HCOO <sup>1</sup> H*	Fe <sub>B</sub>	0.56	0.28	−1.28
4c	HCOO* + H* → HCOO <sup>2</sup> H*	Fe <sub>A</sub>	1.28	0.19	−0.42
4d	HCOO* + H* → HCOO <sup>2</sup> H*	Fe <sub>B</sub>	2.12	0.71	−0.84
4e	HCOO* + H* → H <sub>2</sub> CO + O*	Fe <sub>A</sub>	1.83	1.51	1.74
4f	HCOO* + H* → H <sub>2</sub> COO*	Fe <sub>B</sub>	2.12	1.30	−0.26

considerably more likely than the formation of formaldehyde (4e and 4f), although this species has been identified on other catalysts as a potential intermediate in methanol production from CO<sub>2</sub>.<sup>17,90</sup> Once HCOO is hydrogenated to form formaldehyde, its precursor (H<sub>2</sub>COO) remains adsorbed on Fe<sub>B</sub>, but on Fe<sub>A</sub>, the C–O bond is completely broken and H<sub>2</sub>CO is released from the surface, leaving an O ad-atom strongly adsorbed on Fe<sub>A</sub>, thereby poisoning the active site. Formaldehyde is also a product of CO hydrogenation as described below.

Similarly to the formate intermediate, further hydrogenation of COOH leads to thermodynamically favorable HCOOH, but the activation energy ( $E_A > 1.2$  eV) makes the reaction kinetically implausible (reactions 5a and 5b). As summarized in Table 5, dihydroxycarbene (HOCOH) is an alternative hydrogenation route as experimentally proposed in the methanol synthesis on oxide catalysts,<sup>91</sup> but its formation is highly inaccessible from a kinetic point of view (5c and 5d). Nevertheless, we have considered HOCOH formation and dissociation to COH\* + OH\*, as suggested on Cu{111}.<sup>17</sup> However, on Fe<sub>3</sub>S<sub>4</sub>{111}, the reaction pathway is inhibited not only by the activation energy forming HOCOH but also by the unlikely scission of HO–C, which has  $E_R > 0.8$  eV and  $E_A > 1.4$  eV on both Fe sites. Under certain conditions, HOCOH may be observable experimentally but it is not part of the main reaction pathway on greigite. The hydrogenation of the OH group on the COOH intermediate takes place mostly on Fe<sub>B</sub> and leads to the formation



**Fig. 3** Schematic representation of HCOO<sup>1</sup>H (from 4a) on Fe<sub>A</sub> (left) and CO + H<sub>2</sub>O (from 5f) on Fe<sub>B</sub> (right). The light grey and yellow balls represent Fe and S, respectively, and the red and dark grey balls represent O and C, respectively.



**Table 5** Elementary reaction energies for the COOH hydrogenation on the Fe<sub>3</sub>S<sub>4</sub>{111} surface. The structures are represented in the ESI, Fig. S3.4†

Label	Reaction	Site	$E_A$ (eV)	$E_R$ (eV)	$\Delta E$ (eV)
5a	COOH* + H* → HCOOH*	Fe <sub>A</sub>	1.21	−0.74	−1.05
5b	COOH* + H* → HCOOH*	Fe <sub>B</sub>	1.38	−0.24	−0.70
5c	COOH* + H* → HOCOH*	Fe <sub>A</sub>	1.39	−0.13	−0.44
5d	COOH* + H* → HOCOH*	Fe <sub>B</sub>	1.67	0.07	−0.40
5e	COOH* + H* → CO* + H <sub>2</sub> O	Fe <sub>A</sub>	1.84	0.07	−0.24
5f	COOH* + H* → CO* + H <sub>2</sub> O*	Fe <sub>B</sub>	0.73	−0.49	−0.95

of co-adsorbed H<sub>2</sub>O and CO (reactions 5e and 5f). While the process is slightly endothermic on Fe<sub>A</sub> with a large energy barrier above the reference of 1.6 eV, on Fe<sub>B</sub> it is energetically favourable, see Fig. 3. The co-adsorbed H<sub>2</sub>O stabilizes the system by 0.58 eV and, compared with HCOOH formation *via* reaction 3e, its energy barrier is higher by less than 0.05 eV.

We have evaluated the movement of CO between both Fe<sub>B</sub> and Fe<sub>A</sub> from 5f and 5e, respectively, and also considered the presence of co-adsorbed H<sub>2</sub>O (on Fe<sub>B</sub>) or hydrogen ad-atoms, see Table 6. Before and after H<sub>2</sub>O desorption from Fe<sub>B</sub>, the migration of CO to Fe<sub>A</sub> is endothermic and kinetically impractical ( $E_A > 1.5$  eV), see Fig. 4. We have found that once water desorbs, the CO molecule shrinks the Fe<sub>B</sub>–C bond by 0.08 Å and lies perpendicular to the surface at 1.754 Å. The intramolecular bond is 1.161 Å, which, together with a shift in its stretching frequency of 103 cm<sup>−1</sup> with respect to the isolated molecule ( $d_{(C-O)} = 1.142$  Å,  $\nu_{(C-O)} = 2129$  cm<sup>−1</sup>), indicates a weak C–O bond. The presence of co-adsorbed hydrogens decreases the energy barrier by up to 0.82 eV, making the process more likely, although (A)CO is 0.16 eV less stable than (B)CO. The effect of the hydrogens is similar to the CO<sub>2</sub> activation process, which is related to the availability of charge density. The stabilization of the CO adsorption on Fe<sub>A</sub> by the H ad-atoms is observable in the Fe–C distance differences – the Fe<sub>A</sub>–C bond is 0.18 Å larger than the Fe<sub>B</sub>–C bond compared to 0.12 Å in the presence of hydrogens – and the asymmetric stretching frequencies vary by 23 and 11 cm<sup>−1</sup>, respectively, without and with H ad-atoms. We have carried out the hydrogenation of CO on both sites, Fe<sub>A</sub> and Fe<sub>B</sub>, independently.

**Methanol.** We have studied the hydrogenation of CO yielding CH<sub>3</sub>OH on the Fe<sub>3</sub>S<sub>4</sub>{111} surface *via* two possible intermediates, CH<sub>3</sub>OH and CH<sub>x</sub>O, where the last intermediate may also produce formaldehyde. We have explored both energy profiles, summarized in Table 7 and 8, respectively. We have also connected both pathways with the hydrogenation of formaldehyde: CH<sub>2</sub>O + H → CH<sub>2</sub>OH.

**Table 6** Elementary reaction energies for the CO movements between Fe<sub>B</sub> and Fe<sub>A</sub> on the Fe<sub>3</sub>S<sub>4</sub>{111} surface. We have labelled each species regarding its position: (A) or (B). The structures are represented in the ESI, Fig. S3.5†

Label	Reaction	$E_A$ (eV)	$E_R$ (eV)	$\Delta E$ (eV)
6a	(B)CO* + (B)H <sub>2</sub> O* → (A)CO* + (B)H <sub>2</sub> O*	1.57	0.46	−0.49
6b	(B)CO* → (A)CO*	1.84	0.39	0.02
6c	(B)CO* + 2H* → (A)CO* + 2H*	0.82	0.16	−0.37



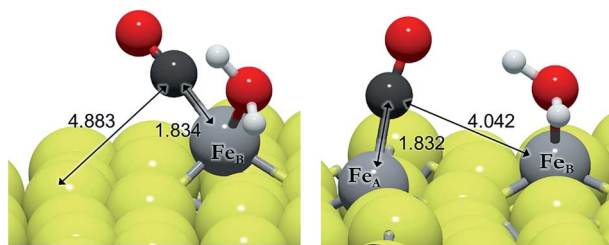


Fig. 4 Schematic representation of CO migration from  $\text{Fe}_\text{B}$  (left) to  $\text{Fe}_\text{A}$  (right) according to the process **6a**. The light grey and yellow balls represent Fe and S, respectively, and the red and dark grey balls represent O and C, respectively.

The carbon monoxide hydrogenation step is slightly unfavorable thermodynamically,  $E_\text{R}(\text{Fe}_\text{B}) < 0.2$  eV, although the overall energy is lower than the reference energy ( $\Delta E$ ), indicating that it is a viable process. On  $\text{Fe}_\text{A}$ , the reaction **7a** is endothermic by 0.3 eV whereas it is also kinetically controlled as the transition state lies above the energy reference. The transition states for the formation of  $\text{HCOH}$  (**7c,d**) and  $\text{H}_2\text{CO}$  (**8a,b**) also lie above the reference energy on both  $\text{Fe}_\text{A}$  and  $\text{Fe}_\text{B}$ , see Fig. 5. These processes, thus, require energy from external sources, such as a natural chemiosmotic or applied potential to surmount the energy barrier. The over-potential needed for the formation of  $\text{HCOH}$  on  $\text{Fe}_\text{A}$  (**7c**) is the smallest one (0.5 eV), leading to a downhill conversion towards  $\text{CH}_3\text{OH}$ . The  $\text{HCOH}$  intermediate has also been detected during CO reduction on transition metal surfaces.<sup>92</sup> The presence of co-adsorbed hydrogens stabilises  $\text{HCOH}$ , whereas the production becomes thermodynamically unfavourable in pathway **8**. The formation of  $\text{HCOH}$  (**7c**) has an energy barrier 0.4 eV lower than that for the production of  $\text{H}_2\text{CO}$  (**8a**), indicating selectivity of this process on  $\text{Fe}_\text{A}$ . On the  $\text{Fe}_\text{B}$  adsorption site, the  $E_\text{A}$  values are bigger than those for  $\text{Fe}_\text{A}$  because the reactants start from a more stable position (by 0.30 eV), although the transition states for **7d** and **8b** are 0.1 and 0.2 eV more favourable than their counterparts on  $\text{Fe}_\text{A}$ .

Although CO reduction is likely to take place following process **7c**, the hydrogenation of  $\text{HCOH}$  (**7e**) has a slightly higher energy barrier than the **8c** process, by 0.1 eV, leading to competing processes. The reduction of  $\text{H}_2\text{CO}$  *via* the **9a** process is 0.2 eV lower than that *via* **7e**, allowing the hydrogenation of the oxy

Table 7 Elementary reaction energies for the CO hydrogenation on the  $\text{Fe}_3\text{S}_4\{111\}$  surface *via* the  $\text{CH}_3\text{OH}$  intermediate. The structures are represented in the ESI, Fig. S3.6†

Label	Reaction	Site	$E_\text{A}$ (eV)	$E_\text{R}$ (eV)	$\Delta E$ (eV)
<b>7a</b>	$\text{CO}^* + 2\text{H}^* \rightarrow \text{HCO}^* + \text{H}^*$	$\text{Fe}_\text{A}$	0.52	0.31	−0.06
<b>7b</b>	$\text{CO}^* + 2\text{H}^* \rightarrow \text{HCO}^* + \text{H}^*$	$\text{Fe}_\text{B}$	0.37	0.17	−0.36
<b>7c</b>	$\text{HCO}^* + \text{H}^* \rightarrow \text{HCOH}^*$	$\text{Fe}_\text{A}$	0.55	0.26	0.20
<b>7d</b>	$\text{HCO}^* + \text{H}^* \rightarrow \text{HCOH}^*$	$\text{Fe}_\text{B}$	1.09	0.26	−0.11
<b>7e</b>	$\text{HCOH}^* + 2\text{H}^* \rightarrow \text{H}_2\text{COH}^* + \text{H}^*$	$\text{Fe}_\text{A}$	1.11	−0.81	−1.04
<b>7f</b>	$\text{HCOH}^* + 2\text{H}^* \rightarrow \text{H}_2\text{COH}^* + \text{H}^*$	$\text{Fe}_\text{B}$	0.86	−0.58	−1.08
<b>7g</b>	$\text{H}_2\text{COH}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^*$	$\text{Fe}_\text{A}$	1.17	−0.75	−1.79
<b>7h</b>	$\text{H}_2\text{COH}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^*$	$\text{Fe}_\text{B}$	0.85	−0.99	−2.07

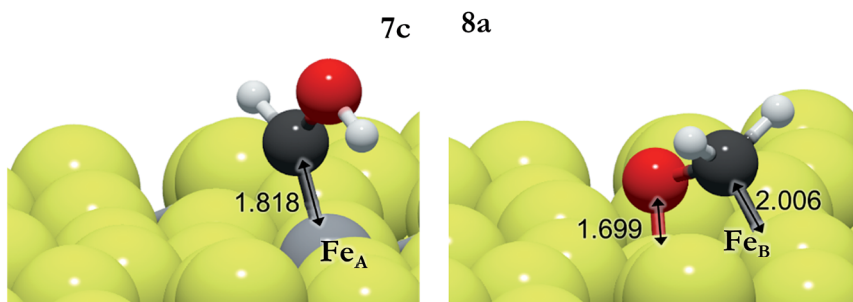


**Table 8** Elementary reaction energies for the HCO hydrogenation on the  $\text{Fe}_3\text{S}_4\{111\}$  surface *via* the  $\text{CH}_x\text{O}$  intermediate. The structures are represented in the ESI, Fig. S3.7†

Label	Reaction	Site	$E_A$ (eV)	$E_R$ (eV)	$\Delta E$ (eV)
<b>8a</b>	$\text{HCO}^* + \text{H}^* \rightarrow \text{H}_2\text{CO}^*$	$\text{Fe}_A$	0.94	0.75	0.69
<b>8b</b>	$\text{HCO}^* + \text{H}^* \rightarrow \text{H}_2\text{CO}^*$	$\text{Fe}_B$	1.11	−0.57	−0.93
<b>8c</b>	$\text{H}_2\text{CO}^* + 2\text{H}^* \rightarrow \text{H}_3\text{CO}^* + \text{H}^*$	$\text{Fe}_A$	0.34	−1.68	−1.23
<b>8d</b>	$\text{H}_2\text{CO}^* + 2\text{H}^* \rightarrow \text{H}_3\text{CO}^* + \text{H}^*$	$\text{Fe}_B$	1.04	−0.58	−1.79
<b>8e</b>	$\text{H}_3\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^*$	$\text{Fe}_A$	0.42	−0.98	−1.79
<b>8f</b>	$\text{H}_3\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^*$	$\text{Fe}_B$	1.14	−0.28	−2.07

group and lying  $-1.04$  eV below the energy reference (Table 9). However, the **7f**, **8d** and **9b** processes on  $\text{Fe}_B$  require less energy to surmount their transition states, leading to intermediates stabilised by up to  $1.8$  eV below the reference. Once methanol is formed through either the **7** or **8** pathway, it binds to  $\text{Fe}_A$  or  $\text{Fe}_B$  with an adsorption energy of  $-0.54$  and  $-0.82$  eV, respectively. Overall, the  $\text{CH}_3\text{OH}$  formation is more feasible on  $\text{Fe}_B$  where only **7d** and **8b** are limiting steps.

**Reaction energy profile.** We have expressed, in energy profiles, all the steps described above for the  $\text{CO}_2$  reduction at both  $\text{Fe}_A$  and  $\text{Fe}_B$  sites on the  $\text{Fe}_3\text{S}_4\{111\}$  surface, see Fig. 6 and 7, respectively. The activation of  $\text{CO}_2$  is known to be an endothermic process, although the presence of atomic H on the surface stabilizes the activated molecule, making this a favourable process on  $\text{Fe}_B$  (**2d**). Upon  $\text{CO}_2$  activation (**2**), the molecule may undergo hydrogenation on either C or O. Although reactions such as **3b** may be driven by favourable thermodynamics, the activation energy is higher than the reference energy, indicating that the molecule would desorb before being hydrogenated. Reaction **3c** is an exception as it has an activation energy of only  $0.1$  eV with a transition state  $0.2$  eV below the reference. Processes that do not require  $\text{CO}_2$  pre-activation and proceed *via* the ER mechanism (**3e–h**) still require an energy input to surmount the activation energy and not all of them are thermodynamically driven. The difference in activation energies for the formation of  $\text{HCOO}$  and  $\text{COOH}$  is only  $0.1$  eV (**3e** vs. **3d**) and therefore the selectivity for specific products, *i.e.*  $\text{HCOOH}$  and  $\text{CH}_3\text{OH}$ , is very low. Many of the following processes studied are energetically inhibited under mild conditions and the pathways are limited to reactions **4a** on  $\text{Fe}_A$ , and **4b**, **4d** and **5f** on  $\text{Fe}_B$ .



**Fig. 5** Schematic representation of  $\text{HCOH}$  (from **7c**) on  $\text{Fe}_A$  (left) and  $\text{H}_2\text{CO}$  (from **8a**) on  $\text{Fe}_B$  (right). The light grey and yellow balls represent Fe and S, respectively, and the red and dark grey balls represent O and C, respectively.

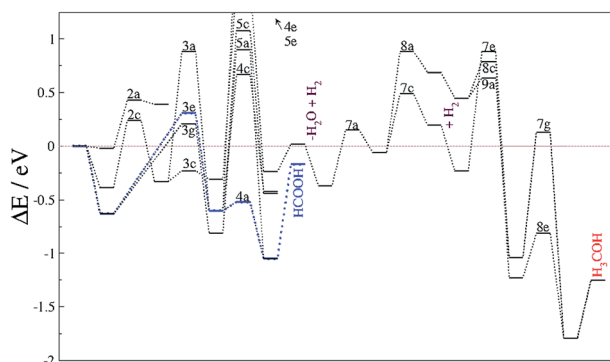


**Table 9** Elementary reaction energies for the  $\text{H}_2\text{CO}$  hydrogenation on the  $\text{Fe}_3\text{S}_4\{111\}$  surface. The structures are represented in Fig. S3.8†

Label	Reaction	Site	$E_A$ (eV)	$E_R$ (eV)	$\Delta E$ (eV)
9a	$\text{H}_2\text{CO}^* + 2\text{H}^* \rightarrow \text{H}_2\text{COH}^* + \text{H}^*$	$\text{Fe}_A$	0.18	−1.49	−1.04
9b	$\text{H}_2\text{CO}^* + 2\text{H}^* \rightarrow \text{H}_2\text{COH}^* + \text{H}^*$	$\text{Fe}_B$	1.14	0.13	−1.08

The formate adsorbed on  $\text{Fe}_A$ , the product of reaction 3e, is followed by a fast process producing  $\text{HCOOH}$ , which remains adsorbed, suggesting the possibility for secondary reactions, *e.g.* C–C formation or combining with  $\text{NH}_2$  to give formamide.<sup>12</sup> This agrees with previous experiments, which observed large amounts of formate on metal surfaces upon exposure to  $\text{CO}_2$  and  $\text{H}_2$  gases.<sup>89,93</sup> Thus, the rate-limiting step for  $\text{HCOOH}$  formation is the first  $\text{CO}_2$  hydrogenation with a TS energy 0.3 eV above the reference.

Recently identified as a key intermediate in the water gas shift reaction,<sup>19,94</sup> we have identified hydrocarboxyl as the first intermediate in the CO formation prior to methanol yield. The reverse water gas shift reaction takes place when oxygen from the  $\text{CO}_2$  molecule reacts with H to produce CO and  $\text{H}_2\text{O}$ , *i.e.* processes 3d and 5f. This pathway on  $\text{Fe}_B$  led to carbon monoxide bonded to  $\text{Fe}_B$  with an adsorption energy of −1.1 eV, which is stabilized by the presence of H ad-atoms (by −0.17 eV). Although the formation of HCO is thermodynamically feasible, its hydrogenation has an energy barrier of at least 0.75 eV, processes (7 and 8), which are driven by very stable intermediates. The reduction of HCO is, hence, the rate-limiting step for  $\text{CH}_3\text{OH}$  formation from  $\text{CO}_2$  on  $\text{Fe}_3\text{S}_4\{111\}$ . Once the limiting step is surmounted, the methoxy route (8) is the most favourable despite the fact that pathway 7 is also downhill energetically. Methoxy intermediates are very stable and remain on the surface for longer, which may lead to interactions with other molecules or intermediates, leading to *e.g.* longer chain hydrocarbons.<sup>12</sup>



**Fig. 6** Reaction energy profiles for the  $\text{CO}_2$  hydrogenation process taking place on  $\text{Fe}_A$ . The blue line highlights the formate pathway. The labels corresponding to elementary steps are placed at the transition state. Processes such as water molecule release ( $-\text{H}_2\text{O}$ ) and surface hydrogenation ( $+\text{H}_2$ ) are also included. The horizontal brown line indicates the energy reference of the naked surface and isolated molecules.



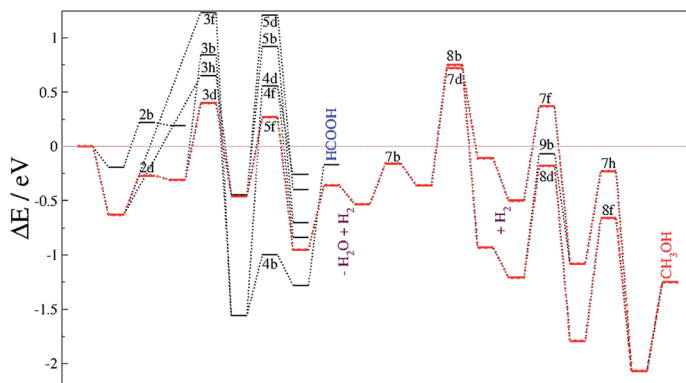


Fig. 7 Reaction energy profiles for the  $\text{CO}_2$  hydrogenation process taking place on  $\text{Fe}_\text{B}$ . The blue line highlights the formate pathway. The labels corresponding to elementary steps are placed at the transition state. Processes such as water molecule release ( $-\text{H}_2\text{O}$ ) and surface hydrogenation ( $+\text{H}_2$ ) are also included. The horizontal brown line indicates the energy reference of the naked surface and isolated molecules.

### Kinetic model results

We have applied a kinetic model, including the adsorption–desorption of the molecules and all the steps described above, in a consistent reaction network. We have characterized the desorption of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{HCOOH}$  and  $\text{CH}_3\text{OH}$  individually and modelled the temperature programmed desorption (TPD) starting with full coverage and raising the temperature by  $1 \text{ K s}^{-1}$ . Molecules like  $\text{CO}_2$ ,  $\text{HCOOH}$  and  $\text{CH}_3\text{OH}$  that have different adsorption sites, *i.e.*  $\text{Fe}_\text{A}$  and  $\text{Fe}_\text{B}$ , were equally distributed among them. For example, there are two configurations of  $\text{HCOOH}$  on  $\text{Fe}_\text{A}$  and two on  $\text{Fe}_\text{B}$ , and we set each configuration at an initial coverage of 0.25 ML. We have also considered secondary reactions like the exchange between  $\text{CO}_2$  adsorption sites and the dissociation–association of the water molecule. The formation of  $\text{H}_2$  is considered as a function of the H-coverage, for which we have investigated the associative desorption with different coverages, *i.e.* 0.25, 0.5, 0.75 and 1 ML, over the eight sulfur sites of an  $\text{Fe}_3\text{S}_4\{111\}$  cell unit. The overlap of these individual TPDs led to Fig. 8.

Physisorbed  $\text{CO}_2$  desorbs from the surface with a minimal thermal energy, in agreement with the weak interaction with either  $\text{Fe}_\text{B}$  or  $\text{Fe}_\text{A}$ . Separately, H adatoms remain scattered on the surface until the temperature reaches 500 K, when they recombine and evolve as  $\text{H}_2$  giving a sharp peak, which is linked to a fast process. Water molecules desorb from  $\text{Fe}_\text{B}$  relatively easily at 135 K with a narrow signal; note that it is a single molecule per unit cell. Formic acid is desorbed in three signals instead of the four expected from the different adsorbed conformations due to the overlapping of two signals around 378 K, from reactions **4a** and **4d**. Methanol TPD also presents multiple signals, at 119 K and at 185 K, related to the molecule adsorbed on  $\text{Fe}_\text{A}$  and  $\text{Fe}_\text{B}$ , respectively.

We have derived the reaction constants for the forward and the reverse reactions, tabulated in Table S1.† The relationship between these constants ( $K = K_+/K_-$ ) provides important information with respect to a particular step. For instance, although reaction **3f** has a high energy barrier compared with other  $\text{CO}_2$



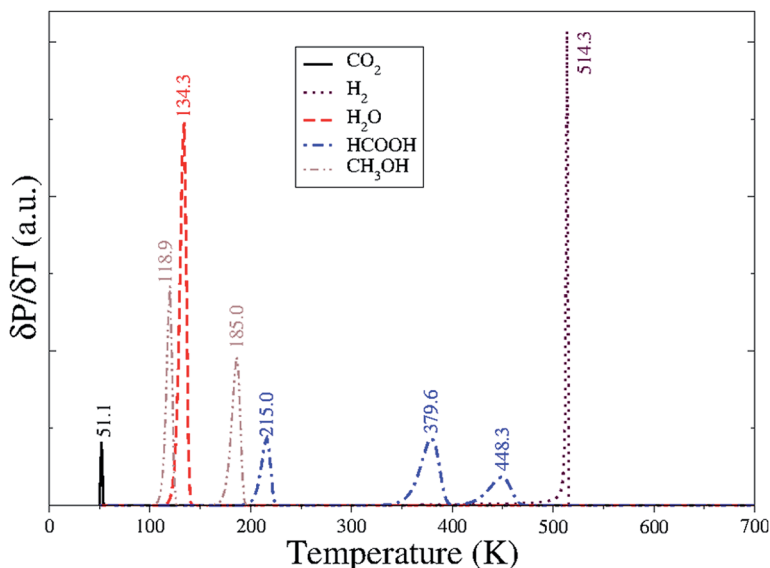


Fig. 8 Temperature programmed desorption of the molecules involved in the reduction mechanism of  $\text{CO}_2$  on  $\text{Fe}_3\text{S}_4(111)$ . The temperature range considered is from 50 to 700 K, evaluated every 2 K each 2 s, leading to a heating rate of  $1 \text{ K s}^{-1}$ .

hydrogenation processes, the driving force of the  $\text{HCOO}$  formation makes  $K_{+1}$  bigger than  $K_{-1}$  and therefore the equilibrium constant ( $K$ ) shifts towards formate. We have plotted the logarithm of  $K$  for every hydrogenation process in Fig. 9.

Although the activation of  $\text{CO}_2$  on the surface is unlikely (reactions **2a–d**), the presence of H ad-atoms enhances its molecular adsorption on either  $\text{Fe}_\text{A}$  or  $\text{Fe}_\text{B}$  as the top left values of Fig. 9 indicate. However, the Eley–Rideal mechanism for the formate formation on  $\text{Fe}_\text{A}$  is preferred and this is followed by a second hydrogenation (**4a**), leading to formic acid, whose desorption, however, is the slowest step, thereby reducing its production. On  $\text{Fe}_\text{B}$ , the formation of formic acid is capped by the second hydrogenation (**4b**) with the reverse process being more favourable, which means that formic acid released from  $\text{Fe}_\text{A}$  would adsorb on  $\text{Fe}_\text{B}$  and remain as formate, limiting the site availability. The processes **5c**, **7a** and **8a** on  $\text{Fe}_\text{A}$  have similar consequences with respect to methanol formation. The methanol formation on  $\text{Fe}_\text{B}$  may take place *via* the highly favourable Eley–Rideal mechanism (**3h**) or through  $\text{CO}_2$  activation and hydrocarboxyl formation (**2b** and **3d**, respectively). The only slightly reverse step is the hydrogenation of CO (**7b**), which limits the process *via* the  $\text{H}_2\text{CO}$  intermediate, mechanism **8**.

The mechanism showed  $\text{HCOOH}$  and  $\text{CH}_3\text{OH}$  as products of the  $\text{CO}_2$  conversion with the reaction constants indicating that intermediate species like formate, carbon monoxide and  $\text{CH}_x\text{O}$  have a long enough residence time on the surface to allow them to react with other C-species, leading to *e.g.* acetic and pyruvic acid. Indeed these  $\text{C}_2$  and  $\text{C}_3$  products were detected experimentally after exposing  $\text{Fe}_3\text{S}_4$  particles to a saturated aqueous solution of  $\text{CO}_2$  under a mild reduction potential.<sup>12</sup>





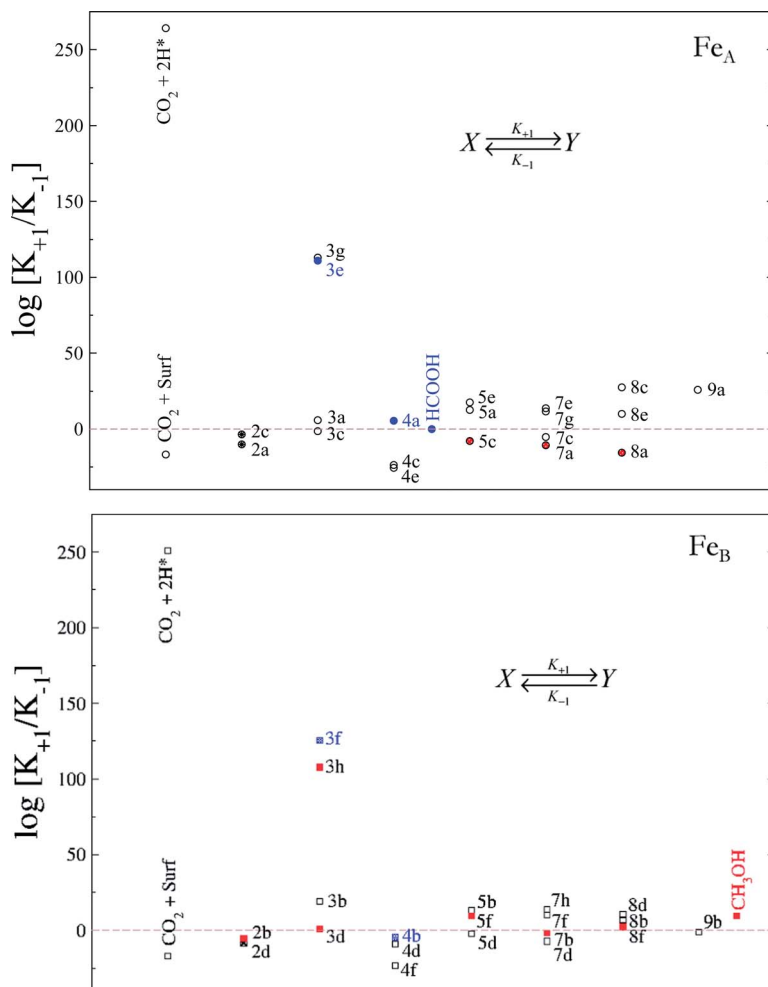


Fig. 9 Relationship between the equilibrium constants ( $\log[K_{+1}/K_{-1}]$ ) at a temperature of 300 K for the  $\text{CO}_2$  reduction towards HCOOH (blue) and  $\text{CH}_3\text{OH}$  (red) on  $\text{Fe}_A$  (circles) and  $\text{Fe}_B$  (squares) sites on the  $\text{Fe}_3\text{S}_4\{111\}$  surface. The labels indicate the processes according to Fig. S3.† Formic acid and methanol desorption/adsorption constants are included on  $\text{Fe}_A$  and  $\text{Fe}_B$ , respectively. The solid symbols show the limiting step for each mechanism.

## Conclusions

We have carried out an extensive density functional theory study to map the  $\text{CO}_2$  reduction mechanism network on the mineral surface  $\text{Fe}_3\text{S}_4\{111\}$ . Among the multiple reaction pathways explored, we have discerned the most favourable by using arguments based on energy profiles and reaction constants. Our results show distinctive behaviour for the different adsorption sites:  $\text{Fe}_A$  and  $\text{Fe}_B$ . On  $\text{Fe}_A$ , the  $\text{CO}_2$  conversion occurs through a formate intermediate *via* Eley–Rideal mechanism, yielding HCOOH. On  $\text{Fe}_B$ , the formation of the hydrocarboxyl intermediate is favoured, which dissociates and yields CO on the surface plus a water molecule. Further hydrogenations of CO are limited by the formation of



the HCO intermediate; despite being energetically favourable compared with the energy reference, the reaction constant towards HCO is smaller than that of the reverse processes. Following reductions are driven by the stability of their products. Methanol, in contrast to formic acid, desorbs from the surface easily, releasing an active site for further CO<sub>2</sub> conversion. Although the production of formic acid or methanol is determined by the adsorption site, CO<sub>2</sub> and intermediates are able to move from one site to another, as shown in step 6.

Thus, Fe<sub>3</sub>S<sub>4</sub>{111} catalyzes the CO<sub>2</sub> transformation by hydrogen, yielding mostly formic acid and methanol, where the rate-limiting step is the CO<sub>2</sub> activation *via* Langmuir–Hinshelwood mechanism, and indicating that the production of methanol is through the formation of the HCO intermediate. The selectivity towards particular products increases, *e.g.* by blocking selectively an Fe site, where capping Fe<sub>A</sub>, for instance, leads to the reduction of CO<sub>2</sub> into methanol.

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