Supporting Information for:

Catalytic formation of oxalic acid on the partially oxidised greigite Fe_3S_4(001) surface

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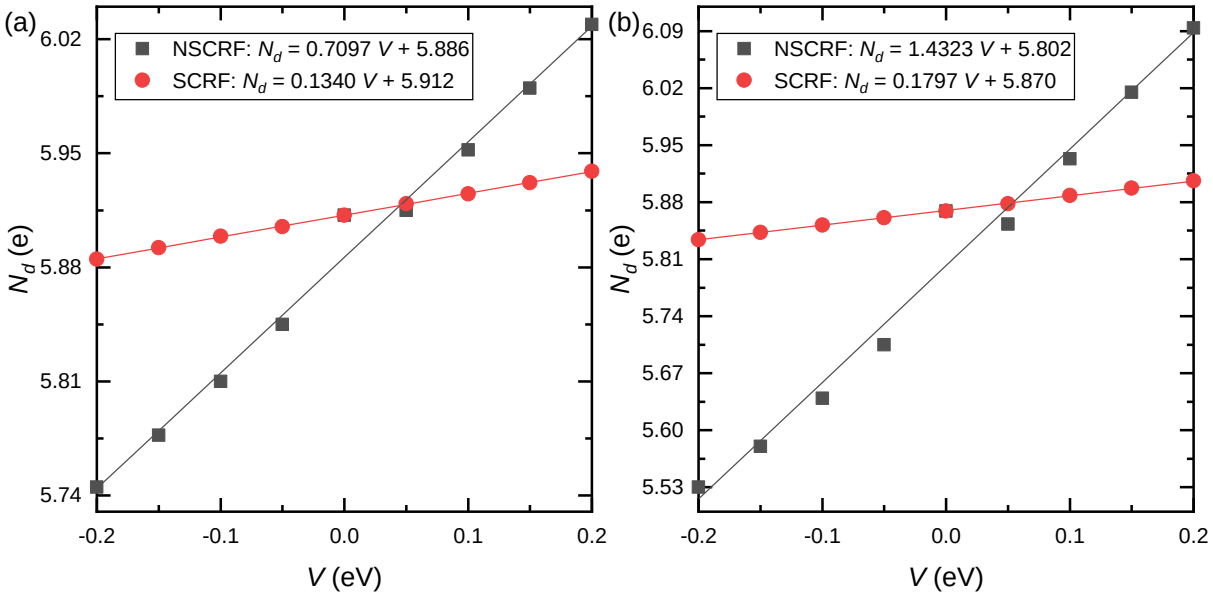

Figure SI1. Linear non-self-consistent (NSCF) and self-consistent response functions (SCF) for the change in the number of *d* electrons on one atomic (a) Fe_A and (b) Fe_B site of Fe_3S_4 as a function of an additional spherical potential (*V*).

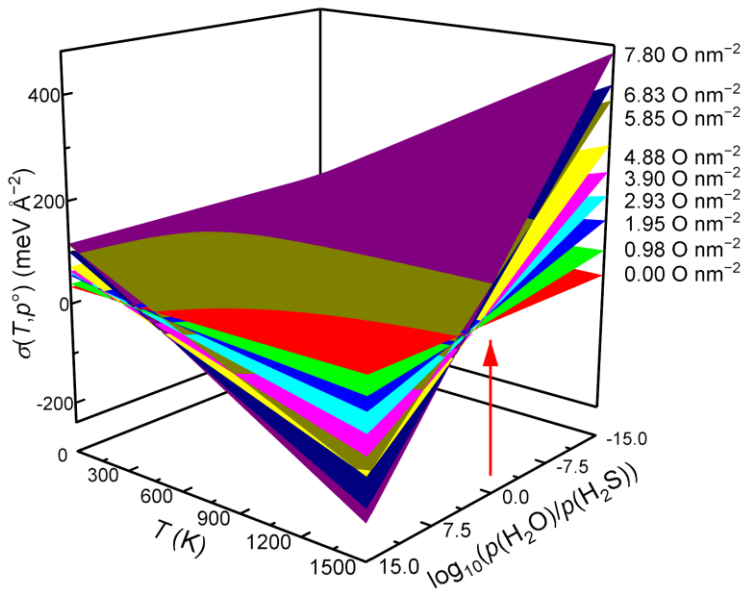

Figure SI2. Bird's eye view of the non-planar potential energy surface representations of the surface free energies for all the coverages of O, indicated in the figure, considered for termination Fe_A of the $Fe_3S_4(001)$ surface. The red arrow indicates the direction for the bi-dimensional projection onto the plane formed by the temperature and ratio of partial pressures of H_2O and H_2S.

Table SI1. Unscaled and scaled wavenumbers for the fundamental vibrational modes calculated for a single CO_2 molecule interacting with the different adsorption sites considered for the partially oxidised 62.5O-Fe_3S_4(001) surface. The presented vibrational modes are the asymmetric stretching (ν_{asym}), symmetric stretching (ν_{sym}) and average bending (δ) modes.

Adsorption site		O	S	Fe_A	Fe_B
Structural type		μ_3–η^3	μ_2–η^2–(C, O)	η^1–O	η^1–O
ν_{asym}(O=C=O) (cm^{-1})	Unscaled	1574	1750	2412	2353
	Scaled	1520	1690	2329	2272
ν_{sym}(O=C=O) (cm^{-1})	Unscaled	1269	1126	1343	1323
	Scaled	1225	1088	1297	1278
δ(O=C=O) (cm^{-1})	Unscaled	823	695	602	615
	Scaled	795	671	581	594

Table SI2. Unscaled and scaled wavenumbers for the fundamental vibrational modes calculated for a single H_2O molecule interacting with the different adsorption sites considered for the partially oxidised 62.5O-Fe_3S_4(001) surface. The presented vibrational modes are the asymmetric stretching (ν_{asym}), symmetric stretching (ν_{sym}) and average bending (δ) modes.

Adsorption site		Fe_A	Fe_A, Fe_A		Fe_B	
Type		Molecular	Molecular	Dissociative	Molecular	Dissociative
Structural type		μ_3–η^3	μ_4–η^4	μ_3–η^3	μ_3–η^3	μ_3–η^3
ν_{asym}(H–O–H) (cm^{-1})	Unscaled	3602	3693	3749	3654	3724
	Scaled	3461	3549	3602	3511	3578
ν_{sym}(H–O–H) (cm^{-1})	Unscaled	3177	2435	3493	2084	2690
	Scaled	3053	2339	3356	2003	2585
δ(H–O–H) (cm^{-1})	Unscaled	1576	1527	840	1576	940
	Scaled	1514	1468	807	1514	904

Table SI3. Vibrational entropies calculated for the adsorbed species observed in the oxalate, carboxylate and bicarbonate pathways at 300 and 600 K. Adsorbed species are presented followed by the symbol * and saddle points are represented by capital letters.

Adsorption species	TS_{vib} (eV)	
	300 K	600 K
$2CO_2$* + H_2O*	0.133	0.682
C_2O_4* + H_2O*	0.167	0.759
HC_2O_4* + OH*	0.172	0.770
$H_2C_2O_4$* + O*	0.165	0.747
CO_2H* + CO_2* + OH*	0.120	0.652
$2CO_2H$* + O*	0.125	0.654
CO_3H* + CO_2* + H*	0.131	0.670
CO_3H* + CO_2H*	0.132	0.661
A	0.153	0.695
B	0.170	0.761
C	0.168	0.761
D	0.125	0.679
E	0.123	0.651
F	0.144	0.736
G	0.131	0.672
H	0.131	0.668
I	0.158	0.707

Table SI4. Entropy extracted from the thermodynamic tables for the isolated CO_2, H_2O, $H_2C_2O_4$ and O_2 molecules.

Adsorption species	*TS* (eV)	
	300 K	600 K
CO_2	0.667	1.518
H_2O	0.588	1.326
$H_2C_2O_4$	0.952	2.361
O_2	0.639	1.409

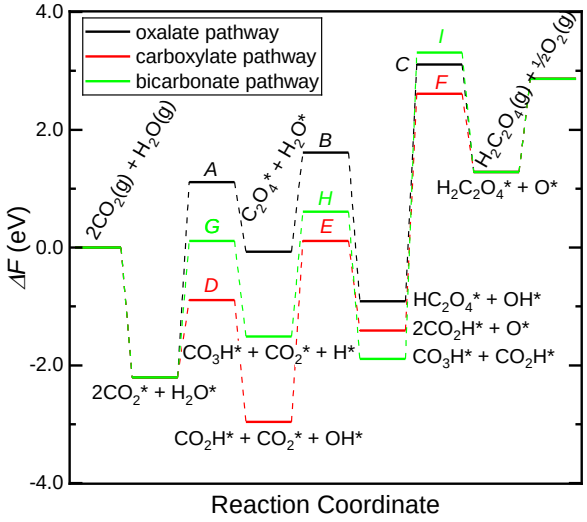

Figure SI3. Minimum energy pathways (MEPs) for the conversion of CO_2 and H_2O into $H_2C_2O_4$ on the partially oxidised 62.5O-Fe_3S_4(001) surface at 0 K. Minimum states are denoted by bold lines and saddle point are represented by narrow lines linked by dashed lines. Energies are referenced to the isolated $2CO_2$(g) + H_2O(g) molecules, including the surface slab. Adsorbed species are presented followed by the symbol *.

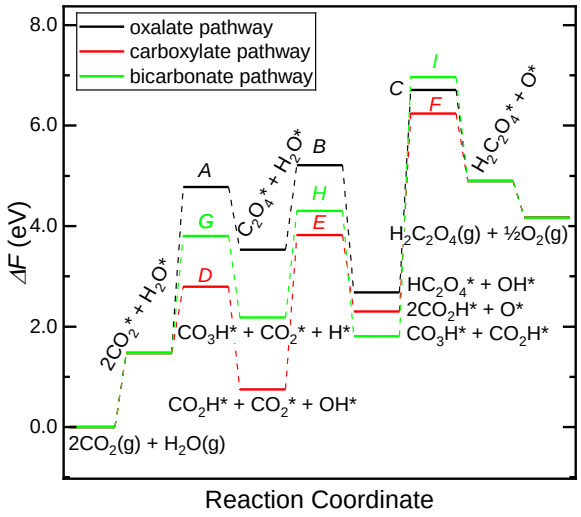

Figure SI4. Minimum energy pathways (MEPs) for the conversion of CO_2 and H_2O into $H_2C_2O_4$ on the partially oxidised 62.5O-Fe_3S_4(001) surface at 600 K. Minimum states are denoted by bold lines and saddle point are represented by narrow lines linked by dashed lines. Energies are referenced to the isolated $2CO_2(g)$ + $H_2O(g)$ molecules, including the surface slab. Adsorbed species are presented followed by the symbol *.