Supporting Information

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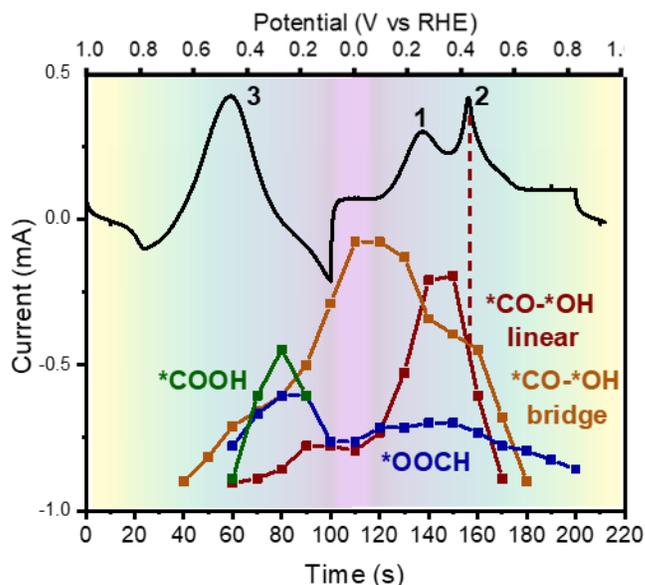
Figure S1: the black line shows the cyclic voltammogram in 1M NaOH and 1M formic acid. The cycle starts at OCP (0.9V vs RHE), then the potential is scanned anodically up to 1V vs RHE and cathodically to 0V vs RHE, at a reduced scan rate of $2mVs^{-1}$. Data were collected in an in-situ cell, described in the experimental section, at 25°C. The working electrode is polycrystalline Pt deposited on a Si optical prism. The coloured lines refer to the magnitude of the peaks associated with different adsorbed species. The peak magnitude was determined from the background-subtracted in-situ surface-enhanced FTIR spectra, collected during the cyclic voltammogram shown in part a
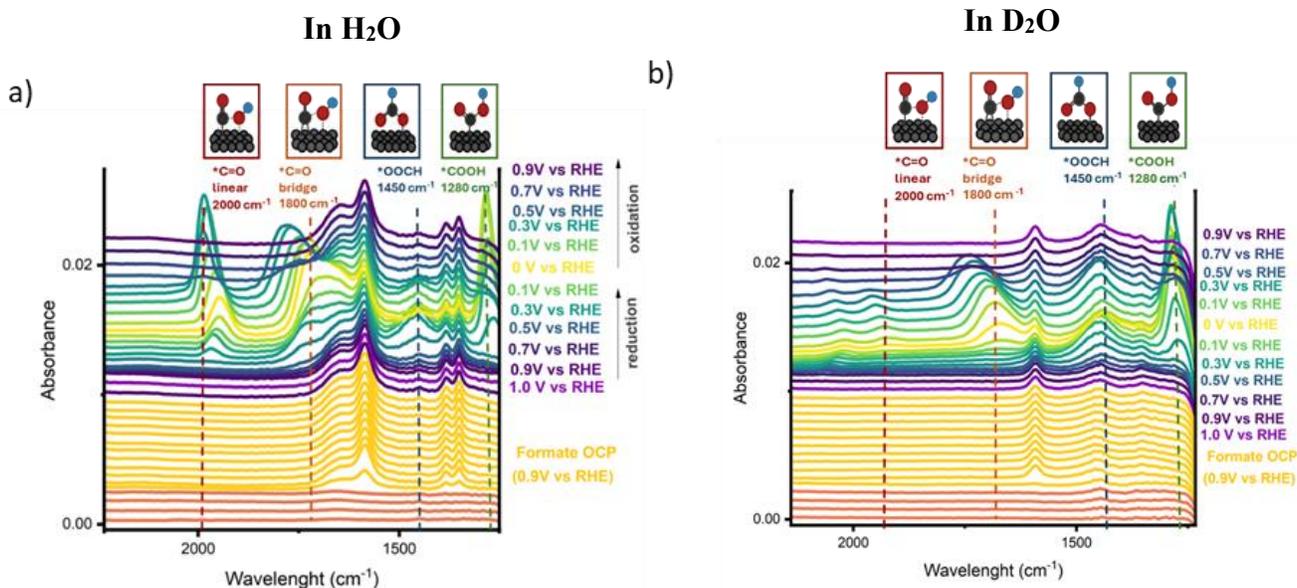
Figure S2: Background-subtracted in-situ surface-enhanced FTIR spectra, collected during a cyclic voltammogram in presence of 1M formic acid, in 1M NaOH in H_2O (a) and 1M NaOD in D_2O (b), strating at OCP (0.9V vs RHE), then scanned anodically up to 1V vs RHE and cathodically to 0V vs RHE, at a scan rate of $10mVs^{-1}$. The time increases from the bottom to the top of the graph. The background was collected at OCP in 1M NaOH (orange curves at the bottom of the graph), then formic acid was added and spectra were collected at OCP (light orange curves). Finally, the potential was cycled and the spectra are color-coded according to the applied potential.
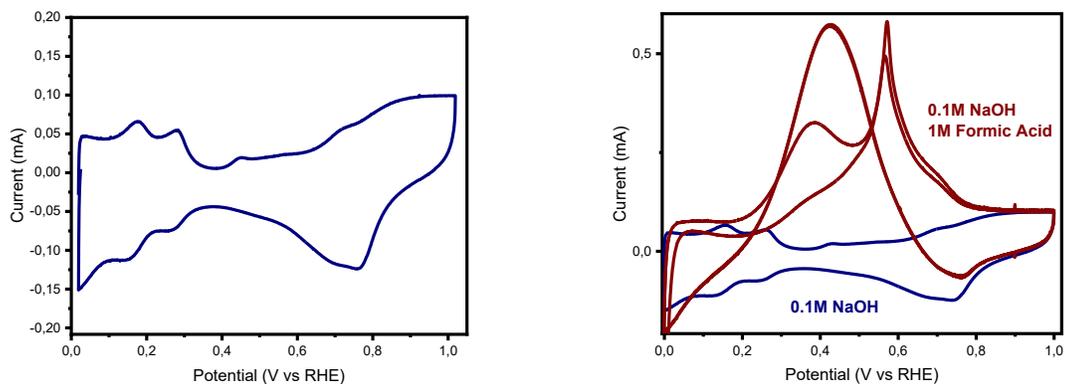
Figure S3: Cyclic voltammogram in 1M NaOH (blue) and 1M NaOH+1M formic acid (red). Data were collected in an in-situ cell, described in the experimental section, at 25˚C. The working electrode is polycrystalline Pt deposited on a Si optical prism.
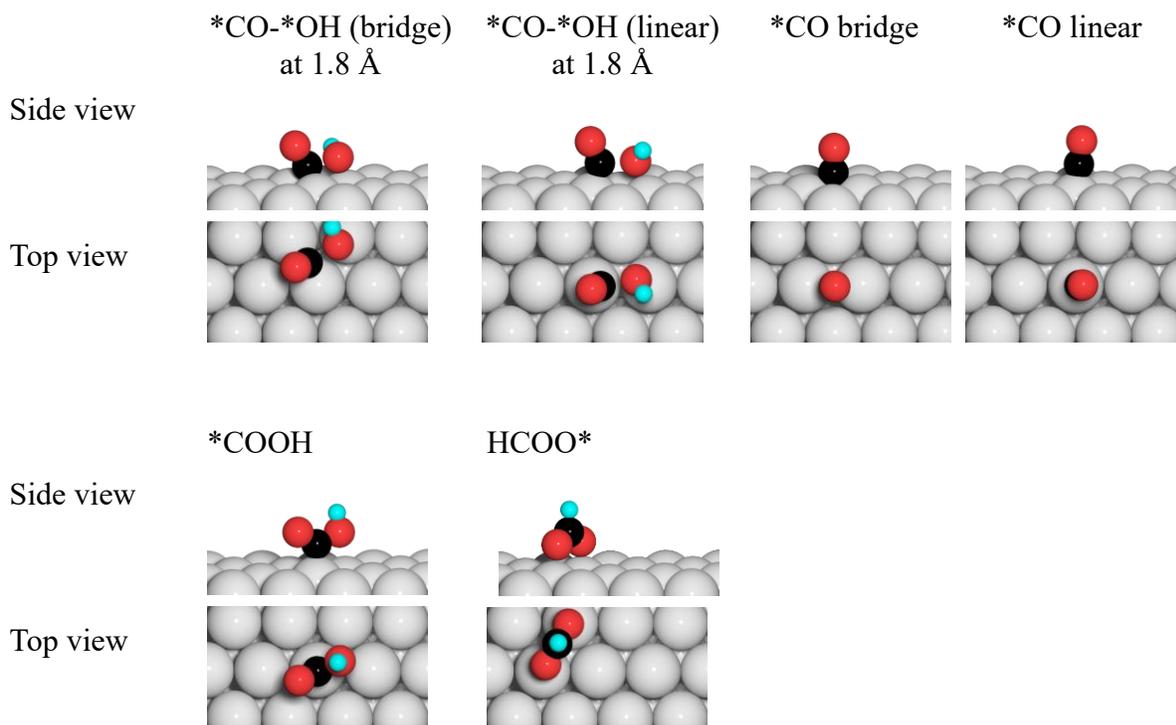
Figure S4: atomic configuration of the proposed intermediates, after DFT optimization

Table S1. The frequency and DFT energy for C-bonded formate (*COOH).

*COOH	cm^{-1}
0	592i
1	154i
2	66
3	272
4	322
5	358
6	538
7	609
8	985
9	**1189**
10	**1686**
11	3397
Energy/eV	0.00

Notes:

1. The DFT energy for C-bonded formate (*COOH) is set to be 0 eV.

2. 9th mode (1189 cm^{-1}): asymmetric stretching in **C-OH**.

   10th mode (1686 cm^{-1}): asymmetric stretching in **O=C**.

Table S2. The frequency and DFT energy for O-bonded formate (*OOCH).

*OOCH	cm^{-1}
0	529i
1	230i
2	83
3	252
4	342
5	410
6	730
7	766
8	1131
9	**1305**
10	**1555**
11	2888
Energy/eV	0.36

Notes:

1. The DFT energy for C-bonded formate (*COOH) is set to be 0 eV.

2. 9th mode (1305 cm^{-1}): symmetric stretching in **O-C-O**.

   10th mode (1555 cm^{-1}): asymmetric stretching in **O-C-O**.

Table S3. The frequency and DFT energy for *CO on linear(top), bridge and fcc sites.

cm^{-1}	Linear *CO	Bridge *CO	Fcc *CO
0	194i	62	21
1	207	173	170
2	371	316	273
3	382	428	343
4	501	454	362
5	**2019**	**1820**	**1717**
Energy/eV	0.42	0.35	0.32

Notes:

1. To compare the DFT energy for *CO on three sites with *COOH, *CO-*OH(linear), *CO-*OH(bridge), same atom type and number should be guaranteed. Therefore, the DFT energy for *CO on three sites use the energy for one *CO and a very far *OH on Pt slab.

2. 5th mode: stretching in **C=O**.

Table S4. The frequency and DFT energy for *CO-*OH (bridge).

*CO-*OH (bridge) /cm^{-1}	Case 1 1.80 Å	Case 2 1.90 Å	Case 3 2.00 Å	Case 4 2.10 Å	Case 5 2.20 Å	Case 6 2.30 Å	Case 7 2.40 Å	Case 8 2.50 Å
0	702i	646i	662i	696i	778i	808i	842i	870i
1	227i	259i	306i	302i	361i	309i	294i	310i
2	94i	152i	144i	119i	207i	222i	245i	267i
3	203	97	176	227	135	223	171	237
4	286	214	229	234	196	231	246	271
5	294	286	264	268	197	251	282	294
6	367	354	341	336	320	315	315	334
7	396	380	385	391	375	358	353	362
8	444	445	419	424	414	410	402	407
9	634	573	525	525	489	496	487	504
10	**1718**	**1720**	**1744**	**1773**	**1777**	**1786**	**1782**	**1803**
11	3432	3427	3445	3441	3448	3446	3448	3450
Energy/eV	0.90	0.89	0.86	0.82	0.77	0.71	0.65	0.59

Notes:

1. Case 1/2…8 here are the different structures for *CO-*OH (C at bridge site, OH at top site), with bond length in C-OH 1.80, 1.90 Å, … 2.50 Å, respectively.

2. The DFT energy for C-bonded formate (*COOH) is set to be 0 eV.

3. 10th mode: asymmetric stretching in **C=O**.

Table S5. The frequency and DFT energy for *CO-*OH (linear).

*CO-*OH (linear) /cm^{-1}	Case 1 1.58 Å	Case 2 1.70 Å	Case 3 1.80 Å	Case 4 1.90 Å	Case 5 2.00 Å	Case 6 2.10 Å	Case 7 2.20 Å	Case 8 2.30 Å	Case 9 2.40 Å	Case 10 2.50 Å
0	867i	845i	1154i	681i	707i	726i	731i	763i	818i	834i
1	216i	386i	288i	333i	368i	329i	310i	327i	295i	346i
2	78i	119i	138i	206i	169i	172i	242i	257i	232i	224i
3	167	136	165	63	52	159	116i	86i	111i	141
4	262	210	241	197	156	190	143	198	277	209
5	317	271	302	254	218	236	246	278	327	286
6	378	365	418	382	375	384	382	361	373	336
7	454	425	511	441	446	433	430	404	400	389
8	580	542	538	500	473	465	475	472	457	487
9	918	759	713	635	599	569	564	548	528	529
10	**1771**	**1800**	**1822**	**1866**	**1895**	**1916**	**1944**	**1961**	**1980**	**1990**
11	3413	3438	3429	3459	3458	3460	3461	3467	3466	3470
Energy/eV	0.55	0.67	0.70	0.70	0.69	0.67	0.63	0.59	0.54	0.50

Notes:

1. Case 1/2…10 here are different structures for *CO-*OH (linear), with bond length between C-OH 1.58, 1.70, …, 2.50 Å, respectively.

2. The DFT energy for C-bonded formate (*COOH) is set to be 0 eV.

3. 10th mode: asymmetric stretching in **C=O**.