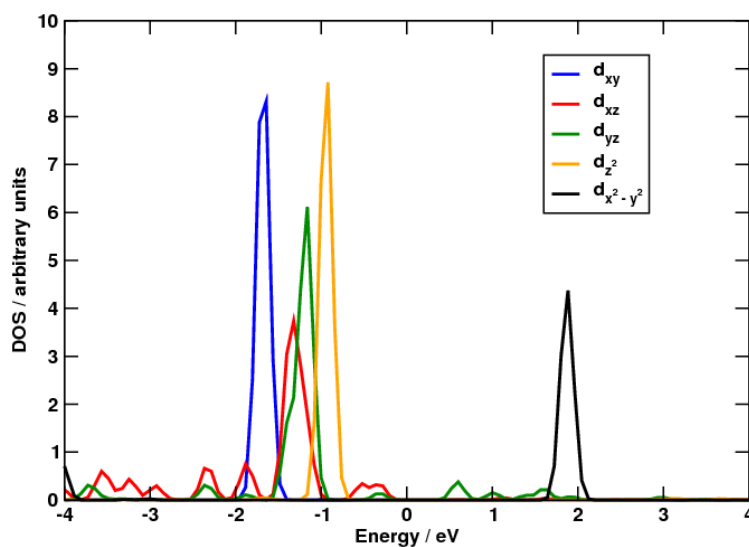


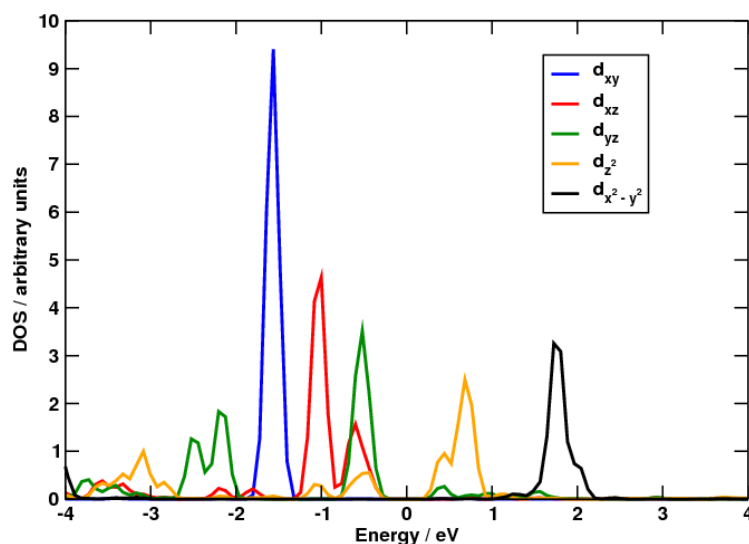
### Supplementary Information

**Spin Analysis:** In the following we will explain in detail the analysis used to determine the oxidation states of the transition metals in the active sites taking Co with and without \*OH as case study. First, we checked the Density of States (DOS) in order to determine the energetic ordering of the d states. Figure s.1 shows the DOS projected onto the d-states of the Co atom for the spin-up channel, in cell B with and without \*OH.

a)



b)

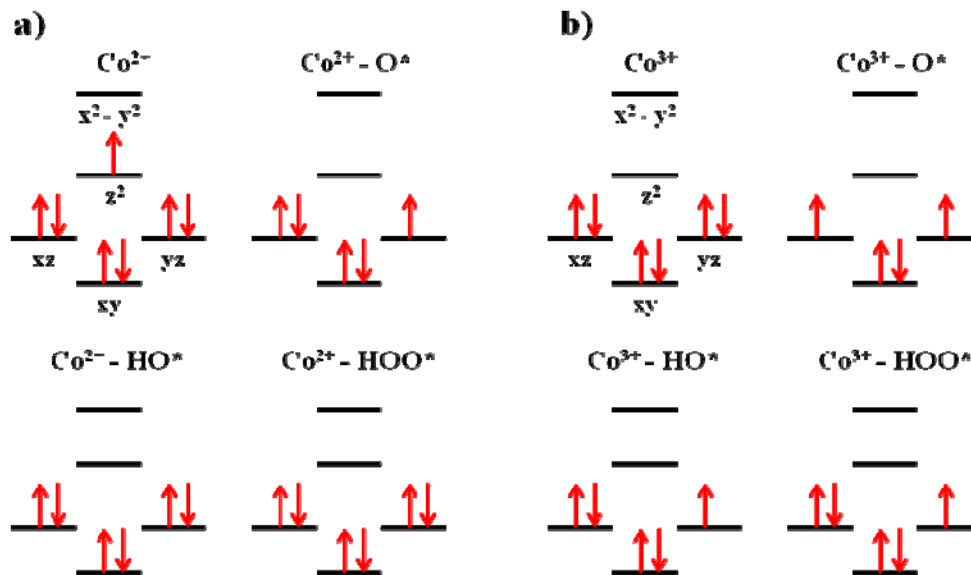


**Figure s.1.** DOS projected onto the d-states of the Co atom for the spin-up channel, in cell B. a) without adsorbates, b) with \*OH adsorbed on atop position on Co.

From Figure s.1 is possible to determine that the increasing energetic ordering of the d-states is the following:  $d_{xy} < d_{xz} \approx d_{yz} < d_z^2 < d_{x^2-y^2}$ . This ordering is typical of square planar complexes where  $d_{xy}$  may also be located over  $d_z^2$ . Furthermore, the ordering remains untouched as expected upon adsorption on atop position, when the complex is now square pyramidal. Interestingly, the  $d_{x^2-y^2}$  is in all cases unoccupied and above the Fermi level, whereas the  $d_z^2$  is occupied when the active site is clean, but unoccupied when \*OH is adsorbed.

The question to solve now is whether Co will have an oxidation state of +2 or +3. The electronic distribution of a neutral Co atom is as follows:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ . Therefore, the distribution ends in  $s^2d^7$ . If we had  $Co^{2+}$ , the orbital splitting would be that of a  $d^7$  atom. On the other hand, if we had  $Co^{3+}$ , the orbital splitting would be that of a  $d^6$  atom. Our spin polarized calculations show that the resulting magnetic moment on Co is  $S = 1$ . Moreover, in the presence of \*O,  $S = 1$ ; whereas in the presence of \*OH and \*OOH,  $S = 0$ .

Figure 2.s shows the low-spin state electronic distribution in the d-bands of  $Co^{2+}$  and  $Co^{3+}$ , taking into account the orbital ordering inferred from Fig1.s.



**Figure 2.s.** Low-spin state Distribution of electrons in the d-band of Co ions a)  $Co^{2+}$ , and b)  $Co^{3+}$ , in a square planar complex with 4 nitrogen ligands. The distribution resulting upon adsorption of the ORR intermediates is also shown.

According to Figure 2.s, the expected magnetic moments of a  $\text{Co}^{2+}$  would be:  $S = 1$  or  $S = 3$  with no adsorbates;  $S = 1, 3,$  or  $5$  with  $\ast\text{O}$ ; and  $S = 0, 2,$  or  $4$  with  $\ast\text{OH}$  and  $\ast\text{OOH}$ . Besides, the expected magnetic moments of a  $\text{Co}^{3+}$  ion would be:  $S = 0, 2,$  or  $4$  with no adsorbates;  $S = 2$  or  $4$  with  $\ast\text{O}$ ; and  $S = 1, 3,$  or  $5$  with  $\ast\text{OH}$  and  $\ast\text{OOH}$ . The different possibilities in each case correspond to low-spin, intermediate-spin, and high-spin states. The ground-state spin will correspond to the arrangement with the least energy. Based on this, we find that the ion present in the complex is  $\text{Co}^{2+}$  and has a low-spin ordering of its d-states.

**Adsorption Energies:** in Table 1.s we present the calculated DFT and Gibbs energies of adsorption.

**Table 1.s.** Energies of Adsorption of the ORR/OER intermediates.

Metal atom / Cell	$\Delta E_{\text{O}}$	$\Delta E_{\text{OH}}$	$\Delta E_{\text{OOH}}$	$\Delta G_{\text{O}}$	$\Delta G_{\text{OH}}$	$\Delta G_{\text{OOH}}$
Cr / A	0.86	0.26	3.52	0.91	0.66	3.92
Mn / A	1.86	0.79	3.99	1.91	1.19	4.39
Fe / A	2.09	0.95	4.02	2.14	1.35	4.42
Co / A	2.91	1.13	4.02	2.96	1.53	4.42
Ni / A	4.13	2.06	4.83	4.18	2.46	5.23
Cu / A	4.49	2.23	5.02	4.54	2.63	5.42
Ru / A	1.69	0.49	3.54	1.74	0.89	3.94
Rh / A	2.81	1.15	4.10	2.86	1.55	4.50
Pd / A	4.62	2.42	4.99	4.67	2.82	5.39
Ag / A	4.74	2.44	5.04	4.79	2.84	5.44
Ir / A	2.39	1.16	4.17	2.44	1.56	4.57
Pt / A	4.58	2.33	5.02	4.63	2.73	5.42
Au / A	4.81	2.53	5.02	4.86	2.93	5.42
Cr / B	0.10	-0.19	3.16	0.15	0.21	3.56
Mn / B	1.03	0.33	3.27	1.08	0.73	3.67
Fe / B	1.41	0.41	3.42	1.46	0.81	3.82
Co / B	2.64	0.75	3.72	2.69	1.15	4.12
Ni / B	4.06	1.83	4.74	4.11	2.23	5.14
Cu / B	3.87	1.72	4.79	3.92	2.12	5.19
Ru / B	1.28	0.15	3.14	1.33	0.55	3.54
Rh / B	2.51	0.90	4.10	2.56	1.30	4.50
Pd / B	4.43	2.21	4.88	4.48	2.61	5.28
Ag / B	4.30	2.01	4.74	4.35	2.41	5.14
Ir / B	2.14	0.97	4.18	2.19	1.37	4.58
Pt / B	4.44	2.19	4.97	4.49	2.59	5.37
Au / B	4.34	1.98	4.69	4.39	2.38	5.09

Moreover, the entropy and Zero-Point Energy corrections used to convert DFT energies of adsorption into Gibbs energies of adsorption, through the formula  $\Delta G = \Delta E^{DFT} + \Delta ZPE - T\Delta S$ , are the following:

**Table 2.s.** Entropy and ZPE corrections to gas and liquid phase molecules and adsorbed species. Taken from Refs [36, 40] in the main text and references therein.

species	TS	ZPE
*O	0.00	0.07
*OH	0.00	0.30
*OOH	0.00	0.39
H <sub>2</sub> O	0.67	0.56
H <sub>2</sub>	0.41	0.27
O <sub>2</sub>	0.64	0.10

**Formation Energies:** the formation of the active sites consists basically of two steps: 1) addition of N atoms into the C substrate, and 2) anchoring of the transition metal (M) into the 4-fold site created by 4 nitrogen atoms (see Ref. 10 in the manuscript). Therefore, we will consider the following two separate reactions:



Where  $aC$  is a pristine graphite sheet with  $a$  atoms (20 and 26 for cells A and B, respectively), and  $aC - 4N$  is the active site created in the graphite sheet with 4 pyridinic N atoms. We remark that Cell A has 25 atoms (20C + 4N + 1M, with M = Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, Au) and Cell B has 31 (26C + 4N + 1M, with M as defined before). The DFT formation energies of the two cells from their elements in their respective reference states at 0K are 0.28 eV / atom and 0.13 eV / atom, respectively. In both cases the reaction is endothermic, which agrees well with experiments (see Ref. 10 in the manuscript) in which the addition of N atoms takes place via pyrolysis at  $T \geq 800K$ .

The anchoring energy of the transition metals into the 4-fold sites made of nitrogen atoms can be represented in the following way:



The anchoring energy depends on the transition metal used and the various energies for the systems considered are shown in the second column in Table 1.

**Table 1.** Anchoring and formation energies in eV atom<sup>-1</sup> for the considered systems.

Metal atom / cell	$\Delta E_{ANC} / \text{eV atom}^{-1}$	$\Delta E_F / \text{eV atom}^{-1}$
Cr / A	-0.24	0.05
Mn / A	-0.22	0.06
Fe / A	-0.18	0.10
Co / A	-0.19	0.10
Ni / A	-0.18	0.11
Cu / A	-0.13	0.15
Ru / A	-0.12	0.16
Rh / A	-0.18	0.10
Pd / A	-0.16	0.12
Ag / A	-0.10	0.18
Ir / A	-0.17	0.11
Pt / A	-0.18	0.10
Au / A	-0.12	0.16
Cr / B	-0.09	0.04
Mn / B	-0.09	0.05
Fe / B	-0.06	0.07
Co / B	-0.08	0.05
Ni / B	-0.08	0.05
Cu / B	-0.04	0.09
Ru / B	0.02	0.15
Rh / B	-0.05	0.09
Pd / B	-0.03	0.10
Ag / B	0.03	0.16
Ir / B	-0.03	0.10
Pt / B	-0.04	0.09
Au / B	0.03	0.16

Furthermore, the heat of formation of a system is defined as the reaction energy of a process in which only the system is the product of the combination of all composing elements in their standard states. In this particular case, the reaction is the following:



Therefore, the formation energies of these systems are equivalent to the addition of Reactions (1) and (2). These energies are shown in the third column in Table 1. In all cases, the formation energies are positive, indicating that the addition of nitrogen in the graphite sheets is the most energy-demanding part in the formation on the active sites.