Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental material

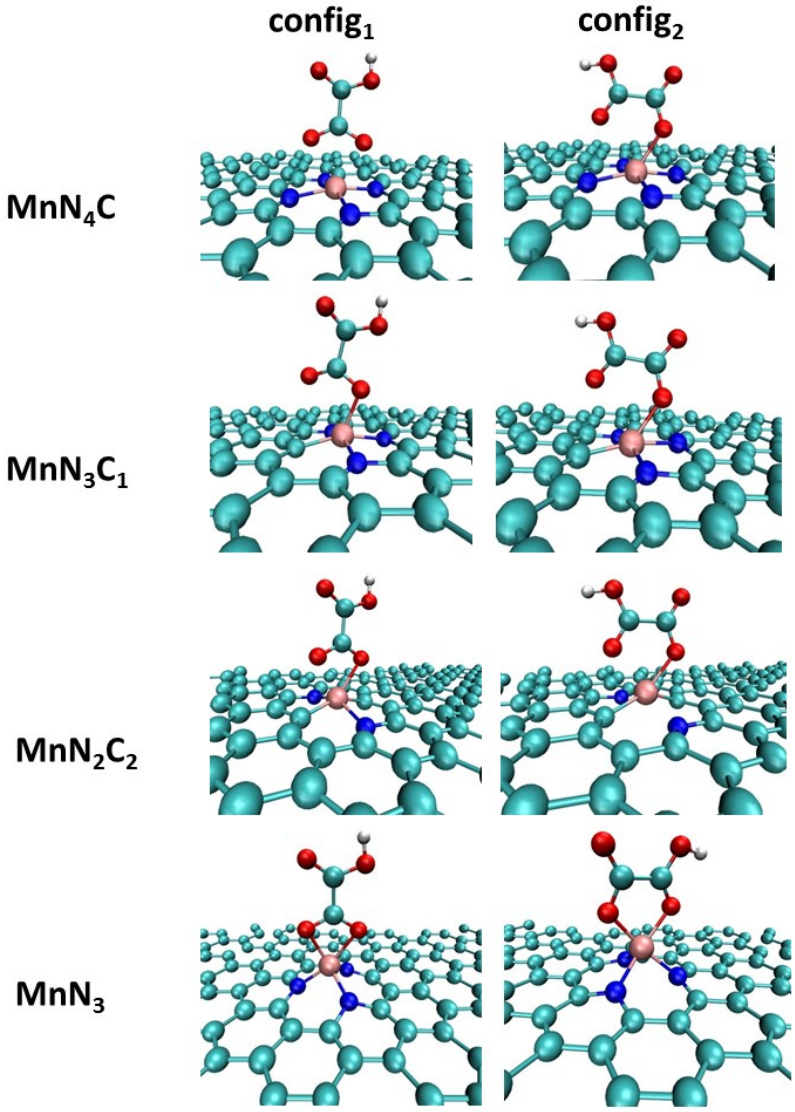

Figure S1. Most stable adsorption sites of $C_2O_4H^-$ anion on proposed active sites of Mn-AAPyr. Two possible adsorption configurations are shown.

Table S1. Change in the electronic energy, zero-point energy, and $T\Delta S$ term used to obtain the free energy diagram for oxalate oxidation mechanism on MnN_4 active sites of Mn-AAPyr at pH=0 .

Reaction:	ΔE/eV	ΔZPE/eV	$T\Delta S$/eV	$\Delta_r G$/eV
$* C_2O_4H + \mathrm{H}^+ + e^- \rightarrow * C_2O_4H + \mathrm{H}^+ + e^-$	+0.49	+0.09	-0.80	+1.38
$* C_2O_4H + \mathrm{H}^+ + e^- \rightarrow CO_2H * + CO_2 + \mathrm{H}^+$	-0.31	-0.305	+0.66	-1.28
$CO_2H * + CO_2 + \mathrm{H}^+ + e^- \rightarrow 2CO_2 + 2\mathrm{H}^+ +$	-0.03	-0.18	+0.86	-1.06

Table S2. Change in the electronic energy used to obtain the free energy diagram for oxalate oxidation mechanism on MnN_3C, MnN_2C_2, $MnN_2C_2(2)$ and MnN_3 active sites of Mn-AAPyr at pH=0. Change in zero-point energy and $T\Delta S$ term are assumed to be the same for all active sites and are given in Table 1 .

	ΔE/eV			
Reaction:	MnN_3C	MnN_2C_2	$MnN_2C_2(2)$	MnN_3
$* C_2O_4H + \mathrm{H}^+ + e^- \rightarrow * C_2O_4H + \mathrm{H}^+ + e$	0.03	-0.25	0.06	-1.79
$* C_2O_4H + \mathrm{H}^+ + e^- \rightarrow CO_2H * + CO_2 + \mathrm{H}^+$	0.18	0.39	0.13	1.13
$CO_2H * + CO_2 + \mathrm{H}^+ + e^- \rightarrow 2CO_2 + 2\mathrm{H}^+ +$	-0.04	+0.02	-0.03	+0.82