Role of Oxometallic Complex in OH Dissociation during Water Oxidation: A Microscopic Insight from DFT Study

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Initial and final geometries for the NEB calculations:

The Activation barrier for the OH → O + H reaction in the presence of different oxometallic unit is calculated using the climbing-image nudged elastic band (NEB) method. In NEB calculations we considered a set of 13 intermediate states (images), which are distributed along the reaction path connecting optimized initial and final states. For example, the initial and final configurations for the M_4O_4 complex is shown in Figure S1.

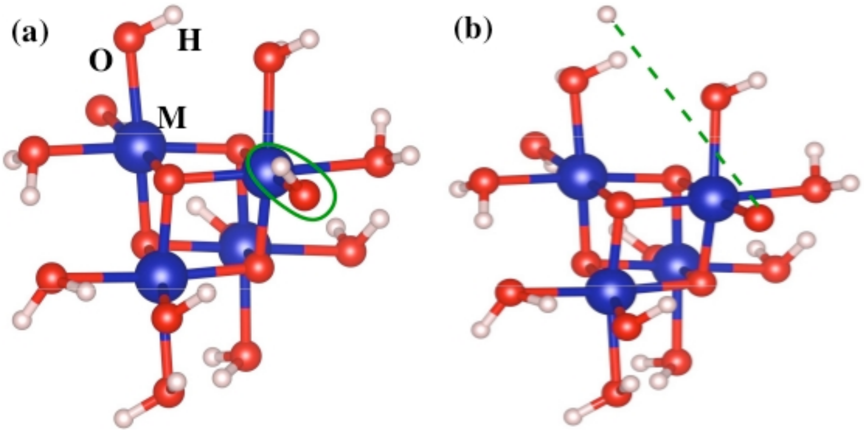

Figure S1: Initial [left panel (a)] and final [right panel (b)] configuration of M_4O_4 unit adopted in NEB calculation. The marked circle in green in left panel indicates OH bond of typical bond length ~ 0.9 Å. In the right panel that particular H ion gets detached from O ion and remains at a distance about 7-8 Å (indicated by dotted line).

The Electron Localization Function

The Electron localization function (ELF)[1] at OH bond has been computed in order to study the metal-oxygen hybridization. ELF has been found to be extremely useful for elucidating the bonding characteristics of a variety of systems.[2] For a single determinantal wave function ψ_i, the ELF is defined as,

$$\chi_{ELF} = \left[1 + (D/D_h)^2\right]^{-1}$$

where

$$D_h = (3/10)(3\pi^2)^{5/3}\rho^{5/3}$$

$$D = (1/2)\sum_i |\nabla\psi_i|^2 - (1/8)|\nabla\rho|^2/\rho$$

$\rho \equiv \rho(\vec{r})$ is the valence-electron density. D is the excess local kinetic energy due to the Pauli repulsion obtained from the difference between the definite positive kinetic energy density of actual fermionic system and that of the von Weiszacker kinetic energy functional and D_h is the Fermi constant. By construction, ELF can adopt values in the interval [0,1], with 1 representing perfect localization of valence electron, the value for uniform electron gas being 1/2. The large values (typically 0.7 or more) of isosurface of ELF in the bonding region between two bonds represent a localized bond in that region, while low values of ELF reflect a delocalized region as in metallic systems. The present ELF calculations are based on the valence electrons, while the core electrons are replaced by the pseudopotential.

Magnetic moments of individual ions

Single oxometallic unit

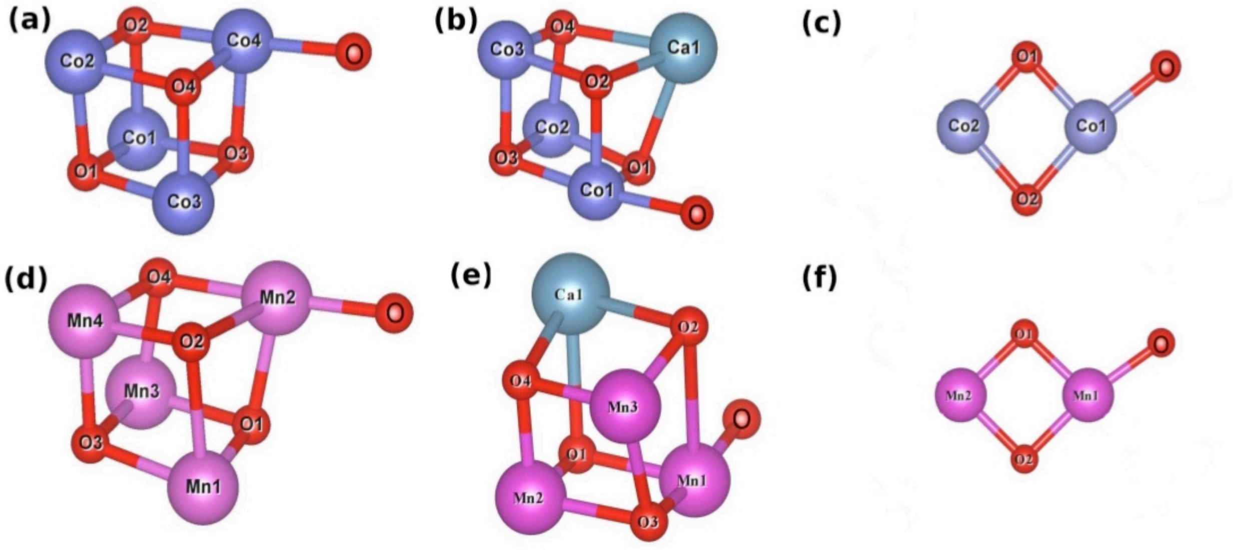

Figure S2: Schematic diagram of different oxo-metallic units, (a) Co_4O_4, (b) $CaCo_3O_4$, (c) Co_2O_2, (d) Mn_4O_4, (e) $CaMn_3O_4$, (f) Mn_2O_2. The site marked as "O", is the particular O from which H gets detached. For clarity, other OH and H_2O molecules, which are attached to the metal ion center, are not shown.

Table S1: Calculated magnetic moments on individual ions of Co1-Co4 and O1-O4 forming the core unit Co_4O_4, and on O, the oxygen ion from which H gets detached. For numbering of ions refer to panel (a) of Figure S2. The major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f - m_i
	Before reaction (m_i)	After reaction (m_f)	
Co1	0.0	0.03	0.03
Co2	0.0	-0.05	-0.05
Co3	0.0	-0.03	-0.03
Co4	0.0	0.43	**0.43**
O1	0.0	0.01	0.01
O2	0.0	0.04	0.04
O3	0.0	0.04	0.04
O4	0.0	0.02	0.02
O	0.0	0.27	**0.27**

Table S2: Calculated magnetic moments for $CaCo_3O_4$ unit, before and after the removal of H from the hydroxyl. Ca, Co1-Co3 and O1-O4 form the core unit $CaCo_3O_4$, and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (b) of Figure S2. The major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f - m_i
	Before reaction (m_i)	After reaction (m_f)	
Ca	0.0	0.0	0.0
Co1	0.0	0.38	**0.38**
Co2	0.03	0.05	0.02
Co3	0.0	0.03	0.03
O1	0.0	0.01	0.01
O2	0.0	0.02	0.02
O3	0.02	0.04	0.02
O4	0.0	0.02	0.02
O	0.0	0.45	**0.45**

Table S3: Calculated magnetic moments for Co_2O_2 unit, before and after the removal of H from the hydroxyl. Co1, Co2, O1, O2 form the core unit Co_2O_2 and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (c) of Figure S2. The major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f - m_i
	Before reaction (m_i)	After reaction (m_f)	
Co1	1.55	1.68	**0.13**
Co2	1.55	1.60	0.05
O1	0.22	0.26	0.04
O2	0.22	0.30	0.08
O	0.0	0.66	**0.66**

Table S4: Calculated magnetic moments for Mn_4O_4 unit, before and after the removal of H from the hydroxyl. Mn1-Mn4 and O1-O4 form the core unit Mn_4O_4, and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (d) of Figure S2. The major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f - m_i
	Before reaction (m_i)	After reaction (m_f)	
Mn1	3.64	3.62	-0.02
Mn2	3.61	3.30	**-0.31**
Mn3	3.60	3.55	-0.05
Mn4	3.61	3.50	-0.09
O1	0.01	0.02	0.01
O2	0.01	0.1	0.09
O3	0.04	0.1	0.06
O4	0.01	0.01	0.0
O	0.0	0.25	**0.25**

Table S5: Calculated magnetic moments for $CaMn_3O_4$ unit, before and after the removal of H from the hydroxyl. Ca, Mn1-Mn3 and O1-O4 form the core unit $CaMn_3O_4$, and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (e) of Figure S2. The major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f -m_i
	Before reaction (m_i)	After reaction (m_f)	
Ca	0.0	0.0	0.0
Mn1	3.58	3.32	**-0.26**
Mn2	3.60	3.52	-0.08
Mn3	3.61	3.54	-0.06
O1	0.01	0.05	0.04
O2	0.01	0.04	0.03
O3	0.04	0.09	0.05
O4	0.01	0.01	0.0
O	0.0	0.25	**0.25**

Table S6: Calculated magnetic moments for Mn_2O_2 unit, before and after the removal of H from the hydroxyl. Mn1, Mn2, O1 and O2 form the core unit Mn_2O_2, and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (f) of Figure S2. The major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f -m_i
	Before reaction (m_i)	After reaction (m_f)	
Mn1	3.53	3.28	**-0.34**
Mn2	3.53	3.45	-0.08
O1	0.09	0.06	-0.03
O2	0.01	0.02	0.01
O	0.0	0.54	**0.54**

Multiple oxo-metallic unit

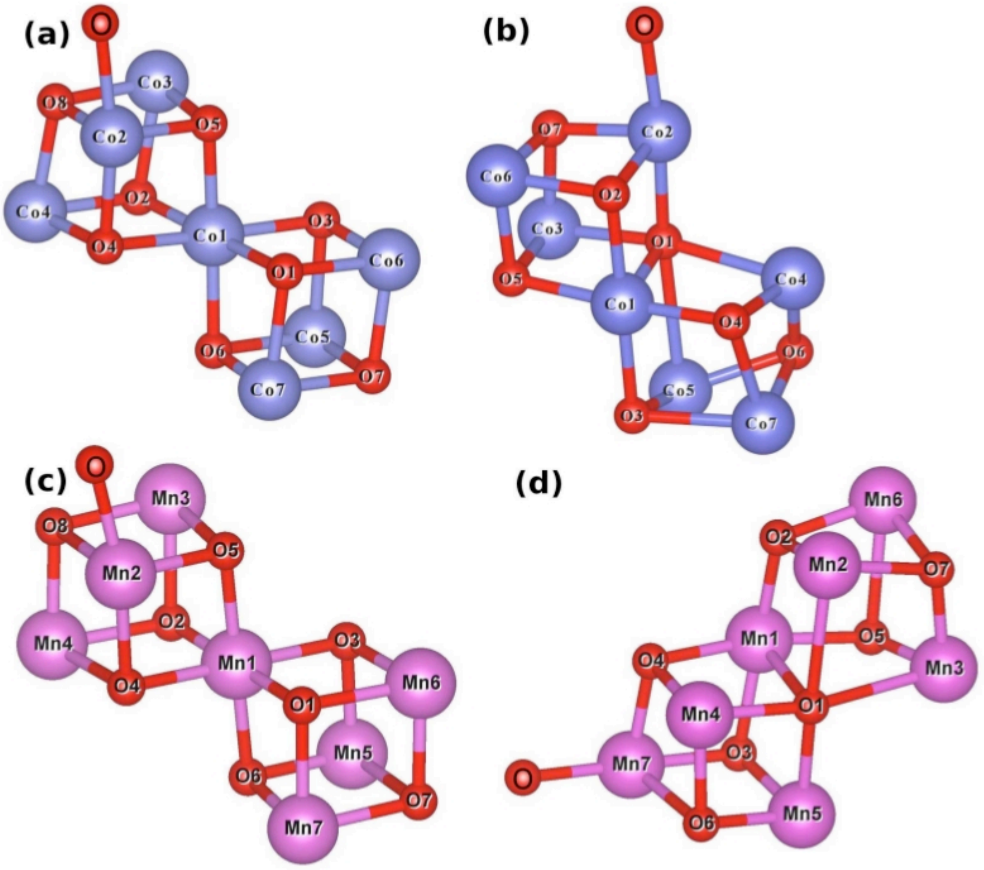

Figure S3: Schematic diagram of different multiple oxo-metallic units, (a) corner shared Co_7O_8, (b) edge shared Co_7O_7, (c) corner shared Mn_7O_8,(d) edge shared Mn_7O_7. The site marked as "O", is the particular O from which H gets detached. For better clarity of the figures, other OH and H_2O molecules, which are attached to the metal ion center, are not shown.

Table S7: Calculated magnetic moments, before and after the OH → O + H reaction, for the corner shared Co_7O_8, where the active metal site is in LS state. Co1-Co7 and O1-O8 form the core unit of corner shared Co_7O_8, and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (a) of Figure S3. The major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f -m_i
	Before reaction (m_i)	After reaction (m_f)	
Co1	0.01	0.1	0.09
Co2	0.02	0.48	**0.46**
Co3	0.04	0.22	0.18
Co4	0.01	0.02	0.01
Co5	2.60	2.57	-0.03
Co6	0.05	0.1	0.05
Co7	0.06	0.1	0.04
O1	0.0	0.0	0.0
O2	0.03	0.01	-0.02
O3	0.14	0.13	-0.01
O4	0.0	0.0	0.0
O5	0.02	0.0	-0.02
O6	0.07	0.01	-0.06
O7	0.13	0.15	0.02
O8	0.01	0.02	0.01
O	0.0	0.62	**0.62**

Table S8: Calculated magnetic moments, before and after the OH → O + H reaction, for the corner shared Co_7O_8, where the active metal site is in IS state. Co1-Co7 and O1-O8 form the core unit of corner shared Co_7O_8, and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (a) of Figure S3. Note that the O from which H gets detached oxygen, in this case is attached to Co5, instead of Co2 as shown in the figure for the LS case.

Ion	Magnetic moments in μ_B		m_f -m_i
	Before reaction (m_i)	After reaction (m_f)	
Co1	0.01	0.24	0.23
Co2	0.02	0.1	0.08
Co3	0.04	0.29	0.25
Co4	0.01	0.05	0.04
Co5	2.60	2.06	-0.54
Co6	0.05	0.1	0.05
Co7	0.06	-0.2	-0.26
O1	0.0	0.0	0.0

O2	0.03	0.03	0.0
O3	0.14	0.04	-0.1
O4	0.0	0.0	0.0
O5	0.02	0.02	0.0
O6	0.07	0.07	0.0
O7	0.13	0.07	-0.06
O8	0.01	-0.01	-0.02
O	0.0	0.66	**0.66**

Table S9: Calculated magnetic moments, before and after OH → O + H reaction, for edge shared Co_7O_7 unit. Co1-Co7 and O1-O7 form the core unit of edge shared Co_7O_7, and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (b) of Figure S3. Major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f -m_i
	Before reaction (m_i)	After reaction (m_f)	
Co1	0.24	0.24	0.0
Co2	0.04	0.52	**0.48**
Co3	0.07	0.05	0.02
Co4	0.01	0.05	0.04
Co5	0.02	0.07	0.05
Co6	0.05	0.1	0.05
Co7	0.06	0.12	0.06
O1	0.0	0.0	0.0
O2	0.03	0.03	0.0
O3	0.01	0.04	0.03
O4	0.0	0.0	0.0
O5	0.01	0.2	0.01
O6	0.07	0.05	-0.02
O7	0.03	0.05	0.02
O	0.0	0.61	**0.61**

Table S10: Calculated magnetic moment, before and after OH → O + H reaction, for corner shared Mn_7O_8 unit. Mn1-Mn7 and O1-O8 form the core unit of corner shared Mn_7O_8 and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (c) of Figure S3. Major changes have been marked in bold.

Ion	Magnetic moments in μ_B		m_f -m_i
	Before reaction (m_i)	After reaction (m_f)	
Mn1	2.68	2.77	0.09
Mn2	3.62	3.35	**-0.27**
Mn3	3.56	3.51	-0.04
Mn4	3.63	3.55	-0.08
Mn5	3.62	3.62	0.0
Mn6	3.56	3.62	0.08
Mn7	3.62	3.54	-0.08
O1	0.02	0.02	0.0
O2	0.02	0.01	-0.01
O3	0.07	0.07	0.0
O4	0.07	0.05	-0.02
O5	0.12	0.08	-0.04
O6	0.12	0.10	-0.02
O7	0.07	0.08	0.01
O8	0.07	0.07	0.0
O	0.0	0.32	**0.32**

Table S11: Calculated magnetic moments, before and after OH → O + H reaction, for the edge shared Mn_7O_7 unit. Mn1-Mn7 and O1-O7 form the core unit of edge shared Mn_7O_7 and O, is the oxygen ion from which H gets detached. For numbering of ions refer to panel (d) of Figure S3. Major changes are marked in bold.

Ion	Magnetic moments in μ_B		m_f -m_i
	Before reaction (m_i)	After reaction (m_f)	
Mn1	3.45	3.50	0.05
Mn2	3.62	3.60	-0.02
Mn3	3.68	3.60	-0.08
Mn4	3.63	3.59	-0.04
Mn5	3.65	3.60	-0.05
Mn6	3.68	3.64	-0.04
Mn7	3.58	3.35	**-0.23**
O1	0.07	0.14	0.07

O2	0.12	0.07	-0.05
O3	0.13	0.08	-0.05
O4	0.05	0.13	0.08
O5	0.09	0.09	0.0
O6	0.11	0.08	-0.03
O7	0.05	0.03	-0.02
O	0.0	0.25	**0.25**

Density of states (DOS)

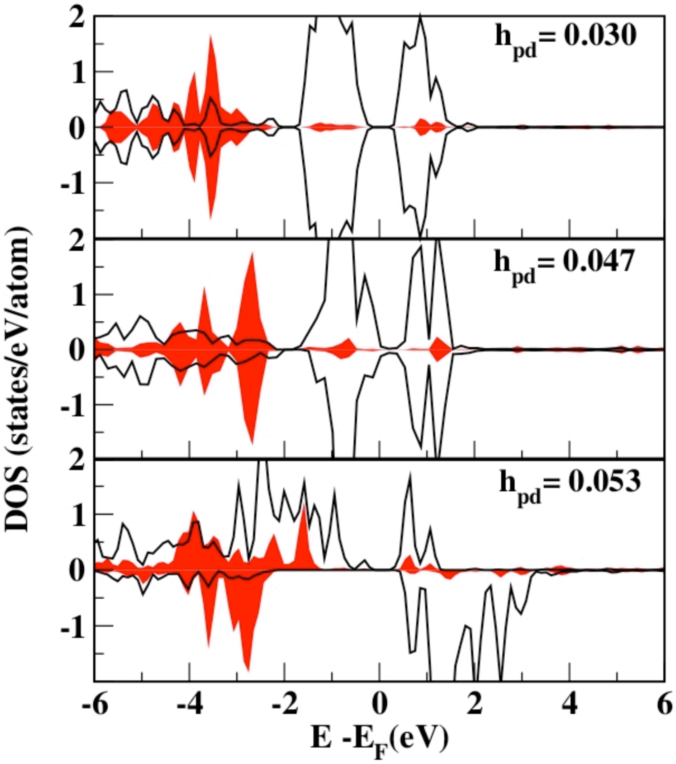

Figure S4: DOS projected to M-*d* (solid black line) and O-*p* (shaded red area) states of Co_4O_4, $CaCo_3O_4$ and Mn_4O_4, shown from top to bottom panel respectively. Fermi energy (E_F) is set at zero. Hybridization index (h_{pd}) decreases as one moves from top to bottom panel, supported by the increase in the mixing between M-*d* and O-*p* states.

Energy barrier of O-O bond formation

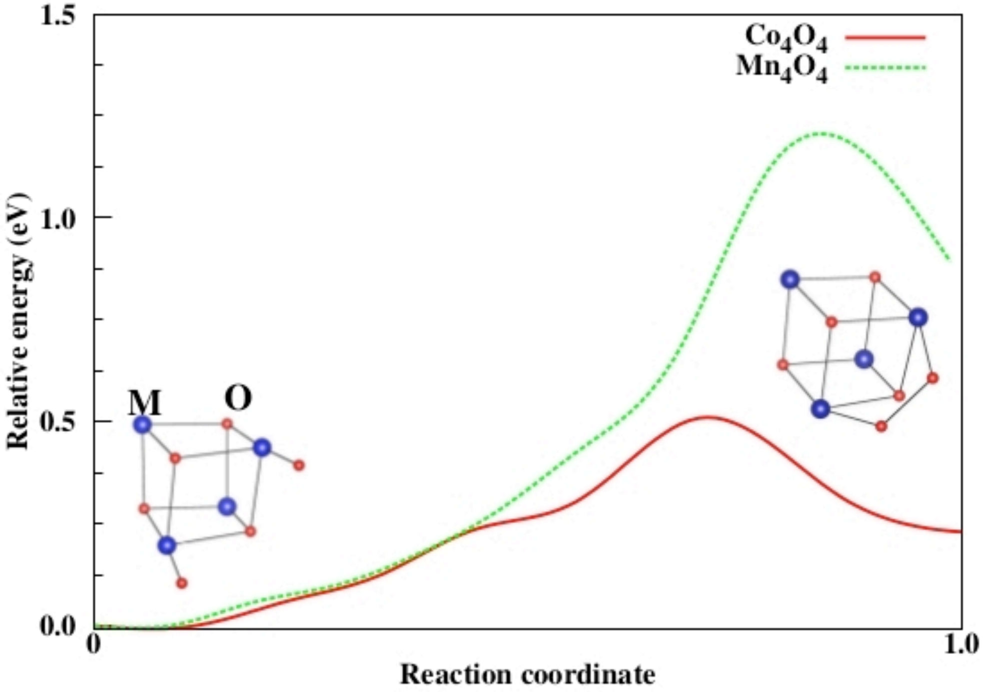

Figure S4: Energy barrier for O-O bond formation in presence of M_4O_4 oxo-metallic unit. Two inset figures show the schematic structure of initial (x=0 of x-axis) and final (x=1.0 of x-axis) configuration. The barrier heights are estimated to be 0.5 eV for Co_4O_4 and 1.18 eV for Mn_4O_4. The corresponding energy barrier calculated for the OH → O + H reaction for Co_4O_4 and Mn_4O_4 units are 3.67 eV and 3.13 eV respectively, and therefore dominate the water oxidation process.

References:

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