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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Mechanism of water oxidation by nanolayered manganese oxide: A step forward†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We, for the first time, estimate the rate of H₂¹⁸O exchange for μ-O groups on the surface of nanolayered Mn-K oxide by diffuse reflectance infrared Fourier transform spectroscopy. These results, in addition to results from previously reported membrane-inlet mass spectrometry, provide new insights into mechanism of water oxidation by nanolayered Mn oxide.

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The renewable energies, such as wind and solar, are typically very fluctuating and thus storing of these energies is necessary to use these renewable energies. In this context, water splitting is a promising route for the conversion of solar, wind, ocean currents, tides or waves energy, into hydrogen as a “fuel”.¹⁻³ However, water oxidation reaction is the bottleneck for water splitting and the development of energy-conversion schemes based on renewable energies.¹⁻³ Plants, algae and cyanobacteria efficiently use a Mn₄CaO₅ cluster (known as water oxidizing complex (WOC) or oxygen-evolving complex (OEC)) to oxidize water.^{4,5} Since the WOC consists of four Mn ions, particular attention has been given to the Mn compounds aimed at simulating the WOC⁶⁻⁹ but a few artificial Mn complexes have been discovered so far that are able to act as a homogeneous catalyst for the oxidation of water.⁶⁻⁹ However, Mn oxides were reported as heterogeneous catalysts toward water oxidation by some groups.¹⁰⁻¹⁴ Among Mn oxides, layered Mn oxides are reported as efficient water-oxidizing catalysts¹⁰ but the mechanism of water oxidation by these, and other, catalysts is not known.¹⁵ In 2011, membrane-inlet mass spectrometry (MIMS) was used to detect the oxygen produced in the reactions of Mn oxides in the presence of cerium(IV) ammonium nitrate (Ce(IV)) or Ru^{III}(bpy)₃³⁺ in H₂¹⁸O and the signals for the O₂ isotopologues ¹⁶O₂ (m/z = 32), ¹⁶O¹⁸O (m/z = 34) and ¹⁸O₂ (m/z = 36) were determined.¹⁶ The total fraction of ¹⁸O atoms in the product O₂ according $^{18}\alpha = ([^{18}\text{O}_2] + 0.5 [^{16}\text{O}^{18}\text{O}])/[\text{O}_2]_{\text{total}}$ was reported that provides [O₂] measurements, and traces of the development of ¹⁸α over time could then be plotted for the course of the catalytic O₂-formation.¹⁶ The incorporation of oxygen atoms from μ-O of the Mn oxide into the released O₂ during the early stages of the reaction was also determined.¹⁶ Experiments showed that the reaction of Mn oxides in the presence of Ce(IV) or Ru^{III}(bpy)₃³⁺ is a real water oxidation.¹⁶

¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂ in the reaction of a layered Mn oxide and Ce(IV) in water (5% H₂¹⁸O) is shown in Fig. S5 (ESI†).¹⁶ The ¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂ species rise fast after the addition of Ce(IV)

and the formation of ¹⁸O₂ is detected.¹⁶ ¹⁸α shows that the theoretically expected ¹⁸O fraction of 5% is reached within only 30 s after the addition of Ce(IV) to the oxide suspension. These results show that the oxygen formed in reactions with Ce(IV) indeed originates from the oxidation of bulk water. From these experiments, it was concluded that:¹⁶

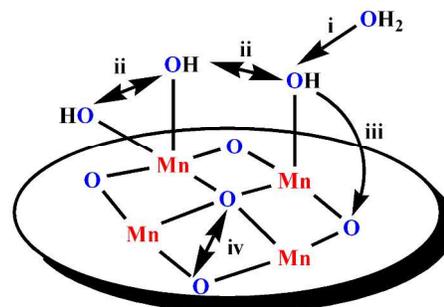
a) μ-O groups, bridging oxido ligands, on the surface are themselves not involved in the O-O bond formation (**i** and **ii** in Scheme 1).

b) μ-O groups on the surface are oxidised to form O₂ (**iii** and **iv** in Scheme 1). However, in this condition μ-O groups on the surface should exchange with the bulk solution very rapidly. If the exchange is slow, more ¹⁶O₂ and ¹⁶O¹⁸O will be formed because μ-O groups are not isotopic when O₂ is evolved.

Thus, without data for the rate of exchange of μ-O groups on the surface of Mn oxide, discrimination between routes **a** or **b** is not possible. If very fast exchange occurs between bulk water and μ-O on the surface of these oxides then μ-O may participate in water oxidation and all four mechanisms are possible (**i-iv** in Scheme 1).¹⁶

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Scheme 1 Proposed mechanisms for water oxidation by the layered Mn oxide:¹⁶ Nucleophilic attack of hydroxide on a terminal oxido (**i**); coupling of terminal oxido ligands (**ii**), attack of hydroxide on a bridging oxido ligand (**iii**), coupling of bridging oxido ligands (**iv**).

In those oxygen evolution experiments by H_2^{18}O ,¹⁶ $^{18}\alpha$ shows that bulk water molecules are oxidized to oxygen. Thus, if the exchange of $\mu\text{-O}$ on the surface of oxide is slow, it is concluded that $\mu\text{-O}$ are not involved in the water oxidation. Slow rate in this condition means the rates that all $\mu\text{-O}$ groups exchange in more than 30 seconds because only 30 seconds after reaction $^{18}\alpha$ shows bulk water oxidation.¹⁶ If we assume that the water exchange for $\mu\text{-O}$ on the surface of oxide in 30 seconds takes to be 95% complete then for a first order reaction we need $k_{\text{exchange}} \sim 0.1 \text{ s}^{-1}$ that is most probably very fast for a $\mu\text{-O}$ in a Mn(III,IV) compound.¹⁷ In other words, regarding data from many groups, it is clearly observed that time for completed water exchange of $\mu\text{-O}$ groups in Mn(III)($\mu\text{-O}$)Mn(IV) or Mn(IV)($\mu\text{-O}$)Mn(IV) are longer than 30 seconds;¹⁷ A view of surface of layered Mn oxide (such as layered K-Mn oxide) shows that each $\mu\text{-O}$ on the surface of these oxides is coordinated, at least, to two Mn ions (Fig. 1). However, many of $\mu\text{-O}$ groups on the surface of Mn oxides are coordinated to three Mn ions and thus the water exchange is, most probably, slow for these $\mu\text{-O}$ groups but the rate of such water exchange on the surface of Mn oxides is not measured.

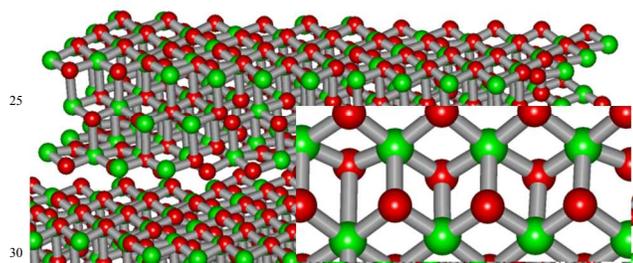
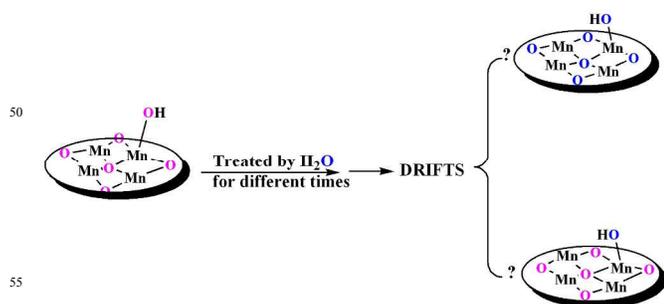


Fig. 1 Structure of layered Mn oxide (such as layered K-Mn oxide) shows that each $\mu\text{-O}$ on the surface of these oxides is coordinated, at least, to two Mn ions (O: red and Mn: green). Although, many $\mu\text{-O}$ groups on the surface of these oxides are usually coordinated to three Mn ions (inserted image).

With low exchange of $\mu\text{-O}$ groups on the surface of Mn catalyst, lower values are expected from $^{18}\alpha$ if $\mu\text{-O}$ groups are involved in water oxidation (Fig. S5 (ESI[†])). To find more about the rate of exchange between bulk water and $\mu\text{-O}$ on the surface of nano-sized Mn oxide, we used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).¹⁸ Our procedure is shown in Scheme 2. In this procedure, we treated layered Mn oxides by H_2^{18}O for different times (For details see ESI[†]). Then we used DRIFTS to find if in this special time $\mu\text{-}^{18}\text{O}$ is observed in the vibrational area of Mn-O-Mn or not.



Scheme 2 The procedure for finding the rate of exchange for $\mu\text{-O}$ on the surface of layered Mn oxides by DRIFTS.

This procedure can be used to indicate an estimated rate of exchange for $\mu\text{-O}$ groups on the surface of Mn catalyst with bulk water, and thus it is a new step toward understanding mechanism of water oxidation by the Mn oxide. Our results show that the peaks in the area of $\mu\text{-O}$ show no changes even after a few hours treatment by H_2^{18}O . Only after 48 hours, a few peaks related to partial $\mu\text{-}^{18}\text{O}$ formation were observed. Slow water exchange was also reported for a few metal-oxide structure.¹⁹ In water exchange issue, the $\mu\text{-O}$ bridged among three Mn ions ($\mu_3\text{-O}$) in the nanolayered Mn-K oxide is very similar to $\mu_3\text{-O}$ in a cubane oxo, $[\text{Mn}_4\text{O}_4\text{L}_6]^+$ (L: $[\text{O}_2\text{P}(\text{C}_6\text{H}_4\text{OCH}_3)_2]^+$), complex.^{17b} It is interesting because the structure of motif in nanolayered Mn-K oxide is also cubic.^{11b} Thus, the rate of exchange for $\mu\text{-O}$ groups on the surface of the Mn catalyst is too slow and hardly can be very fast in the presence of $\text{Ru}(\text{bpy})_3^{2+}$ or $\text{Ce}(\text{IV})$.¹⁶

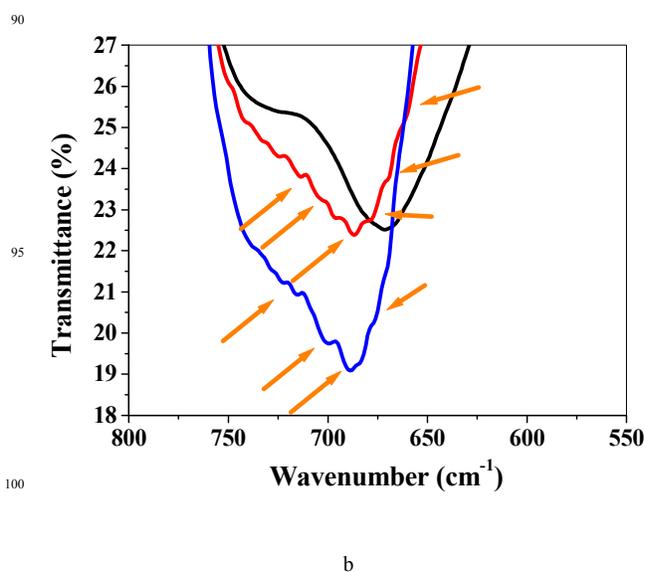
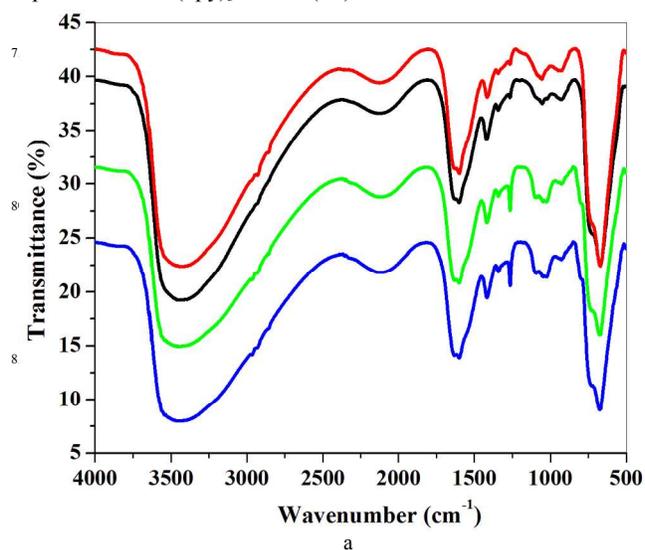
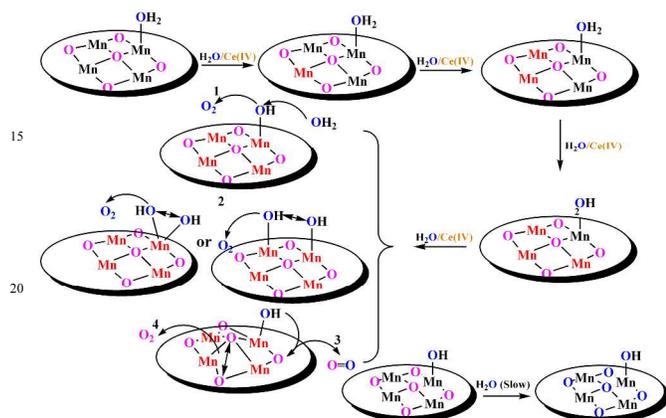


Fig. 2 DRIFT spectra of reference compound (black), reference compound after 30 s (red), 120 s (green) and 600 s (blue) treated by H_2^{18}O (a). DRIFT spectra of reference compound (black), reference compound after 48 hours (red) or one week (blue) treated by H_2^{18}O .

Orange arrows show the peaks related to $\mu\text{-}^{18}\text{O}$ groups (for details see Fig. S6 (ESI†)).

In other words, the results show that water exchange for $\mu\text{-O}$ is slower than water oxidation. Thus, we conclude that $\mu\text{-O}$ groups are not involved in water oxidation, and **1** or **2** in Scheme 3 is, most probably, real mechanism for water oxidation. It is important to note that if water exchange for $\mu\text{-O}$ was very fast, distinguish among different mechanisms (**1-4** in Scheme 3) would not be possible.



Scheme 3 Proposed mechanisms of oxygen evolution by Mn oxide.¹⁶ Red Mn ions show oxidized Mn ions.

The water oxidation can occur as a four-electron reaction, or in multiple steps with intermediates such as $\cdot\text{OH}$, H_2O_2 or $\text{O}_2^{\cdot-}$ (Table S1).⁸ As shown in Table S1 (ESI†), comparing the standard reduction potentials shows that the potential of Ce(IV)/Ce(III) under experimental conditions¹⁶ was smaller than the redox potential of $\text{H}_2\text{O}/\cdot\text{OH}$, $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ or $\text{H}_2\text{O}/\text{O}_2^{\cdot-}$, and thus the potential of Ce(IV)/Ce(III) would not be enough to oxidize water to $\cdot\text{OH}$, H_2O_2 or $\text{O}_2^{\cdot-}$.²⁰ Most probably, in Mn oxides, multiple Mn sites are involved in charge delocalization and accumulation to a four-electron water oxidation step.²¹

As shown in Scheme 3, pathway **1** or **2**, four Ce(IV) ions oxidize four Mn ions step-by-step such that, after four charge-accumulation steps, a multi-electron oxidation proceeds yielding O_2 from water in one step regarding two proposed mechanisms.

We proposed that the O-O bond may be formed by attack of an outer-sphere water to OH that is attached to high-valent Mn ion in oxide structure or by the reaction between two OH that are coordinated to high-valent Mn ions. As layered Mn oxides are real catalysts for water oxidation by many Mn based compounds,^{12,22} this step is very important to understand of water oxidation. Interestingly, recent calculations on the mechanism of water oxidation by Mn oxide or other transition metal oxides proposed similar water-oxidation mechanisms reported here.²³

Regarding these proposed mechanisms,²³ we suggested two pathways for water oxidation by these oxides: the first a mechanism with very low overpotential related to the reaction between two OH groups that are coordinated to high-valent Mn ion(s) (pathway **2** in Scheme 3), and the second a mechanism with high overpotential related to attack of an outer-sphere water to an OH that is attached to high-valent Mn ion in oxide (pathway **1** in Scheme 3). We have observed these two areas for water oxidation for Mn oxides: the first area for water oxidation that is

near to the peak related to Mn(III)/Mn(IV) ^{14a} and another is 0.5 V higher than the first area.²⁴ We relate these points to pathways **2** and **1** in Scheme 3, respectively.

In conclusion, we used diffuse reflectance infrared Fourier transform spectroscopy to estimate the rate of water exchange for $\mu\text{-O}$ groups on the surface of nanolayered Mn-K oxide. We found that water exchange for $\mu\text{-O}$ groups on the surface of nanolayered Mn oxides is very slow. Regarding these results and those results from previously reported membrane-inlet mass spectrometry we proposed the O-O bond may be formed by attack of an outer-sphere water to an OH attached to high-valent Mn ion in oxide structure or by reaction between two OH that are coordinated to high-valent Mn ions depends on the potential used in water oxidation.

The authors are grateful to the Institute for Advanced Studies in Basic Sciences and the National Elite Foundation for financial support.

Notes and references

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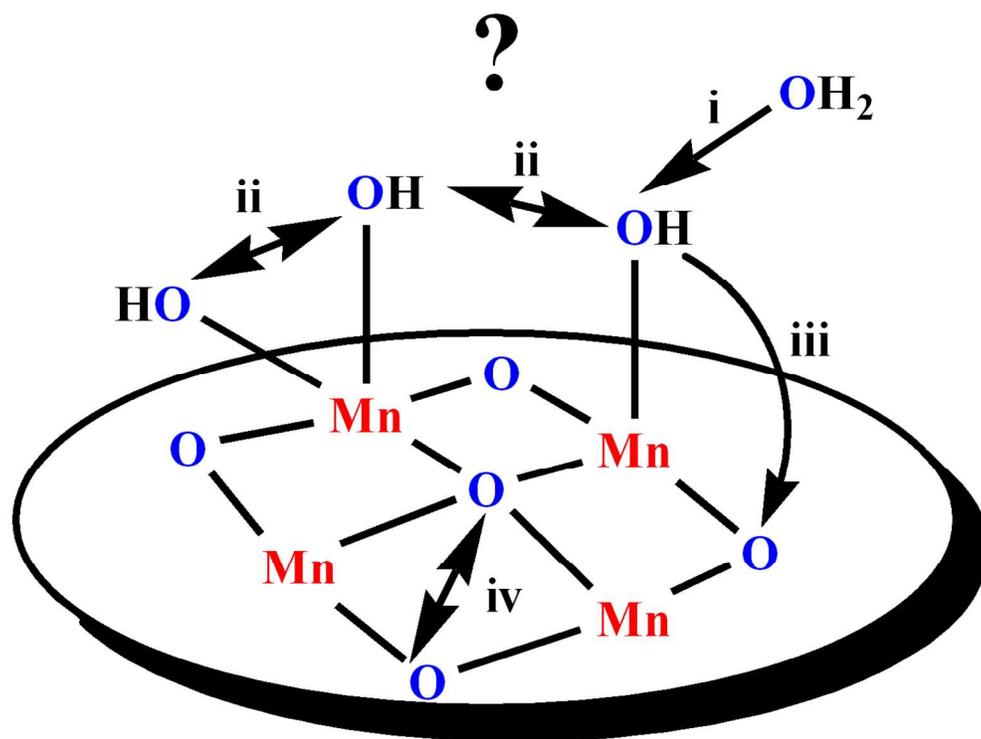
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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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New insights into mechanism of water oxidation by layered Mn oxide are reported.



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