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

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We, for the first time, estimate the rate of H$_2^{18}$O 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.

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 Mn$_6$CaO$_2$ 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.10,12 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$_{10}^{16}$ (bpy)$_3^{3+}$ in H$_2^{18}$O and the signals for the O$_2$ isotopologues $^{16}$O$_2$ (m/z = 32), $^{18}$O$^{16}$O (m/z = 34) and $^{18}$O$_2$ (m/z = 36) were determined.16 The total fraction of $^{18}$O atoms in the product O$_2$ according to $^{18}$O = $^{[18}$O$_2$ + 0.5 $^{[16}$O$^{18}$O] [O$_2$]$_{total}$ was reported that provides O$_2$ measurements, and traces of the development of $^{18}$O over time could then be plotted for the course of the catalytic O$_2$-formation.16 The incorporation of oxygen atoms from µ-O of the Mn oxide into the released O$_2$ 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$_{10}^{16}$ (bpy)$_3^{3+}$ is a real water oxidation.16 $^{16}$O$_2$, $^{18}$O$^{16}$O and $^{18}$O$_2$ in the reaction of a layered Mn oxide and Ce(IV) in water (5% H$_2^{18}$O) is shown in Fig. S5 (ESI†).16 The $^{16}$O$_2$, $^{18}$O$^{16}$O and $^{18}$O$_2$ species rise fast after the addition of Ce(IV) and the formation of $^{18}$O$_2$ is detected.16 $^{18}$O shows that the theoretically expected $^{18}$O 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 O$_2$ (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 $^{16}$O$_2$ and $^{18}$O$^{16}$O will be formed because µ-O groups are not isotopic when O$_2$ 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

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

This procedure can be used to indicate an estimated rate of exchange for \( \mu\)-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 \( \mu\)-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 \( \mu\)-O formation were observed. Slow water exchange was also reported for a few metal-oxide structure. In water exchange issue, the \( \mu\)-O bridged among three Mn ions (\( \mu_3\)-O) in the nanolayered Mn-K oxide is very similar to \( \mu_3\)-O in a cubane oxo, \([\text{Mn}_3\text{O}_2\text{L}_6]^+ \) (L: \([\text{O}_2\text{P(C}_6\text{H}_4\text{OCH}_3)_2]\)), complex. It is interesting because the structure of motif in nanolayered Mn-K oxide is also cubic. Thus, the rate of exchange for \( \mu\)-O groups on the surface of the Mn catalyst is too slow and hardly can be very fast in the presence of Ru(bpy)_3^{2+} or Ce(IV).

With low exchange of \( \mu\)-O groups on the surface of Mn catalyst, lower values are expected from \( \alpha \) if \( \mu\)-O groups are involved in water oxidation (Fig. S5 (ESI†)). To find more about the rate of exchange between bulk water and \( \mu\)-O on the surface of nanosized Mn oxide, we used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). 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 \( \mu\)-O is observed in the vibrational area of Mn-O-Mn or not.

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

In other words, the results show that water exchange for $\mu$-O is slower than water oxidation. Thus, we conclude that $\mu$-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 $\mu$-O was very fast, distinguish among different mechanisms (1-4 in Scheme 3) would not be possible.

The water oxidation can occur as a four-electron reaction, or in multiple steps with intermediates such as $\text{OH}, \text{H}_2\text{O}_2,$ or $\text{O}_2^+$ (Table S1). As shown in Table S1 (ESI†), comparing the standard reduction potentials shows that the potential of Ce(IV)/Ce(III) would not be enough to oxidize 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 $\text{O}_2$ 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 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 depending on the potential used in water oxidation.

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Notes and references

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