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'Old' Clusters with New Function: Oxidation Catalysis by High Oxidation State Manganese and Cerium/Manganese Clusters Using O_2 Gas

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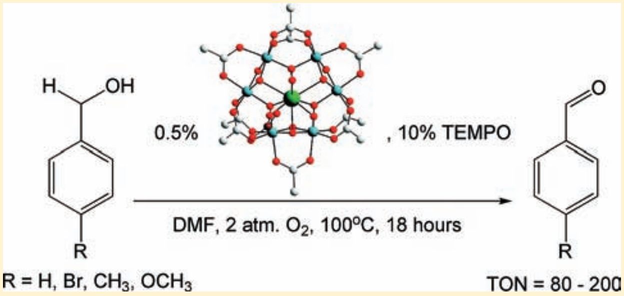
S *Supporting Information*

ABSTRACT: The family of polynuclear manganese clusters of formula $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = Et, Ph, etc.) has been investigated in great detail over the years for their ability to function as single-molecule magnets (SMMs), but they have not been employed as oxidation catalysts. In the present report, the ability is described of these clusters to act as catalysts in the selective oxidation of benzyl alcohol to benzaldehyde using molecular O_2 as the primary oxidant and the nitroxyl radical TEMPO as a cocatalyst. A systematic investigation of Mn clusters varied in their R group, oxidation state, and size was conducted in order to realize the electronic requirements that will lead to the best catalytic activity. The best reactivity (>99%) was obtained when the catalyst was the mixed-metal cluster $[CeMn_6O_9(O_2CMe)_9(NO_3)(H_2O)_2]$, which contains $Ce^{4+}Mn^{4+}{}_6$ ions; in this case, lower loadings of catalysts (cluster and TEMPO) are required and the reaction can proceed even without a solvent. In addition, it has been demonstrated that the high efficiency can be only achieved when both high oxidation Ce^{4+} and Mn^{4+} ions are present within the same cluster.



■ INTRODUCTION

Polynuclear oxide-bridged clusters such as the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (Mn_{12}; R = Me, Et, Ph, etc.) family have been well investigated by our group and others,[1] as have many other polynuclear high oxidation state Mn and mixed-metal Mn complexes. The main interest to date in these clusters has been their often unusual magnetic properties, such as their ability to behave as single-molecule magnets.[1,2] What has not been investigated to date is whether they might exhibit useful function as oxidation catalysts in homogeneous solution. In contrast, some smaller nuclearity Mn_x clusters ($x \leq 4$) containing Mn^{3+} and/or Mn^{4+} have been shown to function as homogeneous oxidation catalysts for reactions such as organic oxidations and water oxidation, using H_2O_2, organic peroxides, or other activated O-atom sources as oxidants;[3] there are also reports of electrocatalysis using a variety of such small clusters.[4] As the Mn nuclearity increases and the number of oxide bridges between the metal ions correspondingly increases, the clusters can acceptably be described as small pieces of a Mn oxide stabilized and solubilized by the organic ligands. In this regard, they could be considered as smaller, molecular ('bottom-up') versions of the 'top-down' Mn oxide nanoparticles, such as those that have recently been employed as supported heterogeneous oxidation catalysts.[5] As such, the question that then arises is whether these clusters can behave as "molecular Mn oxide nanocatalysts" for homogeneous oxidation transformations. If so, one advantage of molecular species is that their exact size and structure are well defined and the sample is truly a single-size (monodisperse) collection of identical molecules, allowing catalytic activity vs molecular nuclearity to be assessed. Further, there are also available well-characterized heteronuclear analogues, particularly Mn_yLn_z (Ln = lanthanide) clusters of a known and variable y:z ratio, that could be explored.[6] For such reasons, we have begun an investigation of the ability of high-nuclearity Mn_x and heteronuclear Mn_yLn_z clusters to act as homogeneous nanocatalysts. Since we accumulated a wealth of experience in the synthesis and modification of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (henceforth Mn_{12}) clusters, we chose these for our initial studies.

In fact, the Mn_{12} clusters (Figure 1) have several properties that make them particularly attractive as potential oxidation catalysts: (i) they contain high oxidation state metal ions ($8Mn^{3+}$, $4Mn^{4+}$); (ii) they are prepared by convenient, high-yield procedures from readily available, environmentally benign and inexpensive metal salts and solvents, e.g., $Mn(O_2CMe)_2$ and aqueous acetic acid;[7,8] (iii) they are well-defined crystalline compounds, stable over time under aerobic conditions; (iv) they are soluble in a variety of solvents; (v) they have a high O^{2-}:Mn ratio of 1:1, and the $[Mn_{12}O_{12}]$ central core is akin to a small, soluble piece of Mn oxide, as mentioned above; and (vi) they display multiple one-electron reversible reductions at high potentials, and the latter can be varied by almost 1 V depending

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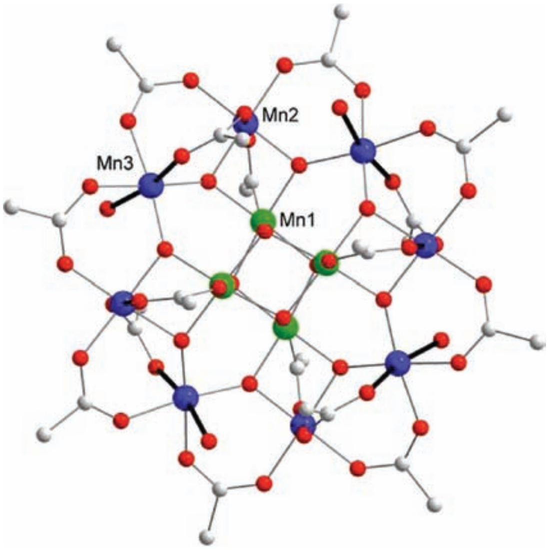


Figure 1. Structure of $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$: green, Mn^{4+}; blue, Mn^{3+}; red, O; gray, C. Numbering identifies the three groups of symmetry-inequivalent Mn atoms; the point group is S_4.

on the R groups.[9,10] In spite of this, they have never been explored as catalysts. However, they contain only carboxylate and water as peripheral ligands, and they are consequently not stable in aqueous conditions and decompose in the presence of H_2O_2 or other highly reactive oxidants. Thus, we targeted the use of O_2 gas as oxidant, which is environmentally friendly, readily available, and cheap but more difficult to activate. Activation of O_2 by Mn species has been previously demonstrated only in a few systems, including (i) heterogeneous oxidation of alcohols by high oxidation state heterogeneous Mn oxides[11] and (ii) homogeneous oxidation of catechols to quinines[12] and of amines to aldehydes[13] by mononuclear and dinuclear Mn complexes, respectively.

The main objective of our initial work was not to achieve the oxidative transformation of a particular substrate but to assess in general whether such molecular clusters do indeed have the capability to function as oxidation catalysts with O_2. Thus, we chose an organic transformation as our test system that has already been well explored[14] and is indeed often employed as a benchmark for development of new oxidation catalysts, oxidation of benzyl alcohol in the presence of 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) as cocatalyst.[15] We herein report the use of Mn_{12} clusters as homogeneous catalysts for activation of molecular O_2 and its oxidation of benzyl alcohol selectively to benzaldehyde. In addition, we will show that we also extended the studies to heteronuclear, high oxidation state $CeMn_6$ clusters and will also describe the results of that study.

■ EXPERIMENTAL SECTION

Materials and Methods. The Mn_{12}, Mn_3, Mn_4, and $CeMn_6$ clusters were prepared using published procedures referenced in the text. All reagents and solvents were purchased form commercial sources and used without further purification. The samples were analyzed with a Shimadzu GC-17A chromatograph using either an Alltech EC-WAX (15 m × 0.45 mm with a 1.0 μm film) column or a J&W Scientific DB-5 (15 m × 0.53 mm with a 1.5 μm film) column. Both columns were attached to the injection port with a neutral 5 m × 0.32 mm deactivated guard column. GC-MS analysis was conducted on a TraceGC Ultra DSQ mass spectrometer (Thermo Scientific) that was equipped with a Stabilwax-DA column (Restek; 30 m × 0.25 μm i.d. × 0.25 μm d_f).

Table 1. TEMPO-Assisted Aerobic Oxidation of $PhCH_2OH$ Catalyzed by Different Mn Clusters

entry	catalyst[a]	PhCHO (%)[b,c]
1	$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$[d]	10
2	$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$	62
3	$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$[e]	8
4	none (only TEMPO)	6
5	$[Mn_{12}O_{12}(O_2CC_6H_4OMe)_{16}(H_2O)_4]$	73
6	$[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$	57
7	$[Mn_{12}O_{12}(O_2CC_6H_4C_6H_5)_{16}(H_2O)_4]$	75
8	$[Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4]$	64
9	$[Mn_{12}O_{12}(O_2CC_6H_4F)_{16}(H_2O)_4]$	80
10	$[Mn_3O(O_2CMe)_6(py)_3]^{+}$[f]	72
11	$[Mn_4O_2(O_2CMe)_7(bpy)_2]^{+}$[f]	76
12	$Mn(O_2CMe)_2{\bullet}4H_2O$	16

[a] Reaction conditions: $PhCH_2OH$ (6×10^{-4} mol), catalyst (6×10^{-6} mol, 1 mol %), TEMPO (18 mg, 22 mol %), 0.3 mL of DMF (0.02 M catalyst), 2 atm O_2, 100 °C, 18 h. [b] Benzylaldehyde was the only product, and no benzoic acid was detected by either GC or GC-MS. [c] The TON is the same as the conversion for this catalyst:substrate ratio (1:100). [d] No TEMPO. [e] No O_2. [f] py = pyridine, bpy = 2,2′-bipyridine, ClO_4^- anions.

General Procedure for Catalytic Oxidation. All oxidation reactions were conducted in 15 mL pressure tubes. The tubes were charged with cluster catalyst (typically 1 mol %, 6×10^{-6} mol), TEMPO (10−22 mol %, 8−18 mg, 1.32×10^{-4} mol) and 300 μL of DMF and $PhCH_2OH$ (typically 60 μL, 6×10^{-4} mol), purged three times with 2 bar O_2, sealed under pressure, and placed in an oil bath preheated to 100 °C. After 18 h, a 20 μL sample from the pressure tube was added to 1.5 mL of toluene and analyzed by GC.

■ RESULTS AND DISCUSSION

TEMPO-Assisted Oxidation of $PhCH_2OH$ Catalyzed by Mn_{12} Clusters. Combinations of metal ions such as Ru,[16] Cu,[17] Ce,[18] V,[19] or Mn[20−22] with stable nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) have been used extensively as homogeneous catalytic systems, and their mechanism of action in the oxidation of primary alcohols to aldehydes has been previously established (see details below).[14] In the present study, we tested mixtures of Mn_{12} acetate (1 mol %) and different amounts of TEMPO (5−30 mol %) in DMF for the catalytic oxidation of benzyl alcohol at 100 °C for 18 h. DMF was chosen as solvent to ensure good solubility and stability of the R = Me Mn_{12} derivative under these reaction conditions that we initially explored. We found this system to be catalytically active for conversion of $PhCH_2OH$ to PhCHO but with only a small conversion (10%) and turnover number (TON = 10)[23] after 18 h at 100 °C in the absence of TEMPO (Table 1, entry 1). Addition of TEMPO greatly improved conversion and TON, and 22 mol % was found to be optimum, giving 62% conversion of $PhCH_2OH$ selectively to PhCHO (Table 1, entry 2). The fact that no benzoic acid is produced in the TEMPO-assisted catalytic system has been demonstrated before[17c,19] and is consistent with the well-known propensity of TEMPO for scavenging free radicals, thereby acting as an effective autoxidation inhibitor.[14]

As controls, when the reaction of entry 2 was repeated without O_2 (entry 3) or without Mn_{12} acetate (entry 4), only 8% (TON = 8) and 6% (TON = 6) conversions, respectively, were obtained. Since the electron-donating or -accepting nature of the carboxylates is known to have a significant effect on the Mn_{12} redox potentials, we explored how they might consequently also affect the catalytic activity. We thus prepared five Mn_{12} derivatives with different R groups and explored them as catalysts with 22 mol % TEMPO in the oxidation of $PhCH_2OH$ (Table 1, entries 5−9). Only small variations in TON were observed, with the highest being for $[Mn_{12}O_{12}(O_2CC_6H_4F)_{16}(H_2O)_4]$ (entry 9), which has the highest reduction potential of those explored (0.23 V in CH_2Cl_2 vs ferrocene).[1] Notably, the use of the Mn^{2+} salt $Mn(O_2CMe)_2 \cdot 4H_2O$ gave poor conversion (16%), indicating that a high oxidation state Mn_x cluster is required for efficient activity.

In the context of Mn oxidation state, the high-symmetry Mn_{12} molecule contains two types of high-oxidation Mn ions: the four inner Mn^{4+} ions (Mn1 in Figure 1) and the eight outer Mn^{3+} ions that separate into two groups of four by S_4 symmetry (Mn2 and Mn3). Any or all of these three groups of Mn ions could potentially enable the catalytic transformation. However, it is well known that reduction of Mn_{12} to $[Mn_{12}]^{n-}$ (n = 1, 2, 3) takes place selectively at one group of outer Mn^{3+} ions (Mn3), converting them to Mn^{2+}, not at the other Mn^{3+} group or at the inner Mn^{4+} ions. In addition, the Mn^{3+} ions of type Mn3 each possess a labile water molecule bound on the Jahn−Teller elongation axis[1] and are thus more likely to be involved in the redox activity than the Mn^{4+} ions or even the Mn^{3+} ions of type Mn2. We consequently presumed that the Mn^{3+} ions of type Mn3 are those primarily responsible for the catalytic activity of the Mn_{12} clusters. In order to test this assumption, we explored two molecular Mn clusters that contain only Mn^{3+} ions, $[Mn_3O(O_2CMe)_6(py)_3](ClO_4)$[24] and $[Mn_4O_2(O_2CMe)_7(bpy)_2](ClO_4)$,[25] and these both proved to be efficient alcohol oxidation catalysts with TON comparable to those of the Mn_{12} clusters (Table 1, entries 10 and 11). These results indicate that it is indeed the Mn^{3+} ions of the Mn_{12} clusters that represent the redox-active sites in the catalytic reaction. Our results also suggest that the exact number of Mn ions and the size of the cluster do not determine the catalytic activity.

The mechanism of the TEMPO-assisted aerobic oxidation of alcohols catalyzed by metal ions has been well investigated over the last few decades, as summarized by Sheldon et al.[14] We do not therefore wish to suggest a new mechanism but rather to determine which of the proposed mechanisms in the literature is compatible with our system. On the basis of the results from the control experiments (entries 1, 3, 4) as well as the structural features of the Mn_{12} cluster (Figure 1), we believe the mechanism previously reported by Neumann and co-workers[19] is also valid in our catalytic system. This proposed mechanism suggests that the alcohol is oxidized by TEMPO, TEMPO is reoxidized by a high-oxidation metal ion, and the latter is reoxidized by O_2. First, the observation in Table 1 that low conversion can be obtained in the absence of TEMPO is consistent with the same control experiment done by the Neumann group. This result also excludes the possibility that the active catalyst is a metal−TEMPO complex as proposed by Sheldon and co-workers,[17b,c] who reported no conversion in the same control experiment. Second, the structural similarities between our Mn_{12} cluster, which has a well-established redox-active $Mn^{3+/2+}$ site in the outer region of its metal−oxo core,[1] and the polyoxometalate used in the study by the Neumann group, which has a redox-active $V^{5+/4+}$ in its exterior, also support our assumption regarding the mechanistic pathway.

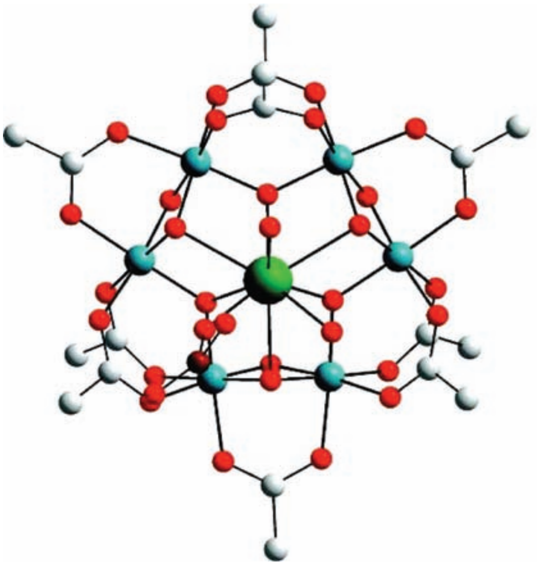


Figure 2. $[CeMn_6O_9(O_2CMe)_9(NO_3)(H_2O)_2]$: green, Ce^{4+}; sky blue, Mn^{4+}; red, O; gray, C.

Improved Catalytic Oxidation of Benzyl Alcohol Using a $CeMn_6$ Cluster. Encouraged by the above initial results, we sought to improve the system by achieving full conversion, further improving the TON and decreasing the amount of TEMPO needed for catalysis. On consideration of available high-oxidation Mn clusters, we were particularly attracted to mixed-metal ones that also contain a second type of high oxidation state metal ion, namely, Ce^{4+}/Mn^{4+} species. Although Ce^{4+} is a useful oxidation catalyst,[26] the combination of Ce^{4+} and a manganese ion in a molecular compound has not previously been explored as a catalytic system for oxidation of alcohols. In previous reports, we described the synthesis, characterization, and magnetic properties of a family of Ce^{4+}/Mn^{4+} molecular complexes and suggested that they might have application as oxidation catalysts.[27] One of the reasons for believing this was that these clusters were all prepared from oxidation of Mn^{2+} reagents with Ce^{4+} at stoichiometries that should have yielded Ce^{3+}/Mn^{3+} or Ce^{3+}/Mn^{4+} products, but instead, they were all Ce^{4+}/Mn^{4+}, indicating the involvement of atmospheric O_2 to raise the metal oxidation states to +4. Since both Mn^{4+} and Ce^{4+} are strongly oxidizing, the possibility that their reduced forms generated by substrate oxidation could be reoxidized by O_2 suggested a potentially attractive catalytic system involving O_2 as the ultimate oxidant. We have thus explored this possibility using the cluster $[CeMn_6O_9(O_2CMe)_9(NO_3)(H_2O)_2]$ ($CeMn_6$; Ce^{4+}, $6Mn^{4+}$) (Figure 2) in the oxidation of $PhCH_2OH$ with molecular O_2. This complex is relatively easy to synthesize and soluble and stable in a variety of solvents. For reliable comparisons, the same conditions were used as for the Mn_{12} clusters in Table 1.

The results obtained with $CeMn_6$ clearly indicate it to be a superior catalyst (Table 2): not only did we achieve full conversion selectively to benzaldehyde but we could also (i) reduce the amount of TEMPO to only 10 mol % (Table 2, entry 5), (ii) employ air instead of oxygen pressure (Table 2, entry 6), and (iii) decrease the reaction time (Table 2, entry 7), all without any loss

Table 2. TEMPO-Assisted Oxidation of $PhCH_2OH$ with O_2 Catalyzed by $CeMn_6$ or a Combination of Ce and Mn Salts

entry	catalyst[a]	PhCHO (%)[b,c]
1	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$	>99
2	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[d]	12
3	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[e]	6
4	none (only TEMPO)	6
5	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[f]	>99
6	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[g]	>99
7	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[h]	>99
8	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[i]	>99
9	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[j]	>99
10	$[CeMn_6O_9(O_2CMe)_9NO_3(H_2O)_2]$[k]	>99
11	$(NH_4)_2[Ce(NO_3)_6]$ (CAN)	6
12	$Mn(O_2CMe)_2{\bullet}4H_2O$ + CAN	11
13	$Mn(O_2CMe)_3{\bullet}2H_2O$ + CAN	12

[a] Reaction conditions: $PhCH_2OH$ (6×10^{-4} mol), catalyst (6×10^{-6} mol, 1 mol %), TEMPO (18 mg, 22 mol %), 0.3 mL of DMF (0.02 M catalyst), 2 atm O_2, 100 °C, 18 h. [b] PhCHO was the only product; no $PhCO_2H$ acid was detected by either GC or GC-MS. [c] The TON is the same as the conversion in this catalyst:substrate ratio (1:100). [d] No TEMPO. [e] No O_2. [f] TEn mole percent TEMPO. [g] Air instead of O_2. [h] Thirteen hours. [i] No solvent. [j] Acetone was used as a solvent. [k] Polyethyleneglycol (PEG)-1000 was used as a solvent.

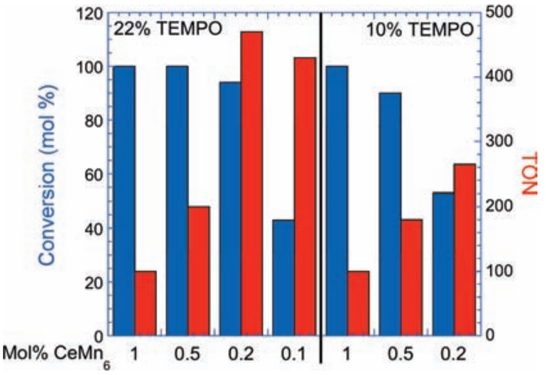


Figure 3. Variation in TON with decreasing amounts of $CeMn_6$ catalyst. Conditions: 0.3−0.5 mL DMF, 2 atm O_2, 100 °C, 18 h.

in catalytic efficiency. Importantly, we were also able to dispense with the high boiling point solvent DMF and perform the reaction with no solvent at all, with low boiling point acetone, or with PEG-1000 (a solid at room temperature), again with full conversion (Table 2, entries 8−10). As we found for the Mn_{12} acetate/TEMPO catalytic system, all three components—the metal cluster, molecular O_2, and TEMPO—are essential for high conversion; the absence of any resulted in a very poor TON. Moreover, the use of $(NH_4)_2[Ce^{4+}(NO_3)_6]$ (CAN), either alone or as mixtures with either Mn^{2+} or Mn^{3+} acetate reagents, afforded only poor conversions (Table 2, entries 11−13). These observations collectively demonstrate that full conversion requires the use of a heterometallic Mn^{4+}/Ce^{4+} species (see below for proposed mechanism).

Since $CeMn_6$ catalyzes $PhCH_2OH$ oxidation with full conversion, we next targeted further improvement in the TON. We reduced the amount of catalyst systematically and evaluated its activity in the presence of either 22 or 10 mol % TEMPO (Figure 3). For 22 mol % TEMPO, complete conversion of $PhCH_2OH$ to PhCHO was obtained with both 1 and 0.5 mol % catalyst; a slight decrease in conversion (94%) was observed with 0.2 mol % catalyst, and only 43% conversion was achieved with 0.1 mol % catalyst. The highest TON of 470 was obtained with 0.2 mol % catalyst. For 10 mol % TEMPO, the conversion decreased linearly with the amount of catalyst, and the highest TON (TON = 260) was again achieved at 0.2 mol % catalyst.

Role of Ce^{4+} and Mn^{4+} in the Catalytic Activity of the $CeMn_6$ Cluster. The observation that all three components—metal cluster, O_2, and TEMPO—are essential for high conversion suggests that the same reaction mechanism applies for the heteronuclear Ce^{4+}/Mn^{4+} catalyst as for the homonuclear Mn_{12} catalyst described above. In this case, however, all Ce and Mn ions are in the M^{4+} oxidation state. The two labile water molecules and one nitrate ion on the central Ce^{4+} ion of the $CeMn_6$ cluster (Figure 2) suggest this site is likelier than the Mn^{4+} ions to be accessible and thus involved in the redox chemistry during catalysis. We can therefore propose that it is the Ce^{4+} that oxidizes TEMPO while being reduced to Ce^{3+} and then reoxidized by the O_2. The proposed mechanism is depicted in Scheme 1. According to standard redox potentials, O_2 is not thermodynamically capable of oxidizing Ce^{3+} to Ce^{4+}; however, we emphasize again the oxide-rich environment of the Ce (and Mn) in the $CeMn_6$ cluster, which will serve to stabilize the higher oxidation state, i.e., make it easier to oxidize Ce^{3+}.[27] Indeed, the cyclic voltammogram (CV) and differential pulse volammogram (DPV) of the $CeMn_6$ cluster in DMF shows multiple reduction peaks at relatively low potentials, the first at only 0.54 V vs NHE (Figure S1, Supporting Information). This is much lower than the reduction potential of CAN in DMF, which is 1.47 V vs NHE (Figure S2, Supporting Information), and it is thus consistent with the synthesis of this cluster at the $Ce^{4+}Mn^{4+}{}_6$ oxidation level, as described above. Therefore, the complete, oxide-rich $\{CeMn_6O_9\}$ core stabilized by the Mn^{4+} ions plays a crucial role in the efficient catalytic activity of the $CeMn_6$ cluster by stabilizing Ce^{4+} and thereby lowering the $Ce^{4+/3+}$ potential. Thus, under our aerobic catalytic conditions, the reduced form of the $CeMn_6$ cluster generated by TEMPO oxidation can be reoxidized by O_2 back to the $Ce^{4+}Mn^{4+}{}_6$ level. In addition, the control experiments in Table 2 (entries 11−13) show that the Ce^{4+} salt $(NH_4)_2[Ce(NO_3)_6]$ (CAN), with or without the additional presence of a Mn^{2+} or Mn^{3+} salt, is not an efficient catalyst under these reaction conditions, suggesting that the presence of Mn^{4+} ions in combination with the Ce^{4+} are required for the catalysis. Finally, to test this conclusion, we used a member of the $[CeMn_8O_8(O_2CR)_{12}L_4]$ ($CeMn_8$; Ce^{4+}, $8Mn^{3+}$) family of clusters with a lower oxide:metal ratio,[28] which like the $CeMn_6$ cluster are heteronuclear but unlike them contain only Mn^{3+}; there is a Ce^{4+} inside a loop of eight Mn^{3+} ions rather than six Mn^{4+} ions. The synthesis of these clusters does not involve oxidation of Mn^{2+} ions by Ce^{4+} but rather uses smaller clusters containing Mn^{3+} ions as precursors. We chose the R = Bu^t and L = DMF member:[29] using 0.5 mol % catalyst and 10 mol % TEMPO in 0.3 mL of DMF at 100 °C, we obtained after 18 h only 22% conversion of $PhCH_2OH$ to PhCHO with TON = 44. This activity is much lower than that of $CeMn_6$ (90% conversion, TON = 180) under the same reaction conditions. Further, the use of 0.5 mol % Mn_{12} acetate under the same conditions afforded 24% conversion with TON = 48, a result very similar to that with $CeMn_8$. The picture that emerges is that high conversion and high TON require an intimate association of

Scheme 1. Proposed Mechanism for the TEMPO-Assisted Catalytic Oxidation of Benzylalcohol by the $CeMn_6$ Catalyst

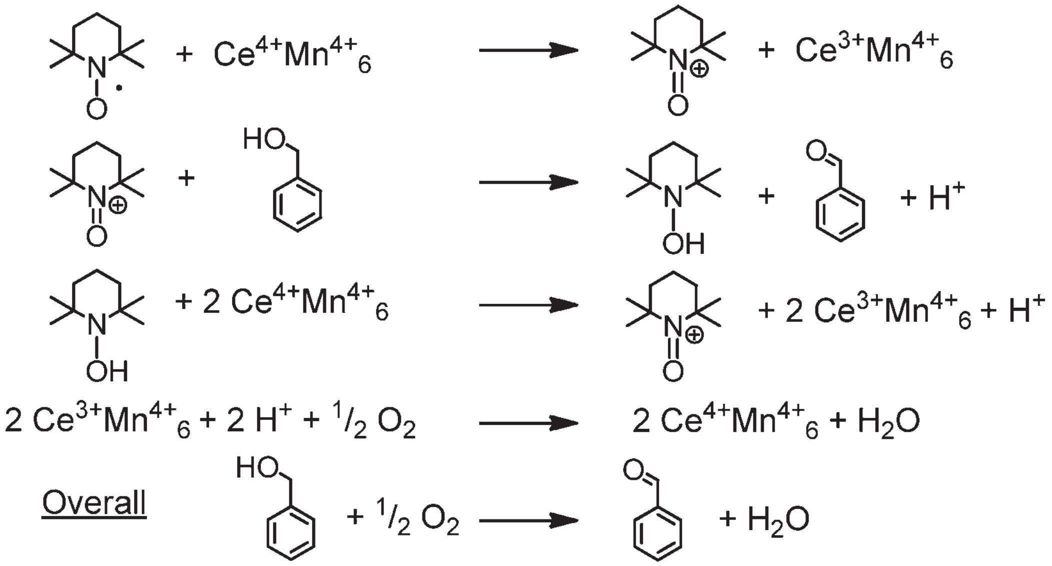
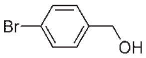
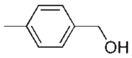
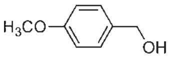


Table 3. TEMPO-Assisted Oxidation of Para-Substituted $PhCH_2OH$ with O_2 Catalyzed by $CeMn_6$

Alcohol	Aldehyde % (TON) [a]		
	No $CeMn_6$ [b]	$CeMn_6$ + 22 mol% TEMPO	$CeMn_6$ + 10 mol% TEMPO
	9 (4.5)	>99 (200)	52 (104)
	6 (3)	>99 (200)	63 (126)
	5.5 (3)	>99 (200)	38 (76)

[a] Reaction conditions: para-substituted $PhCH_2OH$ (1.2×10^{-3} mol), catalyst (6×10^{-6} mol, 0.5 mol %), 0.3 mL of DMF (0.02 M catalyst), 2 atm O_2, 100 °C, 18 h. [b] Only TEMPO (18 mg, 22 mol %).

Ce^{4+} and Mn^{4+} within a heteronuclear cluster, i.e., that the Mn^{4+} in $CeMn_6$ and the resulting high oxide:metal ratio does indeed enable the aerobic oxidation of Ce^{3+} to Ce^{4+} and consequently to the observed high catalytic activity.

Reaction Scope. Since full conversion was obtained at a catalyst-to-substrate ratio as low as 1:200 with 22 mol % TEMPO and high conversion was observed at the same catalyst-to-substrate ratio with only 10 mol % TEMPO, these conditions were employed for the aerobic oxidation of para-substituted primary benzylic alcohols (Table 3). The results obtained with 22 or 10 mol % TEMPO seem to indicate that there is no significant substituent effect. This observation is consistent with a similar study done by Neumann and co-workers, where all the para-substituted benzyl alcohols tested in their catalytic system gave the same conversion within experimental error.

Catalyst Stability. An important issue to be investigated was whether the catalysts we used are stable under the reaction conditions. In this context, we also wished to determine whether the final yields in the case of the family of Mn_{12} clusters are a consequence of catalyst deactivation or low activity. To this aim, we measured benzyl alcohol conversion to aldehyde over time with the two representative catalysts, Mn_{12} (R = Me) and $CeMn_6$. The time−conversion plots are shown in Figure 4. Figure 4A clearly shows that for Mn_{12} the final conversion is a consequence of the low activity of the catalyst, as the conversion does not reach 100% even after 30 h of reaction, and the reported conversion is indeed the final one. For $CeMn_6$, the conversion reached 100% after 13 h, which suggests no decrease in activity over time or deactivation of the catalyst. Additionally, solid-state IR (KBr) spectra of both catalysts were taken before and after the reaction (Figures S3 and S4, Supporting Information). In both cases, ether was added to the reaction mixture and the precipitated solid washed with ether and dried in air prior to IR analysis. For Mn_{12},

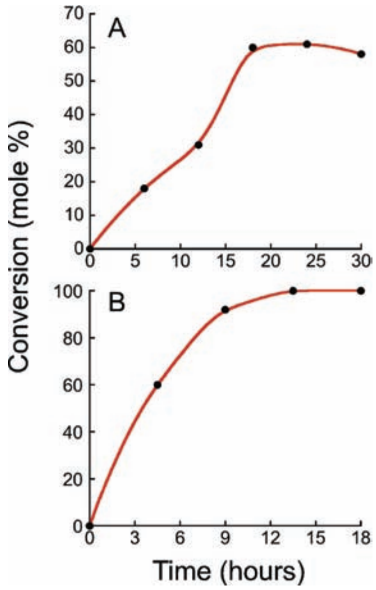


Figure 4. Time-dependent catalytic oxidation of $PhCH_2OH$ with Mn_{12} acetate (A) and $CeMn_6$ (B). Reaction conditions: $PhCH_2OH$ (6×10^{-4} mol), catalyst (6×10^{-6} mol, 1 mol %), TEMPO (18 mg, 22 mol %), 0.3 mL of DMF (0.02 M catalyst), 2 atm O_2, 100 °C.

a noticeable broadening of the peaks was observed, suggesting that the cluster had undergone some structural change and/or decomposition. This observation is consistent with its low catalytic activity. In contrast, the IR spectrum of $CeMn_6$ that was obtained after the reaction looks much more similar to that taken before the reaction, suggesting that the catalyst is much more stable under the reaction conditions. This is consistent with its high catalytic activity.

■ CONCLUSIONS

We have demonstrated for the first time the catalytic activity of high oxidation state manganese species including $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ and $[CeMn_6O_9(O_2CMe)_9(NO_3)(H_2O)_2]$, employing the well-established TEMPO-assisted aerobic oxidation of benzyl alcohol as the test system. Although many efficient catalysts for the TEMPO-assisted oxidation of alcohols are known, the present systems have some distinct advantages, such as (i) the catalysts are easily prepared from cheap and readily available metal salts, e.g., Mn and Ce rather then precious metals such as Ru, (ii) the synthesis involves environmentally benign reagents and solvents, e.g., water and acetic acid rather then highly concentrated nitric and sulfuric acids, as in the systems that utilize polyoxometalates,[18] and (iii) the catalytic mixture contains only the metal cluster and TEMPO, addition of base[17b,c] not being required. We also discovered that the $CeMn_6$ cluster shows the best catalytic performance due to the presence of both high oxidation state Ce^{4+} and Mn^{4+} ions intimately connected via oxide bridges. In addition, we were able to show that these new oxidation catalysts are capable of utilizing O_2 as the terminal oxidant using 'green' solvents such as acetone and polyethylene glycol or without any solvent (neat). Work is now in progress to expand both the scope of the reaction and utilization of these clusters as catalysts in other important oxidation transformations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Cyclic voltammograms and differential pulse voltammograms of $CeMn_6$ and CAN. IR spectra of Mn_{12} acetate and $CeMn_6$ before and after catalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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