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Review

Applications of the "nano to bulk" Mn oxides: Mn oxide as a Swiss army knife

Mohammad Mahdi Najafpour[a,b,*], Małgorzata Hołyńska[c], Saeideh Salimi[a]

[a] Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran
[b] Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran
[c] Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften (WZMW), Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany

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This review is dedicated to Professor Habib Firouzabadi for all his kinds, considerations, helps and encouragement

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ABSTRACT

Mn oxides are inexpensive, environmentally friendly, stable and redox-active compounds. Thus, they are among the most promising compounds for different applications. In this short review we discuss the importance of Mn oxides in different catalytic reactions, such as alcohol, sulfide and water oxidations, and also promising applications of these compounds as supercapacitors, in batteries and water treatment.

* Corresponding author at: Institute for Advanced Studies in Basic Sciences (IASBS), Department of Chemistry, Gavazang, Zanjan 1159-45195, Iran. Tel.: +98 24 3315 3201.
E-mail addresses: mmnajafpour@iasbs.ac.ir, mmnajafpour@yahoo.com (M.M. Najafpour).

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1. Introduction

Mn oxides are materials displaying a variety of applications and interest in different areas [1–6]. In particular, they are currently gaining importance for energy-issue concerns acting as super capacitors [7], being catalysts in water oxidation [8] and finding applications in batteries [9–11]. These compounds are flexible, with a wide diversity of crystal forms and can be prepared with different defects, morphology, porosity and textures. Being environmentally friendly and often mimicking biosystems [8], they also exhibit a variety of useful physical, chemical and electrochemical properties as representatives of reducible oxides [12]. In addition to bulk, they can also be used in supported, colloidal and nano-sized forms with high surface areas [5,13]. Different facile methods are available for their synthesis. Specific bulk and surface structures of Mn oxides could assist the occurrence of multi-electron and complicated reactions [5,13].

In this review, we will briefly describe the structure of Mn oxides. Subsequently, we introduce a variety of important processes catalyzed by Mn oxides: oxidation of various substrates, epoxidation of olefins and more, on representative examples. With this respect Mn oxides truly deserve to be called a "catalytic Swiss army knife".

2. Structure of Mn oxides

In the structure of some Mn oxides, other cations such as Na(I) or K(I), are present. Other Mn oxides, such as MnO, Mn_2O_3, Mn_3O_4, Mn_5O_8 or MnO_2, do not contain additional ions.

Mn(II) oxide [14–29], found in nature as the mineral manganosite, crystallizes in the cubic crystal system, with rock salt type with octahedral coordination sphere of the Mn(II) ion (Fig. 1, [14]). Under the temperature of 120 K, corresponding to the Neél temperature of this antiferromagnetic material, a rhombohedral distortion is observed [2,25].

The most well-known form of Mn_3O_4 ($Mn^{2+}Mn^{3+}{}_2O_4$) is tetragonal hausmannite, crystallizing in an $I4_1/amd$ space group type and displaying a range of possible stoichiometries (Table 1) [30–37]. This form has a spinel structure with a *cpp* sublattice formed by the O^{2-} ions. The Mn(II) ions occupy the tetrahedral sites and the Mn(III) ions lie in the octahedral voids, displaying the expected Jahn–Teller distortion.

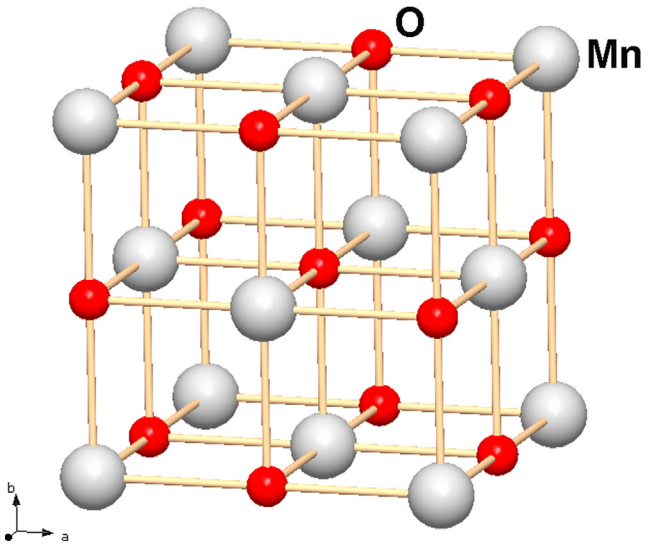

Fig. 1. Structure of the cubic Mn(II) oxide.

Table 1
Structures of Mn oxides.

Formula	Space group symbol
MnO	$Fm\bar{3}m$
MnO with a rhombohedral distortion	$F\bar{3}m$
$Mn_{0.999}O$	$Fm\bar{3}m$
$Mn_{0.995}O$	$Fm\bar{3}m$
$Mn_{0.990}O$	$Fm\bar{3}m$
$Mn_{0.986}O$	$Fm\bar{3}m$
$Mn_{0.977}O$	$Fm\bar{3}m$
$Mn_{0.965}O$	$Fm\bar{3}m$
$Mn_{0.959}O$	$Fm\bar{3}m$
$Mn_{0.95}O$	$Fm\bar{3}m$
$Mn_{0.944}O$	$Fm\bar{3}m$
$Mn_{0.910}O$	$Fm\bar{3}m$
$Mn_{0.76}O_{0.90}$	$Fm\bar{3}m$
Mn_3O_4	$Fd\bar{3}m$
Mn_3O_4	$Pbcm$
Mn_3O_4	$I4_1/amd$
$Mn_{2.933}O_4$	$I4_1/amd$
$Mn_{2.978}O_4$	$I4_1/amd$
$Mn_{2.972}O_4$	$I4_1/amd$
$Mn_{2.963}O_4$	$I4_1/amd$
$Mn_{2.956}O_4$	$I4_1/amd$
$Mn_{2.937}O_4$	$I4_1/amd$
$Mn_{2.907}O_4$	$I4_1/amd$
Mn_2O_3	$R\bar{3}c$
Mn_2O_3	$Ia\bar{3}$
Mn_2O_3	$Pbca$
Mn_5O_8	$C2/m$
MnO_2	$Pnnm$
MnO_2	$Pnma$
MnO_2	$I4/m$
MnO_2	$Fd\bar{3}m$
MnO_2	$P4_2/mnm$
$Mn_{0.5}O$	$P6_3/mmc$
Mn_2O_7	$P2_1/c$

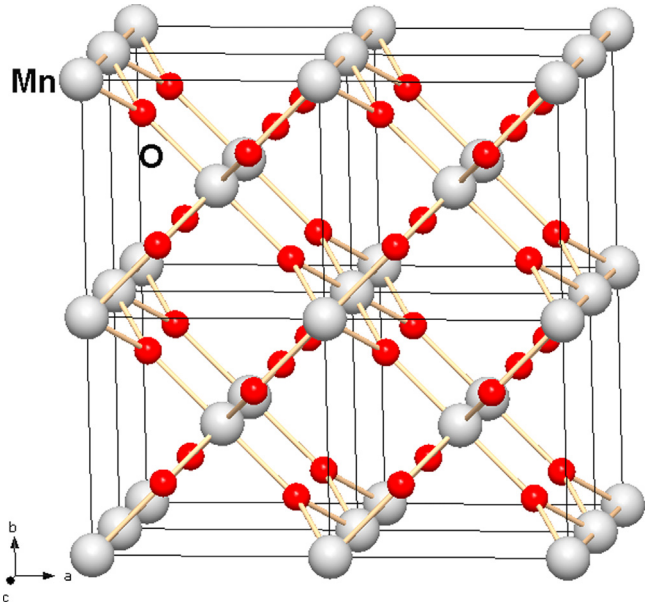

Fig. 2. Tunnel structure of pyrolusite with channels along *c*.

Several forms of Mn_2O_3 [38–45] include the orthorhombically-distorted bixbyite structure, in a *P*bca space group type [42–45]. Above 300 K a phase transition to a cubic form is observed [42].

The polymorphic forms of MnO_2 are listed in Table 1 [48–59]. The thermodynamically stable form, pyrolusite [57–59], forms a tunnel structure (Fig. 2), similar to rutile, crystallizing in a $P4_2/mnm$ space group type. Here a range of compositions from $MnO_{1.93}$ to $MnO_{2.0}$ is possible [57–59]. Thus, distorted octahedral edge-sharing