



# Nanolayered manganese-calcium oxide as an efficient and environmentally friendly catalyst for alcohol oxidation

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## ABSTRACT

Here, we report that nanolayered Mn-Ca oxide is an efficient catalyst toward alcohol oxidation in the presence of O<sub>2</sub>.

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## 1. Introduction

The design of new types of catalysts using abundant, low-cost and environmentally friendly compounds is very attractive field in recent years [1]. Mn oxides are among the most attractive inorganic materials not only because of their physical and chemical properties but also because of their low cost and environmentally friendly [2]. They were used as bulk, supported and colloidal forms and synthesized easily by different methods. Mn oxides can be also prepared as nano-sized nanostructures with large surface area, and thus many of their active sites are accessible for the reactants [2]. The structures of these compounds are polynuclear and could favor the occurrence of multi-electron and complicated reactions. In Mn oxides, no easily oxidizable ligands are present that make the compound stable in different conditions.

Mn oxides were used as oxidant in organic chemistry. The compounds were also used as efficient catalysts for oxidation of organic [3–7] and inorganic compounds such as carbon monoxide [8,9], nitrogen oxides [10] and water [11]. Among different oxidation reactions, selective oxidation of alcohols to aldehydes is an

important reaction [12]. Different stoichiometric oxidizing reagents are used in the reaction. O<sub>2</sub> is a very promising oxidant for the reaction regarding low-cost and environmentally friendly issues [12]. In this context, homogeneous catalysis provides powerful environment to use this oxidant, but in an industrial scale a heterogeneous catalysts are preferred [12].

Among heterogeneous catalysts, Pt-group metals can oxidize alcohols in the presence of O<sub>2</sub> under close to ambient conditions to produce carbonyl or carboxylic compounds in high yields [12].

Regarding our previous studies on water-oxidation by Mn oxides [13–18], here we report catalytic oxidation of alcohols to aldehydes by the nanolayered Mn oxides in presence of O<sub>2</sub>. MnO<sub>2</sub> was usually used as an oxidant, but oxidation by catalytic amounts of Mn oxides was also reported [19].

Suib's group for the first time reported aerobic oxidation of alcohols with octahedral molecular sieves (OMS) without the use of additives [19]. Benzylic and allylic alcohols were readily converted into aldehydes and ketones in the presence of sub-stoichiometric amounts of activated MnO<sub>2</sub> under oxygen atmosphere [19]. No over-oxidation to carboxylic acid happened. Kamimura's group reported oxidation of benzyl alcohols by semi-stoichiometric amounts of cobalt doped birnessite-type layered MnO<sub>2</sub> under oxygen atmosphere [20].

Among different Mn oxides, nanolayered Mn oxides are efficient catalyst toward oxidation-reactions [13–18]. The probable reasons for enhancement of catalytic activity of them involve a combination of factors. They have a layered structure with considerable

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thermodynamic stability and high surface area, they include mixed valent Mn with internal oxidation enthalpy smaller in magnitude than for the  $\text{Mn}_2\text{O}_3$ - $\text{MnO}_2$  couple, and low surface enthalpy, which suggests relatively loose binding of substrate on the nanoparticle surfaces [21]. In the layered structure, bulk metal ions are able to participate as catalytically active sites regarding the prevalence of di- $\mu$ -oxo-bridging between metal ions and their large interlayer space caused by water and further ions [22].

Here, we report nanolayered Mn oxides as catalysts for alcohol oxidation in the presence of oxygen.

## 2. Materials and methods

All reagents and solvents were purchased from commercial sources (Merck or Sigma-Aldrich) and were used without further purification. MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and  $4000\text{ cm}^{-1}$ . TEM and SEM were carried out with JEOL JEM 2010 Fas TEM operating at 200 kV and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu- $K\alpha$  radiation). Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (10.0 mg metal) were added to 1 mL of concentrated nitric acid and  $\text{H}_2\text{O}_2$ , left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS. The products of oxidation of alcohols were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column and flame-ionization detector.

### 2.1. Synthesis of compound

The compound was synthesized by a previously reported method [7]:

Briefly, it was synthesized by mixing a solution contain  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  (2.70 mmol, 0.494 g) and  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (5.6 mmol, 1372 mg) in water (5 mL) and a solution of  $\text{KMnO}_4$  (2.4 mmol, 379 mg) and  $\text{KOH}$  (17.0 g) in 100 mL water. The obtained suspension was filtered and washed with distilled water (3 L) before being allowed to dry for 12 h at  $60^\circ\text{C}$  in an oven. Then the solid was heated to  $400^\circ\text{C}$  for 10 h in air to obtain a brown powder. Yield: >90%; at  $400^\circ\text{C}$  the oxide could be formulated as  $\text{Ca}_{0.16}\text{MnO}_2 \cdot 2\text{H}_2\text{O}$ .

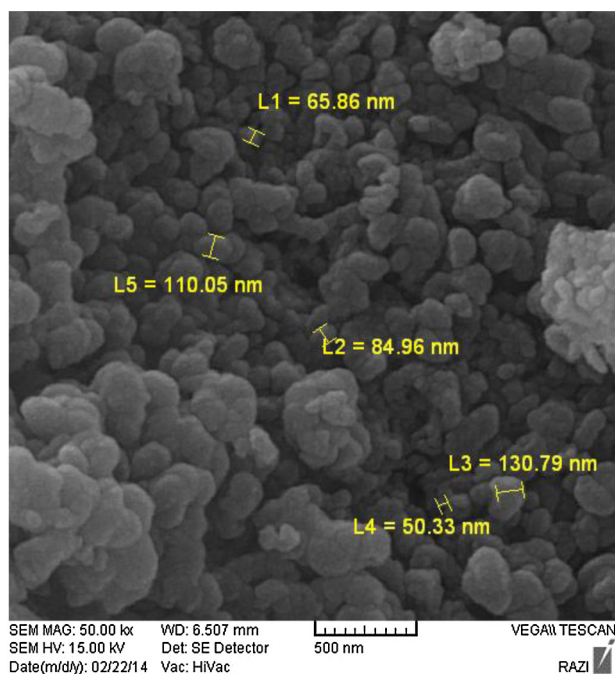
### 2.2. Oxidation of alcohols catalyzed by $\text{Ca}_{0.16}\text{MnO}_2 \cdot 2\text{H}_2\text{O}$

To a solution of alcohols (1.0 mmol), and catalyst (1.0 mg) in  $\text{CH}_3\text{CN}$  (1 mL) was bubbled  $\text{O}_2$  as the oxidant. The reaction was vigorously stirred at room temperature for a defined time. After the reaction, the product mixtures were analyzed by gas chromatography (GC).

## 3. Results and discussion

The procedure to synthesize of the nanolayered Mn oxides was simple, easily and cheap by the reaction of  $\text{KMnO}_4$ ,  $\text{Mn}(\text{II}) (\text{OAc})_2$  and  $\text{CaCl}_2$  in the presence of  $\text{KOH}$ . In IR spectra of the compound, a broad band at  $\sim 3200$ – $3500\text{ cm}^{-1}$  related to antisymmetric and symmetric O–H stretchings and at  $\sim 1630\text{ cm}^{-1}$  related to H–O–H bending are observed [7,23,13]. The peaks at  $\sim 700\text{ cm}^{-1}$  are related to Mn–O–Mn bonds.

XRD data for the compound are of very poor resolution. However, the peak near the  $2.4\text{ \AA}$  spacing ( $2\theta \sim 38$ ), observed in all octahedrally coordinated Mn oxide materials, was observed in XRD



(a)

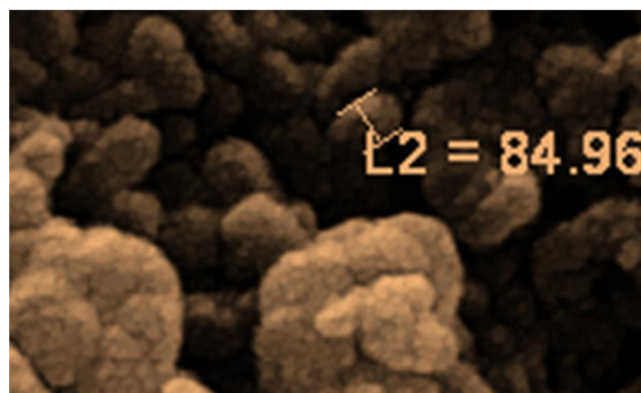


Fig. 1. SEM micrographs of nano-sized Mn-Ca oxide (a,b).

patterns of the compound. The peaks near  $2\theta \sim 11, 25, 36$  and  $65$  found in most layered materials such as layered oxides, are observed in XRD patterns of these compounds that are related to the previously reported structure of layered Mn oxides. The weak peak in  $2\theta \sim 11$  related (001), reveals the absence of long-range order of the layer stacking [7,23,13].

In 2011, the structures of these compounds were considered using extended-range X-ray absorption spectroscopy (XAS) at the K-edges of both Ca and Mn. Two different Ca-containing motifs were identified. One of the motifs was the formation of  $\text{Mn}_3\text{CaO}_4$  cubes while the other Ca(II) ions probably interconnected oxide-layer fragments [24].

We used scanning electron microscopy (SEM) (Fig. 1), and transmission electron microscopy (TEM) to find about morphology of compound [23]. EDX-Mapping images show the homogeneous elemental distributions [23]. Regarding TEM and SEM images, most probably, morphology of each nanoparticle is similar to crumpled paper.

Dynamic light scattering (DLS) in condition similar to alcohol oxidation, shows that particles are in the range of 100–200 nm (Fig. 2). Comparing with SEM (<100 nm), we found aggregation of catalyst particles in this condition.

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