



## Manganese oxide-based catalysts for toluene oxidation



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### ABSTRACT

Four different catalysts based on manganese oxide were prepared: a perovskite ( $\text{LaMnO}_3$ ), via sol-gel method;  $\text{Mn}_2\text{O}_3$ , rapid method and an Octahedral Molecular Sieve (OMS-2) by two different preparation methods, via solid state (OMS<sub>s</sub>) and hydrothermal method (OMS<sub>h</sub>). The physicochemical properties of these catalysts were characterized by X-ray diffraction (XRD),  $\text{N}_2$  adsorption–desorption at  $-196^\circ\text{C}$ , thermogravimetric and differential thermal analysis (TGA/DTA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and temperature-programmed reduction with hydrogen ( $\text{H}_2$ -TPR). Their catalytic performances were evaluated in the catalytic oxidation of toluene. Three consecutive catalytic cycles were performed for each catalyst in order to reach steady state performances. In order to assess the stability of the catalysts under reaction conditions, the catalytic performances were studied upon long term experiments running for 24 h at 25% of toluene conversion. For comparison purposes, the catalytic activity of the present manganese oxide catalysts was compared with that of typical industrial catalysts such as a commercial  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst containing 0.78% Pd. The crystalline features detected in the XRD patterns, are well-consistent with the formation of the desired structures. Based on their specific surface area and their low-temperature reducibility, the catalysts were ranked as follows:  $\text{OMS}_s > \text{Mn}_2\text{O}_3 > \text{OMS}_h > \text{LaMnO}_3$ . This trend was in good agreement with the performances observed in the catalytic removal of toluene. A kinetic model was proposed and a good agreement was obtained upon fitting with the experimental data.

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### 1. Introduction

Volatile Organic Compounds (VOCs) emitted from industrial processes and automobile are not only harmful to human health because they are malodorous, mutagenic and/or carcinogenic but also because they can form toxic photochemical oxidants and suspended particulate matters through photochemical reactions. Many countries have already enacted stringent legislations to abate VOC emissions [1].

In order to efficiently remove VOCs, various technologies have been developed, including adsorption, bio-degradation, membrane separation, thermal incineration and photo-catalytic oxidation [2]. Among these technologies, catalytic oxidation is considered as the most promising process for limiting VOCs' emissions. Indeed, catalytic oxidation might be operated at temperatures much lower compared to thermal incineration. The advantage of the low

temperature oxidation is the reduction of fuel consumption, particularly for large volumes of diluted VOC contaminated air. The optimization of the catalyst formulation is not an easy task due to the large variety of VOCs and the complexity of VOC-containing mixtures. Primarily, the catalyst has to allow ignition temperatures as low as possible. Moreover, it has to be very active, due to the low concentration of VOCs and the large volumes to be treated, and also highly selective in the sense that only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  should be produced. Finally, the catalyst has to withstand the reaction conditions over long periods of operation, i.e., has to be thermally stable.

Noble metal catalysts demonstrated higher activity compared to base metal catalysts; however, their cost is much higher. Therefore, many efforts are being paid to the development of transition metal oxide-based catalysts with high catalytic activity. Among them, manganese oxide-based catalysts are the most active ones [3,4]; although such oxides usually exhibit low specific surface area and poor thermal stability. An interesting way to obtain new manganese oxide-based structures ( $\text{LaMnO}_3$ , OMS and  $\text{Mn}_2\text{O}_3$ ), with smaller crystallite size (i.e. higher specific surface area) and

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improved stability, is the implementation of new preparation methods.

As one of the possible substitutes for precious metal catalysts in redox processes, perovskite-type metal oxides, more specifically LaMnO<sub>3</sub>-based perovskites, have attracted much attention due to their adequate catalytic activity and good thermal stability in the catalytic oxidation of various hydrocarbons. For example, Spinicci et al. [5] investigated the catalytic combustion of acetone, isopropanol and benzene over LaMnO<sub>3</sub> perovskites. The presence of surface oxygen species, easily available and sufficiently mobile, was proposed as a fundamental requirement for the high catalytic activity of LaMnO<sub>3</sub>. Alvarez-Galvan et al. [6] have studied the combustion of methyl ketone over La-transition metal (Cr, Co, Ni, Mn) perovskites. The LaMnO<sub>3</sub> catalyst exhibited the best catalytic performances with complete methyl ketone conversion being achieved at 297 °C. However, in order to ascertain the formation of the perovskite structure, calcination of the precursor material at high temperature (typically above 600 °C) is necessary, leading to relatively low specific surface area and poor reducibility at low temperature in comparison with other transition metal oxides. Therefore, in order to obtain perovskites with high specific surface area and outstanding redox ability, selection and optimization of the synthesis method is a key parameter. For example, the sol-gel method was earlier shown to yield well-crystallized samples with larger specific areas [7].

In addition, OMS-2 is a type of manganese oxide with edge and corner-shared MnO<sub>6</sub> octahedra, forming a 2 × 2 tunnel structure, with K<sup>+</sup> ions inside the tunnel for charge compensation. Because of its unique structural characteristics, OMS-2 has been extensively investigated for various applications in thermocatalytic oxidations such as the chemical synthesis or the cleanup of organic pollutants [8,9]. The activity of OMS-2 catalysts was tentatively attributed to their physicochemical properties, such as their specific surface area, their morphology and/or their surface acidity [10,11].

Similarly, cryptomelane-type of OMS was used in the catalytic oxidation of a variety of VOCs; namely, benzene [12,13], toluene [14], ethanol [10,15] and ethyl acetate [10]. The high activity of such catalysts was alternatively attributed to the presence of the redox Mn(III)/Mn(IV) couple, the high mobility of lattice oxygen, the open structure of cryptomelanes and/or the high hydrophobicity of these solids. Ding et al. [16] used a solvent-free method (solid state method) to synthesize cryptomelane-type of catalysts and investigated the possible correlation between the specific surface area of the catalysts and their catalytic performances. The results showed that the catalysts with the highest surface area (95 m<sup>2</sup> g<sup>-1</sup>) exhibited the best catalytic performances in the oxidation of toluene. The same trend was observed when OMS-2 was synthesized using the hydrothermal method. The best performances in the oxidation of toluene also corresponded to higher surface area, higher reducibility and/or higher mesopore diameter.

Finally, it is reported in the literature that manganese oxide catalysts, such as Mn<sub>2</sub>O<sub>3</sub>, exhibit high performances in the catalytic oxidation of VOCs. The most active manganese oxide catalysts were those with the best redox properties and the highest oxygen mobility [16,17]. Various methods have been used to prepare Mn<sub>2</sub>O<sub>3</sub>, such as co-precipitation, hydrothermal process, sol-gel method and microwave synthesis. However, the gas-liquid reaction method (referred as rapid preparation method in the following) was shown to be the most appropriate since it is simple, easy to control, low-cost and fast [18]. Moreover, large surface area solids could be obtained.

In the present study, Mn catalysts have been prepared using different procedures. All catalysts were characterized by BET, XRD, TGA-DTA, H<sub>2</sub>-TPR and ICP-OES and evaluated in the catalytic oxidation of toluene, chosen as target VOC molecule.

## 2. Experimental

### 2.1. Catalyst preparation

Based on the state-of-the-art, different synthesis routes were selected for the preparation of different families of Mn oxide catalysts. The sol-gel method was the most appropriate for perovskites (LaMnO<sub>3</sub>) [2], the solid state route for OMS<sub>s</sub> [19], the hydrothermal synthesis for OMS<sub>h</sub> [16] and the rapid preparation method for Mn<sub>2</sub>O<sub>3</sub> (Mn<sub>2</sub>O<sub>3R</sub>) [20].

#### 2.1.1. LaMnO<sub>3</sub> (Sol-gel method)

Nitrates (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Fluka, 99 wt.% and Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Alfa Aesar, 98 wt%) were used as metal precursors to prepare the LaMnO<sub>3</sub> perovskite-type oxides. Equimolar amounts of the nitrates were weighed and mixed in a beaker. Distilled water was used to prepare the aqueous nitrates solution. Citric acid (CA) was purchased from Alfa Aesar (>99.5 vol%). The CA to total metal ions (La<sup>3+</sup> + Mn<sup>2+</sup>) molar ratio was fixed at 1.5. After CA addition, the solution was heated up to 80 °C under magnetic stirring to evaporate the excess water. The preparation was dried at 120 °C overnight and subsequently treated in a muffle furnace at 200 °C (2 °C min<sup>-1</sup>) for 1 h. Finally, the solid was calcined at 750 °C (5 °C min<sup>-1</sup>) for 2 h in a quartz tubular reactor under static air.

#### 2.1.2. OMS<sub>s</sub> (Solid state method)

9.48 g of KMnO<sub>4</sub> (Sigma-Aldrich, 99.0 wt%), and 22.05 g Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O (Sigma-Aldrich, 99.0 wt%) were homogeneously grounded in an agate mortar. The powder was further introduced in a capped glass bottle and maintained at 80 °C for 4 h. A black powder was received. After washing with deionized water, the solid was dried at 100 °C for 12 h. Then, the resulting material was calcined at 500 °C (5 °C min<sup>-1</sup>) for 2 h in a quartz tubular reactor under static air.

#### 2.1.3. OMS<sub>h</sub> (Hydrothermal method)

0.04 mol (6.76 g) of MnSO<sub>4</sub>·H<sub>2</sub>O (Sigma-Aldrich, 99.0 wt%) was dissolved in 40 mL of water. The pH of the solution was adjusted to 1.0 using concentrated HNO<sub>3</sub> (Sigma-Aldrich, 90 vol%). An aqueous permanganate solution, prepared by dissolving 0.028 mol (4.40 g) of KMnO<sub>4</sub> (Sigma-Aldrich, 99.0 wt%) in 150 mL of water, was then slowly added to the previous solution under vigorous stirring. The pH of the mixture was again adjusted to 1.0. The mixture was subsequently transferred in a glass liner and sealed in a stainless steel autoclave.

The autoclave was placed in an oven and maintained at 100 °C for 16 h. After cooling, the received black precipitate was filtered and then washed thoroughly with water. The sample was finally dried at 120 °C for 16 h and calcined at 500 °C (5 °C min<sup>-1</sup>) for 2 h in a quartz tubular reactor under static air.

#### 2.1.4. Mn<sub>2</sub>O<sub>3</sub> (Rapid preparation method)

4.9018 g (20 mmol) of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Sigma-Aldrich, 99.0 wt%) was dissolved in 100 mL of ethanol. After addition of 40 mL NH<sub>3</sub>·H<sub>2</sub>O (Sigma-Aldrich, 25.0 vol%), the solution, from colourless turned to light red. However, no precipitate was formed. Subsequently, 1.5 L min<sup>-1</sup> air was bubbled into the solution for 5 min at 50 °C. The solution gradually changed to deep black as colloids were formed. These colloids appeared to be evenly dispersed in the bulk of the solution and stable. Finally, the suspension was centrifuged, dried at 110 °C over night and calcined at 500 °C (the heating rate of 5 °C min<sup>-1</sup>) for 2 h in a quartz tubular reactor under air atmosphere.

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