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# The role of lattice oxygen on the activity and selectivity of the OMS-2 catalyst for the total oxidation of toluene

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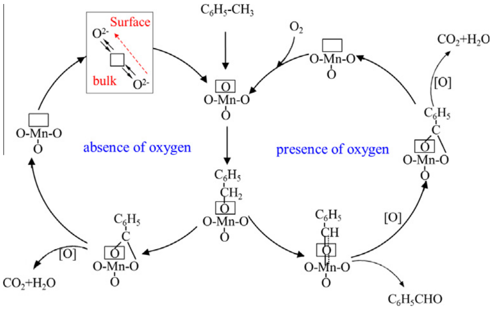
## HIGHLIGHTS

- OMS-2 exhibited excellent activity for catalytic oxidation of toluene.
- The active species and the adsorption sites on OMS-2 are lattice oxygen.
- The selectivity to $CO_2$ is influenced by the nature of replenished lattice oxygen.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The role of lattice oxygen on the activity and selectivity of the OMS-2 catalyst synthesized by the hydrothermal method was investigated for the catalytic oxidation of toluene. The OMS-2 catalyst exhibited excellent activity for the catalytic oxidation of toluene, but the by-product benzaldehyde was detected at low temperatures. A DRIFT study showed that the lattice oxygen was both the adsorption site and active catalytic site. The nature of the replenished surface lattice oxygen was found to influence the selectivity, and toluene that was adsorbed on the lattice oxygen replenished by gaseous oxygen could be oxidized easily into benzaldehyde. A possible reaction mechanism has been proposed that could elucidate the toluene oxidation activity over OMS-2 involving two reaction routes, either with or without gaseous oxygen.

## 1. Introduction

Catalytic oxidation is considered to be a promising technique to remove volatile organic compounds (VOCs) because of its advantages over thermal incineration, such as its high destruction efficiency and its low operation temperature [1,2]. For VOCs oxidation, noble metal catalysts have been demonstrated to be effective. However, some attention has been given to transition metal catalysts due to the limited availability of precious metals and their low resistance to humidity and $SO_2$. Lahousse et al. compared the activity of $\gamma$-$MnO_2$ and some noble metal catalysts for the total oxidation of benzene, ethyl-acetate, and *n*-hexane, and found that manganese oxide catalyst was more active than Pt-$TiO_2$ catalysts for the conversion of ethyl-acetate, and *n*-hexane [3]. Thus, manganese-based catalysts are explored as a possible substitute for noble metal catalysts for catalytic oxidation of VOCs because of their unique redox properties [4,5].

OMS-2 ($KMn_8O_{16}\cdot nH_2O$) is a microporous tunnel-structured manganese oxide having a tunnel size of 4.6 × 4.6 Å, constructed

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by edge and corner sharing of $MnO_6$ octahedra to form one-dimensional tunnel structures. It has been reported that OMS-2 is an active catalyst for the total oxidation of VOCs [6–9], and its good oxidation ability is mainly related to two factors: the coexistence of mixed valence Mn to form $Mn_2^+/Mn_4^+$ or $Mn_3^+/Mn_4^+$ redox couples and the effects of lattice oxygen [9,10].

Although many studies have been carried out to investigate the activity of OMS-2 for oxidizing different types of VOCs, the reaction mechanism involving lattice oxygen is not clear. In addition, some toxic partial-oxidation by-products are usually observed when OMS-2 is adopted as the catalyst, especially at low temperatures [9,11]. In our previous work, the partial oxidation product benzaldehyde was observed in the total oxidation of toluene over the OMS-2 catalysts [12]. However, the reasons for the formation of theses by-products are not still known.

Therefore, the aim of the present paper is to study the reaction mechanism for complete oxidation of toluene over the OMS-2 catalysts, and to understand the role of lattice oxygen on total oxidation and/or partial oxidation. The OMS-2 catalyst was prepared by the hydrothermal method. The catalytic activity of the OMS-2 thus prepared was investigated, and its physical properties were characterized by SEM, TEM, XRD and $O_2$-TPD. Furthermore, DRIFT experiments were carried out to explore the reaction mechanism and to analyze the role of lattice oxygen because lattice oxygen was found to influence the activity and selectivity of the OMS-2 catalyst for the catalytic oxidation of toluene.

## 2. Experimental

### 2.1. Catalyst synthesis

To synthesize the OMS-2 catalysts via a hydrothermal reaction, a solution of $KMnO_4$ was added slowly to a mixture solution of $HNO_3$ and $MnSO_4$ with a $KMnO_4/MnSO_4$ molar ratio of 0.46:1. The black precipitate thus formed was transferred into a Teflon-lined autoclave. Subsequently, the hydrothermal treatment was conducted at 100 °C for 24 h. The product was washed with deionized water to reach a neutral pH, and then dried at 120 °C for 12 h. Before the catalytic activity test, the sample of catalyst was calcined at 250 °C for 2 h.

### 2.2. Characterization

The phase of the OMS-2 materials was identified by a X-ray diffraction (Shimadzu 6000, Japan) instrument with a Cu K$\alpha$ X-ray source with a beam voltage of 45 kV and a 40 mA beam current. The morphology and crystal structure of OMS-2 was studied using a FEI-Tecnai-20 transmission electron microscope (TEM) operated at 200 kV. The temperature programmed desorption of $O_2$ (TPD-$O_2$) was conducted in a Quantachrome Chemisorption Analyzer (ChemBET 3000). In all, 100 mg of the catalysts were placed in a quartz reactor, and then were purged with helium for 1 h at room temperature. Subsequently, the sample was heated from 25 to 900 °C with a ramp of 10 °C/min under the same atmosphere. A TCD was employed to quantify the oxygen.

### 2.3. Catalytic evaluation

Catalytic oxidation reactions were carried out in a 10 mm i.d. tubular quartz reactor at atmospheric pressure. The catalysts (particles size 0.42–0.84 mm) were packed in the bed of the reactor. Toluene vapor was introduced into the reactor by $N_2$ which flowed through a toluene-containing bubbler placed in an ice bath. The reaction mixture consisting of toluene (0.10 vol%), $O_2$ (21%) and $N_2$ (balance of gases) was passed continuously through the catalyst bed with a total flow rate of 100 $cm^3$/min. The toluene concentrations of inlet and outlet gases were analyzed by an on-line gas chromatograph equipped with an FID detector.

### 2.4. FTIR studies

The in-situ infrared experiments were performed with a Bruker (Vertex 70, Bruker Optics) FTIR spectrometer equipped with an MCT detector cooled with liquid nitrogen. The FTIR experiments were carried out in situ by using an FTIR cell with KBr windows, which was connected with the reaction system.

## 3. Results and discussion

### 3.1. Catalyst characterization

The TEM, HRTEM images and selected area electron diffraction pattern (SAED) of the OMS-2 catalyst prepared by the hydrothermal method are shown in Fig. 1. It can be seen that OMS-2 displays nanorod-shaped morphology. The diameter of these nanorods is approximately 7–10 nm with lengths of 300–400 nm. The HRTEM images show these nanorods exhibit well-defined lattice fringes and four main types of lattice fringes are observed. Electron diffraction pattern and the clear lattice fringes show that the OMS-2 tetragonal prisms are single crystalline, as shown in Fig. 1B–D. The width of 0.68 nm two neighboring lattice fringes corresponds to the (1 1 0) planes. The fringe distances of 0.50 nm are good agreement with lattice spacings of the (2 0 0) planes. The fringe spacings of 0.24 and 0.30 nm with a cross angle of 60° can be attributed to the (2 1 1) and (3 1 0) planes in crystal structures, respectively.

The XRD pattern of the fresh sample is shown in Fig. 2. It can be found that all reflections in the XRD patterns of the sample are in good agreement with the standard patterns of the tetragonal cryptomelane ($KMn_8O_{16}$, JCPDS). The intensity and sharp diffraction peaks appear at $2\theta$ = 12.9°, 18.2°, 28.9°, 37.7°, 49.9° and 60.5° can be primarily attributed to the (1 1 0), (2 0 0), (3 1 0), (2 1 1), (4 1 1), (5 2 1) planes, respectively. Furthermore, no impurity phase is observed, demonstrating that the synthetic sample has only the cryptomelane-type structure. According to the Scherrer equation, the average size of the crystallite particles is calculated as 7.9 nm with a reflection at $2\theta$ = 37°. The BET surface area of OMS-2 is 97.6 $m^2$/g.

The $O_2$-TPD profile of the OMS-2 catalyst is presented in Fig. 3. To avoid the effect of $H_2O$, a cold trap was installed before the released gas entered the TCD. It can be observed that there are three desorption peaks at 307, 654, and 823 °C, respectively. The weak peak at 307 °C is attributed to desorption of oxygen adspecies located at surface vacancies because the decomposition of pure $MnO_2$ begins at 535 °C [13,14]. The major peak at 654 °C with a clear shoulder peak is ascribed to desorption of the surface oxygen species ($O^-$ and $O_2^-$) and of lattice oxygen [15]. At the same time, the transformation of cryptomelane to $Mn_2O_3$ occurs. The high temperature peak (823 °C) is ascribed to the successive transformations to $Mn_3O_4$ [16].

### 3.2. Catalytic performance for toluene oxidation

Fig. 4 shows the toluene conversion and benzaldehyde selectivity over the OMS-2 catalyst as a function of temperature in the catalytic combustion reaction. It is found that OMS-2 is the active combustion catalyst and the total conversion into $CO_2$ is achieved at 240 °C. However, it is worth noting that the by-product benzaldehyde is monitored. The yields of benzaldehyde increase with increasing the reaction temperature, and reach a maximum value of 14.0% near 160 °C. Further increasing the temperature can