

# $\alpha$ -MnO<sub>2</sub> CATALYSTS FOR COMPLETE OXIDATION OF ISOPROPANOL: EFFECT OF SYNTHESIS METHOD

## XÚC TÁC $\alpha$ -MnO<sub>2</sub> CHO PHẢN ỨNG OXI HÓA HOÀN TOÀN ISOPROPANOL: ẢNH HƯỞNG CỦA PHƯƠNG PHÁP TỔNG HỢP

Minh Tuan Nguyen Dinh\*

The University of Danang - University of Science and Technology, Danang, Vietnam

\*Corresponding author: ndmtuan@dut.udn.vn

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**Abstract** - This study investigates the effect of synthesis methods on the physicochemical properties and catalytic activity of  $\alpha$ -MnO<sub>2</sub> catalysts in the complete oxidation of isopropanol. The catalysts were synthesized via redox-precipitation reactions by using dropwise and reflux methods and characterized by XRD, SEM, and N<sub>2</sub> adsorption-desorption. The results show that the synthesis methods significantly affect the properties and catalytic activity of  $\alpha$ -MnO<sub>2</sub> catalysts. The dropwise method facilitates the formation of  $\alpha$ -MnO<sub>2</sub> nanofibers with lower crystallite size (12 nm), higher surface area (68 m<sup>2</sup>/g), and pore volume (0.16 cm<sup>3</sup>/g), resulting in enhanced performance for the complete oxidation of isopropanol into CO<sub>2</sub> in comparison with  $\alpha$ -MnO<sub>2</sub> nanorods synthesized by the reflux method. Over  $\alpha$ -MnO<sub>2</sub> nanofibers, the T<sub>50(CO<sub>2</sub>)</sub> and T<sub>90(CO<sub>2</sub>)</sub> temperatures, at which 50% and 90% of isopropanol are converted to CO<sub>2</sub>, were found to be 155°C and 166°C, respectively.

**Key words** - MnO<sub>2</sub>; catalyst; isopropanol; complete oxidation; VOCs

### 1. Introduction

The complete catalytic oxidation of volatile organic compounds (VOCs) is a promising approach to reducing air pollution, which is a major environmental issue in household activities, industrial productions, and automobiles [1]. Among VOCs, isopropanol is widely used as a solvent in various industrial processes like cosmetics paint and coating, printing, electronics, and adhesives. Isopropanol is known to have harmful effects on human health and the environment [2], [3].  $\alpha$ -MnO<sub>2</sub> has been reported as a good catalyst for the complete oxidation of isopropanol and other volatile organic compounds (VOCs) and is considered a promising alternative to expensive noble catalysts like Pt, Au, and Pd [4]. However, it should be noted that the synthesis method of  $\alpha$ -MnO<sub>2</sub> materials can significantly affect its catalytic performance [4]. Several synthesis methods have been reported in the literature such as hydrothermal, co-precipitation, ball-milling, combustion, redox-precipitation, and sol-gel [4] – [8]. Among them, redox-precipitation between KMnO<sub>4</sub> and a reducing agent such as oxalic acid, glycerol, and H<sub>2</sub>O<sub>2</sub> shows good catalytic activity for the complete oxidation of different VOCs molecules like benzene, toluene, formaldehyde, acetone, and isopropanol [8] – [10]. However, the reflux method, which is a promising method to prepare the  $\alpha$ -MnO<sub>2</sub> catalysts in large scales for total oxidation of VOCs, is rarely reported.

Therefore, this study aims to investigate the effect of synthesis methods on the catalytic activity of  $\alpha$ -MnO<sub>2</sub>

**Tóm tắt** - Nghiên cứu này đánh giá ảnh hưởng của phương pháp tổng hợp lên các đặc tính hóa lý và hoạt tính của xúc tác  $\alpha$ -MnO<sub>2</sub> cho phản ứng hoàn toàn isopropanol. Xúc tác được tổng hợp từ các phản ứng oxi hóa khử kết tủa bằng hai phương pháp nhỏ giọt và hồi lưu. Các tính chất đặc trưng được xác định bằng phương pháp nhiễu xạ tia X (XRD), kính hiển vi điện tử SEM và hấp phụ giải hấp nitơ. Kết quả cho thấy phương pháp tổng hợp ảnh hưởng lớn đến tính chất và hoạt tính của xúc tác  $\alpha$ -MnO<sub>2</sub>. Phương pháp nhỏ giọt tạo ra  $\alpha$ -MnO<sub>2</sub> dạng sợi nano với kích thước tinh thể thấp hơn (12 nm), bề mặt riêng (68 m<sup>2</sup>/g) lớn hơn, thể tích xốp cao hơn (0,16 cm<sup>3</sup>/g) và có hiệu quả oxi hóa hoàn toàn isopropanol thành CO<sub>2</sub> tốt hơn khi so sánh với  $\alpha$ -MnO<sub>2</sub> dạng que nano tổng hợp bằng phương pháp hồi lưu. Nhiệt độ chuyển hóa 50% và 90% isopropanol thành CO<sub>2</sub> trên xúc tác này lần lượt là 155°C và 166°C.

**Từ khóa** - MnO<sub>2</sub>; xúc tác; isopropanol; oxi hóa hoàn toàn; VOCs

catalysts in the complete oxidation of isopropanol. In particular, the dropwise and reflux methods were employed to synthesize  $\alpha$ -MnO<sub>2</sub> catalysts via redox-precipitation reactions, and their catalytic performances were compared. The physicochemical properties are evaluated by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and nitrogen adsorption-desorption isotherms.

### 2. Experimental

#### 2.1. Catalyst preparation

##### 2.1.1. Dropwise method

230 mL of the 0.05 M KMnO<sub>4</sub> solution was dropwise added to 100 mL of the solution containing ethanol with a flow rate of 2 mL/min. The molar ratio of ethanol to KMnO<sub>4</sub> ( $R_{\text{Ethanol/KMnO}_4}$ ) is 18. The pH of the reaction mixture varies from 11 to 8. The precipitate was filtered and washed with distilled water (1 L). The obtained solid was dried at 110°C for 16 hours and then calcined at 400°C for 4 hours. The catalyst is denoted as  $\alpha$ -MnO<sub>2</sub>-DW.

##### 2.1.2. Reflux method

1.185 gram of KMnO<sub>4</sub> and 8 mL of acetic acid (AC) (96%) was added to 300 mL of water. The obtained mixture is poured into a flask fitted with a reflux condenser. The reaction is refluxed for 24 hours. The obtained brown precipitate was filtered, washed, dried, and calcined with the same procedure as the dropwise method. The catalyst is denoted as  $\alpha$ -MnO<sub>2</sub>-RF.

## 2.2. Characterization

The phase and crystalline structure of  $\alpha$ -MnO<sub>2</sub> catalysts are characterized by XRD on a Smartlab (Rigaku). The mean crystallite size ( $D_c$ ) is calculated by PDXL software (Rigaku) via the Scherrer equation:  $D_c = K\lambda/\beta\cos\theta$ ; where  $\lambda$  is the wavelength of CuK $\alpha$  radiation,  $\beta$  is full width at half maximum of peaks,  $\theta$  is the Bragg angle, and  $K$  is shape factor. The morphology is observed by SEM via a JSM-6020LV apparatus (Jeol). The adsorption-desorption isotherms are analyzed by ASAP2020 physico-adsorber (Micromeritics). The surface area is determined by BET (Brunauer-Emmett-Teller) theory. The pore volume and pore size distribution are determined from the desorption branch of the isotherms by BJH (Barrett-Joyner-Halenda) method.

## 2.3. Catalytic test

The catalytic test of complete oxidation of isopropanol are evaluated by the same previous procedure [9]. Typically, 0.1 gram of  $\alpha$ -MnO<sub>2</sub> catalyst was load into a microreactor and pretreated at 250°C for 2 hours in a dried air stream to remove moist and CO<sub>2</sub> adsorbed on the catalyst surface. The catalytic test is performed from 30 – 300°C using a gas hourly space velocity (GHSV) of  $\sim 120000\text{ h}^{-1}$  and an air feed stream consisting of synthetic air containing 1000 ppm isopropanol. The isopropanol vapor is generated via passing an air flow into a bubble system (5°C) and is then diluted with another air stream to obtain a total flow of 160 mL/min. The outlet stream is directly connected to a Gas Chromatograph (Agilent). The gas composition is analyzed by FID and TCD detectors. The IPA conversion ( $\eta$ ), acetone yield ( $Y_{\text{Acetone}}$ ), and CO<sub>2</sub> yield ( $Y_{\text{CO}_2}$ ) are calculated by the formula (1), (2), and (3), respectively.

$$\eta = \frac{[C_3H_8O]_{in} - [C_3H_8O]_{out}}{[C_3H_8O]_{in}} \times 100 \quad (1)$$

$$Y_{\text{Acetone}} = \frac{[C_3H_6O]}{[C_3H_8O]_{in}} \times 100 \quad (2)$$

$$Y_{\text{CO}_2} = \frac{[CO_2]}{3 \times [C_3H_8O]_{in}} \times 100 \quad (3)$$

Where,  $[C_3H_8O]_{in}$ ,  $[C_3H_8O]_{out}$  are the concentration of isopropanol in the inlet and outlet streams of microreactor, respectively.  $[CO_2]$  and  $[C_3H_6O]$  are the concentration of CO<sub>2</sub> and acetone, respectively, in the outlet stream of the microreactor.

## 3. Result and discussion

### 3.1. Phase and crystalline structure

Firstly, the XRD technique is used to characterize the phase and crystalline structure of the  $\alpha$ -MnO<sub>2</sub> catalysts synthesized by drop-wise or reflux methods. As shown in Figure 1, all the diffraction peaks are indexed to cryptomelane-type MnO<sub>2</sub> (re-called  $\alpha$ -MnO<sub>2</sub>) (JCPDS card No. 44-0141). The diffraction intensity of  $\alpha$ -MnO<sub>2</sub>-DW is much lower than that of  $\alpha$ -MnO<sub>2</sub>-RF, indicating the lower crystallite size. The mean crystallite size calculated by the Scherrer Equation is 12 nm for  $\alpha$ -MnO<sub>2</sub>-DW and 38 nm for  $\alpha$ -MnO<sub>2</sub>-RF. The low crystallite size of  $\alpha$ -MnO<sub>2</sub>-DW may

favor the diffusion of oxygen, reactant, and product molecules like IPA, acetone, and CO<sub>2</sub> during the oxidation at high temperatures [11].

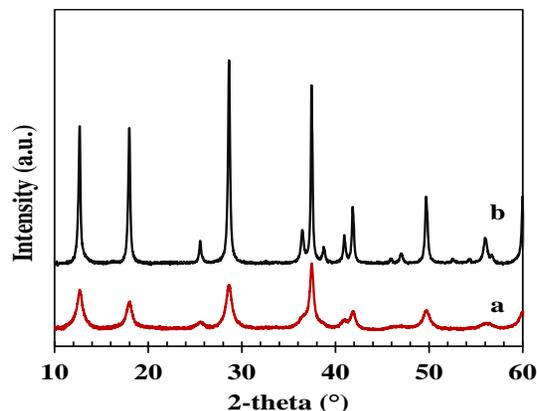


Figure 1. XRD patterns of  $\alpha$ -MnO<sub>2</sub> synthesized by a) dropwise and b) reflux methods using ethanol and acetic acid as reductants, respectively, with  $R_{R/KMnO_4}$  ratio of 18

### 3.2. Morphology

Secondly, the SEM technique is used to observe the morphology of  $\alpha$ -MnO<sub>2</sub> catalysts, as illustrated in Figure 2. The drop-wise method yields the  $\alpha$ -MnO<sub>2</sub>-DW nanofibers while the reflux method generates  $\alpha$ -MnO<sub>2</sub> nanorods with lengths up to 450 nm and a diameter up to 140 nm.

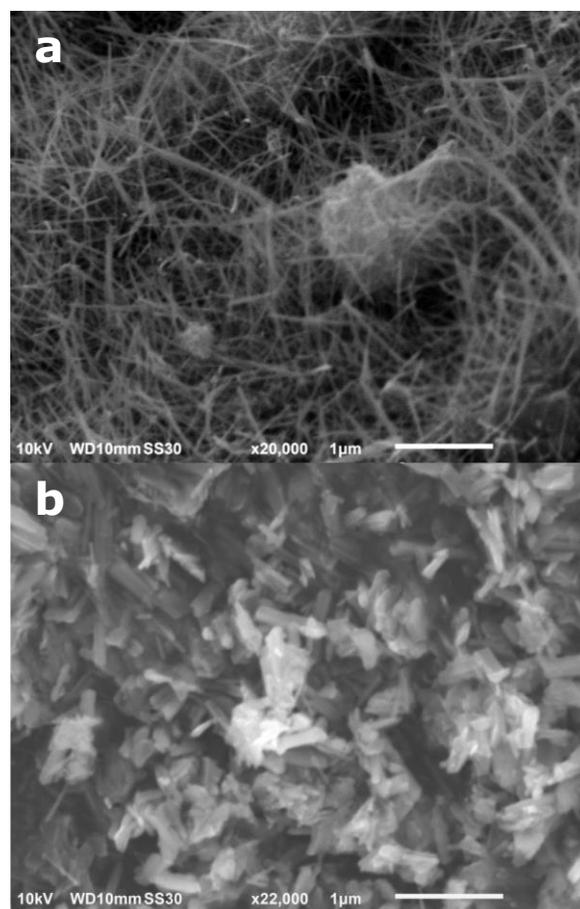
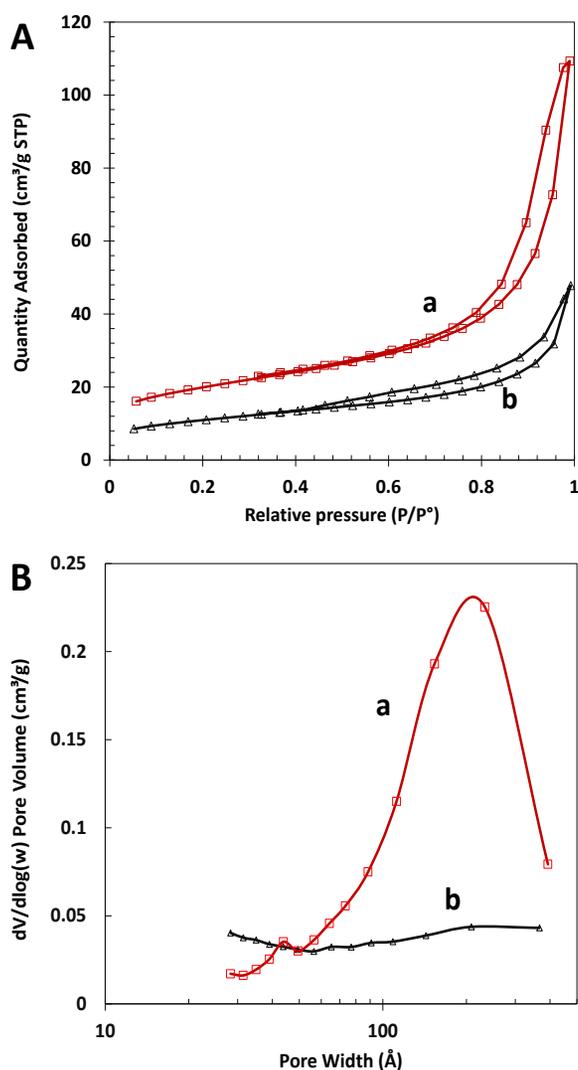


Figure 2. SEM images of a)  $\alpha$ -MnO<sub>2</sub>-DW, and b)  $\alpha$ -MnO<sub>2</sub>-RF

### 3.3. Surface area, pore volume and pore distribution

The adsorption-desorption curves of the  $\alpha$ -MnO<sub>2</sub> catalysts show the type IV isotherm with an H<sub>3</sub> hysteresis loop ranging from P/P<sup>0</sup> of 0.4 to 1.0, as depicted in Figure 3, indicating the presence of parallel plate-shaped mesopores. The pore sizes of  $\alpha$ -MnO<sub>2</sub>-RF catalyst are distributed in the range of 20 Å – 400 Å and reach the maximum at 230 Å, whereas the pore sizes of  $\alpha$ -MnO<sub>2</sub>-MW catalyst vary in a wider range and have much lower volume. The BET surface area and pore volume of the  $\alpha$ -MnO<sub>2</sub>-DW catalyst are 68 m<sup>2</sup>/g and 0.16 cm<sup>3</sup>/g, respectively, which are much higher than those of  $\alpha$ -MnO<sub>2</sub>-RF (35 m<sup>2</sup>/g and 0.07 cm<sup>3</sup>/g, respectively). The high surface area could enhance the number of active sites available for the oxidation reaction, while the large pore volume is believed to facilitate rapid access of isopropanol molecules into the active sites and efficient release of the reaction products during high conversion reaction.



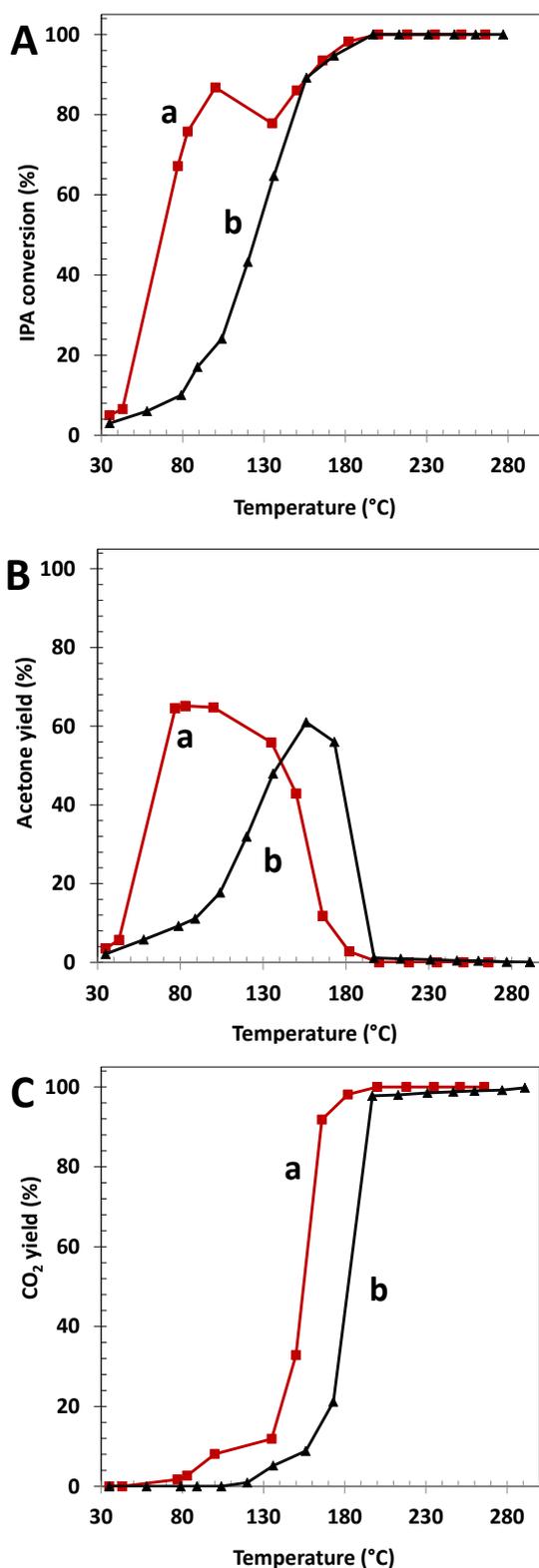
**Figure 3.** A) Nitrogen adsorption-desorption isotherms and B) pore size distribution of  $\alpha$ -MnO<sub>2</sub> synthesized by a) drop-wise and b) reflux methods using ethanol and acetic acid as reductant, respectively

### 3.4. Catalytic performance of complete oxidation of isopropanol

The catalytic activities of oxidation of isopropanol over the  $\alpha$ -MnO<sub>2</sub> catalysts are evaluated in the temperature range of 30 – 300°C. The obtained IPA conversion curve shown in Figure 4, line b illustrates a slight increase of IPA conversion over  $\alpha$ -MnO<sub>2</sub>-RF catalyst when temperature raises from 30 to 80°C, then steeply rises to 95% at 173°C, before slowly reaching 100% at 197°C. The use of  $\alpha$ -MnO<sub>2</sub>-DW catalyst rapidly enhance IPA conversion is to 86.8% at 100°C then decreased to 77.8% at temperatures up to 135°C before increasing to 100% (line b). This can be attributed to the formation of acetone, which possibly partially blocks the active sites and/or the desorption of IPA due to heating [12]. Overall, the conversion of IPA is much better at lower temperatures, below 156°C, compared to  $\alpha$ -MnO<sub>2</sub>-RF. The temperature values corresponding to the 50% and 90% IPA conversions were determined from the IPA conversion curves and denoted as T<sub>50</sub> and T<sub>90</sub>, respectively (Table 1). T<sub>50(CO<sub>2</sub>)</sub> and T<sub>90(CO<sub>2</sub>)</sub> values, which are calculated from the CO<sub>2</sub> yield curves, are also used to assess the complete oxidation activity. In comparison with  $\alpha$ -MnO<sub>2</sub>-RF, the T<sub>50</sub> value of  $\alpha$ -MnO<sub>2</sub>-DW is much lower at 67°C, while the T<sub>90</sub> value is nearly the same. This is consistent with the higher yield acetone of  $\alpha$ -MnO<sub>2</sub>-DW catalyst at low temperature (T ≤ 130°C), as depicted in Figure 3B (line a). CO<sub>2</sub> yield is also enhanced with  $\alpha$ -MnO<sub>2</sub>-DW with T<sub>50(CO<sub>2</sub>)</sub> of 155°C and T<sub>90(CO<sub>2</sub>)</sub> of 166°C, which are much lower than that of  $\alpha$ -MnO<sub>2</sub>-RF, indicating the improvement of catalytic activity toward the complete oxidation. Accordingly, a considerable amount of acetone is produced with a yield of up to 62% by using  $\alpha$ -MnO<sub>2</sub>-DW catalyst. However, at low temperature (T ≤ 130°C), the yield of CO<sub>2</sub> was poor, less than 10%, indicating that the catalyst is only able to convert IPA molecules into the undesired oxygenate compound though the surface oxygen species available on the catalyst surface. At higher temperature than 190°C, the yield of acetone is almost depleted, and the yield of CO<sub>2</sub> is nearly 100%. This indicates that the catalyst can oxidize IPA and acetone molecules into CO<sub>2</sub>, which could be assigned to two reasons: i) High reactivity of surface oxygen molecules/surface oxygen vacancies; ii) The participation of bulk oxygen molecules and oxygen vacancies in catalytic cycles. It can be seen that the  $\alpha$ -MnO<sub>2</sub>-DW catalyst, which possesses a large surface area and pore volume, demonstrates a better catalytic activity of the oxidation reaction of isopropanol into acetone and CO<sub>2</sub> than that of  $\alpha$ -MnO<sub>2</sub>-RF.

**Table 1.** Properties and catalytic performances of  $\alpha$ -MnO<sub>2</sub> catalysts

Catalysts	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	Catalytic performances			
			T <sub>50</sub> (°C)	T <sub>90</sub> (°C)	T <sub>50(CO<sub>2</sub>)</sub> (°C)	T <sub>90(CO<sub>2</sub>)</sub> (°C)
$\alpha$ -MnO <sub>2</sub> -DW	68.3	0.16	67	158	155	166
$\alpha$ -MnO <sub>2</sub> -RF	35.0	0.07	125	158	182	195



**Figure 4.** A) Light-off curves representative of IPA conversion versus temperature; B) Acetone selectivity; and C) CO<sub>2</sub> selectivity over; a)  $\alpha$ -MnO<sub>2</sub>-DW and b)  $\alpha$ -MnO<sub>2</sub>-RF catalysts

#### 4. Conclusion

To conclude,  $\alpha$ -MnO<sub>2</sub> catalysts were successfully synthesized through the oxidation-reduction precipitation reactions between KMnO<sub>4</sub> and acetic acid or ethanol with the molar ratio of Ac/KMnO<sub>4</sub> (or ethanol/KMnO<sub>4</sub>) of 15 using reflux and dropwise methods, respectively. The dropwise method proved to be a good way to prepare the  $\alpha$ -MnO<sub>2</sub> catalyst ( $\alpha$ -MnO<sub>2</sub>-DW) as it results in nanofibers with lower crystallite size, higher surface area, pore volume, and better catalytic performance for the complete oxidation of isopropanol into CO<sub>2</sub> compared to the reflux method. These findings provide valuable insights into the development of  $\alpha$ -MnO<sub>2</sub>-based catalysts for the complete oxidation of VOCs and contribute to reducing air pollution caused by VOC emissions.

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