



# Enhanced effect of water vapor on complete oxidation of formaldehyde in air with ozone over $\text{MnO}_x$ catalysts at room temperature

De-Zhi Zhao<sup>a</sup>, Chuan Shi<sup>a</sup>, Xiao-Song Li<sup>a</sup>, Ai-Min Zhu<sup>a,\*</sup>, Ben W.-L. Jang<sup>b,\*\*</sup>

<sup>a</sup> Laboratory of Plasma Physical Chemistry, School of Physics and Optoelectronic Engineering & School of Chemistry, Dalian University of Technology, Dalian 116024, China

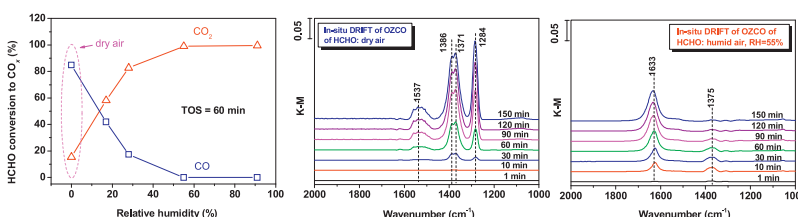
<sup>b</sup> Department of Chemistry, Texas A&M University Commerce, PO Box 3011, Commerce, TX 75429, United States

## HIGHLIGHTS

- ▶ Enhanced effect of  $\text{H}_2\text{O}$  on OZCO of HCHO to  $\text{CO}_2$  and reaction stability is reported.
- ▶ The carbonates formed on catalysts increased gradually with TOS in the dry stream.
- ▶ Almost no accumulation of carbonates on catalysts was observed in the humid stream.
- ▶ Reaction pathways are proposed for OZCO of HCHO in dry and humid air streams.

## GRAPHICAL ABSTRACT

In humid air streams ( $\text{RH} \geq 55\%$ ),  $\sim 100\%$  of formaldehyde could be oxidized into  $\text{CO}_2$  by ozone over  $\text{MnO}_x$  catalysts and the reaction stability was significantly enhanced. On  $\text{MnO}_x$  catalysts, the carbonate species increased gradually with TOS in the dry stream and almost no accumulation of carbonate species was observed in the humid stream.



## ARTICLE INFO

### Article history:

Received 9 July 2012

Received in revised form 14 August 2012

Accepted 5 September 2012

Available online 12 September 2012

### Keywords:

Catalytic oxidation

Ozone

Enhanced effect

Formaldehyde removal

## ABSTRACT

At room temperature, the enhanced effect of water vapor on ozone catalytic oxidation (OZCO) of formaldehyde to  $\text{CO}_2$  over  $\text{MnO}_x$  catalysts and the reaction stability was reported. In a dry air stream, only below 20% of formaldehyde could be oxidized into  $\text{CO}_2$  by  $\text{O}_3$ . In humid air streams ( $\text{RH} \geq 55\%$ ),  $\sim 100\%$  of formaldehyde were oxidized into  $\text{CO}_2$  by  $\text{O}_3$  and the reaction stability was significantly enhanced. Meanwhile, in situ Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of OZCO of HCHO demonstrate that the amount of both monodentate and bidentate carbonate species on  $\text{MnO}_x$ , in the dry stream, increased gradually with time on stream (TOS). However, in the humid stream, almost no accumulation of carbonate species on the catalysts was observed. To clarify the enhanced mechanism, formaldehyde surface reactions and  $\text{CO}_2$  adsorption/desorption on the fresh,  $\text{O}_3$  and  $\text{O}_3 + \text{H}_2\text{O}$  treated  $\text{MnO}_x$  catalysts were examined comparatively.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Ozone catalytic oxidation (OZCO) method, in which the reaction proceeds at room temperature using a non-noble metal catalyst, is effective for the removal of volatile organic compounds (VOCs), especially at a low concentration level. The process has been

extensively studied for the removal of various kinds of VOCs due to its simplicity and low cost operation at room temperature [1–7]. In most of these studies, unsupported and supported manganese oxides ( $\text{MnO}_x$ ) were employed as the catalysts [8–11], because manganese oxide catalysts are highly active for  $\text{O}_3$  decomposition [12,13]. However, the key problems in the OZCO method are catalyst deactivation and incomplete oxidation byproducts, such as CO [1]. Einaga et al. reported that water vapor could suppress the catalyst deactivation in OZCO of benzene over  $\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3$  catalysts, and promoted complete oxidation of formate species formed on the catalyst surface [14]. They recently reported that the stability of OZCO of benzene at room temperature was achieved in

\* Corresponding author. Fax: +86 411 84706094.

\*\* Corresponding author. Fax: +1 903 468 6020.

E-mail addresses: [amzhu@dlut.edu.cn](mailto:amzhu@dlut.edu.cn) (A.-M. Zhu), [Ben.Jang@tamuc.edu](mailto:Ben.Jang@tamuc.edu) (B.W.-L. Jang).

the presence of water vapor using manganese oxides supported on ultra-stable Y (USY) zeolite catalysts. But, CO still accounted for 10% of CO<sub>x</sub> produced [10].

Formaldehyde (HCHO) is a typical volatile organic compound (VOC) in indoor air and can cause serious health disorders for human beings [15,16]. However, very few studies have been reported for the removal of formaldehyde in air using the OZCO method [11,17]. In our previous communication [11], complete oxidation of formaldehyde with ~100% selectivity to CO<sub>2</sub> was reported using the OZCO method in humid air over MnO<sub>x</sub> catalysts at room temperature. Generally, in normal catalytic oxidation reactions, water vapor has a marked poisoning effect on the catalysts, especially at room temperature [18,19]. Herein, the enhanced effect of water vapor on OZCO of formaldehyde to CO<sub>2</sub> over MnO<sub>x</sub> catalysts at room temperature and the reaction stability is reported. Moreover, HCHO surface reactions and CO<sub>2</sub> adsorption/desorption on the fresh, O<sub>3</sub> and O<sub>3</sub> + H<sub>2</sub>O treated MnO<sub>x</sub> catalysts are examined comparatively to clarify the enhanced mechanism of water vapor.

## 2. Experimental

### 2.1. Catalyst preparation

MnO<sub>x</sub> catalysts were prepared by the redox reaction of potassium permanganate (KMnO<sub>4</sub>) with manganese(II) acetate (Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O) [11,18]. A solution of KMnO<sub>4</sub> (4.75 g in 50 ml H<sub>2</sub>O) was added dropwise to a solution of Mn(CH<sub>3</sub>COO)<sub>2</sub> (11.03 g in 30 ml H<sub>2</sub>O) under stirring at room temperature for 24 h. The black slurry was filtered, washed with deionized water, and dried at 100 °C for 6 h. The resultant precipitate was crushed and calcined in air at 300 °C for 3 h. The obtained powders of MnO<sub>x</sub> catalysts were in turn grounded, tableted, crushed and sieved to 20–40 mesh.

### 2.2. BET and XRD characterization

The Brunauer Emmett Teller (BET) surface area of MnO<sub>x</sub> catalysts was 208 m<sup>2</sup>/g, as measured by N<sub>2</sub> adsorption-desorption isotherms at −196 °C (QuadraSorb SI, Quantachrome, USA). The catalysts mainly showed amorphous in X-ray diffraction (XRD) characterization using an X-ray diffractometer (D/Max-2400, Rigaku, Japan) [11].

### 2.3. OZCO tests on MnO<sub>x</sub> catalysts

The schematic diagram of the experimental setup is shown in Fig. 1. OZCO of formaldehyde experiments were performed in a U-shape quartz tubular reactor (i.d. 6 mm) with 100 mg of MnO<sub>x</sub> catalysts, placed in a water bath at 25 °C. Formaldehyde was produced via catalytic depolymerization of trioxymethylene vapor in a N<sub>2</sub>-diluted gas stream at 160 °C over glass pellets coated with 85% phosphoric acid [11,20,21]. Water vapor was carried by N<sub>2</sub> and O<sub>2</sub> flowing through a bubbler placed in a water bath at 25 °C. The water concentration was measured online using a dew point hygrometer (635-2, Testo, Germany), which was expressed as relative humidity (RH) at 25 °C. The desired RH was adjusted by varying the carrier gas flow rate(s). The reaction gas mixture, dry or humid, simulated air (80% N<sub>2</sub> + 20% O<sub>2</sub>) containing HCHO and O<sub>3</sub> was flowed through the catalyst bed at a total flow rate of 500 ml/min, which corresponded to a gas hourly space velocity (GHSV) of 2 × 10<sup>5</sup> h<sup>−1</sup>. HCHO initial concentration was measured by its conversion to CO<sub>2</sub> using a homemade VOC-to-CO<sub>2</sub> converter (10%Cu/10%Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalysts) at 400 °C, and the concentration of CO<sub>2</sub> was monitored online by a CO<sub>x</sub> analyzer (S710, Sick-Maihak, Germany) [11,20]. The reason for measuring HCHO concentration by this method was explained in our previous paper [20]. Ozone was generated from O<sub>2</sub> by a homemade ozone generator. High (>500 ppm) and low (≤500 ppm)

concentrations of O<sub>3</sub> were monitored online by an ozone analyzer (Mini-HiCon, INUSA, USA) and a Fourier transform-infrared (FT-IR) spectrometer (Nicolet-Antaris IGS Analyzer, Thermo, USA), respectively. The concentrations of CO and CO<sub>2</sub> in the reactor outlet gas were measured online using the CO<sub>x</sub> analyzer. The definitions of HCHO conversion to CO and CO<sub>2</sub>, and O<sub>3</sub> decomposition were as follows, respectively:

$$\text{HCHO conversion to CO}_2 \text{ (\%)} = \frac{C_{\text{CO}_2}^{\text{out}}}{C_{\text{HCHO}}^{\text{in}}} \times 100\% \quad (1)$$

$$\text{HCHO conversion to CO (\%)} = \frac{C_{\text{CO}}^{\text{out}}}{C_{\text{HCHO}}^{\text{in}}} \times 100\% \quad (2)$$

$$\text{O}_3 \text{ decomposition (\%)} = \frac{C_{\text{O}_3}^{\text{in}} - C_{\text{O}_3}^{\text{out}}}{C_{\text{O}_3}^{\text{in}}} \times 100\% \quad (3)$$

where  $C_{\text{CO}}^{\text{out}}$  and  $C_{\text{CO}_2}^{\text{out}}$  are the concentrations of CO and CO<sub>2</sub> in the reactor outlet gas, respectively;  $C_{\text{HCHO}}^{\text{in}}$  is the initial concentration of HCHO;  $C_{\text{O}_3}^{\text{in}}$  and  $C_{\text{O}_3}^{\text{out}}$  are the concentrations of O<sub>3</sub> in the reactor inlet and outlet gas, respectively.

Before OZCO experiments, all catalysts were pretreated in a dry simulated air stream at 300 °C for 1 h, and then cooled down to room temperature in the same air stream.

### 2.4. In situ DRIFT OZCO reaction

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on an FT-IR spectrometer (Tensor 27, Bruker, Germany) equipped with a liquid N<sub>2</sub> cooled MCT detector. Scans were collected from 4000 cm<sup>−1</sup> to 1000 cm<sup>−1</sup> with a resolution of 4 cm<sup>−1</sup> and accumulating 128 scans. MnO<sub>x</sub> catalysts were placed in a DRIFT cell equipped with CaF<sub>2</sub> window. The experimental procedures of in situ DRIFT OZCO reaction were similar with those in Section 2.3. The total flow rate and gas mixture used are 100 ml/min and 80 ppm of HCHO and 700 ppm of ozone in dry or humid simulated air streams.

### 2.5. HCHO surface reaction, TPO, CO<sub>2</sub> adsorption/desorption and TPD of the used catalysts experiments

Three different catalysts, including fresh, ozone treated and O<sub>3</sub> + H<sub>2</sub>O treated MnO<sub>x</sub> catalysts, were investigated for HCHO surface reaction, including in situ DRIFT analysis and product analysis for CO and CO<sub>2</sub>. The procedures to prepare the ozone treated catalyst include flowing 500 ml/min (for product analysis) or 100 ml/min (for in situ DRIFT analysis) of a dry simulated air stream containing 80 ppm O<sub>3</sub> to MnO<sub>x</sub> catalysts at room temperature for 30 min followed by purging with a dry simulated air stream at the same temperature for 30 min. Subsequently, a 500 ml/min (for product analysis) or 100 ml/min (for in situ DRIFT analysis) dry simulated air stream containing HCHO was switched to the catalyst for in situ DRIFT analysis of catalyst surface and gas product analysis with the CO<sub>x</sub> analyzer. The procedures to prepare the O<sub>3</sub> + H<sub>2</sub>O treated catalyst are the same as the ozone treated sample except that the step includes O<sub>3</sub> plus H<sub>2</sub>O (RH = 55%) instead of ozone only.

Temperature Programmed Oxidation (TPO) experiments were carried out over the catalysts, including fresh, ozone treated and O<sub>3</sub> + H<sub>2</sub>O treated MnO<sub>x</sub> catalysts, after the HCHO surface reaction. The catalysts were purged with a dry simulated air stream at a flow rate of 100 ml/min at room temperature for 30 min before TPO. The temperature was raised linearly from room temperature to 300 °C at 5 °C/min. The gas products were analyzed by the on-line CO<sub>x</sub> analyzer.

CO<sub>2</sub> adsorption/desorption experiments were also carried out over three catalysts, including fresh, ozone treated and O<sub>3</sub> + H<sub>2</sub>O

Download English Version:

<https://daneshyari.com/en/article/577764>

Download Persian Version:

<https://daneshyari.com/article/577764>

[Daneshyari.com](https://daneshyari.com)