室温 MnO_x 上 O_3 氧化脱除空气中甲醛赵德志¹, 丁天英², 李小松¹, 刘景林¹, 石川¹, 朱爱民^{1,*}¹大连理工大学等离子体物理化学实验室, 辽宁大连 116024²大连理工大学机械工程学院, 辽宁大连 116024

摘要: 采用氧化还原法制备了 MnO_x 催化剂, X 射线衍射结果表明其主要为无定形结构。在甲醛和臭氧浓度分别为 137 和 642 mg/m^3 , 相对湿度为 56% (25 °C), GHSV 为 $2 \times 10^5 \text{ h}^{-1}$ 条件下, MnO_x 催化剂上 O_3 可将甲醛全部氧化为 CO_2 , 反应 150 min 内甲醛转化率和 CO_2 选择性一直保持在~100%。另外, 当臭氧与甲醛的摩尔比约为 2:3, 即显著低于化学计量比时, CO_2 选择性仍可达~100%。采用傅里叶变换红外光谱仪在线分析了甲醛氧化反应产物, 未检测到任何副产物, 从而确认了 MnO_x 催化剂上 O_3 对甲醛的完全氧化。

关键词: 氧化锰催化剂; 甲醛; 完全氧化; 臭氧

中图分类号: O643 **文献标识码:** A

收稿日期: 2011-11-28. 接受日期: 2011-12-27.

*通讯联系人. 电话/传真: (0411)84706094; 电子信箱: amzhu@dlut.edu.cn

基金来源: 国家自然科学基金 (11079013); 国家高技术研究发展计划 (863 计划, 2007AA06Z311).

本文的英文电子版(国际版)由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).

Ozone Catalytic Oxidation of HCHO in Air over MnO_x at Room TemperatureZHAO Dezhi¹, DING Tianying², LI Xiaosong¹, LIU Jinglin¹, SHI Chuan¹, ZHU Aimin^{1,*}¹Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian 116024, Liaoning, China²School of Mechanical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

Abstract: The complete oxidation of HCHO in air with O_3 over MnO_x catalysts at room temperature was studied. The MnO_x catalysts were prepared by a redox method. The catalysts showed amorphous patterns in X-ray diffraction characterization. Formaldehyde in simulated air containing 137 mg/m^3 HCHO with 56% relative humidity (RH, 25 °C) was totally oxidized to CO_2 by 642 mg/m^3 O_3 over the MnO_x catalysts at GHSV (gas hourly space velocity) = $2 \times 10^5 \text{ h}^{-1}$. The formaldehyde conversion and CO_2 selectivity were maintained at ~100% during 150 min time-on-stream. The effect of the molar ratio of O_3 to HCHO was also investigated. At a O_3 to HCHO molar ratio of 2:3, which was significantly lower than the stoichiometric ratio, a CO_2 selectivity of 100% was still achieved. No byproduct was detected during HCHO oxidation with O_3 over the MnO_x catalysts using an online Fourier transform infrared spectrometer.

Key words: manganese oxide; formaldehyde; complete oxidation; ozone

Received 28 November 2011. Accepted 27 December 2011.

*Corresponding author. Tel/Fax: +86-411-84706094; E-mail: amzhu@dlut.edu.cn

This work was supported by the National Natural Science Foundation of China (11079013) and the National High Technology Research and Development Program (863 Program, 2007AA06Z311).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

甲醛是一种典型的室内挥发性有机化合物 (VOCs), 对人体的危害很大。脱除甲醛的方法有吸附法、光催化氧化法、等离子体氧化法、催化氧化法和臭氧催化氧化法等。其中, 吸附法仅将甲醛从

气相转移到固相, 容易造成二次污染, 且吸附剂受吸附容量的限制而很快失效^[1,2]; 光催化氧化法需要紫外光源和薄膜型光催化剂, 反应速率较低^[3]; 等离子体氧化法存在能耗高和二次副产物等问题^[4]; 催化

氧化法可在室温下进行, 但需要昂贵的贵金属催化剂^[5,6]. 而臭氧催化氧化法具有不需要贵金属催化剂且在室温下进行等优点, 因而近年来广泛应用于脱除苯^[7]和甲苯^[8]等 VOCs 污染物. 该法大多采用负载或非负载的氧化锰 (MnO_x) 基催化剂^[9,10], 这是因为氧化锰是一种高活性的臭氧分解催化剂^[11]. 然而对空气中甲醛污染物的脱除, 除光催化结合臭氧的报道^[12]外, 采用臭氧催化氧化法的很少^[13], 且仅考察了甲醛的脱除率, 未涉及反应产物. 至今尚未见臭氧催化完全氧化甲醛的报道.

本文首次在室温下将 MnO_x 催化剂用于臭氧完全氧化脱除湿空气中甲醛, 考察了臭氧与甲醛摩尔比的影响, 并采用傅里叶红外吸收光谱 (FT-IR) 对反应产物进行在线分析.

MnO_x 催化剂通过 KMnO_4 和 $\text{Mn}(\text{CH}_3\text{COO})_2$ 氧化还原反应制得, 其中 MnO_4^- 与 Mn^{2+} 的摩尔比为 0.72. 将高锰酸钾溶液逐滴加入到醋酸锰溶液中, 室温水浴搅拌 24 h, 得到黑色的悬浊液. 抽滤并经去离子水洗涤后, 于 100 °C 干燥 6 h. 所得样品经粉碎后在空气中于 300 °C 焙烧 3 h, 研磨, 压片, 破碎, 过筛, 即得所需催化剂 (20~40 目).

采用 X 射线衍射 (XRD, 日本 Rigaku D/Max-2400) 表征所制 MnO_x 催化剂. $\text{Cu K}\alpha$ 射线源 ($\lambda = 0.1542 \text{ nm}$), 管电压 40 kV, 管电流 100 mA.

臭氧催化氧化脱除甲醛反应在内径为 6 mm 的 U 形石英管固定床反应器中进行. 将反应器置于恒温水浴中, 使其保持在室温. 实验所需的各路气体流量均由质量流量计调控, 混合后流入反应器. 甲醛气体通过 N_2 携带三聚甲醛蒸气在涂有 85% 浓磷酸的玻璃小球上于 160 °C 催化解聚产生^[14]. 湿度通过氮气鼓泡携带室温水蒸气来调节, 并由温湿度计 (德国 Testo 635-2) 在线监测. 将入口气体通过一个装有 10%Cu/10%Mn/ $\gamma\text{-Al}_2\text{O}_3$ 催化剂的转化炉 (400 °C), 使甲醛完全转化为 CO_2 , 在线检测出口 CO_2 浓度, 由此得出反应器入口气体中甲醛浓度^[14]. 反应器出口气体中 CO 和 CO_2 的浓度采用 CO_x 红外气体分析仪 (德国 Sick-Maihak S710) 在线检测. 臭氧通过自制的臭氧发生器产生, 其浓度通过臭氧分析仪 (美国 INUSA Mini-HiCon) 在线检测. 同时, 采用傅里叶变换红外光谱仪 (美国 Thermo Nicolet-Antaris IGS Analyzer) 对反应器出口气体进

行在线检测, 气体池体积 200 ml, 光程 2 m, 检测器 MCT-A, 光谱分辨率 2 cm^{-1} , 扫描次数 64.

甲醛转化率 (X_{HCHO})、臭氧转化率 (X_{O_3}) 以及 CO_2 选择性 (S_{CO_2}) 分别定义如下:

$$X_{\text{HCHO}} = (\text{C}_{\text{CO}} + \text{C}_{\text{CO}_2}) / \text{C}_{\text{HCHO}}^{\text{in}} \times 100\%$$

$$X_{\text{O}_3} = \text{C}_{\text{O}_3}^{\text{out}} / \text{C}_{\text{O}_3}^{\text{in}} \times 100\%$$

$$S_{\text{CO}_2} = \text{C}_{\text{CO}_2} / (\text{C}_{\text{CO}} + \text{C}_{\text{CO}_2}) \times 100\%$$

其中, C_{CO} 和 C_{CO_2} 分别为反应器出口气体中 CO 和 CO_2 浓度, $\text{C}_{\text{HCHO}}^{\text{in}}$ 为反应器入口气体中甲醛浓度, $\text{C}_{\text{O}_3}^{\text{in}}$ 和 $\text{C}_{\text{O}_3}^{\text{out}}$ 分别为反应器入口和出口气体中 O_3 的浓度.

图 1 为 MnO_x 催化剂的 XRD 谱. 可以看出, 样品在 $2\theta = 37.5^\circ$ 处出现微弱的衍射峰, 对应于隐钾锰矿 ($\text{KMn}_8\text{O}_{16}$) (211) 晶面^[15,16], 表明所制 MnO_x 催化剂主要以无定形结构存在, 仅含有少量的隐钾锰矿物相, 与文献[17]结果一致.

图 1 MnO_x 催化剂的 XRD 谱

Fig. 1. XRD pattern of the MnO_x catalyst.

图 2 为相对湿度 $\text{RH} = 56\%$ (25 °C), 空速 $\text{GHSV} = 2 \times 10^5 \text{ h}^{-1}$, 甲醛和臭氧浓度分别为 137 和 642 mg/m^3 时 MnO_x 催化剂上 O_3 和甲醛的转化率以及 CO_2 选择性随反应时间的变化. 由图可见, MnO_x 催化剂上 O_3 可将甲醛全部氧化为 CO_2 , 反应 150 min 内, 甲醛转化率和 CO_2 选择性一直保持在 ~100%, 且未检测到 CO 生成. 由此可见, MnO_x 催化剂具有优良的催化臭氧完全氧化甲醛能力. 另外, O_3 转化率由初始的 100% 降低到 10 min 时的 80%, 随后稍有降低, 至 60 min 后基本稳定在 73% 左右. 需要说明的是, 臭氧和含甲醛的模拟空气混合气流在不流经催化剂床层时, 甲醛和 O_3 几乎不发生反应, 故臭氧氧化甲醛气相反应可以忽略.

图2 MnO_x 催化剂上臭氧和甲醛的转化率以及 CO_2 选择性随时间的变化

Fig. 2. Time plots for conversions of HCHO and ozone and CO_2 selectivity over MnO_x catalysts. Reaction conditions: 100 mg catalysts, flow rate of simulated air 500 ml/min, RH = 56% (25 °C), GHSV = $2 \times 10^5 \text{ h}^{-1}$, HCHO 137 mg/m^3 , ozone 642 mg/m^3 , room temperature.

为进一步确证 MnO_x 的催化作用, 图3给出了臭氧和含甲醛的模拟空气混合后流经石英砂床层时 O_3 和甲醛的浓度随时间的变化. 由图可见, 甲醛浓度几乎不变, 而 O_3 浓度在初始 5 min 由 857 mg/m^3 降至 763 mg/m^3 , 但随即迅速回升, 并在 10 min 后一直基本稳定在 850 mg/m^3 左右. 这说明 O_3 对甲醛的完全氧化无疑应归因于 MnO_x 的催化作用.

图3 石英砂上臭氧和甲醛的浓度随时间的变化

Fig. 3. Time plots for HCHO and ozone concentrations over quartz sand. Reaction conditions: 160 mg quartz sand (20–40 mesh), flow rate of simulated air 500 ml/min, RH = 51% (25 °C), GHSV = $2 \times 10^5 \text{ h}^{-1}$, room temperature.

图4为 RH = 56% (25 °C), GHSV = $2 \times 10^5 \text{ h}^{-1}$ 条件下, 反应器入口臭氧与甲醛的摩尔比分别约为 2:3 ($C_{\text{O}_3}^{\text{in}} = 128 \text{ mg/m}^3$, $C_{\text{HCHO}}^{\text{in}} = 122 \text{ mg/m}^3$) 和 3:1 ($C_{\text{O}_3}^{\text{in}} = 642 \text{ mg/m}^3$, $C_{\text{HCHO}}^{\text{in}} = 137 \text{ mg/m}^3$) 时, MnO_x 催化剂上 O_3 氧化甲醛的转化率对比. 由图可以看出, 当臭氧与甲醛的摩尔比从 3:1 降至 2:3 时, 即从高于化学计量比 (等于 2, 化学方程式 $2\text{O}_3 + \text{HCHO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{O}_2$) 降至显著低于该值时, 甲醛转化率从约为 100% 降至 58%, 但 CO_2 的选择性仍然为 100%. 这说明 MnO_x 催化剂上甲醛完全氧化为 CO_2 并非由于 O_3 过量所致, 而应归因于 MnO_x 优良的催化性能. 另外, O_3 转化率随臭氧与甲醛摩尔比的升高而下降.

图4 不同臭氧与甲醛摩尔比下 MnO_x 催化剂上臭氧和甲醛转化率以及 CO_2 选择性

Fig. 4. Conversions of HCHO and ozone and CO_2 selectivity at different molar ratios of O_3 to HCHO over MnO_x catalysts. Reaction conditions: 100 mg catalysts, flow rate of simulated air 500 ml/min, RH = 56% (25 °C), GHSV = $2 \times 10^5 \text{ h}^{-1}$, room temperature. Data were taken at 60 min.

为了确认该反应是否有副产物生成, 采用 FT-IR 对反应产物进行了在线分析, 结果见图5. 可以看出, 反应器出口气体中除主产物 CO_2 (2360 cm^{-1}) 和剩余的 O_3 (1060 和 2120 cm^{-1}) 外, 未检测到甲酸 (1107, 1775 和 2921 cm^{-1}) 和 CO (2180 cm^{-1}) 等副产物, 与前文结果一致.

综上所述, 采用氧化还原法制备的无定形 MnO_x 催化剂在本文所考察的条件下, 可催化 O_3 完全氧化甲醛为 CO_2 . 当臭氧与甲醛摩尔比降至约为 2:3, 即显著低于化学计量比时, 虽然甲醛转化率降至 58%, 但 CO_2 的选择性仍可达 ~100%. 另外,

图5 MnO_x 催化剂上臭氧氧化甲醛反应产物的 FT-IR 谱
Fig. 5. FT-IR spectra of the product of HCHO oxidation with O_3 over MnO_x catalysts. Reaction conditions were the same as those in Fig. 2.

MnO_x 催化剂上 O_3 催化氧化甲醛反应产物中, 未检测到任何副产物, 从而确认了甲醛的完全氧化。

参 考 文 献

- 李晶, 李忠, 刘冰, 夏启斌, 奚红霞. 化学工程学报 (Li J, Li Zh, Liu B, Xia Q B, Xi H X. *Chin J Chem Eng*), 2008, **16**: 871
- Domingo-García M, Fernández-Morales I, López-Garzón F J, Moreno-Castilla C, Pérez-Mendoza M. *Langmuir*, 1999, **15**: 3226
- Di L B, Li X S, Shi C, Xu Y, Zhao D Z, Zhu A M. *J Phys D*, 2009, **42**: 032001
- Ding H X, Zhu A M, Lu F G, Xu Y, Zhang J, Yang X F. *J Phys D*, 2006, **39**: 3603
- Tang X F, Chen J L, Huang X M, Xu Y D, Shen W J. *Appl Catal B*, 2008, **81**: 115
- Huang H B, Leung D Y C. *J Catal*, 2011, **280**: 60
- Einaga H, Futamura S. *J Catal*, 2006, **243**: 446
- 龙丽萍, 赵建国, 杨利娟, 付名利, 吴军良, 黄碧纯, 叶代启. 催化学报 (Long L P, Zhao J G, Yang L X, Fu M L, Wu J L, Huang B Ch, Ye D Q. *Chin J Catal*), 2011, **32**: 904
- Harling A M, Glover D J, Whitehead J C, Zhang K. *Appl Catal B*, 2009, **90**: 157
- Einaga H, Teraoka Y, Ogas A. *Catal Today*, 2011, **164**: 571
- Oyama S T. *Catal Rev-Sci Eng*, 2000, **42**: 279
- 齐虹, 孙德智, 迟国庆. 哈尔滨工业大学学报 (Qi H, Sun D Z, Chi G Q. *J Harbin Inst Technol*), 2006, **38**: 1051
- 杨俊鹏, 史文晶, 施建伟, 上官文峰. 分子催化 (Yang J P, Shi W J, Shi J W, Shangguan W F. *J Mol Catal (China)*), 2009, **23**: 334
- Zhao D Z, Li X S, Shi C, Fan H Y, Zhu A M. *Chem Eng Sci*, 2011, **66**: 3922

- Wang R H, Li J H. *Catal Lett*, 2009, **131**: 500
- Sidheswaran M A, Destailhats H, Sullivan D P, Larsen J, Fisk W J. *Appl Catal B*, 2011, **107**: 34
- Njagi E C, Chen C H, Genuino H, Galindo H, Huang H, Suib S L. *Appl Catal B*, 2010, **99**: 103

英 译 文

English Text

Formaldehyde (HCHO) is a typical volatile organic compound (VOC) in indoor air and can cause serious health disorders for human beings. A number of studies have been made for removing formaldehyde from gas streams using adsorption, photocatalytic oxidation, plasma oxidation, catalytic oxidation, and ozone catalytic oxidation (OZCO) methods. For the adsorption method, formaldehyde is only transferred from the gas phase to a solid phase without being destroyed, which can potentially result in secondary pollution. Moreover, the capacity of the adsorbent is limited [1,2]. For the photocatalytic oxidation method, an ultraviolet light source and photocatalysts in the form of films are required, and the reaction rate is relatively low [3]. For the plasma oxidation method, the problems are high energy cost and harmful byproducts [4]. For the catalytic oxidation method, noble metal catalysts are required for formaldehyde removal at room temperature [5,6]. Recently, the OZCO method, in which the reaction proceeds at room temperature and non-noble metal catalysts are used, has been extensively studied for the removal of various kinds of VOCs such as benzene [7] and toluene [8]. In most of these studies, unsupported and supported manganese oxides (MnO_x) were employed as the catalyst [9,10] because manganese oxide catalysts are highly active for O_3 decomposition [11]. However, for the OZCO of formaldehyde, except for studies on photocatalytic oxidation combined with O_3 [12], there has been only one report [13]. In this literature report [13], the removal efficiency of formaldehyde was investigated, but the reaction products were not given. Therefore, the OZCO of formaldehyde to CO_2 for purifying air has not been completely reported.

Here, the complete oxidation of HCHO in air with O_3 over MnO_x catalysts at room temperature is reported. The effect of the molar ratio of O_3 to HCHO was investigated. An online Fourier transform infrared spectrometer (FT-IR) was used to detect the possible gaseous products of OZCO of formaldehyde.

The MnO_x catalysts were prepared by the redox reaction of potassium permanganate (KMnO_4) with manganese (II) acetate ($\text{Mn}(\text{CH}_3\text{COO})_2$) using 0.72 molar ratio of MnO_4^- to Mn^{2+} . A solution of KMnO_4 was added dropwise to a solution of $\text{Mn}(\text{CH}_3\text{COO})_2$ under stirring at room temperature for 24 h. The black slurry was filtered, washed with deion-

ized water, and dried at 100 °C for 6 h. The resultant precipitate was crushed and calcined in air for 3 h at 300 °C. The powders of the MnO_x catalyst obtained were ground, made into tablets, crushed, and sieved to 20–40 mesh.

X-ray diffraction (XRD) patterns were obtained using a X-ray diffractometer (D/Max-2400, Rigaku, Japan). The wavelength of $\text{Cu } K_\alpha$ radiation used was 0.1542 nm and the beam voltage and current were 40 kV and 100 mA, respectively.

OZCO of HCHO was carried out in a fixed-bed reactor. The catalytic reactor was a U-shape quartz tube (i.d. 6 mm) placed in a water bath at room temperature. The gas flow rates were adjusted and controlled by mass flow controllers (SevenStar Co., China). A feed gas mixture of O_3 and HCHO as simulated air was flowed into the reactor. The formaldehyde was produced by the catalytic depolymerization of trioxymethylene vapor in a N_2 diluted gas stream at 160 °C over glass pellets coated with 85% phosphoric acid [14]. Water vapor was carried into the gas stream by passing N_2 through a bubbler in a water bath at room temperature. The humidity was measured online using a dew point hygrometer (635-2, Testo, Germany). The CO and CO_2 concentrations were measured online using an infrared absorption spectrometer (S710, Sick-Maihak, Germany). HCHO was measured by its conversion to CO_2 using a homemade VOC-to- CO_2 converter (10%Cu/10%Mn/ γ - Al_2O_3 catalysts) at 400 °C [14]. Ozone was synthesized from O_2 by a homemade ozone generator and was monitored by an ozone analyzer (Mini-HiCon, INUSA, USA). An online FT-IR spectrometer (Nicolet-Antaris IGS Analyzer, Thermo, USA) equipped with a 2 m optical path length gas cell (volume 200 ml) and an MCT-A detector was used to determine possible byproducts in the reactor outlet gas. The FT-IR spectra were averaged over 64 scans at a resolution of 2 cm^{-1} .

The conversions of HCHO (X_{HCHO}) and O_3 (X_{O_3}), and CO_2 selectivity (S_{CO_2}) were calculated as

$$X_{\text{HCHO}} = (C_{\text{CO}} + C_{\text{CO}_2})/C_{\text{HCHO}}^{\text{in}} \times 100\%$$

$$X_{\text{O}_3} = C_{\text{O}_3}^{\text{out}}/C_{\text{O}_3}^{\text{in}} \times 100\%$$

$$S_{\text{CO}_2} = C_{\text{CO}_2}/(C_{\text{CO}} + C_{\text{CO}_2}) \times 100\%$$

where C_{CO} and C_{CO_2} are the concentrations of CO and CO_2 in the reactor outlet gas, respectively, $C_{\text{HCHO}}^{\text{in}}$ is the concentration of HCHO in the reactor inlet gas, and $C_{\text{O}_3}^{\text{in}}$ and $C_{\text{O}_3}^{\text{out}}$ are the concentrations of O_3 in the reactor inlet and outlet gas, respectively.

The crystal structure of the MnO_x catalysts was characterized by XRD. The result is shown in Fig. 1. A weak diffraction peak appeared at $2\theta = 37.5^\circ$, which can be attributed to the (211) crystal plane of cryptomelane ($\text{KMn}_8\text{O}_{16}$) [15,16]. These MnO_x catalysts prepared using the redox method did not have distinct diffraction peaks, indicating they were mainly amorphous with a small amount of crystalline cryptomelane. This is in agreement with the literature

[17].

Figure 2 shows the time plots for conversions of HCHO and ozone, and CO_2 selectivity over the MnO_x catalysts from a simulated air stream containing 137 g/m^3 HCHO and 642 g/m^3 O_3 with 56% RH (25 °C) at GHSV of $2 \times 10^5 \text{ h}^{-1}$. Formaldehyde was totally oxidized to CO_2 by O_3 over the MnO_x catalysts, and the HCHO conversion and CO_2 selectivity were maintained at ~100% during all of the 150 min time-on-stream. Moreover, no CO was detected during the whole process of OZCO. Therefore, the MnO_x catalysts possessed excellent catalytic performance for the complete oxidation of HCHO with O_3 . In addition, the conversion of O_3 decreased dramatically from 100% to 80% in 10 min during the initial 10 min time-on-stream, and then it became slightly less and was maintained at 73% after 60 min. Formaldehyde did not react with O_3 if the feed gas stream did not flow through the catalyst bed. Thus, the gas phase reaction of HCHO with O_3 was negligible.

To further confirm the catalysis by MnO_x , Fig. 3 shows time plots for the concentrations of HCHO and ozone when a feed gas stream was flowed through a quartz sand bed. It can be seen from Fig. 3 that the HCHO concentration was almost constant. The O_3 concentration decreased from 857 to 763 mg/m^3 during the initial 5 min, but recovered rapidly and was maintained at ~850 mg/m^3 after 10 min. This experimental result confirmed that the complete oxidation of HCHO with O_3 was due to catalysis by MnO_x .

The effect of the molar ratio of O_3 to HCHO on the conversions of HCHO and O_3 , and CO_2 selectivity was examined with a simulated air stream with 56% RH (25 °C) at GHSV of $2 \times 10^5 \text{ h}^{-1}$ over the MnO_x catalysts. According to the reaction equation for the complete oxidation of HCHO with O_3 , $2\text{O}_3 + \text{HCHO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{O}_2$, the stoichiometric ratio of O_3 to HCHO is 2. As shown in Fig. 4, when the molar ratio of O_3 to HCHO was decreased from 3:1 (> the stoichiometric ratio) to 2:3 (< the stoichiometric ratio), the conversion of HCHO decreased from ~100% to 58%, but the CO_2 selectivity was still maintained at ~100%. The result showed that the CO_2 selectivity of ~100% should be attributed to the excellent catalytic performance of the MnO_x catalysts for the complete oxidation of HCHO with O_3 , even when O_3 is not in excess. In addition, the O_3 conversion decreased with the increase in the molar ratio of O_3 to HCHO.

To detect possible byproducts from the OZCO of HCHO over MnO_x , an online FT-IR spectrometer was used. From Fig. 5, it can be seen that no absorption peaks of byproducts such as HCOOH (1107, 1775, and 2921 cm^{-1}) and CO (2180 cm^{-1}) were observed. The only absorption peaks were those of the CO_2 product (2360 cm^{-1}) and the remaining O_3 (1060 and 2120 cm^{-1}). This is in agreement with Fig. 2.

With amorphous MnO_x prepared by a redox method as

catalyst, the OZCO of HCHO in air at room temperature and its products was investigated. Formaldehyde in simulated air containing 137 mg/m^3 HCHO and 642 mg/m^3 O_3 (molar ratio of O_3 to HCHO was about 3:1) was totally oxidized to CO_2 at 56% relative humidity (25 °C) and GHSV of $2 \times 10^5 \text{ h}^{-1}$. Formaldehyde conversion and CO_2 selectivity were maintained at ~100% during 150 min time-on-stream. When the molar ratio of O_3 to HCHO was decreased to 2:3

(significantly lower than the stoichiometric ratio), the conversion of HCHO decreased to 58%, but a CO_2 selectivity of ~100% was still achieved. No byproduct was detected during the OZCO of HCHO over MnO_x using an online FT-IR spectrometer.

Full-text paper available online at Elsevier ScienceDirect
<http://www.sciencedirect.com/science/journal/18722067>