

Role of Surface Carboxylates in the Gas Phase Ozone-Assisted Catalytic Oxidation of Toluene

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Abstract Ozone-assisted catalytic oxidation of toluene was conducted over MnO_x/γ -Al₂O₃ to identify and differentiate the role of reaction byproducts. It was found that not only alumina acted as a reservoir for toluene, but also it interacted effectively with toluene to create surface carboxylate intermediates. Surface carboxylates were essential for an effective oxidation process, and they did not directly cause catalyst deactivation. The presence of Mn sites was necessary for further oxidation of the surface carboxylates. At 90 °C, a stable catalytic activity with 95% conversion was achieved. However, at 25 °C, byproducts such as acetic acid and formic acid accumulated on the surface of the catalyst and decreased the catalyst activity.

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Graphical Abstract



T: toluene, RCOO: carboxylate, RCOOH: carboxylic acid

1 Introduction

Volatile organic compounds (VOCs) are important indoor and outdoor air pollutants. VOCs can have adverse health effects on eyes, skin, lungs and the central nervous system [1]. A number of techniques have been used for removal of VOCs from air. The most common methods are adsorption [2], photocatalytic oxidation [3], non-thermal plasma [4], biological treatment [5], catalytic oxidation and ozoneassisted catalytic oxidation (i.e. catalytic ozonation) [6]. Among these, catalytic ozonation has gained increasing attention in the recent years due to its advantages over

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catalytic oxidation. Compared to catalytic oxidation, the reaction temperature for catalytic ozonation is significantly lower, leading to energy saving. In addition, catalysts based on transition metal oxides have high efficiencies in removal of VOCs by catalytic ozonation, eliminating the need for expensive noble metals that are commonly used in catalytic oxidation of VOCs by oxygen [7].

Manganese oxides (MnO_x) are the most active metal oxides for gas phase VOC removal in the presence of ozone [8]. Manganese oxides supported on different supports have been used for catalytic ozonation of acetone [9], benzene [10], toluene [11], formaldehyde [12], cyclohexane [13] and chlorobenzene [14]. It has been shown that catalytic ozonation can oxidize the listed VOCs at temperatures below 100 °C. Supported manganese oxide possesses higher catalytic activity than unsupported manganese oxide [15]. In addition, studies on catalytic ozonation of VOCs, using manganese oxide supported on γ -alumina, silica, titania, and zirconia, found that VOC removal rates normalized by surface area of the catalysts were comparable or slightly lower than those with the γ -alumina supported catalysts [16–18].

Catalytic ozonation of VOCs at room temperature is advantageous. However, catalyst deactivation is a serious impediment. There have been a number of studies aimed at understanding the nature of catalyst deactivation and formation of reaction byproducts in catalytic ozonation. Reed et al. [9] used in-situ Raman spectroscopy to study catalytic ozonation of acetone on 10 wt% MnO_x/SiO₂. It was concluded that acetone was physisorbed molecularly on the silica surface. It was suggested that the silica support was a reservoir for the adsorbed acetone, then the adsorbed acetone migrated to Mn site and reacted with atomic oxygen species produced from ozone decomposition. Einaga et al. used in-situ Fourier transform infrared (FTIR) spectroscopy to investigate room temperature catalytic ozonation of benzene over 5 wt% Mn/USY zeolite [19] and 5 wt% MnO_2/Al_2O_3 [16]. It was observed that two types of intermediates were formed on the surface of the catalysts. These intermediates were categorized as weakly bound and strongly bound compounds. Zhao et al. [12] employed insitu FTIR spectroscopy to investigate room temperature catalytic ozonation of formaldehyde on MnOx catalyst. Bidentate and monodentate carbonate species were found on the catalyst surface and both increased gradually with time. These studies have limited their investigations to ozonation operating temperatures in the range of 22-35 °C, at which severe catalyst deactivation occurs. In addition, they have not identified a mechanism for production of the observed compounds, and therefore, have not differentiated between the roles of reaction intermediates and byproducts.

It is known that catalytic ozonation of VOCs at a relatively high temperature (i.e. 90 °C) shows stable activity

with no or negligible catalyst deactivation [7, 18, 20]. Study of catalytic ozonation of VOCs at a relatively high temperature, with stable catalytic activity, and comparison of the reaction characteristics with those at the room temperature reaction, with catalyst deactivation, can provide more clear understanding of the reaction intermediates and catalyst stability. It is important to investigate the nature and roles of intermediates and byproducts that are formed on the surface of the catalyst during room temperature operation. This can help us develop a better understanding of the reaction mechanism and catalyst stability.

In this work, catalytic ozonation of toluene was investigated at two temperatures of 25 and 90 °C on MnO_x/γ -alumina catalyst. A combination of in-situ diffuse reflectance infrared Fourier transform spectroscopy, chemical analysis of the reaction products by GC-MS analysis, and a number of temperature programmed techniques were used to investigate the reaction pathways by differentiating the roles of reaction intermediates and byproducts that are formed on the surface of the catalyst.

2 Materials and Methods

2.1 Experimental Setup

Figure 1 shows a schematic diagram of the experimental setup that was used for catalyst activity and gas phase analyses. A gas cylinder with ppm level concentration of toluene balanced with nitrogen (Praxair, accuracy of $\pm 2\%$) was used to supply toluene. An ozone generator (AZCO Industries LTD, HTU-500S) was employed to produce ozone from a high purity oxygen stream (Praxair, 99.993%). Nitrogen gas was supplied from a high purity nitrogen cylinder (Praxair, 99.999%) for dilution and purging purposes. Gas flows were controlled by mass flow controllers (Brooks, SLA 5850, accuracy of $\pm 1\%$). Total flow rate of 250 ml/min (at STP) was used for all experiments. Gas streams were combined and passed through a horizontal Pyrex tube, filled with glass beads, to improve mixing before entering the reactor. A reaction chamber (Harrick, HVC) was used as an atmospheric pressure reactor to conduct all the reaction experiments. The reaction chamber was equipped with a heater that allowed operations up to 900 °C. Exhaust gas from the reactor was analyzed by a long-path gas cell (PIKE, volume 0.1 l 2.4 m optical length, KBr window) coupled with a Nicolet iS50 FTIR spectrometer equipped with a Deuterated L-alanine doped triglycine sulfate (DLaTGS) detector. Spectra were collected at a resolution of 4 cm⁻¹ in the range of 4000–400 cm⁻¹. Homogeneous reaction between ozone and toluene was negligible in this system.



Fig. 1 Schematic of the experimental setup for the catalyst activity measurements

An ozone analyzer (Teledyne API M454) was used to measure concentration of ozone in the exhaust gas stream.

Another configuration (Figure S.1 in the supplementary document) was used for in-situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) analyses, in which the long-path gas cell was replaced with a DRIFTS accessory (Harrick, Praying Mantis) on the FTIR spectrometer. Then, the reaction chamber, equipped with ZnSe windows, was coupled with the DRIFTS accessory and the FTIR spectrometer. To achieve higher sensitivity and faster scanning, a narrow band mercuric cadmium telluride (MCT-A) detector was used for in-situ DRIFTS operations. Spectra were collected at a resolution of 4 cm^{-1} in the range of 3900-1300 cm⁻¹ to avoid saturation of the MCT-A detector. Exhaust stream of the reaction chamber was analyzed by the ozone analyzer. A gas cylinder with ppm level concentrations of carbon dioxide and carbon monoxide balanced with nitrogen (Praxair, accuracy of $\pm 2\%$) was used for calibration purposes. CO_x yield was calculated using Eq. (1):

$$CO_{x} \text{ yield} = 100 \times ([CO] + [CO_{2}]) / (7 * [C_{7}H_{8, \text{ reacted}}])$$
(1)

2.2 Catalyst Preparation

MnO_x/ γ -Al₂O₃ catalyst was prepared by dry impregnation of powdered γ -alumina (powder size less than 0.208 mm) by using manganese(II) nitrate tetrahydrate (Sigma Aldrich, 97%) solution as manganese precursor. Nominal mass of Mn per mass of the catalyst was 10%. The impregnated support was dried for 10 h at 100 °C and calcined for 4 h at 500 °C in air. Then, the catalyst was crushed and sieved to a final powder size of less than 0.208 mm. For each experiment, 0.06 g of the catalyst was heated for 1 h at 475 °C under 140 ml/min oxygen and 110 ml/ min nitrogen. Then, the catalyst was cooled down under 250 ml/min nitrogen flow and its temperature was fixed at the desired reaction temperature of 25 or 90 °C. The catalyst was saturated by toluene before introducing ozone to the reaction chamber.

2.3 Catalyst Characterization

Manganese loading on the catalyst was verified by inductively coupled plasma mass spectrometry (ICP-MS) using a Nexion 300D (PerkinElmer) instrument. N₂ adsorption by ASAP 2020 (Micromeritics) instrument was used to determine pore volume and Brunauer–Emmett–Teller (BET) surface area of the catalyst. Topography of the catalyst was recorded by transmission electron microscopy (Philips CM10). Prior to measurements, the catalyst was ultrasonically dispersed in ethanol to produce a suspension. A drop of the suspension was deposited onto the holey carbon film and was left to dry. Then, it was used for the transmission electron microscopy (TEM).

X-ray absorption near edge structure (XANES) of Mn *K-edge* was collected at hard X-ray micro analysis beamline of the Canadian Light Source (CLS). Catalyst was diluted with boron nitride (BN), ground and pressed to thin disks. The prepared disks were protected by Kapton tape. Measurements were conducted in transmission mode using straight ion chamber detectors filled with helium gas, a Si(1 1 1) monochromator crystal, and Rh mirrors. For the preedge and XANES regions, scan step-sizes were 10 eV/step and 0.25 eV/step, respectively. ATHENA software [21] was used for data processing. The reference materials including Mn_2O_3 (Sigma-Aldrich, 99%, bixibyite), MnO_2 (Alfa Aesar, 99.9%, pyrolusite), MnO (Alfa Aesar, 99%, manganosite), and Mn_3O_4 (Sigma-Aldrich, 97%, hausmannite) were also analyzed to provide reference points.

Raman spectroscopy was performed by Renishaw InVia Raman microscope. A 514.5 nm Ar+laser (Spectra Physics) and a CCD detector were used. A 10 s detector exposure time and 32–128 spectra accumulations were used for the measurement and the instrument was operated in the line focus mode [8].

Thermo-gravimetric analysis was used to analyze temperature programmed weight loss of the spent catalyst. A thermal analyzer (TGA Q500, TA Instruments) with standard furnace type was employed for this purpose. Samples were heated at 20 °C/min to 790 °C under a pure nitrogen flow.

Carbonaceous species accumulated on the catalyst were extracted with dichloromethane and were analyzed by injecting the extracted sample into a gas chromatograph (Agilent, 7890A) coupled with mass spectrometer (Agilent, 5975C). An Agilent standard HP-5MS column was used in the gas chromatograph.

For temperature programmed oxidation (TPO), spent catalyst was immediately purged with nitrogen for 10 min. Then, the catalyst was heated at a rate of $10 \,^{\circ}C/$ min to 745 $^{\circ}C$ under a 250 ml/min atmospheric flow of oxygen–nitrogen (20–80 v%). Similarly, for temperature programmed desorption (TPD), spent catalyst was immediately purged with nitrogen for 10 min. Then, the sample was heated at 20 $^{\circ}C$ /min to 870 $^{\circ}C$ under a 250 ml/min atmospheric flow of nitrogen.

3 Results and Discussion

3.1 Catalyst Characterization

Table 1 presents manganese loading, BET surface area and pore volume of the catalyst. ICP-MS analysis verified that the manganese loading on the catalyst (9.8 wt%) was close to its nominal 10 wt% loading. Also, surface area and pore volume results showed that addition of manganese on γ -alumina decreased the pore volume and surface area by 15 and 16%, respectively.

 Table 1
 Manganese loading, BET surface area and pore volume of the catalyst

Catalyst	γ-alumina	MnO _x /γ- Alumina
Mn loading (wt %)		9.8
BET (m^2/g)	219	183
Pore volume (cm^3/g)	0.60	0.51

Figure 2 shows Mn K-edge XANES spectra of the catalyst along with spectra of MnO, Mn₃O₄, Mn₂O₃ and MnO₂ as the pure reference materials. At energies higher than 6550 eV, catalyst spectra were a mix of spectra of the reference materials. On the other hand, at energies below 6550 eV, catalyst spectra followed the Mn₂O₃ spectra. Quantification of the results by Linear Combination Fitting (LCF) of Mn K-edge XANES data showed that Mn₂O₃ (82%) was the major manganese phase in the catalyst followed by MnO₂ (11%) and Mn₃O₄ (7%). Raman spectra of the catalyst confirm that Mn₂O₃ was the major manganese phase. Figure 3 shows Raman spectra of the catalyst and the reference materials [8]. There were four distinct peaks at 199, 312, 614, and 698 cm^{-1} on the spectra of the catalyst, which indicate a significant presence of the Mn₂O₃ phase.

Figure 4 depicts transmission electron microscopy image of the catalyst. TEM image showed that the catalyst consists of metal cluster sizes of about 20 nm. This is confirmed by X-ray diffraction (XRD) results (Figure S.2) that showed Mn_2O_3 and MnO_2 in the catalyst had metal cluster sizes of 23 and 17 nm, respectively. Mn_3O_4 was not detected by XRD. This is due to detection limit of the XRD analyzer. XRD analyzer can detect particles larger than 5 nm, indicating that metal clusters of Mn_3O_4 phase were highly dispersed [22].

3.2 Catalyst Activity

Catalytic ozonation of toluene was carried out at 25 and 90 °C. The experiments were conducted over MnO_x/γ -Al₂O₃, pure γ -alumina, and pure Mn_2O_3 . Toluene and ozone conversion profiles along with carbon dioxide and carbon monoxide concentrations in the exhaust stream



Fig. 2 XANES spectra of Mn *K-edge*; (*a*) Mn_2O_3 , (*b*) Mn_3O_4 , (*c*) MnO_2 , (*d*) MnO, (*e*) MnO_3/γ -alumina



Fig. 3 Raman spectra; (a) MnO_x/γ -alumina, (b) Mn_3O_4 , (c) Mn_2O_3 , (d) MnO_2 , (e) MnO



Fig. 4 Transmission electron microscopy image of MnO_x/γ -alumina catalyst

are presented in Fig. 5. Standard error for toluene and ozone conversion was within $\pm 3\%$. Also, Standard errors for carbon dioxide and carbon monoxide concentrations were within ± 7 and ± 3 ppm, respectively.

For catalytic ozonation over MnO_x/γ -alumina at 90 °C, a stable reaction was observed with a high conversion of 95% for both toluene and ozone. However, at 25 °C operation, a decline in toluene and ozone conversions was observed. After 150 min of the reaction at 25 °C, toluene and ozone conversions dropped to 71 and 35%, respectively. At 90 °C, CO and CO₂ concentrations increased gradually with reaction time and reached constant concentrations of 167 and 413 ppm, respectively. On the other hand, at 25 °C reaction, CO and CO₂ concentrations increased initially and reached maximum values of 58 (at 105 min) and 178 ppm (at 55 min), respectively, followed by a decline in CO₂ concentration. After 150 min of reaction, CO_x yields for the 25 and 90 °C reactions were 35 and 87% with CO₂/CO ratios of 2.38 and 2.47, respectively.

For catalytic ozonation over pure γ -alumina, rapid catalyst deactivation was observed at both 25 and 90 °C. However, toluene and ozone conversions were relatively higher at 90 °C compared to those at the 25 °C reaction. This observation emphasizes the important role of the Mn sites in the catalytic activity of the MnO_x/ γ -alumina catalyst. Moreover, this observation suggests that γ -alumina is not an inert support and it can oxidize toluene in the presence of ozone, although the reaction is not stable and a rapid catalyst deactivation is observed.

For catalytic ozonation over pure Mn_2O_3 , a decline in toluene and ozone conversions was observed at 25 °C operation. However, at 90 °C a stable reaction with relatively low conversions of toluene (37%) and ozone (46%) was observed. CO and CO₂ concentrations for reactions over pure γ -alumina and Mn_2O_3 were significantly lower than those for reactions over MnO_x/γ -Al₂O₃ catalyst. Unlike pure Mn_2O_3 , manganese oxides in the MnO_x/γ -alumina are dispersed on the large surface area of γ -alumina. Also, it was indicated that γ -alumina is not inert and interacts with toluene. These factors help the MnO_x/γ -alumina catalyst to achieve a stable reaction at 90 °C with high toluene and ozone conversions.

To better understand the effect of temperature on catalyst activity and byproduct formation, in-situ DRIFTS studies were conducted. Figure 6 depict in-situ DRIFTS spectra of the catalytic ozonation of toluene at different reaction times. Figure 6a, b show in-situ DRIFTS spectra of the catalytic ozonation of toluene over MnO_x/γ -Al₂O₃ catalyst at 25 and 90 °C, respectively. Toluene adsorption on the catalyst did not change spectra of the fresh catalyst, due to low concentration of toluene in the inlet stream. Once ozone was introduced into the reactor, a number of peaks appeared. The peaks at around 1429, 1740, and



Fig. 5 Catalytic ozonation of toluene at 25 and 90 °C, $[O_3] = 1150$ ppm, [toluene] = 100 ppm; **a** Conversions of toluene and ozone, **b** CO and CO₂ concentrations in the exhaust stream; (1) MnO_x/ γ -Al₂O₃, (2) γ -Al₂O₃, (3) Mn₂O₃



Fig. 6 In-situ DRIFTS spectra of catalytic ozonation of toluene, $[O_3]=1150$ ppm, [toluene]=100 ppm; **a** MnO_x/ γ -Al₂O₃ at 25 °C, **b** MnO_x/ γ -Al₂O₃ at 90 °C, **c** γ -Al₂O₃ at 25 °C, **d** Mn₂O₃ at 25 °C

1603 cm⁻¹ were the main bands corresponding to C–H asymmetric deformation vibration, C=O stretching, and overlap of aromatic ring stretching and COO⁻ stretching of surface carboxylates, respectively. Moreover, there was a broad band from 2400 to 3750 cm⁻¹ corresponding to the overlap of OH stretching of alcohols, carboxylic acids and water. Complete list of significant bands and corresponding functional groups are summarized in Table 2 [16, 22, 23]. The in-situ spectra suggest that catalytic ozonation started with a similar mechanism at both 25 and 90 °C. This caused appearance and initial increase of similar bands at both temperatures. However, the bands corresponding to the byproduct formation (i.e. 1740, and the broad band at 2400–3750 cm⁻¹) were stronger at 25 °C, which is in agreement with the deactivation pattern of the catalyst at 25 °C.

In-situ DRIFTS spectra for catalytic ozonation of toluene using pure γ -alumina at 25 °C are depicted in Fig. 6c. The significant bands were at around 1325–1393, 2896, and 1600 cm⁻¹ corresponding to COO⁻ stretching of the surface carboxylates, saturated C–H stretching, and overlap of aromatic ring stretching and another COO⁻ stretching, respectively. In addition, there was a broad band from 2500 to 3750 cm⁻¹ corresponding to the overlap of OH stretching of alcohols, carboxylic acids and water. The most important difference between the spectra obtained from MnO_x/ γ - alumina and γ -alumina was the presence of a very strong band at around 1740 cm⁻¹ (corresponding to C=O stretching) on the spectra of the MnO_x/ γ -alumina catalyst. The same band appeared only as a shoulder on the spectra of the γ -alumina catalyst. This implies that the presence of manganese oxide

Table 2Assignment of FT-IRbands for catalytic ozonation oftoluene

Significant band (cm ⁻¹)	Assigned functional groups	
1308–1393	Antisymmetric and symmetric COO ⁻ stretching of carboxylates	
1429	C-H asymmetric deformation vibration	
1453	Aromatic ring stretching	
1498	Aromatic ring stretching	
1568	Antisymmetric COO ⁻ stretching of carboxylates	
1603	Overlap of aromatic ring stretching and COO ⁻ stretching of carboxylates	
1720-1780	C=O stretching	
2350	Adsorbed carbon dioxide	
2893–2944	Saturated C-H stretching	
3036-3072	Unsaturated C-H and aromatic C-H stretching	
2400-3750	OH stretching of alcohols, carboxylic acids and water	



Fig. 7 Weight loss during thermo-gravimetric analysis for fresh and spent MnO_x/γ -Al₂O₃ catalysts used in catalytic ozonation of toluene at 25 and 90 °C

is essential to effectively oxidize carbonaceous materials on the surface of the catalyst.

In-situ DRIFTS spectra for catalytic ozonation of toluene using pure Mn_2O_3 at 25 °C are depicted in Fig. 6d. Interestingly, the only significant band was at around 1760 cm⁻¹ corresponding to C=O stretching. Also, surface carboxylates, with a significant band at around 1600 cm⁻¹, were not formed in the absence of γ -alumina. Therefore, both γ -alumina and manganese oxide play important but different roles in catalytic ozonation of toluene over the MnO_x/ γ -alumina catalyst.

3.3 Temperature Programmed Analysis

Thermo-gravimetric analysis was conducted under inert N_2 environment. Figure 7 shows weight loss profile during thermo-gravimetric analysis of the catalyst. After heating



Fig. 8 In-situ DRIFTS spectra during TPD analysis of spent MnO_x/γ -Al₂O₃ catalyst used in catalytic ozonation of toluene at 25 °C

the spent MnO_x/γ -alumina catalysts at a rate of 20 °C/min to 790 °C, the spent catalysts of 25 and 90 °C reactions lost 22.9 and 5.9% of their weights, respectively. This indicates that higher amount of byproduct was deposited on the catalyst at the 25 °C operation.

Figure 8 depicts in-situ DRIFTS spectra at different temperatures of 325, 525 and 870 °C during temperature programmed desorption (TPD) of the catalyst used in the 25 °C catalytic ozonation. TPD was carried out under inert N₂ flow and the spent catalyst was heated up to 870 °C at a rate of 20 °C/min. By heating the spent catalyst to 325 °C, intensities of all bands decreased to some extent. Further increase in temperature to 525 °C, reduced intensities of the band at 1740 cm⁻¹ (C=O stretching) and the broad band at 2400–3750 cm⁻¹ (OH stretching). On the other hand, it increased intensities of the bands at 1429 (C–H asymmetric deformation vibration) and 1600 cm⁻¹ (overlap of aromatic

Sample	Temperature range (°C)	Detected compounds	
25 °C reaction	25–325	Acetic acid, formic acid, water vapor, CO, CO ₂	
25 °C reaction	325-525	Water vapor, CO, CO ₂	
25 °C reaction	525-870	Benzene, methane, CO, CO ₂	
90 °C reaction	25-525	Water vapor, CO, CO ₂	
90 °C reaction	525-870	Benzene, methane, CO, CO ₂	

Table 3 Compounds detected in the exhaust gas during TPD

ring stretching and COO⁻ stretching of surface carboxylates). At 525 °C, there were still two other bands at 2930 and 3060 cm⁻¹ corresponding to saturated and unsaturated C–H stretching, respectively. Further increase in temperature to 870 °C, removed the bands at 1740 and 2930 cm⁻¹ and reduced intensity of the bands at 1429 and 1600 cm⁻¹. Therefore, even at 870 °C, the bands at 1429, 1530–1600, and 3060 cm⁻¹ remained on the spectra.

Evolved gases during TPD were analyzed and Table 3 presents a summary of the detected compounds at each temperature range. CO and CO₂ were found in the exhaust gas during TPD of the spent catalyst at almost all TPD temperatures (25–870 °C) and their concentrations varied by temperature (Figure S.3). The presence of significant amounts of CO and CO₂ in a wide range of temperature and variation of their concentrations with temperature indicates that the detected CO_x not only originated from desorption of isolated CO and CO₂, but also they evolved from decomposition of larger carbonaceous compounds that were deposited on the surface of the catalyst.

During TPD of the catalyst used for the 25°C catalytic ozonation, acetic acid, formic acid and water were desorbed by heating the spent catalyst to 325 °C. Benzene and methane were detected during TPD from 525 to 870°C. This is the same temperature range at which the bands corresponding to saturated C-H stretching, aromatic ring stretching and COO⁻ stretching of surface carboxylates were decreased/removed as well (Fig. 8). This implies that benzene and methane evolved from decomposition of larger surface carboxylate compounds. Surface carboxylates have been found in catalytic ozonation of VOCs using SiO₂-based catalysts as well [18]. During TPD of the catalyst used for the 90 °C catalytic ozonation, benzene and methane were detected at 525-870 °C temperature range. This indicates that the surface carboxylates, associated with benzene and methane, were present at the 90 °C catalytic ozonation as well.

Temperature programmed oxidation (TPO) of the spent catalysts was conducted under atmospheric flow of oxygen–nitrogen (20–80 v%) and heating rate of 10 °C/min. Figure 9 depicts in-situ DRIFTS spectra during TPO of the



Fig. 9 In-situ DRIFTS spectra during TPO analysis of the spent MnO_x/γ -Al₂O₃ catalyst used in catalytic ozonation of toluene at 25 °C

catalyst used in the 25 °C catalytic ozonation. By increasing temperature to 745 °C almost all bands corresponding to carbonaceous materials disappeared. This is different from TPD (under N₂) results that even at 870 °C, some bands at 1429, 1530–1600, and 3060 cm⁻¹ remained on the spectra.

Figure 10 shows the variations in CO and CO₂ concentrations during TPO analysis. For the catalyst used in the 25 °C catalytic ozonation (Fig. 10a), maximum CO generation was at 346 °C with a concentration of 511 ppm. Also, maximum CO₂ concentration was 1861 ppm that was obtained at 394 °C. Most of the CO₂ was generated in the temperature range of 275-525 °C. This is an agreement with the DRIFTS spectra during TPO (Fig. 9) that increasing temperature to 525 °C decreased the intensity of the band at 1740 cm⁻¹ (C=O stretching) significantly. Benzene and methane gases were not found during TPO analysis. This indicates that the surface carboxylates, associated with benzene and methane, were oxidized to CO and CO_2 . Similar results were obtained for the catalyst used in the 90 °C catalytic ozonation (Fig. 10b), however, CO and CO₂ concentrations were relatively lower. In this case, maximum CO concentration was 95 ppm that was obtained at 292 °C, and CO₂ concentration reached a maximum value of 333 ppm at 357 °C. For the catalyst used in the 25 °C reaction, total amount of the evolved CO_v during TPO was 4.6 times higher than that of the 90 °C reaction (Table 4), indicating that higher amount of carbonaceous materials accumulated on the catalyst in the 25 °C reaction.

Table 4 shows the quantitative data for the overall carbon balance in the process. For the 25 °C operation, about 15.03 mg carbon entered the reactor during the saturation and reaction time. On the other hand, 13.76 mg carbon was



Fig. 10 Variation of CO and CO₂ concentrations during TPO analysis of the spent MnO_x/γ -Al₂O₃ catalyst used in catalytic ozonation of toluene at a 25 °C, b 90 °C

 Table 4
 Breakdown of carbon distribution and overall carbon balance (values are in mg)

	25 °C reaction	90 °C reaction
Total carbon in ^a	15.03	14.17
Total carbon out before TPO ^b	7.62	12.17
Total carbon evolved during TPO ^c	6.14	1.51
Total carbon out	13.76	13.68

^aDuring reaction and catalyst saturation with toluene

^bAs CO_x and unreacted toluene

^cAs evolved CO_x during TPO

detected in the exhaust of the reactor as unreacted toluene, produced CO_x during reaction, and CO_x during TPO. This resulted in a 92% overall carbon balance. For the 90 °C operation, about 14.17 mg carbon entered to the system and 13.68 mg carbon was detected in the exhaust stream resulting in a 97% overall carbon balance.

3.4 Carbonaceous Deposits on the Spent Catalysts

The carbonaceous species accumulated on the spent MnO_v/γ -alumina catalyst were extracted with dichloromethane and were analyzed with GC-MS. For the catalyst used at 25 °C, a number of organic compounds were found such as formic acid, acetic acid, acetol, methylglyoxal, formyl acetate, acetic anhydride, acetoxyacetic acid, maleic anhydride, and isopropyl methyl ketone. These compounds are listed in order of increasing the number of carbon atoms in their structures. In another attempt, the catalyst that was used in the catalytic ozonation at 25 °C, was heated to 325 °C under N2 flow. Then it was washed with dichloromethane and the extract was analyzed with GC-MS. The results did not show any extracted byproduct. This indicates that all of the mentioned byproducts were desorbed from the surface of the catalyst by heating the spent catalyst to 325 °C. For the catalyst used at 90 °C, none of the mentioned compounds were found by GC-MS analysis in the extract.

3.5 Effect of the Surface Carboxylates

According to the thermo-gravimetric analysis results (Fig. 7) for the catalyst used in 25 °C operation, almost 70% of the observed weight loss occurred by heating the catalyst to 325 °C. TPD results (Table 3) showed that heating up to 325 °C was enough to desorb formic acid and acetic acid from the surface of the catalyst. Also, other byproducts that were detected by GC-MS analysis, were not found after heating the catalyst to 325 °C. Therefore, mainly surface carboxylates remained on the surface of the catalyst after heating it to 325 °C.

The catalyst that was used for catalytic ozonation at 25 °C, was regenerated by heating to 325 °C under N₂ flow, then the regenerated catalyst was used for a second catalytic ozonation of toluene. The reaction conditions were the same as the first catalytic ozonation. Figure 11 shows toluene and ozone conversion profiles along with produced CO and CO₂ concentrations for the first and second catalytic ozonations. Up to 75 min from the beginning of the reaction, toluene conversion results for the first and second catalytic ozonations were almost identical. Then, the regenerated catalyst showed more deactivation. After 150 min, toluene conversions for the first and second catalytic ozonations dropped to 71 and 56%, respectively. On the other hand, ozone conversion for the second catalytic ozonation, dropped significantly after 10 min from the beginning of the reaction, followed by a gradual decline. After 150 min,



Fig. 11 Catalytic ozonation of toluene at 25 °C by using fresh and regenerated MnO_x/γ -Al₂O₃ catalysts, $[O_3] = 1150$ ppm, and [toluene] = 100 ppm; **a** conversions of toluene and ozone, **b** CO and CO₂ concentrations in the exhaust stream

ozone conversions were 35 and 17% for the first and second catalytic ozonations, respectively.

At the beginning, CO and CO_2 concentrations for the second catalytic ozonation were higher than those of the first catalytic ozonation. However, their concentrations deceased more rapidly and after 150 min CO and CO_2 concentrations for the second catalytic ozonation were lower than those of the first reaction.

Identical toluene conversions in the first 75 min of the both reactions suggest that the presence of the surface carboxylates did not directly prevent toluene conversion. In addition, high ozone conversion at the first 10 min of the second catalytic ozonation indicates that the active sites of the catalyst (i.e. Mn sites) were regenerated by heating the spent catalyst up to 325 °C and desorbing byproducts such as formic acid and acetic acid. Also, higher CO and CO₂ concentrations at the beginning of the second catalytic ozonation are attributed to two factors. First, the active sites of the catalyst were regenerated, and improved oxidation of the toluene. Second, the presence of the regenerated active sites and better ozone decomposition helped with further oxidation of the previously deposited surface carboxylates. It seems that improved oxidation of the surface carboxylates generated more byproducts such as formic acid and acetic acid, which subsequently reduced ozone decomposition and CO_x formation. It has been reported [24] that increase in ozone concentration enhances transformation from species with COO⁻ group (representing carboxylates) to species containing C=O and C-O functional groups such as carboxylic acids.

If byproducts such as formic acid and acetic acid are mainly produced from oxidation of the surface carboxylate intermediates, then these intermediates should be formed on the surface of the catalyst before the appearance of formic acid and acetic acid. To investigate this possibility, a one-minute catalytic ozonation reaction was conducted by using fresh MnO_x/γ -alumina at 25 °C. Figure 12 depicts insitu DRIFTS spectra of the 1 min reaction. The significant bands on the DRIFTS spectra are listed in Table 2. It can be seen that the surface carboxylases were formed on the surface of the catalyst from the early moments of the reaction. Therefore, these compounds were present from the early moments of the reaction, however, they did not reduce the toluene and ozone conversions (See Fig. 11). The surface carboxylates were observed during the catalytic ozonation



Fig. 12 In-situ DRIFTS spectra of the one-minute catalytic ozonation of toluene at 25 °C using MnO_x/γ -Al₂O₃

at 90 °C as well, while a stable catalytic ozonation was observed. The surface carboxylates were found in the catalytic ozonation with pure γ -alumina as well (Fig. 6c), while they were not found in the catalytic ozonation with pure Mn₂O₃ (Fig. 6d). Therefore, it is plausible that the surface carboxylases resided mainly on the γ -alumina part of the MnO_x/ γ -alumina catalyst, and therefore they did not reduce the catalytic activity. This conclusion is different from previous studies [16, 18, 19, 24] that have assumed all accumulated materials are detrimental to the catalytic activity, without differentiating between their roles in the reaction.

As discussed earlier, formic acid and acetic acid were found during TPD of the catalyst used for catalytic ozonation at 25 °C (see Table 3). In addition to formic acid and acetic acid, byproducts such as acetoxyacetic acid, formyl acetate, acetol, methylglyoxal, acetic anhydride, maleic anhydride, and isopropyl methyl ketone were detected in the extract of the spent catalyst (see Sect. 3.4). It is believed that these byproducts, which were found only in the 25 °C operation, accumulated on the surface of the catalyst and caused catalyst deactivation.

3.6 Reaction Mechanism

It has been reported [9, 13] that ozone decomposition on the surface of the catalyst generates highly reactive atomically adsorbed oxygen species (**•**O) that rapidly oxidize adsorbed VOCs:

$$O_3 + {}^{\bullet} \to O_2 + {}^{\bullet}O \tag{2}$$

$$^{\bullet}\mathrm{O} + \mathrm{O}_3 \to \mathrm{O}_2 + ^{\bullet}\mathrm{O}_2 \tag{3}$$

$$^{\bullet}O_2 \to O_2 + ^{\bullet} \tag{4}$$

where \blacksquare represents a surface metal site. As discussed earlier, ozone decomposition occurs on both γ -alumina and Mn sites of the MnO_x/ γ -alumina catalyst. Therefore, \blacksquare can be either an alumina or Mn site.

Figure 13 shows breakthrough curves of toluene adsorption on MnO_x/γ -alumina, pure γ -alumina, and pure Mn_2O_3 . Adsorption breakthrough times for MnO_x/γ -alumina, and pure γ -alumina were 6 and 8 min, respectively. However, breakthrough time for pure Mn_2O_3 was very short (<1 min). Therefore, toluene is mainly adsorbed on γ -alumina sites of the MnO_x/γ -alumina catalyst.

As discussed in Sect. 3.2, alumina not only acts as a reservoir for toluene, but also it interacts effectively with toluene, in the presence of ozone, to create surface carboxylate intermediates. The presence of highly reactive atomic oxygen species, resulted from ozone decomposition, creates an oxidative environment. Many quick reactions can occur in this oxidative environment, which makes it difficult to identify unstable reaction intermediates. However, studies on interaction of



Fig. 13 Breakthrough curves of toluene adsorption on MnO_x/γ -Al₂O₃, γ -Al₂O₃, and Mn_2O_3 at 25 °C and [toluene] = 100 ppm

toluene with metal oxides have shown [25–28] that toluene interacts with the surface of metal oxides via abstraction of H atoms from the methyl group. Therefore, a possible pathway for catalytic ozonation of toluene on the MnO_x/γ -alumina catalyst is as follows:

$$C_6H_5 - CH_3 + ^{\blacktriangle} \rightleftharpoons ^{\blacktriangle}C_6H_5 - CH_3 \tag{5}$$

$${}^{\blacktriangle}C_6H_5 - CH_3 + {}^{\bigstar} \rightarrow {}^{\bigstar}C_6H_5 - CH_2 + {}^{\bigstar}H$$
(6)

$${}^{\bullet}C_{6}H_{5}-CH_{2}+2{}^{\bullet}O \rightarrow {}^{\bullet}C_{6}H_{5}-COO+2{}^{\bullet}H$$
(7)

where \blacktriangle represents an alumina site. Equation (5) shows adsorption of toluene on the first alumina site. Equation (6) is based on dissociation of one H atom from the methyl group of toluene [25–28]. Then, the unstable benzyl species ($\degree C_6H_5-CH_2$) reacts with oxygen species (Eq. 7) to produce adsorbed benzoate ($\degree C_6H_5-COO$), which is a stable surface carboxylate intermediate. Equation (7) may include multiple steps as described in the supplementary document (Section S.4). The adsorbed protons (\degree H) can react with the oxygen species and produce water (Eqs. 8, 9, 10) [28, 29]:

$$^{\bullet}H + ^{\bullet}O \rightleftharpoons ^{\bullet}OH \tag{8}$$

$$2^{\bullet} OH \rightleftharpoons {}^{\bullet} H_2 O + {}^{\bullet} O \tag{9}$$

$$^{\bullet}\mathrm{H}_{2}\mathrm{O} \rightleftharpoons ^{\bullet} + \mathrm{H}_{2}\mathrm{O} \tag{10}$$

Pure γ -alumina cannot further oxidize surface carboxylates (see Sect. 3.2) and the presence of Mn sites is necessary for further oxidation of the surface carboxylates (Eqs. 11, 12):

$$^{\bullet}C_6H_5 - COO + ^* \rightleftharpoons ^*C_6H_5 - COO \tag{11}$$

$$^{*}C_{6}H_{5}$$
-COO + n $^{*}O \rightarrow$ products (12)

where * represents a surface Mn site. At 90 °C, the surface carboxylates are quickly oxidized to carbon dioxide and carbon monoxide. At 25 °C, in addition to carbon dioxide and carbon monoxide, byproducts such as acetic acid and formic acid are produced and reduce the catalyst activity.

4 Conclusions

Catalytic ozonation of toluene at 25 and 90 °C was conducted over MnO_x/γ -alumina catalyst. Distinguishing the role of surface carboxylates from that of byproducts such as acetic acid and formic acid helped to develop a better understanding of the reaction mechanism and catalyst stability. In the presence of ozone, alumina interacts with toluene to produce surface carboxylate intermediates. These intermediates are further oxidized on the manganese sites. At 25 °C, a decline in toluene and ozone conversions is observed. It is believed that at 25 °C, byproducts such as acetic acid and formic acid accumulated on the surface of the MnO_x/γ -alumina catalyst and decreased the catalyst activity. However, at 90°C, these byproducts are quickly oxidized to carbon dioxide and carbon monoxide. Therefore, a stable catalytic activity is observed at 90 °C. The catalyst deactivation at 25 °C is reversible, as a high catalytic activity is restored by heating the spent catalyst to 325 °C and desorbing the byproducts such as acetic acid and formic acid.

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References

- Guieysse B, Hort C, Platel V, Munoz R, Ondarts M, Revah S (2008) Biotechnol Adv 26:398–410
- 2. Li M-S, Wu SC, Shih Y-H (2016) J Hazard Mater 315:35-41
- Huang Y, Ho SSH, Lu Y, Niu R, Xu L, Cao J, Lee S (2016) Molecules 21:56
- Rodrigues A, Tatibouet J-M, Fourre E (2016) Plasma Chem Plasma Process 36:901–915
- Mohamed EF, Awad G, Andriantsiferana C, El-Diwany AI (2016) Environ Technol 37:1197–1207
- 6. Naydenov A, Mehandjiev D (1993) Appl Catal A Gen 97:17-22
- Rezaei E, Soltan J, Chen N, Lin J (2013) Chem Eng J 214:219–228
- 8. Rezaei E, Soltan J (2012) Chem Eng J 198–199:482–490
- 9. Reed C, Xi Y, Oyama ST (2005) J Catal 235:378–392
- Huang H, Ye X, Huang W, Chen J, Xu Y, Wu M, Shao Q, Peng Z, Ou G, Shi J, Feng X, Feng Q, Huang H, Hu P, Leung DYC (2015) Chem Eng J 264:24–31
- Jung S-C, Park Y-K, Jung HY, Kang U II, Nah JW, Kim SC (2016) Res Chem Intermed 42:185–199
- 12. Zhao D-Z, Shi C, Li X-S, Zhu A-M, Jang BW-L (2012) J Hazard Mater 239:362–369
- 13. Einaga H, Futamura S (2004) React Kinet Catal Lett 81:121-128
- 14. Jin D, Ren Z, Ma Z, Liu F, Yang H (2015) Rsc Adv 5:15103-15109
- 15. Einaga H, Maeda N, Teraoka Y (2013) Appl Catal B 142:406–413
- 16. Einaga H, Futamura S (2004) J Catal 227:304-312
- 17. Einaga H, Futamura S (2005) Appl Catal B 60:49–55
- 18. Einaga H, Ogata A (2009) J Hazard Mater 164:1236-1241
- 19. Einaga H, Teraoka Y, Ogata A (2013) J Catal 305:227-237
- Wang HC, Liang HS, Chang MB (2011) J Hazard Mater 186:1781–1787
- 21. Ravel B, Newville M (2005) J Synchrotron Radiat 12:537-541
- 22. Rezaei E, Soltan J, Chen N (2013) Appl Catal B Environ 136–137:239–247
- Coates J (2000) In: Meyers RA (ed) Encyclopedia of analytical chemistry. John Wiley & Sons Ltd., Chichester, pp 10815–10837
- Liping L, Jianguo Z, Lixian Y, Mingli F, Junliang W, Bichun H, Daiqi Y (2011) Chinese J Catal 32:904–916
- 25. Andersson SLT (1986) J Catal 98:138–149
- Busca G, Cavani F, Trifirò F (1987) J Catal 106:471–482
- 27. Irigoyen B, Juan A, Larrondo S, Amadeo N (2003) Surf Sci 523:252-266
- 28. Menon U, Galvita VV, Marin GB (2011) J Catal 283:1-9
- 29. Rezaei E, Soltan J (2014) Appl Catal B Environ 148-149:70-79