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# Heterogeneous Catalytic Ozonization of Sulfosalicylic Acid

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**Abstract:** This paper describes the potential of heterogeneous catalytic ozonization of sulfo-salicylic acid (SSal). It was found that catalytic ozonization in the presence of Mn-Zr-O (a modified manganese dioxide supported on silica gel) had significantly enhanced the removal rate (72%) of total organic carbon (TOC) compared with that of ozonization alone (19%). The efficient removal rate of TOC was probably due to increasing the adsorption ability of catalyst and accelerating decomposition of ozone to produce more powerful oxidants than ozone.
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**Keywords:** Ozone, catalytic ozonization , total organic carbon , sulfosalicylic acid.

Ozone is a powerful oxidant and is capable of oxidative degradation of many organic compounds. However, ozonization alone still has low removal rate of total organic carbon (TOC) and chemical oxygen demand (COD) owing to some refractory small molecule of organic compounds, such as acetic acid, oxalic acid, produced in the system. Therefore many researchers try to improve the efficiency of ozonization for various applications. Some combination oxidation processes (AOPs), such as $O_3$+$H_2O_2$[1], UV/$O_3$[2, 3] catalytic ozonization[4], have been developed. Among them the heterogeneous catalytic ozonization is the most promising process for industrial effluent depollution because of its low cost and easy operation. $MnO_2$ is the most efficient catalyst for decomposition of ozone in gas[5], so the characteristic of $MnO_2$ used in catalytic ozonization of contaminants in aqueous solution is interested too. A few papers[6-9] have reported on heterogeneous catalytic efficiency of $MnO_2$, the removal rate of TOC is less than 60%. In order to raise the removal rate of TOC, a modified $MnO_2$ supported on silica gel (Mn-Zr-O) heterogeneous catalytic ozonization was investigated.

The ozonization system consisted of an oxygen purge apparatus, ozone generator (CFS-1A ,Ozonia), ozone reactor (40 cm height × 3 cm internal diameter) and ozone destructor oven (ODT-003,Ozonia). The sintered inlet at the bottom of the reactor produced small bubbles into solution. The semi-continuous test was applied to evaluate the activity of solid catalyst. The concentration of ozone in the gas was measured by iodometeric titration (Ozone Standards Committee Method). The TOC content in the aqueous solution was measured with Apollo 9000 apparatus (TEKMAR DOHRMANN). Some organic acids were identified by high pressure liquid chromatography (HP1100, Spherisorb S5C6 column, liquid phase: phosphoric acid buffer solution (pH=7.0) (80%)

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and methanol (20%), UV detector). The pH-value of the solution was measured by using pH S-3C meter. Salicylic acid (SSal) is a typical nonbiodegradable aromatic compound ($BOD_5$/ COD<0.1)[10]. The catalytic efficiency of Mn-Zr-O was tested during ozonization of SSal. The catalyst Mn-Zr-O was prepared by the following process: 1 g $Mn(Ac)_2{\cdot}4H_2O$ and suitable amount of $ZrOCl_2{\cdot}8H_2O$ were dissolved into the double-distilled water, then 8 g silica gel was added into the solution for impregnation. After drying for 2 hours at 150°C, the catalyst was calcined for two stages before use: the first stage at 550°C for 3 hours and the second stage at 900°C for 6 hours. The catalyst $MnO_2$/silica gel was prepared from $Mn(Ac)_2{\cdot}4H_2O$ by the same process. $MnO_2$ was a commercial reagent without any further treatment. The ozonised oxygen was maintained at constant flow rate (0.67 L/min). The experimental temperature was kept at 20°C. The initial SSal concentration was 2.5 mmol/L and its corresponding $TOC_0$ was 193.2 mg/L. All solutions were prepared by double-distilled water.

In order to compare the oxidative degradation effects of catalytic ozonization of different catalysts with that of ozonization alone, the experiments were carried out in a semi-continuous flow reactor where ozone gas (prepared from pure oxygen) was bubbling continuously into 250 mL unbuffered aqueous solution of SSal. Each set of experiments consisted of: (1) catalytic ozonization, with 1575 mg/h $O_3$ in the presence of 2000 mg of catalyst; (2) ozonization alone with 1575 mg/h $O_3$; (3) ozonization plus adsorption test, after ozonization 20 min, the dissolved ozone was quenched by thiosulfate, then to the mixture 2000 mg catalyst was added and bubbled with pure oxygen at the same flow rate for 20 min. During each run, samples were taken for TOC analysis at appropriate intervals.

**Figure 1** The removal rate of TOC during ozonization of SSal

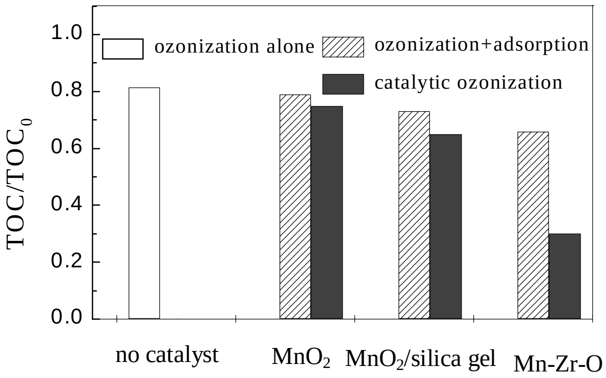
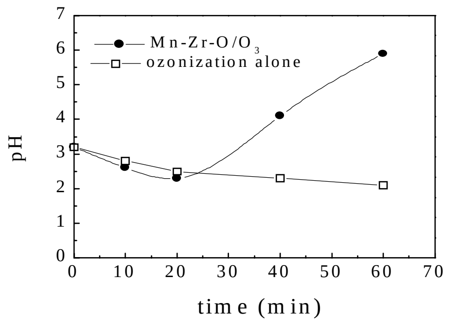


**Figure 1** shows that: (1) the removal rate of TOC is low without the catalyst; (2) the adsorption abilities of preozonised aqueous of SSal on the catalyst Mn-Zr-O/silica gel and $MnO_2$/silica gel are stronger than on the catalyst $MnO_2$; (3) a better TOC abatement is achieved when the ozonization is carried out with either catalyst $MnO_2$/silica gel or Mn-Zr-O, especially catalyst Mn-Zr-O, the remaining TOC is only 30% of its initial

$TOC_0$. The experimental results show that Mn-Zr-O is the most efficient catalyst in this condition.

In order to confirm the catalytic effect of Mn-Zr-O, the evolution of pH was measured. The results are shown in **Figure 2**. The pH of the solution declines gradually for ozonization alone, which is according with the results that some organic acids, such as oxalic acid, acetic acid, accumulate in the solution owing to their refractory to ozone ($k<10^{-2}$ $M^{-1}\cdot s^{-1}$)[11]. The pH of Mn-Zr-O/$O_3$ system declines at first and then increases later. These data show that Mn-Zr-O/$O_3$ is a more powerful oxidative system than ozonization alone because it can oxidize refractory organic compounds with ozone.

**Figure 2** Evolution of pH during ozonization and catalytic ozonization of SSal



Bielanski and Haber[12] have divided the oxides into three groups: (1) oxides on which oxygen is adsorbed mainly in the form of electron-rich speices, such as $O^-$ and $O^{2-}$ (oxides of Ni, Mn *etc.*); (2) oxides on which oxygen is adsorbed in the form of speices less rich in electrons, such as $O_2^-$ (oxides of V, Zr *etc.*) and oxides on which oxygen do not adsorbed (oxides of Mo, W *etc.*). The experimental results show that $MnO_2$ with a high amount of electron-donor centers has the low removal rate of TOC compared with catalyst Mn-Zr-O, so the suitable catalyst for catalytic ozonization may exist appropriate electron-donor centers in spite of electrophilic properties of ozone. Obviously, the increasing adsorption ability of catalyst Mn-Zr-O for organic compounds also probably plays an important role for the efficient removal rate of TOC compared with that of $MnO_2$. The detailed catalytic mechanism will be reported later.

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