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# Catalytic activity of Ru/Al<sub>2</sub>O<sub>3</sub> for ozonation of dimethyl phthalate in aqueous solution

Zhou Yunrui <sup>\*</sup>, Zhu Wanpeng, Liu Fudong, Wang Jianbing, Yang Shaoxia

*Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China*

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## Abstract

With dimethyl phthalate as the model pollutant and Ru/Al<sub>2</sub>O<sub>3</sub> as catalyst, this paper systemically investigates the removal of total organic carbon (TOC) of system. Our results have confirmed that Ru/Al<sub>2</sub>O<sub>3</sub> can significantly increase the effect of ozonation. TOC removal in 120 min can reach 72% while only 24% with ozone alone. The optimal catalyst preparing condition was 0.1 wt% Ru content, 600 °C calcination temperature, 0.5–1.0 mm particle diameter, which is characterized by a high surface area and a large population of surface active sites. The contrasting experiments of ozone alone, catalyst adsorption after ozonation, and catalytic ozonation confirmed that catalytic reaction was the most important process to TOC removal in system with Ru/Al<sub>2</sub>O<sub>3</sub> as catalyst.

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**Keywords:** Catalytic oxidation; Ozone; Ruthenium; Aluminum leaching; Advanced oxidation processes

## 1. Introduction

Phthalates are widely used as plasticizers to improve the flexibility and durability of consumer products, food packaging materials and polyvinyl chloride (PVC) plastics (Marttinena et al., 2003). Since they are not chemically bound to the PVC polymer, they may leach from solid products during use or after disposal. In addition, several industrial plants produce large amounts of wastewater containing high concentration of phthalates, which have negative effects on the water environment (Alatrisme-Mondragona et al., 2003). A study of phthalic acid esters (PAEs) in the municipal sludges of China showed that PAEs with lighter molecular weight, such as dimethyl phthalate (DMP), diethyl phthalate, di-*n*-butyl phthalate, and butyl-benzyl phthalate were detected in almost all the investigated sludge of China (Mo et al., 2001). Another investigation on phthalates in Chinese drinking water

showed that phthalate compounds were found in water samples from all investigated water plants (Wu et al., 1999). Indeed, experimental evidences have consistently shown that phthalates may have endocrine disrupting effects on aquatic species by altering the action of endogenous steroid hormones and may lead to reproductive tract malformations (Knudsen and Pottinger, 1999; Hoyer, 2001; Scholz, 2003).

The most common method for phthalates removal from wastewater is biological treatment, which is based on the metabolic degradation of phthalates by microorganisms under aerobic or anaerobic conditions (Wang et al., 1998; Adhoum and Monser, 2004). However, several studies found that PAEs with long alkyl-chains are poorly degraded and some of them are considered recalcitrant to biological treatment (Ejlertsson et al., 1997).

Heterogeneous catalytic ozonation is a novel type of advanced oxidation that combines ozone with the adsorptive and oxidative properties of solid phase metal oxide catalysts to achieve mineralization of some dissolved organics at room temperature (Paillard et al., 1991; Legube and Karpel, 1999). The main advantage of supported catalyst

<sup>\*</sup> Corresponding author. Tel.: +86 10 62784527x814.

E-mail address: zyr02@mails.tsinghua.edu.cn (Z. Yunrui).

is the ability to avoid the separation of the solid and liquid phases. Also other characteristics of the supported catalyst can increase ozone capability for the abatement of refractory organic pollutants (Gracia et al., 2000). Clearly, it is a promising advanced oxidation technology for water treatment (Cooper and Robbie, 1999). In literature on this subject, different metal oxides such as  $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ , or transition metals deposited on several porous materials (alumina, Titanium dioxide, activated carbon) were investigated (Andreozzi et al., 1996; Beltran et al., 2003, 2004; Tong et al., 2003; Qu et al., 2004). But the reports about ruthenium as catalyst are scarce (Fu et al., 2000). In this work, Ru was chosen as a catalyst because of its extensive use in catalytic oxidation processes, mainly in wet air oxidation (Delanoe et al., 2001). Furthermore, Ru was reported to decompose ozone into hydroxyl radicals (Qin and Aika, 1998) and, in consequence, its application with ozone could be considered a potential catalyst. In previous papers, we studied the catalytic ozonation performance using  $\text{Al}_2\text{O}_3$  and found the catalytic reactivity improved. We concluded that those results were attributable to the external surface area and catalytic surface hydroxyl groups (Zhou and Zhu, 2006). The main objective of this study was to investigate the mineralization of DMP in the heterogeneous Ru/ $\text{Al}_2\text{O}_3$  catalyzed ozonation.

## 2. Methods

### 2.1. Experimental procedures

The test installation is shown in Fig. 1. Ozone was generated by a laboratory ozone generator (Harbin Jiujiu Electric Chemistry Engineering and Technique Co., Ltd., DHX-SS-03C, China) rated at  $118 \text{ mg O}_3 \text{ h}^{-1}$ . After eliminating water through a silica gel column, oxygen was used as the gas source. The input gas pressure was 0.04 Mpa and the gas flow rate was arranged from 100 to  $400 \text{ ml min}^{-1}$  with a flow-meter. The experiments were conducted in a glass reactor (1200 mm in high, 50 mm in diameter), equipped with a glass sand porous plate (10–30  $\mu\text{m}$  porous size) at its bottom to obtain gas bubbles. The effective volume was 1000 ml. The excess ozone in the outlet gas was absorbed by 5%

$\text{Na}_2\text{S}_2\text{O}_3$  solution. Temperature-control system including heated belt, thermocouple and XMT temperature controller maintained the temperature at  $15 \pm 0.5^\circ\text{C}$ . DMP concentration, total organic carbon (TOC) and leaching metals were determined after different time periods.

### 2.2. Materials

DMP was obtained from Tianjin Chemical Reagent No.1 Plant (China). The potassium indigotrisulfonate was purchased from Acros organics (USA). Methanol of HPLC grade was purchased from Fisher Scientific International Inc. (USA). Other chemicals (KI,  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_3$ ) were reagent grade. DMP solution was prepared by dissolving 50  $\mu\text{l}$  DMP with 10 l deionized water to afford a solution of about  $6.0 \text{ mg l}^{-1}$  with pH of 6.6.

### 2.3. Analytical methods

The concentration of ozone in in-gas and off-gas was measured with iodometric method. Gaseous ozone in in-gas and off-gas was continuously introduced to two sets of glass bottles, each filled with 100 ml of 1% KI, through a ceramic sparger. The concentration of ozone dissolved in aqueous phase was determined using the indigo method (Bader and Hoigne, 1981). DMP concentration was determined by HPLC (Shimadzu, LC-10AD, Japan) with an UV-vis detector (Shimadzu, SPD-10AV, Japan) and a Kromasil KR100-5C18 column (250 mm long, 4.6 mm i.d., AKZONOBEL, USA). The mobile phase was a mixture of water/methanol (the ratio of volume is 50:50) at a rate of  $1.0 \text{ ml min}^{-1}$  with a column temperature of  $40^\circ\text{C}$ . The injection volume of our sample for analysis was 40  $\mu\text{l}$ . Under these conditions, the DMP retention time was 9 min. NPOC (non-purgeable organic carbon) in water was determined with a TOC analyzer (Shimadzu, TOC-Vwp, Japan) after filtration through 0.70  $\mu\text{m}$  glass fiber pre-filter. Since experiments were carried out under aeration with mixture gas of ozone and oxygen, NPOC values corresponded, in fact, to the TOC in water. Leaching metals were determined by ICP (inductively coupled plasma) (Thermo Elemental, IRIS Intrepid, USA). The X-ray diffraction (XRD) powder patterns were recorded on a diffractometer (Rigaku, D/max-RB, Japan) using Cu K $\alpha$  radiation. The chemical composition of catalytic support was estimated by sequential X-ray fluorescence spectrometer (Shimadzu, XRF-1700, Japan). The textural properties such as specific surface area, pore volume, pore size were determined by nitrogen adsorption. Nitrogen adsorption and desorption isotherms were recorded on commercial gas adsorption system (Micromeritics, ASAP 2010M, USA).

### 2.4. Preparation of catalysts

The catalyst support used in this study, which had a particle size of 0.5–5 mm and a specific surface area of  $113\text{--}183 \text{ m}^2 \text{ g}^{-1}$ , was obtained from Jiangyan Chemical

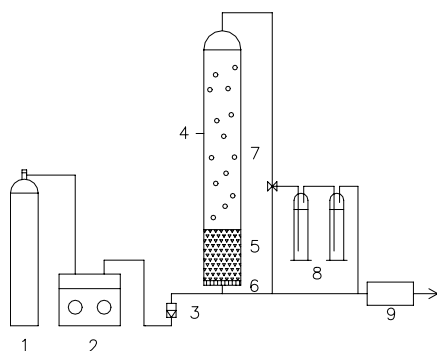


Fig. 1. The schematic diagram of experiment. 1 oxygen cylinder, 2 ozone generator, 3 gas flow-meter, 4 sample tap, 5 catalyst, 6 gas diffuser, 7 glass reactor, 8 KI trap, 9 ozone absorber.

Table 1  
Element composition of  $\text{Al}_2\text{O}_3$

$\text{Al}_2\text{O}_3$	MgO	$\text{SiO}_2$	$\text{SO}_3$	$\text{Cr}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{Fe}_2\text{O}_3$	$\text{Ga}_2\text{O}_3$	CaO
99.31%	0.20%	0.17%	0.13%	0.05%	0.05%	0.03%	0.03%	0.02%

Auxiliary Agent Factory (Jiangyan, China). The element composition is shown in Table 1. Before use, the  $\text{Al}_2\text{O}_3$  was thoroughly washed with distilled water and dried in an oven at  $105^\circ\text{C}$  for 24 h. The  $\text{Ru}/\text{Al}_2\text{O}_3$  catalysts with different Ru loading were prepared by the dipping method with an aqueous solution of ruthenium chloride in a shaking incubator at 160 rpm and  $30^\circ\text{C}$  for 2 h. The wet sample was dried at  $105^\circ\text{C}$  for 3 h and then calcinated at a different temperature for 3 h.

### 3. Results and discussion

#### 3.1. The catalytic activity of $\text{Ru}/\text{Al}_2\text{O}_3$

Fig. 2 shows the removal of DMP and TOC of system along with ozonation time. DMP could be effectively degraded above 95% within 20 min ozonation in the uncatalyzed, the blank support catalyzed, and the  $\text{Ru}/\text{Al}_2\text{O}_3$  catalyzed ozonation processes. Among the three processes, DMP removal with ozone alone was slightly higher because of its better gas diffusion. However, TOC removal presented noticeable differences in the three cases. After reacting for 120 min, the  $\text{Ru}/\text{Al}_2\text{O}_3$  catalyzed ozonation led to more than 72% TOC removal, and 56%

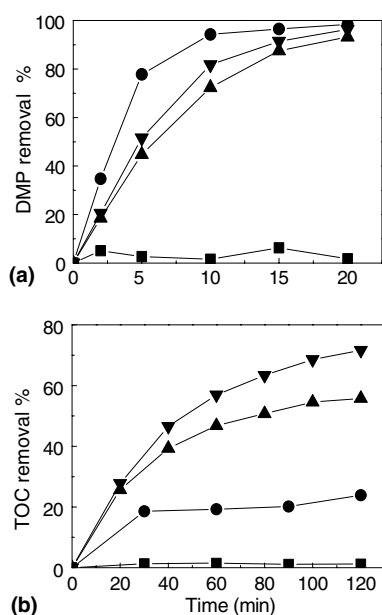


Fig. 2. Evolution of removal of (a) DMP concentration and (b) TOC with time corresponding to different experiments: (■)  $\text{O}_2 + \text{Ru}/\text{Al}_2\text{O}_3$ , (●)  $\text{O}_3$ , (▲)  $\text{O}_3 + \text{Al}_2\text{O}_3$ , (▼)  $\text{O}_3 + \text{Ru}/\text{Al}_2\text{O}_3$ . Conditions: Ru content: 0.1 wt%, calcination temperature:  $600^\circ\text{C}$ , particle diameter: 2–3 mm, catalyst dosage:  $10\text{ g l}^{-1}$ , ozone dosage:  $116\text{ mg O}_3\text{ h}^{-1}$ ,  $\text{TOC}_0 = 4.03\text{ mg l}^{-1}$ , gas flow rate:  $400\text{ ml min}^{-1}$ , temperature:  $15^\circ\text{C}$ .

for the blank catalyzed process. The ozone alone process gave only a modest decrease in TOC of 24%. The pH value is one of the important parameters which influence the catalytic reaction. During the process of catalytic ozonation, the pH value declines slightly and reaches 6.12 after 120 min. In addition, there was about 5% DMP adsorbed onto the  $\text{Ru}/\text{Al}_2\text{O}_3$  catalyst with oxygen. The results demonstrated that, in the experimental condition of our study, DMP could not be degraded to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  completely by ozone alone.  $\text{Ru}/\text{Al}_2\text{O}_3$  showed a great catalytic effect on the mineralization of DMP in the ozonation process.

#### 3.2. Preparing an optimal supported $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst

##### 3.2.1. Determining the optimal Ru content of $\text{Ru}/\text{Al}_2\text{O}_3$

Because Ru is the active species in the supported catalyst of  $\text{Ru}/\text{Al}_2\text{O}_3$ , it might be expected that increasing amounts of Ru would lead to increasing activity of the catalyst, and then an increasing removal of TOC of the system. We evaluated the effect of altering the Ru content of the catalyst on its catalytic performance in the ozonation. Fig. 3 showed that, when Ru content is above 0.1 wt%, the TOC removal begins declining from their best values. Similar results (Chen et al., 2004) were found when they studied the effect of Ce content of  $\text{CeO}_2/\text{Al}_2\text{O}_3$  catalyst on its catalytic performance in the catalytic wet air oxidation of phenol. They have indicated that this decline probably occurred because of the content of active species exceeding some threshold value. The active species on the support formed larger crystals, resulting in a decrease in the amount of active sites, followed by a decline in activity. At the same time, increasing Ru content will plug the pores of  $\text{Al}_2\text{O}_3$  by its crystals, which will decrease the BET surface area and have negative effects on its catalytic activity.

##### 3.2.2. Determining the optimal calcination temperature

The effect of the catalyst calcination temperature on TOC removal is shown in Fig. 4. The catalytic performance reached the uppermost value at  $600^\circ\text{C}$  and then declined with the increasing calcination temperature. In the low-temperature range ( $300\text{--}800^\circ\text{C}$ ), the alumina is mainly

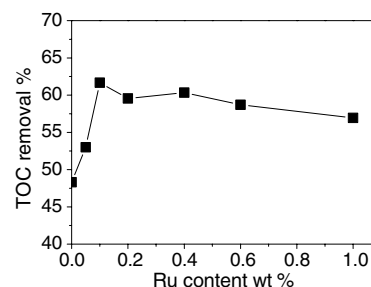


Fig. 3. Effect of Ru content on TOC removal. Conditions: calcination temperature:  $600^\circ\text{C}$ , particle diameter: 2–3 mm, catalyst dosage:  $10\text{ g l}^{-1}$ , ozone dosage:  $116\text{ mg O}_3\text{ h}^{-1}$ ,  $\text{TOC}_0 = 4.03\text{ mg l}^{-1}$ , gas flow rate:  $400\text{ ml min}^{-1}$ , temperature:  $15^\circ\text{C}$ .

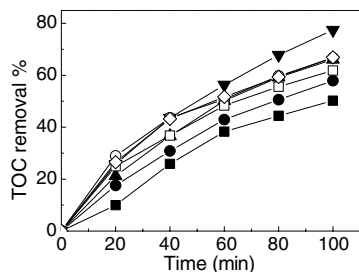


Fig. 4. Effect of calcination temperature on TOC removal: (■) 1000 °C, (●) 800 °C, (▲) 700 °C, (▼) 600 °C, (○) 500 °C, (□) 400 °C, (◇) 300 °C. Conditions: Ru content: 0.1 wt%, particle diameter: 2–3 mm, catalyst dosage: 20 g l<sup>-1</sup>, ozone dosage: 116 mg O<sub>3</sub> h<sup>-1</sup>, TOC<sub>0</sub> = 4.03 mg l<sup>-1</sup>, gas flow rate: 400 ml min<sup>-1</sup>, temperature: 15 °C.

amorphous alumina and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (see Fig. 5), which is characterized by higher surface area and open porosity than in the high-temperature range (see Table 2). When the calcination temperature is 1000 °C, the alumina is mainly  $\theta$ -Al<sub>2</sub>O<sub>3</sub> ( $2\theta$  = 31.24°, 32.76°, 36.76°, 44.82°, 67.38°) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $2\theta$  = 25.62°, 35.20°, 37.82°, 43.40°, 52.60°, 57.54°, 68.24°) (see Fig. 5). The surface area is smaller. So low-temperature Ru/Al<sub>2</sub>O<sub>3</sub> are better used as catalysts and adsorbents in the catalytic ozonation process,

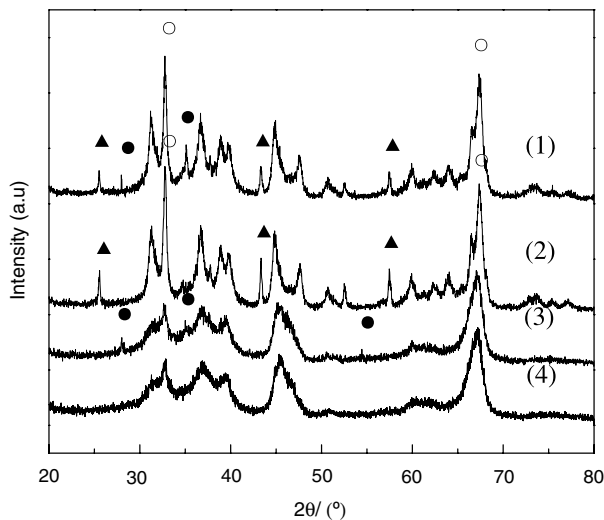


Fig. 5. XRD patterns of catalysts under different calcination temperature. (1) 1000 °C 1.0 wt% Ru/Al<sub>2</sub>O<sub>3</sub>, (2) 1000 °C Al<sub>2</sub>O<sub>3</sub>, (3) 600 °C 1.0 wt% Ru/Al<sub>2</sub>O<sub>3</sub>, (4) 600 °C Al<sub>2</sub>O<sub>3</sub>.

not only for their high surface area (lower order and smaller average pore diameter), but also because they have larger population of surface active sites (Morterra and Magnacca, 1996).

### 3.2.3. The effect of particle size on activity of Ru/Al<sub>2</sub>O<sub>3</sub>

Gas–liquid–solid catalytic ozonations are heterogeneous reaction systems that involve chemical reactions on the catalyst surface and a series of consecutive-parallel steps of mass transfer, which mainly are the external diffusions of reactant molecules (or ozone molecules) between the bulk liquid (or bulk gas) and gas–liquid interface and the internal diffusion of reactant molecules (or byproduct molecules) between the catalyst pores and external surfaces. The influences of the catalyst particle sizes on TOC removal are shown in Fig. 6. The TOC removal increased with the decrease of the particle size, while the surface areas of different catalysts were similar. Thus, it can be concluded that the surface reactions develop mainly in the outer section of the pores.

### 3.3. The leaching and lifetime of catalyst

In order to investigate the Ru/Al<sub>2</sub>O<sub>3</sub> lifetime and the leaching of components, experiments were carried out in the same reactor under a continuous flow condition. The liquid flow rate was 20 ml min<sup>-1</sup> (retention time was 50 min) and catalyst dosage was 40 g. The TOC removal and component leaching were measured continuously for 42 h. The experimental results are shown in Fig. 7. The

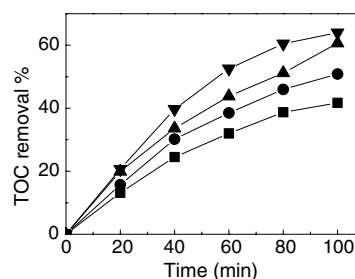


Fig. 6. Effect of catalyst's particle diameter on TOC removal: (■) 3.0–5.0 mm, (●) 2.0–3.0 mm, (▲) 1.0–2.0 mm, (▼) 0.5–1.0 mm. Conditions: Ru content: 0.1 wt%, calcination temperature: 600 °C, catalyst dosage: 10 g l<sup>-1</sup>, ozone dosage: 116 mg O<sub>3</sub> h<sup>-1</sup>, TOC<sub>0</sub> = 4.05 mg l<sup>-1</sup>, gas flow rate: 400 ml min<sup>-1</sup>, temperature: 15 °C.

Table 2

Surface areas, pore volume and pore diameter of Ru/Al<sub>2</sub>O<sub>3</sub>

Sample	Calcination temperature (°C)	$A_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$A_{\text{micro}}$ (m <sup>2</sup> g <sup>-1</sup> )	$A_{\text{ext}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{tol}}$ (ml g <sup>-1</sup> )	$V_{\text{micro}}$ (ml g <sup>-1</sup> )	$V_{\text{max}}$ (ml g <sup>-1</sup> )	$D_{\text{ave}}$ (nm)	$D_{\text{med}}$ (nm)
Al <sub>2</sub> O <sub>3</sub>	1000	85.0	8.8	76.2	0.31	0.0031	213.7	0.020	24.0
2.0–3.0 mm	800	125.1	9.2	115.9	0.38	0.0028	175.7	0.034	24.1
	600	136.3	8.9	129.8	0.40	0.0013	170.1	0.036	22.3
	400	154.7	9.5	145.2	0.40	0.0026	150.2	0.039	19.8

$V_{\text{micro}}$ —microporous surface area;  $A_{\text{ext}}$ —external surface area;  $V_{\text{tol}}$ —total pore volume;  $V_{\text{micro}}$ —microporous volume;  $V_{\text{max}}$ —maximum pore volume;  $D_{\text{ave}}$ —average pore diameter;  $D_{\text{med}}$ —median pore diameter.



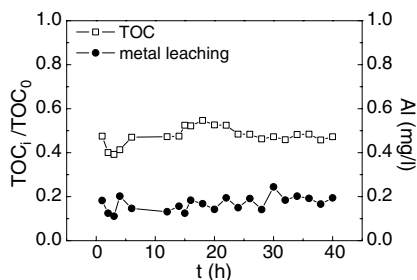


Fig. 7. TOC removal and aluminum leaching along with the time.

TOC removal efficiency kept to a nearly constant rate, which suggested that the catalytic capacity of Ru/Al<sub>2</sub>O<sub>3</sub> was not decreasing with time under such treatment conditions. At the same time, the leaching of Ru was not detected in solution by ICP, but the leaching of aluminum was significant, nearly 0.15 mg l<sup>-1</sup>. This demonstrated that the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst was effective in the ozonation of organic pollutants. The leaching aluminum, though detrimental to the stability of the catalyst, has no direct effect on the catalytic activity.

### 3.4. Mechanisms

As for the mechanisms occurring in catalytic ozonation, we can propose three main possibilities: first, ozone would oxidize the initial organic compound or its byproducts; second, the catalyst would behave as an adsorbent; and third, the catalyst would take part in the reaction between ozone and organic compound, behaving as a real catalyst, and improve the removal of TOC. The catalytic ozonation with Al<sub>2</sub>O<sub>3</sub> as catalyst to remove oxalic, acetic, salicylic and succinic (Ernst et al., 2004) was investigated. Their results indicated the catalyst exhibited different adsorption abilities to different model compounds. The adsorption of the organic model substances on the catalyst's surface was not necessary for effective oxidation. It actually inhibits the catalytic effect. As seen in Fig. 2, the TOC removal of catalytic ozonation was much higher than non-catalytic ozonation, while non-catalytic ozonation performed better than catalytic ozonation for DMP removal. It is believed that the adsorption and removal of byproducts is important for catalytic ozonation. In order to reveal the mechanisms in catalytic ozonation, three experiments were conducted: direct ozonation for 60 min (the TOC removal are mainly based on the ozonation); stripping the residual ozone with nitrogen for 5 min, followed by adsorption for another 60 min after oxidation by direct ozonation for 60 min (the increment of TOC removal are mainly based on the adsorption of DMP and its byproduct during degradation); and catalytic ozonation for 60 min (The TOC removal is ascribed to ozonation, adsorption of organic compounds and catalytic reaction). As seen above (Fig. 2), the adsorption of DMP on Al<sub>2</sub>O<sub>3</sub> ozone was slight, but higher for its byproduct as shown on Fig. 8. The byproduct adsorption could not be neglected during

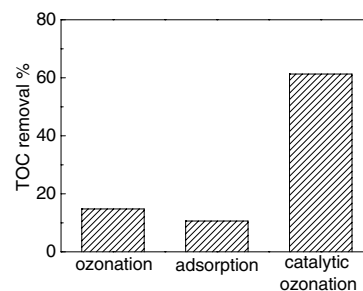


Fig. 8. TOC removal after 60 min corresponding to different experiments.

ozonation. Among the three processes, adsorption rate is 12% for system TOC removal, 21% for direct ozonation, and 67% for catalytic ozonation.

### 4. Conclusions

Ru/Al<sub>2</sub>O<sub>3</sub> is an effective catalyst in the ozonation process. Although the degradation rates of DMP were almost the same in the direct ozonation and Ru/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation, the TOC removal efficiency of catalytic ozonation is much higher than that of ozonation. The catalyst can increase the TOC removal to 72% after 120 min, compared to only 15% for direct ozonation.

Preparing conditions have an important effect on Ru/Al<sub>2</sub>O<sub>3</sub> catalytic activity. 0.1 wt% Ru loading content and 600 °C calcination represent optimal conditions. The catalytic activity increased with the decrease of particle size.

Despite the fact that aluminum leaching was detected, Ru/Al<sub>2</sub>O<sub>3</sub> is still an efficient catalyst for catalytic ozonation. Ru/Al<sub>2</sub>O<sub>3</sub> has a long lifetime; however, after a long period of use, Al<sub>2</sub>O<sub>3</sub> leaching will become a serious problem. Further work will be focused on increasing the stability of the catalyst and avoiding the problem of aluminum leaching.

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