



Efficient mineralization of dimethyl phthalate by catalytic ozonation using $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst

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ABSTRACT

The removal of dimethyl phthalate (DMP), which is a pollutant of concern in water environments, was carried out by catalytic ozonation with $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts. The heterogeneous catalytic ozonation was an ozonation process combined with the catalytic and adsorptive properties of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts to significantly accelerate the mineralization efficiency. Semi-batch ozonation was performed under various experimental conditions including the fed ozone concentration, catalyst type, catalyst dosage, and ultraviolet radiation on the degradation of DMP. The complete removal of DMP was efficiently achieved by both sole and catalytic ozonation; meanwhile, the presence of the catalysts slightly accelerated the elimination rate of DMP. On the other hand, the mineralization efficiency, in terms of total organic carbon (TOC) removal, was substantially enhanced by employing the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst. The mineralization efficiency using the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst was the highest, followed in decreasing order by the Al_2O_3 catalyst, the TiO_2 catalyst, and sole ozonation. In addition, the use of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst would increase the utilization efficiency of the fed ozone, especially in the late ozonation period. Furthermore, the decrease in the catalytic activity of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst after multi-run experiments can be mostly recovered by an incineration process at a high temperature.

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1. Introduction

Many environmental hormones, such as phthalic acid esters, have been found in the wastewater that comes from urban sewage and factories, and this phenomenon has been accelerated by rapid economic development in recent decades [1]. Large amounts of phthalic acid esters are often leached from the plastics that are dumped at municipal landfills. These pollutants are harmful to microorganisms and accumulate in natural bodies of water, ultimately becoming widely distributed within aqueous systems such as rivers, lakes, and groundwater and exerting a noticeable influence on the environment [2]. Thus the endocrine system of the human body may be disturbed when phthalic acid esters are ingested or inhaled [3].

Dimethyl phthalate (DMP), which is composed of a benzene ring with methyl ester groups attached at the ortho-positions, is one of the most common phthalic acid esters. DMP has been used as a plasticizer in many products, including tools, automotive parts, toothbrushes, food packaging, cosmetics, and insecticides. Thus DMP has been frequently detected in wastewater effluents and

river water because of its high mobility in the aquatic system [4]. DMP would disrupt the endocrine system of aquatic species by altering the action of endogenous steroid hormones, making it an aqueous pollutant of concern in water and wastewater systems.

The common method for DMP removal from wastewater is biological treatment, which is based on the metabolic degradation of DMP by microorganisms under aerobic or anaerobic conditions. However, several studies have found that some phthalates with long alkyl-chains may be refractory to biological treatment. Bauer et al. [2] studied hydrolysis, anaerobic transformation, and ozonation/ultraviolet radiation (O_3/UV) processes to destroy some phthalic acid esters and concluded that only the O_3/UV process was able to efficiently decompose di-(2-ethylhexyl) phthalate and benzyl butyl phthalate.

In ozonation treatment, the phthalates are attacked through two different reaction mechanisms: (1) direct ozonation by the ozone molecules, especially of specific functional groups (double bonds, nucleophilic positions) and (2) radical oxidation by highly oxidative free radicals such as hydroxyl free radicals (OH^\bullet), which are generated from the decomposition of ozone in an aqueous solution [5,6]. This radical oxidation is nonselective and vigorous. The purpose of introducing UV radiation into the ozonation process is to enhance ozone decomposition, yielding more free radicals for greater oxidation [7].

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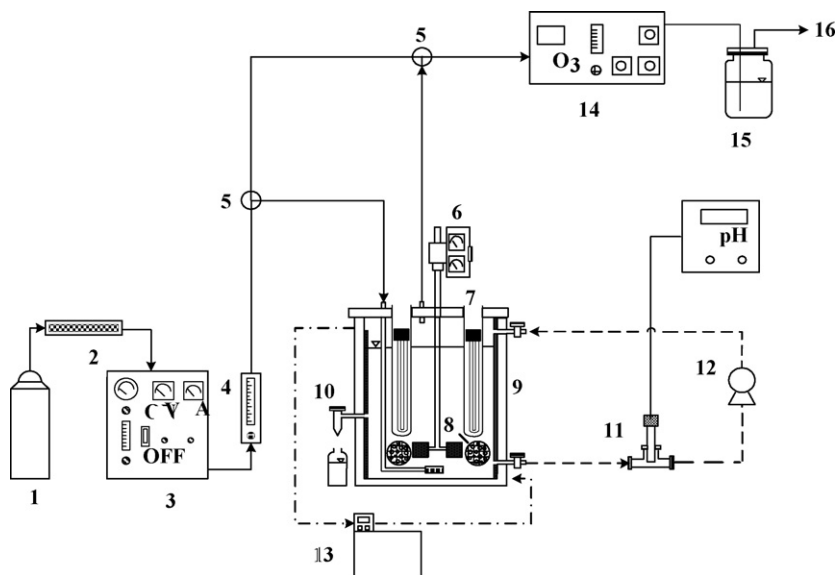


Fig. 1. Sketch of the experimental apparatus. —, — —, and - - -: ozone gas stream, circulating experimental solution, and isothermal water. Components: 1. oxygen cylinder, 2. drying tube, 3. ozone generator, 4. mass flow controller, 5. three-way valves, 6. stirrer, 7. UV lamps, 8. packed Al_2O_3 -based catalysts, 9. reactor, 10. sample port, 11. pH sensor, 12. circulation pump, 13. thermostat, 14. UV-photometric analyzer, 15. KI solution, and 16. vent to hood.

Ozonation has been employed as an effective way to eliminate DMP from aqueous solutions. Furthermore, the removal of the total organic carbons (TOC) is commonly used as a mineralization index of the ozonation. Nevertheless, sole ozonation resulted in a limited removal percentage of TOC (η_{TOC}) of about 37% [8]. Recently, Zhou et al. [9], Chen et al. [8], and Chang et al. [10] employed heterogeneous ruthenium-containing ($\text{Ru}/\text{Al}_2\text{O}_3$), high silica zeolites, and commercial platinum-containing ($\text{Pt}/\text{Al}_2\text{O}_3$) catalysts, respectively, to enhance the η_{TOC} in the catalytic ozonation of DMP. However, the novel catalyst with superior catalytic activity is still desirable to approach higher η_{TOC} in the treatment of DMP-containing solution.

Compared to the previous studies, this study successfully presented a $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst to obtain a distinguished improvement on the mineralization of DMP and its derivatives in the catalytic ozonation process. The synthesized $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst was composed of approximately 10.0 wt.% TiO_2 and 87.3 wt.% Al_2O_3 and then applied to catalyze the ozonation of DMP. The effect of the cat-

alytic ozonation conditions, such as the inlet ozone concentration (C_{AGi0}), catalyst dosage (W_{cat}), and UV radiation, was examined. Moreover, the catalytic ozonation of DMP using commercial TiO_2 and Al_2O_3 catalysts was also performed for comparison. The concentrations of DMP (C_{Blb}) and TOC (C_{TOC}) in the solution were analyzed at specified time intervals to study the decomposition of DMP.

2. Materials and methods

2.1. Materials

The commercial Al_2O_3 catalyst, with a particle size of 3–5 mm, was obtained from Advantage Chemical Co., Ltd. (Taichung, Taiwan). Titanium tetrachloride (TiCl_4 , 99%) was purchased from Hayashi Pure Chemical Ind. (Osaka, Japan). Degussa P25 TiO_2 (Dusseldorf, Germany), with a primary particle size and a specific surface area of 21 nm and $50 \text{ m}^2/\text{g}$, respectively, was employed.

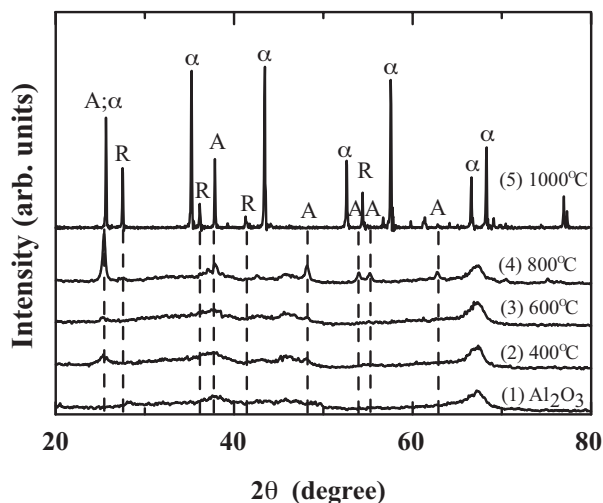


Fig. 2. XRD patterns of the (1) Al_2O_3 catalyst and the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts calcined at (2) 400 °C, (3) 600 °C, (4) 800 °C, and (5) 1000 °C.

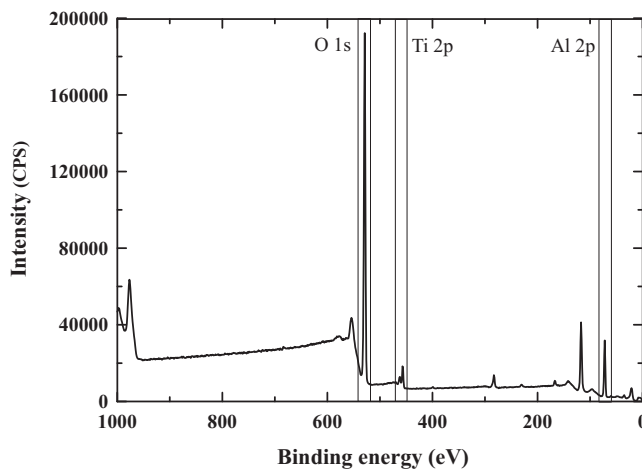


Fig. 3. XPS spectra of the O 1s, Ti 2p, and Al 2p regions of the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst calcined at 400 °C.

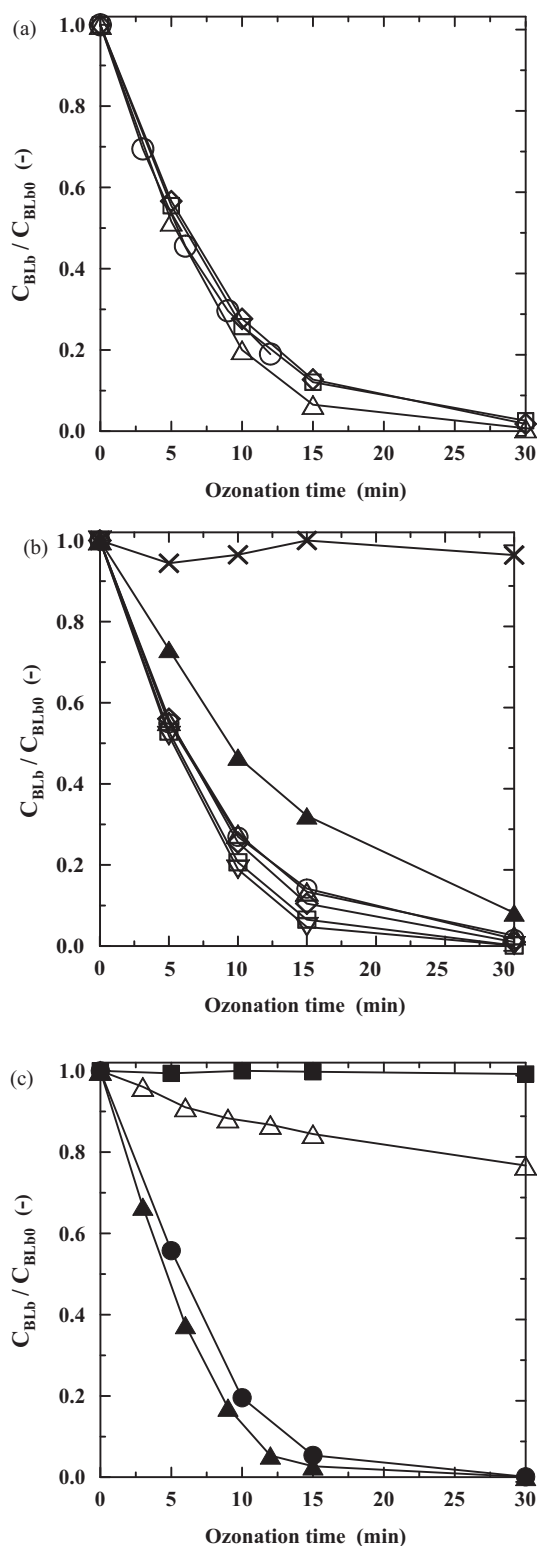


Fig. 4. Variation of C_{BLb}/C_{BLb0} with time in the ozonation of DMP. (a) Ozonation using the TiO_2 and Al_2O_3 catalysts. $C_{AGIO} = 14$ mg/L. \circ : sole ozonation. Δ : TiO_2 catalyst with $W_{cat} = 1$ g/L. \square : Al_2O_3 catalyst with $W_{cat} = 10$ g/L. \diamond : TiO_2 catalyst with $W_{cat} = 1$ g/L and Al_2O_3 catalyst with $W_{cat} = 10$ g/L. (b) Ozonation using the TiO_2/Al_2O_3 catalyst. \times : adsorption experiment, $W_{cat} = 10$ g/L. Δ : $C_{AGIO} = 8$ mg/L, $W_{cat} = 10$ g/L. \square , \circ , \diamond , and ∇ : $C_{AGIO} = 14$ mg/L, $W_{cat} = 1, 5, 10, 20,$ and 40 g/L. (c) Ozonation using UV and the catalysts. $[I] = 0.648$ W/L. Δ : TiO_2 catalyst with $W_{cat} = 1$ g/L. \square : TiO_2/Al_2O_3 catalyst with $W_{cat} = 10$ g/L. \bullet : $C_{AGIO} = 14$ mg/L, TiO_2/Al_2O_3 catalyst with $W_{cat} = 10$ g/L. \blacktriangle : $C_{AGIO} = 14$ mg/L, TiO_2 catalyst with $W_{cat} = 1$ g/L.

2.2. Preparation of the TiO_2/Al_2O_3 catalyst

The TiO_2/Al_2O_3 catalyst was prepared with $\gamma-Al_2O_3$ particles using a wet-impregnation method followed by an incineration procedure [11]. The $\gamma-Al_2O_3$ particles (100 g) were immersed in 100 mL of an aqueous solution containing 20 vol.% $TiCl_4$ for 24 h. The loaded $TiCl_4$ was converted through hydrolysis to form the TiO_2 sites on the alumina support. One should note that the TiO_2 content may increase with the ratio of $TiCl_4$ to $\gamma-Al_2O_3$ in the preparation procedure. However, the $\gamma-Al_2O_3$ particles would apparently collapse found in the preliminary tests with higher $TiCl_4$ concentration because of the high acidity. Subsequently, the excess water was removed by evaporation at $80^\circ C$ over 48 h. The dry titanium-loaded $\gamma-Al_2O_3$ particles prepared from the same batch were further calcined at temperatures of 400, 600, 800, or $1000^\circ C$ for 3 h to obtain the TiO_2/Al_2O_3 catalysts. The TiO_2/Al_2O_3 catalyst was washed with deionized water several times and then dried and stored.

2.3. Experimental apparatus

An airtight reactor with an inner diameter of 17.2 cm and an effective volume of 5.5 L was made of Pyrex glass and equipped with a water jacket to maintain a constant solution temperature of $25^\circ C$ for all experiments. The design of the reactor was based on the criteria for the shape factors of a standard six-blade turbine [12]. Two quartz tubes with outer diameters of 3.8 cm, symmetrically installed inside the reactor, were used to house the UV lamps. A volume of 3.705 L of the DMP-containing solution (V_L) was used in each experiment, and the total sampling volume was less than 5% of the experimental solution. The stirring speed was 800 rpm to ensure the complete mixing of the system, in accordance with the previous study [8]. A pH meter (model 300T, Suntex, Taipei, Taiwan) was used to measure the pH value of the solution. A circulation pump was used to transport the liquid from the reactor to the pH sensor with a flow rate of 0.18 L/min and to re-flow it back during the ozonation. All fittings, tubings, and bottles were made of stainless steel, Teflon, or glass. The experimental apparatus employed in this work is shown in Fig. 1.

The ozone was generated from pure oxygen by an ozone generator (model LAB2B, Ozonia, Dübendorf, Switzerland) with a gas flow rate (Q_G) of 1.95 L/min. The C_{AGIO} and discharged ozone concentration (C_{AGe}) were determined with a UV-photometric analyzer (model SOZ-6004, Seki, Tokyo, Japan), which was calibrated with the KI titration method [13]. Low-pressure mercury lamps (model PL-S 9W, Philips, Eindhoven, Netherlands) were employed to generate UV radiation at a wavelength of 254 nm. The intensity of UV radiation ($[I]$) was measured by a digital radiometer (Ultra-Violet Products, Upland, CA, USA) with a radiation sensor (model DIX-254A). The UV radiation intensity, in units of W/L, was defined as the average applied power of UV radiation per unit volume in the well-mixed system relative to the number of photons absorbed by the solution per unit volume and time. The $[I]$ value was calculated from the product of $[I_{UV}] (Aq/V_L)Fs$, where $[I_{UV}]$ is the light intensity measured on the outer surface of the quartz tubes by the radiation sensor in units of W/cm^2 , Aq is the outer area (cm^2) of the quartz tubes submerged in the solution, and Fs is the fraction of the emitting UV light absorbed by the solution. The value of Fs was determined close to the unit by measuring the negligible transmittance of UV radiation through the solution.

All experimental solutions were prepared with deionized water without other buffers. The initial concentration of DMP (C_{BLb0}) in the aqueous solution was 0.4 mM (77.7 mg/L). The initial TOC concentration (C_{TOC0}) and initial pH values of the prepared solution were measured to be approximately 45 mg/L and 5.60, respectively.

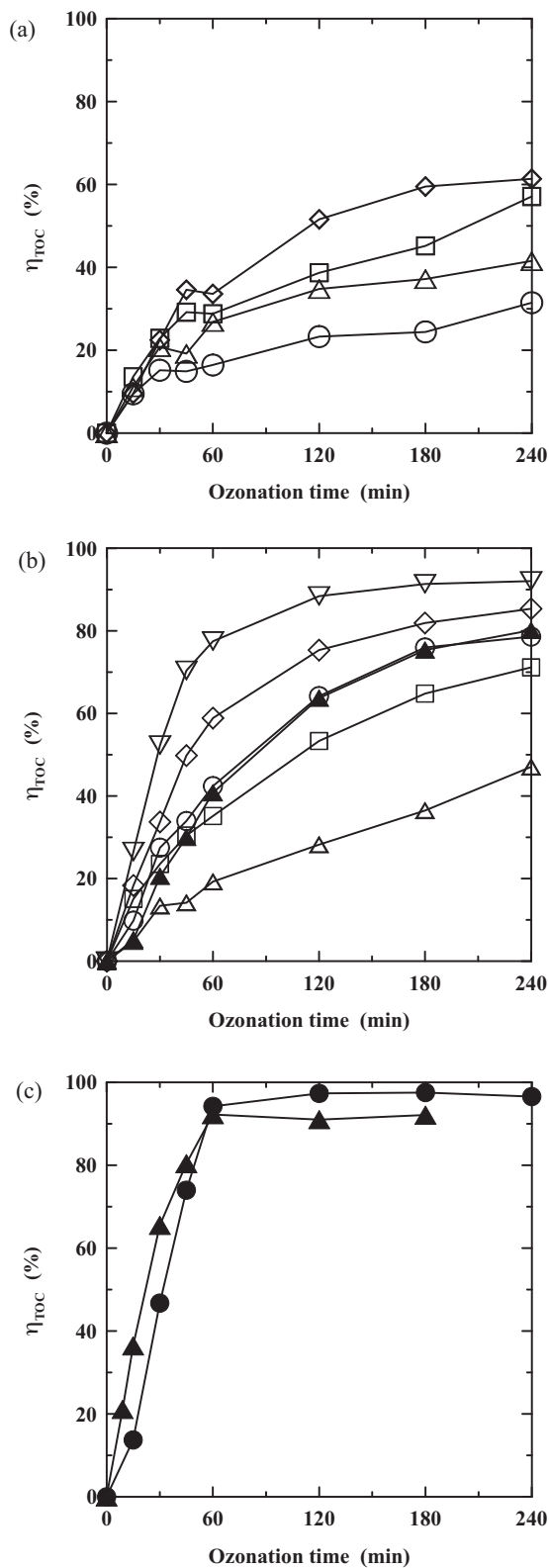


Fig. 5. Variation of TOC removal percentage in the ozonation of DMP. The experimental conditions and notations are the same as those specified in Fig. 4.

Two values of C_{AGi0} , 8 and 14 mg/L, were used in the experiments. The effect of the TiO_2/Al_2O_3 catalyst on the catalytic ozonation of DMP was examined at five W_{cat} : 1, 5, 10, 20, and 40 g/L. The contribution of UV radiation was tested with an I value of 0.648 W/L. Samples were drawn out from the reactor at desired time intervals

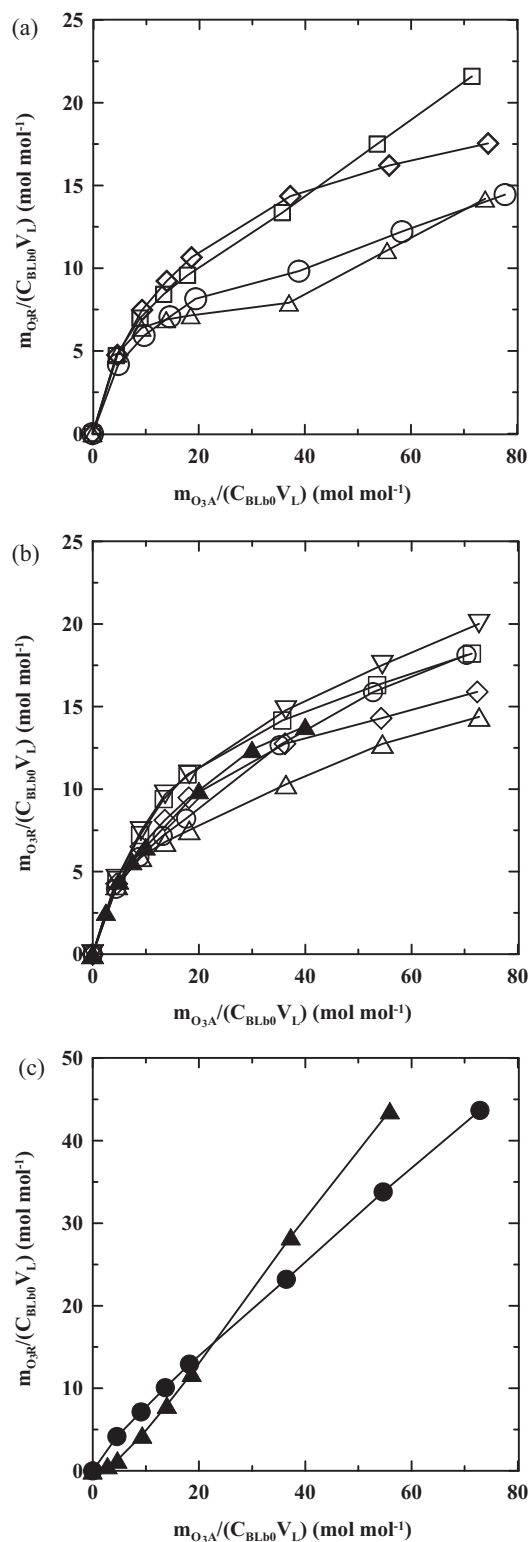


Fig. 6. Amount of ozone consumed per mole of DMP vs. the amount of ozone applied per mole of DMP in the ozonation of DMP. The experimental conditions and notations are the same as those specified in Fig. 4.

in the course of the experiments, and the samples were quenched and stored at 4 °C for subsequent analyses. The dissolved ozone concentration (C_{ALb}) was analyzed by the indigo method [14]. Successive multi-run experiments of the catalytic ozonation were performed to test the durability of the TiO_2/Al_2O_3 catalysts.

2.4. Analytic instrumentation

The crystal structure and oxidation state profiles of the TiO₂/Al₂O₃ catalyst were analyzed using wide-angle X-ray diffraction (XRD, Bruker AXS, model D8-Advance, Karlsruhe, Germany) and X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., model Axis Ultra DLD, Manchester, England), respectively. The chemical composition of the catalysts was estimated by X-ray fluorescence analysis (Spectro Analytical Instruments GmbH, Kleve, Germany). The Brunauer–Emmett–Teller (BET) specific surface area of the catalysts was analyzed with a Micrometrics ASAP 2010 BET surface area analyzer (Atlanta, GA, USA).

The DMP concentration was analyzed using a high-performance liquid chromatography (HPLC) system, with a 250 mm × 4.6 mm column (model ODS-2, GL Sciences Inc., Tokyo, Japan) and a diode array detector (model L-2455, Hitachi, Tokyo, Japan) at a wavelength of 230 nm. The HPLC solvent, at a flow rate of 1.0 mL/min, was composed of methanol and water at a 1:1 ratio. The injection volume of the analytical solution was 40 μL, and the detection limit of DMP concentration was 0.01 mg/L. The intermediates in the samples were further identified by HPLC coupled with a triple quadrupole mass spectrometer (LC–MS) with highly selective reaction monitoring (Thermo Fisher Scientific Inc., Waltham, MA, USA). The TOC concentration was analyzed with a TOC instrument (model 1030W, OI Corporation, College Station, TX, USA), using the UV-persulfate technique to convert the organic carbon compounds into carbon dioxide for subsequent quantification by an infrared carbon dioxide analyzer calibrated with a potassium hydrogen phthalate standard. In addition, the residual organic content on the TiO₂/Al₂O₃ catalyst, which was dried at 110 °C under vacuum for 1 h prior to the fabrication of the KBr pellet, was characterized on a Thermo Nicolet Avatar 370 Fourier transform infrared (FT-IR) spectrometer (Madison, WI, USA) with a resolution of 2 cm⁻¹.

3. Results and discussion

3.1. Characterization of the TiO₂/Al₂O₃ catalysts

The XRD patterns of the Al₂O₃ and synthesized TiO₂/Al₂O₃ catalysts, which confirm the chemical structures, are illustrated in Fig. 2. The intensity of the peaks including anatase TiO₂ (A), rutile TiO₂ (R), and α-alumina (α) increased with the calcination temperature. Compared to standard XRD patterns, the peaks of the five samples matched the peaks of the reference crystalline metals obtained from the Joint Committee on Powder Diffraction Standards. The results demonstrated that the TiO₂/Al₂O₃ catalysts contained the expected components, including crystalline alumina and TiO₂. In the following ozonation experiments, the TiO₂/Al₂O₃ catalyst calcined at 400 °C was used because of its superior catalytic activity as discussed in Section 3.6. Fig. 3 shows the high-resolution XPS spectra of the TiO₂/Al₂O₃ catalyst calcined at 400 °C. The chemical bonding states in terms of the O 1s (529 eV), Ti 2p (456 eV), and Al 2p (72 eV) peaks further confirmed the existence of the expected chemical compounds. The physical properties and compositions of the catalysts are shown in Table 1. The BET surface area and total pore volume decreased with the calcination temperature, probably because of the collapse of the porous structure at high calcination temperatures. The synthesized TiO₂/Al₂O₃ catalyst was composed of approximately 10.0 wt.% TiO₂ and 87.3 wt.% Al₂O₃.

3.2. Decomposition of DMP during catalytic ozonation

Fig. 4a–c shows the time variations of the dimensionless DMP concentration ($C_{\text{BLb}}/C_{\text{BLb0}}$) in the catalytic ozonation using various catalysts, C_{AGi0} , W_{cat} , and $[I]$. As shown in Fig. 4, DMP is immedi-

ately decomposed in the early period of the catalytic ozonation. The degradation rate of DMP was almost identical in the presence or absence of the catalysts because the oxidation of DMP was easily carried out via the direct ozonation [8]. Furthermore, the adsorption of DMP on the TiO₂/Al₂O₃ catalyst was negligible as shown in Fig. 4b, which may be due to the molecular size and steric hindrance of DMP [15]. The effect of the W_{cat} on the degradation rate was slight. In addition, the degradation efficiency of DMP in the catalytic ozonation process increased moderately with the introduction of UV radiation because of the accelerated generation rate of OH• (Fig. 4c). By comparison, the O₃/UV treatment of DMP using the Degussa P25 TiO₂ catalyst resulted in a better destruction efficiency of DMP compared to treatment using the TiO₂/Al₂O₃ catalyst because of higher external surface area of the Degussa P25 TiO₂ catalyst.

The time required to reduce the concentration of DMP by more than 98% in the ozonation process was marked as a characteristic time ($t_{f,\text{DMP}}$). A comparison of the ozonation results in terms of $t_{f,\text{DMP}}$, under various experimental conditions is summarized in Table 2. The C_{AGi0} was the most important factor in the degradation rate of DMP, as the $t_{f,\text{DMP}}$ value with an C_{AGi0} of 14 mg/L was about half of that with an C_{AGi0} of 8 mg/L. A pseudo first-order reaction rate equation, $C_{\text{BLb}}/C_{\text{BLb0}} = e^{-k_{\text{B}}t}$, was applied to describe the degradation rate of DMP from the experimental data in Fig. 4, where k_{B} is the reaction rate constant. The value of k_{B} in the catalytic ozonation process with the TiO₂/Al₂O₃ catalyst was determined to be $k_{\text{B}}(\text{min}^{-1}) = 0.0164C_{\text{AGi0}}^{0.767}W_{\text{cat}}^{0.06}$ (where C_{AGi0} is in units of mg/L), with a determination coefficient (R^2) of 0.834. The pH value of the solution decreased from an initial value of 5.60 to a final value ranging from 1.67 to 3.54 in the early ozonation period ($t < t_{f,\text{DMP}}$), suggesting that acidic groups such as organic acids are generated in the decomposition of DMP. Although the decomposition of DMP was accompanied by a significant decrease in TOC (Table 2), the generated intermediates still contributed a large amount of TOC.

3.3. TOC removal in the catalytic ozonation of DMP

The time variations of η_{TOC} with the experimental conditions specified in Fig. 4 are shown in Fig. 5 where the η_{TOC} was calculated as $(C_{\text{TOC0}} - C_{\text{TOC}})/C_{\text{TOC0}}$. The TOC removal in sole ozonation rapidly increased with time in the initial period because of the rapid decomposition of DMP and then slowly reached approximately 31% at reaction time of 240 min (Fig. 5a). The ozone dipolar cyclo-addition of the benzene ring is considered to be the major oxidation pathway of DMP because the two methyl carboxylate groups are strongly electron-withdrawing and deactivate the electrophilic substitution reaction [16]. The generated intermediates are highly resistant to react with ozone molecules [7]. As shown in Fig. 5a, catalytic ozonation significantly improved the TOC removal compared to sole ozonation. The activity of the catalysts in terms of the TOC removal was the highest in combining Degussa P25 TiO₂ and Al₂O₃ catalysts followed in order by using the Al₂O₃ catalyst, the Degussa P25 TiO₂ catalyst, and sole ozonation. For example, the η_{TOC} was increased by approximately 32% and 81% compared to sole ozonation with the employment of the Degussa P25 TiO₂ and Al₂O₃ catalysts, respectively, at reaction time of 240 min.

As shown in Fig. 5b, the TiO₂/Al₂O₃ catalyst exhibited significantly higher catalytic efficiency than did the catalysts in Fig. 5a. Furthermore, the TOC removal was enhanced with a higher W_{cat} and was relatively independent on the C_{AGi0} , in contrast to DMP reduction. At a reaction time of 240 min, the Langmuir-like relationship between the TOC removal and catalyst dosage was given by $\eta_{\text{TOC}}(\%) = W_{\text{cat}}/(1 + 1.13W_{\text{cat}})$ with an R^2 value of 0.983. It indicated that the TOC removal with the use of the TiO₂/Al₂O₃ catalyst may also be caused by the adsorption of intermediates, which are

Table 1
Physical properties and compositions of the TiO₂, Al₂O₃, and TiO₂/Al₂O₃ catalysts.

Catalyst	Calcination temperature (°C)	BET surface area (m ² /g)	Average pore diameter (Å)	Total pore volume (cm ³ /g)	Bulk density (kg/m ³)	Composition (wt.%)					
						TiO ₂	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	HCl
TiO ₂	None	50	NA	NA	NA	99.5	<0.3	<0.2	ND	<0.01	<0.3
Al ₂ O ₃	None	152	116	0.441	2.97	0.003	96.6	2.28	0.654	0.02	0.431
TiO ₂ /Al ₂ O ₃	400	143	105	0.376	3.31	9.72	86.9	1.79	0.287	0.034	1.271
	600	130	110	0.356	3.26	10.9	85.7	2.04	0.320	0.039	0.948
	800	96	143	0.343	3.37	9.48	88.7	1.21	0.234	0.052	0.357
	1000	4.2	63	0.0066	4.03	9.77	88.0	1.60	0.416	0.036	0.238

NA: not applicable.

ND: not detected.

generally more hydrophilic and with smaller molecular size than DMP, thereby increasing the η_{TOC} . The adsorption of some intermediates on the TiO₂/Al₂O₃ catalyst was also confirmed by the FT-IR analysis of the used TiO₂/Al₂O₃ catalyst. Subsequently, the adsorbed intermediates could further advance the surface reaction on the TiO₂/Al₂O₃ catalyst by reacting with ozone or OH^{*}.

Fig. 5c compares the O₃/UV processes of DMP using the TiO₂/Al₂O₃ and Degussa P25 TiO₂ catalysts. The O₃/UV process with the Degussa P25 TiO₂ catalyst had the maximal η_{TOC} of approximately 90%, which is close to the value obtained in the sole O₃/UV process reported by Chen et al. [8]. On the other hand, the O₃/UV process with the TiO₂/Al₂O₃ catalyst nearly reached complete mineralization with a maximal η_{TOC} of approximately 98%, which was mainly attributed to the catalytic ozonation happened in the bulk solution. Another advantage of using the TiO₂/Al₂O₃ catalyst in the catalytic ozonation is easy to recover while the small particle size of Degussa P25 TiO₂ tends to accumulate or cause blockages in instruments.

3.4. Ozone utilization and TOC removal associated with ozone consumption

To further investigate the catalytic ozonation, the variation of the amount of ozone consumed per mole of DMP ($m_{\text{O3R}}/(C_{\text{BLb0}}V_{\text{L}})$) with the amount of ozone applied per mole of DMP ($m_{\text{O3A}}/(C_{\text{BLb0}}V_{\text{L}})$) was studied, as shown in Fig. 6. The masses of ozone applied (m_{O3A}) and consumed (m_{O3R}) were calculated by Eqs. (1) and (2), respectively, where V_{F} is the volume of free space in the reactor.

$$m_{\text{O3A}} = Q_{\text{G}} \times C_{\text{AGi0}} \times t \quad (1)$$

Table 2
Comparison of the ozonation results at the time to reduce DMP concentration greater than 98% ($t_{\text{r,DMP}}$) under various experimental conditions.^a

Catalyst types	C_{AGi0} (mg/L)	W_{cat} (g/L)	$[I]$ (W/L)	$t_{\text{r,DMP}}$ (min)	η_{TOC} (%)	pH	k_{B} (min ⁻¹)	R^2
None	14	0	0	30	15.19	3.11	0.131	0.997
	14	0	0.648	30 ^b	32.6 ^b	3.26 ^b	0.177 ^b	0.949
TiO ₂	14	1	0	30	20.78	3.07	0.167	0.994
TiO ₂	14	1	0.648	30	65.50	1.67	0.245	0.985
Al ₂ O ₃	14	10	0	30	22.89	3.54	0.127	0.991
TiO ₂ + Al ₂ O ₃ ^c	14	11	0	30	22.47	3.28	0.134	0.998
TiO ₂ /Al ₂ O ₃	8	10	0	60	40.80	2.80	0.086	0.998
	14	1	0	30	13.40	3.08	0.125	0.996
	14	5	0	30	23.54	2.81	0.171	0.978
	14	10	0	30	27.48	2.61	0.111	0.984
	14	10	0.648	30	46.74	3.03	0.180	0.964
	14	20	0	15	18.35	2.87	0.144	0.988
	14	40	0	15	26.52	2.99	0.187	0.966

^a Initial values of pH and DMP concentration were 5.60 and 0.4 mM.^b Obtained from Chen et al. [8].^c Degussa P25 TiO₂ catalyst: $W_{\text{cat}} = 1$ g/L; Al₂O₃ catalyst: $W_{\text{cat}} = 10$ g/L.

$$m_{\text{O3R}} = \int_0^t (C_{\text{AGi0}} - C_{\text{AGe}}) dt - C_{\text{ALb}} V_{\text{L}} - C_{\text{AGe}} V_{\text{F}} \quad (2)$$

The slope of the curves in Fig. 6 represents the utilization efficiency of the fed ozone.

As shown in Fig. 6a, the utilization efficiency of the fed ozone was significantly improved in the presence of the Al₂O₃ catalyst compared to the efficiencies with no catalyst or with the Degussa P25 TiO₂ catalyst. This result may be caused by the catalytic mechanism of the Al₂O₃ catalyst, resulting in an increase in the mass of consumed ozone [17–19]. The utilization efficiency of the fed ozone with the Degussa P25 TiO₂ catalyst had a similar trend as did sole ozonation, indicating insignificant enhancement of ozone utilization with this catalyst. Moreover, the ozone utilization obtained with the TiO₂/Al₂O₃ catalyst was found to be similar to that obtained with the Al₂O₃ catalyst at the same catalyst dosage (Fig. 6b). In addition, the introduction of UV radiation was advantageous to the utilization efficiency of the fed ozone, especially when the $m_{\text{O3A}}/(C_{\text{BLb0}}V_{\text{L}})$ was greater than 20 (Fig. 6c). For example, the ozone utilization ranged from 12 to 16% and from 34 to 43% in the catalytic ozonation without and with UV radiation, respectively, at the $m_{\text{O3A}}/(C_{\text{BLb0}}V_{\text{L}})$ of 55. The information would be advantageous to evaluate the ozone dose in large scale applications.

The relationship between the η_{TOC} and $m_{\text{O3R}}/(C_{\text{BLb0}}V_{\text{L}})$ is illustrated in Fig. 7. Sole ozonation had the low $m_{\text{O3R}}/(C_{\text{BLb0}}V_{\text{L}})$ and η_{TOC} (Fig. 7a), indicating that further oxidation of the intermediates cannot proceed in this non-catalytic process. A comparison of Fig. 7a and b shows that the addition of the TiO₂/Al₂O₃ catalyst increased the extent of TOC removal. A greater dosage of the TiO₂/Al₂O₃ cat-

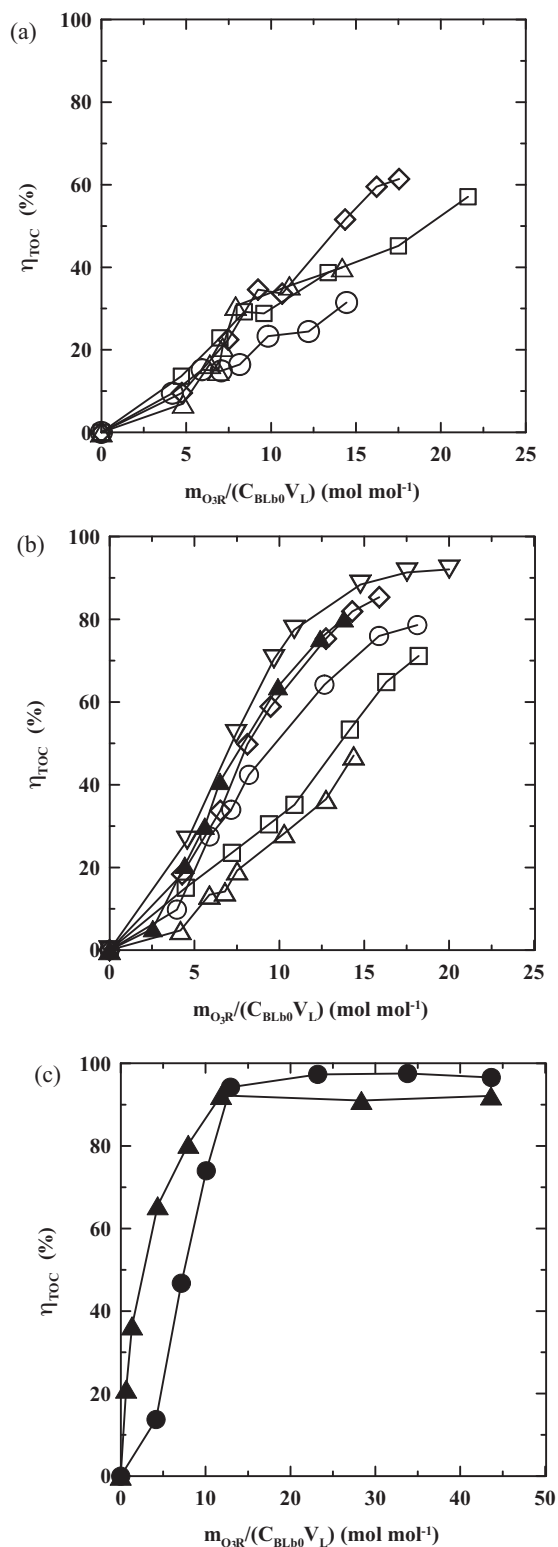


Fig. 7. TOC removal percentage vs. the amount of ozone consumed per mole of DMP in the ozonation of DMP. The experimental conditions and notations are the same as those specified in Fig. 4.

alyst increased the TOC removal at the same $m_{O_3R}/(C_{BLb0}V_L)$, as shown in Fig. 7b. In the catalytic ozonation with UV radiation using the TiO_2/Al_2O_3 catalyst (Fig. 7c), approximately 94% of the TOC was removed at the $m_{O_3R}/(C_{BLb0}V_L)$ of 12.9, revealing the greatest mineralization ability.

3.5. Mechanism of the catalytic ozonation of DMP

Furthermore, the present study showed superior mineralization performance in both the O_3 and O_3/UV processes of DMP with the use of the TiO_2/Al_2O_3 catalyst compared to the findings in the literatures as indicated in Table 3. It is mainly attributed to the catalytic mechanism of the TiO_2/Al_2O_3 catalyst which led to better oxidation ability. To illustrate the possible roles of ozone and the TiO_2/Al_2O_3 catalyst in the ozonation of DMP and its intermediates, a simplified scheme showing the catalytic ozonation of DMP with the TiO_2/Al_2O_3 catalyst is depicted in Fig. 8. The direct attack of ozone is primarily on the substituted benzene ring of DMP at certain positions around the ring [8,21], suggesting a rapid oxidation rate via pathway I. Because intermediates are usually inhibitory to the ozone molecules, pathway II is slow relative to pathway I. The catalytic ozonation process consists of the generation of OH^\bullet from the surface reaction of the TiO_2/Al_2O_3 catalyst, marked as pathway III. This pathway was the principal pathway of the consumption of the fed ozone in the late DMP ozonation stage. The presence of OH^\bullet led to successive oxidation reactions of DMP and its intermediates, marked as pathways IV and V, respectively, accounting for the enhancement of the TOC removal in these reactions. The purpose of introducing UV radiation was to promote the generation of OH^\bullet , as shown in pathway VI [22]. Furthermore, catalytic ozonation involved the adsorption of intermediates, denoted pathway VII. In this study, the adsorption of the intermediates on the TiO_2/Al_2O_3 catalyst contributes to the increase in the TOC removal and may also be beneficial for the subsequent oxidation reactions.

Consequently, the difference between sole and catalytic ozonation resulted from the contributions of reactions IV, V, and VII. Based on the experimental data, several conclusions were made: (1) the introduction of the TiO_2/Al_2O_3 catalyst exerted the catalytic ozonation to enhance the TOC removal, (2) the increase of the TOC removal involves the synergistic effect of adsorption and radical oxidation by the TiO_2/Al_2O_3 catalyst, and (3) the TiO_2/Al_2O_3 catalyst has superior performance in the catalytic ozonation in terms of the ozone utilization and TOC removal compared to the other catalysts.

Based on the results of the LC-MS analysis, a mechanism of the DMP degradation during the catalytic ozonation with the TiO_2/Al_2O_3 catalyst was proposed (Fig. 9). Both reaction pathways A and B were observed in both the sole and catalytic ozonation of DMP. However, sole ozonation likely proceeds through pathway A, in which the hydroxylation of DMP to generate 3-hydroxy dimethyl phthalate was the first ozonated step. The next step is the oxidative cleavage of the benzene ring as carboxylation forms 3,4-di-methyloxycarbonyl 2,4-hexadienedioic acid. Intermediates including 3-hydroxy 3-formyl propanoic acid, 2-hydroxy pentanedioic acid, and 2, 3-dihydroxy pentanedioic acid, resulted from further oxidation. On the other hand, the catalytic ozonation would preferably cleave the benzene ring at the ortho position of the methyloxycarbonyl group to generate 5,6-dimethyloxycarbonyl 2,4-hexadienedioic acid through pathway B on the surface of the TiO_2/Al_2O_3 catalyst. The following intermediates included 2-hydroxy dimethyl succinate, 2,4-hexadienedioic acid, and 4-hydroxy 2-pentenoic acid, etc. In consequence, the resulting products such as malonic and oxalic acids were associated with the generation of carboxylic groups and accounted for the significant decrease in the pH of the solution during the ozonation.

3.6. Durability of TiO_2/Al_2O_3 catalysts

The variations of η_{TOC} using the TiO_2/Al_2O_3 catalysts which were prepared at different calcination temperatures (400, 600, 800, or 1000 °C) during repetitive DMP ozonation cycles were studied to

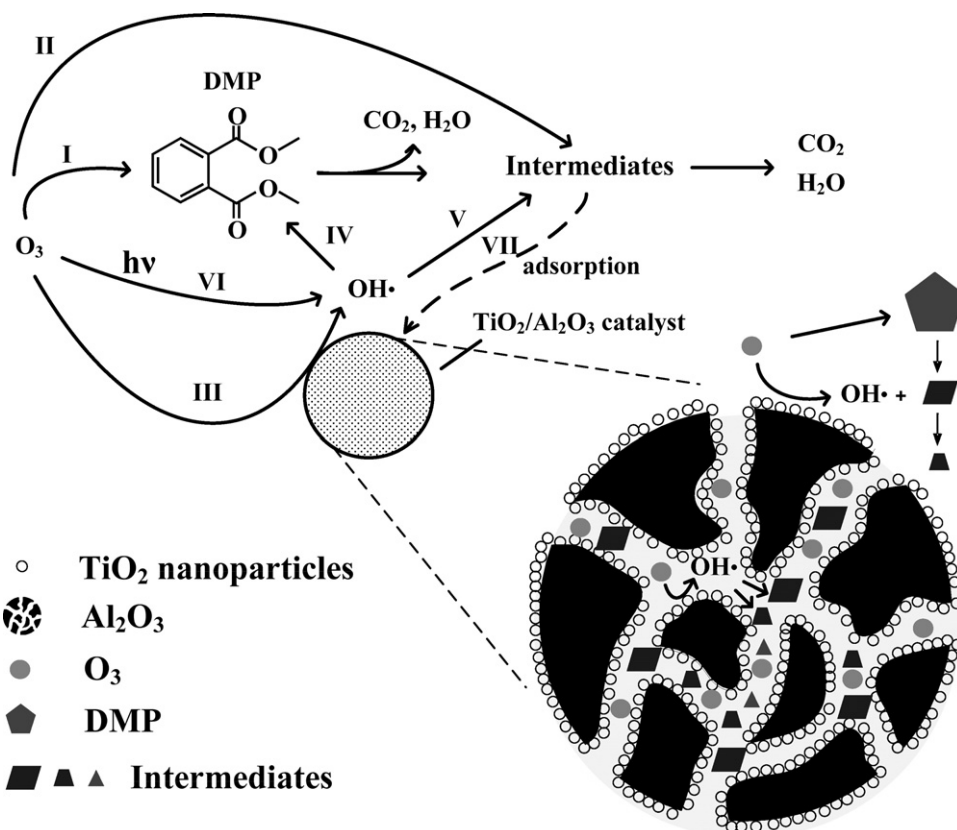


Fig. 8. Simplified reaction mechanism of catalytic ozonation of DMP using the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst.

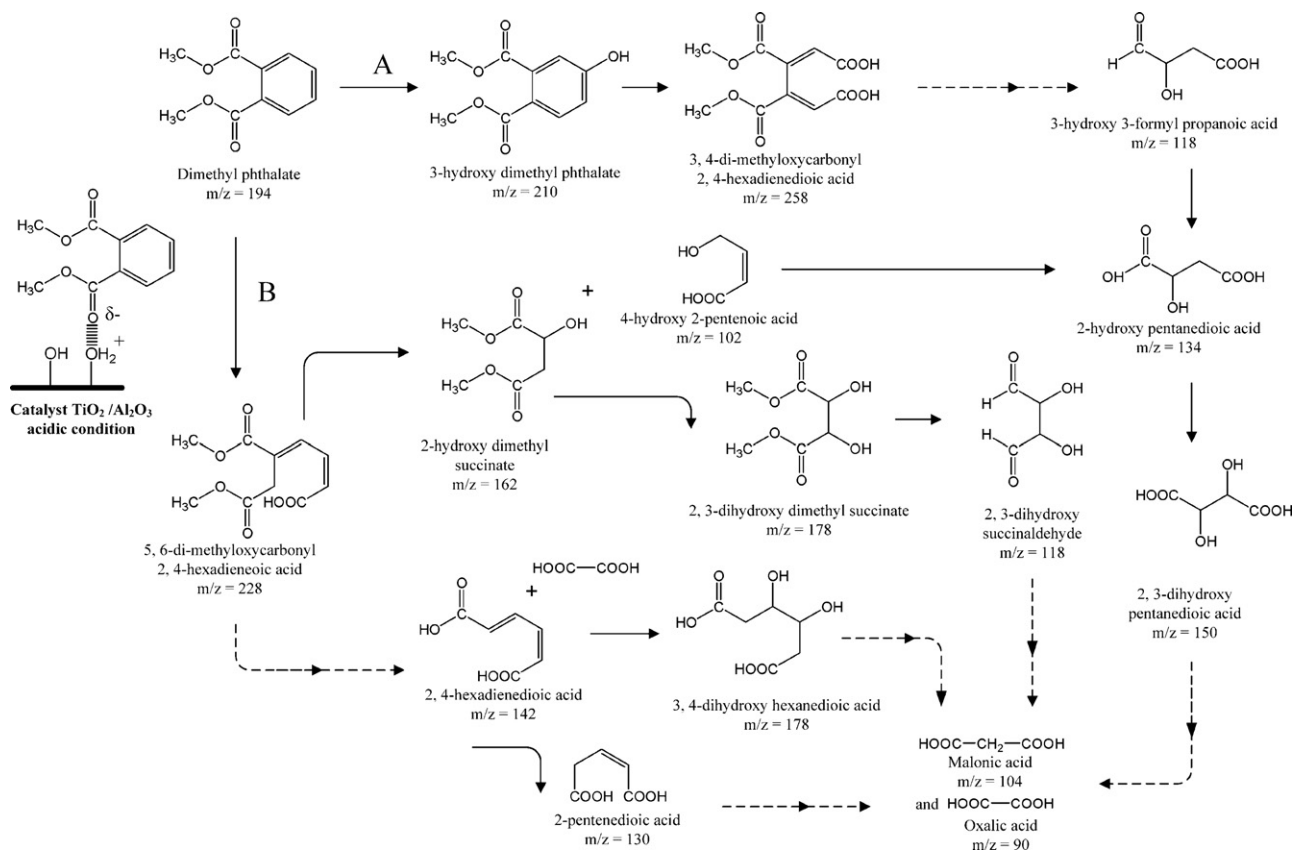


Fig. 9. Degradation mechanism of DMP in catalytic ozonation with the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst.

Table 3
Comparison of the mineralization results in catalytic ozonation of DMP.

Authors	Catalyst	Process	C_{BLD0} (mg/L)	$m_{\text{O}_3\text{A}}/(C_{\text{BLD0}}V_1)$ (mol mol ⁻¹)	W_{cat} (g/L)	η_{TOC} (%)
Zhou et al. [9]	Ru/Al ₂ O ₃	O ₃	6	156	10	72
Chen et al. [8]	High silica zeolites	O ₃	77.7	142	1	36
		O ₃ /UV	77.7	69	1	91
Chang et al. [10]	Pt/Al ₂ O ₃	O ₃	100	61	220	57
		O ₃ /UV	100	61	220	65
Jing et al. [20]	TiO ₂	O ₃	10	8	1	48.3
		O ₃ /UV	10	8	1	79.9
Present work	TiO ₂ /Al ₂ O ₃	O ₃	77.7	69	10	76
		O ₃ /UV	77.7	69	10	98

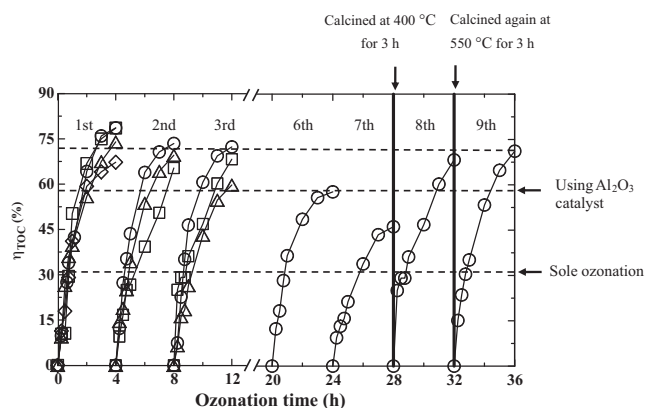


Fig. 10. Variation of TOC removal percentage for repetitive DMP ozonation cycles with the TiO₂/Al₂O₃ catalysts. $W_{\text{cat}} = 10$ g/L. ○, △, □, and ◇: TiO₂/Al₂O₃ catalysts calcined at 400 °C, 600 °C, 800 °C, and 1000 °C, respectively.

examine the durability of the catalysts (Fig. 10). The TiO₂/Al₂O₃ catalyst that was calcined at 400 °C had the greatest catalytic activity, possibly due to its high BET surface area (Table 1). After repetitive ozonation runs, the activity of the TiO₂/Al₂O₃ catalyst decreased noticeably because of the residual contaminant inside the catalyst. It was worth to note that the catalytic activity of the used TiO₂/Al₂O₃ catalyst can be recovered by an incineration process at a high temperature (≥ 400 °C), a process which removed the residual contaminant. A slight decrease in catalytic activity remained after the incineration process compared to the fresh catalyst that may be attributed to the possible residual contaminant or property changes of the used TiO₂/Al₂O₃ catalyst.

4. Conclusions

Ozonation using a TiO₂/Al₂O₃ catalyst was developed as an effective means to eliminate dimethyl phthalate (DMP) from aqueous solutions. The TiO₂/Al₂O₃ catalyst is composed of approximately 10.0 wt.% TiO₂ and 87.3 wt.% Al₂O₃ and was the most active when it was calcined at 400 °C. The removal percentage of total organic carbons (η_{TOC}) was the most efficient in the process employing the TiO₂/Al₂O₃ catalyst, followed by the Al₂O₃ catalyst, the Degussa P25 TiO₂ catalyst, and sole ozonation. In the catalytic ozonation, the relationship between the η_{TOC} and catalyst dosage followed the relation $\eta_{\text{TOC}} (\%) = W_{\text{cat}} / (1 + 1.13W_{\text{cat}})$, where W_{cat} is the dosage of the TiO₂/Al₂O₃ catalyst in units of g/L. Moreover, the combination of the catalytic ozonation with UV radiation resulted in the η_{TOC} of approximately 98%. The activity of the TiO₂/Al₂O₃ catalyst, which decreased after multi-run experiments, was effectively recovered by an incineration process at high temperature (≥ 400 °C).

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References

- Q.Y. Cai, C.H. Mo, Q.T. Wu, Q.Y. Zeng, A. Katsoyiannis, Occurrence of organic contaminants in sewage sludges from eleven wastewater treatment plants, China, *Chemosphere* 68 (2007) 1751–1762.
- M.J. Bauer, R. Herrmann, A. Martin, H. Zellmann, Chemodynamics, transport behavior and treatment of phthalic acid esters in municipal landfill leachates, *Water Sci. Technol.* 38 (1998) 185–192.
- G. Latini, Monitoring phthalate exposure in humans, *Clin. Chim. Acta* 361 (2005) 20–29.
- P. Roslev, K. Vorkamp, J. Aarup, K. Frederiksen, P.H. Nielsen, Degradation of phthalate esters in an activated sludge wastewater treatment plant, *Water Res.* 41 (2007) 969–976.
- M.D. Gurof, P.C. Singer, Kinetic of ozone decomposition: a dynamic approach, *Environ. Sci. Technol.* 16 (1982) 377–383.
- M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- B.S. Oh, Y.J. Jung, Y.J. Oh, Y.S. Yoo, J.W. Kang, Application of ozone, UV and ozone/UV processes to reduce diethyl phthalate and its estrogenic activity, *Sci. Total Environ.* 367 (2006) 681–693.
- Y.H. Chen, N.C. Shang, D.C. Hsieh, Decomposition of dimethyl phthalate in an aqueous solution by ozonation with high silica zeolites and UV radiation, *J. Hazard. Mater.* 157 (2008) 260–268.
- Y. Zhou, W. Zhu, F. Liu, J. Wang, S. Yang, Catalytic activity of Ru/Al₂O₃ for ozonation of dimethyl phthalate in aqueous solution, *Chemosphere* 66 (2007) 145–150.
- C.C. Chang, C.Y. Chiu, C.Y. Chang, C.F. Chang, Y.H. Chen, D.R. Ji, Y.H. Yu, P.C. Chiang, Combined photolysis and catalytic ozonation of dimethyl phthalate in a high-gravity rotating packed bed, *J. Hazard. Mater.* 161 (2009) 287–293.
- F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, A TiO₂/Al₂O₃ catalyst to improve the ozonation of oxalic acid in water, *Appl. Catal. B: Environ.* 47 (2004) 101–109.
- W.L. McCabe, J.C. Smith, P. Harriott, *Unit Operations of Chemical Engineering*, fifth ed., McGraw-Hill, New York, 1993.
- K. Rankness, G. Gordon, B. Langlais, W. Masschelein, N. Matsumoto, Y. Richard, C.M. Robson, I. Somyia, Guideline for measurement of ozone concentration in the process gas from an ozone generator, *Ozone Sci. Eng.* 18 (1996) 209–229.
- H. Bader, J. Hoigné, Determination of ozone in water by the indigo method, *Water Res.* 15 (1981) 449–456.
- R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental Organic Chemistry*, second ed., John Wiley & Sons, New York, 2003.
- B. Langlais, D.A. Reckhow, D.R. Brink, *Ozone in Water Treatment: Application and Engineering*, first ed., Lewis Publishers, Chelsea, Michigan, 1991.
- M. Ernst, F. Lurot, J.C. Schrotter, Catalytic ozonation of refractory organic model compounds in aqueous solution by aluminum oxide, *Appl. Catal. B: Environ.* 47 (2004) 15–25.
- M. Trapido, Y. Veressina, R. Munter, J. Kallas, Catalytic ozonation of m-dinitrobenzene, *Ozone Sci. Eng.* 27 (2005) 359–363.
- C. Tizaoui, R.I. Bickley, M.J. Slater, W.J. Wang, D.B. Ward, A. Al-Jaberi, A comparison of novel ozone-based systems and photocatalysis for the removal of water pollutants, *Desalination* 227 (2008) 57–71.
- Y. Jing, L. Li, Q. Zhang, P. Lu, P. Liu, X. Lü, Photocatalytic ozonation of dimethyl phthalate with TiO₂ prepared by a hydrothermal method, *J. Hazard. Mater.* 189 (2011) 40–47.
- J. Hoigné, Chemistry of aqueous ozone and transformation of pollutants by ozone and advanced oxidation processes, in: J. Hrubec (Ed.), *The Handbook of Environmental Chemistry*, vol. 5, part C Quality and Treatment of Drinking Water, Part II, Springer, Berlin, Heidelberg, 1998, pp. 83–141.
- Y.H. Chen, C.Y. Chang, S.F. Huang, C.Y. Chiu, D.R. Ji, N.C. Shang, Y.H. Yu, P.C. Chiang, Y. Ku, J.N. Chen, Decomposition of 2-naphthalenesulfonate in aqueous solution by ozonation with UV radiation, *Water Res.* 36 (2002) 4144–4154.