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3 **The role of cobalt oxide or magnesium oxide in ozonation of ammonia nitrogen in water**

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19

20 **Abstract**

21 In this study, the reaction mechanisms for ozonation of ammonia nitrogen in the presence of  
22  $\text{Co}_3\text{O}_4$  or  $\text{MgO}$  were investigated. For the reaction over  $\text{Co}_3\text{O}_4$ ,  $\text{Cl}^-$  in the reaction solution was  
23 indispensable and  $\text{ClO}^-$  was formed by a non-catalytic oxidation of  $\text{Cl}^-$ .  $\text{Co}_3\text{O}_4$  promoted the  
24 reaction of  $\text{NH}_4^+$  with  $\text{ClO}^-$  to give the products including  $\text{NO}_3^-$ , chloramines and gaseous  
25 products. In contrast,  $\text{Cl}^-$  was unnecessary for the reaction with  $\text{MgO}$ . pH of the reaction  
26 solution was maintained at around 9 throughout the reaction owing to partial dissolution of  
27  $\text{MgO}$ . Ammonia nitrogen was decomposed to mainly  $\text{NO}_3^-$  by non-catalytic radical reaction  
28 involving  $\text{OH}\cdot$ , which was formed by the reaction of  $\text{OH}^-$  with  $\text{O}_3$  in weakly basic solution. To  
29 keep the reaction solution weakly basic,  $\text{H}^+$  formed with the decomposition of  $\text{NH}_4^+$  was  
30 neutralized. As a result, about the same amount of  $\text{Mg}^{2+}$  as that of decomposed ammonia  
31 nitrogen was dissolved.

32

33 Keywords: ozonation; ammonia nitrogen; cobalt oxide; magnesium oxide; wastewater  
34 treatment

35

36 **1. Introduction**

37 While ammonia ( $\text{NH}_3$ ) and ammonium ion ( $\text{NH}_4^+$ ), which are collectively called  
38 ammonia nitrogen, are indispensable nutrient for plants, excess ammonia nitrogen in water  
39 often causes eutrophication of rivers, lakes, and inland seas. In addition, ammonia nitrogen is  
40 toxic to fish species even if the concentration in water is less than  $10 \text{ mg L}^{-1}$  [1]. High  
41 concentration ammonia nitrogen in natural environment comes from inadequate treatments of  
42 industrial wastewater, household sewage, and livestock manure and runoff water from farmland  
43 with excess fertilization. Nitrogen-containing organic matters, such as urea, amino acids,  
44 polypeptides and proteins can be a source for ammonia nitrogen in wastewater with microbial  
45 action [2]. For environmental protection, ammonia nitrogen in environmental water should be  
46 below  $0.5 \text{ mg L}^{-1}$  [3,4]. To achieve this criteria, highly efficient and feasible processes for the  
47 purification of water containing ammonia nitrogen are absolutely necessary.

48 So far, many treatment processes have been studied and some of them including  
49 adsorption [5], ion exchange [6], activated sludge [7], stripping [8] and breakpoint chlorination  
50 [2] are commercially used for the treatment of wastewater containing ammonia nitrogen.  
51 However, each process has some limitations and disadvantages from technical and economic  
52 standpoints. For example, because ion exchange is the processes only removing ammonia  
53 nitrogen, waste brine containing high concentration ammonia nitrogen is generated, which  
54 should be further treated. Activated sludge process consumes a lot of energy and oxygen, and  
55 burdensome treatment of produced generated sludge is necessary [7]. Ammonia stripping  
56 technique requires a large stripping tower, strict control of  $\text{CaCO}_3$  dose, and is ineffective in  
57 winter due to the low volatility of  $\text{NH}_3$  under low temperature environment [8]. In addition, it  
58 potentially causes air pollution if the stripped  $\text{NH}_3$  is not appropriately treated.

59 Catalytic wet air oxidation (CWAO) is a process to oxidatively decompose  
60 contaminants in water by reaction with air ( $O_2$ ) in the presence of a catalyst. CWAO is  
61 considered to be applicable for purification of wastewater containing ammonia nitrogen. So far,  
62 several precious metals supported on carriers like metal oxides have been investigated for the  
63 reaction [9-14]. Taguchi and Okuhara reported that Pt/TiO<sub>2</sub> [9] and Pd/ZrO<sub>2</sub> [10] effectively  
64 and selectively promoted the oxidation of ammonia nitrogen into N<sub>2</sub> at relatively low  
65 temperature (433 K) and low pressure (0.5 MPa) in mild acidic solution (pH 5.5). These  
66 previous studies showed high potential of CWAO for the purification of wastewater containing  
67 ammonia nitrogen. However, harsh reaction conditions are still indispensable for achieving  
68 high decomposition rate to make up for low oxidizing ability of O<sub>2</sub> even by using highly active  
69 catalysts [14].

70 Catalytic ozonation is the reaction for oxidative decomposition of contaminants with  
71 O<sub>3</sub>. Because O<sub>3</sub> is a strong oxidant comparing with O<sub>2</sub>, the reaction often proceeds even under  
72 mild reaction conditions, e.g., low temperature and ambient pressure [15-17]. While non-  
73 catalytic ozonation of ammonia nitrogen in water [18] and catalytic one with a homogeneous  
74 catalyst [19] were reported in 1975 and 1984, respectively, the first paper on the latter over  
75 heterogeneous catalysts was reported in 2014 [20]. After that, Chen et al. reported Mg-Co  
76 mixed metal oxide catalyst with different Mg to Co ratios for the reaction [21] and found that  
77 MgO-Co<sub>3</sub>O<sub>4</sub> with Mg/Co = 4/1 calcined at 773 K was the best catalyst in terms of  
78 decomposition rate of ammonia nitrogen and selectivity to gaseous nitrogen compounds.

79 In our previous paper [20], eight metal oxides (MO<sub>x</sub>, M = Co, Ni, Fe, Sn, Mn, Cu, Mg  
80 and Al) were tested as a catalyst for the ozonation of ammonia nitrogen in mild-acidic solution  
81 under atmospheric pressure at 333 K in the presence of Cl<sup>-</sup>. It was found that the highest  
82 decomposition rate of ammonia nitrogen was obtained in the presence of MgO, but undesirable

83  $\text{NO}_3^-$  was predominantly formed. In addition, a part of MgO was dissolved during the reaction  
84 and pH of the reaction solution was increased up to around 9. The increase in pH of the reaction  
85 solution for the same reaction in the presence of MgO was also reported by Liu et al [22]. In  
86 stark contrast,  $\text{Co}_3\text{O}_4$  gave the highest selectivity to gaseous nitrogen products with more than  
87 85% selectivity and was insoluble in the reaction solution, while the catalytic activity was the  
88 third best among them. Furthermore, we found that the reaction proceeded only in the presence  
89 of  $\text{Cl}^-$ , demonstrating that  $\text{Cl}^-$  was indispensable for the reaction over  $\text{Co}_3\text{O}_4$ . However, it is  
90 not known how  $\text{Cl}^-$  is involved in the reaction over  $\text{Co}_3\text{O}_4$  and why the selectivity is so different  
91 for the reactions between in the presence of MgO and that of  $\text{Co}_3\text{O}_4$ .

92 In the present study, we conducted an in-depth investigation to provide a clear  
93 overview on the reaction mechanism for the ozonation of ammonia nitrogen in water in the  
94 presence of  $\text{Co}_3\text{O}_4$  or MgO. For the former, we focused on the behavior of  $\text{Cl}^-$  in the reaction  
95 solution during the reaction and tried to identify gaseous nitrogen products. The results clearly  
96 demonstrated that  $\text{Co}_3\text{O}_4$  effectively promoted the formation of chloramines ( $\text{NH}_{3-x}\text{Cl}_x$ ,  $x = 1,$   
97  $2,$  and  $3$ ) as gaseous nitrogen products. Meanwhile, we found that the reaction proceeded with  
98 a non-catalytic radical reaction in the presence of MgO and that MgO was just a reactant for  
99 the reaction.

100

## 101 **2. Experimental**

### 102 *2.1. Materials*

103 Analytical grade reagents of  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , KOH,  $\text{HNO}_3$ ,  
104  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ , NaClO, NaCl and aqueous ammonia were purchased from Wako Pure  
105 Chem. Ind. Ltd. and used without further purification.

106

107 *2.2. Preparation of Co<sub>3</sub>O<sub>4</sub> and MgO*

108 Cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) was prepared by a conventional precipitation method [20]. An  
109 aqueous ammonia (1.0 mol L<sup>-1</sup>) was added to a solution of Co(NO<sub>3</sub>)<sub>2</sub> (1.0 mol L<sup>-1</sup>) until pH of  
110 the solution was stably at 8.1. The suspension was stirred for 10 min at room temperature. The  
111 formed blue-green precipitate was separated by filtration, washed with distilled water, and dried  
112 at 373 K for 24 h. The solid was ground with a mortar and then was calcined in air at 773 K for  
113 4 h.

114 Magnesium oxide (MgO) was prepared by calcining Mg(OH)<sub>2</sub> at 773 K for 5 h [20].  
115 Calcium oxide (CaO) was also prepared with the same manner to that of MgO except for using  
116 Ca(OH)<sub>2</sub>.

117

118 *2.3. Characterization*

119 Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer  
120 (Rigaku, Miniflex) with Cu K $\alpha$  radiation ( $\lambda$ = 0.154 nm, 30 kV, 15 mA) at room temperature.  
121 Specific surface area was estimated by applying the Brunauer–Emmett–Teller (BET) equation  
122 to an adsorption isotherm of N<sub>2</sub> at 77 K, which was acquired on a Belsorp-mini instrument  
123 (BEL Japan Inc.). The sample was pretreated in N<sub>2</sub> flow at 473 K for 3 h before the  
124 measurement.

125

126 *2.4. Ozonation of ammonia nitrogen in water*

127 Ozonation of ammonia nitrogen in water was performed by using a semi-batch reactor  
128 connected to a gas flow line and traps (Fig. 1). Two reaction solutions containing 10 mM NH<sub>4</sub><sup>+</sup>,  
129 which was present as NH<sub>3</sub> when the solution was alkaline, were prepared from NH<sub>4</sub>Cl and  
130 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and are denoted as **Sol(Cl)** and **Sol(SO<sub>4</sub>)**, respectively. Typically, 0.1 g of Co<sub>3</sub>O<sub>4</sub>

131 or MgO was added to the reactor containing 100 mL of the reaction solution and the suspension  
132 was vigorously stirred in a stream of O<sub>2</sub> (100 cm<sup>3</sup> min<sup>-1</sup>). After temperature of the suspension  
133 reached to predetermined one (298 or 333 K), the gas was changed to a mixture of O<sub>3</sub>/O<sub>2</sub> (1.88  
134 mmol L<sup>-1</sup> as O<sub>3</sub>, total flow rate = 100 cm<sup>3</sup> min<sup>-1</sup>) to start the ozonation of ammonia nitrogen.  
135 O<sub>3</sub> was generated from O<sub>2</sub> using an ozone generator (Tokyu Car Co., SO-03UN-OX).

136 A small portion of the reaction solution was periodically withdrawn and analyzed to  
137 determine the concentrations of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> by using two ion chromatographs  
138 (Tosoh Co. Ltd., IC-2001). A column containing an anion-exchange resin (TSK gel Super IC-  
139 AZ, Tosoh) and an aqueous solution of NaHCO<sub>3</sub> (2.9 mmol L<sup>-1</sup>) and Na<sub>2</sub>CO<sub>3</sub> (3.1 mmol L<sup>-1</sup>)  
140 were used as stationary and mobile phases, respectively, for anion analysis. For cation analysis,  
141 a column containing a cation-exchange resin (TSK gel IC-Cation 1/2 HR, Tosoh) and an  
142 aqueous solution of methanesulfonic acid (2.2 mmol L<sup>-1</sup>) and 18-crown-6 (1.0 mmol L<sup>-1</sup>) were  
143 used as stationary and mobile phases, respectively. Since the eluting solution used for the cation  
144 analysis was highly acidic, all ammonia nitrogen in the solution was detected as NH<sub>4</sub><sup>+</sup> even if  
145 NH<sub>3</sub> was present in the solution. The yield of and selectivity to NO<sub>3</sub><sup>-</sup> were calculated by Eqs.  
146 1 and 2, respectively.

147

$$148 \quad \text{Yield of NO}_3^- = \frac{\text{Formed NO}_3^-}{\text{Initial NH}_4^+} \quad (1)$$

$$149 \quad \text{Selectivity to NO}_3^- = \frac{\text{Formed NO}_3^-}{\text{Consumed NH}_4^+} \quad (2)$$

150

151 Because basically gaseous nitrogen products were not analyzed in this study, the selectivity to  
152 them was calculated by subtracting the selectivity to NO<sub>3</sub><sup>-</sup> from 100%.



153 While pH of both **Sol**(SO<sub>4</sub>) and **Sol**(Cl) was around 5.5, it was adjusted to 7 and 9 for  
154 some reactions by the addition of aqueous solution of KOH. For the reaction in the presence of  
155 MgO, the concentration of Mg<sup>2+</sup> in the reaction solution was determined by the ion  
156 chromatograph in a similar manner to that of NH<sub>4</sub><sup>+</sup>.

157 ClO<sub>x</sub><sup>-</sup> in solutions were determined by using another ion chromatograph (Thermo  
158 Scientific, Dionex ICS-900) equipped with a column of Dionex IonPac AS16 RFIC. An  
159 aqueous solution of NaOH (35 mmol L<sup>-1</sup>) was used as a mobile phase.

160 Total chlorine in the reaction solution was quantified by using an inductively coupled  
161 plasma mass spectrometer (ICP-MS, Agilent Technology, 8800 ICP-QQQ). Gas  
162 chromatography mass spectroscopy (GC-MS) analysis was performed by using GCMS-  
163 QP2010 SE (Shimadzu) equipped with a capillary column (SH-Rxi-5 Sil MS, 30 m × 0.25 mm  
164 × 0.25 μm, Shimadzu). Mass spectrum was obtained with electron impact mode, and the  
165 interface and ion source were heated at 333 and 423 K, respectively.

166

#### 167 2.5. Reaction of NH<sub>4</sub><sup>+</sup> with ClO<sup>-</sup> without O<sub>3</sub>

168 Reaction of NH<sub>4</sub><sup>+</sup> with ClO<sup>-</sup> without O<sub>3</sub> was carried out in a similar manner to that for  
169 the ozonation of ammonia nitrogen in water, while O<sub>2</sub> was fed into the reactor instead of O<sub>3</sub>/O<sub>2</sub>  
170 mixture. The reaction solution was prepared by adding NaClO to **Sol**(Cl) and the concentrations  
171 of NH<sub>4</sub><sup>+</sup> and ClO<sup>-</sup> in the solution were 10 and 20 mmol L<sup>-1</sup>, respectively. The pH of the reaction  
172 solution was adjusted to 5.5 with dilute nitric acid.

173

### 174 3. Results and discussion

#### 175 3.1. Physical properties of Co<sub>3</sub>O<sub>4</sub> and MgO

176 Fig. 2 shows the XRD patterns of as-prepared  $\text{Co}_3\text{O}_4$  and  $\text{MgO}$ . The typical diffraction  
177 lines due to spinel type  $\text{Co}_3\text{O}_4$  were observed at  $2\theta = 19.08, 31.32, 36.90, 38.68, 44.82, 55.82,$   
178  $59.34, 65.26$  and  $77.42^\circ$ , which were ascribed to (111), (220), (311), (222), (400), (422), (511),  
179 (440) and (533), respectively.  $\text{MgO}$  gave the diffraction lines at  $2\theta = 36.91, 42.88, 62.27, 74.65$   
180 and  $78.58^\circ$ , which were assignable to (111), (200), (220), (311) and (222), respectively, for  
181 cubic  $\text{MgO}$ . The sizes of the crystallites estimated by applying a Scherrer's equation to the  
182 diffraction lines at  $36.90$  and  $42.88^\circ$  of  $\text{Co}_3\text{O}_4$  and  $\text{MgO}$  were 26 and 36 nm, respectively. The  
183 specific surface areas of  $\text{Co}_3\text{O}_4$  and  $\text{MgO}$  were 12 and  $252 \text{ m}^2 \text{ g}^{-1}$ , respectively.

184

### 185 *3.2 Involvement of $\text{Cl}^-$ for ozonation of ammonia nitrogen*

186 Fig. 3 shows the conversion and selectivity at 6 h for the ozonation of ammonia nitrogen  
187 in **Sol(Cl)** and **Sol(SO<sub>4</sub>)** at 333 K in the presence of  $\text{Co}_3\text{O}_4$  and  $\text{MgO}$ . In the absence of neither  
188 solid materials, only a small amount of  $\text{NH}_4^+$  was decomposed in **Sol(Cl)** and no reaction  
189 occurred in **Sol(SO<sub>4</sub>)**. In the presence of  $\text{Co}_3\text{O}_4$ ,  $\text{NH}_4^+$  was decomposed only in **Sol(Cl)**,  
190 forming gaseous nitrogen products with ca. 83% selectivity, while no reaction occurred in  
191 **Sol(SO<sub>4</sub>)**, suggesting involvement of  $\text{Cl}^-$  in the reaction. To further confirm the participation of  
192  $\text{Cl}^-$ , we examined influence of the concentration of  $\text{Cl}^-$  on the conversion of  $\text{NH}_4^+$  and  
193 selectivities by the addition of  $\text{NaCl}$  into **Sol(SO<sub>4</sub>)** (Fig. 4). With an increase in the  
194 concentration of  $\text{Cl}^-$ , the conversion of  $\text{NH}_4^+$  increased. The selectivity to gaseous products  
195 with  $10 \text{ mmol L}^{-1} \text{Cl}^-$  was almost the same as that for the reaction in **Sol(Cl)**. Therefore, it was  
196 concluded that  $\text{Cl}^-$  played a critical role for the reaction over  $\text{Co}_3\text{O}_4$ .

197 In contrast to the reactions over  $\text{Co}_3\text{O}_4$ , there was little difference in the reaction results  
198 with **Sol(Cl)** and **Sol(SO<sub>4</sub>)** in the presence of  $\text{MgO}$ . Almost all  $\text{NH}_4^+$  was decomposed at 6 h in  
199 the presence of  $\text{MgO}$  and  $\text{NO}_3^-$  was a main product regardless of the reaction solutions. These

200 results indicate that  $\text{Cl}^-$  in the solution was not involved in the reaction with  $\text{MgO}$ . This  
201 significant difference in the reaction behavior between  $\text{Co}_3\text{O}_4$  and  $\text{MgO}$  strongly suggest a  
202 difference in reaction mechanism in the presence of each solid.

203

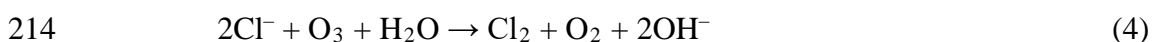
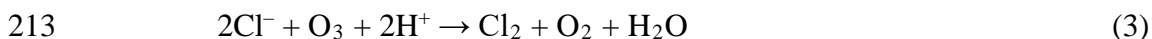
### 204 3.3. Reaction mechanism over $\text{Co}_3\text{O}_4$

#### 205 3.3.1. Behavior of $\text{Cl}^-$ during the reaction

206 As mentioned in 3.2,  $\text{Cl}^-$  was indispensable for the reaction over  $\text{Co}_3\text{O}_4$ . To investigate  
207 how  $\text{Cl}^-$  was involved in the reaction, time course in the concentration of  $\text{Cl}^-$  was examined in  
208 **Sol(Cl)** in the presence of  $\text{Co}_3\text{O}_4$  (Fig. S1). It should be noted that the concentration of  $\text{Cl}^-$  was  
209 decreased with reaction time and more than 85% of  $\text{Cl}^-$  in the reaction solution was lost at 6 h.

210 One possibility for the loss of  $\text{Cl}^-$  was the formation of  $\text{Cl}_2$  by the oxidation of  $\text{Cl}^-$  with  
211  $\text{O}_3$  (Eqs. 3 and 4) and then it went out from the reactor with the flow of  $\text{O}_3/\text{O}_2$  mixture.

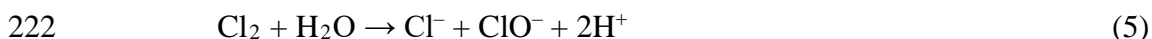
212



215

216 In fact, no formation of  $\text{Cl}_2$  occurred as was confirmed by the following experiment. The  
217 reaction was performed in **Sol(Cl)** in the presence of  $\text{Co}_3\text{O}_4$  and the outlet gas from the reactor  
218 was absorbed by pure water in the three traps connected in series. If  $\text{Cl}_2$  was formed,  $\text{Cl}^-$  should  
219 be detected in the water along with  $\text{ClO}^-$  because  $\text{Cl}_2$  is easily reacted with water to form  $\text{Cl}^-$   
220 and  $\text{ClO}^-$  (Eq. 5).

221



223

224 Neither  $\text{Cl}^-$  nor  $\text{ClO}^-$  was detected in water of the traps. To further investigate the possibility of  
225 the formation of  $\text{Cl}_2$  by the oxidation of  $\text{Cl}^-$  with  $\text{O}_3$ , we carried out the reaction in an aqueous  
226 solution of NaCl with a similar manner to that in **Sol(Cl)**. However, no formation of  $\text{Cl}^-$  nor  
227  $\text{ClO}^-$  was confirmed. Thus, the formation of  $\text{Cl}_2$  was improbable.

228 Another possibility for the loss of  $\text{Cl}^-$  was the formation of  $\text{ClO}_x^-$  ( $x = 1-4$ ) by the  
229 reaction with  $\text{O}_3$ . To check the formation of  $\text{ClO}_x^-$  during the reaction in **Sol(Cl)** in the presence  
230 of  $\text{Co}_3\text{O}_4$ , we applied analytical conditions for ion-chromatography analysis being able to  
231 detect them in the solution (see the experimental section). Unfortunately,  $\text{ClO}^-$  and  $\text{ClO}_3^-$   
232 cannot be analyzed individually even with the analytical conditions if they exist together in the  
233 solution because unavoidable reduction of  $\text{ClO}_3^-$  to  $\text{ClO}^-$  occurs in the column. Thus, we only  
234 knew the total amount of  $\text{ClO}^-$  and  $\text{ClO}_3^-$ . The ion-chromatography analysis showed no  
235 formation of  $\text{ClO}_2^-$  and  $\text{ClO}_4^-$  in the reaction solution at any reaction time. On the other hand,  
236  $\text{ClO}^-$ , some of which could come from  $\text{ClO}_3^-$ , was found in the solution, but the amount of  
237  $\text{ClO}^-$  at 6 h corresponded to only 5% or less of that of the lost  $\text{Cl}^-$ . Thus, the formation of  $\text{ClO}^-$   
238 or  $\text{ClO}_3^-$  was not the main cause for the loss of  $\text{Cl}^-$  during the reaction in **Sol(Cl)**.

239

### 240 3.3.2. Formation of chloramines

241 To investigate the involvement of  $\text{NH}_4^+$  in the loss of  $\text{Cl}^-$ , we evaluated the  
242 consumption rate of  $\text{Cl}^-$  in an aqueous solution of NaCl in the presence of  $\text{Co}_3\text{O}_4$ . It was found  
243 that the consumption rate of  $\text{Cl}^-$  in the aqueous solution of NaCl was about only one-tenth of  
244 that in **Sol(Cl)**, which were 0.087 and 0.92  $\text{mmol h}^{-1}$ , respectively. These results strongly  
245 suggest that the reaction of  $\text{Cl}^-$  with  $\text{NH}_4^+$  gave some chlorinated nitrogen compounds that were  
246 undetected by ion chromatography, namely non-ionic compounds.

247 To confirm the formation of such compounds, the reaction solution of **Sol(Cl)** in the  
248 presence of  $\text{Co}_3\text{O}_4$  was analyzed by an inductively coupled plasma-mass spectrometry (ICP-  
249 MS). The analysis with ICP-MS gives total concentration of chlorine in the solution. At 3 h of  
250 the reaction, the total concentration of chlorine in the solution was  $9.5 \text{ mmol L}^{-1}$ , while the  
251 concentration of  $\text{Cl}^-$  in the solution analyzed by ion chromatography was  $7.0 \text{ mmol L}^{-1}$  (Fig.  
252 S1). The fact that the total concentration of chlorine was higher than that of  $\text{Cl}^-$  indicated the  
253 presence of non-ionic chlorinated nitrogen compounds in the reaction solution.

254 It is known that monochloramine ( $\text{NH}_2\text{Cl}$ ) is formed by the reaction of  $\text{NH}_4^+$  with  
255 hypochlorite ( $\text{ClO}^-$ ) in weakly acidic aqueous solution even without any catalyst [23].  
256 Monochloramine is further transformed into dichloramine ( $\text{NHCl}_2$ ) and trichloramine ( $\text{NCl}_3$ )  
257 by the reaction with hypochloric acid ( $\text{HClO}$ ) if pH of the solution is around 4 or less [24].  
258 Initial pH of **Sol(Cl)** was 5.5 and pH was decreased to 3 at 6 h in the presence of  $\text{Co}_3\text{O}_4$  due to  
259 the oxidation of  $\text{NH}_4^+$  into neutral products as well as anionic  $\text{NO}_3^-$ . Thus, the formation of  
260 chloramines was possible for the reaction in **Sol(Cl)**.

261 Chloramines easily undergo decomposition in strongly basic solution, giving  $\text{Cl}^-$  [25].  
262 Thus, we took out an aliquot of the reaction solution and pH of the solution was increased to  
263 11 by the addition of an aqueous KOH solution. If chloramines were present in the solution, the  
264 concentration of  $\text{Cl}^-$  was increased after the pH increase. Furthermore, the outlet gas of the  
265 reactor was absorbed into a strongly basic KOH solution (pH 11), in which fine powder of MgO  
266 was further dispersed, in traps during the reaction in **Sol(Cl)** in the presence of  $\text{Co}_3\text{O}_4$ . Because  
267 chloramines especially trichloramine are less soluble in water, chloramines formed in the  
268 reaction solution could go out from the reactor with a flow of  $\text{O}_3/\text{O}_2$  mixture. To avoid slipping  
269 chloramines from the trap solution, three traps containing the strongly basic KOH solution with  
270 MgO fine powder were connected in series at the outlet of the reactor (Fig. 1) and we confirmed

271 that there was nothing detected in the third trap. The reaction solution and trap solutions were  
272 analyzed by ion chromatography to determine the concentration of  $\text{Cl}^-$ .

273 Fig. 5 displays time-course changes in the concentrations of  $\text{Cl}^-$  in the reaction solution  
274 as it was and in the reaction solution after the pH increase, and the concentration of  $\text{Cl}^-$  in the  
275 trap solution. For easy understanding, amounts of  $\text{Cl}^-$  found in the three trap solutions are  
276 combined and is displayed as if those exist in the reaction solution. It should be noted that the  
277 concentration of  $\text{Cl}^-$  in the reaction solution was increased after the pH increase. Especially at  
278 3 h, the increment was significant. This behavior strongly suggested the formation of  
279 chloramines. The amount of chlorine being incorporated in chloramines, which was estimated  
280 from the difference in the concentrations of  $\text{Cl}^-$  before and after the pH increase, corresponded  
281 to  $2.5 \text{ mmol L}^{-1}$  at 3 h. At 6 h, at which almost all  $\text{NH}_4^+$  disappeared in the reaction solution  
282 (Fig. S1), the increase in the concentration of  $\text{Cl}^-$  by the pH increase was only little, suggesting  
283 that the formed chloramines went out from the reactor. In fact, the concentration of  $\text{Cl}^-$  in the  
284 trap solution was drastically increased at 6 h. However, chlorine balance defined as Eq. 6 at 6  
285 h was about 85%, suggesting that some chlorine-containing compounds that were stable even  
286 in the strong alkaline solution were formed and/or were slipped out of the traps.

287

$$288 \quad \text{Chlorine balance (\%)} = \frac{[\text{Cl}^-]_{\text{reaction solution after pH increase}} + [\text{Cl}^-]_{\text{trap}}}{[\text{Cl}^-]_0} \times 100 \quad (6)$$

289

290 Unfortunately, we do not have any evidence to explain it and now it is still under investigation.

291 Next, we tried to detect chloramines directly by using GC-MS. The reaction solution at 3  
292 h was analyzed, but chloramines were not detected probably because the concentrations were  
293 below the detection limits. Thus, we applied a head-space GC-MS method to demonstrate the  
294 formation of chloramines during the reaction. A head-space GC-MS method is suitable for

295 analyzing minute amounts of volatile compounds present in solution, because such compounds  
296 are enriched in a gas phase of a vial container with the solution, namely head space, when the  
297 solution is allowed to stand in the sealed container [26]. Unfortunately, no standard solution of  
298 chloramines is available for analysis, because chloramines are unstable and are easy to strip  
299 into air. Thus, we performed only a qualitative analysis here.

300 According to Fig. 5, it seemed that the concentration of chloramines in the reaction  
301 solution was the highest at 3 h for the reaction in **Sol(Cl)** in the presence of  $\text{Co}_3\text{O}_4$ . Thus, we  
302 analyzed that reaction solution with the head-space GC-MS method. However, no peak due to  
303 chloramines was found on the gas chromatogram, probably because their concentrations in the  
304 solution were below detection limits for the head-space GC-MS analysis.

305 Thus, we collected chloramines formed during the reaction in **Sol(Cl)** in the presence  
306 of  $\text{Co}_3\text{O}_4$  by making the outlet gas of the reactor absorbed into pure water in a trap for 6 h and  
307 analyzed the trap solution. Fig. 6a gives the chromatogram of the trap solution obtained by the  
308 head-space GC-MS method. The large peak at 1.1 min on the chromatogram was due to air.  
309 The chromatogram had a large peak at 2.4 min, while very small ones were observed at 1.4 and  
310 1.6 min. Mass spectrum for the peak at 2.4 min showed the peaks at  $m/z = 119$  and 121 (Fig.  
311 6b), which was assignable to the molecular ions of trichloramine with  $\text{N}^{35}\text{Cl}^{35}\text{Cl}^{35}\text{Cl}$  and  
312  $\text{N}^{35}\text{Cl}^{35}\text{Cl}^{37}\text{Cl}$ , respectively. Since the abundance ratios of  $\text{N}^{35}\text{Cl}^{37}\text{Cl}^{37}\text{Cl}$  and  $\text{N}^{37}\text{Cl}^{37}\text{Cl}^{37}\text{Cl}$   
313 among trichloramine were small, being 0.07 and 0.02, respectively, the peaks at  $m/z = 123$  and  
314 125 assignable to their molecular ions were not observed. In addition to the molecular ion peaks,  
315 various fragment ion peaks were observed at 84, 86 and 88 ( $\text{NCl}_2^+$ ) and 49 and 51 ( $\text{NCl}^+$ ) with  
316 reasonable intensity ratios. Therefore, it was concluded that the formation of trichloramine was  
317 successfully confirmed by using the head-space GC-MS method. The small peaks at 1.4 and

318 1.6 min on the chromatogram seemed to be monochloramine and dichloramine, but the  
319 identifications were impossible due to low intensities.

320

### 321 *3.3.3. Re-evaluation of the selectivity for the reaction over $Co_3O_4$*

322 In our previous paper, only  $NO_3^-$  was analyzed as a product and the rest of the products  
323 was regarded as gaseous nitrogen products, which were presumed to  $N_2$  and  $N_2O$  [20].  
324 However, as was demonstrated in 3.3.2, the formation of chloramines was confirmed, though  
325 it is still unknown which chloramine and how much amount of them were formed. Thus, we re-  
326 evaluated the selectivity for the reaction in **Sol(Cl)** in the presence of  $Co_3O_4$  by taking the  
327 formation of chloramines into account. At 6 h, conversion of  $NH_4^+$  was 97%. At the time,  
328 selectivity to  $NO_3^-$  was 17%. The combined concentration of  $Cl^-$  derived from the formed  
329 chloramines in the reaction solution ( $1.9\text{ mmol L}^{-1}$ ) and trap solutions ( $5.8\text{ mmol L}^{-1}$ ) was  $7.7$   
330  $\text{mmol L}^{-1}$  at 6 h. If all the chloramines were trichloramine ( $NCl_3$ ), the selectivity to it was 26%.  
331 Thus, the selectivity to other gaseous nitrogen products, which might be  $N_2$ ,  $N_2O$ ,  $NO$ , and  
332  $NO_2$ , was 57%. On the other hand, if all the chloramines were monochloramine ( $NH_2Cl$ ), the  
333 selectivity to it was 79% and that to other gaseous nitrogen products was 4%. According to the  
334 head space GC-MS analysis, it was presumed that trichloramine was predominant among three  
335 chloramines. Thus, the selectivity to chloramines is thought to be close value to the former  
336 estimation. However, to obtain accurate selectivity, the gaseous nitrogen products should be  
337 qualitatively analyzed, and it is still in progress.

338

### 339 *3.3.4. Reaction pathway for the reaction over $Co_3O_4$*

340 As mentioned before, it is reported that chloramines are formed by the reaction of  
341  $NH_4^+$  with hypochlorite ion (or hypochlorous acid) in acid solution [23]. Under the reaction



342 conditions in **Sol(Cl)** in this study, hypochlorite ion was formed. Thus, it was plausible that  
343 monochloramine was formed by the reaction of  $\text{NH}_4^+$  with  $\text{ClO}^-$ , and dichloramine and  
344 trichloramine were successively formed by the reaction of mono- and dichloramine,  
345 respectively, with  $\text{ClO}^-$  (or  $\text{HClO}$ ). As Fig. 3 showed, the decomposition rate of  $\text{NH}_4^+$  in the  
346 presence of  $\text{Co}_3\text{O}_4$  was higher than that in its absence. There are two possibilities for the  
347 promotion by  $\text{Co}_3\text{O}_4$ :  $\text{Co}_3\text{O}_4$  accelerated (i) the formation of  $\text{ClO}^-$  and (ii) the reaction of  $\text{NH}_4^+$   
348 with  $\text{ClO}^-$ . However, the former was improbable, because the formation of  $\text{ClO}^-$  by the reaction  
349 of  $\text{Cl}^-$  with  $\text{O}_3$  was rather inhibited by the presence of  $\text{Co}_3\text{O}_4$  for the reaction in an aqueous  
350 solution of  $\text{NaCl}$  (Fig. S2).

351 To confirm the possibility of the latter, we carried out the reactions of  $\text{NH}_4^+$  with  $\text{ClO}^-$   
352 under  $\text{O}_2$  flow without  $\text{O}_3$  in the presence and absence of  $\text{Co}_3\text{O}_4$  (Fig. 7). As Fig. 7 clearly  
353 demonstrates, the conversion of  $\text{NH}_4^+$  in the presence of  $\text{Co}_3\text{O}_4$  was much higher than that in  
354 its absence. Furthermore, we confirmed the formation of chloramines found in the reaction  
355 solution and trap solutions by similar manners to those performed for the reaction shown in Fig.  
356 5. Therefore, it was concluded that  $\text{Co}_3\text{O}_4$  accelerated the reaction of  $\text{NH}_4^+$  with  $\text{ClO}^-$ .

357 Based on the results, we propose the reaction pathway for the reaction over  $\text{Co}_3\text{O}_4$  as  
358 Fig. 8. In the first step,  $\text{Cl}^-$  is non-catalytically oxidized with  $\text{O}_3$  to form  $\text{ClO}^-$ .  $\text{Co}_3\text{O}_4$  rather  
359 inhibits this reaction. Thereafter,  $\text{NH}_4^+$  is reacted with  $\text{ClO}^-$  on  $\text{Co}_3\text{O}_4$  to form  $\text{NO}_3^-$ ,  
360 chloramines, and other gaseous nitrogen compounds.

361

### 362 *3.4 Reaction mechanism for ozonation of $\text{NH}_4^+$ in the presence of $\text{MgO}$*

#### 363 *3.4.1. Role of $\text{MgO}$ for the ozonation of ammonia nitrogen*

364 Fig. 9 shows time-course changes in the concentrations of ammonia nitrogen as well  
365 as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  for the reactions in **Sol(Cl)** and **Sol(SO<sub>4</sub>)** in the presence of  $\text{MgO}$ . In contrast

366 to  $\text{Co}_3\text{O}_4$ , the ozonation of ammonia nitrogen proceeded even in **Sol**( $\text{SO}_4$ ) in the presence of  
367  $\text{MgO}$ , and the presence of  $\text{Cl}^-$  did not affect the reaction rate and selectivity. In fact,  $\text{Cl}^-$  was  
368 not lost over the reaction time in **Sol**( $\text{Cl}$ ), suggesting that the reaction did not follow the reaction  
369 mechanism as it occurred over  $\text{Co}_3\text{O}_4$ .

370 A stark difference between  $\text{Co}_3\text{O}_4$  and  $\text{MgO}$  for the reaction was their dissolution  
371 behavior. In contrast to insoluble  $\text{Co}_3\text{O}_4$ , about 40% of  $\text{MgO}$  was dissolved in **Sol**( $\text{SO}_4$ ) for 6  
372 h, though  $\text{MgO}$  is known to be poorly soluble in water. Interestingly, pH of the reaction solution  
373 rose from 5.5 to around 9 just by the addition of  $\text{MgO}$  even before the flowing of  $\text{O}_3$  and the  
374 pH was maintained throughout the reaction. This pH increase could be caused by the forward  
375 reaction of Eq. 7.

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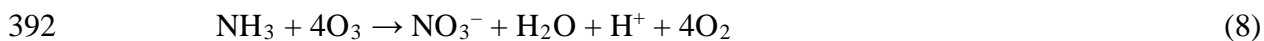
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379 Ideally, a small amount of  $\text{MgO}$  less than 0.1% of the amount added in the reaction solution is  
380 sufficient to cause the pH increase. Liu et al. also proposed a similar mechanism for the pH  
381 increase of the solution by the addition of  $\text{MgO}$  [22]. Since the pH was quickly increased just  
382 by the addition of  $\text{MgO}$  and was maintained near constant throughout the reaction, the reaction  
383 of Eq. 7 must reach equilibrium quickly under the reaction conditions with  $\text{MgO}$ .

384 To get an insight into the role of  $\text{MgO}$ , firstly, a reaction in the absence of  $\text{MgO}$  at pH  
385 9 was carried out. Because  $K_b$  of  $\text{NH}_3$  ( $= [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$ ) is  $10^{-4.8}$ , ammonia nitrogen  
386 existed predominantly as  $\text{NH}_3$  in the reaction solution. As shown in Fig. S3, 16% of ammonia  
387 nitrogen was decomposed at 1 h and concomitantly  $\text{NO}_3^-$  that was equivalent to the consumed  
388 ammonia nitrogen was formed. After that, however, the reaction was completely stopped. At

389 the time, the solution turned to acidic because of charge compensation for the formation of  
390 anionic product ( $\text{NO}_3^-$ ) from neutral reactants ( $\text{NH}_3$  and  $\text{O}_3$ ) (Eq. 8).

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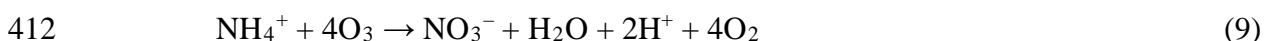


393

394 We further carried out a similar reaction, but pH of the reaction solution was repeatedly restored  
395 to 9 at each sampling time (Fig. S4). For that reaction, the decomposition of ammonia nitrogen  
396 continually proceeded. Under the reaction conditions, stripping of  $\text{NH}_3$  from the reaction  
397 solution was only little. These results clearly demonstrated that in mildly alkaline solution,  
398 ammonia nitrogen can be oxidized into mainly  $\text{NO}_3^-$  even without any catalysts.

399 As mentioned above, to increase pH to around 9, only less than 0.1% of MgO added  
400 to the reaction solution was sufficient, but the fact was that much amount of MgO was dissolved  
401 with the reaction, implying the presence of another mechanism for the dissolution of MgO. To  
402 get a clue for it, we carried out the ozonation of ammonia nitrogen with different initial  
403 concentrations of ammonia nitrogen in the presence of MgO and investigated the relationship  
404 between the amount of decomposed ammonia nitrogen and that of dissolved  $\text{Mg}^{2+}$  at each  
405 reaction time with different initial concentrations of ammonia nitrogen. The results are shown  
406 in Fig. 10. Notably, the amount of  $\text{Mg}^{2+}$  dissolved was linearly increase with increase in the  
407 amount of ammonia nitrogen decomposed. It should be noted that the slope of the line in Fig.  
408 10 was nearly unity. Because ammonia nitrogen exists originally as  $\text{NH}_4^+$  in the as-prepared  
409 reaction solution before the addition of MgO, the stoichiometric equation for the oxidation of  
410 ammonia nitrogen to  $\text{NO}_3^-$  is as follows.

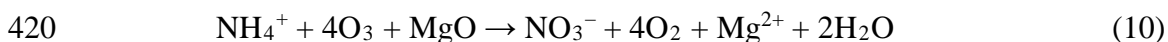
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414 Since the pH of the solution was maintained at around 9 throughout the reaction in the presence  
415 of MgO, H<sup>+</sup> formed by the reaction of Eq. 9 was neutralized with OH<sup>-</sup> that was formed by the  
416 forward reaction of Eq. 7, inducing further dissolution of MgO. Consequently, a single  
417 decomposition reaction of ammonia nitrogen yielded the dissolution of one Mg<sup>2+</sup> as represented  
418 by Eq. 10.

419



421

422 In short, MgO was a reactant for the ozonation of ammonia nitrogen in water.

423 In addition to MgO, CaO, which is another alkaline-earth metal oxide, acted in the  
424 same way as MgO did for the reaction. The reaction solution turned into strong basic (pH around  
425 11) immediately by the addition of CaO to it. The ozonation of ammonia nitrogen proceeded  
426 smoothly in the presence of CaO and the decomposition rate of ammonia nitrogen was about  
427 1.5-times faster than that in the presence of MgO. This supports our conclusion above  
428 mentioned in the case of MgO.

429

#### 430 *3.4.2. Possibility of involvement in homogeneous catalysis by Mg<sup>2+</sup>*

431 Because Mg<sup>2+</sup> was present in the reaction solution for the reaction with MgO, it could  
432 be that Mg<sup>2+</sup> acted as a homogeneous catalyst. Thus, we performed the ozonation of ammonia  
433 nitrogen in **Sol**(SO<sub>4</sub>) with 10 mmol L<sup>-1</sup> of Mg<sup>2+</sup>, which was prepared by adding  
434 Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to the reaction solution. The initial pH of the reaction solution was adjusted  
435 to 9 by the addition of KOH. The result showed that the conversion of ammonia nitrogen was  
436 only 12% at 1 h and after that the reaction stopped, which was the same as that for the blank

437 test in the absence of MgO (Fig. S3). Therefore, it was concluded that there was no contribution  
438 of homogeneous catalysis by  $Mg^{2+}$  to the ozonation of ammonia nitrogen.

439

#### 440 3.4.3. Reaction pathway for the reaction in the presence of MgO

441 The effect of radical scavenger was investigated for the reaction in **Sol**(SO<sub>4</sub>) in the  
442 presence of both MgO and *tert*-butyl alcohol (TBA, 100 mmol L<sup>-1</sup>) and the result was compared  
443 to that in the absence of TBA (Fig. 11). Since TBA acts as a radical scavenger, the addition of  
444 TBA decreases the concentration of radicals in the solution [27]. Thus, if the reaction follows  
445 radical mechanism, the decomposition rate of ammonia nitrogen is decreased along with  
446 decrease in the leaching amount of MgO. As Fig. 11 clearly shows, the decomposition of  
447 ammonia nitrogen was inhibited by the presence of TBA and the leaching amount of MgO was  
448 also decreased, indicating the involvement of a radical mechanism. Liu et al. also investigated  
449 the effect of TBA for ozonation of ammonia nitrogen in the presence of MgO and reached a  
450 totally opposite conclusion that TBA did not interfere the reaction [22]. In the reaction in Fig.  
451 11, tenfold amount of TBA to ammonia nitrogen was used, while only one-tenth of it was added  
452 to the reaction solution in the study by Liu et al. [22]. Such difference in the amount of TBA  
453 added may bring about the discrepancy of the reaction mechanism.

454 Based on the results mentioned so far and the fact that OH· radical is formed by the  
455 reaction of OH<sup>-</sup> with O<sub>3</sub> at pH more than 9 [28], we propose the reaction pathway for the  
456 reaction in the presence of MgO as Fig. 12. The reaction of solid MgO with H<sub>2</sub>O giving Mg<sup>2+</sup>  
457 and OH<sup>-</sup> is in equilibrium and thus pH of the solution is maintained at mildly alkaline pH.  
458 Ammonia nitrogen is decomposed to mainly NO<sub>3</sub><sup>-</sup> by the reaction with OH·. Proton formed  
459 with the decomposition of ammonia nitrogen is neutralized, leading to further dissolution of

460 MgO. Thus, the same amount of  $Mg^{2+}$  as that of decomposed ammonia nitrogen is dissolved in  
461 the reaction solution.

462

#### 463 **4. Conclusion**

464 In the present study, we investigated the reaction mechanisms for ozonation of  
465 ammonia nitrogen in the presence of  $Co_3O_4$  or MgO. For the reaction over  $Co_3O_4$ ,  $Cl^-$  in the  
466 solution was indispensable and chloramines ( $NH_{3-x}Cl_x$ ), being predominantly trichloramine  
467 ( $NCl_3$ ), were formed as a gaseous nitrogen product. The selectivities to  $NO_3^-$ , chloramines and  
468 other gaseous nitrogen products ( $N_2$ ,  $N_2O$ , and  $NO_x$ ) were estimated to 17, 26, and 57%, if only  
469 trichloramine was formed in chloramines. Hypochlorite ion ( $ClO^-$ ) that was formed by a non-  
470 catalytic reaction of  $Cl^-$  with  $O_3$  acted as an oxidizer for  $NH_4^+$  and  $Co_3O_4$  accelerated the  
471 reaction of  $NH_4^+$  with  $ClO^-$  to give the products.

472 In contrast to the reaction with  $Co_3O_4$ ,  $Cl^-$  was not involved in the reaction with MgO.  
473 During the reaction in the presence of MgO, pH of the reaction solution was maintained at  
474 around 9 owing to the reaction of MgO with  $H_2O$  to give  $OH^-$  ( $MgO(s) + H_2O \rightleftharpoons Mg^{2+} + 2OH^-$   
475 ). Ammonia nitrogen is decomposed to form mainly  $NO_3^-$  by a non-catalytic radical reaction  
476 with  $OH^\cdot$ , which was formed by the reaction of  $OH^-$  with  $O_3$  in mildly alkaline solution. Protons  
477 formed with the decomposition of ammonia nitrogen ( $NH_4^+ + 4O_3 \rightarrow NO_3^- + H_2O + 2H^+ +$   
478  $4O_2$ ) were neutralized with  $OH^-$  to keep the pH of the reaction solution at around 9. As a result,  
479 much the same amount of  $Mg^{2+}$  as that of decomposed ammonia nitrogen was dissolved in the  
480 reaction solution. In short, MgO was a reactant for the ozonation of ammonia nitrogen in water.

481

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486

#### 487 **Appendix A. Supplementary data**

488 Supplementary material related to this article can be found, in the online version, at  
489 doi:<https://doi.org/10.1016/j.apcata.????????>.

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#### 491 **References**

492 [1] D.J. Randall, T.K.N. Tsui, *Mar. Pollut. Bull.* 45 (2002) 17–23.

493 [2] T.A. Pressley, D.F. Bishop, S.G. Roan, *Environ. Sci. Technol.* 6 (1972) 622–628.

494 [3] H.B. Perry, R. Zulliger, M.M. Rogers, *Annu. Rev. Public Heal.* 35 (2014) 399–421.

495 [4] M. Owens, G. Wood, *Water Res.* 2 (1968) 151–159.

496 [5] Y. Tu, P. Feng, Y. Ren, Z. Cao, R. Wang, Z. Xu, *Fuel* 238 (2019) 34–43.

497 [6] A. Thornton, P. Pearce, S.A. Parsons, *J. Hazard. Mater.* 147 (2007) 883–889.

498 [7] Y. Wei, M. Ji, R. Li, F. Qin, *Waste Manag.* 32 (2012) 448–455.

499 [8] P.H. Liao, A. Chen, K.V. Lo, *Bioresour. Technol.* 54 (1995) 17–20.

500 [9] J. Taguchi, T. Okuhara, *Appl. Catal. A* 194–195 (2000) 89–97.

501 [10] J. Taguchi, Y. Yoshinaga, T. Okuhara, *Chem. Lett.* 30 (2001) 112–113.

502 [11] J. Barbier, L. Oliviero, B. Renard, D. Duprez, *Catal. Today* 75 (2002) 29–34.

503 [12] D.K. Lee, S.C. Jeong, L.Y. Wang, *Chemosphere* 61 (2005) 573–578.

504 [13] C. Lousteau, M. Besson, C. Descorme, *Catal. Today* 241 (2015) 80–85.

505 [14] S.K. Bhargava, J. Tardio, J. Prasad, K. Föger, D.B. Akolekar, S.C. Grocott, *Ind. Eng. Chem.*  
506 *Res.* 45 (2006) 1221–1258.

- 507 [15] S.T. Oyama, *Catal. Rev. Sci. Eng.* 42 (2000) 279–322.
- 508 [16] B. Kasprzyk-Hordern, M. Ziółek, J. Nawrocki, *Appl. Catal. B Environ.* 46 (2003) 639–  
509 669.
- 510 [17] J. Nawrocki, B. Kasprzyk-Hordern, *Appl. Catal. B* 99 (2010) 27–42.
- 511 [18] P.C. Singer, W.B. Zilli, *Water Res.* 9 (1975) 127–134.
- 512 [19] W.R. Haag, J. Hoigné, H. Bader, *Water Res.* 18 (1984) 1125–1128.
- 513 [20] S. Ichikawa, L. Mahardiani, Y. Kamiya, *Catal. Today* 232 (2014) 192–197.
- 514 [21] Y. Chen, Y. Wu, C. Liu, L. Guo, J. Nie, Y. Chen, T. Qiu, *J. Environ. Sci.* 66 (2018) 265–  
515 273.
- 516 [22] H. Liu, L. Chen, L. Ji, *J. Hazard. Mater.* 376 (2019) 125–132.
- 517 [23] P.J. Vikesland, K. Ozekin, R.L. Valentine, *Water Res.* 35 (2001) 1766–1776.
- 518 [24] R.M. Chapin, *J. Am. Chem. Soc.* 51 (1929) 2112–2117.
- 519 [25] V.C. Hand, D.W. Margerum, *Inorg. Chem.* 22 (1983) 1449–1456.
- 520 [26] K. Kosaka, K. Seki, N. Kimura, Y. Kobayashi, M. Asami, *Water Sci. Technol.: Water*  
521 *Supply* 23 (2010) 23–29.
- 522 [27] A. Ikhlaiq, D.R. Brown, B. Kasprzyk-Hordern, *Appl. Catal. B Environ.* 165 (2015) 408–  
523 418.
- 524 [28] J. Hoigne, H. Bader, *Environ. Sci. Technol.* 12 (1978) 79–84.
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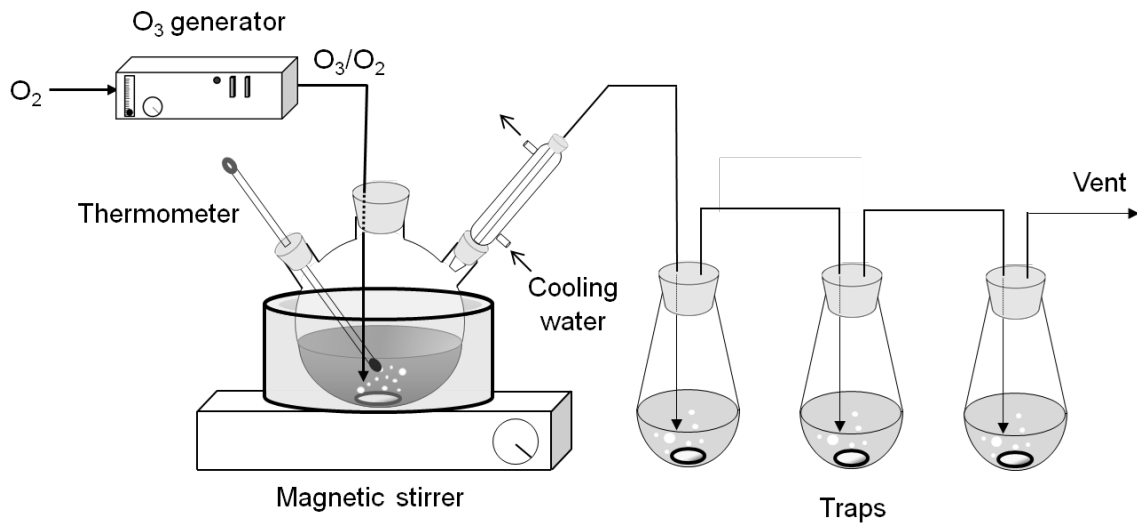
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538 **Fig. 1.** Illustration of the semi-batch reactor used for ozonation of ammonia nitrogen in water.

539 Pure water or an aqueous KOH solution (pH 11) with fine powder of MgO was put in three

540 traps.

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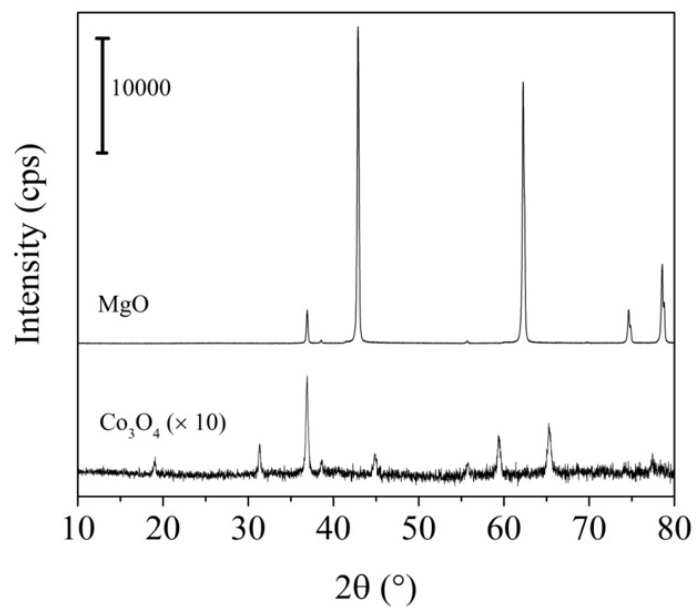
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**Fig. 2.** XRD patterns of  $\text{Co}_3\text{O}_4$  and MgO.

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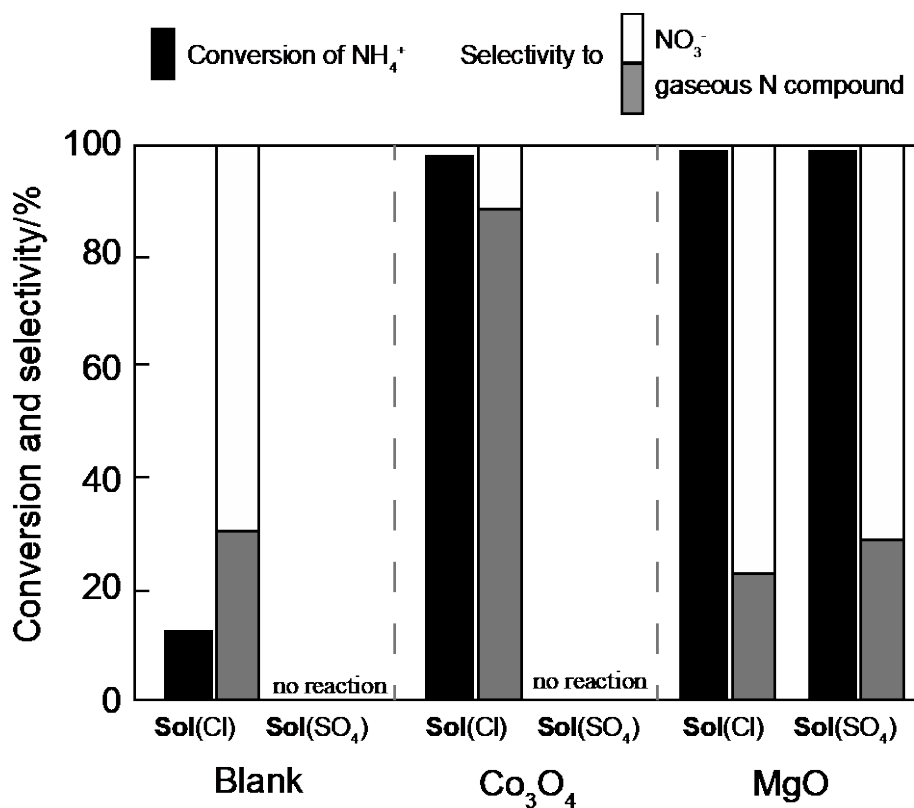
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574 **Fig. 3.** Conversions and selectivity for ozonation of ammonia nitrogen in Sol(Cl) and  
575 Sol(SO<sub>4</sub>) in the presence of Co<sub>3</sub>O<sub>4</sub> or MgO. Sol(Cl) and Sol(SO<sub>4</sub>) represent the reaction  
576 solutions prepared from NH<sub>4</sub>Cl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, respectively. Reaction conditions: Co<sub>3</sub>O<sub>4</sub> or  
577 MgO, 0.1 g; 10 mmol L<sup>-1</sup> NH<sub>4</sub><sup>+</sup> solution, 100 mL; total flow rate of O<sub>3</sub>/O<sub>2</sub> mixture, 100 mL  
578 min<sup>-1</sup>; concentration of O<sub>3</sub> in the mixture, 0.7 vol%; reaction temperature, 333 K; reaction time,  
579 6 h.

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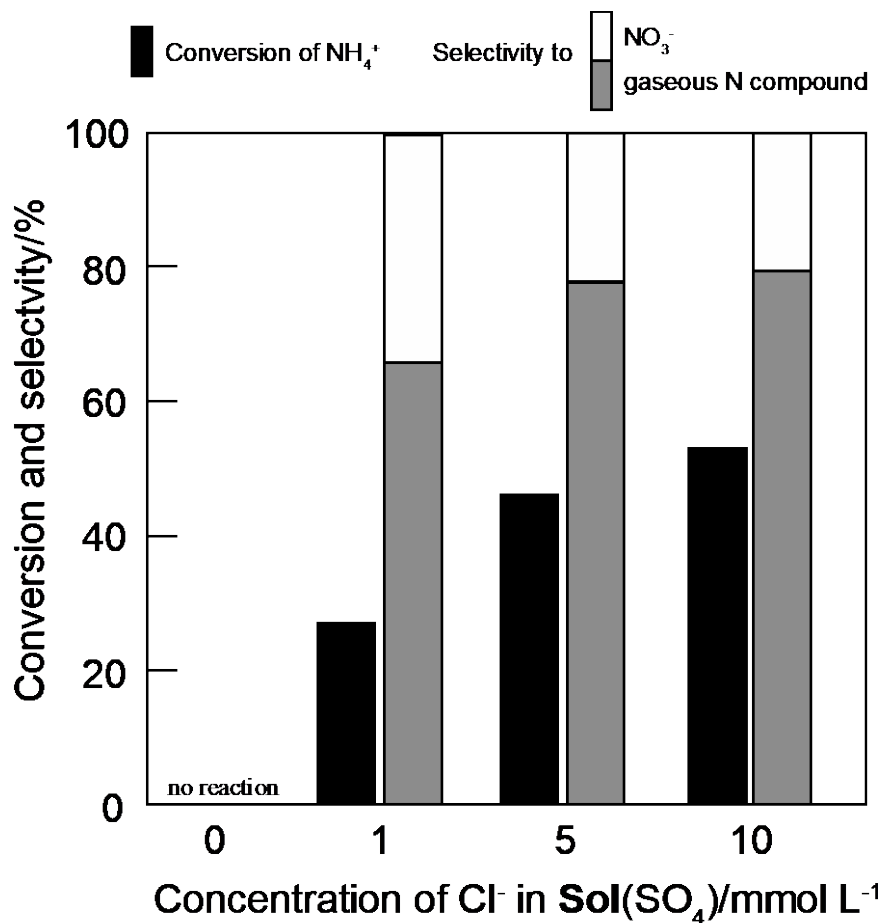
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595 **Fig. 4.** Influence of Cl<sup>-</sup> concentration in Sol(SO<sub>4</sub>) on the ozonation of ammonia nitrogen in

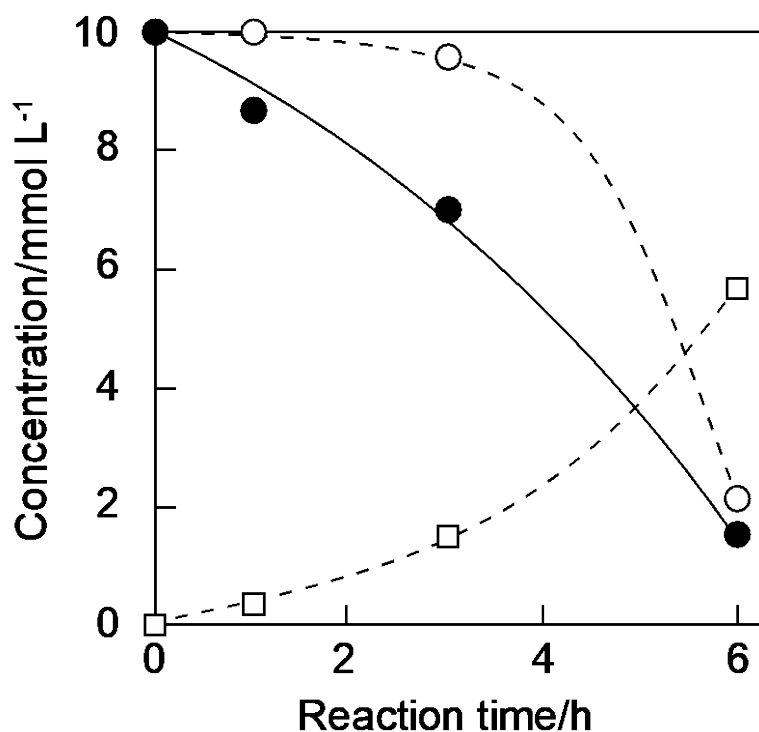
596 the presence of Co<sub>3</sub>O<sub>4</sub>. The reaction solution was prepared by adding NaCl to Sol(SO<sub>4</sub>).

597 Reaction conditions: Co<sub>3</sub>O<sub>4</sub>, 0.1 g; 10 mmol L<sup>-1</sup> NH<sub>4</sub><sup>+</sup>, 100 mL; O<sub>3</sub>/O<sub>2</sub> flow rate, 100 mL min<sup>-1</sup>;

598 <sup>1</sup>; concentration of O<sub>3</sub>, 0.7 vol%; reaction temperature 333 K; reaction time, 6 h.

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**Fig. 5.** Time-course changes in the concentrations of Cl<sup>-</sup> in the reaction solution (●) as it is and (○) after increasing the pH to 11 and (□) in the trap solution for ozonation of ammonia nitrogen in Sol(Cl) in the presence of Co<sub>3</sub>O<sub>4</sub>. Reaction conditions: Co<sub>3</sub>O<sub>4</sub>, 0.1 g; 10 mmol L<sup>-1</sup> NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>, 100 mL; O<sub>3</sub>/O<sub>2</sub> flow rate, 100 mL min<sup>-1</sup>; concentration of O<sub>3</sub>, 0.7 vol%; reaction temperature, 333 K. An aqueous KOH solution was added to the reaction solution taken at each time to increase pH of the solution to 11. An aqueous KOH solution with fine powder of MgO was used as a trap solution to decompose formed chloramines to give Cl<sup>-</sup>.

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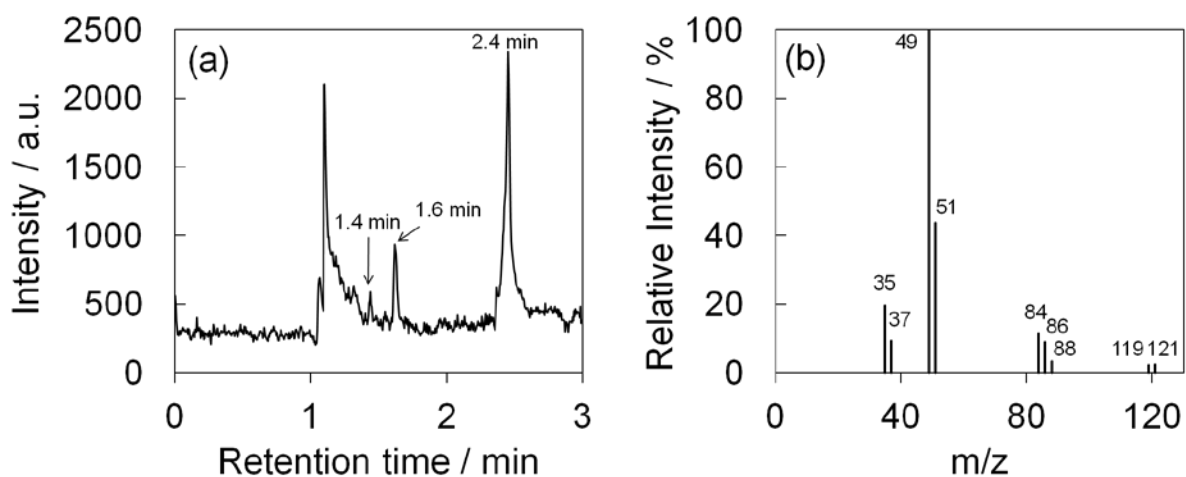
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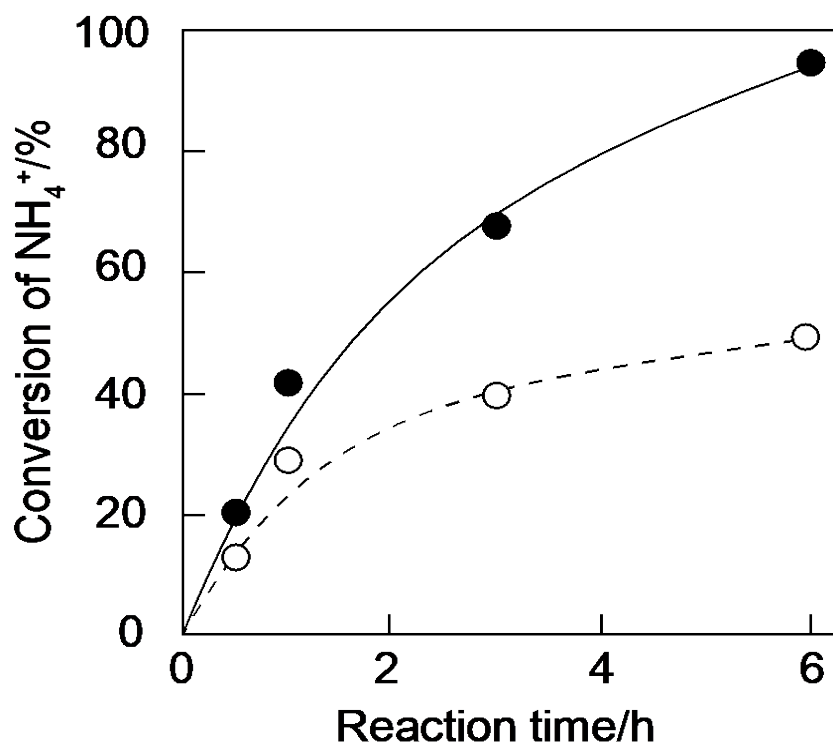
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636 **Fig. 6.** The results of a head-space GC-MS analysis for the solution obtained by passing the  
637 outlet gas of the reactor through pure water in the traps for 6 h in ozonation of ammonia nitrogen  
638 in  $\text{Sol}(\text{Cl})$  over  $\text{Co}_3\text{O}_4$ . The trap was cooled at 273 K. (a) total ion chromatogram and (b)  
639 mass spectra for the peak at 2.4 min. Reaction conditions were the same as those in Fig. 5,  
640 but pure water was used as a trap solution instead of an aqueous KOH solution with fine powder  
641 of MgO.

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**Fig. 7.** Time-course changes in the conversion of  $\text{NH}_4^+$  for the reaction of  $\text{NH}_4^+$  with  $\text{ClO}^-$  under  $\text{O}_2$  flow without  $\text{O}_3$  in the (●) presence and (○) absence of  $\text{Co}_3\text{O}_4$ . Reaction conditions:  $\text{Co}_3\text{O}_4$ , 0.1 g ; concentrations of  $\text{NH}_4^+$  and  $\text{ClO}^-$ , 10 and 20  $\text{mmol L}^{-1}$ , respectively; volume of reaction solution, 100 mL;  $\text{O}_2$  flow rate, 100  $\text{cm}^3 \text{min}^{-1}$ ; reaction temperature, 333 K.

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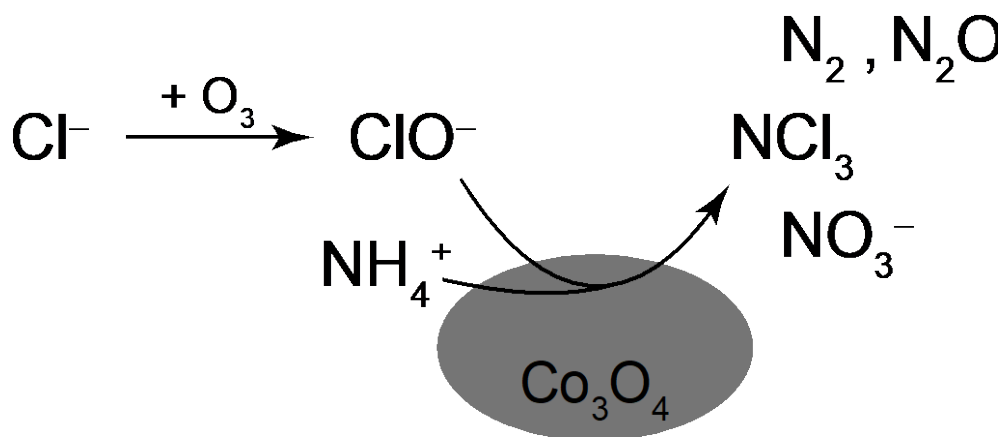
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671 **Fig. 8.** Proposed reaction pathway for ozonation of ammonia nitrogen in the presence of  $\text{Cl}^-$

672 over  $\text{Co}_3\text{O}_4$ .

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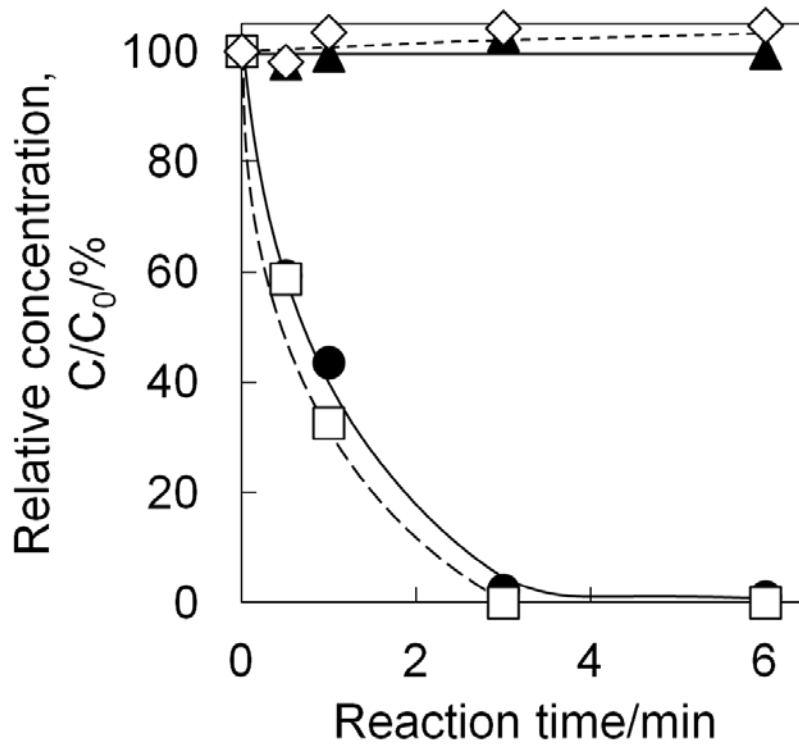
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690 **Fig. 9.** Time-course changes in the concentrations of ammonia nitrogen and anions for

691 ozonation of ammonia nitrogen in **Sol(Cl)** and **Sol(SO<sub>4</sub>)** in the presence of MgO. (●) and (▲)

692 are the concentrations of ammonia nitrogen and  $Cl^-$ , respectively, for the reactions in **Sol(Cl)**,

693 and (□) and (◇) are those of ammonia nitrogen and  $SO_4^{2-}$ , respectively, for the reactions in

694 **Sol(SO<sub>4</sub>)**. Reaction conditions are the same as those for the reaction in Fig. 3.

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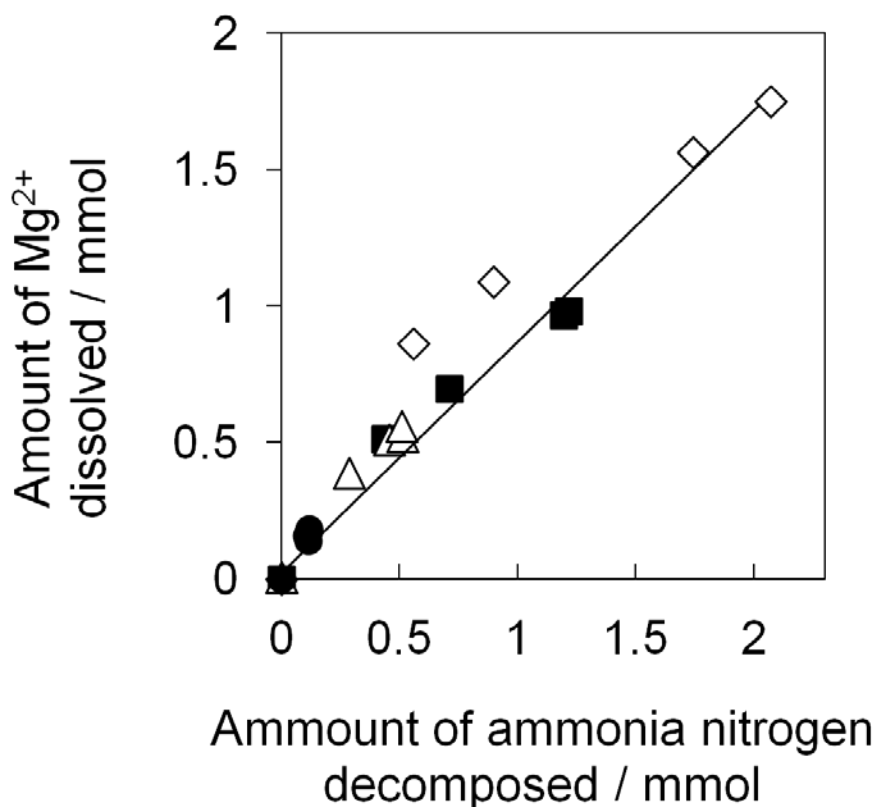
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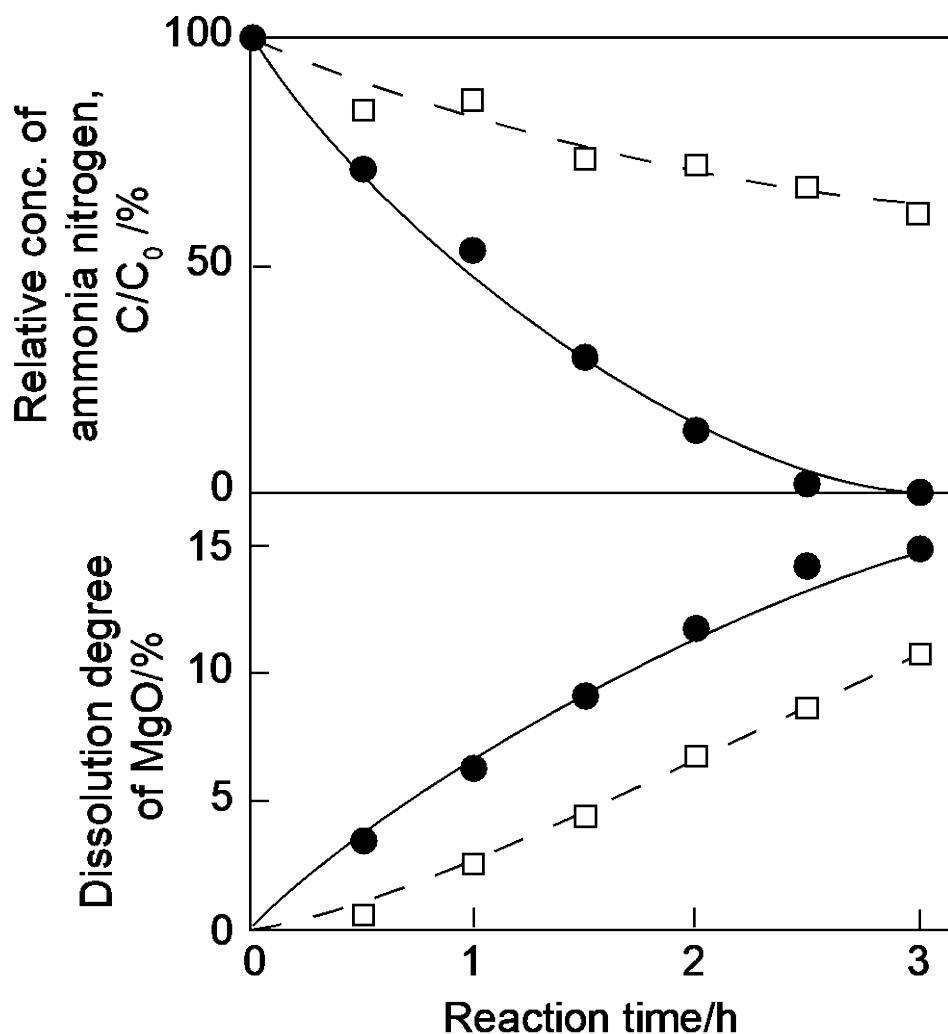
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711 **Fig. 10.** Relationship between the amount of Mg<sup>2+</sup> dissolved and that of decomposed  
712 ammonia nitrogen for ozonation of ammonia nitrogen in the presence of MgO with different  
713 initial concentrations of ammonia nitrogen and reaction time. Reaction conditions: MgO, 0.1  
714 g; reaction solution, 100 mL; O<sub>3</sub>/O<sub>2</sub> flow rate, 100 mL min<sup>-1</sup>; reaction temperature ,333 K.  
715 Initial concentration of ammonia nitrogen: (●) 1 mmol L<sup>-1</sup>, (△) 5 mmol L<sup>-1</sup>, (■) 10 mmol L<sup>-1</sup>,  
716 (◇) 20 mmol L<sup>-1</sup>. The data collected at different reaction times are plotted on the graph.

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**Fig. 11.** Influence of tert-butyl alcohol (TBA) in the reaction solution on the decomposition rate of ammonia nitrogen and dissolution degree of MgO for ozonation of ammonia nitrogen in the presence of MgO. (●) in the absence of TBA and (□) in the presence of TBA. Reaction conditions: MgO, 0.1 g; concentrations of NH<sub>4</sub><sup>+</sup> and TBA, 10 and 100 mmol L<sup>-1</sup>, respectively; reaction solution, 100 mL; O<sub>3</sub>/O<sub>2</sub> flow rate, 100 cm<sup>3</sup> min<sup>-1</sup>; reaction temperature, 298 K.

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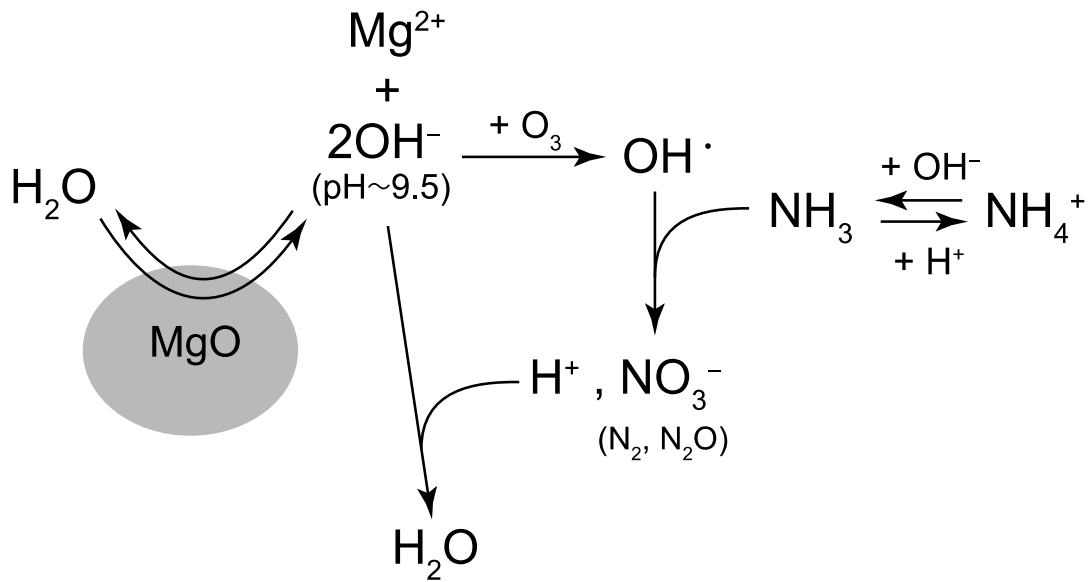
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753 **Fig. 12.** Proposed reaction pathway for ozonation of ammonia nitrogen in the presence of

754 MgO.

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