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

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Abstract

In this study, the reaction mechanisms for ozonation of ammonia nitrogen in the presence of Co_3O_4 or MgO were investigated. For the reaction over Co_3O_4, Cl^- in the reaction solution was indispensable and ClO^- was formed by a non-catalytic oxidation of Cl^-. Co_3O_4 promoted the reaction of NH_4^+ with ClO^- to give the products including NO_3^-, chloramines and gaseous products. In contrast, Cl^- was unnecessary for the reaction with MgO. pH of the reaction solution was maintained at around 9 throughout the reaction owing to partial dissolution of MgO. Ammonia nitrogen was decomposed to mainly NO_3^- by non-catalytic radical reaction involving OH·, which was formed by the reaction of OH^- with O_3 in weakly basic solution. To keep the reaction solution weakly basic, H^+ formed with the decomposition of NH_4^+ was neutralized. As a result, about the same amount of Mg^{2+} as that of decomposed ammonia nitrogen was dissolved.

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

1. Introduction

While ammonia (NH_3) and ammonium ion (NH_4^+), which are collectively called ammonia nitrogen, are indispensable nutrient for plants, excess ammonia nitrogen in water often causes eutrophication of rivers, lakes, and inland seas. In addition, ammonia nitrogen is toxic to fish species even if the concentration in water is less than 10 mg L^{-1} [1]. High concentration ammonia nitrogen in natural environment comes from inadequate treatments of industrial wastewater, household sewage, and livestock manure and runoff water from farmland with excess fertilization. Nitrogen-containing organic matters, such as urea, amino acids, polypeptides and proteins can be a source for ammonia nitrogen in wastewater with microbial action [2]. For environmental protection, ammonia nitrogen in environmental water should be below 0.5 mg L^{-1} [3,4]. To achieve this criteria, highly efficient and feasible processes for the purification of water containing ammonia nitrogen are absolutely necessary.

So far, many treatment processes have been studied and some of them including adsorption [5], ion exchange [6], activated sludge [7], stripping [8] and breakpoint chlorination [2] are commercially used for the treatment of wastewater containing ammonia nitrogen. However, each process has some limitations and disadvantages from technical and economic standpoints. For example, because ion exchange is the processes only removing ammonia nitrogen, waste brine containing high concentration ammonia nitrogen is generated, which should be further treated. Activated sludge process consumes a lot of energy and oxygen, and burdensome treatment of produced generated sludge is necessary [7]. Ammonia stripping technique requires a large stripping tower, strict control of $CaCO_3$ dose, and is ineffective in winter due to the low volatility of NH_3 under low temperature environment [8]. In addition, it potentially causes air pollution if the stripped NH_3 is not appropriately treated.

Catalytic wet air oxidation (CWAO) is a process to oxidatively decompose contaminants in water by reaction with air (O_2) in the presence of a catalyst. CWAO is considered to be applicable for purification of wastewater containing ammonia nitrogen. So far, several precious metals supported on carriers like metal oxides have been investigated for the reaction [9-14]. Taguchi and Okuhara reported that Pt/TiO_2 [9] and Pd/ZrO_2 [10] effectively and selectively promoted the oxidation of ammonia nitrogen into N_2 at relatively low temperature (433 K) and low pressure (0.5 MPa) in mild acidic solution (pH 5.5). These previous studies showed high potential of CWAO for the purification of wastewater containing ammonia nitrogen. However, harsh reaction conditions are still indispensable for achieving high decomposition rate to make up for low oxidizing ability of O_2 even by using highly active catalysts [14].

Catalytic ozonation is the reaction for oxidative decomposition of contaminants with O_3. Because O_3 is a strong oxidant comparing with O_2, the reaction often proceeds even under mild reaction conditions, e.g., low temperature and ambient pressure [15-17]. While non-catalytic ozonation of ammonia nitrogen in water [18] and catalytic one with a homogeneous catalyst [19] were reported in 1975 and 1984, respectively, the first paper on the latter over heterogeneous catalysts was reported in 2014 [20]. After that, Chen et al. reported Mg-Co mixed metal oxide catalyst with different Mg to Co ratios for the reaction [21] and found that $MgO\text{-}Co_3O_4$ with Mg/Co = 4/1 calcined at 773 K was the best catalyst in terms of decomposition rate of ammonia nitrogen and selectivity to gaseous nitrogen compounds.

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

NO_3^- was predominantly formed. In addition, a part of MgO was dissolved during the reaction and pH of the reaction solution was increased up to around 9. The increase in pH of the reaction solution for the same reaction in the presence of MgO was also reported by Liu et al [22]. In stark contrast, Co_3O_4 gave the highest selectivity to gaseous nitrogen products with more than 85% selectivity and was insoluble in the reaction solution, while the catalytic activity was the third best among them. Furthermore, we found that the reaction proceeded only in the presence of Cl^-, demonstrating that Cl^- was indispensable for the reaction over Co_3O_4. However, it is not known how Cl^- is involved in the reaction over Co_3O_4 and why the selectivity is so different for the reactions between in the presence of MgO and that of Co_3O_4.

In the present study, we conducted an in-depth investigation to provide a clear overview on the reaction mechanism for the ozonation of ammonia nitrogen in water in the presence of Co_3O_4 or MgO. For the former, we focused on the behavior of Cl^- in the reaction solution during the reaction and tried to identify gaseous nitrogen products. The results clearly demonstrated that Co_3O_4 effectively promoted the formation of chloramines ($NH_{3-x}Cl_x$, x = 1, 2, and 3) as gaseous nitrogen products. Meanwhile, we found that the reaction proceeded with a non-catalytic radical reaction in the presence of MgO and that MgO was just a reactant for the reaction.

2. Experimental

2.1. Materials

Analytical grade reagents of $Mg(OH)_2$, $Ca(OH)_2$, $Co(NO_3)_2 \cdot 6H_2O$, KOH, HNO_3, $(NH_4)_2SO_4$, NH_4Cl, NaClO, NaCl and aqueous ammonia were purchased from Wako Pure Chem. Ind. Ltd. and used without further purification.

2.2. Preparation of Co_3O_4 and MgO

Cobalt oxide (Co_3O_4) was prepared by a conventional precipitation method [20]. An aqueous ammonia (1.0 mol L^{-1}) was added to a solution of $Co(NO_3)_2$ (1.0 mol L^{-1}) until pH of the solution was stably at 8.1. The suspension was stirred for 10 min at room temperature. The formed blue-green precipitate was separated by filtration, washed with distilled water, and dried at 373 K for 24 h. The solid was ground with a mortar and then was calcined in air at 773 K for 4 h.

Magnesium oxide (MgO) was prepared by calcining $Mg(OH)_2$ at 773 K for 5 h [20]. Calcium oxide (CaO) was also prepared with the same manner to that of MgO except for using $Ca(OH)_2$.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku, Miniflex) with Cu Kα radiation (λ= 0.154 nm, 30 kV, 15 mA) at room temperature. Specific surface area was estimated by applying the Brunauer–Emmett–Teller (BET) equation to an adsorption isotherm of N_2 at 77 K, which was acquired on a Belsorp-mini instrument (BEL Japan Inc.). The sample was pretreated in N_2 flow at 473 K for 3 h before the measurement.

2.4. Ozonation of ammonia nitrogen in water

Ozonation of ammonia nitrogen in water was performed by using a semi-batch reactor connected to a gas flow line and traps (Fig. 1). Two reaction solutions containing 10 mM NH_4^+, which was present as NH_3 when the solution was alkaline, were prepared from NH_4Cl and $(NH_4)_2SO_4$ and are denoted as **Sol**(Cl) and **Sol**(SO_4), respectively. Typically, 0.1 g of Co_3O_4

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_2 (100 cm^3 min^{-1}). After temperature of the suspension
133 reached to predetermined one (298 or 333 K), the gas was changed to a mixture of O_3/O_2 (1.88
134 mmol L^{-1} as O_3, total flow rate = 100 cm^3 min^{-1}) to start the ozonation of ammonia nitrogen.
135 O_3 was generated from O_2 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_3^-, NO_2^- and NH_4^+ 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 $NaHCO_3$ (2.9 mmol L^{-1}) and Na_2CO_3 (3.1 mmol L^{-1})
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^{-1}) and 18-crown-6 (1.0 mmol L^{-1}) 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_4^+ even if
145 NH_3 was present in the solution. The yield of and selectivity to NO_3^- were calculated by Eqs.
146 1 and 2, respectively.

147

148 $$\text{Yield of } NO_3^- = \frac{\text{Formed } NO_3^-}{\text{Initial } NH_4^+} \quad (1)$$

149 $$\text{Selectivity to } NO_3^- = \frac{\text{Formed } NO_3^-}{\text{Consumed } NH_4^+} \quad (2)$$

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_3^- from 100%.

While pH of both **Sol**(SO_4) and **Sol**(Cl) was around 5.5, it was adjusted to 7 and 9 for some reactions by the addition of aqueous solution of KOH. For the reaction in the presence of MgO, the concentration of Mg^{2+} in the reaction solution was determined by the ion chromatograph in a similar manner to that of NH_4^+.

ClO_x^- in solutions were determined by using another ion chromatograph (Thermo Scientific, Dionex ICS-900) equipped with a column of Dionex IonPac AS16 RFIC. An aqueous solution of NaOH (35 mmol L^{-1}) was used as a mobile phase.

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

2.5. Reaction of NH_4^+ with ClO^- without O_3

Reaction of NH_4^+ with ClO^- without O_3 was carried out in a similar manner to that for the ozonation of ammonia nitrogen in water, while O_2 was fed into the reactor instead of O_3/O_2 mixture. The reaction solution was prepared by adding NaClO to **Sol**(Cl) and the concentrations of NH_4^+ and ClO^- in the solution were 10 and 20 mmol L^{-1}, respectively. The pH of the reaction solution was adjusted to 5.5 with dilute nitric acid.

3. Results and discussion

3.1. Physical properties of Co_3O_4 and MgO

Fig. 2 shows the XRD patterns of as-prepared Co_3O_4 and MgO. The typical diffraction lines due to spinel type Co_3O_4 were observed at 2θ = 19.08, 31.32, 36.90, 38,68, 44.82, 55.82, 59.34, 65.26 and 77.42°, which were ascribed to (111), (220), (311), (222), (400), (422), (511), (440) and (533), respectively. MgO gave the diffraction lines at 2θ = 36.91, 42.88, 62.27, 74.65 and 78.58°, which were assignable to (111), (200), (220), (311) and (222), respectively, for cubic MgO. The sizes of the crystallites estimated by applying a Scherrer's equation to the diffraction lines at 36.90 and 42.88° of Co_3O_4 and MgO were 26 and 36 nm, respectively. The specific surface areas of Co_3O_4 and MgO were 12 and 252 $m^2\ g^{-1}$, respectively.

3.2 Involvement of Cl^- for ozonation of ammonia nitrogen

Fig. 3 shows the conversion and selectivity at 6 h for the ozonation of ammonia nitrogen in **Sol**(Cl) and **Sol**(SO_4) at 333 K in the presence of Co_3O_4 and MgO. In the absence of neither solid materials, only a small amount of NH_4^+ was decomposed in **Sol**(Cl) and no reaction occurred in **Sol**(SO_4). In the presence of Co_3O_4, NH_4^+ was decomposed only in **Sol**(Cl), forming gaseous nitrogen products with ca. 83% selectivity, while no reaction occurred in **Sol**(SO_4), suggesting involvement of Cl^- in the reaction. To further confirm the participation of Cl^-, we examined influence of the concentration of Cl^- on the conversion of NH_4^+ and selectivities by the addition of NaCl into **Sol**(SO_4) (Fig. 4). With an increase in the concentration of Cl^-, the conversion of NH_4^+ increased. The selectivity to gaseous products with 10 mmol L^{-1} Cl^- was almost the same as that for the reaction in **Sol**(Cl). Therefore, it was concluded that Cl^- played a critical role for the reaction over Co_3O_4.

In contrast to the reactions over Co_3O_4, there was little difference in the reaction results with **Sol**(Cl) and **Sol**(SO_4) in the presence of MgO. Almost all NH_4^+ was decomposed at 6 h in the presence of MgO and NO_3^- was a main product regardless of the reaction solutions. These

results indicate that Cl^- in the solution was not involved in the reaction with MgO. This significant difference in the reaction behavior between Co_3O_4 and MgO strongly suggest a difference in reaction mechanism in the presence of each solid.

3.3. Reaction mechanism over Co_3O_4

3.3.1. Behavior of Cl^- during the reaction

As mentioned in 3.2, Cl^- was indispensable for the reaction over Co_3O_4. To investigate how Cl^- was involved in the reaction, time course in the concentration of Cl^- was examined in **Sol**(Cl) in the presence of Co_3O_4 (Fig. S1). It should be noted that the concentration of Cl^- was decreased with reaction time and more than 85% of Cl^- in the reaction solution was lost at 6 h.

One possibility for the loss of Cl^- was the formation of Cl_2 by the oxidation of Cl^- with O_3 (Eqs. 3 and 4) and then it went out from the reactor with the flow of O_3/O_2 mixture.

$$2Cl^- + O_3 + 2H^+ \rightarrow Cl_2 + O_2 + H_2O \quad (3)$$

$$2Cl^- + O_3 + H_2O \rightarrow Cl_2 + O_2 + 2OH^- \quad (4)$$

In fact, no formation of Cl_2 occurred as was confirmed by the following experiment. The reaction was performed in **Sol**(Cl) in the presence of Co_3O_4 and the outlet gas from the reactor was absorbed by pure water in the three traps connected in series. If Cl_2 was formed, Cl^- should be detected in the water along with ClO^- because Cl_2 is easily reacted with water to form Cl^- and ClO^- (Eq. 5).

$$Cl_2 + H_2O \rightarrow Cl^- + ClO^- + 2H^+ \quad (5)$$

Neither Cl^- nor ClO^- was detected in water of the traps. To further investigatr the possibility of the formation of Cl_2 by the oxidation of Cl^- with O_3, we carried out the reaction in an aqueous solution of NaCl with a similar manner to that in **Sol**(Cl). However, no formation of Cl^- nor ClO^- was confirmed. Thus, the formation of Cl_2 was improbable.

Another possibility for the loss of Cl^- was the formation of ClO_x^- (x = 1–4) by the reaction with O_3. To check the formation of ClO_x^- during the reaction in **Sol**(Cl) in the presence of Co_3O_4, we applied analytical conditions for ion-chromatography analysis being able to detect them in the solution (see the experimental section). Unfortunately, ClO^- and ClO_3^- cannot be analyzed individually even with the analytical conditions if they exist together in the solution because unavoidable reduction of ClO_3^- to ClO^- occurs in the column. Thus, we only knew the total amount of ClO^- and ClO_3^-. The ion-chromatography analysis showed no formation of ClO_2^- and ClO_4^- in the reaction solution at any reaction time. On the other hand, ClO^-, some of which could come from ClO_3^-, was found in the solution, but the amount of ClO^- at 6 h corresponded to only 5% or less of that of the lost Cl^-. Thus, the formation of ClO^- or ClO_3^- was not the main cause for the loss of Cl^- during the reaction in **Sol**(Cl).

3.3.2. Formation of chloramines

To investigate the involvement of NH_4^+ in the loss of Cl^-, we evaluated the consumption rate of Cl^- in an aqueous solution of NaCl in the presence of Co_3O_4. It was found that the consumption rate of Cl^- in the aqueous solution of NaCl was about only one-tenths of that in **Sol**(Cl), which were 0.087 and 0.92 mmol h^{-1}, respectively. These results strongly suggest that the reaction of Cl^- with NH_4^+ gave some chlorinated nitrogen compounds that were undetected by ion chromatography, namely non-ionic compounds.

To confirm the formation of such compounds, the reaction solution of **Sol**(Cl) in the presence of Co_3O_4 was analyzed by an inductively coupled plasma-mass spectrometry (ICP-MS). The analysis with ICP-MS gives total concentration of chlorine in the solution. At 3 h of the reaction, the total concentration of chlorine in the solution was 9.5 mmol L^{-1}, while the concentration of Cl^- in the solution analyzed by ion chromatography was 7.0 mmol L^{-1} (Fig. S1). The fact that the total concentration of chlorine was higher than that of Cl^- indicated the presence of non-ionic chlorinated nitrogen compounds in the reaction solution.

It is known that monochloramine (NH_2Cl) is formed by the reaction of NH_4^+ with hypochlorite (ClO^-) in weakly acidic aqueous solution even without any catalyst [23]. Monochloramine is further transformed into dichloramine ($NHCl_2$) and trichloramine (NCl_3) by the reaction with hypochloric acid (HClO) if pH of the solution is around 4 or less [24]. Initial pH of **Sol**(Cl) was 5.5 and pH was decreased to 3 at 6 h in the presence of Co_3O_4 due to the oxidation of NH_4^+ into neutral products as well as anionic NO_3^-. Thus, the formation of chloramines was possible for the reaction in **Sol**(Cl).

Chloramines easily undergo decomposition in strongly basic solution, giving Cl^- [25]. Thus, we took out an aliquot of the reaction solution and pH of the solution was increased to 11 by the addition of an aqueous KOH solution. If chloramines were present in the solution, the concentration of Cl^- was increased after the pH increase. Furthermore, the outlet gas of the reactor was absorbed into a strongly basic KOH solution (pH 11), in which fine powder of MgO was further dispersed, in traps during the reaction in **Sol**(Cl) in the presence of Co_3O_4. Because chloramines especially trichloramine are less soluble in water, chloramines formed in the reaction solution could go out from the reactor with a flow of O_3/O_2 mixture. To avoid slipping chloramines from the trap solution, three traps containing the strongly basic KOH solution with 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 Cl^-.

273 Fig. 5 displays time-course changes in the concentrations of Cl^- in the reaction solution
274 as it was and in the reaction solution after the pH increase, and the concentration of Cl^- in the
275 trap solution. For easy understanding, amounts of 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 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 Cl^- before and after the pH increase, corresponded
281 to 2.5 mmol L^{-1} at 3 h. At 6 h, at which almost all NH_4^+ disappeared in the reaction solution
282 (Fig. S1), the increase in the concentration of Cl^- by the pH increase was only little, suggesting
283 that the formed chloramines went out from the reactor. In fact, the concentration of 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 $$\text{Chlorine balance (\%)} = \frac{[Cl^-]_{\text{reaction solution after pH increase}} + [Cl^-]_{\text{trap}}}{[Cl^-]_0} \times 100 \quad (6)$$

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

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

According to Fig. 5, it seemed that the concentration of chloramines in the reaction solution was the highest at 3 h for the reaction in **Sol**(Cl) in the presence of Co_3O_4. Thus, we analyzed that reaction solution with the head-space GC-MS method. However, no peak due to chloramines was found on the gas chromatogram, probably because their concentrations in the solution were below detection limits for the head-space GC-MS analysis.

Thus, we collected chloramines formed during the reaction in **Sol**(Cl) in the presence of Co_3O_4 by making the outlet gas of the reactor absorbed into pure water in a trap for 6 h and analyzed the trap solution. Fig. 6a gives the chromatogram of the trap solution obtained by the head-space GC-MS method. The large peak at 1.1 min on the chromatogram was due to air. The chromatogram had a large peak at 2.4 min, while very small ones were observed at 1.4 and 1.6 min. Mass spectrum for the peak at 2.4 min showed the peaks at m/z = 119 and 121 (Fig. 6b), which was assignable to the molecular ions of trichloramine with $N^{35}Cl^{35}Cl^{35}Cl$ and $N^{35}Cl^{35}Cl^{37}Cl$, respectively. Since the abundance ratios of $N^{35}Cl^{37}Cl^{37}Cl$ and $N^{37}Cl^{37}Cl^{37}Cl$ among trichloramine were small, being 0.07 and 0.02, respectively, the peaks at m/z = 123 and 125 assignable to their molecular ions were not observed. In addition to the molecular ion peaks, various fragment ion peaks were observed at 84, 86 and 88 (NCl_2^+) and 49 and 51 (NCl^+) with reasonable intensity ratios. Therefore, it was concluded that the formation of trichloramine was successfully confirmed by using the head-space GC-MS method. The small peaks at 1.4 and

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

3.3.3. Re-evaluation of the selectivity for the reaction over Co_3O_4

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

3.3.4. Reaction pathway for the reaction over Co_3O_4

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

conditions in **Sol**(Cl) in this study, hypochlorite ion was formed. Thus, it was plausible that monochloramine was formed by the reaction of NH_4^+ with ClO^-, and dichloramine and trichloramine were successively formed by the reaction of mono- and dichloramine, respectively, with ClO^- (or HClO). As Fig. 3 showed, the decomposition rate of NH_4^+ in the presence of Co_3O_4 was higher than that in its absence. There are two possibilities for the promotion by Co_3O_4: Co_3O_4 accelerated (i) the formation of ClO^- and (ii) the reaction of NH_4^+ with ClO^-. However, the former was improbable, because the formation of ClO^- by the reaction of Cl^- with O_3 was rather inhibited by the presence of Co_3O_4 for the reaction in an aqueous solution of NaCl (Fig. S2).

To confirm the possibility of the latter, we carried out the reactions of NH_4^+ with ClO^- under O_2 flow without O_3 in the presence and absence of Co_3O_4 (Fig. 7). As Fig. 7 clearly demonstrates, the conversion of NH_4^+ in the presence of Co_3O_4 was much higher than that in its absence. Furthermore, we confirmed the formation of chloramines found in the reaction solution and trap solutions by similar manners to those performed for the reaction shown in Fig. 5. Therefore, it was concluded that Co_3O_4 accelerated the reaction of NH_4^+ with ClO^-.

Based on the results, we propose the reaction pathway for the reaction over Co_3O_4 as Fig. 8. In the first step, Cl^- is non-catalytically oxidized with O_3 to form ClO^-. Co_3O_4 rather inhibits this reaction. Thereafter, NH_4^+ is reacted with ClO^- on Co_3O_4 to form NO_3^-, chloramines, and other gaseous nitrogen compounds.

3.4 Reaction mechanism for ozonation of NH_4^+ in the presence of MgO

3.4.1. Role of MgO for the ozonation of ammonia nitrogen

Fig. 9 shows time-course changes in the concentrations of ammonia nitrogen as well as Cl^- and SO_4^{2-} for the reactions in **Sol**(Cl) and **Sol**(SO_4) in the presence of MgO. In contrast

366 to Co_3O_4, the ozonation of ammonia nitrogen proceeded even in **Sol**(SO_4) in the presence of
367 MgO, and the presence of Cl^- did not affect the reaction rate and selectivity. In fact, Cl^- was
368 not lost over the reaction time in **Sol**(Cl), suggesting that the reaction did not follow the reaction
369 mechanism as it occurred over Co_3O_4.

370 A stark difference between Co_3O_4 and MgO for the reaction was their dissolution
371 behavior. In contrast to insoluble Co_3O_4, about 40% of MgO was dissolved in **Sol**(SO_4) for 6
372 h, though 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 MgO even before the flowing of 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.

376

377 $$MgO(s) + H_2O \rightleftarrows Mg^{2+} + 2OH^- \quad (7)$$

378

379 Ideally, a small amount of 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 MgO [22]. Since the pH was quickly increased just
382 by the addition of MgO and was maintained near constant throughout the reaction, the reaction
383 of Eq. 7 must reach equilibrium quickly under the reaction conditions with MgO.

384 To get an insight into the role of MgO, firstly, a reaction in the absence of MgO at pH
385 9 was carried out. Because K_b of NH_3 (= $[NH_4^+][OH^-]/[NH_3]$) is $10^{-4.8}$, ammonia nitrogen
386 existed predominantly as NH_3 in the reaction solution. As shown in Fig. S3, 16% of ammonia
387 nitrogen was decomposed at 1 h and concomitantly NO_3^- that was equivalent to the consumed
388 ammonia nitrogen was formed. After that, however, the reaction was completely stopped. At

the time, the solution turned to acidic because of charge compensation for the formation of anionic product (NO_3^-) from neutral reactants (NH_3 and O_3) (Eq. 8).

$$NH_3 + 4O_3 \rightarrow NO_3^- + H_2O + H^+ + 4O_2 \quad (8)$$

We further carried out a similar reaction, but pH of the reaction solution was repeatedly restored to 9 at each sampling time (Fig. S4). For that reaction, the decomposition of ammonia nitrogen continually proceeded. Under the reaction conditions, stripping of NH_3 from the reaction solution was only little. These results clearly demonstrated that in mildly alkaline solution, ammonia nitrogen can be oxidized into mainly NO_3^- even without any catalysts.

As mentioned above, to increase pH to around 9, only less than 0.1% of MgO added to the reaction solution was sufficient, but the fact was that much amount of MgO was dissolved with the reaction, implying the presence of another mechanism for the dissolution of MgO. To get a clue for it, we carried out the ozonation of ammonia nitrogen with different initial concentrations of ammonia nitrogen in the presence of MgO and investigated the relationship between the amount of decomposed ammonia nitrogen and that of dissolved Mg^{2+} at each reaction time with different initial concentrations of ammonia nitrogen. The results are shown in Fig. 10. Notably, the amount of Mg^{2+} dissolved was linearly increase with increase in the amount of ammonia nitrogen decomposed. It should be noted that the slope of the line in Fig. 10 was nearly unity. Because ammonia nitrogen exists originally as NH_4^+ in the as-prepared reaction solution before the addition of MgO, the stoichiometric equation for the oxidation of ammonia nitrogen to NO_3^- is as follows.

$$NH_4^+ + 4O_3 \rightarrow NO_3^- + H_2O + 2H^+ + 4O_2 \quad (9)$$

Since the pH of the solution was maintained at around 9 throughout the reaction in the presence of MgO, H^+ formed by the reaction of Eq. 9 was neutralized with OH^- that was formed by the forward reaction of Eq. 7, inducing further dissolution of MgO. Consequently, a single decomposition reaction of ammonia nitrogen yielded the dissolution of one Mg^{2+} as represented by Eq. 10.

$$NH_4^+ + 4O_3 + MgO \rightarrow NO_3^- + 4O_2 + Mg^{2+} + 2H_2O \quad (10)$$

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

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

3.4.2. Possibility of involvement in homogeneous catalysis by Mg^{2+}

Because Mg^{2+} was present in the reaction solution for the reaction with MgO, it could be that Mg^{2+} acted as a homogeneous catalyst. Thus, we performed the ozonation of ammonia nitrogen in **Sol**(SO_4) with 10 mmol L^{-1} of Mg^{2+}, which was prepared by adding $Mg(NO_3)_2 \cdot 6H_2O$ to the reaction solution. The initial pH of the reaction solution was adjusted to 9 by the addition of KOH. The result showed that the conversion of ammonia nitrogen was 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_4) in the
442 presence of both MgO and *tert*-butyl alcohol (TBA, 100 mmol L^{-1}) 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^- with O_3 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_2O giving Mg^{2+}
457 and OH^- is in equilibrium and thus pH of the solution is maintained at mildly alkaline pH.
458 Ammonia nitrogen is decomposed to mainly NO_3^- by the reaction with OH·. Proton formed
459 with the decomposition of ammonia nitrogen is neutralized, leading to further dissolution of

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

4. Conclusion

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

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

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Appendix A. Supplementary data

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

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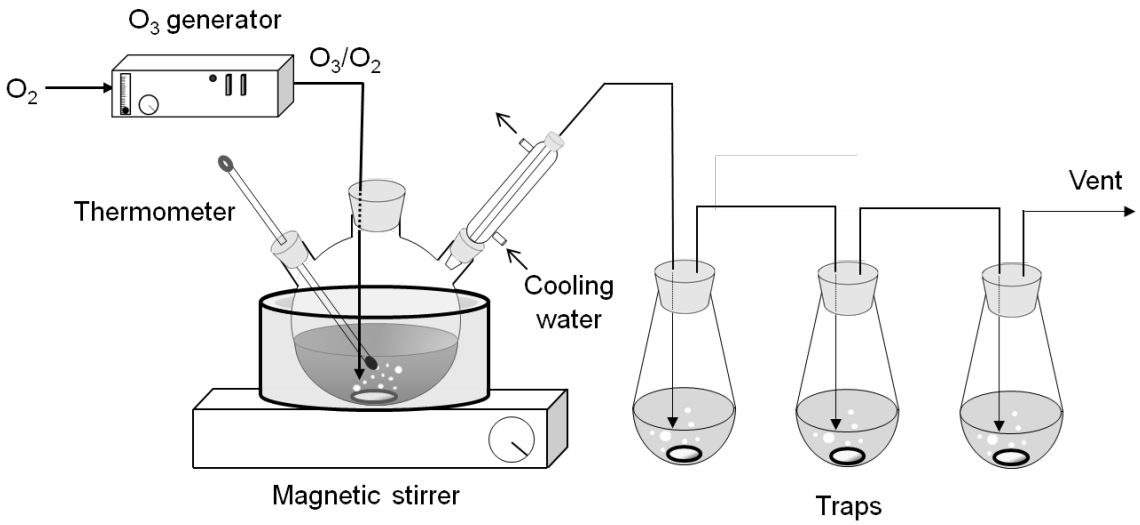

Fig. 1. Illustration of the semi-batch reactor used for ozonation of ammonia nitrogen in water. Pure water or an aqueous KOH solution (pH 11) with fine powder of MgO was put in three traps.

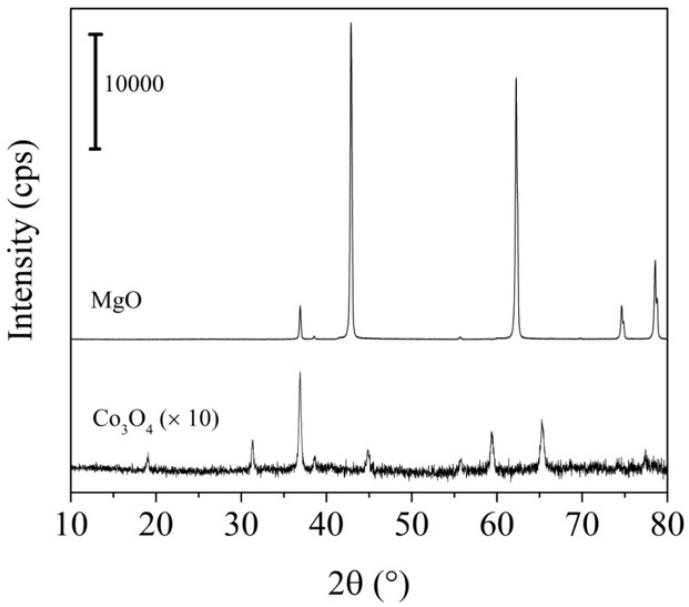

Fig. 2. XRD patterns of Co_3O_4 and MgO.

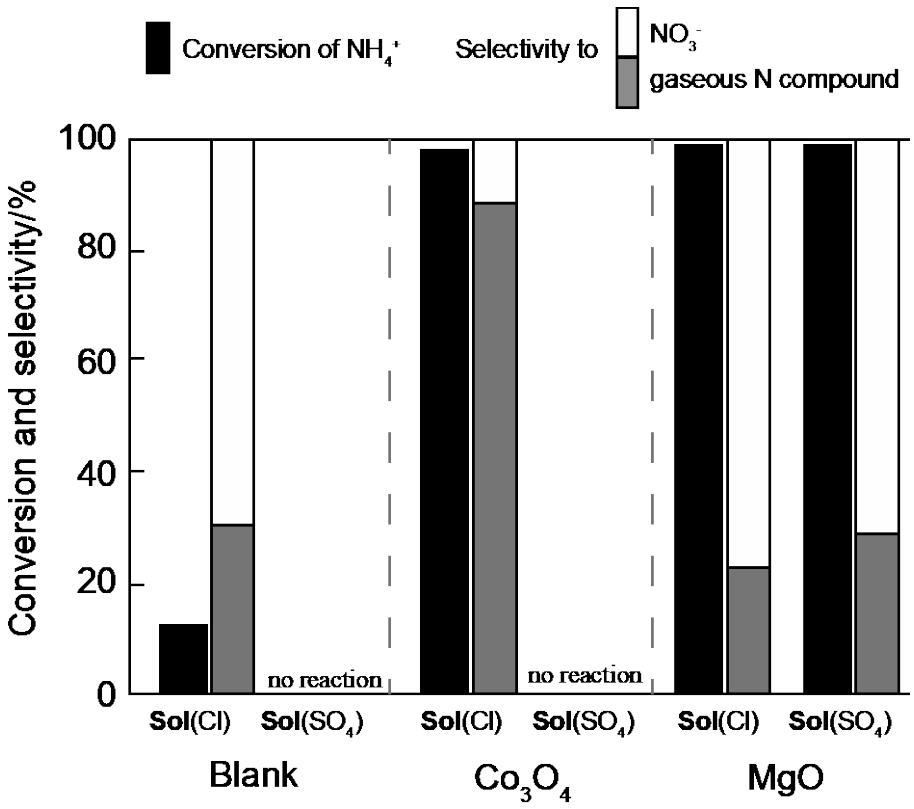

Fig. 3. Conversions and selectivity for ozonation of ammonia nitrogen in **Sol**(Cl) and **Sol**(SO_4) in the presence of Co_3O_4 or MgO. **Sol**(Cl) and **Sol**(SO_4) represent the reaction solutions prepared from NH_4Cl and $(NH_4)_2SO_4$, respectively. Reaction conditions: Co_3O_4 or MgO, 0.1 g; 10 mmol L^{-1} NH_4^+ solution, 100 mL; total flow rate of O_3/O_2 mixture, 100 mL min^{-1}; concentration of O_3 in the mixture, 0.7 vol%; reaction temperature, 333 K; reaction time, 6 h.

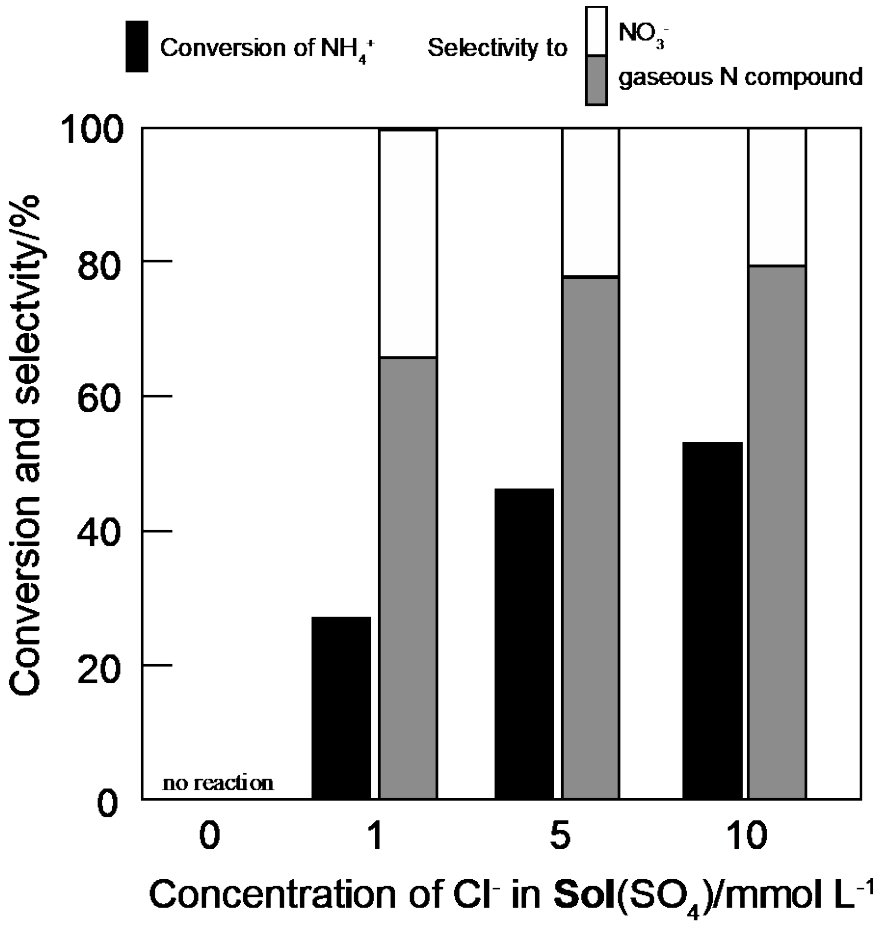

Fig. 4. Influence of Cl^- concentration in **Sol**(SO_4) on the ozonation of ammonia nitrogen in the presence of Co_3O_4. The reaction solution was prepared by adding NaCl to **Sol**(SO_4). Reaction conditions: Co_3O_4, 0.1 g; 10 mmol L^{-1} NH_4^+, 100 mL; O_3/O_2 flow rate, 100 mL min^{-1}; concentration of O_3, 0.7 vol%; reaction temperature 333 K; reaction time, 6 h.

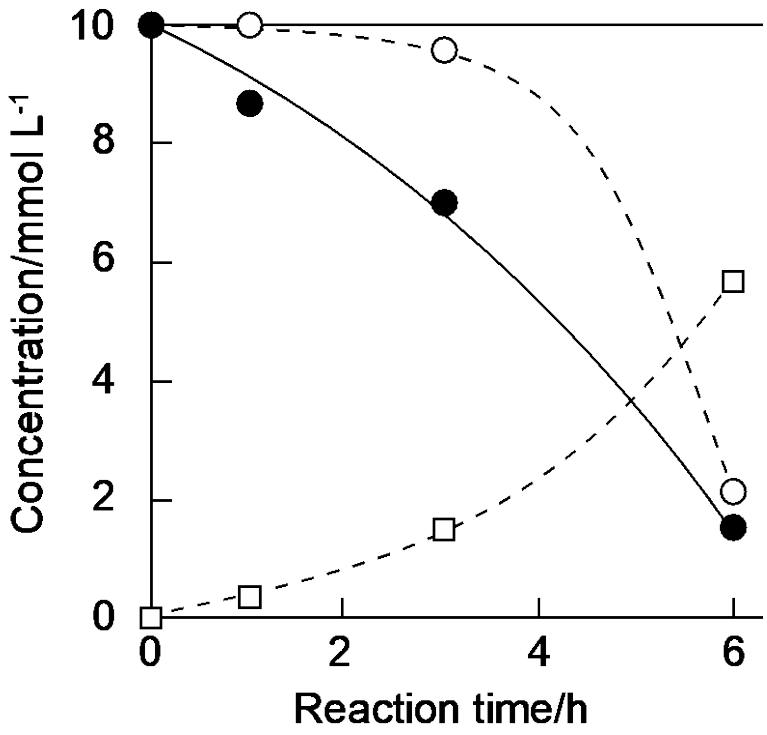

Fig. 5. Time-course changes in the concentrations of Cl^- in the reaction solution (●) as it is and (○) after increasing the pH to 11 and (□) in the trap solution for ozonation of ammonia nitrogen in **Sol**(Cl) in the presence of Co_3O_4. Reaction conditions: Co_3O_4, 0.1 g; 10 mmol L^{-1} NH_4^+ and Cl^-, 100 mL; O_3/O_2 flow rate, 100 mL min^{-1}; concentration of O_3, 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^-.

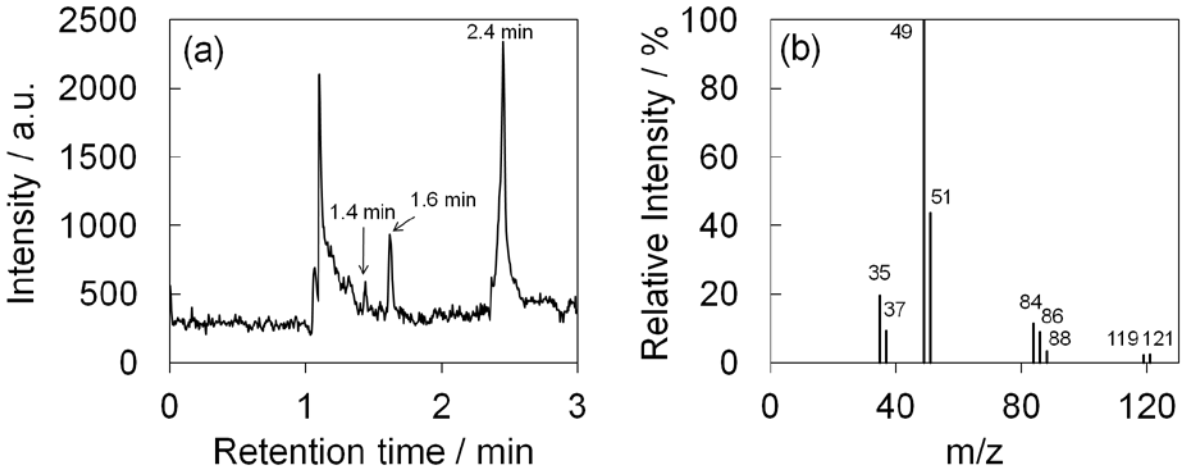

Fig. 6. The results of a head-space GC-MS analysis for the solution obtained by passing the outlet gas of the reactor through pure water in the traps for 6 h in ozonation of ammonia nitrogen in **Sol**(Cl) over Co_3O_4. The trap was cooled at 273 K. (a) total ion chromatogram and (b) mass spectra for the peak at 2.4 min. Reaction conditions were the same as those in Fig. 5, but pure water was used as a trap solution instead of an aqueous KOH solution with fine powder of MgO.

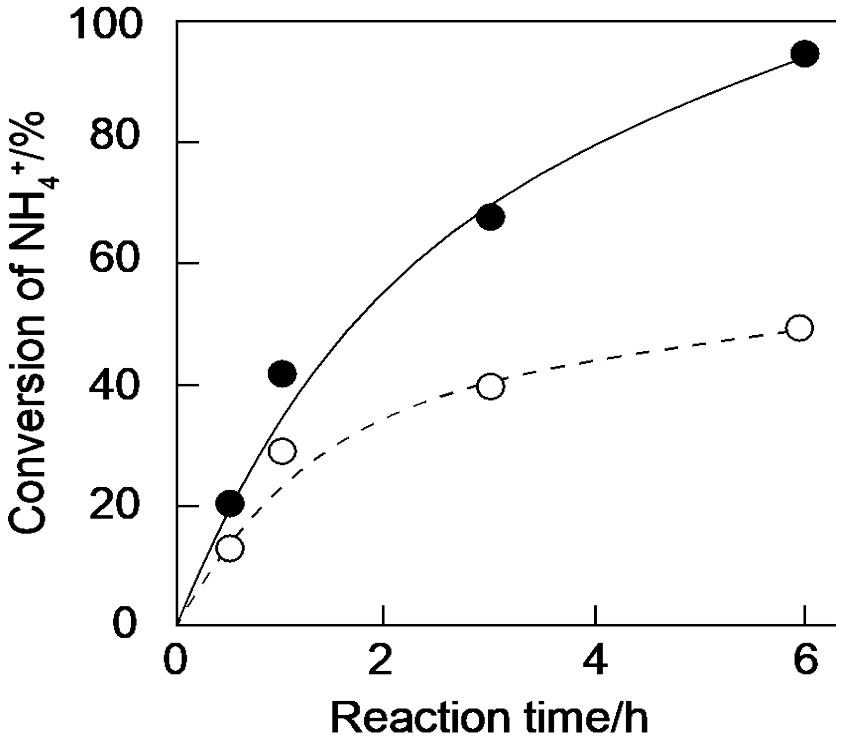

Fig. 7. Time-course changes in the conversion of NH_4^+ for the reaction of NH_4^+ with ClO^- under O_2 flow without O_3 in the (●) presence and (○) absence of Co_3O_4. Reaction conditions: Co_3O_4, 0.1 g ; concentrations of NH_4^+ and ClO^-, 10 and 20 mmol L^{-1}, respectively; volume of reaction solution, 100 mL; O_2 flow rate, 100 cm^3 min^{-1}; reaction temperature, 333 K.

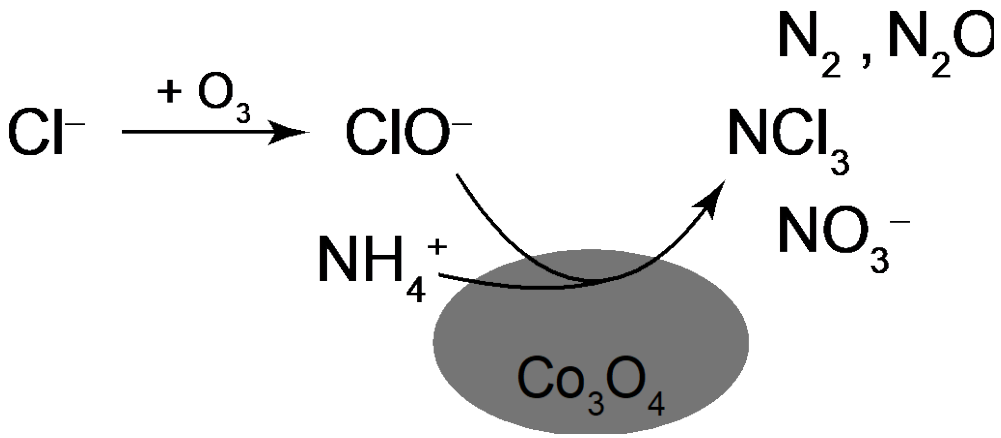

Fig. 8. Proposed reaction pathway for ozonation of ammonia nitrogen in the presence of Cl^- over Co_3O_4.

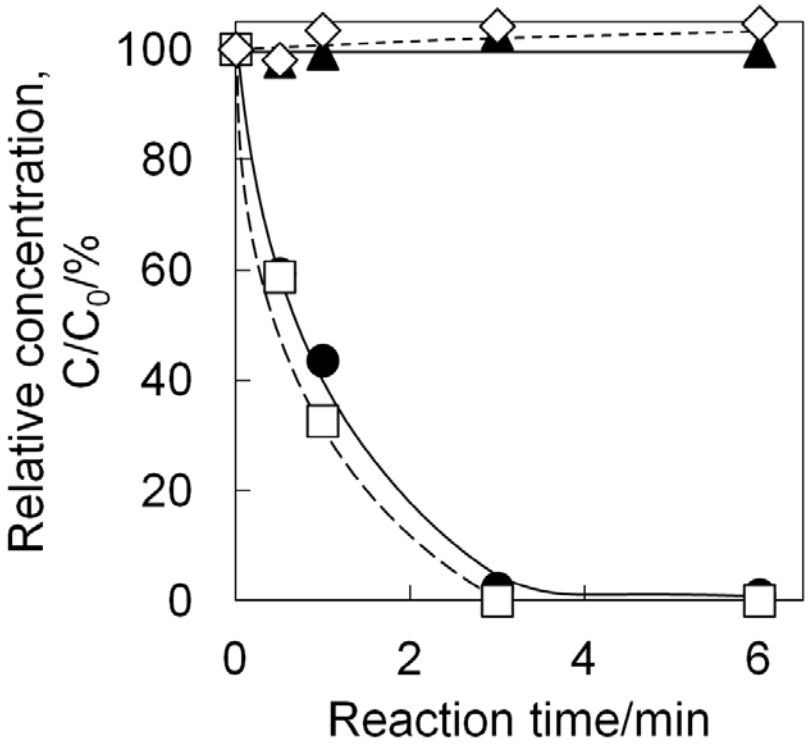

Fig. 9. Time-course changes in the concentrations of ammonia nitrogen and anions for ozonation of ammonia nitrogen in **Sol**(Cl) and **Sol**(SO_4) in the presence of MgO. (●) and (▲) are the concentrations of ammonia nitrogen and Cl^-, respectively, for the reactions in **Sol**(Cl), and (□) and (◇) are those of ammonia nitrogen and SO_4^{2-}, respectively, for the reactions in **Sol**(SO_4). Reaction conditions are the same as those for the reaction in Fig. 3.

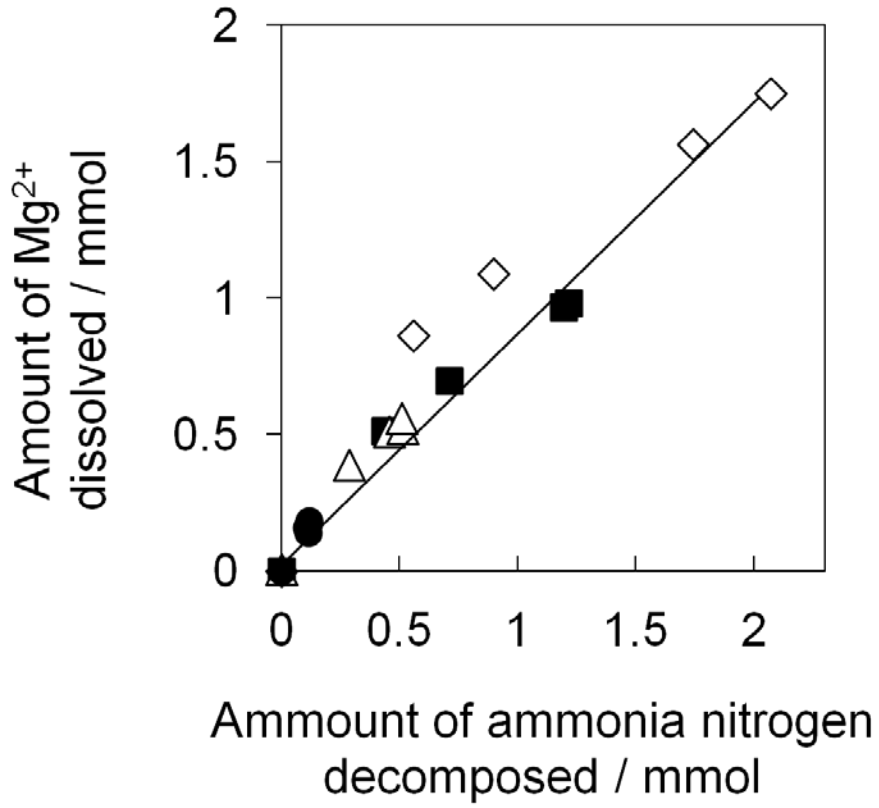

Fig. 10. Relationship between the amount of Mg^{2+} dissolved and that of decomposed ammonia nitrogen for ozonation of ammonia nitrogen in the presence of MgO with different initial concentrations of ammonia nitrogen and reaction time. Reaction conditions: MgO, 0.1 g; reaction solution, 100 mL; O_3/O_2 flow rate, 100 mL min^{-1}; reaction temperature ,333 K. Initial concentration of ammonia nitrogen: (●) 1 mmol L^{-1}, (△) 5 mmol L^{-1}, (■) 10 mmol L^{-1}, (◇) 20 mmol L^{-1}. The data collected at different reaction times are plotted on the graph.

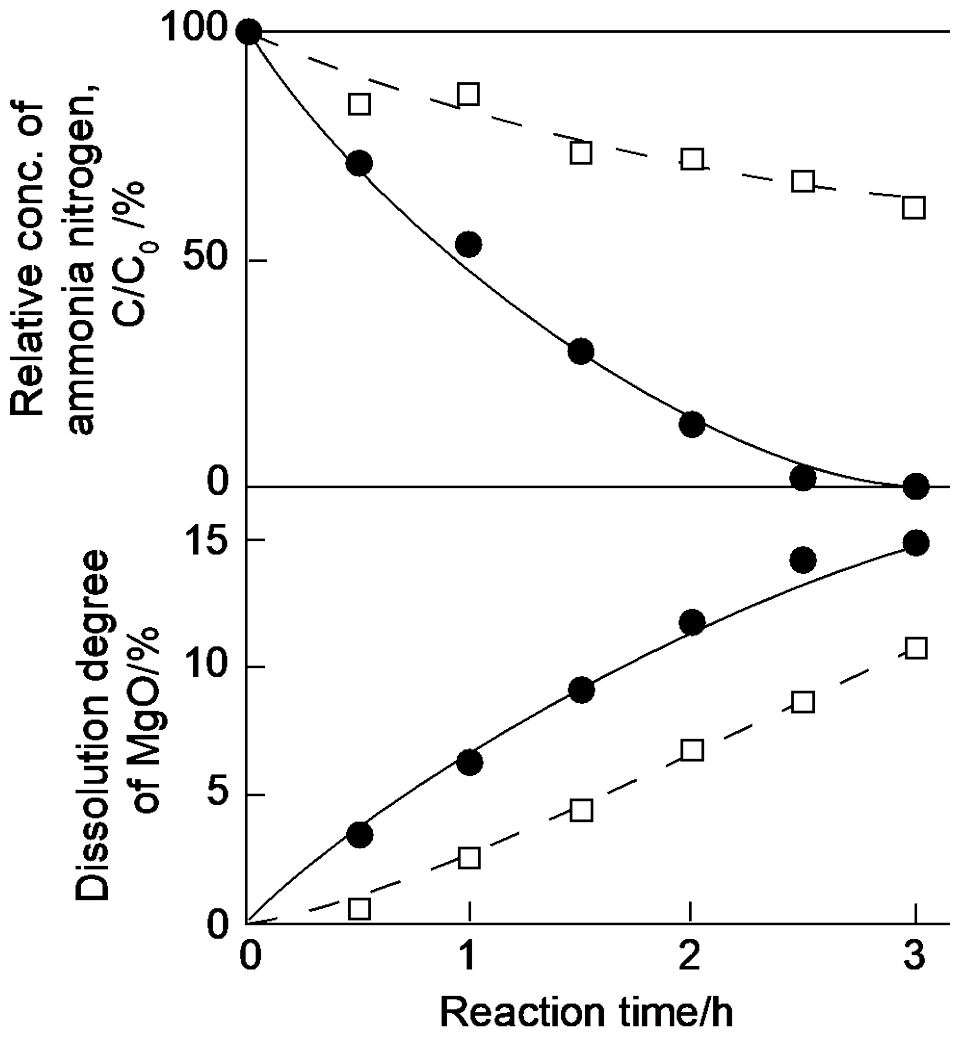

Fig. 11. Influence of tert-butyl alcohol (TBA) in the reaction solution on the decomposition rate of ammonia nitrogen and dissolution degree of MgO for ozonation of ammonia nitrogen in the presence of MgO. (●) in the absence of TBA and (□) in the presence of TBA. Reaction conditions: MgO, 0.1 g; concentrations of NH_4^+ and TBA, 10 and 100 mmol L^{-1}, respectively; reaction solution, 100 mL; O_3/O_2 flow rate, 100 cm^3 min^{-1}; reaction temperature, 298 K.

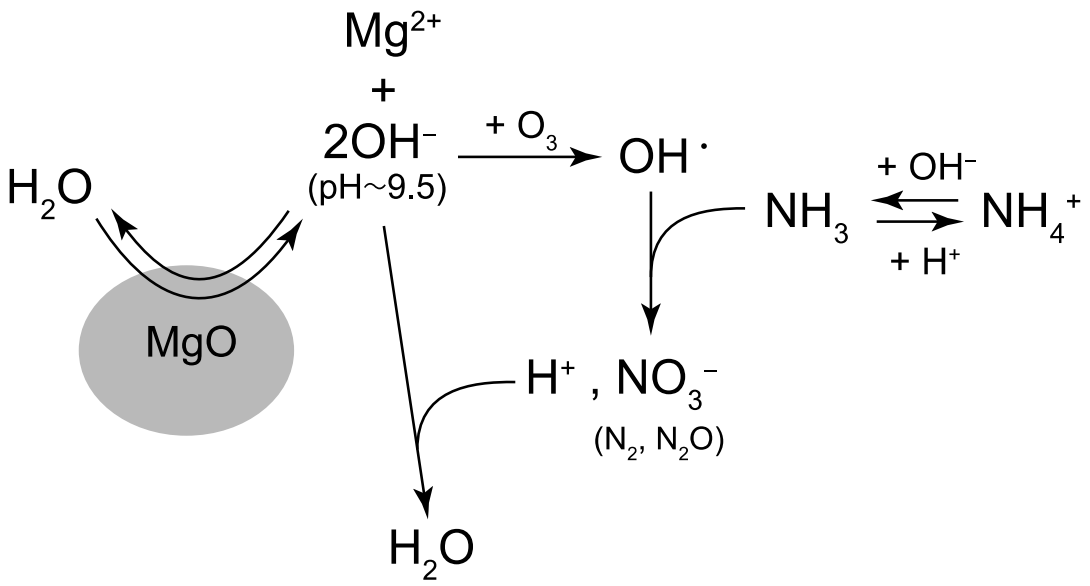

Fig. 12. Proposed reaction pathway for ozonation of ammonia nitrogen in the presence of MgO.