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Oxidative decomposition of ammonium ion with ozone in the presence of cobalt and chloride ions for the treatment of radioactive liquid waste

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Abstract

To prevent unexpected accidents at nuclear facilities caused by accumulated ammonium nitrate in an aqueous liquid waste containing ammonium salts and nitric acid, NH_4^+ in the liquid waste must be decomposed under mild reaction conditions. In this study, we investigated the oxidative decomposition of NH_4^+ with O_3 at 333 K in the presence of a homogeneous Co^{2+} catalyst and Cl^- in the wide pH range of the test solution. The reaction behavior was greatly affected by pH of the test solution. In a basic solution at pH 12, high conversion of NH_4^+ was obtained even in the absence of Co^{2+} and Cl^-, and the main product was NO_3^-. However, Co^{2+} and Cl^- in the solution greatly enhanced the decomposition rate of NH_4^+ in acidic to mild basic solutions (pH 1−8), while only low conversion of NH_4^+ was observed unless both Co^{2+} and Cl^- were present. For the reaction with Co^{2+} and Cl^- in the solutions, NH_4^+ was transformed mainly into chloramines (NH_xCl_{3-x}, x = 1−3) by the reaction with HClO, which was formed by the reaction of Cl^- with O_3 catalyzed by the homogeneous Co^{2+} catalyst, and led to the high decomposition rate of NH_4^+. Cl^- suppressed the formation of the precipitate CoO(OH) during the reaction and consequently the Co^{2+} catalyst stably existed in the reaction solution, which was another reason for the high decomposition rate of NH_4^+ in the presence of Cl^-. Owing to the swift decomposition of NH_4^+ under mild reaction conditions and small formation of secondary waste, the oxidative decomposition of NH_4^+ in the presence of the homogeneous Co^{2+} catalyst and Cl^- is suitable and applicable for the treatment of the aqueous liquid waste containing ammonium salts and nitric acid.

Keywords: radioactive liquid waste, ammonium ion, ozone oxidation, cobalt ion, pH dependence

1. Introduction

Many types of liquid wastes containing radio isotopes and/or nuclear materials have been being generated through research and development (R&D) activities at nuclear facilities. These radioactive liquid wastes contain various chemical reagents. Because some of them are highly reactive and explosive, the radioactive liquid wastes should be stored or disposed of with special attention to the risks of the chemical reagents according to their properties.

To develop technologies for the treatment of radioactive liquid wastes with various compositions, Japan Atomic Energy Agency (JAEA) launched a study project named STRAD (Systematic Treatment of RAdioactive liquid wastes for Decommissioning) (Watanabe et al., 2019). In this project, the Chemical Processing Facility (CPF) of JAEA was selected as a test case of the liquid waste source, and fundamental studies for the treatment of the wastes generated through R&D activities in CPF were conducted. CPF is a laboratory used for the development of fuel reprocessing and vitrification technology for advanced nuclear fuel cycle. Currently, the analysis on contaminated water from the Fukushima daiichi nuclear power plant is an important task imposed on CPF in addition to the usual R&D activities.

The long-standing R&D activities performed at CPF for more than 30 years have generated many types of radioactive liquid wastes containing various chemical reagents. These liquid wastes are broadly categorized into four types: (i) aqueous liquid waste generated through analyses, (ii) aqueous liquid waste generated through process experiments, (iii) organic liquid waste generated through analyses, and (iv) organic liquid waste generated through process experiments. The targeted liquid wastes used in this study are the aqueous liquid waste generated through analyses including acid–base titration, absorption spectrometry, and radioactivity measurements. The aqueous liquid wastes contain many chemical reagents with complicated composition, and the appropriate treatment of such liquid wastes is a challenging task.

Currently, approximately 300 L of the aqueous liquid waste generated through the analyses is stored in a shielded area at CPF. As pretreatment for the analyses, various chemical reagents were added to sample solutions, which generated aqueous liquid wastes with various compositions. Ammonium sulfate [$(NH_4)_2SO_4$], ammonium persulfate [$(NH_4)_2S_2O_8$], ammonium iron(II) sulfate [$(NH_4)_2Fe(SO_4)_2$], and tetraammonium cerium(IV) sulfate dihydrate [$Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$] are ammonium salts that are commonly used during pretreatments to mask uranium species by forming uranium complexes and to adjust the valence of plutonium species appropriate for the analyses. The pretreatments using ammonium salts are also employed in the reprocessing of spent nuclear fuels (Hayashi and Wachi, 1986), and large quantities of liquid wastes containing ammonium salts have been generated at the experimental laboratories. Because such liquid wastes contain ammonium salts and nitric acid, the formation of solid ammonium nitrate is possible during storage. Ammonium nitrate is a hazardous material; it explodes upon impact and in contact with specific materials (United States Environmental Protection Agency, 2013). To prevent accidents at the facilities, ammonium ion in aqueous liquid wastes should be removed for safe keeping. However, the separation of ammonium ions through the formation of a precipitate is impossible because they are typically highly soluble in water; thus, ammonium ions should be decomposed into gaseous compounds before the storage of wastes.

Gas-phase oxidation after ammonia stripping (Imamura and Doi, 1985, Huang et al., 2000), breakpoint chlorination (Eilbeck, 1984, Keenan and Hegemann, 1978), and biological treatment (Schmidt, 2003) are commercially available methods for the treatment of common industrial wastewater containing ammonium ion. Indeed, high removal and decomposition rates for ammonium ion can be achieved using these methods. However, they require severe conditions such as high temperature and pressure, and high chloride concentration for gas-phase oxidation after ammonia stripping and breakpoint chlorination, respectively, and strict control of the treatment conditions is needed for biological treatment, which are impossible inside shielded spaces at nuclear facilities. Therefore, other methods that are suitable for the operation inside shielded spaces, i.e., decomposition of ammonium ion under mild reaction conditions (ideally ambient temperature and pressure), should be developed for the appropriate management of aqueous liquid wastes.

The oxidative decomposition of organic pollutant in water with ozone (O_3), which is known as an advanced oxidation process, has gained considerable attention for water treatment because the decomposition reaction proceeds even under mild reaction conditions (Singer and Zilli, 1975, Rice, 1996, Wang and Xu, 2012, Khuntia et al., 2013). To enhance the decomposition efficiency, the reaction is often performed in the presence of a catalyst, which is called catalytic ozonation (Hordern et al., 2003, Nawrocki and Hordern, 2010, Wang and Bai, 2017). For the catalytic ozonation of ammonium ion in water, Co_3O_4 is reported to be a highly active heterogeneous catalyst, and the decomposition reaction over the catalyst proceeds under mild conditions, i.e., 333 K and ambient pressure (Ichikawa et al., 2014, Mahardiani and Kamiya, 2016, Krisbiantoro et al., 2020). The target of those studies with Co_3O_4 is the treatment of common wastewater containing ammonium ion, and the treated water is intended to be eventually released into the environment (Ichikawa et al., 2014, Mahardiani and Kamiya, 2016). Thus, use of heterogeneous catalysts, such as Co_3O_4, which are insoluble in the aqueous reaction solution, is favorable to prevent secondary pollution caused by the catalyst itself.

However, the target of this study is radioactive liquid wastes, and the treated water will be further treated (e.g., via solidification) but not released into the environment. While an essential problem in homogeneous catalysis is the separation of the catalyst from the reaction solution after the reaction, it does not matter for the treatment of radioactive liquid wastes, because catalyst separation is unnecessary. All metal ions that are present in the reaction solution can act as an active center in homogeneous catalysis unlike heterogeneous catalysis, in which the reaction proceeds only on the surface of the catalyst material. Thus, homogeneous catalysts often exhibit higher performance than heterogeneous ones especially under mild reaction conditions (Beller et al., 2012) .

It is known that some metal ions work as a homogeneous catalyst during catalytic ozonation. Cobalt ion has been reported to promote the formation of active radical species, including hydroxyl radical ($OH\cdot$), by the reaction with O_3 and water (eq. 1) and to quench radicals (eqs. 2 and 3) (Hill, 1948, Wang and Chan, 2020):

$$Co^{2+} + O_3 + H_2O \rightarrow Co(OH)^{2+} + O_2 + OH\cdot \quad (1)$$

$$OH\cdot + O_3 \rightarrow HO_2\cdot + O_2 \quad (2)$$

$$HO_2\cdot + Co(OH)^{2+} \rightarrow Co^{2+} + H_2O + O_2 \qquad (3)$$

These reactions were considered for the reaction in acidic solutions (Pan et al., 1984, Beltran et al., 2003). Therefore, we assumed that cobalt ion was a promising candidate as a homogeneous catalyst for the oxidative decomposition of ammonium ion with O_3 in radioactive liquid wastes. To our knowledge, such investigations have not been previously reported.

In this study, we performed the oxidative decomposition of ammonium ion with O_3 in the presence of Co^{2+} in a wide pH range of the test solution to examine the applicability of the homogeneous catalytic process with Co^{2+} for the treatment of aqueous liquid waste generated through analyses. In addition, we investigated the influence of Cl^- on the reaction and determined that Cl^- was involved in the reaction. Finally, we proposed a reaction mechanism for the reaction that was based on the reaction behavior at different pH, the roles of Cl^- for the reaction, and the chemical state of cobalt species revealed by the in situ XAFS measurement.

2. Experimental method

2.1. Oxidative decomposition of ammonium ion with ozone in water

A reaction apparatus for the oxidative decomposition of ammonium ion is illustrated in Fig. 1. The apparatus consisted of an O_2 cylinder (99.9 vol% O_2), a mass flow controller, an ozone generator, a four-neck separable flask, a hot stirrer, a condenser with a cooling water circulator, and three trap bottles.

(Fig. 1)

Test solutions examined in this study are summarized in Table 1. The presence or absence of Co^{2+} and Cl^{-}, and the pH of the test solution were systematically changed to investigate the influence of these factors on reaction behavior in the oxidative decomposition of ammonium ion with O_3. NH_4Cl and $(NH_4)_2SO_4$ (FUJIFILM Wako Pure Chemicals Co.) were used as an ammonium ion source, and either of the two compounds was dissolved in 200 mL of ultrapure water ($[NH_4^+]_0$ = 50 mmol L^{-1}). For the reactions in the presence of Co^{2+}, $Co(NO_3)_2 \cdot 6H_2O$ (FUJIFILM Wako Pure Chemicals Co.) was added to the test solution so that the concentration of Co^{2+} was 4.5 mmol L^{-1}. The pH of the solution was adjusted by adding dilute nitric acid or an aqueous NaOH solution to reach the target value just before the reaction. While the precipitate was formed in the middle of the pH adjustment for the test reaction of pH 12, the oxidative decomposition of ammonium ion was performed without removing it.

(Table 1)

The test solution (200 mL) was put in a separable flask, and the temperature of the solution was increased and then kept at 333 K throughout the reaction. Ozone was generated from O_2 by the ozone generator, and the concentration of O_3 was 5 vol% in O_2. The mixture of O_3/O_2 was flown into the solution at the flow rate of 360 mL min^{-1} after the temperature of the solution reached 333 K. A total of 100 mL of ultrapure water was put in the first and second trap bottles. In the third trap bottle, 100 ml of the KI solution (1 mol L^{-1}) was put to decompose unreacted O_3 by the reaction with I^-.

A small portion of the reaction and trap solutions were obtained at 1, 3, and 5 h. The concentrations of NH_4^+, NO_3^-, NO_2^-, and co-existing anions (i.e., Cl^- or SO_4^{2-}), and pH were measured by ion chromatographs (ICS-1100, Dionex; and CS16 and AS20 columns for cation and anion analyses, respectively) and a pH meter (Standard ToupH electrode 9615S-10D, Horiba), respectively. Because the pH of the eluting solution for cation analysis for ion chromatography was approximately 1, NH_3 in the solution was detected as NH_4^+, if it existed.

The conversion of NH_4^+ was calculated with eq. 4,

$$\mathrm{NH_4}^+ \text{ conversion } (\%) = \frac{[\mathrm{NH_4}^+]_0 - [\mathrm{NH_4}^+]_t}{[\mathrm{NH_4}^+]_0} \times 100 \tag{4}$$

where $[NH_4^+]_0$ and $[NH_4^+]_t$ are the initial concentration (= 50 mmol L^{-1}) and that at time t (h), respectively. The selectivity to NO_3^- at 5 h was calculated with eq. 5,

$$\text{Selectivity to } \mathrm{NO_3}^- \text{ } (\%) = \frac{[\mathrm{NO_3}^-]_{5\mathrm{h}}}{[\mathrm{NH_4}^+]_0 - [\mathrm{NH_4}^+]_{5\mathrm{h}}} \times 100 \tag{5}$$

where $[NH_4^+]_{5h}$ and $[NO_3^-]_{5h}$ are the concentrations of NH_4^+ and NO_3^- at 5 h, respectively. NO_2^- was not detected in the reaction and trap solutions during the entire reaction time. The concentration of cobalt species dissolved in the reaction solution was measured using ICP-OES (SPS3520UV, Hitachi High-Technologies).

2.2 In situ XAFS analysis

The state of cobalt species in the solution during the operation was evaluated by the in situ XAFS measurement. Co-K edge X-ray absorption spectra were measured by the fluorescence method at the BL5S1 beamline of Aichi Synchrotron Radiation Center, Japan. The spectra were analyzed by Demeter, which is comprehensive system for processing and analyzing X-ray absorption spectroscopy data (Ravel and Newville, 2005).

The experimental setup consisted of a mass flow controller, an ozone generator, a 100 mL bottle (made of polycarbonate), and a hotplate (Fig. 2). The temperature of the test solution was controlled at 333 K, while the mixture of O_3/O_2 was fed into the bottle at the flow rate of 100 mL min^{-1}. The conditions of the test solution were $[(NH_4)_2SO_4]_0$ = 50 mmol L^{-1}, $[NaCl]_0$ = 250 mmol L^{-1}, $[Co(NO_3)_2{\cdot}6H_2O\ ]_0$ = 50 mmol L^{-1}, and pH 4. The volume of the test solution was 50 mL. The concentration of Co^{2+} for the in situ XAFS measurement (50 mmol L^{-1}) was set to be higher than that for the oxidative decomposition of ammonium ion (4.5 mmol L^{-1}) to facilitate the acquisition of spectra. The spectra for an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ with the concentration of 50 mmol L^{-1}, and solid CoO(OH) (Kojundo Chemical Laboratory Co., Ltd.), $CoCl_2$ (FUJIFILM Wako Pure Chemicals Co.), and Co_3O_4 (FUJIFILM Wako Pure Chemicals Co.) were used as references. In addition, the XAFS spectra of the precipitate formed under the conditions of $[(NH_4)_2SO_4]_0$ = 50 mmol L^{-1}, $[Co(NO_3)_2{\cdot}6H_2O]_0$ = 4.5 mmol L^{-1}, initial pH 4, and the blowing of the O_3/O_2 mixture for 10 h were measured.

(Fig. 2)

3. Results and discussion

3.1 Influence of pH on reaction behavior during the oxidative decomposition of ammonium ion with ozone

The oxidative decomposition of NH_4^+ with O_3 was performed in the presence or absence of Co^{2+} and/or Cl^-, and at different pH conditions (Table 1). The conversion of NH_4^+ at 5 h is shown in Fig. 3. Because the reaction was greatly affected by the pH of the test solution, the reaction behavior will be described with respect to each pH.

(Fig. 3)

pH 12

High NH_4^+ conversion was obtained regardless of the presence or absence of Co^{2+}

and Cl^-. As described in detail in 3.2, NO_3^- and gaseous nitrogen compounds (including N_2 and N_2O) were the products under the conditions. There are equilibria between NH_4^+ and NH_3 in an aqueous solution (represented as $NH_{3(aq)}$) and between gaseous NH_3 (represented as $NH_{3(gas)}$) and $NH_{3(aq)}$ (eqs. 6 and 7, respectively).

$$NH_4^+ \rightleftarrows NH_{3(aq)} + H^+ \tag{6}$$

$$NH_{3(aq)} \rightleftarrows NH_{3(gas)} \tag{7}$$

Because pK_a of NH_4^+ is 9.25, the equilibrium of eq. 6 shifts to the right at pH 12. Thus, the escape of NH_4^+ as $NH_{3(gas)}$ from the test solution in the O_3/O_2 mixture was possible. However, the total amount of ammonia species ($NH_{3(aq)}$ and NH_4^+) found in the trap solution at 5 h was only approximately 4% of the initial amount of NH_4^+ regardless of the test solutions, which was too low to explain the high NH_4^+ conversion under the conditions. The formation of gaseous NO_x was also suspected for the high NH_4^+ conversion. If it occurred, NO_3^- and NO_2^- were detected in the trap solution. However, their amount in the trap solution was only approximately 3% of the initial amount of NH_4^+. Therefore, the escape of NH_4^+ as gaseous NH_3 and the formation of gaseous NO_x had a small effect on the observed high NH_4^+ conversion at pH 12.

Because $NH_{3(aq)}$ was the main ammonia species and a large amount of hydroxyl ions was present in the test solution at pH 12, these species had to be involved in the reaction. There are two possible reactions for the oxidation of $NH_{3(aq)}$ with O_3 in the solution. One is the direct oxidation of $NH_{3(aq)}$ with O_3 (eq. 8), followed by the successive oxidation of NO_2^- to NO_3^- (eq. 9) (Holgne and Bader, 1978).

$$NH_{3(aq)} + 3O_3 \rightarrow NO_2^- + 3O_2 + H^+ + H_2O \quad (8)$$

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \quad (9)$$

The other is the reaction involving hydroxyl radical generated by the reaction of hydroxyl ion with O_3 in an aqueous solution at high pH (eqs. 10 and 11) (Tomiyasu et al., 1985).

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (10)$$

$$O_3 + HO_2^- \rightarrow OH\cdot + O_2^-\cdot + O_2 \quad (11)$$

In this reaction, hydroxyl radical works as an oxidant, and $NH_{3(aq)}$ is converted to NO_3^- through $NH_2\cdot$ as an intermediate (eqs. 12–17) (Buxton et al., 1988, Nakamura et al., 2014).

$$NH_{3(aq)} + OH\cdot \rightarrow NH_2\cdot + H_2O \quad (12)$$

$$4NH_2\cdot + 3O_2 \rightarrow 4HNO + 2H_2O \quad (13)$$

$$2HNO + O_2 \rightarrow 2HNO_2 \quad (14)$$

$$HNO_2 \rightleftarrows H^+ + NO_2^- \quad (15)$$

$$NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O \quad (16)$$

$$NO_2^- + O^* \rightarrow NO_3^- \quad (17)$$

Regardless of the mechanisms, the main product is NO_3^-. In direct oxidation, the reaction of eq. 8 gives H^+. However, the reaction involving hydroxyl radical consumes hydroxyl ion according to eq. 10. Thus, the pH of the solution decreases with the progress of the reaction for both mechanisms. Therefore, the reaction rate of ammonia decomposition is gradually decreased with the progress of the reaction, and eventually the reaction stops if pH is not kept sufficiently high. In this study, the pH of the reaction solution was not controlled during the reaction and decreased to approximately 3 at 5 h. In fact, the reaction rate gradually decreased with an increase in the reaction time (data is not shown), which supports the abovementioned reaction mechanisms.

The NH_4^+ conversion was only slightly higher for the reaction in the presence of both Co^{2+} and Cl^- than those for the other three conditions; however, the difference in the conversion was small. The reaction rates for ammonia decomposition were sufficiently high even without Co^{2+} or Cl^- and with either Co^{2+} or Cl^-. In addition, Co^{2+} formed a precipitate before the reaction (see 2.1). Thus, Co^{2+} and Cl^- in the solution had little effect on the reaction at pH 12 unlike the reactions at 1, 4, and 8, as described later.

pH 1

Compared to the reactions at pH 12, the reactions in eqs. 8, 10, and 12 are unlikely to occur at pH 1 because NH_4^+ is predominant, and only a small amount of hydroxyl ions is present in the test solution. Thus, the reactions, which differ from those at pH 12, can occur at pH 1. As shown in Fig. 3, no reaction occurred at pH 1 without Cl^-. Meanwhile, the decomposition reaction of NH_4^+ proceeded in the test solution with Cl^-, and Co^{2+} enhanced the reaction rate, which suggested the involvement of Co^{2+} and Cl^- in the reaction. The products and reaction mechanism will be discussed in detail in 3.2.

pH 4 and 8

The conversions were very low without Co^{2+} and Cl^-, and with either Co^{2+} or Cl^-. In contrast, the high NH_4^+ conversion (i.e., approximately 50%) was obtained in the presence of both Co^{2+} and Cl^-, which suggested that both Co^{2+} and Cl^- were involved in the reaction, while the increment of the conversion caused by the presence of both Co^{2+} and Cl^- was more significant at pH 4 and 8 than that at pH 1. Detailed reaction mechanism and how Co^{2+} and Cl^- are involved in the reaction will be discussed in the following sections.

Utilization efficiency of O_3 was calculated under the reaction conditions that were in the presence of both Co^{2+} and Cl^- and at pH 4. At 5 h, the consumed amount of NH_4^+ was 5.0 mmol, while the total amount of O_3 flown to the rector was 72.5 mmol, which was determined by a titration method. Therefore, the utilization efficiency of O_3 was calculated to be 6.9% (= 5.0 mmol/72.6 mmol × 100).

3.2. Involvement of Cl^{-} in the reaction

To understand the enhancement effect owing to the presence of both Co^{2+} and Cl^{-}, first, reactions at pH 4 were closely examined. Figure 4 shows the time course changes in the concentrations of NH_4^+, NO_3^- and co-existing anion (Cl^- or SO_4^{2-}) at pH 4 in the presence and absence of Co^{2+} and Cl^-. It is noted that 10 mmol L^{-1} of NO_3^- derived from $Co(NO_3)_2$ was present in the test solution from the start of the reactions with Co^{2+} [Figs. 4B and 4D].

(Fig. 4)

Only a small amount of NH_4^+ was decomposed for the reaction without Co^{2+} and Cl^- (Fig. 4A). For the reaction in the presence of only Co^{2+}, NH_4^+ was decomposed with a decent rate, and NO_3^- was formed for the initial 1 h; however, after some time, the decomposition rate of NH_4^+ became slow (Fig. 4B). For the reaction only with Cl^-, the concentration of NH_4^+ decreased along with that of Cl^-; however, the decomposition rate of NH_4^+ was slow (Fig. 4C). In comparison, the decomposition reaction of NH_4^+ proceeded with a decent reaction rate in the presence of both Co^{2+} and Cl^- (Fig. 4D), as mentioned above, while only a small increase in the concentration of NO_3^- was observed, which indicated that the reactions, which afforded products other than NO_3^-, predominantly proceeded. It is noted that the concentration of Cl^- was decreased with a decrease in the concentration of NH_4^+. This concurrency for the consumption of NH_4^+ and Cl^- indicated the progression of the reaction between the two species, which could produce chloramines (NH_xCl_{3-x}, x = 1–3). The formation of chloramines is reported for the oxidative decomposition of NH_4^+ over Co_3O_4 in the presence of Cl^- (Krisbiantoro et al., 2020). Therefore, it was deduced that only the reaction that formed chloramines proceeded at a decent reaction rate with the help of Co^{2+} at pH 4. Because the consumed amount of Cl^- was almost the same as that of NH_4^+, monochloramine (NH_2Cl) was presumably a predominant product among chloramines.

It is known that hypochlorous acid (HClO) is produced by the oxidation of Cl^- with O_3 in neutral to acidic solution even in the absence of any catalysts (eqs. 18–20) (Levanov et al., 2003).

$$Cl^- + O_3 \rightarrow ClO^- + O_2 \quad (18)$$

$$Cl^- + O_3 + H^+ \rightleftarrows HClO_3 \quad (19)$$

$$HClO_3 \rightarrow HClO + O_2 \quad (20)$$

Because p*K*a of hypochlorous acid is 7.53, HClO is predominant in acidic solution, and the abundance ratio of HClO to ClO^- (=[HClO]/[ClO^-]) is calculated to be 3388 at pH 4.

HClO is a strong oxidant and is known to oxidize NH_4^+ to give NH_2Cl in an acidic solution (eq. 21) (Leung and Valentine, 1994).

$$NH_4^+ + HClO \rightarrow NH_2Cl + H_3O^+ \qquad (21)$$

Because the presence of Co^{2+} considerably accelerated the decomposition rate of NH_4^+ at pH 4 (Fig. 4D), it is plausible that Co^{2+} acted as a homogeneous catalyst for the reaction in eq. 21.

Chloramines are easily decomposed in strong alkaline solution and the rection gives Cl^- as a product (eq. 22).

$$3NH_2Cl + 3OH^- \rightarrow 3Cl^- + NH_3 + N_2 + 3H_2O \qquad (22)$$

The formation of chloramines under the reaction conditions was confirmed by using this reaction as follows. The oxidative decomposition of NH_4^+ was performed in the presence of both Co^{2+} and Cl^-, and at pH 4 with the similar manner to that described in 2.1, but an aqueous KOH solution (0.5 mol L^{-1}) was put in the first and second trap bottles, instead of ultrapure water, to decompose formed chloramines in the traps. The result was that about half amount of Cl^- consumed in the reaction solution was found in the trap solutions, clearly demonstrating the formation of chloramines during the reaction.

Figure 5 shows the time course changes in the concentrations of NH_4^+, NO_3^-, and Cl^- for the reactions in the presence of both Co^{2+} and Cl^- at pH 1 and 12. As mentioned in 3.1, the reaction enhancement caused by the co-presence of Co^{2+} and Cl^- was observed at pH 1 but was not significant at pH 12.

(Fig. 5.)

At pH 1, the concentration of Cl^- decreased with an increase in the reaction time (Fig. 5A), which was similar to the reaction at pH 4. NO_3^- was not formed at pH 1, while the high initial concentration of NO_3^- was due to the addition of nitric acid to the test solution for the pH adjustment. Of note, a decrease in the concentration of Cl^- was much larger than that of NH_4^+. Almost all Cl^- disappeared from the reaction solution at 5 h, at which the NH_4^+ conversion was still approximately 30%. Because the consumed amount of Cl^- was approximately 3 times higher than that of NH_4^+, it was plausible that NCl_3 was the dominant chloramine among three of them at pH 1. It is reported that the disproportionation of NH_2Cl and the successive reaction of NH_2Cl with HClO occur to form $NHCl_2$ in an acidic solution (eqs. 23 and 24) (Valentine et al., 1988, Leung and Valentine, 1994).

$$2NH_2Cl + H^+ \rightarrow NHCl_2 + NH_4^+ \quad (23)$$

$$NH_2Cl + HClO \rightarrow NHCl_2 + H_2O \quad (24)$$

The formed $NHCl_2$ is subjected to the successive reaction with HClO to form NCl_3 in the solution (eq. 25).

$$NHCl_2 + HClO \rightarrow NCl_3 + H_2O \quad (25)$$

According to these reactions, NCl_3 was presumably formed at pH 1. Because HClO was consumed to oxidize NH_2Cl and $NHCl_2$ in addition to NH_4^+ (eqs. 24 and 25), and the disproportionation of NH_2Cl occurred to give NH_4^+, the decomposition rate of NH_4^+ at pH 1 was slower than that at pH 4.

Compared to the reactions at pH 1, 4, and 8, NO_3^- was formed at pH 12 (Fig. 5B), while a decrease in the concentration of Cl^- was small. The selectivity to NO_3^- at 5 h was approximately 50%, which suggested that half of NH_4^+, which was present as $NH_{3(aq)}$ in the solution, was decomposed into products other than NO_3^- and chloramines. Thus, such products could be gaseous nitrogen compounds including N_2 and N_2O.

3.3. Suppression of precipitate formation by Cl^-

In some case for the preparation of the test solution and for the oxidative decomposition of NH_4^+ with O_3, a precipitate was formed in the middle of the operations. Judging from the color of the precipitate and from the change in color of the solution with the precipitate (Fig. 6), the precipitate was considered to contain cobalt ion, which was eventually confirmed by the XAFS analysis (described in 3.4). The precipitate formation occurred under two operation conditions. The first one is that the precipitate was formed during the pH adjustment of the test solution to pH 12 by the addition of an aqueous NaOH solution. This is not special because Co^{2+} forms a $Co(OH)_2$ precipitate in alkaline solution.

(Fig. 6)

The other condition was that precipitation occurred during the decomposition reaction of NH_4^+ without Cl^- at pH 4 and 8. Figure 7 shows the time course changes in the concentration of Co^{2+} dissolved in the reaction solution during the oxidative decomposition of NH_4^+ with O_3 in the presence and absence of Cl^- at pH 1, 4, 8, and 12, where the concentration of Co^{2+} in the solution was measured by ICP-OES. The concentration of Co^{2+} was gradually decreased with an increase in the reaction time for the reaction without Cl^- at pH 4 and 8, and the decrease was faster for pH 8 than for pH 4, while the concentration of Co^{2+} dissolved in the solution was constant at pH 1 (Fig. 7A). In contrast, no precipitation occurred even at pH 4 and 8 with Cl^- (Fig. 7B). These results indicated that Cl^- was essential for the suppression of the precipitate formation, which will be discussed later in 3.5. Therefore, Co^{2+} was stably present in the reaction solution, and all Co^{2+} added to the solution acted as a homogeneous catalyst, which resulted in the high NH_4^+ conversion of the reactions at pH 4 and 8 with Cl^-.

(Fig. 7)

3.4. Chemical state of cobalt species in solution and precipitate

To understand the reaction mechanism, first, it was necessary to understand what the precipitate was. Thus, the Co-K edge XANES spectrum of the precipitate, which was obtained by the reaction at pH 4 without Cl^{-}, was measured. Figure 8 shows the XANES spectrum of the precipitate and those of commercially available Co_3O_4, CoO(OH), and $Co(OH)_2$ as references.

(Fig. 8)

The precipitate showed strong X-ray absorption at approximately 7730 eV, which corresponded to the Co-K edge and demonstrated that the precipitate contained cobalt. $Co(OH)_2$ and CoO(OH) have divalent and trivalent cobalt ions, respectively; Co_3O_4 is composed of Co^{2+} and Co^{3+} at the ratio of 1:2. The spectrum of the precipitate was fitted by the linear combination of the spectrum of CoO(OH) and that of $Co(OH)_2$ with 95:5, which indicated that almost all cobalt species in the precipitate were Co^{3+}. The simulated spectrum is shown in Fig. 8.

The EXAFS spectra of the precipitate and CoO(OH) are shown in Fig. 9. The two oscillations showed a reasonable agreement, which allowed to identify them as being the same compound.

(Fig. 9)

According to a previous study (Ichikawa et al., 2014), Co_3O_4 acts as a highly active heterogeneous catalyst for the oxidative decomposition of NH_4^+ with O_3; however, CoO(OH) is not. Thus, only low decomposition rate of NH_4^+ was obtained when the precipitate was formed during the reaction.

Next, the cobalt species dissolved in the reaction solution were examined by the in situ XAFS measurement. Figure 10 shows the XANES spectra of the reaction solution before (0 h) and after O_3/O_2 blowing for 1.5 h. The XANES spectrum of an aqueous solution of $Co(NO_3)_2$ as well as solid $CoCl_2$ and CoO(OH) are shown in Fig. 10. Based on the position of the absorption edge, Co^{2+} was predominant in the reaction solution before O_3/O_2 blowing. In that spectrum, a small pre-edge peak and a shoulder peak were observed at 7707 eV and 7716 eV, respectively, both of which were absent in the XANES spectrum of an aqueous solution of $Co(NO_3)_2$.

(Fig. 10)

In addition, the EXAFS spectrum of the reaction solution before O_3/O_2 blowing was not completely consistent with that of the aqueous solution of $Co(NO_3)_2$ (Fig. 11). In the solution at pH 4, NH_4^+ is present, but normally does not coordinate with Co^{2+}. Thus, it was presumable that Co^{2+} in the reaction solution formed a complex with the co-existing anion (Cl^- or SO_4^{2-}). Because the XANES and EXAFS spectra of an aqueous solution of $Co(NO_3)_2$ with SO_4^{2-} were basically the same as those without SO_4^{2-}, it is reasonable to consider that Co^{2+} did not form a complex with SO_4^{2-}. The EXAFS spectrum of the reaction solution was similar to that of solid $CoCl_2$, especially in the region of small wavenumber, which indicated that the first coordination sphere of Co^{2+} in the reaction solution was similar to that in $CoCl_2$. Therefore, the Co–Cl complex can be formed in the reaction solution. Of note, there are no changes in the XANES and EXAFS spectra even after the O_3/O_2 blowing, which indicates that such Co–Cl complex was stable under the reaction conditions.

(Fig. 11)

3.5. Catalysis of Co^{2+} involving Cl^-

Here, the catalysis of Co^{2+} involving Cl^- will be discussed using the reaction at pH 4 as an example. The reaction mechanisms in the absence and presence of Cl^- are proposed in Fig. 12.

(Fig. 12)

To understand the catalysis of Co^{2+} involving Cl^-, first, the reaction that occurs in the absence of Cl^- is considered. What is important is the formation of the precipitate

[CoO(OH)] (Fig. 6), which did not work as a heterogeneous catalyst for the oxidative decomposition of NH_4^+ with O_3. As described in the Introduction, the reaction of Co^{2+} with O_3 produces $Co(OH)^{2+}$ and OH· in an aqueous solution (eq. 1). Thus, the precipitate can be formed from $Co(OH)^{2+}$ by the reaction with H_2O, as shown in eq. 26 and Fig. 12(a).

$$Co(OH)^{2+} + 3H_2O \rightarrow CoO(OH)\downarrow + 2H_3O^+ \qquad (26)$$

Figure 4B shows that the concentration of NH_4^+ decreased just after the reaction started (<1 h) even in the absence of Cl^-; this suggested that OH·, which was generated with the formation of $Co(OH)^{2+}$, could decompose NH_4^+. However, because the pH of the reaction solution decreased from pH 4 with the progress of the reaction, the decomposition of NH_4^+ almost stopped, which is similar to the reaction at pH 1.

In stark contrast to the reaction in the absence of Cl^-, precipitate was not formed when Cl^- was present in the reaction solution [Fig. 7B]. Figures 10 and 11 show that the predominant cobalt species present in the reaction solution was Co^{2+} in the presence of Cl^- under the reaction conditions with O_3. These results indicated that the Co^{3+}, [$Co(OH)^{2+}$], was promptly reduced to Co^{2+}, and Cl^- was involved in this step. In addition, because the decomposition of NH_4^+ to form chloramines was significantly promoted by the presence of Co^{2+}, it was considered that Co^{2+} accelerated the formation of HClO. Thus, we propose the reaction mechanism for the catalysis of Co^{2+} involving Cl^{-}, as shown in Fig. 12(b). The first step (i.e., the oxidation of Co^{2+} with O_3) is the same as that in the absence of Cl^{-}; however, the formed $Co(OH)^{2+}$ is promptly reduced with Cl^{-} to regenerate Co^{2+}. At the same time, HClO is formed by the reaction and reacts with NH_4^+ to afford chloramine. Thus, Co^{2+}, which is added to the reaction solution, catalyzes the formation of HClO from O_3 and Cl^{-} through a redox between Co^{2+} and Co^{3+}. Therefore, the oxidative decomposition of NH_4^+ with O_3 was significantly accelerated by the presence of both Co^{2+} and Cl^{-}.

According to the abovementioned reaction mechanism, NH_4^+ is decomposed into chloramines by the reaction with HClO, which is generated in situ by the reaction of Cl^{-} with O_3 catalyzed by Co^{2+}. While the reaction decomposing NH_4^+ to chloramines is basically the same as that occurring in a commonly used breakpoint chlorination, the oxidative decomposition of NH_4^+ with O_3 in the presence of both Co^{2+} and Cl^{-} has a considerable advantage of the absence of generation of secondary waste compared to breakpoint chlorination, which generates it from the excess use of hypochlorous acid. Therefore, we believe that the oxidative decomposition of NH_4^+ with O_3 in the presence of both Co^{2+} and Cl^{-} is practically preferable for the treatment of aqueous liquid waste containing nuclear materials.

4. Conclusions

The oxidative decomposition of NH_4^+ with O_3 in the presence of Co^{2+} was performed in a wide pH range of the test solution, and in the presence and absence of $Cl^−$. The reaction behavior was greatly affected by the pH of the test solution. At pH 12, the high conversion of NH_4^+ was obtained even in the absence of Co^{2+} and $Cl^−$, and the main product was $NO_3^−$ regardless of the reaction conditions. Both Co^{2+} and $Cl^−$ in the solution had only small effect on the reaction. In contrast, Co^{2+} and $Cl^−$ were involved in the reaction under acidic to mild basic solutions (pH 1~8), and the decomposition rate of NH_4^+ was significantly enhanced when both of them were present in the solution, while only low conversion of NH_4^+ was observed unless both Co^{2+} and $Cl^−$ were present. In the reaction solution with Co^{2+} and $Cl^−$, NH_4^+ was mainly decomposed into chloramines by the reaction with HClO, which was formed by the reaction of $Cl^−$ with O_3 with the help of the homogeneous Co^{2+} catalyst, which led to the high decomposition rate of NH_4^+. $Cl^−$ suppressed the formation of the precipitate CoO(OH). Thus, the homogeneous Co^{2+} catalyst stably existed in the reaction solution at pH 4 and 8, which was another reason for the high decomposition rate of NH_4^+ in the presence of Co^{2+} and $Cl^−$. Because NH_4^+ in the solution was swiftly decomposed by the reaction with O_3 in the presence of Co^{2+}

and Cl^- under mild reaction conditions and only a small amount of secondary waste was generated, we believe that this process is suitable and applicable for the treatment of aqueous liquid waste generated through analysis that contains ammonium salts and nitric acid.

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Table 1

pH and composition of the test solutions[a]

Run No.	pH[b]	Ammonium salt	Co^{2+} (mmol L^{-1})
1	1	NH_4Cl	4.5
2	4		
3	8		
4	12		
5	1	$(NH_4)_2SO_4$	4.5
6	4		
7	8		
8	12		
9	1	NH_4Cl	0
10	4		
11	8		
12	12		
13	1	$(NH_4)_2SO_4$	0
14	4		
15	8		
16	12		

[a]The concentration of NH_4^+ was 50 mmol L^{-1} for all test solutions.

[b]The pH of the test solution was adjusted by the addition of nitric acid or an aqueous NaOH solution.

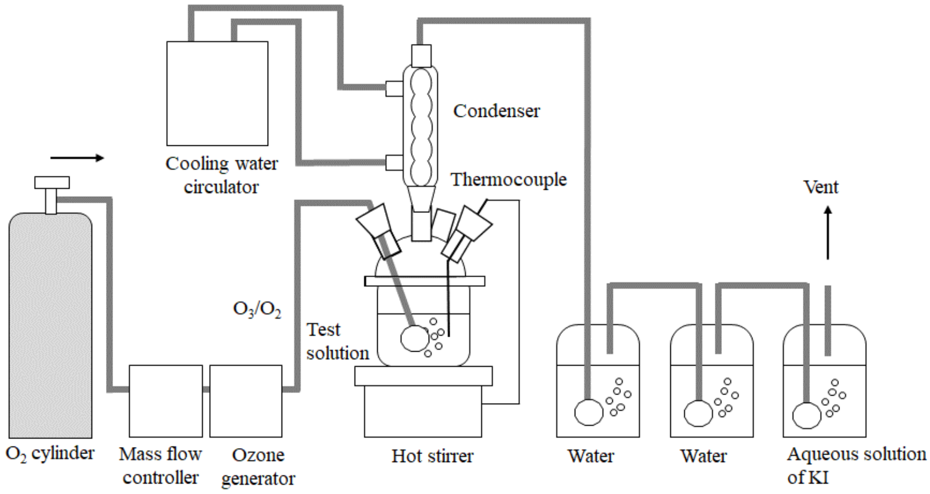


Fig. 1. Reaction apparatus for the oxidative decomposition of NH_4^+ with O_3 in water.

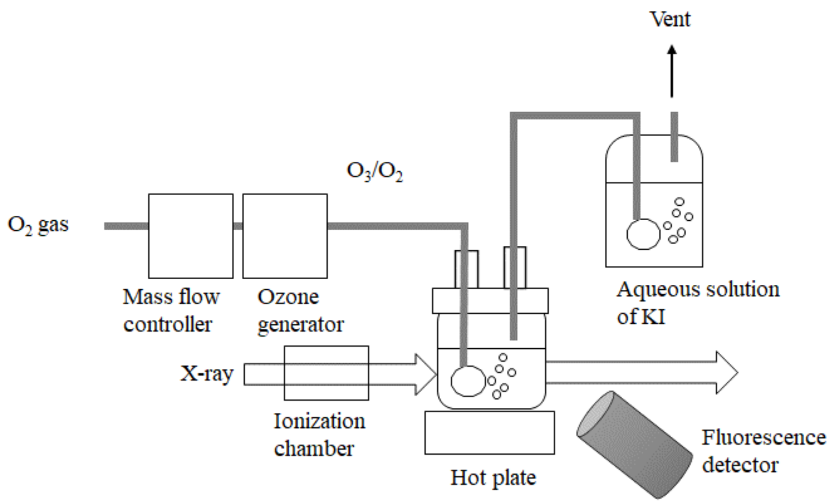


Fig. 2. Apparatus for the in situ XAFS measurement.

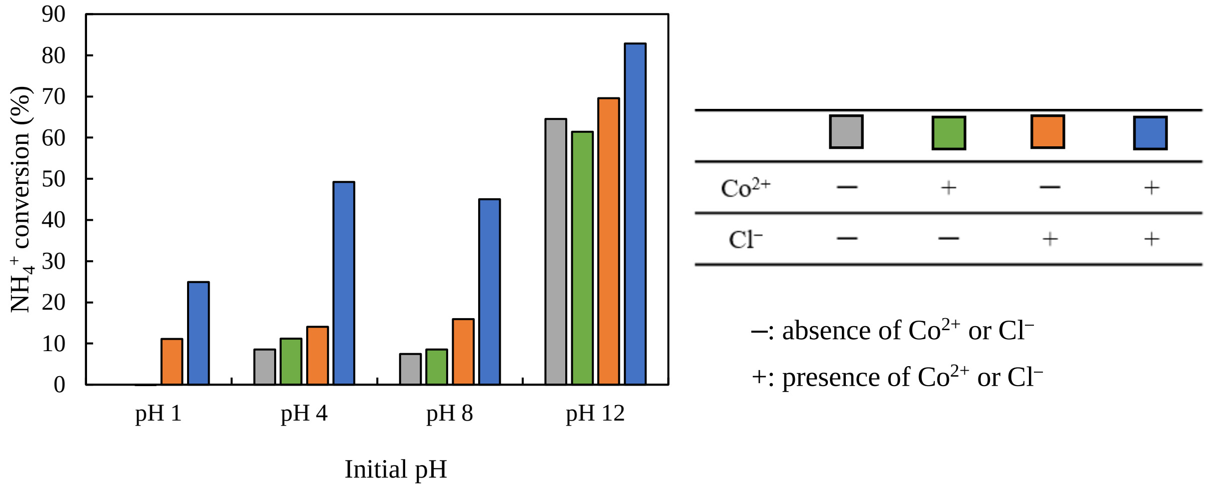
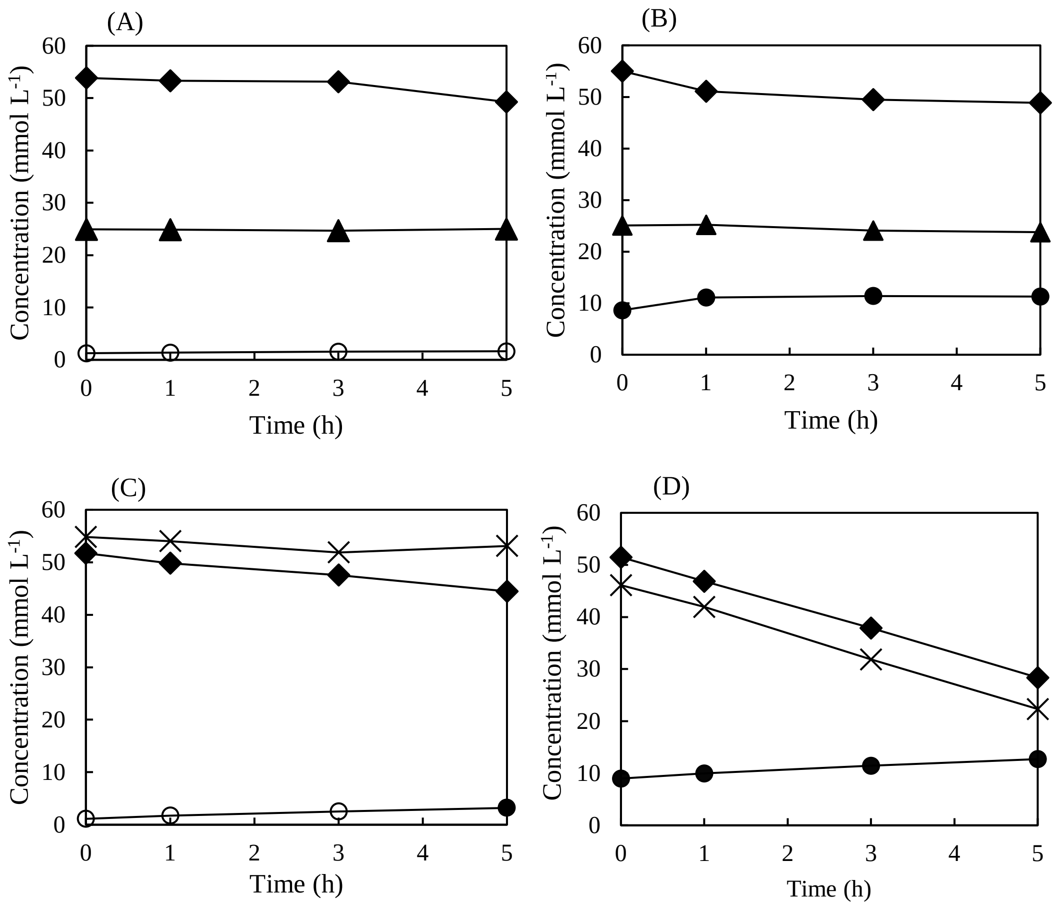


Fig. 3. NH_4^+ conversion at 5 h for the oxidative decomposition of NH_4^+ with O_3 under different conditions.



	(A)	(B)	(C)	(D)
Co^{2+}	–	+	–	+
Cl^{-}	–	–	+	+

Fig. 4. Time course changes in the concentrations of (◆) NH_4^+, (●) NO_3^-, (×) Cl^-, and (▲) SO_4^{2-} for the oxidative decomposition of NH_4^+ with O_3 in the solutions at pH 4. Open symbol in Figs. 4A and D means the value below the lower limit of determination for NO_3^-. Conditions of the test solutions are specified in the table.

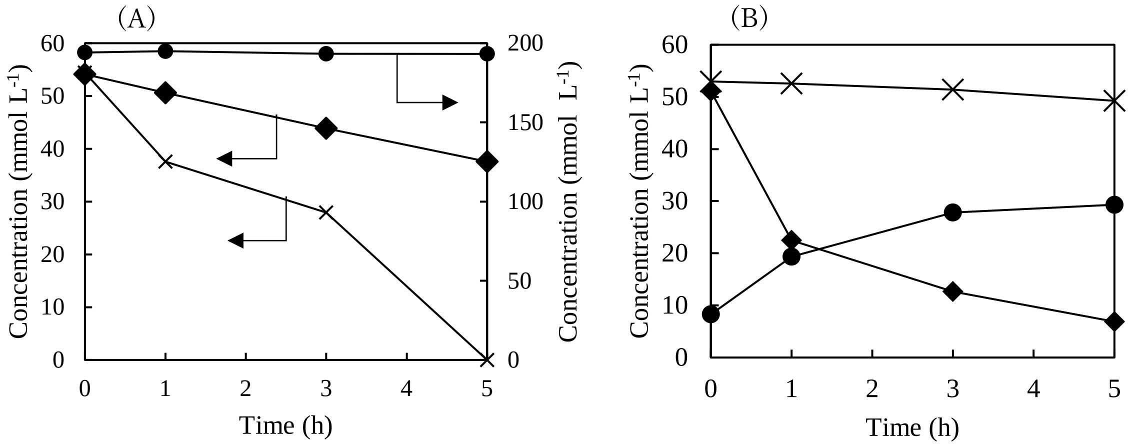


Fig. 5. Time course changes in the concentrations of (◆) NH_4^+, (●) NO_3^-, and (×) Cl^- for the oxidative decomposition of NH_4^+ with O_3 in the presence of both Co^{2+} and Cl^- at (A) pH 1 and (B) pH 12.

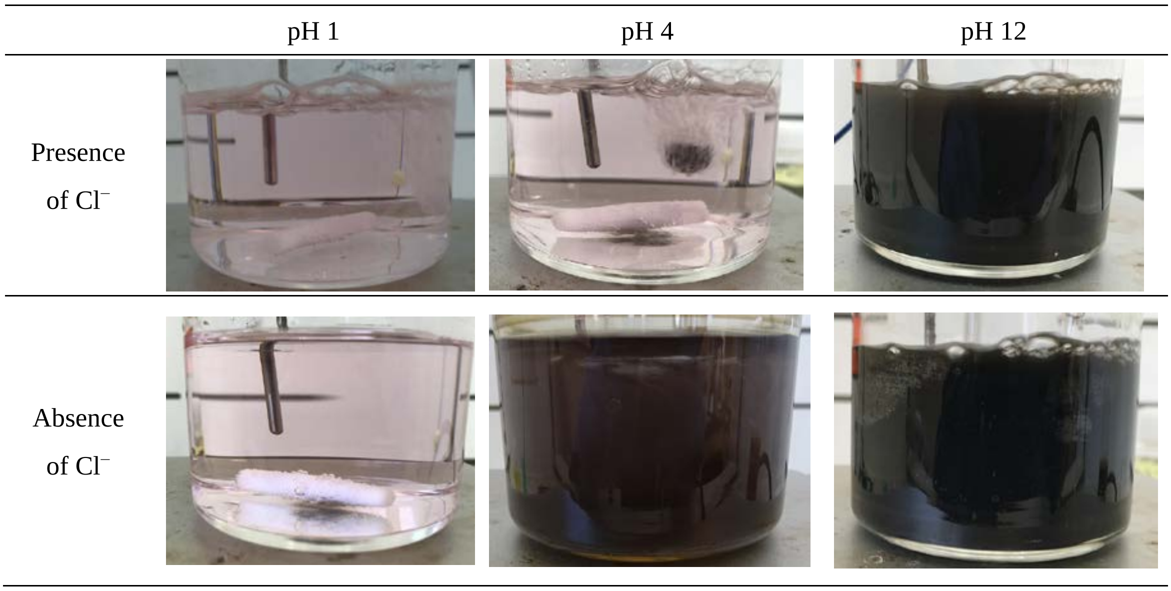


Fig. 6. Appearances of test solutions in the presence or absence of Cl^- at different pH after 5 h of the reaction.

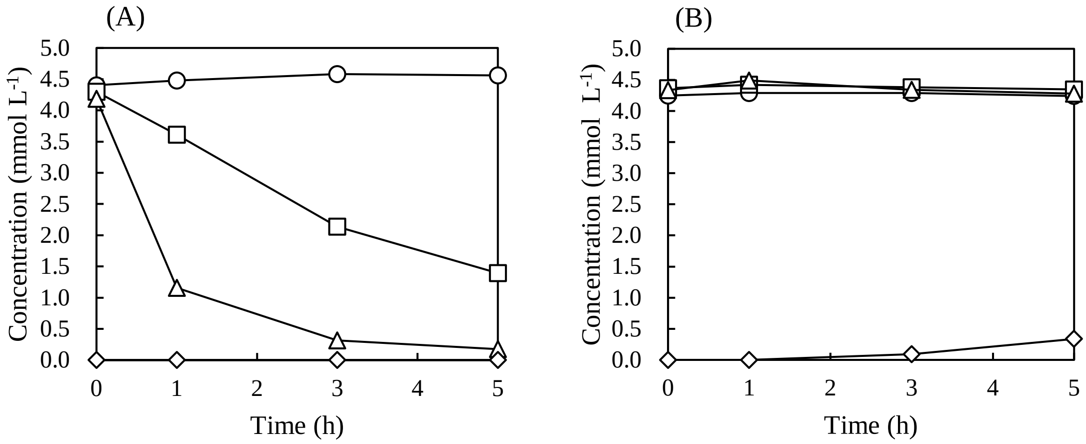


Fig. 7. Time course changes in the concentrations of Co^{2+} in the solution for the oxidative decomposition of NH_4^+ with O_3. (A) Absence of Cl^- (ammonium sulfate) and (B) presence of Cl^- (ammonium chloride). (○) pH 1, (□) pH 4, (△) pH 8, and (◇) pH 12.

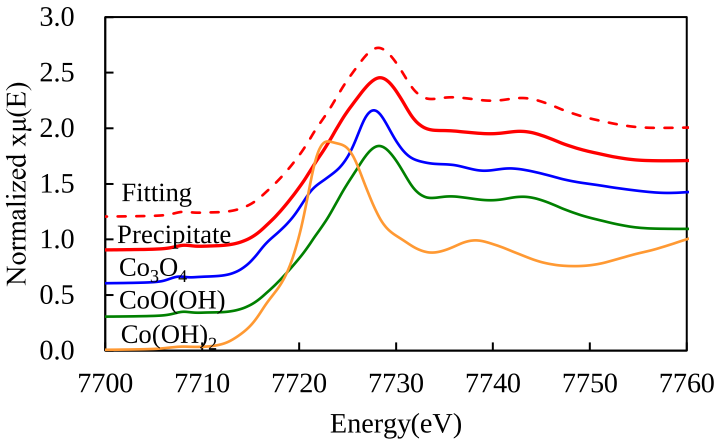


Fig. 8. XANES spectra of the precipitate and reference samples. Dashed line is the spectrum obtained by the linear combination of the spectrum of CoO(OH) (95%) with that of $Co(OH)_2$ (5%).

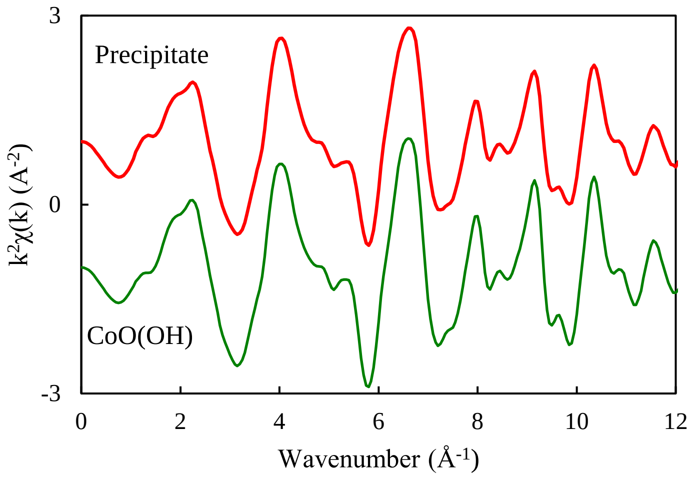


Fig. 9. EXAFS spectra of the precipitate and CoO(OH).

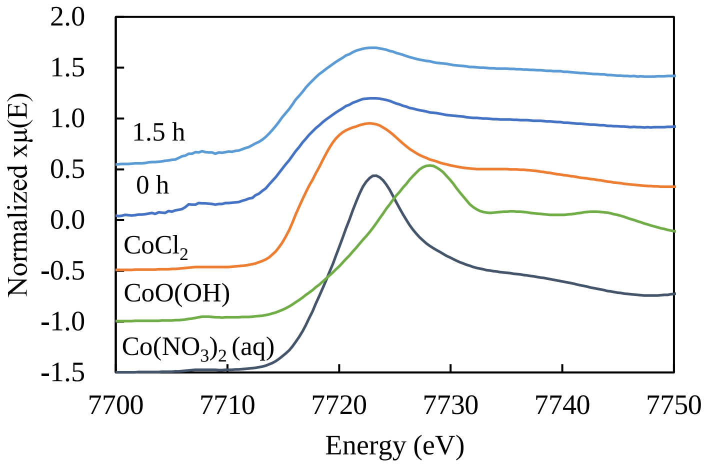


Fig. 10. XANES spectra of the solution before (0 h) and after the O_3/O_2 blowing (1.5 h), and reference samples.

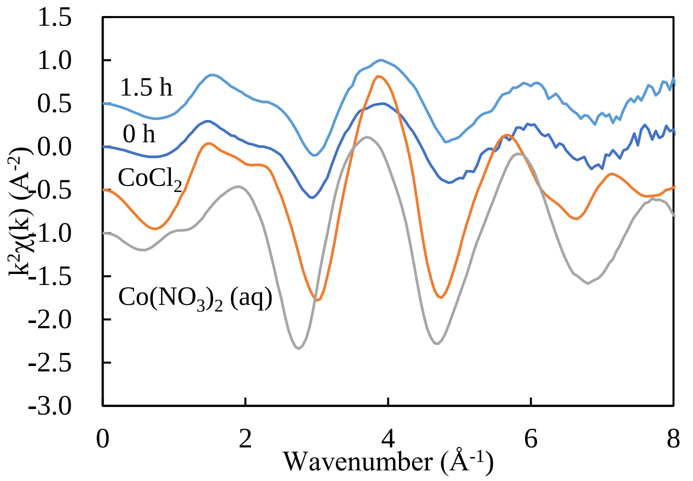
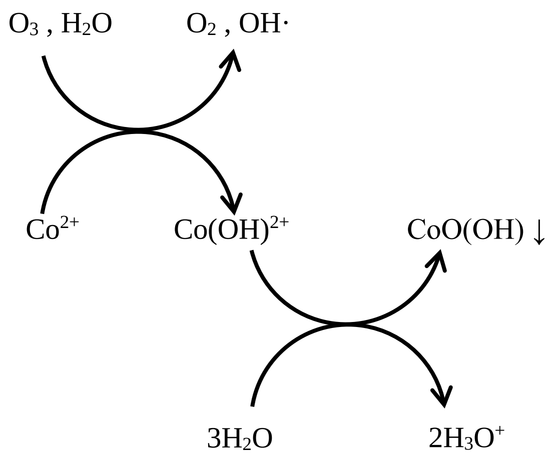


Fig. 11. EXAFS spectra of the solutions before (0 h) and after the O_3/O_2 blowing (1.5 h) and the reference samples.

(a)



(b)

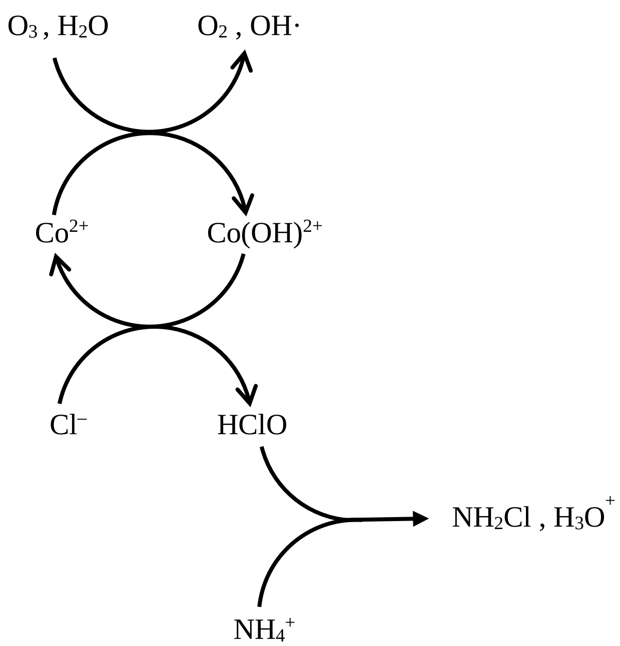


Fig. 12. Proposed reaction mechanisms for the reactions at pH 4 (a) in the absence and (b) presence of Cl^-.