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Cobalt Oxide (Co_3O_4) as an Active and Selective Catalyst for Catalytic Ozonation of Ammonia Nitrogen in Water

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Contents

Chapter 1	**General Introduction**	**1**
1.1	Ammonia pollution problem in water	2
1.2	Established and known methods for removal of ammonia nitrogen	4
1.3	Catalytic ozonation	6
1.4	Deactivation of Catalyst	9
1.5	Reaction mechanism of ozonation	12
1.6	Scope of this thesis	14
	References	17
Chapter 2	**Survey of active and selective metal oxide catalyst for catalytic ozonation of ammonium ion in water**	**21**
2.1	Introduction	22
2.2	Experimental	23
	2.2.1 Preparation of catalysts	23
	2.2.2 Catalytic ozonation of NH_4^+ in water	25
	2.2.3 Characterization	26
2.3	Results and Discussion	28
	2.3.1 Physical properties of metal oxide catalysts	28
	2.3.2 Catalytic performances of metal oxide catalysts	32
2.4	Conclusion	39
	References	40
Chapter 3	**Reaction mechanism of catalytic ozonation of ammonium ion in water**	**41**
3.1	Introduction	42
3.2	Experimental	44
	3.2.1 Catalysts and reagents	44
	3.2.2 Catalytic ozonation of NH_4^+ in the absence and presence of Cl^-	44

3.2.3 Catalytic oxidation of Cl^- with ozone in water 44

3.2.4 Catalytic reaction of NH_4^+ with ClO_x^- 45

3.3 Results and Discussion 45

3.3.1 Role of Cl^- in the catalytic ozonation over Co_3O_4 45

3.3.2 Formation of ClO_x^- by oxidation of Cl^- with O_3 in the absence and presence of Co_3O_4 and catalytic cycle for NH_4^+ ozonation over Co_3O_4 50

3.3.3 Reason for high activity of Co_3O_4 56

3.3.4 Catalyst properties controlling selectivity 59

3.4 Conclusion 62

References 63

Chapter 4 Enhancement of catalytic activity of cobalt oxide for catalytic ozonation of ammonium ion in water with repeated use **65**

4.1 Introduction 66

4.2 Experimental 67

4.2.1 Catalysts 67

4.2.2 Repeated use of catalyst for catalytic ozonation of NH_4^+ in water 67

4.2.3 Pretretment of Co_3O_4 prior to catalytic ozonation of NH_4^+ 69

4.2.4 Characterizations 69

4.3 Results and Discussion 70

4.3.1 Changes in catalytic performance by repeated use 70

4.3.2 Changes in physical properties of Co_3O_4 by repeated use 73

4.3.3 Influence of pretreatment of Co_3O_4 for catalytic performance in catalytic ozonation of NH_4^+ 75

4.4 Conclusion 82

References 83

Chapter 5 Summary and General Conclusions **85**

Chapter 1

General Introduction

1.1 Ammonia pollution problem in water

Water is the most widespread substance to be found in the natural environment and it plays vital roles in both environment and human lives. Since more than 97% water on the earth is sea water, fresh water is only 3%. About 0.3% of fresh water is held in rivers, lakes, and reservoirs, while the rest is stored in glaciers, permanent snow and groundwater aquifers [1].

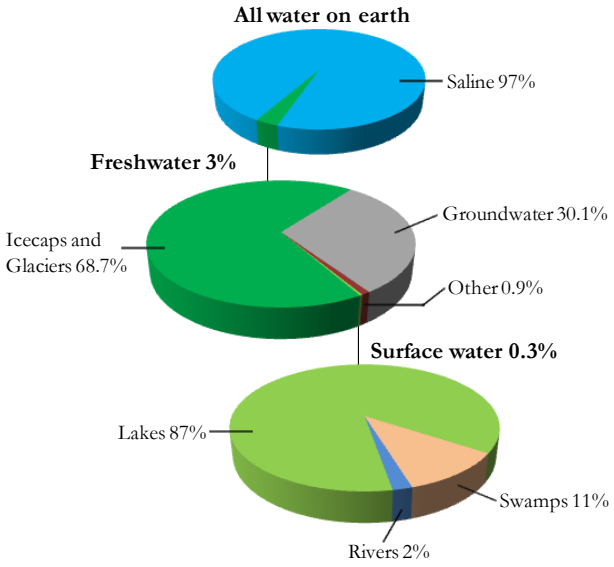

Fig. 1-1 Distribution of water on the earth [1]

Usage of water is different from one region to others. In industrial countries, most of the water is used for manufacturing products, while in developing countries most of the water is used for agricultural activity. Demand of fresh water is becoming a global great concern since the amount of wastewater increases rapidly with the increase of industrialization and population growth. One of the pollutants generated from disposal of industrial wastewater, household sewage discharge, excess fertilization and inappropriate disposal of livestock excreta is ammonia (NH_3) and ammonium ion (NH_4^+). Hereafter

those are called ammonia nitrogen. Ammonia nitrogen can cause eutrophication and is toxic to fish and aquatic organisms [2, 3] in addition to the offensive smell and potential carcinogenesis [4]. Furthermore, growth of algae and bacteria population in drinking water will rise caused by ammonia nitrogen [5].

Ammonia nitrogen is an ordinarily occurring compound originated from metabolic, agricultural and industrial processes and disinfection with chloramines [6, 7]. Ammonia nitrogen is rarely found in unpolluted surface or well water, but the water contaminated with sewage, animal waste and fertilizer runoff may contain an elevated level of it. Thus, the environmental limits for ammonia in surface water have been set in USA ranging from 0.25 to 32.5 mg L^{-1} (ppm). The National Academy of Science and many Europeans nations recommend 0.5 mg L^{-1} (ppm) of concentration of ammonia nitrogen in drinking water [7]. In Indonesia, the limit for ammonia nitrogen in drinking water is set to be 1.5 mg L^{-1} (ppm) [8]. Japan does not have any regulations for ammonia nitrogen in drinking water and in groundwater, while 100 mg L^{-1} (ppm) is the limit for ammonia nitrogen in wastewater [9]. In Japan, there was the regulation for drinking water about 20 years ago. In addition, for aesthetic considerations and equipment maintenance due to its corrosive potential for copper pipes and fittings, the allowable limit for ammonia nitrogen in tap water is recommendation to be 1.5 and 0.5 mg L^{-1} by WHO, and the EU and Australia, respectively [10]. Thus, it is absolutely necessary to treat the wastewater containing ammonia nitrogen by advanced technologies being able to decompose it into harmless compounds like gaseous N_2.

1.2 Established and known methods for removal of ammonia nitrogen

There are some established methods such as biological treatment, ammonia striping, and non-catalytic and catalytic oxidation for removal of ammonia nitrogen in wastewater to meet with the quality criteria.

From an environmental and economic stand point, biological treatment is the most common method for removing low concentration of ammonia nitrogen from wastewater. In the biological treatment, two steps are necessary to convert ammonia nitrogen toward gaseous N_2: oxidation via nitrite (nitrification) and then reduction (denitrification) [11, 12]. Recently some new methods for ammonia oxidation by applying biological treatment, such as partial nitrification, SHARON, Canon and NO_x removal have been developed [13]. Partial nitrification and NO_x removal process can convert ammonia nitrogen into N_2 completely. However, biological treatments have some severe disadvantages. Bacteria used in the processes are very sensitive for environment and cannot withstand wide range of pH and temperature, halogen compounds, cyanides, and other heavy metals present in water [14]. In addition, the biological activities for the nitrification sometimes go silent, when high concentration ammonia nitrogen comes from wastewater [15]. High oxygen demand and energy consumption, huge space requirement and high sludge production are other problems that have been encountered in the biological treatment for removing ammonia nitrogen [16].

Commercially available method for high concentration ammonia nitrogen in wastewater is a stripping. The ammonia stripping has already been established for industrial application to wastewater containing ammonia nitrogen of more than 1000 mg L^{-1}. In this process, addition of lime is needed to convert most of ammonia

nitrogen from ionic NH_4^+ to molecular NH_3 that can be stripped from water into the air [17, 18]. The excess lime causes problems of calcium carbonate scaling and as a result, it decreases the removal efficiency, and rise maintenance frequency and cost [18]. The ammonia stripping has economical advantages, but this method only remove ammonia nitrogen, but does not decompose it [19]. Thus, it causes additional air pollution problems occurred as a result of this process [20], unless the stripped ammonia is adequately treated.

Wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) have been applied for medium concentration organic pollutants in wastewater that contains toxic compounds and thus, are refractory for the biological treatment [21]. Wet air oxidation was first patented over 50 years ago. In this process, organic compounds in liquid phase are decomposed by oxidizing them completely into carbon dioxide and water using an oxidant like O_2 or air. Advantage of WAO/CWAO is the clean process, since no harmful chemical compound is used. If complete oxidation is achieved, the final products are only carbon dioxide and water.

The application of WAO for ammonia nitrogen has been succeeded with a good efficiency, but most studies conclude that a catalyst is necessary for the reaction [22]. When catalytic oxidation is applied for decomposition of nitro and halo aromatic compound, it appears that ammonium ion (NH_4^+) is a by-product of particularly refractory nitrogen containing compound [23]. In 1977, a patent by Okada et al. claimed that the use of transition and noble metals, such as iridium, platinum, gold, palladium, rhodium, iron, nickel, tungsten, copper and cobalt, gave catalytic activity for ammonia oxidation at 265 °C and 70 bar in water when they are supported on alumina [24]. This

reaction over the noble metals supported on TiO_2 was once again carried out by Taguchi and Okuhara [25].

Catalytic wet air oxidation has a good potential for the decomposition of organic and inorganic matters in water. Nevertheless, this process needs high temperature (≥ 200 °C) and high pressure (70 – 250 atm) to high decomposition rate within reasonable reaction time [26, 27] due to the low oxidizing power of O_2 even if catalyst are used. In addition, complex formation with catalysts and formation of the toxic intermediates under the reaction conditions are other problems [24].

1.3 Catalytic ozonation

At present, advanced oxidation processes (AOPs) gain increasing interests and encourage of researchers to investigate their applicability to remove recalcitrant organic pollutants from drinking water. AOPs are defined as *those technologies which involve the generation of hydroxyl radicals ($OH^{\bullet}$) in sufficient quantity to effect water purification via the oxidation of organic solutes* [28, 29]. These processes (e.g., cavitation, photocatalytic oxidation, Fenton's chemistry, ozonation) have been applied successfully for the removal or degradation of recalcitrant pollutants, or used as pretreatment to convert pollutants into shorter-chain compounds that then can be treated by conventional or biological method [28, 29].

Ozone is one of the most powerful oxidizing agents easily available. Oxidizing power of ozone is stronger than those of molecular oxygen and hydrogen peroxide, and ozone is able to react with most substances even at room temperature [30]. Water treatment with ozone improves taste and color along with removing the organic and inorganic

compounds in water [31]. Due to the strong oxidizing power (under acidic conditions $E(O_3/O_2)$ = 2.07 V), it is effective for mineralization of refractory organic compounds [32], but reaction rate for some organic compounds such as inactivated aromatic is slow. Moreover, in many cases, it does not lead to the complete oxidation of organic compounds like natural organic matter [31].

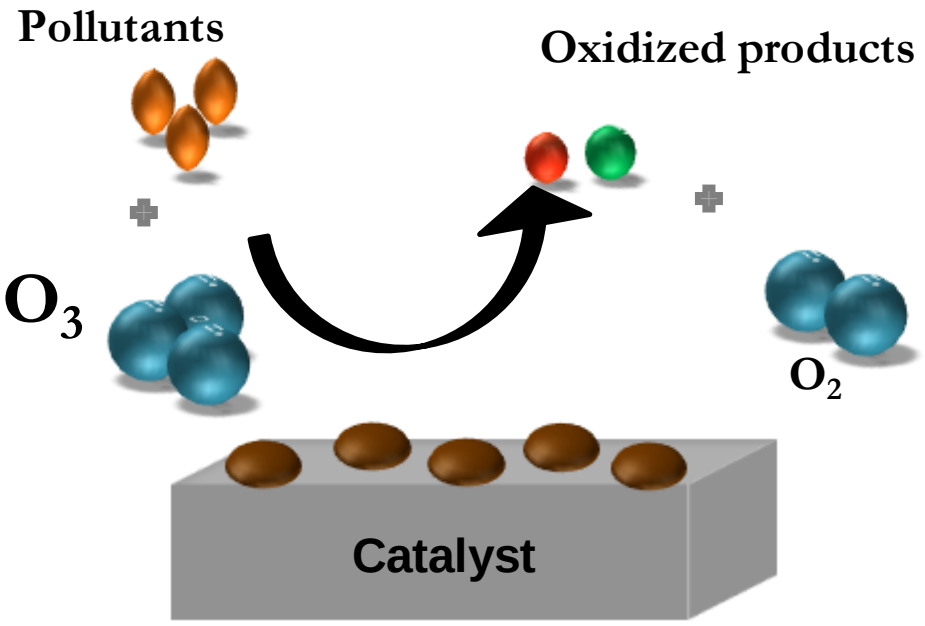

Fig. 1.2 Schematic illustration of catalytic ozonation

Ozonation of ammonia nitrogen in wastewater was first reported in 1970s'. Singer and Zilli have shown that ozonation can be used for oxidation of NH_3 that contained in wastewater to nitrate (eq. 1.1) [33, 34]. In an aqueous phase, the reactivity of NH_3 with ozone changes depends on pH of the solution. At low pH conditions, ammonia nitrogen in the form of electrophilic NH_4^+ is unreactive. In the pH ranging from 7 to 9, ammonia nitrogen is present as free NH_3 and the reaction slowly proceeds to form NO_3^- [34]. In alkaline pH (> 9) much amount of hydroxyl ion (OH^-) exists in water and thus

decomposition of ozone produces HO• radical by the reaction with OH^-. As a result, high decomposition rate of NH_3 is obtained [35].

$$4O_3 + NH_3 \rightarrow H^+ + NO_3^- + H_2O + 4O_2 \qquad (1.1)$$

Non-catalytic ozonation meaning the reaction without any catalysts is a promising way for wastewater treatment. However, in many cases not all pollutants can be completely mineralized in the absence of the catalyst. Therefore, catalyst offers the ability to improve the efficiency of ozonation. Catalytic ozonation, that is the ozonation in the presence of catalysts, has gained a lot of attention again, due to its advantages such as ordinary temperature and pressure, highly effectiveness for organic pollutant degradation, powerful in mineralization of persistent organic pollutants in water and negligible negative effects on water quality.

Catalytic ozonation for water quality improvement is classified into homogeneous and heterogeneous catalysis. In a homogeneous catalysis, catalyst materials were dissolved in water usually as ions. Some transition metals have shown improved reaction rates in the ozonation process. Hewes and Davinson studied that Fe(II), Mn(II), Ni(II) and Co(II) sulfates in solution increase the removal rate of Total Organic Carbon (TOC), comparing to ozonation alone in the absence of the catalyst [36]. Humic substances were also reduced quickly by applying transition metal ion as a catalyst for catalytic ozonation [37]. For catalytic ammonia ozonation, Haag, *et al.* applied bromide as a catalyst in which ammonia was more rapidly oxidized than in the absence of bromide. In this reaction, bromide was oxidized with ozone to HOBr, then NH_2Br was produced by the

reaction with NH_3. Reaction of NH_2Br with ozone gives NO_3^- [38]. The role of bromide as a catalyst in ozonation of ammonia was also studied using microbubbles [20]. This study reported that ammonia was oxidized effectively at high pH and high ozone generation rates and ozonation was occurred by direct reaction of ozone and ammonia at the higher pH. It also showed that hydroxyl radicals were involved in the reaction at the lower pH.

In a heterogeneous catalysis, catalytic effects appear if any of following three processes occurs: ozone adsorbs on the catalyst surface (oxidant activation), substance molecules adsorb on the catalyst surface (reactant activation), or both ozone and substance molecule adsorb on the catalyst surface [39]. It is known that first hydroxyl radicals are formed by decomposition of ozone and the formed radical species make pollutants degraded promptly and effectively. Table 1.1 summarizes some of catalytic ozonation of organic compounds in water. Metal oxides [28, 40, 41, 42, 43, 44, 45], metal supported on oxides [46, 47, 48], mineral [49, 50, 51] and activated carbon [52, 53, 54] have been extensively studied as a catalyst for catalytic ozonation so far.

1.4 Deactivation of Catalyst

In heterogeneous catalyst systems, catalysts must have not only high activity and high selectivity but also good stability and durability. However deactivation of catalyst is often inevitable. Main causes of the catalyst deactivation are poisoning, fouling, thermal degradation (sintering, evaporation) initiated by the often high temperature, mechanical damage, and corrosion/leaching in the reaction mixture [55]. Leaching is a most common cause for the catalyst deactivation in a liquid phase reaction. When the leaching happens,

catalyst loses some of the active components on the catalyst due to dissolution of catalyst during the reaction.

From practical point of view, it is essential to examine catalytic performance of the spent catalyst to establish whether the catalyst is reusable or not, and whether regeneration is possible or not. If the spent catalyst still has good performance, meaning high stability and durability, it is quite beneficial for practical application. For almost all catalysts, their performances are decreased with the use of prolonged reaction time for a flow-type reactor and with the repeated use for a batch-type reactor. Nevertheless, some catalysts show maintained high performances after being used for long period [45, 53, 56]. If the catalytic performance increases with a prolonged reaction time or repeated use, the catalysts would be extremely beneficial and also scientifically interesting. However, catalysts with such properties are very rare [46, 50].

Table 1.1 Some examples for catalytic ozonation of organic compounds

Catalyst	Organic Compound	Reaction Conditions	Remarks	Ref No.
TiO_2	Oxalic acid	Oxalic acid, 8 mM, cat. 1-5 g, 10-40°C, 180 min	Catalyst significantly enhanced the decomposition rate of oxalic acid compared to that of non-catalytic ozonation at 20°C, and 3 h with 3.75 g of catalyst.	[40]
Ce-Mn-O,	Aniline and sulfanilic acid	Aniline and sulfanilic acid, 700 mL, 1 mM, cat. 350 mg, 25°C, 120 min.	TOC removal: 67% aniline and 63% sulfanilic acid.	[43]
Ce-Co-O			TOC removal: 66% aniline and 58% sulfanilic acid.	
CoNiAl-HTLcs	Phenol	Phenol 100 mL, 0.0055 M, cat. 30 mg, 25°C, 240 min	TOC removal: 90 %	[45]
Co(3 wt.%)Al_2O_3/ BaO			TOC removal: 74 %	
Ru/CeO_2	Succinic acid	Succinic acid 500 mL, 1 mM, cat. 0.8 g, 120 min	Succinic acid was completely decomposed after 1 h, and cat. Ru/CeO_2 showed increasing performance with four-time use.	[46]
Ni/Al_2O_3	Oxalic acid	Oxalic acid 1mM, cat. 1 -4 g, 12-32°C, 100 min	Catalyst significantly improved the removal rate of oxalic acid in comparison to the one with non-catalytic process, at 22 °C, and 80 min with 2 g of catalyst.	[47]
Ru/Al_2O_3	Dimethyl phthalate	DMP 6 mM, cat. 10 g, 15°C, 120 min.	TOC removal: 72%	[48]
Perovskite	Pyruvic acid	Pyruvic acid 5 mM, cat. 1 g, 20 °C, 200 min.	The activity of the catalyst is increased after the first use and keeping the stability at least for the first five reuses.	[50]
Zeolite	Phenol	Phenol 120 mL, 100 mM, cat. 0.5 g, 20°C, 60 min	The activity of the catalyst is stable even after being use for ten-times.	[51]
CeO_2/Activated Carbon	Fulvic acid	Fulvic acid 1500 mL, 50 mM, cat. 0.5 g, 20°C, 30 min	CeO_2/AC enhanced the fulvic acid removal efficiency up to 83% compared with ozonation alone. Moreover, CeO_2/AC showed high stability even after six-time use.	[52]

1.5 Reaction mechanism of ozonation

In ozonation in water, efficiency of the reaction depends on the generation of reactive free radicals; the most important of which is the hydroxyl radical (•OH) [29]. The role of •OH generated by ozonation has been studied in the presence of organic matter. The decomposition of ozone is the results of a chain reaction in which hydroxide ion acts as initiators. Decomposition of ozone will lead to the formation of free radical, which is favorable for the oxidation of refractory impurities in water treatment [57]. Therefore, the decomposition rate of organic matter in wastewater can be greatly enhanced by the ozonation.

The ozonation of organic compounds follows two pathways involving either molecular ozone (direct ozonation) or hydroxyl radical reaction, depending on the reaction conditions, such as pH and/or type of pollutant [58]. Direct ozonation dominates and is selective when reaction proceeds at low pH due to low concentration of hydroxyl ions, whereas the indirect pathway prevails at basic conditions [35, 59]. Generation of •OH in the neutral pH region follows following reactions (eq. 1.2 – 1.5) [35, 60, 61]:

$$O_3 + OH^- \rightarrow O_2^{-}\bullet + HO_2\bullet \quad (1.2)$$

$$O_2^{-}\bullet + O_3 \rightarrow O_3^{-}\bullet + O_2 \quad (1.3)$$

$$O_3^{-}\bullet + H^+ \leftrightarrow HO_3^{\bullet} \quad (1.4)$$

$$HO_3\bullet \rightarrow \bullet OH + O_2 \quad (1.5)$$

At higher pH, the generation of •OH proceeds according to following reactions (eq.1.6 – 1.9):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (1.6)$$

$$HO_2^- + O_3 \rightarrow O_3^{-}\bullet + HO_2\bullet \quad (1.7)$$

$$O_2^{-}\bullet + O_3 \rightarrow O_3^{-}\bullet + O_2 \quad (1.8)$$

$$O_3^{-}\bullet + H_2O \rightarrow \bullet OH + O_2 + OH^- \quad (1.9)$$

Decomposition rate of organic matters by ozonation is found to depend on the rate of ozone decomposition, which is independent of the subsequent reaction with organic matters [62]. Moreover, due to the relatively low solubility and stability of ozone in water and slow reaction with some organic compounds, ozonation has been shown to achieve limited mineralization of organic compounds [31].

Homogeneous catalytic ozonation is based on the activation of ozone by metal ions present in aqueous solution, while heterogeneous catalytic ozonation is the catalytic reaction over metal oxides or metals/metal oxide on supports [31, 63]. The homogeneous catalytic ozonation is initiated with an ozone decomposition reaction by the metal ions [31]. Mechanism of homogeneous catalytic ozonation in the presence of transitional metal ions can be expressed briefly as follows:

$$M^{(n-1)+} + O_3 + H^+ \rightarrow Mn^+ + \bullet OH + O_2 \quad (1.10)$$

$$M^{(n-1)+} + \bullet OH \rightarrow Mn^+ + OH^- \quad (1.11)$$

If catalyst dosage exceeds the optimum, hydroxyl radicals are scavenged from the reaction (1.11) and thus degradation rate of organic pollutants is decreased [64].

In the heterogeneous catalytic ozonation, ozone is adsorbed on the catalyst surface and its further decomposition leads to surface-bound O radicals and hydroxyl radicals [31, 40].

At acidic to near-neutral pH (pH 2 – 6), reactions proceed as follows:

$$O_3 + S \leftrightarrows O_3—S \quad (1.12)$$

$$O_3—S \leftrightarrows O—S + O_2 \quad (1.13)$$

$$O_3 + O—S \leftrightarrows 2O_2 + S \quad (1.14)$$

- S is the catalyst surface.

On the other hand, when pH is more than 6, production of •OH occurs along with the direct ozonation, leads to a faster mineralization of organic matters:

$$OH^- + S \leftrightarrows OH—S \quad (1.15)$$

$$O_3 + OH—S \leftrightarrows •O_3—S + •OH \quad (1.16)$$

$$•O_3—S \leftrightarrows •O—S + O_2 \quad (1.17)$$

$$O_3 + •O—S \leftrightarrows O_2^-• + S + O_2 \quad (1.18)$$

1.6 Scope of this thesis

As this author has described so far based on previous papers, there are some established methods, including biological treatment, ammonia stripping, and catalytic oxidation for ammonia nitrogen removal. However, for each established methods have some drawbacks. For examples, biological treatment is impossible to apply to wastewater containing toxic chemicals. Ammonia stripping is not economical even though can remove ammonia nitrogen efficiently, while catalytic oxidation needs high temperature

and high pressure for the decomposition of ammonia nitrogen. Catalytic ozonation is one of the advanced technologies for the treatments of drinking water and wastewater and has advantages such as mild reaction conditions (ordinary temperature and pressure), high effectiveness for organic pollutants degradation, powerful in mineralization of persistent organic pollutants and negligible negative effect on water quality. With such advantages, some researchers have already applied the catalytic ozonation for the decomposition of organic compounds in water. However, there is little paper on the catalytic ozonation of ammonia nitrogen in water.

The research in this thesis aims to apply the catalytic ozonation for ammonia decomposition in water in the presence of heterogeneous catalysts, because catalytic ozonation is expected to be a promising method for the oxidative decomposition of ammonia nitrogen in wastewater. In Chapter 1, ammonia pollution in water, established methods for ammonia removal from water and their problems were described. In addition the objectives of this thesis were described. In Chapter 2, a catalyst screening study was performed in order to find the best catalyst, which is active, selective and stable for the catalytic ozonation of NH_4^+ in water. Cobalt oxide (Co_3O_4) was found to be the most promising catalyst for the catalytic ozonation NH_4^+ in water in terms of activity, selectivity and stability. In Chapter 3, the reaction mechanism of the catalytic ozonation of NH_4^+ mainly over Co_3O_4 was investigated, and the reason for high activity and high selectivity of Co_3O_4 was discussed based on kinetic analysis. It was found that Cl^- in water was indispensable for the catalytic ozonation of NH_4^+, because the reaction did not proceed at all in the absence of Cl^-. Namely, Cl^- was involved in the catalytic cycle. Thus, reaction behaviors of Cl^- with O_3 in the presence and absence of Co_3O_4 were investigated.

In addition, reactions of oxychloride ion, ClO_x^-, with NH_4^+ were carried out to clarify what reactions Co_3O_4 promoted. In Chapter 4, unusual catalytic property of Co_3O_4, in which the catalytic activity was significantly enhanced by repeated used, was reported. This catalytic activity enhancement of Co_3O_4 by repeated use was compared with other metal oxide catalysts including SnO_2, Al_2O_3 and Mn_5O_8. Furthermore, the reasons for its activity enhancement were investigated. Finally, in Chapter 5, the findings of each chapter and general conclusions were described.

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Chapter 2

Survey of active and selective metal oxide catalysts for catalytic ozonation of ammonium ion in water

2.1 Introduction

Presence of ammonia nitrogen (NH_3 and NH_4^+) in aquatic ecosystem, which comes from industrial disposal, household sewage discharge, intensive agriculture activities and excreta of animals, causes eutrophication with offensive smells and is toxic to fish and aquatic life [1-3]. Thus, it is necessary to treat wastewater containing ammonia nitrogen properly, and preferably ammonia nitrogen should be decomposed into harmless compounds such as gaseous N_2.

Recently, catalytic ozonation gains a lot of attention for wastewater treatment, because it proceeds at ordinary temperature and pressure. Operation under such mild reaction conditions is beneficial for practical use. Since the catalytic ozonation is highly effective for degradation of persistent organic pollutants, many studies have been conducted on the catalytic ozonation for the organic pollutant degradation [4-14]. However, there are no reports on the catalytic ozonation of ammonia nitrogen over a heterogeneous catalyst, although non-catalytic ozonation [15] and the catalytic ozonation of ammonia nitrogen with a homogeneous catalyst in water [16] have been investigated.

Decomposition of ammonia nitrogen by catalytic ozonation produces mainly the products formed with eqs. 2.1 – 2.3, where NH_4^+ is represented as a ammonia nitrogen.

$$NH_4^+ + 3/2O_3 \rightarrow 1/2N_2 + 3/2H_2O + 3/2O_2 + H^+ \quad (2.1)$$

$$NH_4^+ + 4O_3 \rightarrow NO_3^- + H_2O + 4O_2 + 2H^+ \quad (2.2)$$

$$NH_4^+ + 3O_3 \rightarrow NO_2^- + H_2O + 3O_2 + 2H^+ \quad (2.3)$$

Among them, N_2 is the best product, because NO_3^- and NO_2^- are more toxic than ammonia nitrogen.

As was mentioned, there is no report on the catalytic ozonation of ammonia nitrogen in the present of a heterogeneous catalyst. Thus, in this chapter the catalytic ozonation of ammonia nitrogen in water was investigated using various metal oxide catalysts to find a good candidate of the heterogeneous catalyst. Under the conditions with mild acidic pH, almost all ammonia nitrogen was present as cationic NH_4^+, not as NH_3 because K_b of NH_3 (=$[NH_4^+][OH^-]/[NH_3]$) is $10^{-4.8}$. Thus, NH_4^+ is used to show ammonia nitrogen. The catalyst was required to have high catalytic activity and high selectivity to gaseous compounds including N_2. In addition, the catalyst should be less soluble in the reaction solution to prevent contamination of the treated water with catalyst materials. Thus, dissolution of the catalysts during the reaction was carefully investigated with ICP-AES analysis.

2.2 Experimental

2.2.1 Preparation of catalysts

Distilled water was used for all experiments. $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_2{\cdot}6H_2O$, $SnCl_4{\cdot}5H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$, MgO, Al_2O_3, NH_4Cl, $(NH_4)_2SO_4$, and 25% aqueous ammonia were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

Cobalt oxide (Co_3O_4) was prepared by a precipitation method. An aqueous ammonia solution (1.0 mol L^{-1}) was added into an aqueous solution of $Co(NO_3)_2$ (1.0 mol L^{-1}) until the pH reached up to 8, leading to the formation of black fine powder. The obtained suspension was allowed to stand for 10 min at room temperature. The precipitate was then filtered, washed with distilled water, and dried at 373 K for two days. Finally, the obtained solid was calcined at 723 K in air for 3 h at a heating rate of $10^oC\ min^{-1}$.

Nickel oxide (NiO) was prepared in a similar manner to that for cobalt oxide calcined at 773 K using a solution of $Ni(NO_3)_2$ instead of $Co(NO_3)_2$. Zinc oxide (ZnO) and iron oxide (Fe_2O_3) were prepared in a similar manner to that for cobalt oxide, except that the pH of the solution was 7, and solutions of $Zn(NO_3)_2$ and $Fe(NO_3)_2$, respectively, were used.

Tin oxide (SnO_2) was prepared as follows. An aqueous ammonia solution (0.5 mol L^{-1}) was added dropwise to an aqueous solution of $SnCl_4$ (1.0 mol L^{-1}) until the pH of the solution was 8. The suspension was stirred at 353 K for 3 h. The precipitate that formed was separated by using centrifugation and dried in air at 383 K for 24 h, followed by calcination in air at 673 K for 2 h.

Manganese oxide (Mn_3O_4) was prepared by using a precipitation method. An aqueous solution of sodium hydroxide (0.5 mol L^{-1}) was added to an aqueous solution of $Mn(CH_3COO)_2$ (0.5 mol L^{-1}) until the pH of the solution was 8. The resulting suspension was stirred at room temperature for 12 h. The precipitate was collected by filtration, washed with distilled water, and dried at 373 K for 24 h. The solid was calcined in air at 673 K for 4 h.

Copper oxide (CuO) was prepared by calcining $Cu(NO_3)_2 \cdot 6H_2O$ in air at 673 K for 4 h. Magnesium oxide (MgO) and aluminum oxide (Al_2O_3) were supplied by Ube Materials Co. (Magnesia 500A) and Japan AEROSIL Co. (Aerosil® Alu C), respectively, and were calcined in air at 773 K for 5 h before use.

2.2.2 Catalytic ozonation of NH_4^+ in water

Catalytic ozonation of NH_4^+ in water was carried out in a three neck flask soaked in a water bath (Fig. 2-1). The reaction solution prepared from NH_4Cl (100 mL, 10 mmol L^{-1}) and 100 mg of metal oxide catalysts were put into the flask. The suspension was heated at 333 K with vigorous stirring using a magnetic stirrer in a stream of O_2 (100 cm^3 min^{-1}). After the temperature reached to 333 K, the gas was changed to a mixture of O_3/O_2 (1.88 mmol h^{-1} as O_3 with total flow rate 100 cm^3 min^{-1}) to start the catalytic ozonation of NH_4^+. Ozone was generated from O_2 using an ozone generator (Tokyo Car Co. SO-03 UN-OX). This reaction conditions are referred as standard conditions.

Compounds in the solution (NH_4^+, NO_3^- and NO_2^-) were analyzed using two ion chromatographs (Tosoh Co. Ltd., IC-2001). For anions, a column containing an anion-exchange resin (TSK gel Super IC-AZ, Tosoh) and an aqueous solution of $NaHCO_3$ (2.9 mmol L^{-1}) and Na_2SO_4 (3.1 mmol L^{-1}) were used as stationary and mobile phase, respectively. For cation analysis, a column containing a cation exchange-resin (TSK gel IC-Cation 1/2 HR, Tosoh) and an aqueous solution of methanesulfonic acid (2.2 mmol L^{-1}) and 18-crown-6 (1.0 mmol L^{-1}) were used as stationary and mobile phase, respectively.

Yield of and selectivity to NO_3^- was calculated by eqs. 2.4 and 2.5, respectively.

$$\text{Yield of } NO_3^- = \frac{\text{Concentration of formed } NO_3^-}{\text{Initial concentration of } NH_4^+} \text{ x } 100\ [\%] \qquad (2.4)$$

$$\text{Selectivity to } NO_3^- = \frac{\text{Concentration of formed } NO_3^-}{\text{Concentration of consumed } NH_4^+} \text{ x } 100\ [\%] \qquad (2.5)$$

Basically, the gas phase was not analyzed, and thus the selectivity to gaseous products was calculated by subtracting the selectivity to NO_3^- from 100%, since NO_3^- was the only product in the solution. However, for some experiments, the gas phase products were analyzed with a gas chromatograph equipped with TCD.

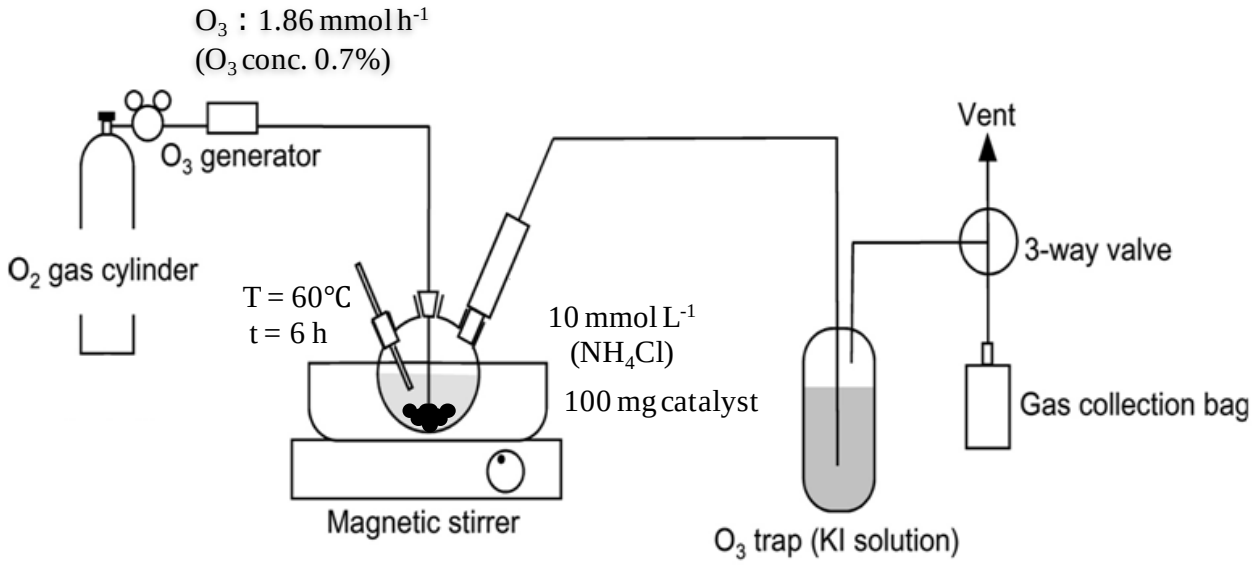


Fig. 2-1 Schematic illustration of a reaction apparatus used for catalytic ozonation of NH_4^+ in water.

2.2.3 Characterization

2.2.3.1 XRD

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 at a scanning rate of 0.02° in 2θ = 4-80°. The crystallite size of metal oxide was calculated using Scherrer's equation with the strongest diffraction line,

$$D = \frac{\lambda 0.9}{\beta \cos\theta} \qquad (2.6)$$

where λ is the X-ray wavelength (0.154 nm), θ is the diffraction angle, and β is the half-line width.

2.2.3.2 Specific surface area

Specific surface area was calculated from N_2 adsorption isotherm at 77 K (Belsorp, Japan Inc.) with the BET equation. Prior to the measurement, the samples were pretreated under N_2 flow for 3 h at 473 K.

2.2.3.3 ICP analysis

Amounts of metals dissolved in the reaction solution from metal oxide catalysts during the catalytic ozonation of NH_4^+ were measured by ICP–AES (Shimadzu Co., ICPS–7000). Dissolution degree (%) of the catalyst during the reaction was calculated by eq. 2.7, where $W_{dissolved}$ and $W_{initial}$ indicate the amount of the metal dissolved in the reaction solution after 6 h and the amount of the metal initially contained in the catalyst, respectively.

$$\text{Dissolution degree} = \frac{W_{dissolved}}{W_{initial}} \text{ x } 100[\%] \qquad (2.7)$$

2.3 Results and Discussion

2.3.1 Physical properties of metal oxide catalysts

Table 2-1 summarizes chemical formula and morphological properties (crystalline and surface area) of nine metal oxide catalysts tested. Tin oxide (SnO_2) and Al_2O_3 had large surface area, being 82 and 93 $m^2\ g^{-1}$, respectively and thus their crystallite sizes were small (8 nm). Meanwhile, ZnO and copper oxide (CuO) had small surface area around 1 $m^2\ g^{-1}$, because of large crystallite sizes, being 45 and 27 nm, respectively. Other catalysts including Co_3O_4, NiO, Fe_2O_3, Mn_3O_4, and MgO had moderate surface areas ranging from 10 – 35 $m^2\ g^{-1}$.

Table 2-1 Chemical formula and morphological properties of catalysts

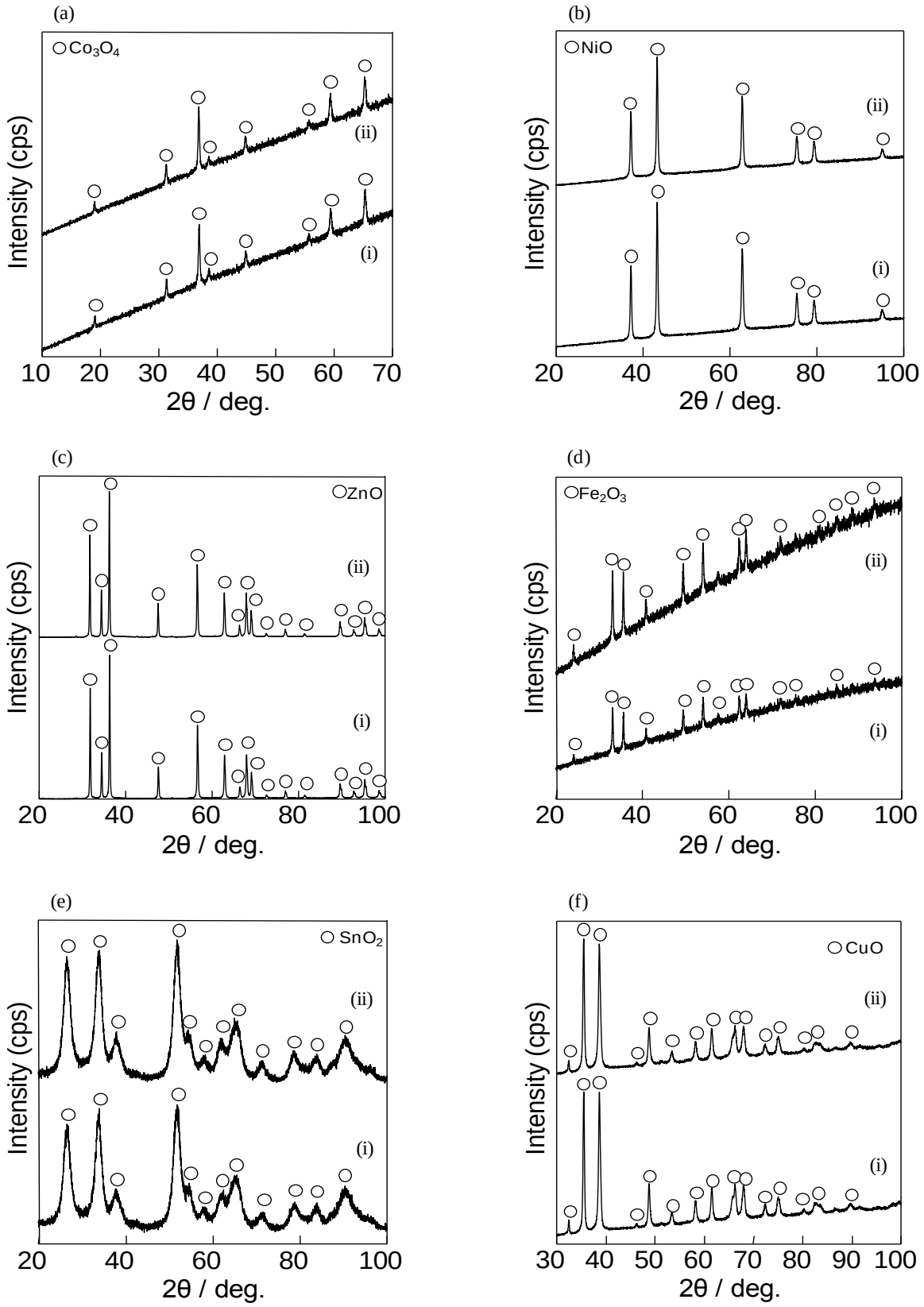
Catalyst	Chemical formula[a]	Crystallite size[b] /nm	Surface area[c] /$m^2\ g^{-1}$
Cobalt oxide	Co_3O_4	28	14
Nickel oxide	NiO	25	22
Zinc oxide	ZnO	45	1
Iron oxide	Fe_2O_3	32	10
Tin oxide	SnO_2	8	82
Manganese oxide	Mn_3O_4	19	23
Copper oxide	CuO	27	1
Magnesium oxide	MgO	30	35
Aluminum oxide	Al_2O_3	8	93

[a]Determined from powder XRD pattern.

[b]Determined by applying Scherrer's equation to the strongest diffraction line in each XRD pattern.

[c]Determined from N_2 adsorption isotherm at 77 K by using the BET equation.

Fig 2-2 shows XRD patterns of the catalysts before and after the catalytic ozonation of NH_4^+. For most of the metal oxide catalysts, their crystalline structures of the spent catalyst (after the reaction) were basically the same as those before the catalytic ozonation. However, the crystalline structure of manganese oxide (Fig. 2-2 (g)) and magnesium oxide (Fig. 2-2 (h)) were changed after the reaction. Mn_3O_4 and MgO were transformed into Mn_5O_8 and $Mg(OH)_2$, respectively, after the reaction due to oxidation and hydration during the catalytic ozonation, respectively.


(a)
Co3O4
(ii)
(i)
Intensity (cps)
10 20 30 40 50 60 70
2θ / deg.
(b)
NiO
(ii)
(i)
Intensity (cps)
20 40 60 80 100
2θ / deg.
(c)
ZnO
(ii)
(i)
Intensity (cps)
20 40 60 80 100
2θ / deg.
(d)
Fe2O3
(ii)
(i)
Intensity (cps)
20 40 60 80 100
2θ / deg.
(e)
SnO2
(ii)
(i)
Intensity (cps)
20 40 60 80 100
2θ / deg.
(f)
CuO
(ii)
(i)
Intensity (cps)
30 40 50 60 70 80 90 100
2θ / deg.

(Continued)

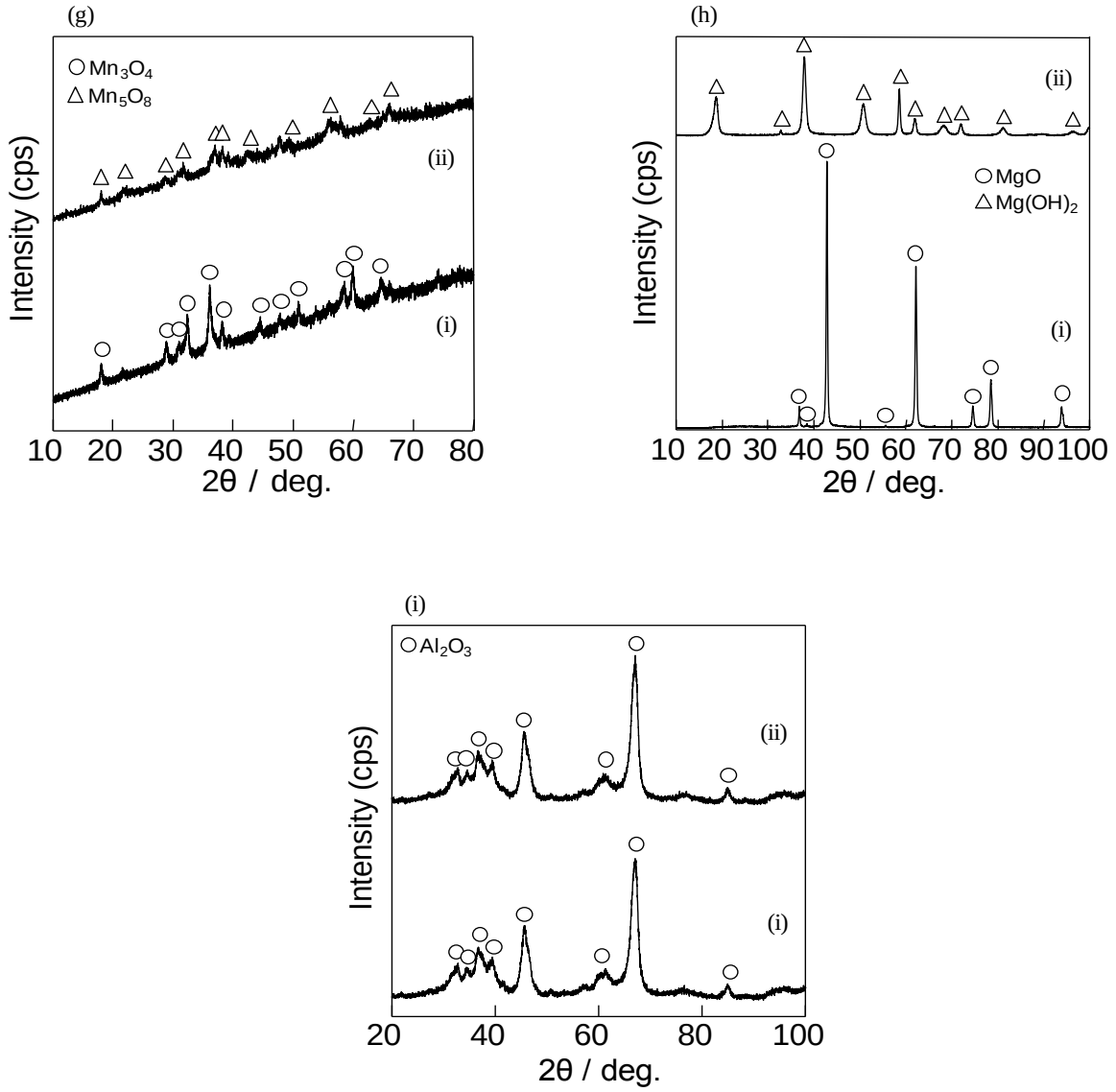


Fig. 2-2 XRD patterns of metal oxide catalysts (i) before and (ii) after catalytic ozonation of NH_4^+.

(a) Co_3O_4, (b) NiO, (c) ZnO, (d) Fe_2O_3, (e) SnO_2, (f) CuO, (g) Mn_3O_4, (h) MgO, and (i) Al_2O_3

2.3.2 Catalytic performances of metal oxide catalysts

Figure 2-3 shows conversion of NH_4^+ in the absence (blank, without catalyst) and presence of the catalyst at 6 h. NH_4^+ underwent to decompose even without catalyst, but the conversion was low (14%). In the presence of catalyst, the conversion of NH_4^+ was higher comparing with the blank experiment. Among the catalysts, NiO was the best catalyst in terms of activity, and MgO was the second best. On the other hand, Fe_2O_3, SnO_2 and Al_2O_3 showed low activity, comparable to no catalyst, meaning inactive catalysts. Meanwhile, Co_3O_4 showed moderate activity and the conversion at 6 h was 74%.

A good catalyst must have high selectivity to gaseous products, including N_2 and N_2O, in the oxidative decomposition of NH_4^+ in water because the formation of soluble nitrogen compounds, including NO_3^- and NO_2^-, must be suppressed to low level due to their high toxicities. Fig. 2-4 shows the selectivity to gaseous compound, which refers to N_2 since N_2O and NOx were not detected, and NO_3^- in the ozonation of NH_4^+ in the absence and presence of metal oxide catalysts at 6 h. NO_2^- did not form at all regardless of the catalyst. MgO and NiO showed low selectivity to N_2 gas, although they had high catalytic activities, as shown in Fig. 2-3. In fact, when they were used, large amount of harmful NO_3^- formed, making them unsuitable for use as catalysts in the purification of wastewater containing ammonia nitrogen.

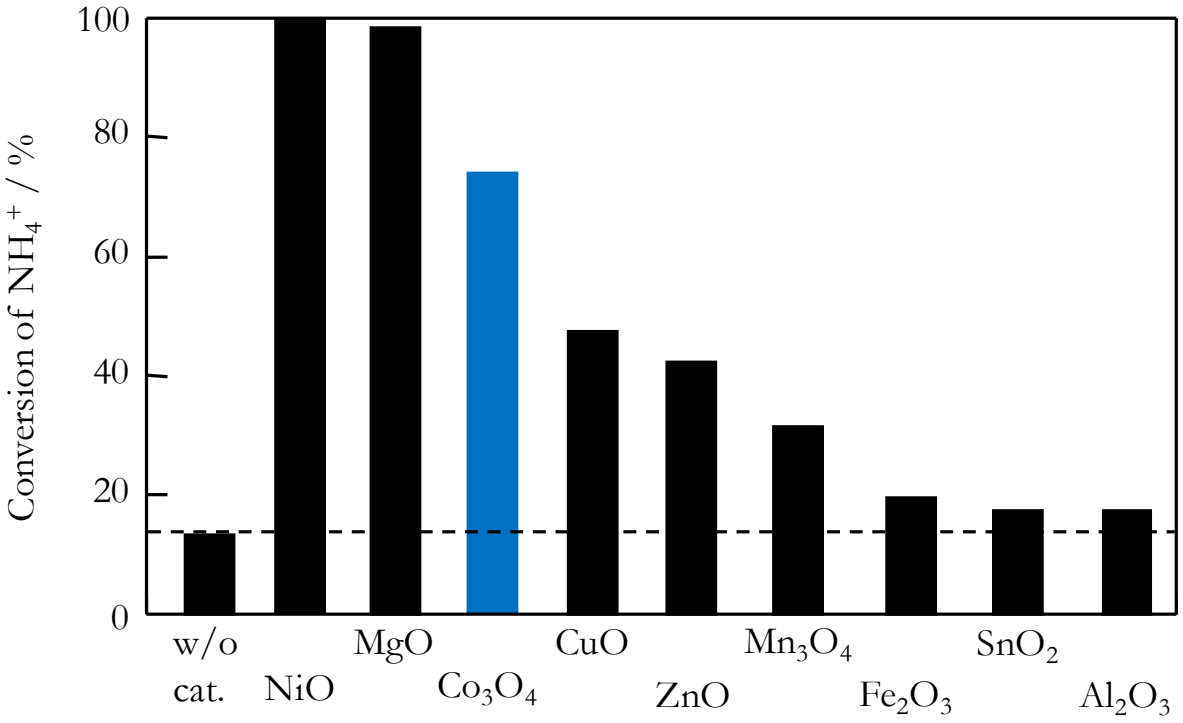


Fig. 2-3 Catalytic activity of metal oxide catalysts for catalytic ozonation of NH_4^+ in water. Reaction conditions: catalyst weight, 0.1 g; [NH_4^+], 10 mmol L^{-1} from NH_4Cl; reaction solution volume, 100 mL; reaction gas, O_3/O_2 mixture; total flow rate, 100 cm^3 min^{-1}; O_3 concentration, 0.7 vol%; reaction temperature, 333 K; and reaction time, 6 h.

CuO and ZnO were less selective to N_2 gas. In contrast, it should be noted that Co_3O_4 exhibited the highest selectivity to N_2 gas (85%) that was detected by using GC analysis. From the conversion (72%) and selectivity to NO_3^- (15%) at 6 h for Co_3O_4, the yield of NO_3^- was calculated to be 9%. When the reaction was conducted in the absence of the catalyst, the yield of NO_3^- was 9%. In other words, almost all of the NO_3^- formed in the presence of Co_3O_4 was produced by homogeneous oxidation of NH_4^+ with O_3 in water.

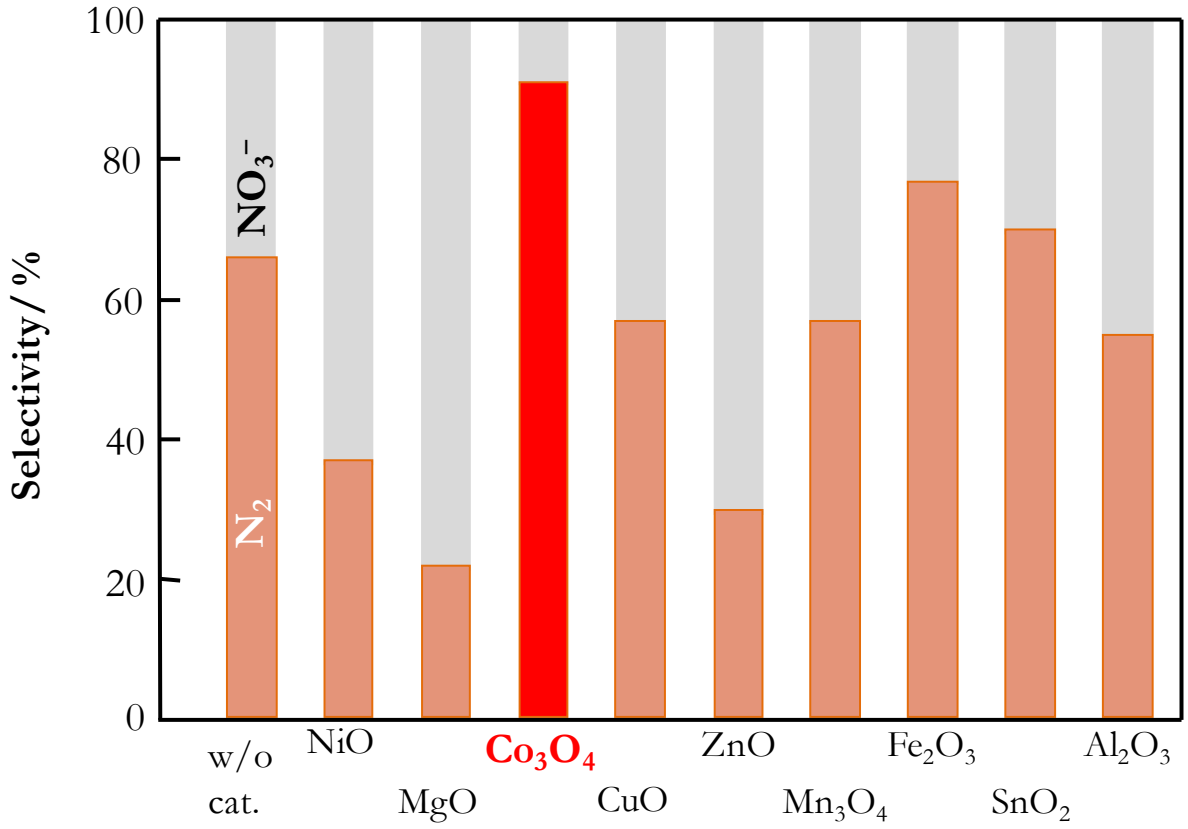


Fig. 2-4 Selectivity to (■) N_2 gas and (■) NO_3^- in catalytic ozonation of of NH_4^+ in water over metal oxide catalysts. Reaction conditions: catalyst weight, 0.1 g; reaction solution, [NH_4^+], 10 mmol L^{-1} from NH_4Cl; reaction solution volume, 100 mL; reaction gas, O_3/O_2 mixture; total flow rate, 100 cm^3 min^{-1}; O_3 concentration, 0.7 vol%; reaction temperature, 333 K; and reaction time, 6 h.

Table 2-2 summarizes the dissolution degree of the metal oxide catalysts during the reaction and pH values of the reaction solution after 6 h. MgO, NiO, CuO and ZnO were highly soluble in the reaction solution. In contrast, Fe_2O_3, SnO_2, and Mn_3O_4 were insoluble in the reaction solution, despite their low activity and/or low selectivity. Meanwhile, only 1% of Co_3O_4 was dissolved during the reaction. According to eqs. 2.1 – 2.3, protons (H^+) were formed by the decomposition of NH_4^+, resulting in the decrease of pH of the reaction solution. The pH after the reaction was less than 2.5 in the case of the insoluble catalysts (Fe_2O_3, SnO_2, and Mn_3O_4). In case of the less soluble catalysts (Co_3O_4 and Al_2O_3), the pH of the reaction solution after the reaction was also around 2-3. In contrast to them, when the soluble catalysts (MgO, NiO, CuO and ZnO) were used, the pH after the reaction was high. The high pH of the reaction solution supports high solubility of these catalysts. From these results, it can be concluded that Co_3O_4 is the best catalyst in terms of activity, selectivity to N_2 gas and stability among the catalysts tested for the catalytic ozonation of NH_4^+.

Table 2-2 Dissolution degrees of the metal oxide catalysts and the pH of the reaction solution after the reaction

Catalyst	Dissolution degree[a] / %	pH after the reaction[b]
MgO	38	9.3
NiO	56	6.3
Co_3O_4	1	2.1
CuO	27	4.6
ZnO	26	6.2
Mn_3O_4	0.1	2.1
Fe_2O_3	below detection limit	2.6
SnO_2	below detection limit	2.7
Al_2O_3	2	3.1

[a]Amount of metal dissolved in the reaction solution was determined by using ICP - AES.
[b]Initial pH of the reaction solution was 5.4.

In addition to the moderate activity, high selectivity and high durability, Co_3O_4 was the reusable catalyst for the reaction. After the reaction, Co_3O_4 was separated by filtration, dried at 373 K overnight and then was afforded to the next reaction. Conversion of the second run was 91% with similar high selectivity to the first one. For the third run, NH_4^+ was completely decomposed at 6 h. The catalytic activity of Co_3O_4 was increased when it was repeatedly used for the reaction. This unique feature of Co_3O_4 will be discussed in detail in Chapter 4.

Since catalytic reaction over a heterogeneous catalyst occurs on its surface, the surface area of the catalyst is one of the important factors controlling the catalyst activity. Thus, catalysts with high surface area may exhibit high catalytic activity, if the specific activity per unit surface area was basically the same regardless the elements composed of the catalyst. However, that was not the case for the catalytic ozonation of NH_4^+ over metal

oxide catalysts. Fig. 2-5 shows the relationship between surface area of the metal oxide catalyst and conversion of NH_4^+. The conversions shown in Fig. 2-5 were obtained by subtracting the conversion for the blank experiment (in the absence of the catalyst) from corresponding conversions in the presence of the catalyst. The data plotted in Fig. 2-5 were only for the catalysts that were not soluble (Fe_2O_3, SnO_2, and Mn_3O_4) or less soluble (Co_3O_4 and Al_2O_3) during the catalytic ozonation. Tin oxide (SnO_2) and Al_2O_3 showed only low activity though they had high surface areas. It was obvious that Co_3O_4 (Fig. 2-5 (a)) showed the highest activity despite its small surface area, meaning that cobalt (Co^{2+} and Co^{3+}) is the component that is intrinsically active for the catalytic ozonation of NH_4^+ in water. The high activity of Co_3O_4 will be discussed in Chapter 3 in conjunction with the reaction mechanism of the catalytic ozonation of NH_4^+ in water.

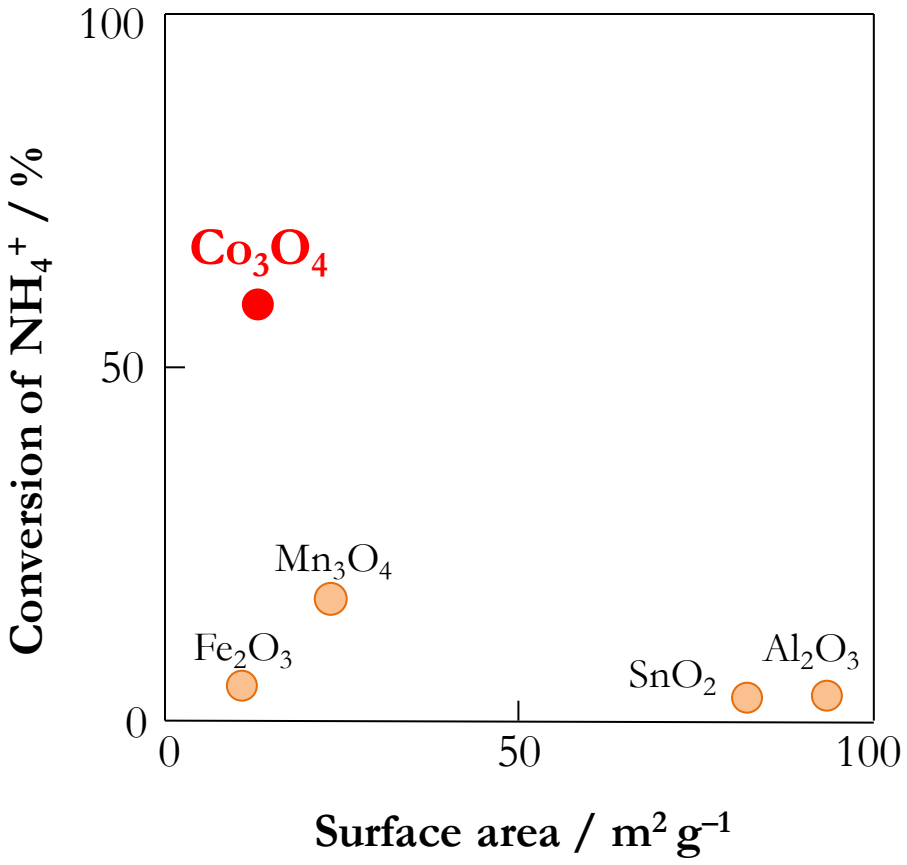


Fig. 2-5 Relationship between conversion of NH_4^+ at 6 h and surface areas of the metal oxide catalysts. The conversions of NH_4^+ shown in the figure were obtained by subtracting the conversion for the blank experiment (without catalyst) from corresponding conversions. The data plotted in the figure are for the catalysts with low degrees of dissolution.

High selectivity to N_2 gas over Co_3O_4 is strongly related to the reaction mechanism and thus the reason for the high selectivity will be discussed in Chapter 3.

2.4 Conclusion

Catalytic oxidation of NH_4^+ with O_3 in water over a variety of metal oxide catalysts, including Co_3O_4, NiO, ZnO, Fe_2O_3, SnO_2, Mn_3O_4, CuO, MgO, and Al_2O_3, without pH control was conducted to find good catalysts for the reaction. MgO and NiO had the highest activity, but large amounts of undesired NO_3^- formed due to their low selectivity to N_2 gas. Although Co_3O_4 was slightly less active than MgO and NiO, it was the best catalyst in terms of activity, selectivity to N_2 gas, and dissolution degree among the metal oxide catalysts tested. The high activity of Co_3O_4 was not due to the high surface area, but because Co_3O_4 intrinsically active. An aqueous solution of NH_4^+ (10 mmol L^{-1}) was effectively oxidized to N_2 with 85% selectivity at 333 K over Co_3O_4.

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Chapter 3

Reaction Mechanism of Catalytic Ozonation of Ammonium Ion in Water

3.1 Introduction

Heterogeneous catalytic ozonation in water is a potential method for organic pollutant degradation or mineralization to treat drinking water and wastewater [1]. Previous reports [1, 2] demonstrate that catalytic ozonation proceed through two pathways. One is the reaction involving hydroxyl radical oxidation and the other is non-hydroxyl radical oxidation. For the heterogeneous catalytic ozonation of organic pollutant, there are furthermore three possible mechanisms [3]: (i) Firstly ozone is activated (adsorbed) on the catalyst surface and •OH is formed by the reaction of the activated ozone with water. The formed •OH is desorbed (release) from the catalyst surface and is reacted with organic pollutant in the bulk of solution (aqueous phase), but not in the surface of the catalyst. (ii) Organic pollutant is firstly activated on the catalyst surface and then ozone directly attacks to the organic pollutant present on the catalyst surface. Finally the formed oxidized product is released from the catalyst surface to regenerate the active site of the catalyst. In this mechanism, ozone is not activated directly on the catalyst surface. (iii) Both ozone and organic pollutant are activated on the surface and then are reacted as a surface reaction. In case of the catalytic ozonation over metal oxide-suported metals, two possible routes have been proposed [4]. One is that first adsorption of organic pollutant (molecule) on the catalyst surface occurs and then it is oxidized with ozone or hydroxyl radical. The other is that generation of •OH by the reaction of reduced form of metal with ozone as well as adsorption of organic molecule occurs first, and then the oxidation of organic molecule by an electron transfer takes place. Finally products are desorbed with simultaneous regeneration of metal site on the catalyst. Though the general reaction mechanisms are proposed as mentioned above, it is difficult to apply such reaction mechanisms for each

reaction systems that are investigated, because catalyst, reactant, reaction conditions, additive, etc. vary according to the target pollutants. Thus, eventually the reaction mechanism should be elucidated in each reaction systems that are investigated by each research group.

In Chapter 2, it was demonstrated that Co_3O_4 showed moderate activity but high selectivity to gaseous products for catalytic ozonation of NH_4^+ in water. In addition, Co_3O_4 was less soluble in the reaction solution, which is beneficial for its practical application. Based on these findings, the author concluded that Co_3O_4 was the best catalyst for the catalytic ozonation of NH_4^+ in water [5]. In this chapter, the reaction mechanism of the catalytic ozonation of NH_4^+ over Co_3O_4 is investigated. Since there is no previous report on the catalytic ozonation of NH_4^+ in the presence of heterogeneous catalysts, nothing is known on the reaction mechanism.

Here, it is focused on the role (involvement) of Cl^- in the reaction solution, because the reaction did not proceed at all without Cl^- even in the presence of Co_3O_4. To clarify the involvement of Cl^- for catalysis cycle, the catalytic ozonation of NH_4^+ was carried out over Co_3O_4 by using the reaction solutions with different Cl^- concentrations. The author speculated that oxychloride ions including ClO^-, ClO_2^-, ClO_3^- and ClO_4^-, which were formed by the oxidation of Cl^- with ozone, acted as oxidizing agent for NH_4^+. Thus, reaction behavior for the oxidation of Cl^- with ozone in the absence of NH_4^+ and the reaction of NH_4^+ with oxychloride ions over Co_3O_4 were investigated. After that, the difference in activity and selectivity for the catalysts shown in Chapter 2 will be discussed based on their catalytic performances for the Cl^- oxidation with ozone and reaction of NH_4^+ with oxychloride ions.

3.2 Experimental

3.2.1 Catalysts and reagents

All catalyst used in this chapter were prepared in the same manner as those described in Chapter 2. NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, KCl, NaCl, NaOCl, $KClO_3$, $NaClO_2$, and $KClO_4$ were purchased from Wako Pure Chemical Industries, Ltd., Kanto Chemical Co. Inc. and Junsei Chemical Co. Ltd, were used without further purification.

3.2.2 Catalytic ozonation of NH_4^+ in the absence and presence of Cl^-

The catalytic ozonation of NH_4^+ in water was conducted in the same manner as that describe in Chapter 2. To investigate influence of Cl^- in the catalytic ozonation of NH_4^+over Co_3O_4, reaction solution of 5 mmol L^{-1} $(NH_4)_2SO_4$ (10 mmol L^{-1} as NH_4^+) with KCl, in which the concentration of KCl was changed from 0 to 10 mmol L^{-1}, were used. In addition, catalytic ozonation of NH4+ from different source namely 5 mmol L^{-1} $(NH_4)CO_3$ (10 mmol L^{-1} as NH_4^+) was conducted to clarify the role of Cl^- and SO_4^{2-}.

3.2.3 Catalytic oxidation of Cl^- with ozone in water

To investigate the possibility of formation of ClO_x^- (x = 1, 2, 3, and 4) by the reaction of Cl^- with ozone during the catalytic ozonation of NH_4^+ in water, where the reaction solution was prepared from NH_4Cl, catalytic oxidation of Cl^- with ozone in the presence of Co_3O_4 but in the absence of NH_4^+ was conducted. Aqueous solution of NaCl (10 mmol L^{-1}) was used as a reaction solution.

The reaction procedure for the oxidation of Cl^- with O_3 was the same as that for the catalytic ozonation of NH_4^+, but the aqueous NaCl solution was used instead of the aqueous

NH_4Cl solution. Small portion of the reactions solution was periodically withdrawn. After the catalyst was separated by filtration, the aqueous phase was analyzed to determine the concentrations of ClO^-, ClO_2^-, ClO_3^- and ClO_4^-.

The concentrations of Cl^-, ClO^- and ClO_2^- in the solution were determined on an ion chromatograph (Tosoh Co. Ltd., IC-2001). A column containing an anion-exchange resin (TSK gel Super IC-AZ, Tosoh) and an aqueous solution of $NaHCO_3$ (2.9 mmol L^{-1}) and Na_2CO_3 (3.1 mmol L^{-1}) were used as stationary and mobile phases, respectively. The concentrations of ClO_3^-, and ClO_4^- in the solution were determined on an ion chromatograph (Dionex ICS-900) equipped with an AS16 column (Dionex, 4x250 mm). The mobile phase was 35 mmol L^{-1} NaOH, and its flow rate was 1.0 mL min^{-1}.

3.2.4 Catalytic reaction of NH_4^+ with ClO_x^- (x = 1, 2, 3 and 4)

Catalytic reaction of NH_4^+ with ClO_x^- was performed in the similar manner to that for the catalytic ozonation of NH_4^+ described in Chapter 2, but the reaction solutions containing both 10 mmol L^{-1} NH_4Cl and 10 mmol L^{-1} ClO_x^- were used but O_3 was not fed into the reactor.

3.3 Result and Discussion

3.3.1 Role of Cl^- in the catalytic ozonation over Co_3O_4.

In Chapter 2, the catalytic ozonation of NH_4^+ was performed with the reaction solution prepared from NH_4Cl and thus not only NH_4^+ but also Cl^- was present in the reaction solution. In such reaction solution, Co_3O_4 showed moderate catalytic activity. However, the reaction did not proceed at all over Co_3O_4, when the reaction solution prepared from

$(NH_4)_2SO_4$, instead of NH_4Cl solution, was applied for the reaction. Figure 3-1 shows conversion and selectivity to N_2 gas for the catalytic ozonation of NH_4^+ over Co_3O_4 at 6 h with the reaction solution prepared from $(NH_4)_2SO_4$ (left three-quarters) and that prepared from NH_4Cl (right one-quarter). In the case of $(NH_4)_2SO_4$ solution, the reactions were carried out with the $(NH_4)_2SO_4$ solution containing KCl (see experimental). As shown in Fig. 3-1, conversion of NH_4^+ at 6 h was 0% for the reaction in the $(NH_4)_2SO_4$ solution without Cl^- (far-left data), while that in the NH_4Cl solution was 72% (far-right data). pH of the reaction solution often affects the reaction rate of the catalytic ozonation in water, but initial pH of the two solution was basically the same each other (pH ≈ 5.2 – 5.4). Thus, it is speculated that Cl^- in water participates in the catalytic cycle for the reaction over Co_3O_4. It should be noted that the conversion of NH_4^+ increased with an increase in the concentration of Cl^- and the conversion at 10 mmol L^{-1} was 54%. The selectivity to N_2 gas was also increased with the increase in the concentration of Cl^-. These results clearly demonstrate that Cl^- is involved in the catalytic cycle for the ozonation of NH_4^+ over Co_3O_4.

The conversion of NH_4^+ and selectivity to N_2 gas with the $(NH_4)_2SO_4$ solution containing 10 mmol L^{-1} Cl^- was slightly lower than that with the NH_4Cl solution, though the concentration of Cl^- were the same each other. Therefore, SO_4^{2-} may cause a weak catalyst deactivation. Many reasons are speculated, e.g. adsorption of SO_4^{2-} on Co_3O_4, promotion of the self decomposition of the active species (O_3, •OH) and so on, but at present there is no direct evidence to support these speculations. Further investigation is absolutely necessary to clarify the influence of SO_4^{2-}.

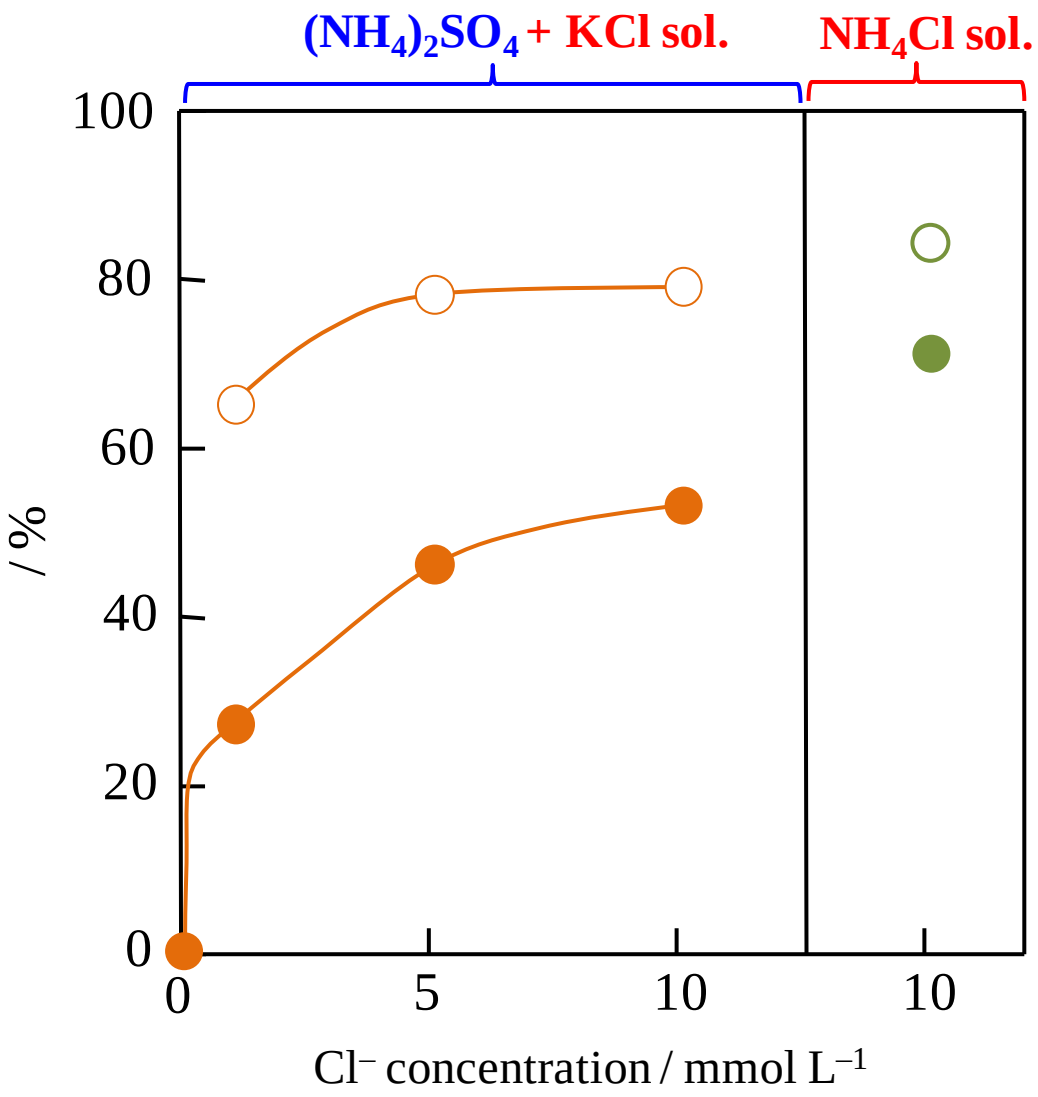


Fig. 3-1 Influence of Cl^- in $(NH_4)_2SO_4$ on the catalytic performance of Co_3O_4. (●,●) conversion of NH_4^+ and (○,○) selectivity to N_2 gas. Reaction conditions: $(NH_4)_2SO_4$, 5 mmol L^{-1}; KCl, 0,1; 5; and 10 mmol L^{-1}; reaction vol, 100 mL; Co_3O_4, 0.1 g; reaction temp. 60°C; O_3/O_2, total flow rate, 100 cm^3 min^{-1}; and reaction time, 6 h. NH_4Cl, 10 mmol L^{-1}; reaction vol, 100 mL; Co_3O_4, 0.1 g; reaction temp. 60°C; reaction time, 6 h; and O_3/O_2, total flow rate, 100 cm^3 min^{-1}

In addition to support the involvement of Cl^- and the role of SO_4^{2-} in catalytic ozonation of NH_4^+, catalytic ozonation of NH_4^+ from different source of NH_4^+ was conducted. When $(NH_4)_2CO_3$ solution (pH adjusted ≈ 5.6 – 5.7) was used as source of NH_4^+ for catalytic ozonation of NH_4^+ in the present of Co_3O_4, 18% of NH_4^+ was decomposed into 83% of N_2 gas. In the absence of SO_4^{2-}, decomposition of NH_4^+ by ozone proceeded in the presence of Co_3O_4. From Fig. 3-2 it confirmed that Cl^- participated in catalytic cycle and SO_4^{2-} was inhibited the catalytic ozonation of NH_4^+.

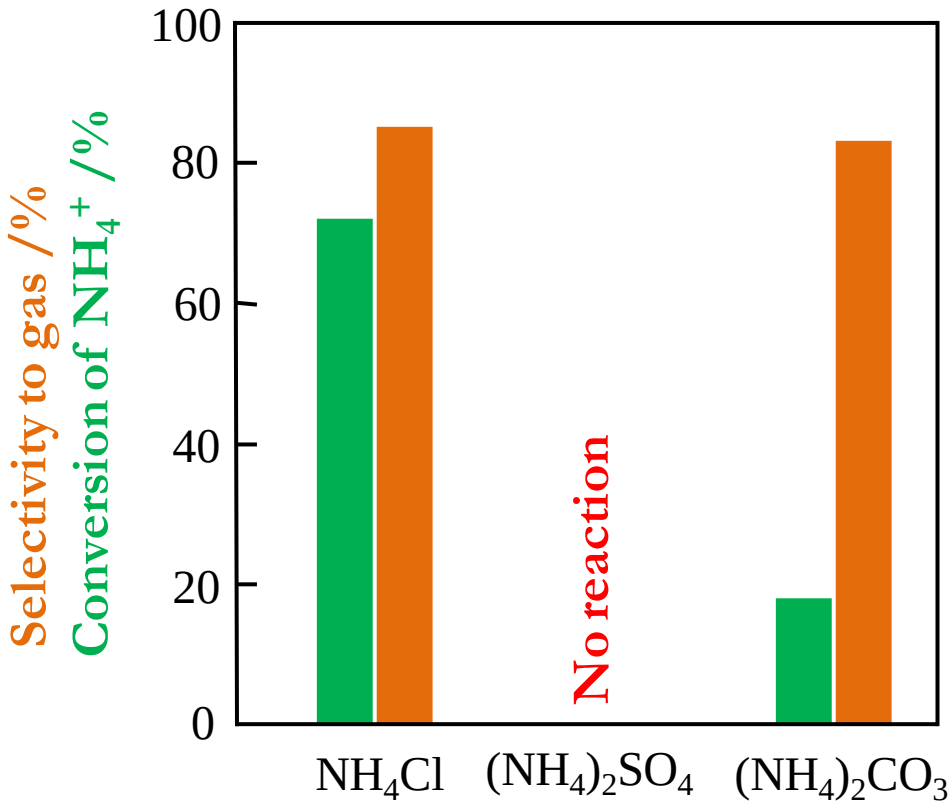


Fig. 3-2 Influence of Cl^- and SO_4^{2-} on the catalytic performance of Co_3O_4. (■) conversion of NH_4^+ and (■) selectivity to N_2 gas. Reaction conditions: NH_4^+, 10 mmol L^{-1} from NH_4Cl, $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$; reaction vol, 100 mL; Co_3O_4, 0.1 g; reaction temp. 60°C; O_3/O_2, total flow rate, 100 cm^3 min^{-1}; and reaction time, 6 h.

Khuntia et al. [6] reported that the decomposition rate of NH_4^+ in the reaction solution prepared from NH_4Cl was almost the same as that in the solution prepared from $(NH_4)_2SO_4$, where ozonation of NH_4^+ was carried out using microbubbles and without any heterogeneous catalyst which was around 19%. In contrast, the data show in Fig. 3-1 clearly shows that Cl^- has a significant positive effect on the decomposition rate of NH_4^+. The difference between Khuntia's experiment and present one was the presence of Co_3O_4 catalyst in the present experiment. This implies that the reaction of Cl^- or ClO_x^- with Co_3O_4 is involved in the catalytic cycle for the NH_4^+ oxidation.

Haag et al. have proposed a reaction mechanism for the ozonation of NH_4^+ in water in the presence of Br^- (homogeneous catalyst) without any heterogeneous catalyst under neutral to mild alkaline conditions [7]. In the reaction mechanism, Br^- is first oxidized with O_3 to form BrOH, then it reacts with NH_3 to form NH_2Br. Finally, NH_2Br reacts with O_3 to form NO_3^-, and at the same time, Br^- is regenerated in the solution. They have demonstrated that the first step (BrOH formation) is the rate-determining step. If the reaction similar to the Br^- system takes place in this study, though Cl^- is less reactive than Br^-, Cl^- may be oxidized with O_3 to form oxychloride ions including ClO^-, ClO_2^-, ClO_3^- and ClO_4^-. Since such oxychloride ions (ClO_x^-) are well-known to act as oxidizing reagent, it is possible that NH_4^+ is oxidized with formed ClO_x^- to produce N_2 and NO_3^-. Thus, in the next section (3.3.2), reaction behavior for the oxidation of Cl^- with O_3 in the absence of NH_4^+ is investigated.

3.3.2 Formation of ClO_x^- by oxidation of Cl^- with O_3 in the absence and presence of Co_3O_4 and catalytic cycle for NH_4^+ ozonation over Co_3O_4

As was demonstrated in 3.3.1, Cl^- was involved in the catalytic cycle for the catalytic ozonation of NH_4^+ over Co_3O_4. It is well known that ClO_x^- is relatively easily formed from Cl^- in water if strong oxidant is present and formed ClO_x^- act as an oxidizing agent. In the catalytic ozonation of NH_4^+ in the presence of Cl^-, ClO_x^- may form by the oxidation of Cl^- with O_3 and oxidize NH_4^+ to decompose it. Thus, here formation behavior of ClO_x^- by oxidation of Cl^- with O_3 in the absence of NH_4^+ was investigated. Figure 3-3 shows time dependences of the concentrations of ClO_x^- by the oxidation of Cl^- with ozone and no NH_4^+ in the absence and presence of Co_3O_4. Only hypochlorite (ClO^-) and chlorate (ClO_3^-) ions were formed in the presence as well as absence of the catalyst, and no formation of chlorite (ClO_2^-) and perchlorate (ClO_4^-) ions was observed regardless of the reaction time. In the absence of the catalyst, concentrations of both ClO^- and ClO_3^- linearly increased with the reaction time and there was no induction period. It is possible that ClO_3^- was formed by a successive reaction through ClO_2^- as an intermediate ($Cl^- \rightarrow ClO^- \rightarrow ClO_2^- \rightarrow ClO_3^-$). However, since ClO_2^- was not detected at all during the oxidation of Cl^- with O_3 and there was no induction period for the ClO_3^- formation, ClO_3^- as well as ClO^- must directly form by the reaction of Cl^- with O_3 (eqs. 3-1 and 3-2).

$$Cl^- + O_3 \rightarrow ClO^- + O_2 \qquad \text{(eq. 3-1)}$$

$$Cl^- + O_3 \rightarrow ClO_3^- \qquad \text{(eq. 3-2)}$$

Some studies also showed that the reaction of Cl^- with O_3 lead to the formation of ClO_3^- [8, 9], but they proposed that ClO_3^- was consecutively formed according to eqs. 3-1, 3-3, and 3-4.

$$ClO^- + O_3 \rightarrow ClO_2^- + O_2 \qquad \text{(eq. 3-3)}$$

$$ClO_2^- + O_3 \rightarrow ClO_3^- + O_2 \qquad \text{(eq. 3-4)}$$

Difference in the reaction conditions between the previous studies and present one may be the reason for the difference in the formation manner.

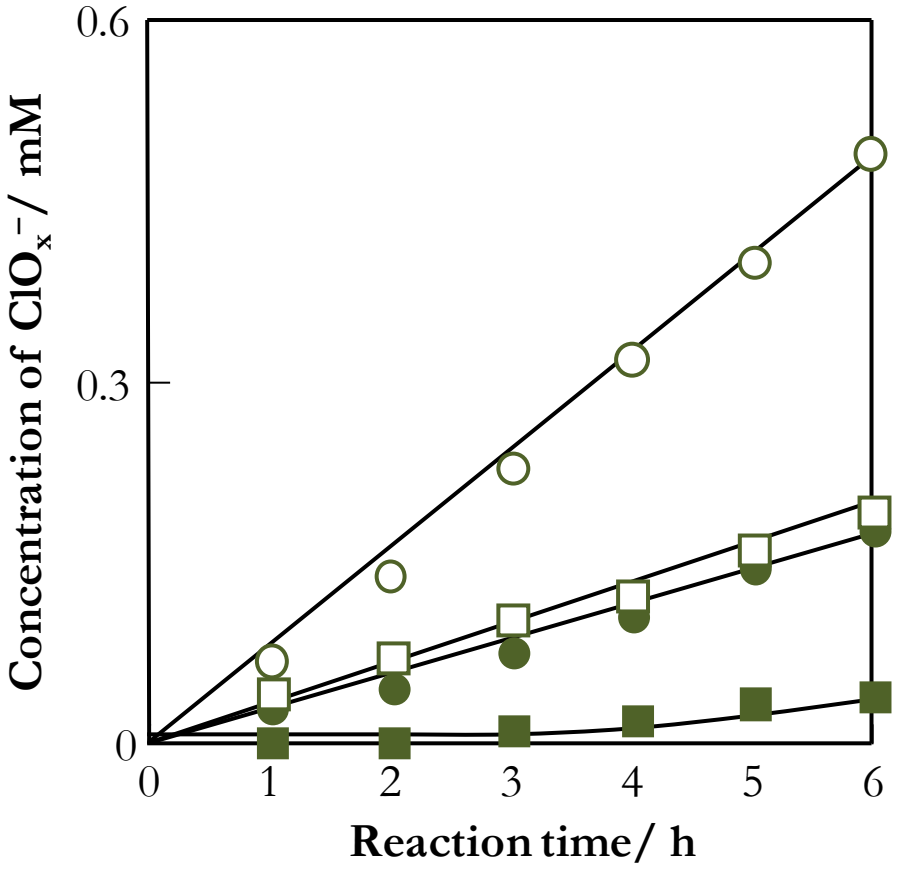


Fig. 3-3 Reaction of Cl^- with O_3 in the absence (open symbol) and presence of Co_3O_4 (close symbol). (□,■) ClO^- and (○,●) ClO_3^-. Reaction conditions: NaCl, 10 mmol L^{-1}; Co_3O_4, 0.1 g; reaction vol, 100 mL; reaction temp. 60°C; reaction time, 6 h; O_3/O_2, total flow rate, 100 cm^3 min^{-1}.

In the presence of Co_3O_4, only ClO^- and ClO_3^- were formed as the reaction in the absence of the catalyst. However, the concentrations of ClO^- and ClO_3^- were much lower than those in the absence of catalyst. In addition, it should be noted that there was an induction period for the ClO^- formation, suggesting that ClO^- was a secondary product, while ClO_3^- was the primary product formed with eq. 3-2. ClO^- might be formed from ClO_3^- with eq. 3-5.

$$ClO_3^- \rightarrow ClO^- + O_2 \qquad \text{(eq. 3-5)}$$

So far, the reaction of Cl^- with O_3 and the decomposition of ClO_3^- have been simply described as eqs. 3-1～3-5, but actual reaction of ozone in water is very complex and many kinds of intermediates are formed [10 – 12]. For example, ozone reacts with water as follows (eqs. 3-6～3-12).

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad \text{(eq. 3-6)}$$

$$O_3 + HO_2^- \rightarrow O_3^- + HO_2 \qquad \text{(eq. 3-7)}$$

$$O_3^- + H^+ \rightleftarrows HO_3 \qquad \text{(eq. 3-8)}$$

$$HO_3 \rightarrow \cdot OH + O_2 \qquad \text{(eq. 3-9)}$$

$$HO_2 \rightleftarrows H^+ + O_2^- \qquad \text{(eq. 3-10)}$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \qquad \text{(eq. 3-11)}$$

$$O_3 + \cdot OH \rightarrow HO_2 + O_2 \qquad \text{(eq. 3-12)}$$

If Cl^- is present in water, it is easy to image that the reactions are much more complex. Thus, at present, it is impossible to fully understand all the reactions of Cl^- with O_3 in water. However, the key component of the reaction is hydroxyl radical (•OH) due to very strong oxidant and it is frequently pointed out that hydroxyl radical is involved in the catalytic cycle for ozonation in water. In this study, hydroxyl radical must be involved for the formation of ClO^- and ClO_3^-. As Fig. 3-3 shows, the formation rates of ClO^- and ClO_3^- in the presence of Co_3O_4 were much slower than those in the absence of the catalyst. However, as shown in Fig. 2-3 in Chapter 2, the decomposition rate of NH_4^+ in the presence of Co_3O_4 was about ten times higher than that in the absence of the catalyst for the catalytic ozonation of NH_4^+. This contradiction suggests that Co_3O_4 promotes the reaction of NH_4^+ with ClO_x^-.

To confirm this speculation, reactions of NH_4^+ with ClO_x^- (x = 1, 2, 3, and 4) in the presence and absence of Co_3O_4 were conducted. Figure 3-4 provides the reaction for the reactions of NH_4^+ with ClO_x^- (x = 1, 2, 3, and 4) for 3 h. In these reactions, O_3 was not fed into the reactor. The reaction proceeded in the presence of Co_3O_4 regardless of the kinds of ClO_x^-. The reaction rate for ClO_2^- was the highest among ClO_x^-, but its contribution may not be significant because ClO_2^- was not formed by the reaction of Cl^- with O_3. In contrast to the reaction in the presence of Co_3O_4, no reaction occurred with ClO^-, ClO_2^-, and ClO_3^- in the absence of the catalyst. These results strongly support our speculation that Co_3O_4 acts as a catalyst for the reaction of NH_4^+ with ClO_x^-, but not for the formation of ClO_x^-. Based on them, the role of Cl^- and Co_3O_4 for the catalytic ozonation of NH_4^+ is proposed as Fig. 3-5.

Since catalyst surface often acts as radical scavenger, the concentration of radical species like •OH must be lower in the presence of Co_3O_4 than the absence of one. It is plausible that the slow rate for the formation of ClO^- and ClO_3^- in the presence of Co_3O_4 (Fig. 3-3) was due to the low concentration of the radical species that oxidize Cl^-.

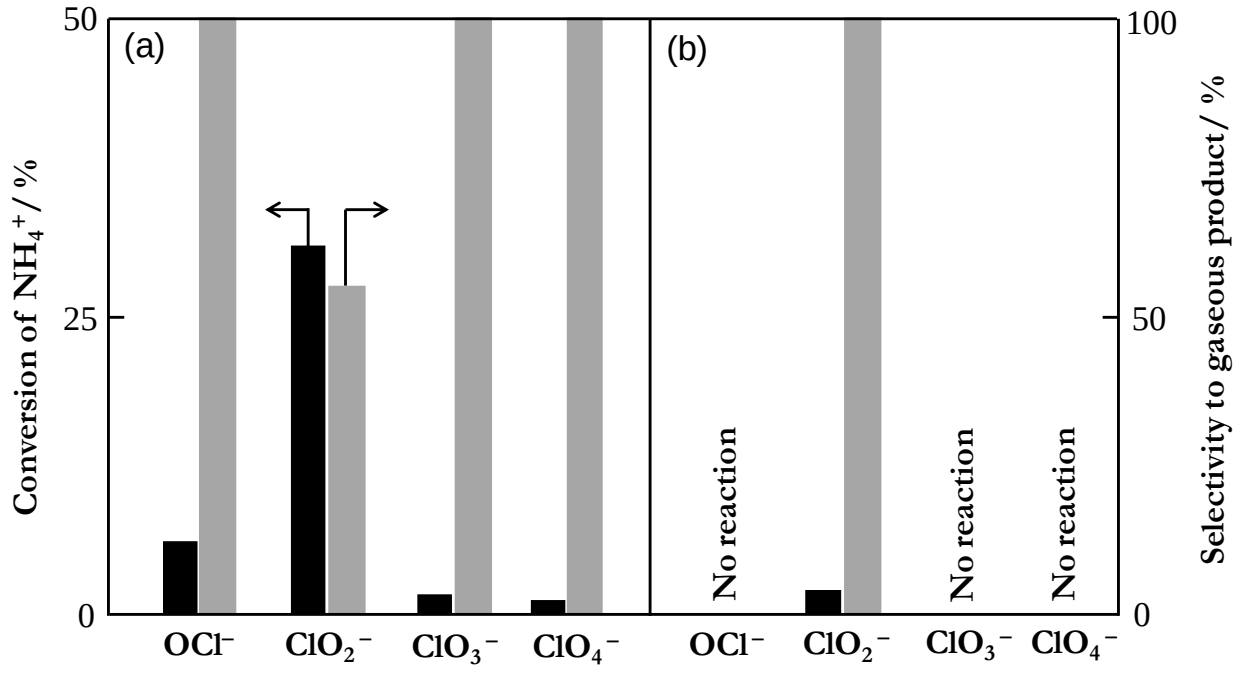
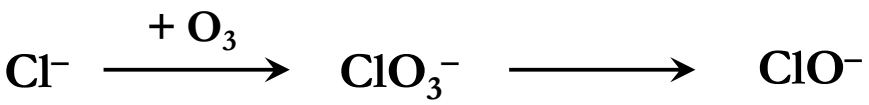


Fig. 3-4 Reaction of NH_4^+ with ClO_x^- (x = 1, 2, 3 and 4) in the absence of O_3. (a) Co_3O_4 and (b) No catalyst. (■) conversion of NH_4^+ and (■) selectivity to gaseous products. Reaction conditions: NH_4Cl, NaOCl, $NaClO_2$, $KClO_3$, and $KClO_4$, 10 mmol L^{-1}; reaction vol, 100 mL; Co_3O_4, 0.1 g; reaction temp. 60°C; O_2, total flow rate, 100 cm^3 min^{-1}; and reaction time, 3 h.

Aqueous phase in the absence of a catalyst



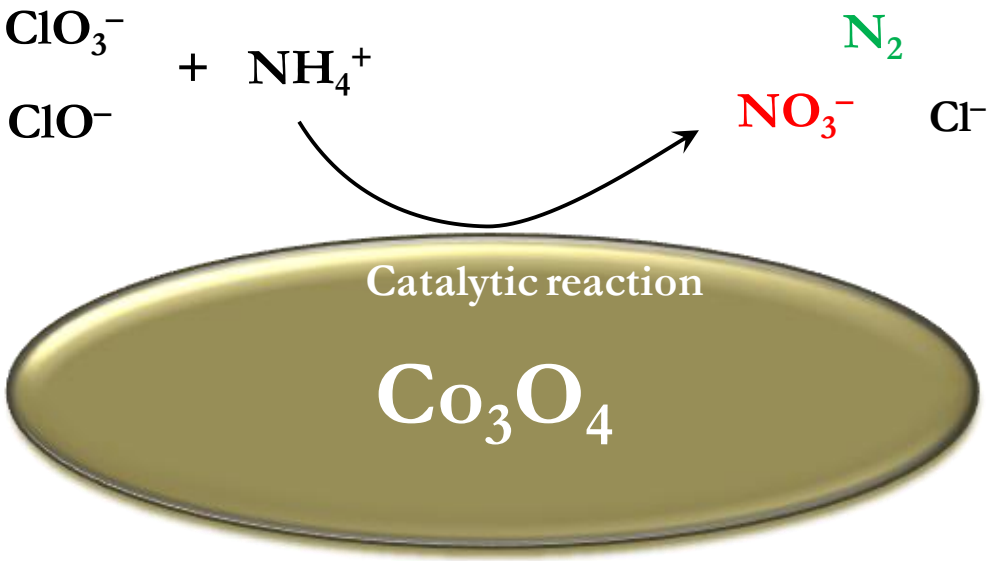


Fig. 3-5 Role of Cl^- and reaction mechanism of catalytic ozonation of NH_4^+ over Co_3O_4

3.3.3 Reason for high activity of Co_3O_4

As Fig. 2-3 and Table 2-2 demonstrate, Co_3O_4 gave the highest activity for the catalytic ozonation of NH_4^+ among insoluble and less soluble catalysts. Al_2O_3 and SnO_2 were basically inactive for the reaction because their conversions were almost the same as that without catalyst. Mn_3O_4 showed activity, but it was much lower than that of Co_3O_4. Two plausible reasons can be considered for the high activity of Co_3O_4 based on the reaction mechanism proposed in Fig. 3.5. One is that Co_3O_4 is highly active for the catalytic reaction of NH_4^+ with ClO_x^- on its surface and another is that Co_3O_4 has low ability to scavenge active radical species formed by the reaction of O_3 with water. Figure 3-6 shows catalytic activities for the reaction of NH_4^+ with ClO^- and ClO_3^-over Co_3O_4, Al_2O_3, Mn_3O_4, and SnO_2. It is obvious that the activity of Co_3O_4 for the reactions was comparable to those of Al_2O_3 and Mn_3O_4. Therefore, the latter is more plausible, but more investigation should be necessary to confirm this hypothesis.

As proposed in Fig 3-5 which confirmed in Fig. 3-3 that ClO_x^-, namely ClO^- and ClO_3^-, was formed in aqueous solution due to the ozonation of Cl^- with ozone in the absence of NH_4^+. And from Fig. 3-4, in the absence of ozone Co_3O_4 promotes the reaction between NH_4^+ and ClO_x^-. In the catalytic ozonation of NH_4^+ in the presence of Co_3O_4, ClO^- and ClO_3^- were not detected until NH_4^+ was completely decomposed as showed in Fig. 3-7. During the catalytic ozonation, ClO_x^- reacted with NH_4^+ to form monochloramine which further react with ozone producing NO_3^-. On complete ozonation of monochloramine solution, no other products including ClO_3^- were detected except NO_3^- and Cl^- since monochloramine react faster than free chlorine at pH < 7.0 [8].

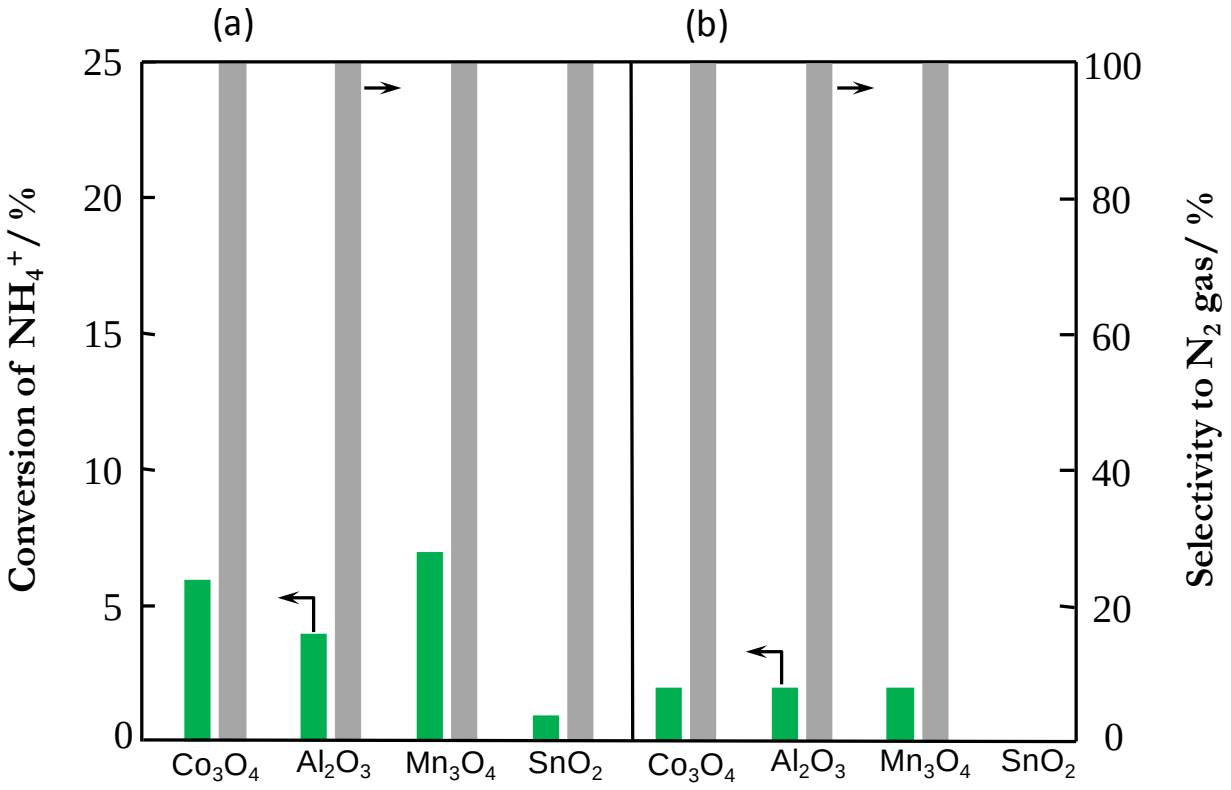


Fig. 3-6 Comparison of catalytic activities for reaction of NH_4^+ with (a) ClO^- and (b) ClO_3^- in the absence of O_3 ( ) conversion of NH_4^+ and ( ) selectivity to N_2 gas. Reaction conditions: NH_4Cl, NaOCl, and $KClO_3$, 10 mmol L^{-1}; cat., 0.1 g; reaction vol., 100 mL; reaction temp. 60°C; reaction time, 3 h; and O_2 total flow rate, 100 cm^3 min^{-1}.

However, since formation of ClO^- and ClO_3^- was observed during catalytic ozonation of NH_4^+ after NH_4^+ completely decomposed, it means that ClO^- and ClO_3^- clearly acted as an oxidant during the catalytic ozonation of NH_4^+. The formation of ClO_x^- during the ozonation of water containing chlorine has caused a growing concern about possible health significance in drinking water. ClO_3^- and ClO_2^- have been shown to cause hemolytic anemia and methaemoglobin formation in laboratory animals [13, 14] and

ClO_4^- can affect the thyroid gland [15]. Nevertheless, ClO_x^- containing drink water can be treated by applying catalyst.

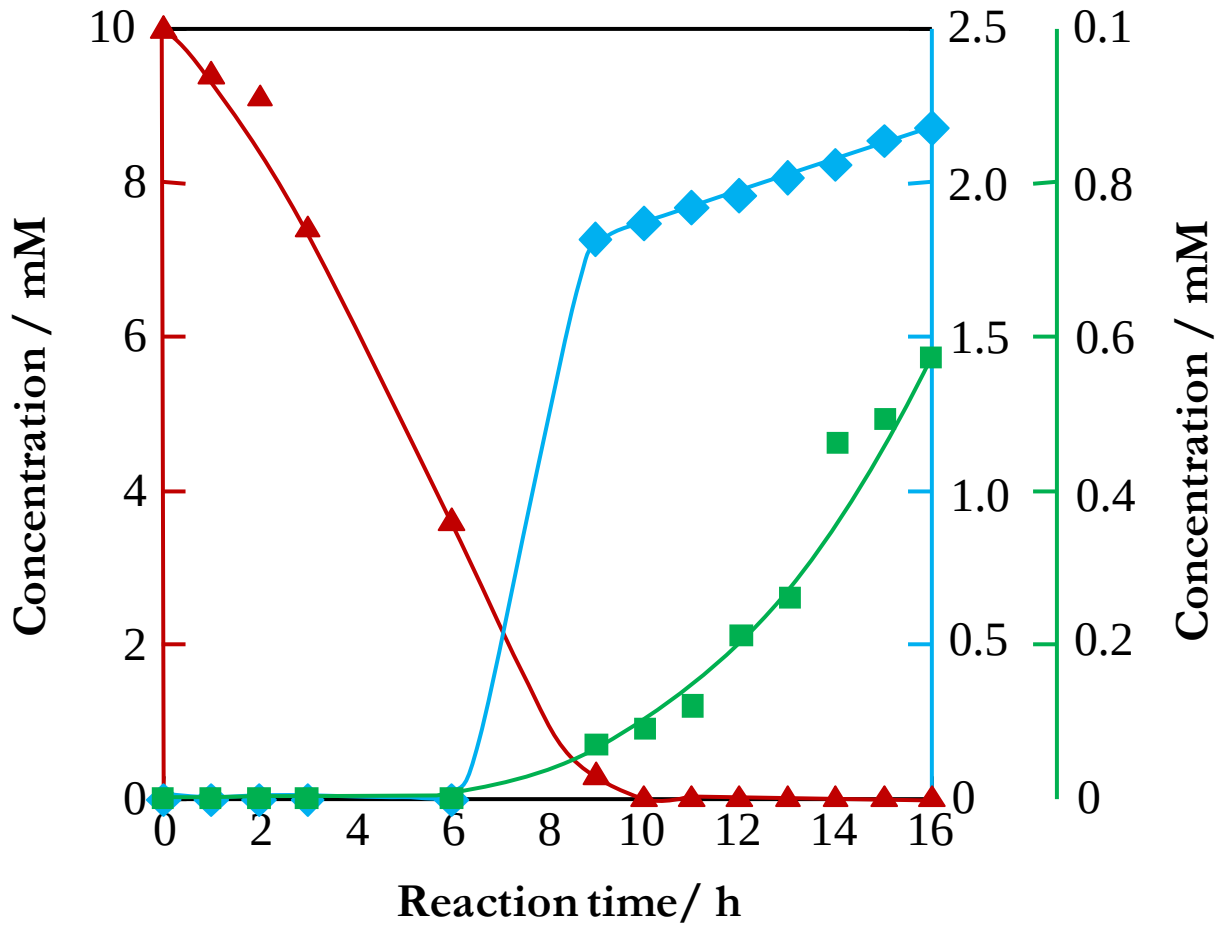


Fig. 3-7 Formation of ClO_x^- during the catalytic ozonation of NH_4Cl over Co_3O_4 catalyst. (▲) concentration of NH_4^+, (■) concentration of ClO^-, and (◆) concentration of ClO_3^-. Reaction conditions: NH_4Cl, 10 mmol L^{-1}; cat. Co_3O_4, 0.1 g; reaction vol., 100 mL; reaction temp. 60°C; reaction time, 16 h; and O_3/O_2 total flow rate, 100 cm^3 min^{-1}.

3.3.4 Catalyst properties controlling selectivity

In this section, the catalyst properties that control the selectivity will be discussed. Figure 3-8 shows a plot of the selectivities to N_2 gas as a function of standard enthalpy change of formation per mol of oxygen atom (ΔH°_f) of the metal oxides. The selectivity to N_2 gas was low for the catalysts with a large value of ΔH°_f, like MgO and ZnO, and increased as ΔH°_f decreased. The catalysts showing moderate to high selectivity to N_2 gas had a value of $\Delta H^\circ_f \leq 60$ kcal (mol of O)$^{-1}$.

In the catalytic oxidation of NH_4^+, two nitrogen intermediate species (NH_x) must react to form gaseous products (bimolecular reaction). On the other hand, NO_3^- is formed when one nitrogen species reacts with active oxygen (O*) (monomolecular reaction), which may form when ClO^- and ClO_3^- react with the catalyst surface. Thus, the ratio of the surface densities of the nitrogen intermediate species and active oxygen atoms ($[NH_x]/[O^*]$) would determine the selectivity. If $[NH_x]/[O^*]$ is high, namely, $[NH_x]$ is high or [O*] is low, the selectivity to gaseous products becomes high. It is reasonable that ΔH_f indicates the bond strength between the metal cation (M) and lattice oxygen (M-O) in the metal oxides. Thus, the metal oxides with small ΔH°_f values have weak M-O bond strengths. If this relationship can be extended to the bond strengths between M on the surface and O* formed by the reaction of O_3 with the surface, O* formed on the catalysts with small ΔH°_f values would be unstable, meaning it is highly active. In other words, O* will be consumed and removed from the surface rapidly due to its high reactivity. As a result, the surface density of the O* is low for the catalysts with small ΔH°_f values, leading to the high selectivity to gaseous products. It can be considered that this is one of the reasons for the high selectivity to gaseous products over catalysts like Co_3O_4. If the hypothesis that

the [NH_x]/[O*] ratio on the surface determines the selectivity is true, the concentration of NH_4^+ in water must affect the selectivity. To demonstrate this, the catalytic ozonation of NH_4^+ over Co_3O_4 using an aqueous solution of NH_4Cl with 5 mmol L^{-1} was carried out. The result showed that the selectivity to gaseous products at 6 h was 66%, which was lower than that with 10 mmol L^{-1} NH_4Cl solution (85%). This result supports the reaction mechanism proposed above.

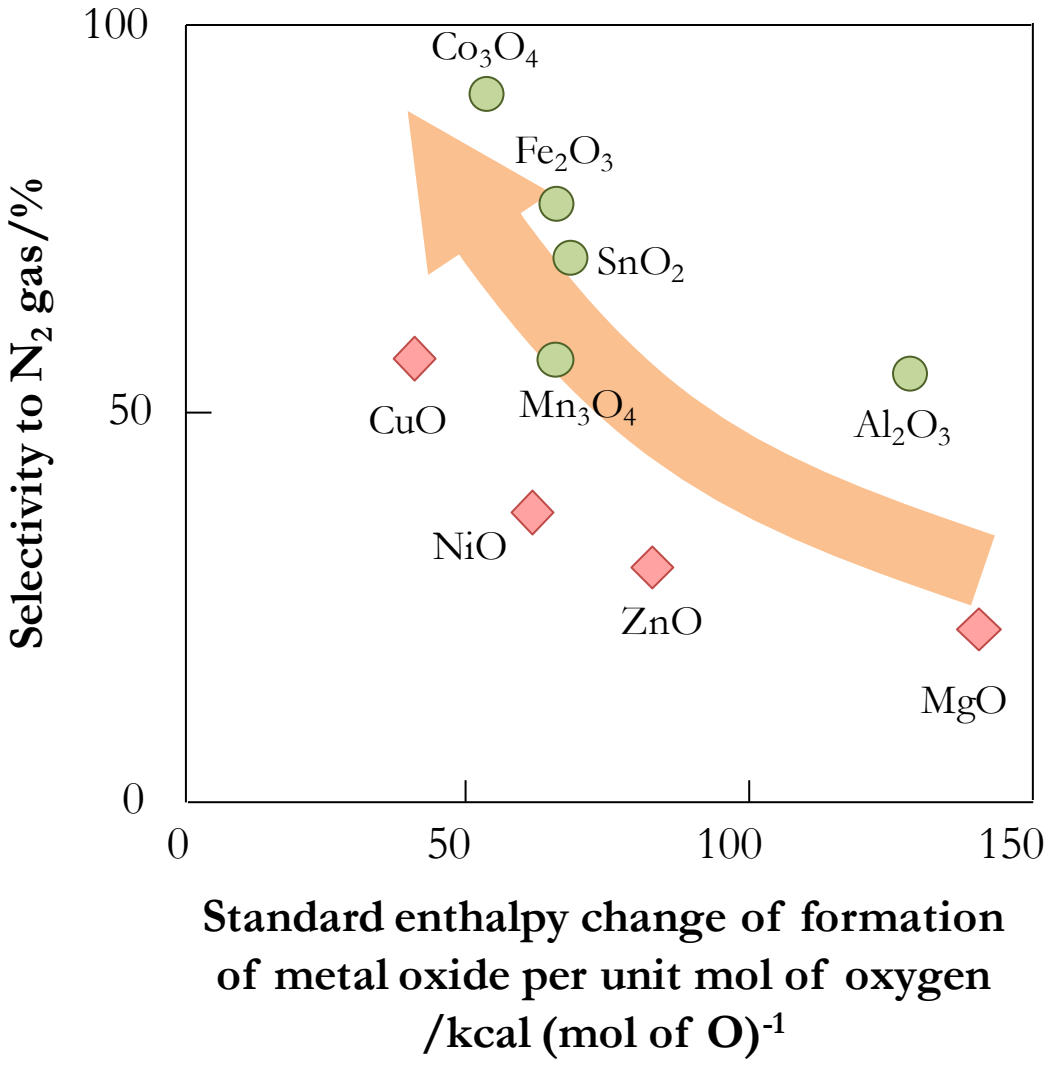


Fig. 3-8 Correlation between selectivity to gaseous products and the standard enthalpy change of formation per mol of one oxygen atom (ΔH°_{f}) of the metal oxide catalyst. (○) catalysts with low solubility and (◇) catalysts with high solubility.

3.4 Conclusion

Cl^- was indispensible for the catalytic ozonation of NH_4^+ in water over Co_3O_4 and the reaction did not proceed at all in the absence of Cl^- even in the presence of Co_3O_4. The reaction of Cl^- with O_3 formed ClO^- and ClO_3^-, but did not form ClO_2^- and ClO_4^-. The formation rates of ClO^- and ClO_3^- with Co_3O_4 were much lower than those without the catalyst. However, Co_3O_4 significantly promoted the reaction of NH_4^+ with ClO^- and ClO_3^-, while these reactions rarely proceeded without any catalyst. Thus, the catalytic role of Co_3O_4 was the promotion for the reaction of NH_4^+ with ClO^- and ClO_3^-. Since the reaction rates for the reaction of NH_4^+ with ClO^- and ClO_3^-over Co_3O_4 were comparable to those over less active catalysts, the reason for the high activity of Co_3O_4 in the catalytic ozonation of NH_4^+ may be that Co_3O_4 had low ability to scavenge active radical species forming ClO^- and $ClO_3^-$from Cl^-. The selectivity to gaseous products were strongly related to the standard enthalpy changes of formation per mole of oxygen atom (ΔH°_f) of the metal oxide, and the catalysts with low ΔH°_f value, like Co_3O_4 showed high selectivity to N_2 gas probably due to a low surface density of the active oxygen formed upon the reaction of O_3 with the catalyst surface.

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Chapter 4

Enhancement of Catalytic Activity of Cobalt Oxide for Catalytic Ozonation of Ammonium Ion in Water with Repeated Use

4.1 Introduction

Heterogeneous catalysts usually become deactivated with prolonged use due to sintering, changes in the crystalline phases and surface structures, catalyst poisoning and so on [1]. Thus, enormous time and efforts have been devoted to develop highly active and selective catalysts with long lifetimes, namely non-deactivated catalysts. This means that, if the catalytic performance of a heterogeneous catalyst increases with each reuse or with a prolonged reaction time, the catalysts would be extremely beneficial and scientifically interesting. However, catalysts with these special properties are rare. Needless to say, catalysts active for the catalytic ozonation are no exception. In fact, as Li et al. [2] reported, catalytic activity of the cobalt-doped red mud catalyst decreased after four times reuse for degradation of a drug compound (bezafibrate) by catalytic ozonation. Catalyst deactivation similar to [2] was also observed for catalytic degradation of phenol with ozone over zerovalent iron [3], in which the catalytic activity was severely depleted after four consecutive uses.

In contrast, some studies on the catalytic ozonation of organic compounds demonstrate that the high catalytic performances are maintained even after several times reuse or long-term usage. Gruttadauria et al. [4] reported that supported cobalt oxide catalysts, namely CoO_x/Al_2O_3 and CoO_x/Al_2O_3-BaO, showed excellent catalytic performances for phenol oxidation with ozone after it being reuse for three consecutive reactions, despite some cobalt species were leached out from the catalyts into the reaction solution during the reactions. Other papers also report the stable catalytic performances of ZnO [5], Fe_3O_4 [6], CeO_2/active carbon [7], and Ni/active carbon [8] for the catalytic ozonation of organic compounds in water. In some special but rare cases, catalytic activity

increases by repeated use for the catalytic ozonation. It was reported that Ru/CeO_2 exhibited enhanced activity after for four times reuse in the catalytic ozonation of succinic acid [9]. Similar enhancement in the catalytic activity by repeated use was also observed for the catalytic ozonation of pyruvic acid over perovskite [10].

In Chapters 2 and 3, Co_3O_4 was demonstrated to be the best catalyst for the catalytic ozonation of NH_4^+ in term of activity, selectivity, and stability, if Cl^- was present in the reaction solution [11]. In this chapter, the author wishes to report the unusual catalytic properties of Co_3O_4 for the catalytic ozonation of NH_4^+, that is, its catalytic activity is significantly enhanced by repeated use for the reaction with a batch-type reactor, whereas other metal oxide catalysts including SnO_2, Al_2O_3 and Mn_5O_8, which have high stability and durability, show little or no activity enhancement with repeated use. In addition, from catalytic data for Co_3O_4 treated under various conditions prior to the catalytic ozonation of NH_4^+ and from changes in the physical and chemical properties of Co_3O_4 with repeated use, the reason for the activity enhancement will be discussed .

4.2 Experiment

4.2.1 Catalysts

Metal oxide catalysts, including Co_3O_4, Al_2O_3, Mn_5O_8, and SnO_2 were prepared in the same manner as those described in Section 2.2.1.

4.2.2 Repeated use of catalyst for catalytic ozonation of NH_4^+ in water

Repeated use of the catalyst for the catalytic ozonation of NH_4^+ was conducted as follows. For the first use, catalytic ozonation of NH_4^+ in water was performed in the same

manner to those described in Section 2.2.3. Catalyst powder (0.1 g) was added to an aqueous solution of NH_4Cl (100 mL, 10 mmol L^{-1}), and the resulting suspension was heated at 333 K with vigorous stirring in a flow of an O_3/O_2 mixture (1.88 mmol L^{-1} of O_3). After 6 h, the concentrations of NH_4^+, NO_3^-, and NO_2^- in the solution were analyzed to evaluate the catalytic performance for the first use. The catalyst collected by filtration was washed with distilled water and dried at 373 K overnight (Fig. 4-1). For the second use, the experiment was conducted with the same manner as that for the first use.

In case of Co_3O_4, since all NH_4^+ was decomposed at 6 h for the third use (second reuse), it was not confirmed how far the catalytic activity of Co_3O_4 was enhanced by repeated use. Thus, the activity enhancement of Co_3O_4 for the catalytic ozonation of NH_4^+ was evaluated with high concentration NH_4Cl (30 mmol L^{-1}) and 0.15 g of the catalyst. The reaction was conducted by the similar manner to those mentioned above, but the reactions were repeated up to ten times.

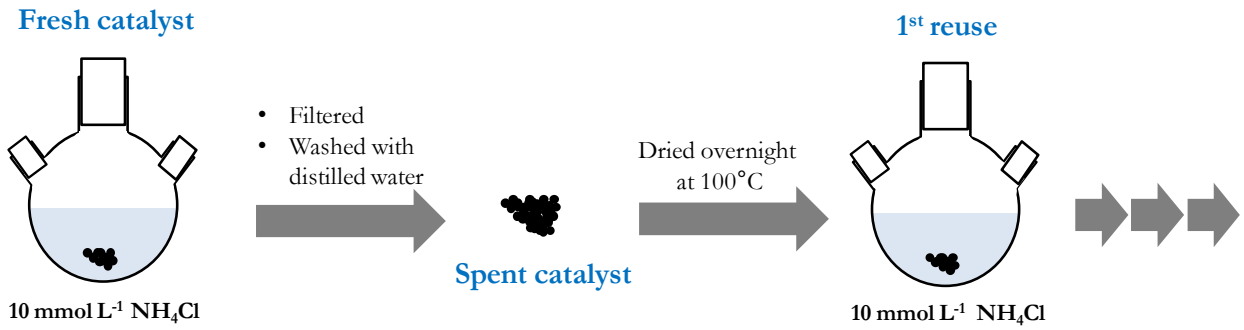


Fig. 4-1 Procedure for repeated use of catalysts.

4.2.3 Pretreatment of Co_3O_4 prior to catalytic ozonation of NH_4^+

Co_3O_4 (0.1 g) was added to an aqueous solution of NH_4Cl (100 mL, 10 mmol L^{-1}), and the resulting suspension was heated at 333 K with stirring. The O_3/O_2 mixture was not flowed into the suspension during the treatment. After 6 h, the solid was collected by filtration, washed with distilled water, and dried at 373 K overnight. The treatment was then repeated for two more times. After the treatment, the obtained catalyst was afforded to the catalytic ozonation of NH_4^+ in water.

Treatment of Co_3O_4 in an aqueous solution of $(NH_4)_2SO_4$ or pure water was conducted using a procedure similar to that of the treatment in an NH_4Cl solution, but the O_3/O_2 mixture was flowed into the suspension during the treatment.

4.2.4 Characterizations

4.2.4.1 XRD

Powder X-ray patterns of samples were obtained on a Rigaku powder diffractometer (RINT-ULTIMA III/NF/B) using Cu Kα radiation (λ = 0.154 nm, 40 kV, and 40 mA) at a scanning rate of 0.02° in a 2θ range of 4°–80°.

4.2.4.2 N_2 adsorption-desorption isotherm

Specific surface area was calculated with the BET equation, which obtained from N_2 adsorption/desorption isotherm at 77 K (Belsorp, Japan Inc.). Prior to the measurement, samples were pretreated under N_2 flow for 3 h at 473 K.

4.2.4.3 FT – IR

The IR spectra of Co_3O_4 were obtained on a Jasco FT/IR – 230x with a resolution of 2 cm^{-1} in the range of 600 to 4000 cm^{-1}. Each sample powder (1% wt) was diluted with KBr powder and subjected to 6 tons pressure for 30 seconds. Prior to the FTIR measurement, the samples powder was pretreated under a He flow for 1 h at 373 K.

4.3 Result and Discussion

4.3.1 Changes in catalytic performance by repeated use.

Figure 4-2 shows the conversion and selectivity to gaseous compounds for the catalytic ozonation of NH_4^+ over Co_3O_4 after each use. For comparison, catalytic data for Al_2O_3, Mn_5O_8 and SnO_2, which are the least soluble MO_x in the reaction solution [1], are also shown in Fig. 3-2. Fresh Co_3O_4 showed high conversion and high selectivity to gaseous compounds. The conversion increased with repeated use, and a slight change in the selectivity was observed. During the second reuse, all of the NH_4^+ decomposed within 6 h. On the other hand, fresh Al_2O_3 and Mn_5O_8 exhibited only low catalytic activities and did not show any activity enhancement, and they became deactivated after the first use. As for SnO_2, the conversion of NH_4^+ increased with each use but only a little.

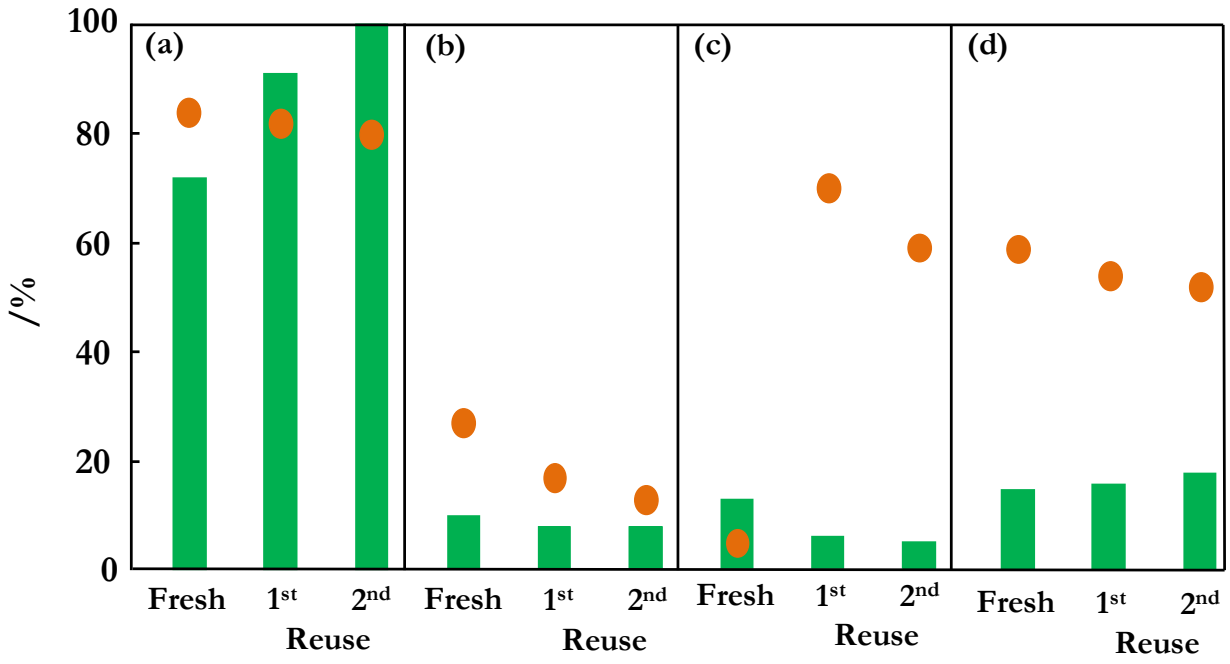


Fig. 4-2 Conversion of NH_4^+ (■) and selectivity (●) for catalytic ozonation of NH_4^+ in water to N_2 gas over fresh and reused samples of (a) Co_3O_4, (b) Al_2O_3, (c) Mn_3O_4 and (d) SnO_2.

This acceleration effect of Co_3O_4 for the repeated use was significantly influenced by the calcination temperature of Co_3O_4. As shown in Fig. 3-2, the activity of Co_3O_4 calcined at 450°C was enhanced by the repeated use. However, when Co_3O_4 was calcined at 650°C, activity was not accelerated for the repeated use and rather steady by the repeated use, which is around 26% (Fig. 4-3).

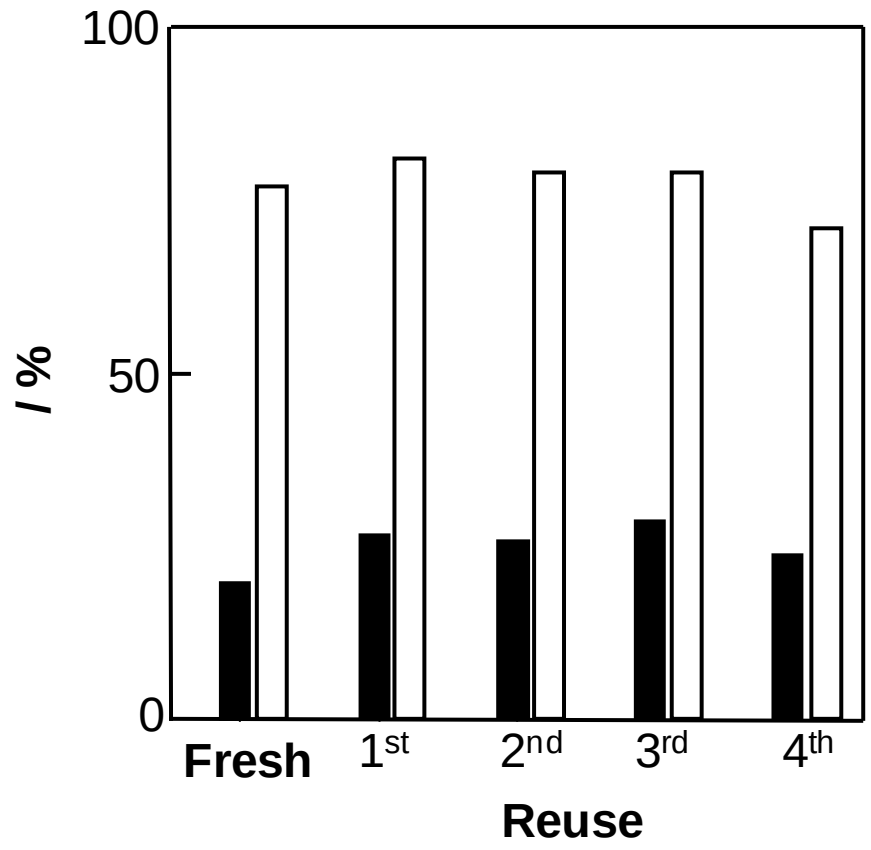


Fig. 4-3 Conversion of NH_4^+ (■) and selectivity to N_2 gas (□) of fresh and reused Co_3O_4 calcined at 650°C for catalytic ozonation of NH_4^+ in water.

Because the conversion of NH_4^+ reached 100% over Co_3O_4 calcined at 450°C during the second reuse under the reaction conditions in Fig. 4-2, the catalytic performance of Co_3O_4 for each use was evaluated using a high concentration of NH_4^+ ion (30 mmol L^{-1}) to suppress the initial conversion. As a result, it can be known how far the catalytic activity of Co_3O_4 was enhanced by repeated use. Under these reaction conditions, fresh Co_3O_4 showed 30% conversion (Fig. 4-4), and the conversion increased with each reuse up to nine times, reaching 80%, with high selectivity.

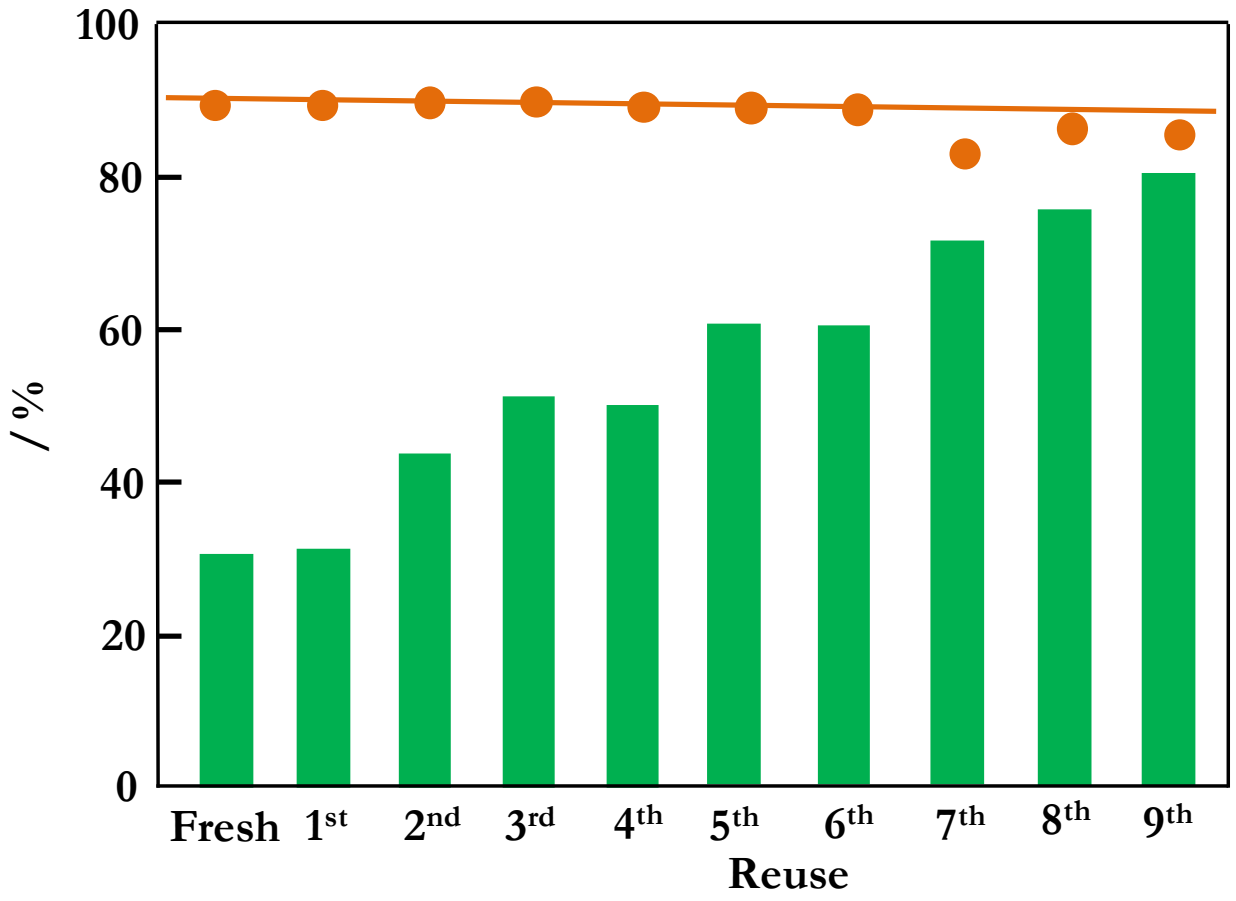


Fig. 4-4 Changes in the catalytic performance of Co_3O_4 reused up to nine times for the catalytic ozonation of high concentrations of NH_4^+. (■) Conversion of NH_4^+ and (●) selectivity to N_2 gas.

4.3.2 Changes in physical properties of Co_3O_4 by repeated use.

One possible reason for the activity enhancement of Co_3O_4 is structural and morphological changes by the repeated use. Thus, the change in the physical properties of Co_3O_4 by the repeated use was investigated. Fig 4-5 shows powder X-ray diffraction (XRD) pattern of fresh Co_3O_4 and that of the catalyst after using it nine times. All of the diffraction lines for the fresh and spent catalysts corresponded to those of Co_3O_4. Thus,

changes in crystalline phase did not cause the activity enhancement. The crystallite sizes of fresh and spent catalysts calculated based on Scherrer's equation were 25 nm.

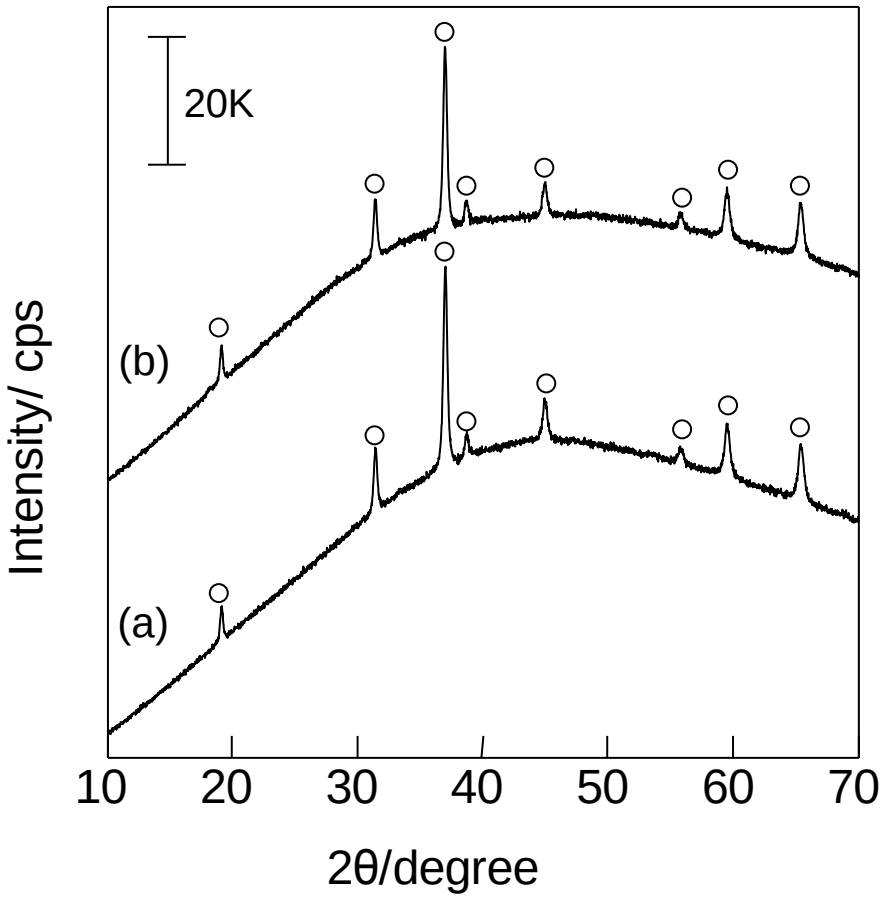


Fig. 4-5 Powder XRD patterns of (a) fresh Co_3O_4 and (b) Co_3O_4 reused nine times. (○) are the peaks.

In addition, the surface area of Co_3O_4 reused nine times was smaller (8 m^2 g^{-1}) than that of the fresh one (20 m^2 g^{-1}). Therefore, the change in the surface structure of Co_3O_4 or modification of the Co_3O_4 surface with reactants and products under the reaction conditions must have cause the increase in the activity with each uses.

4.3.3Influence of pretreatment of Co_3O_4 for catalytic performance in catalytic ozonation of NH_4^+

To elucidate the crucial compound in the reaction solution causing the activity enhancement, Co_3O_4 was treated with various aqueous solutions and under different conditions prior to the catalytic ozonation of NH_4^+. Table 4-1 summaries the catalytic performances of untreated Co_3O_4 and those pretreated. Untreated Co_3O_4, namely fresh Co_3O_4, showed 72% conversion at 6 h for the catalytic ozonation of NH_4^+ (Entry 1). When Co_3O_4 was pretreated with aqueous solutions of NH_4Cl at 333 K but with no O_3, the activity increased (Entry 2). In addition, treatment of Co_3O_4 in the aqueous solutions with NH_4^+ and no Cl^- lead to an increase in the activity (Entry 3) similar to Entry 2. The results clearly indicate that O_3 and Cl^- are not crucial for the activity enhancement. On the other hand, when Co_3O_4 was treated in pure H_2O at 333 K, no activity enhancement occurred (Entry 4). Therefore, it is concluded that NH_4^+ in the reaction solution was essential for the activity enhancement of Co_3O_4 with repeated use. In other words, the reaction of the Co_3O_4 surface with NH_4^+ caused the activity enhancement, because there was no change in the bulk crystalline structure of the catalyst.

Table 4-1 Catalytic performance of untreated and pretreated Co_3O_4

Entry	Conditions	Conversion of NH_4^+ (%)	Selectivity to gaseous (%)
1	untreated[a]	72	85
2	NH_4Cl[b]	95	85
3	$(NH_4)_2SO_4$[c]	98	84
4	only H_2O[d]	77	84

[a]Fresh Co_3O_4 without any pretreatment.
[b]Fresh Co_3O_4 was treated twice with an aqueous solution of NH_4Cl (10 mmol L^{-1}) without O_3 at 333 K for 6 h prior to catalytic ozonation of NH_4^+.
[c]Fresh Co_3O_4 was treated twice with an aqueous solution of $(NH_4)SO_4$ (10 mmol L^{-1}) with O_3 at 333 K for 6 h prior to catalytic ozonation of NH_4^+.
[d]Fresh Co_3O_4 was treated twice with pure water without O_3 at 333 K for 6 h prior to catalytic ozonation of NH_4^+.

If modification of the Co_3O_4 surface during the catalytic ozonation of NH_4^+ caused the activity enhancement of Co_3O_4 by repeated use, it must be confirmed by physicochemical characterization. Figure 4-6 shows IR spectra for fresh Co_3O_4 and after reusing it nine times, which was obtained from the experiment in Fig. 4-4. These spectra were acquired by using a KBr method, and the sample disks were pretreated in a He flow at 373 K for 1 h before acquiring IR spectra. In the spectra for the fresh Co_3O_4 catalyst, two bands at 3365 and 1520 cm^{-1} were assigned to be stretching and bending modes of surface hydroxyl groups, respectively (Fig. 4-6(a)). In the spectra for the Co_3O_4 reused nine times, new bands at 2956, 2921 and 2852 cm^{-1} were observed (Fig. 4-6(b)). Since the IR spectrum for NH_4Cl diluted with KBr (Fig. 4-7) was quite different from that for the Co_3O_4 reused nine times, the new IR bands observed in the spectra for the Co_3O_4 reused nine times were not due to NH_4Cl simply deposited on the Co_3O_4surface.

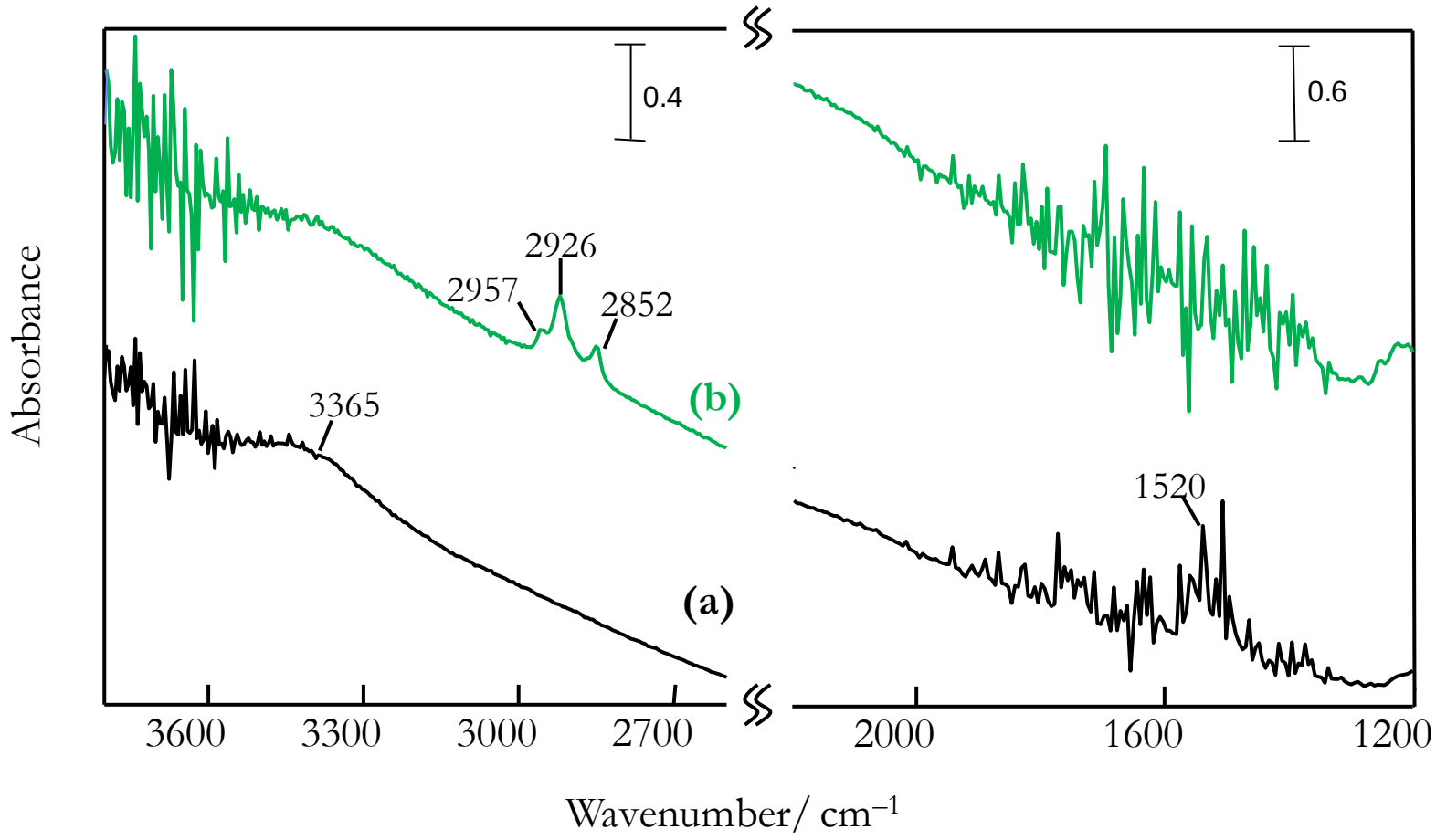


Fig. 4-6 IR spectra for (a) fresh Co_3O_4 and (b) Co_3O_4 reused nine times for catalytic ozonation of NH_4^+ in water. IR spectra were acquired by using a KBr method after pretreatment in He at 373 K for 1 h.

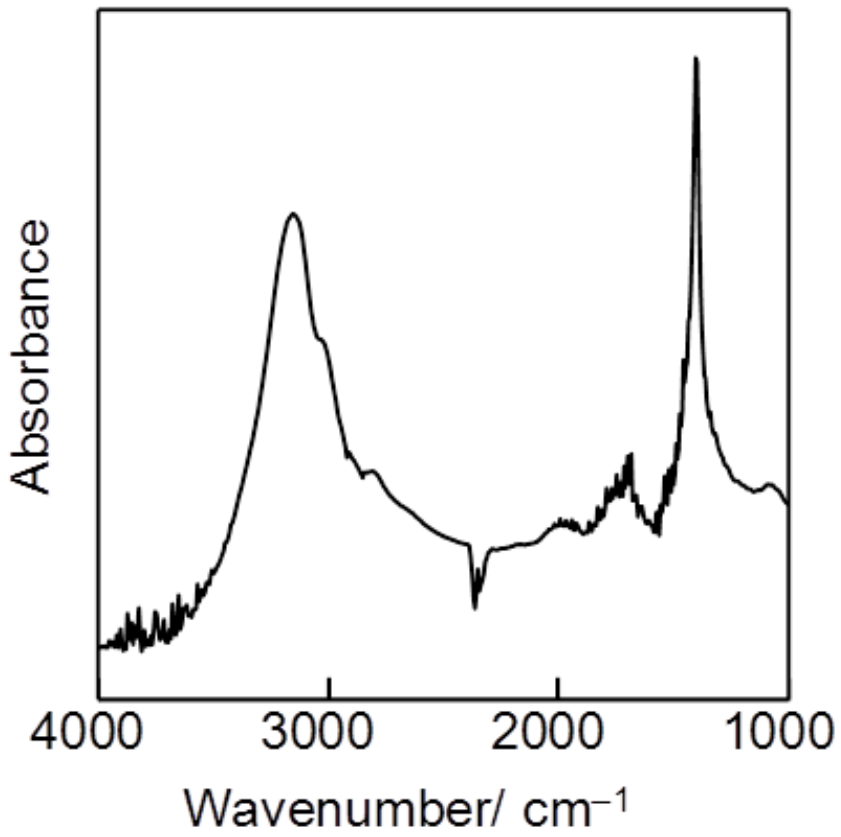
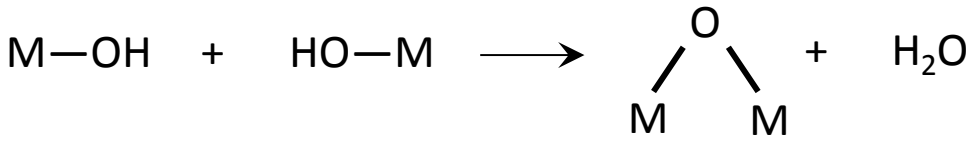


Fig. 4-7 IR spectrum for NH_4Cl. The IR spectrum was acquired by using a KBr method, and the sample disk was treated in He flow at 373 K for 1 h before acquisition of the spectrum.

According to the IR spectra of Co_3O_4 calcined at 450°C, there was a change in its catalyst surface in which $–NH_x$ groups was formed (Fig. 4-6) which led to catalytic activity enhancement by repeated use for catalytic ozonation of NH_4^+. As it mentioned in Chapter 3, Co_3O_4 suppressed the formation of $ClO^–$ and $ClO_3^–$, but promoted the reaction between $ClO_x^–$ and NH_4^+. In repeated use, the presence of $–NH_x$ groups on the surface of Co_3O_4 catalyst, will reduce the role of Co_3O_4 in suppressing the formation of $ClO_x^–$. With more

ClO_x^- formed the more NH_4^+ will be decomposed. In addition, the surface of Co_3O_4 much more reactive with $–NH_x$ groups formed on it compared to the surface of Co_3O_4.

As Fig 4-3 demonstrates, Co_3O_4 calcined at 650°C did not show any activity enhancement, whereas Co_3O_4 calcined at 300°C exhibited a great enhancement in the catalytic activity by the repeated use (data not shown) though the catalyst was a little soluble in the solution. Calcination of metal oxides at high temperature often brings about thermal condensation of surface hydroxyl groups along with dehydration (eq. 4-1).



(4-1)

As a result, metal oxide calcined at high temperature has only a few surface hydroxyl groups. In fact, Co_3O_4 calcined at 650°C had less number of surface hydroxyl groups than those at 300 and 450°C, which were confirmed by using IR spectroscopy (Fig. 4-8).

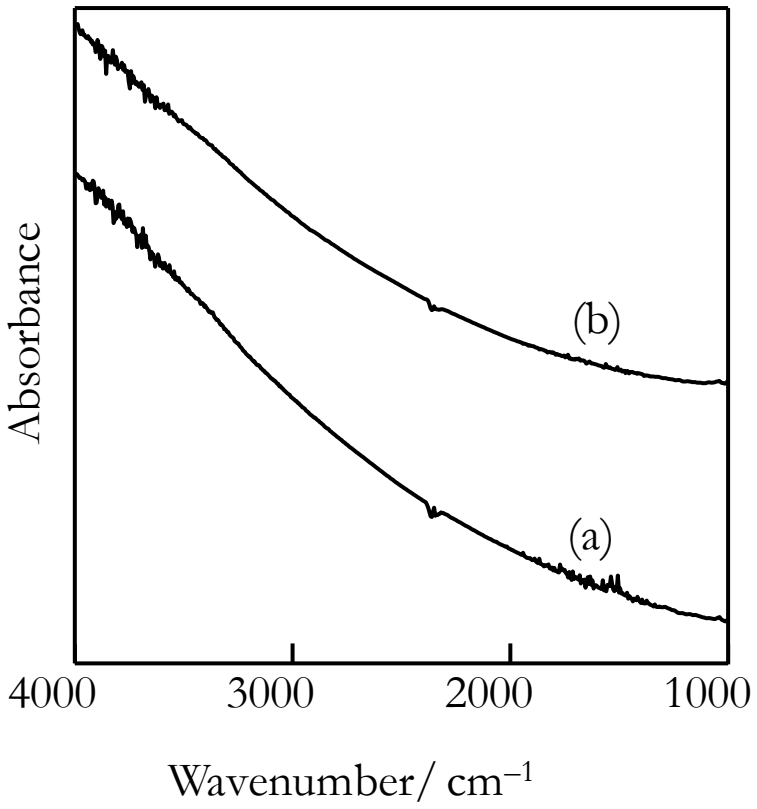


Fig. 4-8 IR spectra for (a) fresh Co_3O_4 and (b) Co_3O_4 reused five times calcined at 650°C for catalytic ozonation of NH_4^+ in water. IR spectra were acquired by using a KBr method after pretreatment in He at 373 K for 1 h.

Since Co_3O_4 calcined at 650°C had only a few surface hydroxyl groups and did not show the activity enhancement, it can be speculated that the hydroxyl groups on the Co_3O_4 surface reacted with NH_4^+ to form Co–NH_x groups on the surface (Fig. 4-9). Thus, if it is true the formation of Co–NH_x groups on the Co_3O_4 surface during the catalytic ozonation of NH_4^+ must cause the activity enhancement.

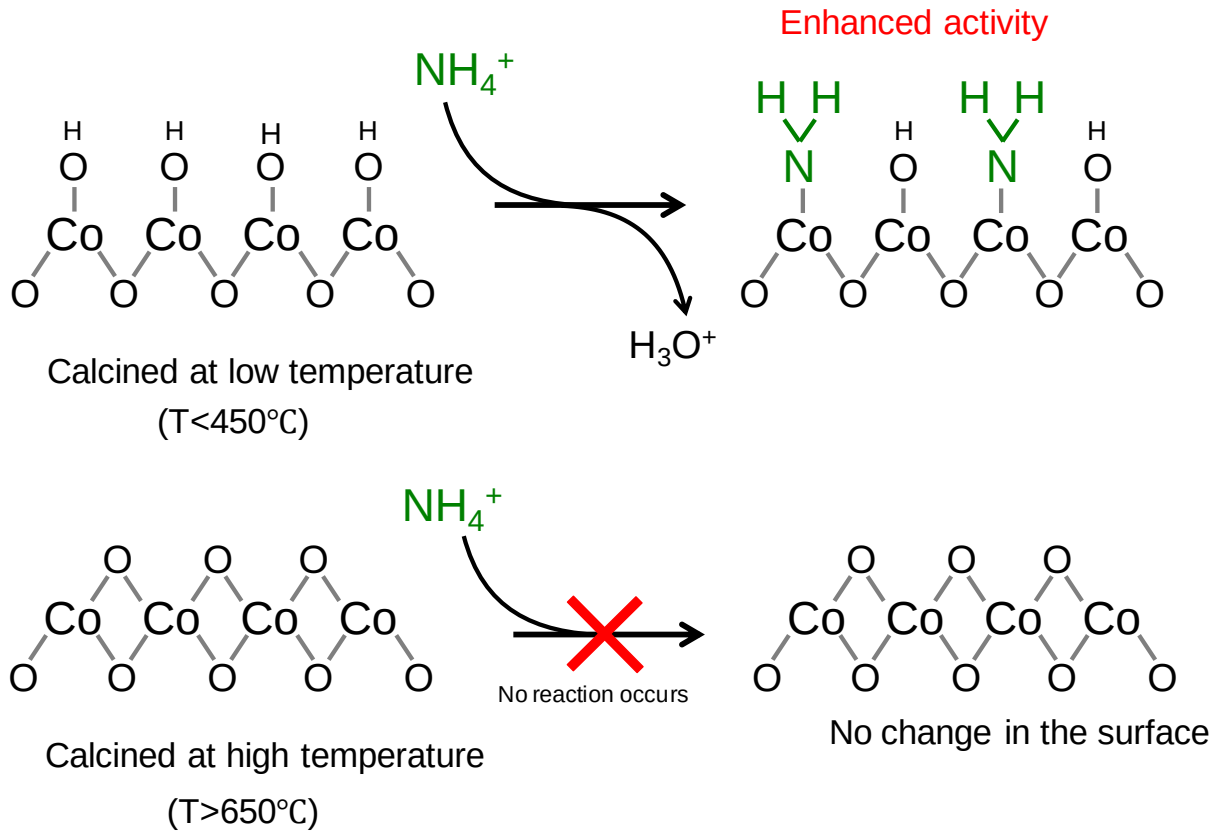


Fig. 4-9 Plausible mechanism activity enhancement for Co_3O_4 calcined at low temperatures.

4.4 Conclusion

Catalytic activity of Co_3O_4 for oxidative decomposition of NH_4^+ with O_3 in water was greatly enhanced with each reuse of the catalyst under the reaction conditions while maintaining its high selectivity towards N_2 gas. However, other metal oxide catalysts including Al_2O_3, Mn_3O_4, and SnO_2 showed no or only a little enhancement of the activity. Formation of $–NH_x$ groups on the surface of Co_3O_4 during the reaction caused the enhancement of the catalytic activity.

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Chapter 5

Summary and General Conclusions

5. Summary and General conclusions

Recently, catalytic ozonation gains increasing interest because it is considered as a potential method to enhance the degradation of recalcitrant organic compounds in water. Previous studies show that catalytic ozonation was successfully applied for decomposition of organic compounds over various catalysts such as metal oxides, metal supported on oxides, minerals and activated carbon. However, the application of catalytic ozonation for decomposition of ammonia nitrogen (NH_3/NH_4^+) has not yet studied, to the best of the author's knowledge. The researches described in this thesis were aimed first to find active, selective and stable metal oxide catalysts for catalytic ozonation of NH_4^+ in water. In addition, elucidation of reaction mechanism for the catalytic ozonation of NH_4^+ over Co_3O_4 was the second objective of this thesis.

In Chapter 2, a metal oxide catalyst screening study was performed in order to find the best catalyst which has high catalytic activity, high selectivity toward gaseous product and also high stability for ozonation of NH_4^+ in water. MgO and NiO had the highest activity, but large amounts of undesired NO_3^- formed due to their low selectivity to gaseous products as well as high activity. Although Co_3O_4 was slightly less active than MgO and NiO, it was the best catalyst in terms of activity, selectivity to gaseous products, and stability (low dissolution degree) among the metal oxide catalysts. An aqueous solution of NH_4^+ (10 mmol L^{-1}) was effectively oxidized to N_2 with 85% selectivity at 333 K over Co_3O_4.

In Chapter 3, the reaction mechanism for the catalytic ozonation of NH_4^+ over Co_3O_4 and the reason for high activity and selectivity of Co_3O_4 were investigated. First the investigation focused on the role of Cl^- since Cl^- was present in the reaction solution. It was found that in the absence of Cl^-, the catalytic ozonation of NH_4^+ could not proceed at even in the presence of Co_3O_4 catalyst. The contribution of Cl^- in the catalytic ozonation process was confirmed

with the formation of oxychloride (ClO_x^-) as the intermediate products of catalytic ozonation of NH_4^+ in water. First ClO_3^- was formed when Cl^- was directly reacted with ozone and then ClO_3^- oxidized into ClO^- in the bulk solution in the presence of Co_3O_4. Then the formed ClO^- and ClO_3^-decompose NH_4^+ over Co_3O_4. The formation of ClO^- and ClO_3^- was higher when Co_3O_4 catalyst was absence. This may be because the active site of the catalyst surface scavenged active radical species such as hydroxyl radicals (•OH) or active oxygen species (O*). The formation of ClO_x^- during the decomposition NH_4^+ may be the reason for high activity in Co_3O_4 catalyst compared to Mn_5O_8, Al_2O_3 and SnO_2. Meanwhile the high selectivity to gaseous products of Co_3O_4 was due to standard enthalphy change of formation per mol of oxygen atom.

In Chapter 4, it was found that the catalytic activity of Co_3O_4 for oxidative decomposition of NH_4^+ with O_3 in water was greatly enhanced with each reuse of the catalyst under the reaction conditions while maintaining its high selectivity towards gaseous compounds. Other catalyst showed no or only a little enhancement of the activity. Changes in the crystalline structure of Co_3O_4 were not the reason for this activity enhancement. From the IR spectra and the catalytic data of Co_3O_4 pretreated under various conditions, it was concluded that formation of $–NH_x$ groups on the surface of Co_3O_4 during the reaction caused the enhancement of the catalytic activity.

The following general conclusions can be drawn based on the findings of each chapter mentioned above.

1. Co_3O_4 is the best catalyst for catalytic ozonation of NH_4^+ in water in terms of activity, selectivity to gaseous products and stability.

2. Cl^- participates in the catalytic ozonation of NH_4^+ in water. The catalytic role of Co_3O_4 was promotes the reaction of NH_4^+ and ClO^- and ClO_3^- formed from the reaction of Cl^- with ozone. In addition, the formation of ClO_x^- was the reason for high activity over Co_3O_4 catalyst. Meanwhile standard enthalpy change of formation per mol of oxygen atom was the reason for high selectivity over Co_3O_4 catalyst.
3. Co_3O_4 showed the enhancement of the catalytic activity by repeated use due to the formation of $–NH_x$ groups on the surface of Co_3O_4 during the catalytic ozonation of NH_4^+ in water.

List of publications

I. Papers corresponding to this thesis

[1] Sho-ichi Ichikawa, Lina Mahardiani, Yuichi Kamiya: "Catalytic oxidation of ammonium ion in water with ozone over metal oxide catalysts", Catal. Today 232 (2014) 192-197.

[2] Lina Mahardiani, Yuichi Kamiya: "Enhancement of Catalytic Activity of Cobalt Oxide for Catalytic Ozonation of Ammonium Ion in Water with Repeated Use", Journal of Japan Petroleum Institute, In Press.

II. Presentations corresponding to this thesis

[1] Lina Mahardiani, Sho-ichi Ichikawa, Yuichi Kamiya: "Decomposition of Ammonium Ion in Water by Catalytic Ozonation using Cobalt Oxide", The 93rd Annual Meeting of Japan Chemical Society, in March 2013, Ritsumekan University.

[2] Lina Mahardiani, Sho-ichi Ichikawa, Yuichi Kamiya: "Catalytic Ozonation of Ammonium Ion over Metal Oxide Catalysts", The 14th Japan-Korea Symposium on Catalysis, in July 2013, Nagoya – Japan.

[3] Lina Mahardiani, Sho-ichi Ichikawa, Yuichi Kamiya: "Decomposition of Ammonium Ion in Water by Catalytic Ozonation using Cobalt Oxide", The 6th Asia-Pacific Congress on Catalysis, in October 2013, Taipei – Taiwan.

[4] Lina Mahardiani, Yuichi Kamiya: "Increase in Catalytic Activity of Cobalt Oxide by Repeated Use for Oxidative Decomposition of Ammonia with Ozone in Water", The 44th Annual Meeting of Japan Petroleum Institute, in October 2014, Asahikawa – Japan.

[5] Lina Mahardiani, Yuichi Kamiya: "Acceleration of Catalytic Ozonation of Ammonium Ion in Water over Cobalt Oxide Catalysts by Repeated Use", The 12th European Congress on Catalysis, August – September 2015, Kazan – Russia.

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