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Catalytic oxidation of ammonium ion in water with ozone over metal oxide catalysts

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Abstract

Oxidative decomposition of NH_4^+ (10 mmol L^{-1}) with O_3 in water was studied at 333 K over a variety of metal oxide catalysts without pH control of the solution. Although MgO and NiO had the highest catalytic activities, large amounts of undesired NO_3^- formed due to low selectivity to gaseous products as well as high activity. Co_3O_4 , which was slightly less active than MgO and NiO, was the best catalyst in terms of activity, selectivity to gaseous products, and dissolution degree among the metal oxide catalysts studied. Over Co_3O_4 , NH_4^+ was selectively oxidized to N_2 with 88% selectivity in water, and the dissolution degree of Co_3O_4 was less than 1%. Fe_2O_3 , SnO_2 , Mn_3O_4 , CuO, MgO, and Al_2O_3 were less selective to gaseous products or much less active for the reaction. The selectivities to gaseous products were strongly related to the standard enthalpy changes of formation per mol of oxygen atom (ΔH_f°) of the metal oxides. The metal oxide catalysts with low ΔH_f° , like Co_3O_4 , showed high selectivity to gaseous products probably due to the low surface density of the active oxygen formed from O_3 on the catalysts. Chloride ions (Cl^-) present in the reaction solution significantly accelerated the reaction rate for NH_4^+ decomposition with O_3 in the presence of Co_3O_4 . This was due to the involvement of Cl^- in the catalytic cycle. For instance, ClO^- , which may form by the reaction of Cl^- with O_3 over Co_3O_4 , could further oxidize NH_4^+ .

Keywords: Catalytic ozonation; Ammonia; Metal oxide catalysts; Wastewater treatment; Cobalt

oxide

1. Introduction

High concentrations of ammonia (NH_3) and ammonium ion (NH_4^+), which are collectively called ammonia nitrogen, in domestic, agricultural, and industrial wastewaters cause eutrophication of rivers, lakes, and epeiric seas. In addition, ammonia nitrogen in environmental water causes acute toxicity in fish species even if the concentration is less than 10 mg L^{-1} . Therefore, ammonia nitrogen needs to be removed from wastewater and preferably decomposed into harmless compounds. Current purification technology for wastewater containing ammonia nitrogen is aerobic biological treatment. However, this treatment method is not applicable to wastewater containing toxic compounds, like heavy metals, and NO_3^- that forms must be reduced to N_2 by anaerobic biodegradation. In addition, this treatment method has some disadvantages, such as the need for tight control of the pH, nutritional sources, and temperature of the wastewater and the need for long reaction times and large areas for installing water-purifier tanks.

A promising method complementing the biological treatment method is catalytic wet oxidation (CWO) of ammonia nitrogen in water with O_2 [1-11]. In 1985, Imamura et al. [1] first reported CWO of NH_3 in water over Ce-based mixed oxides. NH_3 oxidatively decomposes at 536 K and 4.0 MPa of O_2 under strong-alkaline conditions ($\text{pH} = 12$) in the presence of an MnCeOx catalyst. However, about 50 mg L^{-1} of undesired, harmful NO_3^- forms, and the reaction does not proceed at

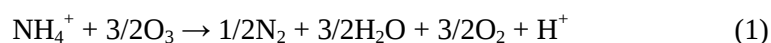
all under neutral or acidic conditions. To conduct CWO of NH_3 under relatively mild reaction conditions, van Santen and co-workers have used supported Pt-group metal catalysts, and they have reported that the reaction proceeds below 473 K over Pt/graphite [3]. Its activity is one order of magnitude higher than the MnCeOx catalyst [1], and N_2 selectively forms at high temperature (453 K). However, undesired by-products, including N_2O and NO_2^- , form, and the catalyst is completely deactivated at relatively low temperature (<433 K) [3]. Taguchi and Okuhara [4,5] have systematically investigated the reactions over supported noble metal (Pt and Pd) catalysts at relatively low temperature (433 K), low pressure (0.5 MPa), and under mild acidic conditions ($\text{pH} = 5.5$). They report that Pt/ TiO_2 decomposes NH_3 into N_2 with 100% selectivity [4].

As mentioned above, CWO of NH_3 is quite attractive because NH_3 is selectively oxidized to N_2 . However, previous reports show that CWO needs reaction temperatures ≥ 423 K, even when noble metal catalysts are used. If the oxidative decomposition of ammonia nitrogen in water could be made to proceed below 373 K, purification of the polluted wastewater could be conducted without a pressure-resistant reactor, which is beneficial from a practical point of view.

Recently catalytic oxidation with O_3 , which is called catalytic ozonation, has attracted much attention as a method for purifying wastewater to decompose organic compounds in water as well as in gas-phase because the oxidation reaction proceeds near room temperature [12-22]. In fact,

various metal oxides and supported precious metal catalysts have been examined for use in catalytic ozonation of organic compounds in water [12,13]. However, to the best of our knowledge, there is no report on the heterogeneous catalytic ozonation of ammonia nitrogen in water, although non-catalytic ozonation of NH_3 [23] and that with a homogeneous catalyst in water [24] have been investigated.

In the present study, to elucidate the catalytic features of metal oxide catalysts, oxidative decomposition of ammonia nitrogen with O_3 (eq. 1) in water was performed using various metal oxide catalysts. Since the reaction was conducted under mild acidic conditions and K_b of NH_3 ($=[\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3]$) is $10^{-4.8}$, almost all of the ammonia nitrogen was present as cationic NH_4^+ , not as NH_3 , in the reaction solution under the present reaction conditions. In the catalytic ozonation of NH_4^+ , it is necessary to prevent both NO_3^- (eq. 2) and NO_2^- (eq. 3) forming because they are much more harmful than ammonia nitrogen. Thus, we carefully examined the formation of these compounds. The reaction mechanism and influence of Cl^- in the reaction solution on the catalytic ozonation over Co_3O_4 are discussed.





2. Experiment

2.1. Catalyst preparation

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$,

$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, aqueous ammonia, and sodium hydroxide were purchased from Wako Pure Chem. Ind. Ltd. and used without further treatment.

Cobalt oxide (Co_3O_4) was prepared by a conventional precipitation method. An aqueous ammonia solution (1.0 mol L^{-1}) was added to a solution of $\text{Co}(\text{NO}_3)_2$ (1.0 mol L^{-1}) until the pH was 8. The suspension was allowed to stand for 10 min at room temperature. The precipitate that formed was separated by filtration, washed with distilled water, and dried at 373 K for two days. The solid was then calcined in air at 773 K for 4 h.

Nickel oxide (NiO) was prepared in a similar manner to that for cobalt oxide calcined at 773 K using a solution of $\text{Ni}(\text{NO}_3)_2$ instead of $\text{Co}(\text{NO}_3)_2$. 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 $\text{Zn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_2$, 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 $\text{Mn}(\text{CH}_3\text{COO})_2$ (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 $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X-Ray diffractometer (Rigaku, Miniflex) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$, 30 kV, 15 mA) at room temperature. Crystallite sizes were estimated by applying Scherrer's equation to the strongest diffraction line for each

sample. Specific surface areas were estimated by applying the Brunauer–Emmett–Teller (BET) equation to an adsorption isotherm of N₂ at 77 K, which was acquired on a Belsorp-mini instrument (BEL Japan Inc.). The samples were dried under N₂ for 3 h at 473 K before the measurements.

2.3 Catalytic ozonation of NH₄⁺ in water

Catalytic ozonation of NH₄⁺ in water was performed by using the batch reactor shown in Fig. 1. An aqueous solution of NH₄Cl (100 mL, 10 mmol L⁻¹, and pH = 5.4) (Wako Pure Chem. Ind. Ltd.) was heated to 333 K with vigorous stirring in a stream of O₂ (100 cm³ min⁻¹). At 333 K, the catalyst powder (0.1 g) was added to the reaction solution, and the gas was changed to a mixture of O₃/O₂ (1.88 mmol L⁻¹ as O₃, total flow rate = 100 cm³ min⁻¹) to start the catalytic ozonation of NH₄⁺. O₃ was generated from O₂ using an ozone generator (Tokyu Car Co. SO-03UN-OX). A portion of the reaction solution was periodically withdrawn, and the concentrations of NO₃⁻, NO₂⁻, and NH₄⁺ in the solution were determined by using two ion chromatographs (Tosoh Co. Ltd., IC-2001). A column containing an anion-exchange resin (TSK gel Super IC-AZ, Tosoh) and an aqueous solution of NaHCO₃ (2.9 mmol L⁻¹) and Na₂CO₃ (3.1 mmol L⁻¹) were used as stationary and mobile phases, respectively, for anion analysis. For cation analysis, a column containing an 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 phases, respectively.

Yield of and selectivity to NO₃⁻ were calculated by eqs. 4 and 5, respectively.

$$\text{Yield of NO}_3^- = \frac{\text{Concentration of formed NO}_3^-}{\text{Initial concentration of NH}_4^+} \times 100 \text{ [\%]} \quad (4)$$

$$\text{Selectivity to NO}_3^- = \frac{\text{Concentration of formed NO}_3^-}{\text{Concentration of consumed NH}_4^+} \times 100 \text{ [\%]} \quad (5)$$

The selectivity to gaseous products was calculated by subtracting the selectivity for NO₃⁻, which was the only product in solution, from 100%. For each experiment, the pH of the reaction solution was measured after the reaction. Dissolution degree (%) of the catalyst during the reaction was calculated by eq. 6, where $W_{\text{dissolved}}$ and W_{initial} indicate the amounts of the metal dissolved in the reaction solution after 6 h and of that initially contained in the catalyst, respectively. $W_{\text{dissolved}}$ was determined by using an ICP-AES instrument (Shimadzu Co., ICPS-7000), and W_{initial} was calculated based on the chemical formula:

$$\text{Dissolution degree} = \frac{W_{\text{dissolved}}}{W_{\text{initial}}} \times 100 \text{ [\%]} \quad (6)$$

For some reactions, we collected the gas phase products at the outlet of the reactor with a gas collection bag and analyzed them by using a gas chromatograph (Shimadzu Co., GC-8A) equipped with a TCD detector and a Porapak[®] Q column. In addition, the catalytic ozonation of NH_4^+ in water over Co_3O_4 was carried out by using a reaction solution prepared from $(\text{NH}_4)_2\text{SO}_4$ in the presence as well as absence of NaCl to investigate the role of Cl^- in the catalytic cycle of the ozonation of NH_4^+ .

3. Results and discussion

3.1 Physical properties of metal oxide catalysts

Fig. 2 shows powder XRD patterns of the catalysts before the catalytic ozonation. All catalysts were crystalline and only exhibited the characteristic diffraction patterns for the metal oxides listed in Table 1. The powder XRD patterns of the catalysts after the reaction were essentially identical to those before the reaction, but MgO and Mn_3O_4 reacted to give $\text{Mg}(\text{OH})_2$ and Mn_5O_8 by oxidation, respectively, during the reaction.

Table 1 lists chemical formulae and crystallite sizes estimated from powder XRD patterns and specific surface areas for the catalysts. SnO_2 and Al_2O_3 had large surface areas, whereas the surface areas of ZnO and CuO were very small due to large crystallite sizes. The other catalysts,

including MgO, NiO, Co₃O₄, Mn₃O₄, and Fe₂O₃, had moderate surface areas in the range of 10–35 m² g⁻¹.

3.2 Catalytic performances of the metal oxide catalysts

Fig. 3 shows the conversion of NH₄⁺ in the absence and presence of the catalysts at 6 h. NH₄⁺ decomposed even when no catalyst was present, as reported previously [20], but the conversion was low (14%). In contrast, high conversions were obtained in the presence of the metal oxide catalysts. Among the catalysts, MgO was the most active catalyst, and NiO was the second. On the other hand, Fe₂O₃, SnO₂, and Al₂O₃ scarcely promoted the reaction, even though the latter two catalysts had large surface areas. Co₃O₄ exhibited moderate catalytic activity with a 74% conversion, whereas CuO, ZnO, and Mn₃O₄ showed lower catalytic activity. The decomposition of NH₄⁺ did not proceed at all when only O₂ was fed into the reaction solution even in the presence of the catalysts.

A good catalyst must have a high selectivity to gaseous products, including N₂ and N₂O, in the oxidative decomposition of NH₄⁺ in water because the formation of soluble compounds, including NO₃⁻ and NO₂⁻, must be suppressed to low levels due to their high toxicities. Fig. 4 shows the selectivities to gaseous compounds and NO₃⁻ in the ozonation of NH₄⁺ in the absence and presence

of the metal oxide catalysts at 6 h. NO_2^- did not form at all regardless of the catalyst. MgO and NiO showed low selectivity to gaseous products, although they had high catalytic activities, as shown in Fig. 3. In fact, when they were used, a large amount of harmful NO_3^- formed, making them unsuitable for use as catalysts in the purification of wastewater containing ammonia nitrogen. CuO and ZnO were less selective to gaseous products. In contrast, it should be noted that Co_3O_4 exhibited the highest selectivity to gaseous products (88%). For the reaction over Co_3O_4 , only N_2 was detected as a gaseous product by using GC analysis. From the conversion (74%) and selectivity to NO_3^- (12%) 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.

In addition to the activity and selectivity, the catalysts must be insoluble to be a good catalyst for practical use. Table 2 summarizes dissolution degrees for the catalysts and the pH values of the reaction solutions after 6 h. MgO, NiO, CuO, and ZnO had the highest dissolution degrees in the reaction solutions. In contrast, Mn_3O_4 , Fe_2O_3 , and SnO_2 were insoluble in the reaction solution, despite being less active and/or less selective to gaseous products. Only 1% of Co_3O_4 dissolved in the reaction solution during the reaction. As eqs. 1–3 indicate, protons were formed by the

ozonation of NH_4^+ in water, resulting in a decrease in the pH of the reaction solution as the reaction progressed. In fact, the pH of the reaction solution after the reaction was less than 2.5 for the insoluble (Mn_3O_4 , Fe_2O_3 , and SnO_2) and less soluble catalysts (Co_3O_4 and Al_2O_3), although the initial pH of the reaction solution was 5.4. On the other hand, when MgO , NiO , ZnO , and CuO were used, the pH of the reaction solution after the reaction was relatively high because they had a higher degree of dissolution during the reaction. From these results, we concluded that Co_3O_4 was the best catalyst in terms of activity, selectivity to gaseous compounds, and dissolution degree among the catalysts that we tested. In addition, Co_3O_4 was reusable for the reaction. After the reaction, Co_3O_4 was separated by filtration, dried at 383 K overnight and then was afforded to the second reaction. The conversion of the second reaction was 91% with similar selectivity to the first one. It should be noted that the conversion of the second reaction was much higher than that of the first one (74%). For the third reaction, the activity was further increased and NH_4^+ was completely decomposed at 6 h. Reconstitution of the surface of Co_3O_4 might occur during the reaction and may be one of the reasons for such improvement in the activity, but further investigation is necessary.

The surface area of the catalyst is one of the factors controlling the catalytic activity because the reaction takes place on the surface, and therefore, a catalyst with high surface area may show

high activity. In Fig. 5, the conversions of NH_4^+ , which were obtained by subtracting the conversion without catalyst from corresponding conversions in the presence of the catalyst, are plotted as a function of the surface areas of the catalysts. In Fig. 5, the data for MgO, NiO, ZnO, and CuO were not plotted because they are soluble. As Fig. 5 clearly shows, Co_3O_4 (Fig. 5(a)) had the highest activity despite its small surface area.

Next we discuss the catalyst properties that control the selectivity. Fig. 6 shows a plot of the selectivities to gaseous products as a function of standard enthalpy change of formation per mol of oxygen atom (ΔH_f°) of the metal oxides. The selectivity to gaseous products 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 gaseous products had a value of $\Delta H_f^\circ \leq 60$ kcal (mol of O)⁻¹.

In the catalytic oxidation of NH_4^+ , two nitrogen intermediate species (NHx) 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 forms when O_3 reacts with the catalyst surface. Thus, the ratio of the surface densities of the nitrogen intermediate species and active oxygen atoms ($[\text{NHx}]/[\text{O}^*]$) would determine the selectivity. If $[\text{NHx}]/[\text{O}^*]$ is high, namely, $[\text{NHx}]$ is high or $[\text{O}^*]$ 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 O₃ 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. We think that this is one of the reasons for the high selectivity to gaseous products over catalysts like Co₃O₄. If the hypothesis that the [NHx]/[O*] ratio on the surface determines the selectivity is true, the concentration of NH₄⁺ in water must affect the selectivity. To demonstrate this, we carried out the catalytic ozonation of NH₄⁺ over Co₃O₄ using an aqueous solution of NH₄Cl with 5 mmol L⁻¹. The result showed that the selectivity to gaseous products at 6 h was 66%, which was lower than that with 10 mmol L⁻¹ solution (88%). This result supports the reaction mechanism we proposed.

3.3 Participation of Cl⁻ in the catalytic cycle over Co₃O₄

Fig. 7 shows time courses of the conversion and selectivity to gaseous products for the ozonation of NH₄⁺ over Co₃O₄. The selectivity was independent of the reaction time. It is noted

that an induction period was observed for the conversion of NH_4^+ . There are two explanations for the appearance of the induction period. One is that the formation rate of O^* on the surface of Co_3O_4 is slow. However, the induction period was also observed for the reaction over Co_3O_4 pretreated with O_3 for 3 h at 333 K in the absence of NH_4^+ in water. In addition, the conversion and selectivity were identical to the reaction without O_3 pretreatment. The second explanation is that Cl^- participates in the ozonation of NH_4^+ ; namely, Cl^- is first oxidized by O_3 over Co_3O_4 to form ClO^- , which oxidizes NH_4^+ . In the reaction solution, Cl^- and NH_4^+ were both present in the same amount because NH_4Cl was used as the source of NH_4^+ . To determine if Cl^- participates in the catalytic cycle for the ozonation of NH_4^+ , we carried out the catalytic ozonation of NH_4^+ over Co_3O_4 using $(\text{NH}_4)_2\text{SO}_4$ as the source of NH_4^+ , i.e., without Cl^- . Even after 6 h, the NH_4^+ conversion was zero, suggesting that Cl^- in water participates in the catalytic cycle for the ozonation of NH_4^+ over Co_3O_4 .

To further confirm the participation of Cl^- , we examined the concentration dependence of Cl^- in the reaction solution on the catalytic ozonation of NH_4^+ over Co_3O_4 . The reaction was conducted in a reaction solution prepared using $(\text{NH}_4)_2\text{SO}_4$ and different concentrations of Cl^- , where the concentration of Cl^- was controlled by adding NaCl to the solution. With an increase in the concentration of Cl^- , the conversion of NH_4^+ increased, and the selectivity to gaseous products

was similar to that for the reaction in the NH_4Cl solution. This result clearly demonstrates that Cl^- is involved in the catalytic cycle for the ozonation of NH_4^+ over Co_3O_4 . Haag et al. have proposed a reaction scheme for the ozonation of NH_4^+ in water in the presence of Br^- without any heterogeneous catalyst under neutral to mild alkaline conditions [24]. In the proposed mechanism, Br^- is oxidized with O_3 to form BrOH , which then 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 (HOBr formation) is the rate-determining step. In the present study, the oxidation of Cl^- with O_3 may take place over Co_3O_4 to form ClO^- , meaning that this reaction is the rate-determining step in the catalytic ozonation of NH_4^+ in the presence of Co_3O_4 . Actually, NO_3^- was produced by a homogeneous reaction, as discussed in Section 3.2. However, gaseous products (N_2 and N_2O) selectively formed over Co_3O_4 (Fig. 4). Thus, Co_3O_4 not only promotes the oxidation of Cl^- with O_3 but also the formation of gaseous N_2 and N_2O . On Co_3O_4 , nitrogen-containing intermediates are preferentially activated to form the gaseous N_2 and N_2O through bimolecular reactions. Further investigations on the reaction mechanism, including kinetic analysis and determination of the surface densities of nitrogen-containing intermediates and active oxygen, are needed.

4. Conclusions

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 studied. 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 dissolution degree among the metal oxide catalysts. An aqueous solution of NH_4^+ (10 mmol L^{-1}) was effectively oxidized to N_2 with 88% selectivity at 333 K over Co_3O_4 . The selectivities to gaseous products were strongly related to the standard enthalpy changes of formation per mol of oxygen atom (ΔH_f°) of the metal oxides, and the catalysts with low ΔH_f° values, like Co_3O_4 , showed high selectivity to gaseous products probably due to a low surface density of the active oxygen formed upon the reaction of O_3 with the catalyst surface. Chloride ions (Cl^-) present in the reaction solution significantly accelerated the reaction rate of NH_4^+ decomposition with O_3 over Co_3O_4 because Cl^- is directly involved in the catalytic cycle, in which Cl^- reacts with O_3 to form ClO^- .

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Table 1

Physical properties of the metal oxide catalysts used

Catalyst	Chemical formula ^a	Crystallite size ^b /nm	Surface area ^c /m ² g ⁻¹
Cobalt oxide	Co ₃ O ₄	28	14
Nickel oxide	NiO	25	22
Zinc oxide	ZnO	45	1
Iron oxide	Fe ₂ O ₃	32	10
Tin oxide	SnO ₂	8	82
Manganese oxide	Mn ₃ O ₄	19	23
Copper oxide	CuO	27	1
Magnesium oxide	MgO	30	35
Aluminum oxide	Al ₂ O ₃	8	93

^adetermined from powder XRD pattern.^bdetermined by applying Scherrer's equation to the strongest diffraction line in each XRD pattern.^cdetermined from N₂ adsorption isotherm at 77 K by using the BET equation.

Table 2

Dissolution degrees of the metal oxide catalysts used 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 ₃ O ₄	1	2.1
CuO	27	4.6
ZnO	26	6.2
Mn ₃ O ₄	0.1	2.1
Fe ₂ O ₃	below detection limit	2.6
SnO ₂	below detection limit	2.7
Al ₂ O ₃	2	3.1

^aAmount of metal dissolved in the reaction solution was determined by using ICP-AES.

^bInitial pH of the reaction solution was 5.4.

Figure captions

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

Fig. 2 Powder XRD patterns of the metal oxide catalysts before catalytic ozonation of NH_4^+ in water.

Fig. 3 Catalytic activities of the metal oxide catalysts used for ozonation of NH_4^+ in water.

Reaction conditions: catalyst weight, 0.1 g; $[\text{NH}_4^+]$, 10 mmol L^{-1} from NH_4Cl ; reaction solution volume, 100 mL; reaction gas, O_3/O_2 mixture; total flow rate, 100 $\text{cm}^3 \text{min}^{-1}$; O_3 concentration, 0.7 vol%; reaction temperature, 333 K; and reaction time, 6 h.

Fig. 4 Selectivities toward ($\square$) NO_3^- and ($\blacksquare$) gaseous products in catalytic ozonation of NH_4^+ in water over various metal oxide catalysts. Reaction conditions: catalyst weight, 0.1 g; reaction solution, $[\text{NH}_4^+]$, 10 mmol L^{-1} from NH_4Cl ; reaction solution volume, 100 mL; reaction gas, O_3/O_2 mixture; total flow rate, 100 $\text{cm}^3 \text{min}^{-1}$; O_3 concentration, 0.7 vol%; reaction temperature, 333 K; and reaction time, 6 h.

Fig. 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 blank (without catalyst) from corresponding conversion. The data plotted in the figure are for the catalysts with low degrees of dissolution. (a) Co_3O_4 , (b) Fe_2O_3 , (c) Mn_3O_4 , (d) SnO_2 , and (e) Al_2O_3 .

Fig. 6 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.

Fig. 7 Time courses of the conversion of NH_4^+ (●) and selectivity to gaseous products (□) for the catalytic ozonation of NH_4^+ in water over Co_3O_4 . Reaction conditions: catalyst weight, 0.1 g; reaction solution, $[\text{NH}_4^+]$, 10 mmol L^{-1} from NH_4Cl ; reaction solution volume, 100 mL; reaction gas, O_3/O_2 mixture; total flow rate, $100 \text{ cm}^3 \text{ min}^{-1}$; O_3 concentration, 0.7 vol%; and reaction temperature, 333 K.

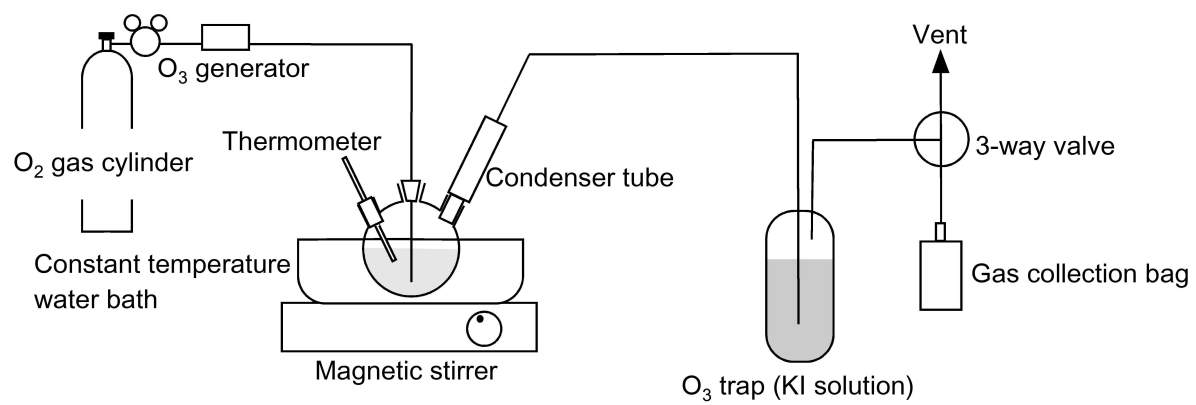


Fig. 1

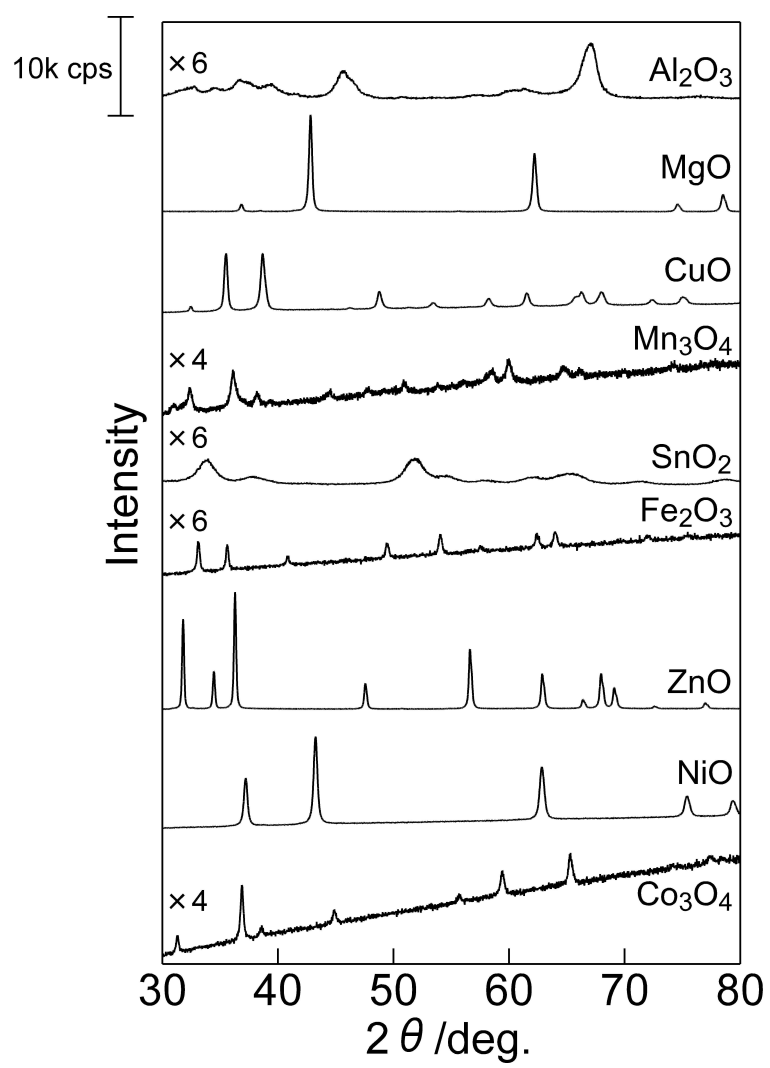


Fig. 2

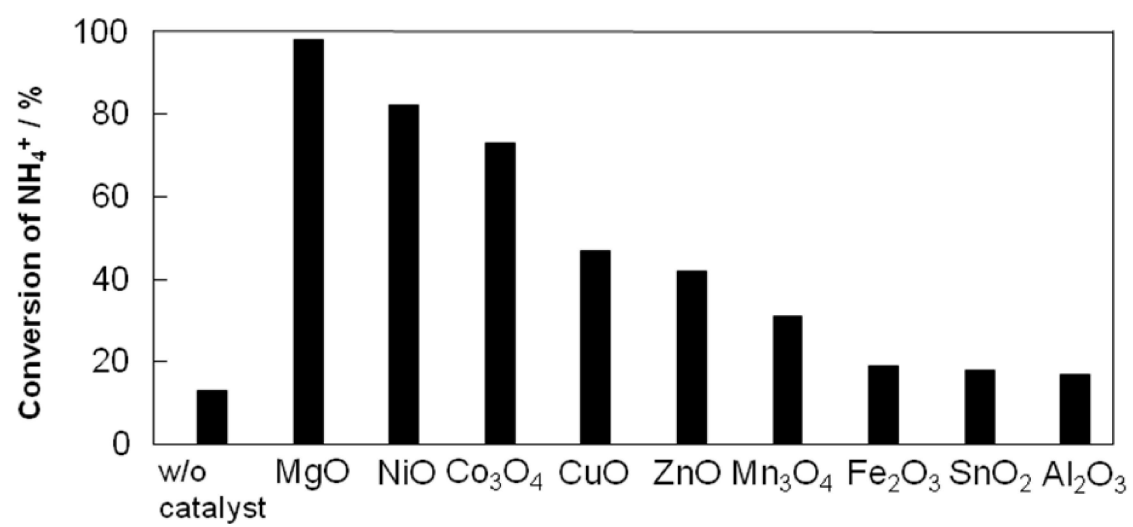


Fig. 3

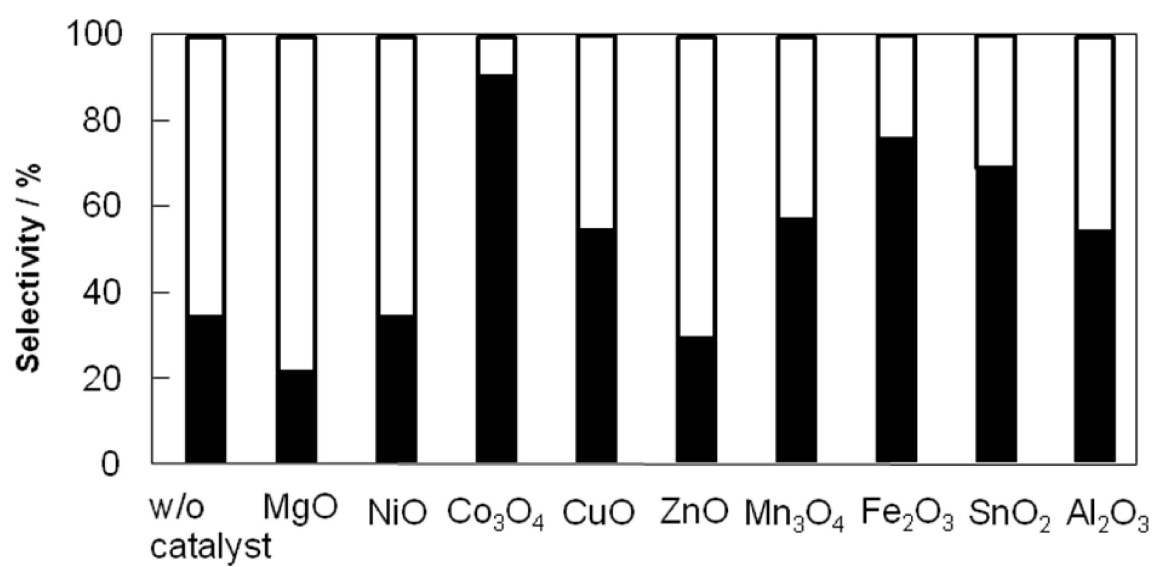


Fig. 4

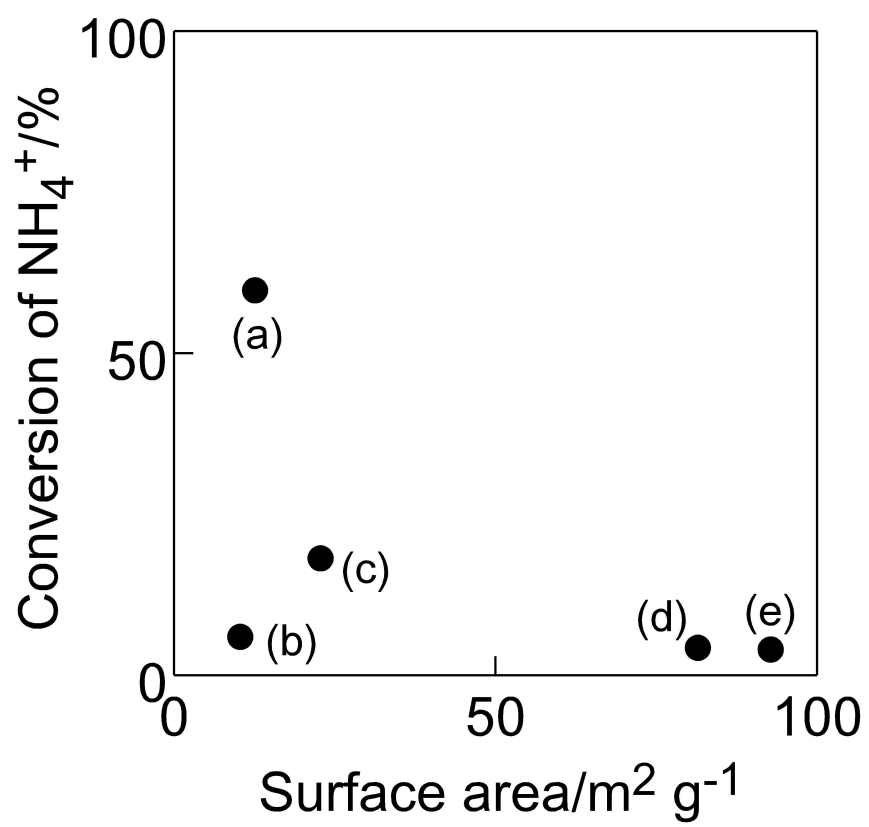


Fig. 5

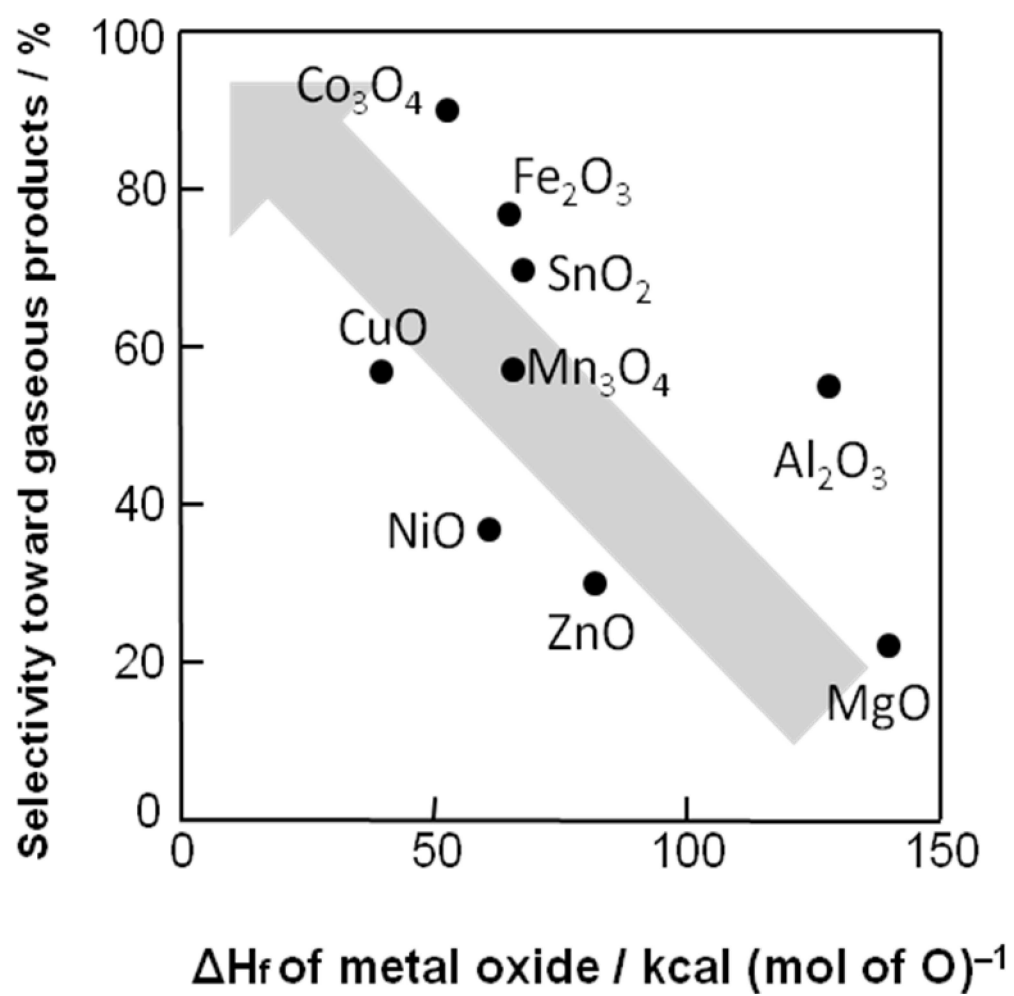


Fig. 6

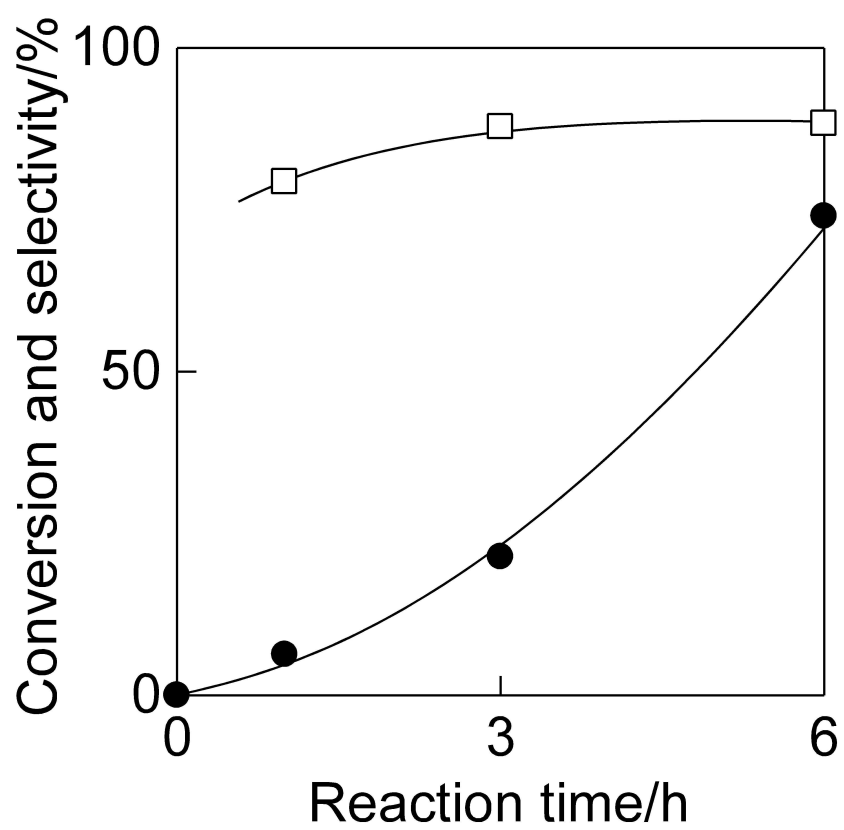


Fig. 7