



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



Sho-ichi Ichikawa^a, Lina Mahardiani^a, Yuichi Kamiya^{b,*}

^a Graduate School of Environmental Science, Hokkaido University, Nishi 5, Kita 10, Kita-ku, Sapporo 060-0810, Japan

^b Research Faculty of Environmental Earth Science, Hokkaido University, Nishi 5, Kita 10, Kita-ku, Sapporo 060-0810, Japan

ARTICLE INFO

Article history:

Received 11 July 2013

Received in revised form

12 September 2013

Accepted 23 September 2013

Available online 16 October 2013

Keywords:

Catalytic ozonation

Ammonia

Metal oxide catalysts

Wastewater treatment

Cobalt oxide

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^+ .

© 2013 Elsevier B.V. All rights reserved.

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 MnCeO_x 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 MnCeO_x 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 $\geq 423 \text{ K}$, even when noble metal catalysts are used. If the oxidative decomposition of ammonia nitrogen in water could be made to proceed below

* Corresponding author. Tel.: +81 11 706 2217; fax: +81 11 706 2217.
E-mail address: kamiya@ees.hokudai.ac.jp (Y. Kamiya).

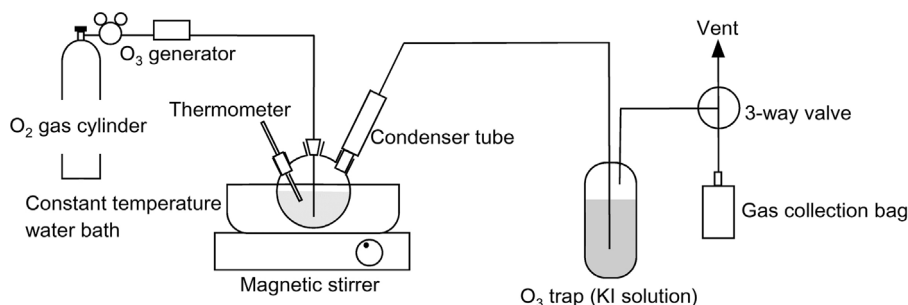
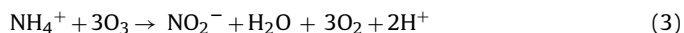
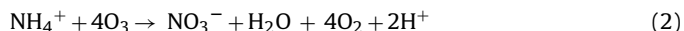
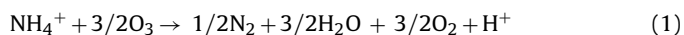


Fig. 1. Schematic illustration of the reaction apparatus used for catalytic ozonation of NH_4^+ in water.

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

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 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 pre-

pared 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 N_2 at 77 K, which was acquired on a Belsorp-mini instrument (BEL Japan Inc.). The samples were dried under N_2 for 3 h at 473 K before the measurements.

2.3. Catalytic ozonation of NH_4^+ in water

Catalytic ozonation of NH_4^+ in water was performed by using the batch reactor shown in Fig. 1. An aqueous solution of NH_4Cl (100 mL , 10 mmol L^{-1} , and $\text{pH} = 5.4$) (Wako Pure Chem. Ind. Ltd.) was heated to 333 K with vigorous stirring in a stream of O_2 ($100 \text{ cm}^3 \text{ min}^{-1}$). At 333 K, the catalyst powder (0.1 g) was added to the reaction solution, and the gas was changed to a mixture of O_3/O_2 (1.88 mmol L^{-1} as O_3 , total flow rate = $100 \text{ cm}^3 \text{ min}^{-1}$) to start the catalytic ozonation of NH_4^+ . O_3 was generated from O_2 using an ozone generator (Tokyu Car Co. SO-03UN-OX). A portion of the reaction solution was periodically withdrawn, and the concentrations of NO_3^- , NO_2^- , and NH_4^+ 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 NaHCO_3 (2.9 mmol L^{-1}) and Na_2CO_3 (3.1 mmol L^{-1}) were used as stationary and mobile phases, respectively, for anion analysis. For cation

Download English Version:

<https://daneshyari.com/en/article/54475>

Download Persian Version:

<https://daneshyari.com/article/54475>

[Daneshyari.com](https://daneshyari.com)