[Letter]

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

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Catalytic activity of Co3O4 for oxidative decomposition of NH4+ with O3 in water was greatly enhanced with each reuse of the catalyst under the reaction conditions while maintaining its high selectivity towards gaseous compounds. On the other hand, other metal oxide catalysts showed no or only a little enhancement of the activity. Formation of −NH2 groups on the surface of Co3O4 during the reaction caused the enhancement of the catalytic activity.

Keywords: Cobalt oxide, Wastewater treatment, Catalytic ozonation, Repeated use, Catalytic activity enhancement, Ammonium ion

1. Introduction

Ammonia is produced by the Haber–Bosch process. In this process, N2 is reacted with H2, which is produced from petroleum and natural gas by a steam reforming. It is obvious that the industrial ammonia production has made a great contribution to construct our modern society, but excess usage of ammonia causes various environmental problems, one of which is water pollution with ammonia. High concentrations of ammonia (NH3) and ammonium ion (NH4+), which are collectively called ammonia nitrogen, in industrial effluents, daily wastewater, household sewage, and runoff water from farmlands can cause eutrophication of rivers, lakes and inland seas, which causes serious damage to aquatic ecosystems1)2). Therefore, it is necessary to decompose ammonia nitrogen into harmless compounds, like N2 and H2O. Catalytic ozonation, in which ozone is utilized as an oxidant in the presence of a catalyst, for decomposition of ammonia nitrogen is an attractive method because the reaction proceeds at ordinary temperatures and pressures3), which are ideal conditions for practical applications. On the other hand, non-catalytic ozonation of ammonia nitrogen exhibits only low reaction rates4)5), and catalytic oxidation with O3 or air needs high reaction temperatures (> 473 K) and consequently high pressures6)-11).

In our previous paper, we reported that Co3O4 showed activity and high selectivity to N2 for the catalytic ozonation of NH4+ in water and high stability among metal oxide catalysts (MOx, M = Mg, Ni, Cu, Zn, Mn, Fe, Sn and Al) tested1). In the present study, we wish to report the unusual catalytic properties of Co3O4 toward the catalytic ozonation of NH4+. Its catalytic activity increased with each reuse, whereas other MOx showed little or no activity enhancement with repeated use. In addition, from catalytic data for Co3O4 treated under various conditions prior to catalytic ozonation of NH4+ and from changes in the physical and chemical properties of Co3O4 with repeated use, we discussed what caused the activity enhancement.
2. Experimental

CO₂O₄ catalyst was prepared by using a precipitation method. An aqueous ammonia solution (1.0 mol L⁻¹) was added to an aqueous solution of Co(NO₃)₂ (1.0 mol L⁻¹) until the pH was 8, leading to the formation of a fine black powder. The 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 2 d. Finally, the obtained solid was calcined at 723 K or 923 K in air for 3 h.

Catalytic ozonation of NH₄⁺ in water was performed in a three-neck flask. Catalyst powder (0.1 g) was added to an aqueous solution of NH₄Cl (100 mL, 10 mmol L⁻¹), and the resulting suspension was heated at 333 K with vigorous stirring in a flow of an O₂/O₃ mixture (1.88 mmol L⁻¹ of O₃, total flow rate = 100 cm² min⁻¹). After 6 h, the catalyst was collected by filtration, washed with distilled water, dried at 373 K overnight, and then used in subsequent reactions. 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.

3. Results and Discussion

Figure 1 shows the conversion and selectivity to gaseous compounds mainly N₂ for the catalytic ozonation of NH₄⁺ over Co₂O₄ after each use. For comparison, catalytic data for Al₂O₃, Mn₃O₄ and SnO₂, which are the least soluble MO₃ in the reaction solution, are also shown in Fig. 1. Fresh Co₂O₄ showed high conversion and high selectivity to gaseous compounds, where most O₃ was consumed to decompose NH₄⁺ as well as its self-decomposition within a few hours. The conversion increased with repeated use, and a slight change in the selectivity was observed. During the second reuse, all of the NH₄⁺ decomposed within 6 h. On the other hand, fresh Al₂O₃ and Mn₃O₄ exhibited only low catalytic activities and did not show any activity enhancement, and they became deactivated after the first use. As for SnO₂, the conversion of NH₄⁺ increased with each use but only a little.

Because the conversion of NH₄⁺ reached 100% over Co₂O₄ during the second reuse under the reaction conditions in Fig. 1, the catalytic performance of Co₂O₄ for each use was evaluated using a high concentration of NH₄⁺ (30 mmol L⁻¹) to suppress the initial conversion. Under these reaction conditions, fresh Co₂O₄ showed 30% conversion (Fig. 2), and the conversion increased with each reuse up to nine times, reaching 80%, with high selectivity.

To investigate the changes in the physical properties of reused Co₂O₄ powder X-ray diffraction (XRD) patterns of fresh Co₂O₄ and that after nine times reuse were acquired (Fig. 3) and compared. All of the diffraction lines corresponded to those of spinel Co₂O₄ and, no significant change was observed between fresh and spent catalysts. Thus, change in the crystalline structure was not the reason for the activity enhancement.

In addition, the surface area of Co₂O₄ reused nine times was rather smaller (8 m² g⁻¹) than that of the fresh one (20 m² g⁻¹). Therefore, the change in the surface structure of Co₂O₄ or modification of the Co₂O₄ surface with reactants and products under the reaction conditions must have caused the increase in the activity with each use.

![Fig. 1 Conversion of NH₄⁺ and Selectivity to Gaseous Compounds for Catalytic Ozonation of NH₄⁺ in Water over Fresh and Reused Samples of (a) Co₂O₄, (b) Al₂O₃, (c) Mn₃O₄ and (d) SnO₂](image)

![Fig. 2 Changes in the Catalytic Performance of Co₂O₄ Reused up to Nine Times for the Catalytic Ozonation of High Concentrations of NH₄⁺](image)
Fig. 3 Powder XRD Patterns of (a) Fresh Co₃O₄ and (b) Co₃O₄ Reused Nine Times [O] are the peaks corresponding to spinel Co₃O₄.

Fig. 4 IR Spectra for (a) Fresh Co₃O₄ and (b) Co₃O₄ Reused Nine Times for Catalytic Ozonation of NH₄⁺ in Water [IR spectra were acquired by using a KBr method after pretreatment in He at 373 K for 1 h.]

To elucidate the crucial compound in the reaction solution causing the activity enhancement, we treated Co₃O₄ with various aqueous solutions and under different conditions prior to the catalytic ozonation of NH₄⁺ (Table 1). Untreated Co₃O₄, namely fresh Co₃O₄, showed 72% conversion at 6 h for the catalytic ozonation of NH₄⁺ (Entry 1). When Co₃O₄ was pretreated with aqueous solutions of NH₄Cl at 333 K but with no O₂, the activity increased (Entry 2). In addition, treatment of Co₃O₄ in the aqueous solutions with NH₄⁺ and no Cl⁻ lead to an increase in the activity (Entry 3). The results clearly indicate that O₂ and Cl⁻ are not crucial for the activity enhancement. On the other hand, when Co₃O₄ was treated in pure H₂O at 333 K, no activity enhancement occurred (Entry 4). Therefore, we concluded that NH₄⁺ in the reaction solution was essential for the activity enhancement of Co₃O₄ with repeated use. In other words, the reaction of the Co₃O₄ surface with NH₄⁺ caused the activity enhancement.

Modification of the Co₃O₄ surface during the catalytic ozonation of NH₄⁺ was confirmed by using IR spectroscopy. Figure 4 shows IR spectra for fresh Co₃O₄ and Co₃O₄ after nine times reuse, which were obtained from the experiment in Fig. 2. These spectra were acquired by using a KBr method, and the sample disks were pretreated in an He flow at 373 K for 1 h before acquiring the IR spectra. In the spectra for the fresh Co₃O₄ catalyst, two bands at 3365 cm⁻¹ and 1520 cm⁻¹ were assigned to be stretching and bending modes of surface hydroxyl groups, respectively (Fig. 4(a)). In the spectra for Co₃O₄ reused nine times, new bands at 2956, 2921, and 2852 cm⁻¹ were observed, while the band at 1520 cm⁻¹ weakened (Fig. 4(b)). The attenuation of the band at 1520 cm⁻¹ suggests that the surface hydroxyl groups were modified under the reaction conditions. Since the IR spectrum for NH₄Cl diluted with KBr (Fig. 5) was quite different from that for Co₃O₄ reused nine times, the new IR bands observed in the spectra for the Co₃O₄ reused nine times were not due to NH₄Cl simply deposited on its surface.

Calcination temperature of Co₃O₄ had an impact on the activity enhancement. As Figs. 2 and 3 show, Co₃O₄ calcined at 723 K exhibited the activity enhancement by repeated use. When Co₃O₄ was calcined at lower temperature like 573 K, the activity enhancement also

Table 1 Catalytic Performance of Untreated and Pretreated Co₃O₄

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Conversion of NH₄⁺ (%)</th>
<th>Selectivity to gas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>untreated</td>
<td>72</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>NH₄Cl</td>
<td>95</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>(NH₄)₂SO₄</td>
<td>98</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>only H₂O</td>
<td>77</td>
<td>84</td>
</tr>
</tbody>
</table>

"a" Fresh Co₃O₄ without any pretreatment. "b" Fresh Co₃O₄ was treated twice with an aqueous solution of NH₄Cl (10 mmol L⁻¹) without O₂ at 333 K for 6 h prior to catalytic ozonation of NH₄⁺. "c" Fresh Co₃O₄ was treated twice with an aqueous solution of (NH₄)₂SO₄ (10 mmol L⁻¹) with O₂ at 333 K for 6 h prior to catalytic ozonation of NH₄⁺. "d" Fresh Co₃O₄ was treated twice with pure water without O₂ at 333 K for 6 h prior to catalytic ozonation of NH₄⁺.
occurred. However, Co$_2$O$_4$ calcined at high temperature (923 K) did not exhibit any activity enhancement with repeated use (Fig. 6). It was confirmed by using IR spectroscopy and thermogravimetric analysis that Co$_2$O$_4$ calcined at 923 K had only a few surface hydroxyl groups. This means that the hydroxyl groups on the Co$_2$O$_4$ surface are strongly related to the activity enhancement. Thus, we concluded that the surface hydroxyl groups reacted with NH$_4^+$ to form Co–NH$_4^+$ groups on the surface and Co–NH$_4^+$ groups caused the activity enhancement. However, the reason why these functional groups have high catalytic activity for the catalytic ozonation reaction remains unclear, and thus, further mechanistic studies are being conducted.

Fig. 6 Conversion of NH$_4^+$ (■) and Selectivity toward Gaseous Compounds (□) for Co$_2$O$_4$ Calcined at 923 K for Catalytic Ozonation of NH$_4^+$ in Water with Repeated Use

4. Conclusions
Catalytic activity of Co$_2$O$_4$ for catalytic ozonation 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. Formation of Co–NH$_4^+$ groups on the surface of Co$_2$O$_4$ during the reaction by the reaction of the surface OH groups with NH$_4^+$ caused the enhancement of the catalytic activity.

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References