Low-temperature conversion of ammonia to nitrogen in water with ozone over composite metal oxide catalyst

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ABSTRACT

As one of the most important water pollutants, ammonia nitrogen emissions have increased year by year, which has attracted people’s attention. Catalytic ozonation technology, which involves production of ·OH radical with strong oxidation ability, is widely used in the treatment of organic-containing wastewater. In this work, MgO-Co₃O₄ composite metal oxide catalysts prepared with different fabrication conditions have been systematically evaluated and compared in the catalytic ozonation of ammonia (50 mg/L) in water. In terms of high catalytic activity in ammonia decomposition and high selectivity for gaseous nitrogen, the catalyst with MgO-Co₃O₄ molar ratio 8:2, calcined at 500°C for 3 hr, was the best one among the catalysts we tested, with an ammonia nitrogen removal rate of 85.2% and gaseous nitrogen selectivity of 44.8%. In addition, the reaction mechanism of ozonation oxidative decomposition of ammonia nitrogen in water with the metal oxide catalysts was discussed. Moreover, the effect of coexisting anions on the degradation of ammonia was studied, finding that SO₄²⁻ and HCO₃⁻ could inhibit the catalytic activity while CO₃²⁻ and Br⁻ could promote it. The presence of coexisting cations had very little effect on the catalytic ozonation of ammonia nitrogen. After five successive reuses, the catalyst remained stable in the catalytic ozonation of ammonia.

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Introduction

In the past few years, the nitrogen content in groundwater has tremendously increased due to various anthropogenic activities like application of animal manure and intensive use of fertilizers on agricultural land (Puckett et al., 2002; Bendahl and Fleming, 2007; Schwientek et al., 2008; Torrento et al., 2010). On the account of groundwater contamination by the resulting nitrates (Trudell et al., 1986; Schwientek et al., 2008) and surface water eutrophication, the removal of ammonia from water is becoming an increasingly important problem. Currently the main treatment technology for water containing ammonia is aerobic biological treatment. However, a number of disadvantages, such as the need for rigid control of the pH, temperature of the water, nutritional sources, and long reaction time, limit its application (Carrera et al., 2004; Terada et al., 2003; Baumgarten and Seyfried, 1996). In particular, due to the toxic nature of ammonia in industrial wastewater, for which biological treatment is not appropriate, catalytic wet oxidation (CWO), where ammonia can be removed as molecular nitrogen, is under development as a promising technology (Taguchi and Okuhara, 2000; Hung et al., 2003; Lee, 2003; Lee et al., 2005; Hung, 2009).

The first reported CWO of NH₃ in water was in 1985, in which NH₃ was found to oxidatively decompose at 536 K and 4.0 MPa of O₂ at pH = 12 in the presence of a MnCeOₓ catalyst, at the expense of forming harmful NOₓ (Imamura et al., 1985).


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Later, under relatively mild reaction conditions (433 K, 0.5 MPa, pH = 5.5), Pt/TiO2 catalysts were found to decompose NH3 into N2 with 100% selectivity (Taguchi and Okuhara, 2000). Although the technology of CWO can oxidize NH3 selectively to N2 rather than hazardous nitrate, the severity of the oxidation reaction conditions (high temperature, high pressure) and the need for noble metal catalysts still inhibit wide-scale use.

Currently, catalytic ozonation is being considered as an alternative method for decomposing organic compounds in water because its reaction conditions are near room temperature (Einaga and Ogata, 2009, 2010). Various metal oxide catalysts have been studied for use in catalytic ozonation of organic compounds in water (Nawrocki and Kasprzyk-Hordern, 2010). Oxidative decomposition of NH3-N with O3 in water was researched at 333 K over non-noble metal oxide catalysts and without a high-pressure reactor (Ichikawa et al., 2014). It was found that MgO had a high catalytic activity but low selectivity for the gaseous product molecular nitrogen (N2), while Co3O4 had high selectivity for N2 but was less active. The simultaneous achievement of high catalytic activity and high selectivity for N2 at low temperature, normal atmospheric pressure, and without the involvement of precious metal catalysts would be very beneficial from a practical point of view. Chen et al. (2015) illustrated potential applications of Mn–Fe–Cu/Al2O3–COS (catalytic ozonation system) for pretreatment of biologically refractory wastewaters. A Mn–Ce–O catalyst showed better catalytic ozonation performance for phenolic wastewater than Co/CeO2–Cu–Al2O3 (cat-

Accordingly, in this study, MgO-Co3O4 composite metal oxide catalysts prepared with different fabrication conditions have been systematically evaluated and compared in the catalytic ozonation of ammonia in water. Meanwhile, the effect of coexisting cations or anions on the decomposition ammonia was also studied. In addition, the reaction mechanism has been discussed.

1. Experimental

1.1. Preparation of catalysts

MgCl2·6H2O, CoCl2·6H2O, and aqueous ammonia were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. and used without further treatment.

MgO-Co3O4 composite metal oxide catalysts were prepared by a co-precipitation (CP) method. Mixed solutions of MgCl2 and CoCl2 with the desired molar ratios were prepared by dissolving solid MgCl2·6H2O (analytical grade) and CoCl2·6H2O (analytical grade) in deionized water. Under continuous stirring, 6.5 mL of aqueous ammonia solution (chemical grade) previously diluted in 10 mL of deionized water was successively added dropwise into the solution. The suspension was stirred continuously for 3 hr and subsequently aged at room temperature for 24 hr. The precipitate that formed was separated by filtration, and washed with deionized water and ethanol. It was then dried at 90°C for 24 hr, and subsequently milled and calcined in air at varying temperatures and times.

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2. Results and discussions

2.1. Properties of composite metal oxide catalysts

Fig. 1 gives the diffractograms of MgO-Co3O4 composite metal oxide catalysts with different molar ratios. As can be seen, Co3O4 (Fig. 1a) shows one sharp peak around $2\theta = 37.03^\circ$ corresponding to the (101) plane and other small peaks of pure crystalline Co3O4. MgO (Fig. 1k) shows two peaks around $2\theta = 42.93^\circ$ and $2\theta = 62.30^\circ$ respectively, which correspond to those of pure MgO. From Fig. 1b to Fig. 1j it can be seen that when the molar ratio of MgO-Co3O4 increased, some diffraction peak intensities decreased, until the peaks of Co3O4 completely disappeared for the molar ratio 9:1. Also, as the molar ratio of MgO-Co3O4 increased, the composite metal oxide crystallinity decreased and the grain size decreased, implying an increase in the specific surface area.

Fig. 2 shows the XRD patterns of MgO-Co3O4 composite metal oxide catalysts with molar ratio 8:2 calcined at 400, 500 and 600°C for 2 hr. Fig. 2 indicates that the thermal treatment of catalysts at elevated temperatures does not give rise to additional reflections. From Fig. 3 it can be seen that with the extension of calcining time for the catalysts, the intensities and the positions of the diffraction peaks were not changed noticeably.

Table 1 lists the specific surface areas for the MgO-Co3O4 composite metal oxide catalysts with different molar ratios calcined at different temperatures for different times. The specific surface area of the catalysts increased with the increase of MgO-Co3O4 molar ratio. The calcination temperature and calcination time had a small effect on the specific surface area of the catalyst with MgO-Co3O4 molar ratio 8:2, with the catalyst calcined at 500°C for 3 hr showing the maximum specific surface area of 28.55 m²/g.

Fig. 4a provides the N2 adsorption–desorption curve of the MgO-Co3O4 composite metal oxide catalyst with molar ratio 8:2 calcined at 500°C for 3 hr. As can be seen, the adsorption–desorption curve of the catalyst has an obvious hysteresis loop, which indicates the existence of a mesoporous structure with large specific surface area and three-dimensional pore structure. Fig. 4b gives the pore size distribution curve of the catalyst.
MgO-Co₃O₄ composite metal oxide catalyst with molar ratio 8:2 calcined at 500°C for 3 hr. From Fig. 4b it can be seen that the catalyst shows a single peak in the distribution, with the pore size range 2–50 nm and the average pore diameter 3.76 nm.

Fig. 5 shows SEM micrographs of the MgO-Co₃O₄ composite metal oxide catalysts with molar ratio 8:2 calcined at different temperatures for different times. Fig. 5a shows that the surface of the catalyst calcined at 400°C for 2 hr is relatively smooth and has a uniform particle size. The catalyst calcined at 500°C shown in Fig. 5b has an uneven surface and smaller particle size, while in Fig. 5c the catalyst calcined at 600°C for 2 hr shows some roasting clumps and sintered bulk.

Fig. 5d shows the SEM image of the catalyst calcined at 500°C for 3 hr. The catalyst surface has a fluffy and floc-like structure, with small and uniform particles that can provide more reactive sites. However, the partial agglomeration phenomenon observed for the catalyst calcined at 500°C for 4 hr (Fig. 5e) could affect the activity of the catalyst.

### Table 1: Specific surface areas for the MgO-Co₃O₄ composite metal oxide catalysts.

<table>
<thead>
<tr>
<th>Molar ratio of MgO-Co₃O₄</th>
<th>Calcining temperature (°C)</th>
<th>Calcining time (hr)</th>
<th>BET (m²/g)</th>
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<tr>
<td>0:10</td>
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<td>2</td>
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</tr>
<tr>
<td>8:2</td>
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<td>4</td>
<td>25.21</td>
</tr>
</tbody>
</table>

BET: specific surface areas determined by the standard Brunauer-Emmett-Teller (BET) method.

MgO-Co₃O₄ composite metal oxide catalyst with molar ratio 8:2 calcined at 500°C for 3 hr. From Fig. 4b it can be seen that the catalyst shows a single peak in the distribution, with the pore size range 2–50 nm and the average pore diameter 3.76 nm.

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### 2.2. Blank experiment

A blank experiment, in the absence of any catalyst, was carried out under ozone with flow rate 12 mg/min at 50°C. The result is presented in Fig. 6, showing that the ammonia decomposed even when no catalyst was present, as Ernst et al. (2004) reported, but the conversion rate of ammonia was only about 20% and most of the ammonia decomposition product was nitrate nitrogen, whose toxicity is higher than that of ammonia nitrogen. As is known to all, ozone is very strongly oxidizing, with a redox potential of 2.07 V. Thus, there was no nitrite nitrogen in solution.

Additional tests were also performed in the presence of the catalysts without ozone in order to evaluate their potential catalytic activities at 50°C (as shown in Fig. 6). When metal oxide catalysts (dosage of catalysts 1 g/L) were employed, whether single metal oxide catalysts (calcined at 500°C for 2 hr) or composite metal oxide catalyst (MgO-Co₃O₄ catalysts with molar ratio 8:2, calcined at 500°C for 3 hr), the decomposition of ammonia did not occur at all in the absence of ozone. The solution contained no nitrate or nitrite nitrogen, and no gaseous nitrogen was generated, since no oxidation took place, indicating that the three bare catalysts were totally inactive in the catalytic oxidation of ammonia under the applied reaction conditions. There was only a small amount of adsorption.

### 2.3. Effect of MgO-Co₃O₄ molar ratio on catalytic performance

Fig. 7 shows the effect of the MgO-Co₃O₄ molar ratio from 0:10 to 10:0 on the catalytic ozonation of ammonia nitrogen at 50°C. The results indicated that pure cobaltous oxide catalyst (MgO-Co₃O₄ molar ratio 0:10, calcined at 500°C for 2 hr) had the lowest removal rate (28.2%) for ammonia nitrogen but a high selectivity for gaseous nitrogen (17.2%), while the pure magnesium oxide catalyst (MgO-Co₃O₄ molar ratio 10:0, calcined at 500°C for 3 hr) produced the opposite result, with the highest removal rate (92.2%) for ammonia nitrogen but the lowest selectivity for gaseous nitrogen (only 7.9%). This result is in agreement with Ichikawa et al. (2014).

From Fig. 7 it can also be seen that the residual ammonia nitrogen in the solution decreased with increasing content of magnesium in the catalyst, yet the concentration of nitrate in
the solution increased gradually. When the molar ratio of magnesium to cobalt was 8:2 (calcined at 500°C for 3 hr), the residual ammonia nitrogen concentration was 7.4 mg/L with an ammonia nitrogen removal rate of 85.2%. Under these conditions the solution total nitrogen content was the lowest, and the selective conversion rate of ammonia nitrogen into gaseous nitrogen was the highest, at 44.8%. The production of nitrite was very low in all reactions. It is accepted that $\Delta H_f$ indicates the bond strength between the metal cation (M) and lattice oxygen (M–O) in metal oxides. Thus, metal oxides with small $\Delta H_f$ values have weak M–O bond strengths. Therefore, the surface density of O is low for catalysts with small $\Delta H_f$.

Fig. 5 – Scanning electron microscope (SEM) images of MgO-Co$_3$O$_4$ composite metal oxide catalysts with molar ratio 8:2 calcined at 400°C(a), 500°C(b), 600°C(c) for 2 hr, at 500°C for 3 hr (d) and 4 hr (e).

Fig. 6 – Wet ozone oxidation of ammonia. Reaction conditions: initial ammonia concentration 50 mg/L, pH 9, contact time 2 hr.
values, leading to the high selectivity for gaseous products (Ichikawa et al., 2014). We believe that this is one of the reasons for the high selectivity for gaseous products over the pure cobaltous oxide catalyst, and the possible degradation mechanism of ammonia using the MgO-Co3O4 ozonation process is the high catalytic activity of MgO with high specific surface area and high selectivity to gaseous products of Co3O4.

Since the reaction was conducted under mild basic conditions (pH 9), most of the ammonia nitrogen was present as molecular NH3, not as NH4+ (Eq. (2)). Under alkaline conditions, the catalytic ozonation with hydroxyl radical is very fast, mainly involving two reactions (Eqs. (3) and (4)) (Li et al., 2016).

\[
\begin{align*}
\text{NH}_4^+ + \text{OH}^- & \rightarrow \text{NH}_3 + \text{H}_2\text{O} \quad (2) \\
\text{O}_3 + \text{OH}^- & \rightarrow \cdot \text{HO}_2 + \cdot \text{O}_2^- \quad (3) \\
\text{O}_3 + \cdot \text{HO}_2 & \rightarrow \cdot \text{OH} + 2\text{O}_2 \quad (4)
\end{align*}
\]

An experimental phenomenon was observed that the pH values of the reaction solutions changed after 2 hr, as shown in Fig. 7. As Eqs. (5)–(9) display, hydrogen ions (H+) are formed by the catalytic ozonation of ammonia in water, causing a decrease in the pH of the reaction solution as the reaction proceeds when the MgO-Co3O4 molar ratio is low (pure metal oxide Co3O4, pH 3.2). As the MgO-Co3O4 molar ratio increased, the pH of the reaction solution after the reaction was relatively high (pure metal oxide MgO, pH 10.7) because MgO had a higher degree of dissolution during the reaction.

2.4. Effect of coexisting ions on catalytic performance

Because actual wastewater usually contains other cations and anions, the influence of coexisting ions should be considered. 50 mg/L of the anions SO4^{2-}, HCO3^−, CO3^{2-} and Br− was added into the solution containing 50 mg/L ammonia respectively to investigate the effect of coexisting anions on the performance...
of the catalyst (MgO-Co3O4 molar ratio 8:2, calcined at 500°C for 3 hr) in catalytic ozonation of ammonia nitrogen at 50°C, as shown in Fig. 8. The presence of SO4 \(^{2-}\) led to increases in the concentrations of both residual ammonia nitrogen and nitrate nitrogen, and the conversion of ammonia nitrogen into gaseous nitrogen decreased. This is mainly due to the capture of \(\cdot\)OH on the \(\cdot\)SO4 \(^{2-}\) radical (Zhou et al., 2010), resulting in the concentration of \(\cdot\)OH decreasing in the solution and thus

![Graph showing the effect of coexisting anions on catalytic activity](image1)

**Fig. 8** – Effect of coexisting anions on catalytic activity. Reaction conditions: Initial ammonia concentration 50 mg/L, pH 9, dosage of catalyst 1 g/L, flow rate of ozone 12 mg/min.

![Graph showing the effect of coexisting cations on catalytic activity](image2)

**Fig. 9** – Effect of coexisting cations on catalytic activity. Reaction conditions: Initial ammonia concentration 50 mg/L, pH 9, dosage of catalyst 1 g/L, flow rate of ozone 12 mg/min.
causing the catalytic activity of ozone oxidation of ammonia nitrogen to decrease. The existence of HCO$_3^-$ brought about a similar result as SO$_4^{2-}$, because HCO$_3^-$ has a strong scavenging effect on ·OH (Zhou et al., 2010). Owing to CO$_3^{2-}$, a very good pH buffering ion, neutralizing H$^+$ produced in the process of the catalytic oxidation of ozone, the addition of CO$_3^{2-}$ promoted the catalytic reaction, and the conversion of ammonia nitrogen into nitrogen increased. As for Br$^-$, Br$^-$ is involved in the catalytic cycle, so a greater proportion of ammonia nitrogen converted into N$_2$. Since in the presence of ozone Br$^-$ will generate the by-product BrO$_3^-$, a potential carcinogen, (Zhang et al., 2011), the catalytic ozonation of ammonia nitrogen should be used carefully in water containing Br$^-$. By the way, the concentration of nitrite in solution was less than 0.1 mg/L in all reaction systems.

Fig. 9 displays the effect of the cations Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$ on the catalyst (MgO-Co$_3$O$_4$ molar ratio 8:2, calcined at 500°C for 3 hr) performance in the catalytic ozonation of ammonia nitrogen at 50°C. The graph shows that the cations Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$ have very little effect on the catalytic ozonation of ammonia nitrogen.

2.5. Practicability of catalyst

The engineering practicability of the catalyst was investigated from two aspects: the dissolution of metal ions in the process of using the catalyst, and whether high activity could be maintained when the catalyst was reused several times.

The dissolution degrees for MgO-Co$_3$O$_4$ composite metal oxide catalysts with molar ratio 8:2 under different calcining temperatures and different calcining times after reaction with ammonia for 2 hr were investigated, as shown in Table 2.

There were small amounts of Mn ions and Co ions dissolved in solution for the MgO-Co$_3$O$_4$ composite metal oxide catalysts with molar ratio 8:2 under the four preparation conditions, for which the maximum dissolution was about 1% of the catalyst dosage for Mn ions, and less than 0.3% for Co ions.

Dissolution degree: amount of metal dissolved in the reaction solution was determined by using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

In order to study the stability of the catalyst with MgO-Co$_3$O$_4$ molar ratio 8:2, calcined at 500°C for 3 hr, the used catalyst was filtered, recovered and reused under the same experimental conditions for catalytic ozonation of ammonia in subsequent experiments. Fig. 10 shows the catalytic activity of the MgO-Co$_3$O$_4$ composite metal oxide catalyst after different reuse cycles, in which can be seen that with the increase in cycles, the removal effect of ammonia decreased slightly. After the catalyst was reused 5 times, the catalytic ozonation of ammonia in water still showed stability.

![Table 2 - Dissolution degrees of the metal oxide catalysts after reaction.](image)

![Fig. 10 - The stability of catalyst on reuse. Reaction conditions: initial ammonia concentration 50 mg/L, pH 9, dosage of catalyst 1 g/L, flow rate of ozone 12 mg/min, contact time 2 hr.](image)
catalytic activity. This is an important condition for the application of a catalyst in actual water treatment.

3. Conclusions

MgO-Co3O4 composite metal oxide catalysts made with different preparation conditions were evaluated by XRD, SEM, BET and pore analysis, and also compared in the catalytic ozonation of ammonia (50 mg/L) in water. Combining the high catalytic activity of MgO and high selectivity for gaseous nitrogen of Co3O4 in ammonia decomposition, the catalyst with MgO-Co3O4 molar ratio 8:2 calcined at 500°C for 3 hr showed the best performance, with an ammonia nitrogen removal rate of 85.2% and gaseous nitrogen selectivity of 44.8%. In addition, the reaction mechanism of ozonation oxidative decomposition of ammonia nitrogen in water with metal oxide catalysts was discussed. Moreover, the effect of coexisting anions and cations on the degrade of ammonia was studied. The experimental results showed that coexisting SO4\(^{2-}\) could inhibit the catalytic activity, while CO3\(^{2-}\) could promote it. Coexisting Br\(^{-}\) greatly promotes the catalytic reaction, but Br\(^{-}\) will generate carcinogenic BrO3 in the presence of ozone. The tested cations had very little effect on the catalytic ozonation of ammonia nitrogen. After five successive reuses, the catalyst remained stable in the catalytic ozonation of ammonia.

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