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THE EFFECT OF CALCINATION TEMPERATURE ON COBALT OXIDE SPECIES AND PERFORMANCE FOR CATALYTIC OZONATION OF NH_4^+ IN WATER

Pengaruh Suhu Kalsinasi pada Cobalt Oksida dan Kinerjanya untuk Ozonasi Katalitik NH_4^+ dalam Air

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ABSTRACT

Cobalt oxide catalysts can be prepared by impregnation and calcined under different temperatures to obtained different species of cobalt oxide, namely CoO(OH), Co_3O_4, and CoO. Co_3O_4 was the most appropriate catalyst for decomposing NH_4^+ with O_3 in the presence of Cl^- because of relatively high activity, 74%, and high selectivity for gas products, 88%, compared to CoO and CoO(OH). Cl^- is necessary to proceed with the catalytic ozonation of NH_4^+ since Cl^- participate in the catalytic ozonation mechanism, while SO_4^{2-} inhibited the process. During the catalytic ozonation of NH_4^+, Co_3O_4 showed no deactivation rather than enhanced the catalytic performance after repeated used up to 100% of NH_4^+ conversion. The Co_3O_4 can be regenerated by recalcining the catalyst under air at high temperatures.

Keywords: *Cobalt oxide species, Co_3O_4, catalytic ozonation NH_4^+, stability, regeneration*

ABSTRAK

Katalis oksida kobalt dapat dibuat dengan cara impregnasi dan kalsinasi pada suhu yang berbeda untuk memperoleh berbagai spesies oksida kobalt, yaitu CoO(OH), Co_3O_4, dan CoO. Co_3O_4 merupakan katalis yang paling tepat untuk mendekomposisi NH_4^+ dengan O_3 dengan adanya Cl^- karena aktivitasnya yang relatif tinggi, 74%, dan selektivitas yang tinggi untuk produk gas, 88%, dibandingkan dengan CoO dan CoO(OH). Cl^- diperlukan untuk memproses ozonasi katalitik NH_4^+ karena Cl^- berpartisipasi dalam mekanisme ozonasi katalitik, sedangkan SO_4^{2-} menghambat proses. Selama ozonasi katalitik NH_4^+, Co_3O_4 tidak menunjukkan deaktivasi melainkan peningkatan performa katalitik setelah penggunaan berulang untuk konversi NH_4^+ hingga 100%. Co3O4 dapat diregenerasi dengan rekalsinasi katalis pada suhu udara tinggi.

Kata Kunci: *Spesies oksida kobalt, Co_3O_4, ozonasi katalitik NH_4^+, stabilitas, regenerasi*

INTRODUCTION

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].

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], it should be removed to prevent environmental damage.

Catalytic ozonation is one of advance oxidation process which is proven effective for treating refractory pollutants [6-8]. Catalytic ozonation gained a lot of attention due to its advantages, such as mild reaction conditions (ordinary temperature and pressure) and high effectiveness for organic pollutants degradation. In catalytic ozonation, even though ozone is one of strong oxidizer, it is not enough for total mineralization of the contaminant in the absence of catalyst [8-10]. Heterogeneous catalyst that usually applied for catalytic ozonation is metal oxide and cobalt oxide is one of them [9, 11-13].

Cobalt oxide has great potential for catalysis [12, 14, 15], electrochemistry [16, 17], sensing devices [18] and magnetic materials [19] to name a few. There are several cobalt oxides that showed significant performance to their potential, namely CoO, CoO_2, Co_2O_3, CoO(OH) and Co_3O_4. However, mostly Co_3O_4 and CoO are used due to their stability [18, 20]. These cobalt oxides were synthesized using various methods such as hydrothermal [21], precipitation [22-24], impregnation [13], femtosecond laser ablation [16], solid-state [14] and core-shell [15].

In the previous study of catalytic ozonation of NH_4^+, Ichikawa et al [13] have reported that Co_3O_4 showed moderate performance with high selectivity of gaseous gas than NO_3^- as product. In the contrary, Liu [14] showed that Co_3O_4 and Co_3O_4-enhanced with surfactant had low activity and selectivity toward nitrogen gas when treating NH_4^+ in water. In this study, the facile synthesis of cobalt oxide was conducted based on the calcination temperature only to form different cobalt oxide catalysts. The purpose of this study was to apply the catalytic ozonation for ammonia decomposition in water in the presence of cobalt oxides. In addition, the stability of Co_3O_4 as heterogeneous catalyst was also have been investigated by repeated use.

EXPERIMENTAL

1. Synthesis of catalysts

The cobalt oxide catalysts were prepared by a precipitation method following the procedure used by Ichikawa et al [13]. Cobalt nitrate, $Co(NO_3)_2$. $6H_2O$, as source of cobalt was mixed with aqueous ammonia until the pH reached 8. The found precipitate was then filtered, washed with distilled water and dried at 100°C for two days, followed by calcination at 450°C for 3 h to obtain Co_3O_4. As for the CoO(OH) and CoO formation were conducted by calcined Co_3O_4 under N_2 gas for 4 h with different temperatures, namely 260 and 850°C, respectively.

2. Catalytic ozonation of NH_4^+

The catalytic ozonation of NH_4^+ was carried out in a batch reactor. The reaction solution containing NH_4Cl (10 mmol/L) and catalyst was heated up to 60°C with stirring. After temperature reached to 60°C, O_3/O_2 mixture was introduced into the reactor to start the reaction. The catalytic ozonation of NH_4^+ was also conducted using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ under same reaction condition. The aqueous phase was analyzed using ion chromatographs to determine the concentrations of NH_4^+ and NO_3^-. NO_2^- was not formed at all under the reaction conditions.

3. Repeated use of Co_3O_4 for catalytic ozonation of NH_4^+

Catalytic ozonation of NH_4^+ in water (NH_4Cl, 10 mmol L^{-1}) was carried out in a batch reactor at 60°C with vigorous stirring in a stream of O_2/O_3. Concentration of NH_4^+ and NO_3^- were determined by using ion chromatographs. After the reaction, the catalyst was separated by filtration, washed with distilled water and dried overnight at 100°C. The spent catalyst was then reused for the catalytic ozonation of NH_4^+ under the reaction conditions similar to those for the first run. The reactions were repeated for several times.

RESULTS AND DISCUSSION

Preparation of cobalt oxide plays important role to determine the cobalt oxide (CoO_x) species. Among the parameters, catalyst precursor and calcination temperature are considered to be crucial [20, 25]. The calcination of $Co(NO_3)_2$ at 300-800°C leads to its decomposition to Co_3O_4, as shown in Eq.1

$$3\ Co(NO_3)_2\ (H_2O)_6 \rightarrow Co_3O_4 + 6\ NO_2 + O_2 + 18\ H_2O \quad (1)$$

Meanwhile, Co_3O_4 can also be obtained from oxidation and decomposition of $Co(OH)_2$, as represented in Eq. 2-4 [25, 26].

$$Co(OH)_2\ NO_3 + KOH \rightarrow Co(OH)_2 + KNO_3 \quad (2)$$

$$4\ Co(OH)_2 + O_2 + H_2O \rightarrow 4\ Co(OH)_3 \quad (3)$$

$$6\ Co(OH)_3 \rightarrow 2\ Co_3O_4 + 9\ H_2O + \tfrac{1}{2}\ O_2 \quad (4)$$

In addition, heating Co_3O_4 under inert gas like N_2 at temperature above 850°C will resulted the formation of CoO [20, 27, 28] and CoO(OH) when CoO_x was thermally decomposed under 270°C [20, 21, 23]. The cobalt oxides collected for this study agrees with the theories mentioned. The cobalt nitrate calcined at 450 and 650°C are Co_3O_4 species and Co_3O_4 which was further calcined at 260 and 850°C are CoO(OH) and CoO, respectively. Next, those cobalt oxide species were utilized for catalytic ozonation of NH_4^+ in water.

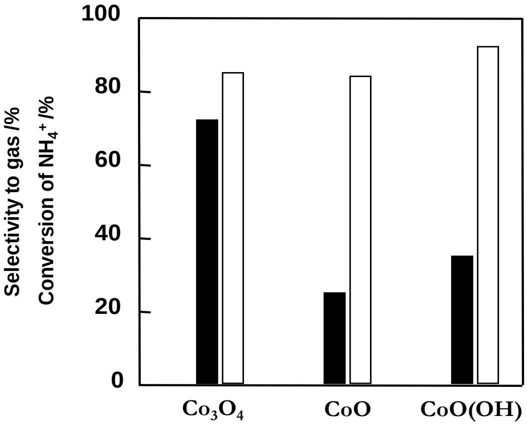

Fig 1. The performance of cobalt oxide catalyst for catalytic ozonation of NH_4^+. (■) conversion of NH_4^+ and (□) selectivity to gaseous product. Reaction parameter: NH_4Cl, 10 mmol L^{-1}; O_3/O_2 total flow rate, 100 cm^3 min^{-1}; T, 60°C; t, 6 h; catalyst, 0.10 g.

Figure 1. exhibits the performance of Co_3O_4, CoO and CoO(OH) based on the conversion of NH_4^+ and selectivity to gaseous product. The activities of those three cobalt oxide species were different. Co_3O_4 showed highest conversion of NH_4^+ at 74% and followed by CoO(OH) and CoO about 36 and 23%, respectively. Co_3O_4 is consist of Co^{2+}, Co^{3+} and O_4^{2-}. The activity of Co_3O_4 is high likely because well-dispersed Co^{2+} species acted as active sites. It is also expected that redistribution of Co^{2+} and Co^{3+} in cobalt happened during ozonation [28]. Meanwhile, all three cobalt oxide species show similar trend in selectivity to gaseous product about 85-90% of NH_4^+. High selectivity was occurred because the surface density of NH_x adsorbed is expected to be high compared to O* adsorbed on the surface of Co_3O_4 [13]. Therefore, it can be said that Co_3O_4 posses more active sites compared to CoO and CoO(OH).

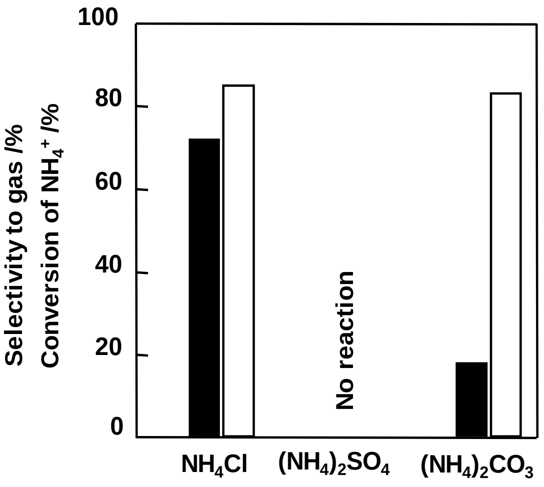

Fig 2. The performance of Co_3O_4 catalyst for catalytic ozonation of NH_4^+ from different source of NH_4^+. (■) conversion of NH_4^+ and (□) selectivity to gaseous product. Reaction parameter: NH_4^+, 10 mmol L^{-1}; O_3/O_2 total flow rate, 100 cm^3 min^{-1}; T, 60°C; t, 6 h; Co_3O_4, 0.10 g.

The catalytic ozonation of NH_4^+ over Co_3O_4 was also performed using different source of NH_4^+, namely $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. In the absence of Cl^-, the conversion of NH_4^+ was low when $(NH_4)_2CO_3$ was used and no catalytic ozonation of NH_4^+ occurred when $(NH_4)_2SO_4$ applied, as shown in Figure 2. Thus, to clarify the role of Cl^- on catalytic ozonation of NH_4^+ over Co_3O_4, once again $(NH_4)_2SO_4$ solution was used as the source of NH_4^+ but this time Cl^- was added into the reaction solution. This graph shows the relationship between Cl^- concentration with the catalytic performance of Co_3O_4. As shown here, the higher the concentration of Cl^-, the higher the conversion of NH_4^+ and so was the selectivity to gaseous product (Figure 3).

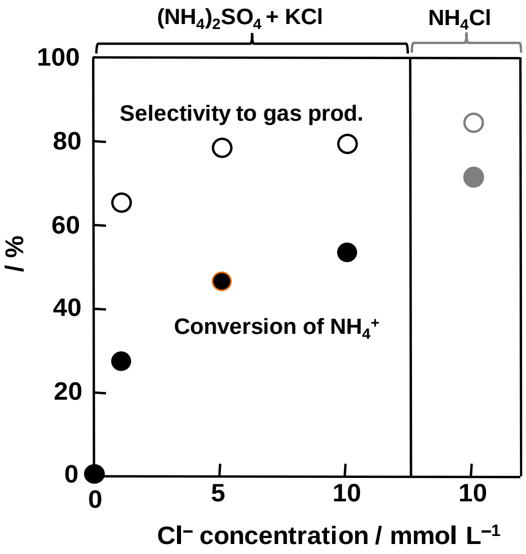

Fig 3. The performance of Co_3O_4 catalyst for catalytic ozonation of NH_4^+ in the presence of KCl. (●) conversion of NH_4^+ and (○) selectivity to gaseous product. Reaction parameter: NH_4^+, 10 mmol L^{-1}; O_3/O_2 total flow rate, 100 cm^3 min^{-1}; T, 60°C; t, 6 h; Co_3O_4, 0.10 g.

The results demonstrate that Cl^- was participated in the catalytic ozonation cycle over Co_3O_4 [13]. However, if we compared the results from $(NH_4)_2SO_4$ as NH_4^+ source with NH_4Cl, we can see that the catalytic performance of Co_3O_4 was a little lower for $(NH_4)_2SO_4$, which suggests that SO_4^{2-} inhibited the reaction.

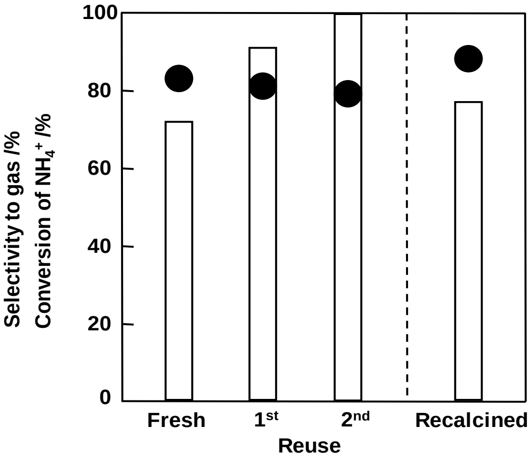

Fig 4. The performance of Co_3O_4 catalyst for catalytic ozonation of NH_4^+ with repeated used and recalcination. (□) conversion of NH_4^+ and (●) selectivity to gaseous product. Reaction parameter: NH_4^+, 10 mmol L^{-1}; O_3/O_2 total flow rate, 100 cm^3 min^{-1}; T, 60°C; t, 6 h; Co_3O_4, 0.10 g. Recalcination: T, 450°C and t, 3 h.

In the previous study [29] reported that conversion of NH_4+ was 100% after repeated used of Co_3O_4 catalyst, due to the formation of Co–NH_x functional group. This clearly showing that Co_3O_4 is an excellent catalyst since no deactivation happened. Deactivation of catalyst can be caused by sintering, fouling, poisoning or thermal degradation [30] and usually able to be generated for reuse in the same or related process [31]. In general, heterogeneous catalyst can be regenerated to regain the active site of the catalyst. Co_3O_4 was washed with distilled water and dried overnight before being used for the next same procedure. The spent Co_3O_4 undergone recalcination after being used for three times at 450°C for 3 h (Figure 4). The recalcination of Co_3O_4 showed slightly better activity compared to fresh Co_3O_4. This is possible because exposing catalyst to oxygen at high temperature will make metal redispersed through gas phase and oxidation may offer a route to removal of poison on catalyst [31]. Nevertheless, to understand the real reason on the effect of recalcination toward the catalyst activity, further investigation is needed.

CONCLUSIONS

Co_3O_4 was the most appropriate catalyst for decomposing NH_4^+ with O_3 in the presence of Cl^- because of relatively high activity and high selectivity for gas products compared to CoO and CoO(OH), due to high dispersion of the Co^{2+} and Co^{3+} active sites. Cl^- is necessary to proceed the catalytic ozonation of NH_4^+ since Cl^- participate in the catalytic ozonation mechanism, while SO_4^{2-} inhibited the process. During the catalytic ozonation of NH_4^+, Co_3O_4 showed no deactivation rather than enhanced the catalytic performance after repeated used up to 100% of NH_4^+ conversion. The Co_3O_4 can be regenerated by recalcining the catalyst under air at high temperature.

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