学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Cobalt oxide (Co_3O_4) as an active and selective catalyst
for catalytic ozonation of ammonia nitrogen in water
（水中アンモニアに高い活性と選択性を示す酸化コバルト触媒）

Water is indispensible in our life, but only 3% of water on the earth is accessible while demand of fresh water is becoming a global great concern since the amount of wastewater increases rapidly with the increase of industrialization and population growth. One of the pollutants generated from disposal of industrial wastewater, household sewage discharge, excess fertilization and inappropriate disposal of livestock excreta is ammonia nitrogen (NH_3/NH_4^+). Ammonia nitrogen can cause eutrophication and is toxic to fish and aquatic organisms in addition to the offensive smell and potential carcinogenesis. Some methods have been established for removal of ammonia nitrogen, including biological treatment, ammonia stripping and catalytic oxidation. However, such established methods have some drawbacks.

Recently, catalytic ozonation gained a lot of attention due to its advantages, such as mild reaction conditions (ordinary temperature and pressure), high effectiveness for organic pollutants degradation, powerful in mineralization of persistent organic pollutants and negligible negative effect on water quality. Therefore, some researchers have been applied catalytic ozonation to treat wastewater. However, there is little paper on catalytic ozonation of ammonium nitrogen in water. Thus, this thesis aimed first to find active, selective and stable metal oxide catalysts for catalytic ozonation of NH_4^+ in water. The second objective was elucidation of reaction mechanism for the catalytic ozonation of NH_4^+ over Co_3O_4.

Catalytic ozonation of NH_4^+ in water was conducted with a variety metal oxide catalysts, including Co_3O_4, NiO, MgO, CuO, Mn_3O_4, Al_2O_3, SnO_2, ZnO, and Fe_2O_3. MgO and NiO had the highest activity, but large amounts of undesired NO_3^- formed due to their low selectivity to gaseous products. 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 stability (low dissolution degree) among the metal oxide catalysts. Ammonia nitrogen (NH_4^+, 10 mmol L^{-1}) in water was effectively decomposed to N_2 with 85% selectivity at 333 K over Co_3O_4.

It was found that Cl^- in the solution was indispensible for the catalytic ozonation of NH_4^+ over Co_3O_4 and Cl^- was involved in the catalytic cycle. In the reaction, Cl^- was first oxidized with ozone to form ClO^- and

ClO_3^-. Formed ClO^- and ClO_3^- were then reacted with NH_4^+ over Co_3O_4 into N_2 and NO_3^-. Co_3O_4 promoted the reaction of NH_4^+ with ClO_x^-, but rather suppressed the oxidation of Cl^- with O_3. Selectivity of the catalytic ozonation reaction was determined by the standard enthalpy change of formation per mol of oxygen atom of the catalysts. The catalysts with the low standard enthalpy 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 ClO_x^- with the catalyst surface.

Catalytic activity of Co_3O_4 for the catalytic ozonation of NH_4^+ in water was greatly enhanced with each reuse of the catalyst under the reaction conditions while maintaining its high selectivity towards gaseous compounds. However, other metal oxide catalysts including Al_2O_3, Mn_5O_8, and SnO_2 showed no or only a little enhancement of the activity. Changes in the crystalline structure of Co_3O_4 were not the reason for this activity enhancement. From the IR spectra and the catalytic data of Co_3O_4 pretreated under various conditions, it was concluded that formation of $–NH_x$ groups on the surface of Co_3O_4 during the reaction caused the enhancement of the catalytic activity.