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学位論文内容の要旨

博士 (環境科学)

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学位論文題名

Electrocatalysis of noble metal alloys for denitrification in the hydrosphere
(水圏における脱窒素のための貴金属合金の電極触媒作用)

Groundwater is the main source of drinking water in many countries, and about more than one-half of the world's population depends on groundwater for their daily activities. Nowadays groundwater is significantly contaminated with nitrate, and nitrate contamination spreads out all over the world. The increasing contamination of groundwater, potable and wastewater by nitrate is an alarming issue due to its adverse effects on health and environment. Among various denitrification technologies, an electrochemical method is promising and effective to eliminate nitrate from the hydrosphere. Previous studies report that noble metal-based binary metal electrodes show good electrocatalytic performances. The objective of this thesis is to clarify the role of noble metals and effect of alloying in binary and ternary metal electrodes in order to develop a guideline for the preparation of the electrodes showing high catalytic activity and N_2 selectivity.

In chapter 3, the effect of pre-reduction of spontaneously adsorbed tin modified Pd electrodes on their physical and electrocatalytic properties was examined. The pre-reduced Sn/Pd exhibited the enhanced activity by several times and the improved N_2 selectivity for the nitrate reduction. The change in physical properties is indicative of the formation of surface alloy, which causes the downshift of d-band center. Consequently such a change leads to weak adsorption of nitrate and loss of hydrogen adsorption and absorption ability by the d-band filling, resulting in the acceleration of the reaction rate and the improvement of the N_2 selectivity by suppressing the hydrogenation reactions.

In chapter 4, the Sn modified PdPt alloy electrodes, prepared by sputtering method followed by the spontaneous Sn adsorption, exhibited higher catalytic activity and N_2 selectivity than those of Sn/Pd and Sn/Pt electrodes and also those expected for a simple mixture of Sn/Pd and Sn/Pt electrodes. The Sn/PdPt also suppressed the formation of NH_3OH^+ and NH_4^+ . The SEIRA spectra showed stronger N=O bond of bidentate NO_3^- with the increasing Pd content. Thus the strong hydrogenation ability of Sn/Pt to produce NH_3OH^+ and NH_4^+ and the relatively weak N-O bond cleavage ability of Sn/Pd to produce N_2O rather than N_2 were harmonized by the formation of the PdPt alloy. The enhanced activity and N_2 selectivity were interpreted by the Sn-induced further downshift of the Pd d-band center already downward shifted by the alloying with Pt.

In chapter 5, the Sn-modified PtRh alloy was chosen to further examine the alloying effect. It is known that Sn/Rh showed the second largest potential of the electrodes for the selective N₂ formation from nitrate, and that the d-band center of Pt shifts downward, which is reverse of Pt in PtPd, and the d-band center of Rh shifts upward by alloying. Although the enhancement of the catalytic activity for the nitrate reduction was observed by the Sn-modification as observed for the other Sn-modified noble metal, the Sn-modified PtRh electrodes did not exhibit distinct effects on the activity, the hydrogenation ability and the N-N formation ability of Sn/Pt and Sn/Rh.

In summary, the electrocatalytic activity and the N₂ selectivity for the reduction of nitrate on Pd electrodes were enhanced by pre-reduction of the electrode and alloying with Pt as well as Sn-modification. It is confirmed that d band center of noble metal in alloys plays an important role for its electrocatalytic properties. It is concluded that the downshift of the d-band weakens the nitrate adsorption and the hydrogen sorption ability, resulting in the improvement of the activity and the product distribution. The present results provide a clear guidance for the electrode design for the denitrification in the hydrosphere.