Study on Catalytic Oxidation/Reduction of Heavy Metal Ions in Aqueous Solution for Wastewater Treatment

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（排水処理のための重金属イオンの水中接触酸化／還元に関する研究）

区　　分：甲

論　文　内　容　の　要　旨

The element of which atomic number is 23 to 92 is frequently called “heavy metal”. Heavy metals are potentially toxic, and some metals such as zinc, mercury, arsenic and selenium are carcinogenic, teratogenic, not biodegradable and prone to accumulate in living organisms. Considering humans’ health, the highly detrimental metal ions beyond their permissible limits (recommended by WHO) should be removed from the wastewater before discharge. The removal of metal ions from contaminated water has attracted worldwide attention of scientists. The removal methods including adsorption, co-precipitation, photo-chemical and biological treatments, have been extensively studied, but their removal efficiency have not satisfied an industrial demand in cases of some stable detrimental ions. For example, it is extremely difficult to remove arsenite ions (As(III)) by any method. In contrast, arsenate ions (As(V)) can be easily removed by precipitation method. Thus it is important that As(III) is effectively oxidized to As(V) in contaminated water. Similarly selenate ions (Se(VI)) should be reduced to Se(0) because Se(VI) have difficulty being eliminated by any method. However, the oxidation or reduction of such chemically stable heavy metal ions is crucial step in aqueous solution.

With the aim to find an effective and rapid oxidation/reduction process of heavy metal ions, I tried for the first time to apply heterogeneous Pt catalysts to the oxidation/reduction of stable heavy metal ions in aqueous solution without extra energy such as ultra-violet irradiation and electric power supply. In this work, the catalytic behaviors of Pt catalysts supported on metal oxides were examined in detail for the oxidation of Fe(II) and As(III) with oxygen, and for the reduction of Se(VI) ions with hydrazine monohydrate, in aqueous solution.

Chapter 1 described various treatment methods by using physical, chemical and biological processes, for removal of toxic heavy metal ions from wastewater.

In chapter 2, catalytic behavior of ZrO_2-supported Pt catalysts (Pt/ZrO_2) was examined for Fe(II) oxidation with oxygen in aqueous solution. It was found that Pt/ZrO_2 significantly promoted the oxidation of Fe(II) ion to goethite FeOOH and ferric oxide Fe_2O_3. The specific oxidation rate per active site on Pt surface was insensitive to Pt particle size of Pt/ZrO_2. The catalytic oxidation rate obeyed first-order kinetics with respect to Fe(II) concentration, and the activation energy was obtained to be 55.5 kJ/mol which was lower than the reported value without any catalyst. The Pt/ZrO_2 showed an excellent reusability in the Fe(II) oxidation. These results suggested that supported Pt catalysts can be useful for the oxidation of more stable

heavy metal ions in aqueous solution.

In chapter 3, catalytic behaviors of supported Pt catalysts were examined for oxidation of As(III) ions with oxygen in aqueous solution. The Pt catalysts remarkably promoted the As(III) oxidation even under neutral conditions, which has not been reported yet. To compare catalyst supports, Pt/ZrO_2 showed higher activity than Pt/Al_2O_3, Pt/TiO_2, and Pt/SiO_2. The Pt size effect was examined using Pt catalysts calcined at a different temperature. As a result, it was found that the Pt particle size of Pt/ZrO_2 scarcely influenced the specific activity of the As(III) oxidation, which indicates that the catalyst with smaller Pt size exhibits a higher conversion of As(III) because of larger Pt surface area. The catalytic oxidation rate of As(III) over Pt/ZrO_2 obeyed first-order kinetics with respect to As(III) concentration, and the activation energy was obtained to be 31.1 kJ/mol which was a little higher than the reported value with a strong oxidant (without any catalyst). The Pt/ZrO_2 catalyst possessed an excellent stability and could be used repeatedly with such high catalytic activity.

In chapter 4, it was shown that Pt catalyst promoted significantly the reduction of Se(VI) ions to Se(0) with hydrazine hydrate in aqueous solution. The effectiveness of supported Pt catalysts for this reaction has not been reported. To compare catalyst supports, Pt/TiO_2 catalyst exhibited a higher activity than Pt/ZrO_2 and Pt/Al_2O_3. During this reaction, however, all the Pt catalysts were deactivated quickly, of which reason was the coverage of Pt surface with Se(0) produced from Se(VI) ions. To improve the catalyst life of Pt/TiO_2, carbon nanotube (CNT) having high surface area and superior electronic property was incorporated with Pt/TiO_2. Actually Pt was immobilized onto TiO_2-covered CNT which was prepared beforehand by alkoxide method. The catalyst life of Pt/TiO_2 was successfully improved by the incorporation.

Finally, conclusions for this work were given in chapter 5. The oxidation/reduction of toxic heavy metal ions over Pt catalysts can be a splendid prospective method for the removal of detrimental ions from contaminated water because Pt catalysts have outstanding catalytic activity in aqueous solution, and high durability and recyclability.