

Title	ポリオール類の化学品への選択酸化反応のための不均一系触媒としての白金ナノ粒子のグリーン調製法の開発に関する研究
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## Abstract of Doctoral Dissertation

Glycerol (GLY) is an eco-friendly compound which is obtained as a by-product from biodiesel production (transesterification of triglycerides with alcohols). As there is an increase in biodiesel production, GLY from their process has also been produced in large quantities. There has been interest from industrial point of view to investigate the value-added products from GLY. In the controlled partial oxidation of GLY and GLY-derived product (1,2-propanediol (PG)), the value-added products such as glyceric acid (GA) and lactic acid (LA) can be obtained, respectively. GA and LA are used in the industrials as cosmetics and pharmaceutical products. Almost all of chemical manufacturing processes (90%) utilize catalysts to control the atomic efficiency of the reaction and the production of desirable products. Therefore, the development of highly efficient and recyclable catalyst with green and sustainable process is a great important issue. This dissertation studied the development of Pt-based NPs heterogeneous catalysts by a green method using eco-friendly material as a reducing and a stabilizing agent in aqueous media to improve the catalytic activity and selectivity for polyols oxidation into value-added chemicals (GA and LA) under mild reaction conditions by tuning the metal compositions and metal ligands.

The research succeeded in the development of novel green method for the preparation of hydrotalcite supported-Pt NPs heterogeneous catalysts (Pt NPs/HT). Pt NPs/HT catalysts were prepared by the immobilization method, in which Pt NPs were pre-generated by the reduction of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  precursor with soluble starch as a reducing and a stabilizing agent under alkaline treatment, and were further immobilized on the HT support. The method resulted in the reproducible particle size distribution which can be controlled by the reduction time. The catalysts showed high activity and selectivity toward GA formation for the aerobic oxidation of GLY in base-free aqueous solution under atmospheric pressure of molecular oxygen and mild conditions. After the reaction, the catalyst was easily removed by hot filtration and no Pt leaching was detected in the solution. The catalyst retained high activity in recycling experiments.

Furthermore, the research investigated the effect of soluble starch onto the catalytic properties of stabilized-Pt NPs/HT comparable to poly(vinyl pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) by probing the electronic structure using XPS and XAFS, and water wettability using contact angle measurement. The structural investigation of polymer stabilized-Pt NPs/HT catalysts with keeping the same particle size (2.2 nm) on the same basic HT support showed that starch has strong electron donation power comparable to PVP and identical to PVA to create negatively charged surface Pt atoms. The catalytic activity was enhanced by the increase of electron density on the Pt NPs surface. In addition, the polymer structure also has effect on the catalytic activity by making the wettability of stabilized-Pt NPs in the water solution. Soluble starch is found to be suitable ligand creating negatively charged Pt surface atoms and providing well-dispersion of catalyst in aqueous media that leads to the highest catalytic PG oxidations. Anionic Pt surface atoms, formed by starch ligand, may transfer electrons to oxygen molecule to form adsorbed  $\text{O}_2^-$  species. This step is proposed to be crucial in the aerobic oxidation of PG in water at room temperature.

The research also modified the developed technique for the preparation of Pt-based bimetallic NPs heterogeneous catalysts (fast co-reduction method). The aerobic oxidation of PG over  $\text{Pt}_x\text{M}_y$  NPs/HT ( $\text{M} = \text{Ru}, \text{Ag}, \text{Pd}, \text{Au}$ ) catalysts exhibited the selectivity toward LA. Especially, PtAu NPs/HT was most selective in base-free aqueous solution under atmospheric pressure of molecular oxygen at 353 K. Further development of synthetic method (slow co-reduction method) explored the very active PtAu NPs/HT which is able to oxidize polyols (PG and GLY) to produce GA and LA in base-free aqueous solution under atmospheric pressure of molecular oxygen at room temperature (298 K). The investigations on catalyst structure by XRD, TEM and XAFS revealed that negative charge on both Au and Pt atoms, in which starch ligand donates electrons, and the excess charge on Au atoms can also transfer to Pt atoms. The negatively-charged Pt atoms cause enhancement of the oxygen absorption and generate anionic  $\text{O}_2^-$  like superoxo or peroxo oxygen to oxidize polyols. The geometric and electronic changes of the catalytically active surface Pt sites by adjacent Au atoms and the starch ligand lead to improvement of the activity and selectivity to target products.

Overall, this research successfully develops technique for the improvement of catalysis of Pt NPs tuned by second metal and ligand. Modification of electronic state of Pt NPs is crucial to improve their catalysis for polyol oxidation. The catalysts effectively transform GLY and PG into the corresponding value-added chemicals via the aerobic oxidation reaction in base-free aqueous solution under an atmospheric pressure of molecular oxygen at room temperature. This research provides a noble route to converting wasted polyols into chemical sources through well-tuned catalytic methodology.

**Keywords:** base-free polyol oxidation, platinum/gold heterogeneous catalyst, hydrotalcite, electronic/geometric effect, starch ligand