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論文題目	Studies on the Development of Platinum-Based Nanoparticles by a Green Synthetic Method as Heterogeneous Catalyst for Selective Oxidation of Polyols into Value-Added Chemicals (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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## 論文の内容の要旨

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  $H_2PtCl_6 \cdot 6H_2O$  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  $O_2^-$  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  $Pt_xM_y$  NPs/HT ( $M = Ru, Ag, Pd, Au$ ) 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  $O_2^-$  like superoxo or peroxy 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

## 論文審査の結果の要旨

化石資源の枯渇が懸念される昨今、資源の多様化を目指し再生可能資源であるバイオマス由来物質から化成品・エネルギーを生産する技術の開発が急務となっている。バイオマス由来物質の中でも、特に木質系バイオマスの有効利用が求められており、トランスエステル化反応によるバイオ燃料生産時に副生するグリセリンを原料とするアプローチが検討されている。本研究では、グリセリンをはじめとする多価アルコール類の常圧酸素存在下での選択酸化反応において、白金ナノ粒子を触媒活性種として用い、安定化配位子（保護剤）や異種金属との複合化による触媒の高機能化を目的とした。

まず、水溶性デンプンを安定化配位子として用い白金ナノ粒子の調製を試みた。デンプンは、配位子としてのみ作用するのではなく、還元剤にもなる事を見出し、層状塩基性粘土鉱物ハイドロタルサイト表面にも固定化できる事を示した。固定化白金ナノ粒子触媒は、常圧酸素存在下、水溶媒中でグリセリンの1級水酸基を酸化し、グリセリン酸を与えた。反応途中で触媒を除去すると酸化反応は停止し、触媒は再使用可能であった事から、デンプン安定化固定化白金ナノ粒子は不均一系触媒として作用している。

次に、デンプン配位子の効果を明らかにするため、一般的な配位子である PVA と PVP を用いて同一粒子径(2.2 nm)を持つ白金ナノ粒子を調製し、触媒作用を検討し、種々キャラクターゼーションを行った。その結果、水溶媒中での 1,2-プロパンジオールの乳酸への酸化反応において、デンプン安定化白金ナノ粒子が最も高い触媒活性を示し、Pt 4f XPS 測定で negative シフトが確認された。XAFS では白金粒子表面への酸素吸着が示唆され、水との接触角測定では中程度の親水性を示した。デンプン安定化白金ナノ粒子表面の負電荷と中程度の親水性が、水溶媒中でのジオールの酸化に重要な役割を果たしていると提案した。

また、Au と複合化させる事で(Pt<sub>60</sub>Au<sub>40</sub>)、グリセリンおよび 1,2-プロパンジオールの酸化反応において、ヒドロキシ酸の選択率が向上する事を見出した。デンプン配位子からの PtAu alloy 様粒子への電子供与が観測され、これが分子状酸素の活性化を促進しているものと推察した。

以上、本論文は、常圧酸素存在下・水溶媒・室温という温和な反応条件で、多価アルコール類の1級水酸基を選択的に酸化する高機能白金ナノ粒子触媒を設計する指針を見いだす事に成功した。

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ノ粒子触媒の設計指針を与え得ると考えられ、学術的・工業的に貢献するところが大きい。  
よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。