学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Direct Synthesis of Chemicals by Acceptorless Dehydrogenation of Alcohols and Cyclic Amines with supported Pt Catalysts
（担持白金触媒によるアルコール・環状アミンの脱水素を利用した化学品の直接合成）

According to the concept of green chemistry, catalysis is an important key for ideal synthesis to prevent waste materials and increase atom economy. This concept urges chemist to develop new methodology to sustainable production of chemicals. Acceptorless catalytic dehydrogenation of alcohols and amines is regarded as one of the most important reactions for sustainable production of chemicals, because the reaction can give industrially important chemicals, carbonyl compounds and imines, without additional reagents. However, most of the reports used homogeneous catalysts, which have serious drawbacks of difficulties in product/catalyst separation and catalyst reuse and needs of additives including expensive ligands. Also, dehydrogenation of alcohols can be a key reaction in one-pot bond formation reaction from alcohols as an atom-efficient synthetic method, but most of the reports have used homogeneous catalysts. Development of heterogeneous catalysts for these reactions addresses the issues of homogeneous catalysts and consequently will provide practical methods for sustainable production of chemicals in industry. The objective of this thesis is to develop new heterogeneous catalysts for acceptorless dehydrogenation of amines and dehydrogenative one-pot bond formation reactions of alcohols. The thesis will show supported Pt nanoparticles are efficient and reusable heterogeneous catalysts for these reactions under additive-free conditions. Characterization of catalysts and model reactions are also studied to discuss catalyst design concept.

In chapter 2, the author investigated various metal loaded carbon catalysts and various supported Pt catalysts for acceptorless dehydrogenation of *N*-heterocycles under additive-free conditions under N_2. Pt metal nanoparticles-loaded carbon (Pt/C) was the best catalyst for the dehydrogenation of 6-methyl-1,2,3,4-tetrahydro-quinoline to 6-methyl-quinoline, and Pt/C was reusable. Various *N*-heterocycles, derivatives of tetrahydroquinoline and indoline, were converted

to quinolines and indole with high yields. For the dehydrogenation of 1,2,3,4-tetrahydroquinoline, turnover number (TON) of Pt/C was more than one order of magnitude higher than those of the previous homogeneous and heterogeneous catalysts. Additionally, the same catalyst was effective for the reverse reaction, hydrogenation of quinoline under 3 bar H_2. Thus, this catalytic method may be useful for a organic halide–based hydrogen storage system.

In chapter 3, a series of transition metal-loaded metal oxide catalysts were examined for the synthesis of indoles via acceptorless dehydrogenative cyclization of 2-(2-aminophenyl) ethanol. Pt/Nb_2O_5 and Pt/HBEA were found to be effective heterogeneous catalysts for the reaction. These catalysts showed higher TON than previously reported catalysts, and the Pt/Nb_2O_5 catalyst was reusable. The reaction consists of dehydrogenation and cyclodehydration steps with elimination of water as byproduct.

In chapter 4, the author examined various metal loaded-SnO_2 and supported Pt catalysts for acceptorless dehydrogenative coupling of primary alcohols to esters under additive-free and solvent-free conditions. Among screened catalysts, Pt/SnO_2 was most active. The method was effective for various primary alcohols under additive-free and solvent-free conditions, and the catalyst was reusable. IR study show that activation of carbonyl groups in aldehydes is the primary important role of the SnO_2 support. Combined with other mechanistic study a reaction pathway is proposed; the reaction of alcohol with the aldehyde coordinated to Sn^{4+} Lewis acid site to give a hemiacetal intermediate followed by its dehydrogenation to the ester. This catalytic system is the first example of heterogeneous catalyst for this reaction, which provides one of the most atom-efficient and step-efficient catalytic routes to esters from readily available starting materials, alcohols.

Chapter 5 is the general conclusion. Chapter 2-4 show systematic examples of new heterogeneous catalysts for acceptorless dehydrogenation reactions of amines (*N*-heterocycles) and alcohols for the synthesis of chemicals under additive-free conditions with liberation of H_2 as a byproduct. The heterogeneous catalysts developed in this work have advantages over the previous homogeneous catalysts, including good catalyst reusability and high TON, and hence will provide practical methods for sustainable production of chemicals.