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Heterogeneous Pt Catalysts for Direct Synthesis of Chemicals from Alcohols by
Borrowing Hydrogen and Acceptorless Dehydrogenation Reactions

(不均一系白金触媒による水素移動・脱水素反応を利用したアルコールからの直接的化学
品合成)

The limited fossil fuel and awareness of green chemistry inspire researchers to develop new green methodology for the synthesis of chemicals with atom-efficiency and step-efficiency. The classical method for the synthesis of C-C and C-N bonds is based on activated substrate such as alkyl halide which produces large amount of salt wastes. With respect to green chemistry, the alcohols based borrowing hydrogen and acceptorless dehydrogenation methodology can be a good option for the classical synthetic method of C-C and C-N bonds formation because this methodology produces H_2O and/or H_2 as byproducts. This thesis focuses on direct C-C and C-N bonds formation using alcohols as green alkylating reagents via borrowing hydrogen and acceptorless dehydrogenation methodology. The objective of this study is the development of efficient and reusable heterogeneous catalyst for the synthesis of chemicals under neutral conditions.

In chapter 2, the author examined various metal loaded- Al_2O_3 and supported Pt catalysts for alkylation of 2-methylquinoline with benzyl alcohol under additive free condition. Among screened catalysts, Pt/ Al_2O_3 was found to be most effective catalyst for the alkylation of 2-methylquinoline with benzyl alcohol. The catalyst was reusable and showed good to moderate yield for the alkylation of 2-methylquinoline with various alcohols. Mechanistic study showed that the reaction was driven by the borrowing hydrogen pathway which showed a sequence of dehydrogenation-condensation-hydrogenation reactions. This result demonstrates the first heterogeneous catalytic system for this reaction.

In chapter 3, the author investigated various metal loaded-CeO₂ and supported Pt catalysts for alkylation of oxindole with alcohols under additive free condition. I found that Pt/CeO₂ was best catalyst for alkylation of oxindole with 1-octanol. The catalyst was reusable and showed good to moderate yield of for the alkylation of oxindoles with various alcohols. Mechanistic study show that the reaction was driven by the borrowing hydrogen pathway which showed a sequence of dehydrogenation-condensation-hydrogenation reactions. This results demonstrate the first additive-free catalytic system for this reaction.

In chapter 4, a series of transition metal-loaded metal oxide catalysts examined for self-coupling of secondary alcohols. Pt/CeO₂ showed the highest activity among various metal loaded-CeO₂ and supported Pt catalysts for self-coupling of 2-octanol, and Pt/CeO₂ was effective catalyst for self-coupling of various secondary aliphatic alcohols. Pt/CeO₂ was also effective for α -alkylation of methyl ketone by secondary alcohols.

In chapter 5, the author demonstrated the first acceptorless method for synthesize of 2-quinazoline from 2-aminobenzylamine with primary alcohols or aldehydes under additive-free condition. CeO₂-supported Pt nanoparticle catalysts showed high activity among various metal supported and Pt loaded catalysts. The author investigated the reusability of catalyst and general applicability of the present catalytic system. Mechanistic study showed that the reaction was driven by the acceptorless dehydrogenation pathway, including dehydrogenation-condensation and cyclization-dehydrogenation steps.

In chapter 6, Pt/Al₂O₃ and Pt/TiO₂ were effective catalysts for the synthesis of 2-substituted benzothiazoles and benzimidazoles from 2-aminothiophenol and 1,2-phenylenediamine with alcohols or aldehydes under acceptor-free and additive-free conditions. With optimized Pt/TiO₂ and Pt/Al₂O₃ catalysts, the author investigated the general applicability of present catalytic system using various alcohols for the synthesis of 2-substituted benzothiazole and 2-substituted benzimidazole respectively.

Chapter 7 is the general summary. Chapters 2-6 show the first systematic examples of heterogeneous catalysis for the synthesis of chemicals via alkylation of nucleophiles by alcohols under additive-free conditions. These eterogeneously catalyzed direct C–C, C–N bond formation reactions by borrowing-hydrogen or acceptorless dehydrogenation methodology are redox neutral, do not require oxidants and reductants, and the byproducts are water and H₂. Hence, the methods will offer practical and atom efficient routes to valuable chemicals from alcohols under neutral conditions.

Considering these research achievements, we conclude that the author is eligible to have a Doctor degree of chemical science and engineering.