学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Sustainable Heterogeneous Catalysis for C-C/C-N Coupling using Methanol and Triglyceride
（メタノールとトリグリセリドを用いた C-C/C-N 結合生成のためのサステナブルな不均一系触媒作用）

Sustainable synthesis of useful chemicals is of the major concerns in the scientific community. To address the issues the areas of catalytic synthesis have dynamically grown over the decades and still in rise. Enormous works have been carried out employing both homogenous and heterogeneous catalysis and these are now advanced viable methods of useful chemical synthesis. Despite sufficient developments in conventional catalysis some challenges still remain unaddressed specially catalysts reusability and easy catalyst/product separation. Besides, expensive ligands are necessary in most of the homogeneous catalysis. In contrast, heterogeneous catalytic systems offer advantages in easy catalysts/products separation and catalysts reusability. From practical point of view, this is highly beneficial and reduces the industrial production cost to a great extent. This is where remains the main focus of this thesis i.e. developing sustainable heterogeneous system for important chemicals synthesis. Heterogeneous methods for methylation of various functional chemicals with methanol using carbon supported Pt-nanoparticle catalyst (Chapter 2&3) comprises one major part of the thesis. The methylation protocols follow transition metal catalyzed borrowing hydrogen methodology. The other part focuses on the research of biomass derived platform molecules, more precisely transformation of renewable triglycerides to various functional chemicals (Chapter 4&5). High-silica Hbeta zeolite was effective catalyst for amidation, nitrillation and methanolysis of triglycerides. For reductive amination of triglycerides into fatty amines with ammonia, Pt-loaded zirconia was developed as the catalyst. Details of all the methods along with studies on structure-activity relationship and reaction mechanism are extensively discussed in the thesis with a view to design new heterogeneous catalysts for sustainable organic synthesis. A brief summary of each title works is presented in the following sections.

The thesis starts with a general introduction followed by five individual chapters. Chapter 2 presents a highly versatile, selective, and recyclable heterogeneous catalytic processes for three types of C-methylation reactions using methanol as a sustainable C1 source. The methods are the beta-methylation of primary alcohols, the alpha-methylation of ketones, and the C3-methylation of indoles. These catalytic systems are driven by a borrowing-hydrogen mechanism, wherein the Pt-nanoparticles-catalyzed dehydrogenation of methanol (and alcohols) to aldehydes is followed by a condensation of formaldehyde with the corresponding nucleophile (aldehyde, ketone, or indole) to yield unsaturated intermediates, which are subsequently hydrogenated by Pt-H species on the catalyst. Compared to previous catalytic methods of borrowing-hydrogen-type C-methylation reactions, this method presents several advantages: (1) easy catalyst/product separation, (2) catalyst recyclability, (3) excellent TONs (up to two orders of magnitude higher than those previously reported), and (4) wide substrate scope. Furthermore, DFT calculations have shown that the adsorption energy of hydrogen correlates well with the catalytic activity of various active metals employed in these reactions. These

results should be helpful to rationalize the properties of catalytic systems and serve as a practical guide for future catalyst design.

Chapter 3 demonstrates a general heterogeneous catalytic method for the selective N-methylation of amines and nitroarenes with methanol using Pt/C and base (NaOH or KOtBu). The presented catalyst system is exclusively effective for four types of N-methylation reactions: dimethylation of aliphatic amines, selective monomethylation of aliphatic and aromatic amines, and monomethylation of nitroarenes. The same Pt/C catalyst is effective for all types of reactions depending only on tuning the reaction conditions such as temperature and atmosphere. Compared to the previously reported methods with homogeneous and heterogeneous catalysts, all these reactions under the same catalytic system showed high yields of the corresponding methylamines for a wide range of substrates, high turnover number (TON), and good catalyst reusability. Mechanistic studies suggested that the reaction proceeded via a borrowing hydrogen methodology. Kinetic results combined with density functional theory (DFT) calculations revealed that the high performance of Pt/C was ascribed to the moderate metal–hydrogen bond strength of Pt.

Chapter 4 describes three heterogeneous catalytic methods for the selective one-pot transformation of triglycerides to value-added chemicals: (i) a reductive amination of triglycerides into fatty amines with aqueous ammonia under hydrogen using Pt metal nanoparticles-loaded zirconia, (ii) an amidation of triglycerides under gaseous ammonia using a high-silica Hbeta zeolite, and (iii) a direct synthesis of nitriles from triglycerides and gaseous ammonia using a high-silica Hbeta zeolite at higher temperature. These methods selectively transform a wide variety of triglycerides (C4-C18) into the corresponding amines, amides, and nitriles, and thus represent a milestone in chemical transformation of triglycerides. A systematic analysis of reaction (ii) and (iii) reveals that the acidity and hydrophobicity of the zeolites are two important factors that affect the catalytic activity of the Hbeta catalysts. Specifically, increasing the number of acid sites and increasing the hydrophobicity may lead to higher reaction rates per weight of the catalyst. Hydrophobicity and acidity of different zeolites were studied by various characterization methods, including NH3-TPD, adsorption experiments in water, and IR spectroscopy.

Chapter 5 shows a simple method for the transesterification of triglycerides with methanol to fatty methyl esters using Hbeta-75 with Si/Al = 75 as an active and reusable catalyst. The fatty acid methyl ester (FAME) is also popular as a biofuel. The developed catalytic system was applicable to the transformation of various triglycerides having C4-C18 frames. Considering the commercial availability and high durability of the Hbeta-75 catalyst, the method could be applicable to a practical process for the conversion of biomass-derived triglycerides into biofuel. The number of Brønsted acid sites and hydrophobicity are two dominant factors that influence the catalytic activity of the presented catalytic system. Quantitative relationships between acidity, hydrophobicity, and reaction rates versus Si/Al ratio of Hbeta zeolite catalysts show that a low affinity to glycerol, which arises from the hydrophobicity of the high-silica zeolites, is an important parameter for controlling the catalytic activity.

Chapter 6 is the general conclusion that summarizes the highlights of this thesis. To reiterate, the key points in two major areas of development i.e. methods in 1) C- and N-methylation using methanol by Pt/C catalyst, and 2) catalytic transformation of biomass derived platform molecule (triglyceride) to valuable chemicals are summarized. All the described methods are highly selective heterogenous systems with reusable catalysts having wide substrate scopes and excellent TONs.