

学位論文の要旨

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Design, Preparation and Application of Noble Metal Catalysts in Biomass Conversion
(バイオマス変換における貴金属触媒の設計、調製と応用)

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Recently, an increasing effort has been devoted to find ways to utilize biomass as feedstocks for the efficient production of value-added organic chemicals and fuels because of its abundance, renewability and worldwide distribution. Unlike petroleum feedstocks, biomass-derived platform molecules possess a high oxygen content that give them low volatility, high solubility in water, high reactivity and low thermal stability, as well as properties that favor the processing of these resources by catalytic aqueous-phase technologies at moderate temperatures. Lignocellulosic biomass encompassing municipal and animal wastes, forestry residues, and others is a specially interesting resource on account of being the most abundant, inedible, and inexpensive biomass.

In this doctoral dissertation, biomass derived 5-hydroxymethylfurfural (HMF), cellulose and bio synthesis gas have emerged as important platform chemicals for the next-generation plastic and basic chemicals for the production of sustainable fuels and chemicals.

Furan derivatives such as 5-hydroxymethyl-2-furaldehyde (HMF) obtained from renewable biomass resource, has the potential to serve as substitutes for the petroleum-based building blocks that are currently used in the production of polymers and fine chemicals. In Section 1 (Chapter 1), reduced graphene oxide (RGO) is one of the most promising catalyst supports since its faintly acidic sites together with large amount of functional groups on its surface. In this report, we prove that, for the first time, Pt loaded RGO (Pt/RGO) is an efficient, robust and durable catalyst oxidizing 5-hydroxymethylfufural (HMF) directly to 2,5-furandicarboxylic acid (FDCA) under mild conditions. The selectivity of FDCA reaches up to 84% along with 100% HMF conversion in the presence of excess base. We deduce that the total reaction on Pt/RGO catalyst includes several consecutive steps, in which 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) acts as an intermediate. The finding in this report is a significant advance not only for RGO-based catalysts development, but also for FDCA scalable production, because the total reaction is performed smoothly without using previously reported harsh reaction conditions.

Furthermore, Cellulose, a polysaccharide mainly composed of glucose via β -1-4 glycosidic linkage, exists widely in biomass resources. The utilization of cellulose is achieved usually through two steps: being selectively hydrolyzed into glucose and further converted into fuels and chemicals. The sugar alcohols, especially sorbitol, are used not only as sweetener in diet foods, but also as an important basic chemical for the production of sustainable fuels and chemicals. In Section 2 (chapter 2-5), Pt nanocatalysts loaded on reduced graphene oxide (Pt/RGO) are prepared via a

convenient microwave-assisted reduction approach with ethylene glycol as reductant. The conversion of cellulose or cellobiose into sorbitol is used as application reaction to investigate their catalytic performance. Various metal nanocatalysts loaded on RGO are compared. Pt/RGO exhibits the highest catalytic activity with 91.5% of sorbitol yield from cellobiose. The catalytic performances are compared with Pt nanocatalysts supported on different carbon materials or on silica support. The result shows that RGO is the best catalyst support, and the yield of sorbitol is as high as 91.5% from cellobiose and 58.9% from cellulose, respectively. The improvement of catalytic activity is attributed to the appropriate Pt particle size and hydrogen spillover effect of Pt/RGO catalyst. Interestingly, the size and dispersion of supported Pt particle are easily regulated by convenient adjustment of the microwave heating temperature. The catalytic performance is found firstly increased and then decreased with increasing particle size. The optimum Pt particle size is 3.6 nm. These findings may offer useful guidelines to design novel catalysts with beneficial catalytic performance for biomass conversion.

Conversion of synthesis gas (a mixture of CO and H₂), derived from biomass, is a hot field in hydrocarbon production. Fischer-Tropsch synthesis is a set of catalytic processes that can be used to produce fuels and chemicals from synthesis gas. Combining a acidic zeolite with common FTS catalyst can produce isoparaffins for gasoline-ranged component. Tuning hydrocarbons distribution in Fischer-Tropsch synthesis is greatly challenging in [Section 3 \(chapter 6\)](#) by employing three different pathways to deposit trace Palladium on Co/H-ZSM5 catalyst, tunable isoparaffin and olefin selectivity is successfully achieved. The impregnated Pd shows a poor promotion of Co dispersion and reducibility, producing a slight enhancement of FTS activity and

isoparaffin selectivity. Pd sputtering induces a re-dispersion of impregnated Co/H-ZSM5 particles and Pd is deposited with an intimate distance to Co species and with a weak interaction combining zeolite, due to which complete hydrogenation of olefins is achieved. But the surface enriched Pd on pre-sputtered Co catalyst was can form Pd-Co nano-alloys, suppressing the chain growth activity by excessive hydrogenation process.