様式第２号（第５条，第１１条関係）

「課程博士用」

学 位 論 文 の 要 旨

専　　攻	安全システム工学　専攻	ふりがな 氏　　名	すらちゃい　かるんじゃなこむ Surachai Karnjanakom
学位論文題目	Development of Highly Active Solid Catalysts for Upgrading of Bio-Oils (バイオオイルアップグレードのための高活性固体触媒の開発)		

学位論文要旨

Pyrolysis of biomass is one of the promising alternatives to generate bio-oil. However, the obtained bio-oil always contains a large amount of oxygenated compounds such as acids, ketones, phenols, sugars and others, which make bio-oil corrosive, unstable and low heating value. Hence, the original bio-oil should be upgraded before utilization of it as transportation fuel. Solid acid catalysts such as alumina, Al-MCM-41 and zeolite are widely utilized for the conversion of oxygenated compounds to hydrocarbons via cracking and deoxygenation. However, their activity and stability are always very low. To solve these problems, in this dissertation work, several catalysts with porous structures were prepared and applied for the upgrading of bio-oil derived from biomass pyrolysis. The detailed investigations were focused on reactions activity, selectivity and stability based adjusting the metal doping on catalyst, catalyst porosity and acidity. The potential challenges and opportunities for upgrading of the bio-oil over prepared porous catalysts were considered and discussed. It is found that when acidity, surface area and pore size of catalysts as well as loaded metal types with their dispersions on catalyst supports were adjusted, the deoxygenating efficiency, the aromatic distribution in the upgraded bio-oil and the coke yield on catalyst were changed significantly. The increasing of acidity exhibited well promoting for deoxygenation, alkylation, aromatization and polymerization, leading to the facile formation of aromatic hydrocarbons and enhancement of coking. The extensive carbon deposition resulted in short catalyst lifetimes. Fortunately, the spent catalysts were easily regenerated by calcination in air. The mechanisms on the catalytic performance and coking formation were proposed and discussed. It is expected that the obtained catalysts can be used for a practical process and the theoretical results can provide a guidance to design an effective catalyst for the bio-oil upgrading. The main conclusions in this dissertation are summarized as follows:

(1) To improve the yield of bio-oil, the biomass was pretreated at first by ultrasound and it is found that the yield of bio-oil was increased from 45% before pretreatment to 56%, due to the destruction of firm lignin structure and releasing more cellulose and hemicellulose from biomass structure. Unfortunately, this pretreating way did not improve the quality of bio-oil and the oxygenated compounds in bio-oil were more than 95%. To solve this problem, the bio-oil was catalytically upgraded over metal/commercial γ-Al_2O_3. It is found that the catalyst effectively promoted the conversion of oxygenated compounds to hydrocarbons, especially to aromatic hydrocarbon. 2.5 wt.% Zn/γ-Al_2O_3 exhibited the highest catalytic activity with the total relative total hydrocarbon amount of 80%.

(2) Mesoporous rod-like alumina with different pore sizes were successfully synthesized by using hydrothermal method with the assistance of Pluronic P123 surfactant, and applied for upgrading of bio-oil derived from biomass pyrolysis. It is found that pore volumes and pore sizes of alumina increased with the increase in the P123/Al molar ratio from 0.005 to 0.05 while surface areas continuously increased until 0.01, indicating that the concentration of P123 had great effect on the textural properties of the obtained alumina. Herein, the alumina with larger pore size resulted in the facile formation of polycyclic aromatic hydrocarbons (PAHs). After doping with Cu and Fe, catalytic upgrading of bio-oil was improved when compared with that without metal doping. Moreover, it is found that 2.5 wt.%Cu/Al_2O_3-0.01 gave the highest relative total hydrocarbon amount of 89%.

(3) It is found that the strong acidity of Al-MCM-41 easily led to the severe coke formation, resulting in the blocking of pores and rapid deactivation of catalyst. Therefore, doping of alkali earth metals such as Mg with different loading amounts as acid–base mesoporous catalysts for upgrading of bio-oils. Interestingly, Mg/Al-MCM-41 showed high selectivity towards BTXs, especially towards benzene production while coke and PAHs yields were decreased to some extent with the increasing of Mg loading amount. Moreover, higher temperature for deoxygenation was required for Al-MCM-41 without Mg doping. Also, no serious reduction of the relative total hydrocarbon amount in the upgraded bio-oil was observed in the catalyst reusability testing for 5 cycles.

(4) Cu loaded on MCM-41 and KIT-6 mesoporous materials were prepared by β-cyclodextrin (CD) assisted impregnation method, and applied for upgrading of bio-oil. It is found that 20 wt.% of Cu loaded MCM-41-CD and KIT-6-CD catalysts had the highest catalytic activity, by which the upgraded bio-oil was rich in monocyclic aromatic hydrocarbons and the total relative maximum hydrocarbon amount of 73.2% and 86.1% were achieved. These results should be attributed to the presence of smaller Cu particles, better dispersion and stronger interaction of active Cu species on support with the assistance of CD.

(5) Mg-Cu-loaded β-zeolite was prepared as an acid–base bifunctional catalyst for the conversion of furfural to monoaromatic compounds. It is firstly found that this catalyst exhibited high selectivity towards benzene, toluene and xylenes (BTXs) production with anti-polycyclic-aromatic-hydrocarbon formation as well as anti-coking ability when compared with Cu-loaded β-zeolite and the parent β-zeolite. The product distribution indicated that addition of Cu significantly promoted the deoxygenation and aromatization of an intermediate product of furan while Mg apparently suppressed the polyaromatization. Especially, an optimum loading amount of 0.5%Mg-1%Cu on β-zeolite was obtained, which showed lower catalytic deoxygenation temperature and interestingly, only benzene was detected in the liquid product at a reaction temperature over 700°C. To the best of our knowledge, this is also the first finding in this field. The significant changing of acidity and basicity of β-zeolite were found after Cu and Mg loadings, which should be the main factors for the improvement of activity, selectivity and stability of the developed catalyst. It is expected that this catalyst can be applied for the upgrading of bio-oil in a practical process.

注）和文 2,000 字以内又は英文 800 語以内　　続紙　有□　無■