

学 位 論 文 の 要 旨

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学位論文題目	Production of High-Value-Added Chemicals and High-performance Catalysts from Lignin（リグニンからの高付加価値化学物質と高性能触媒の製造）		
<p>学位論文要旨</p> <p>The growing global population leads to an increasing demand for fossil-based fuels and chemicals, resulting in many societal problems, including energy security and environmental pollutions. Therefore, development of environmentally friendly fuels, chemical feedstocks, and materials becomes more and more important. Lignin is the largest natural and renewable source of aromatics. Industrial lignin is largely produced as the byproduct, especially in paper and pulping industries and in biorefinery processes. Utilization of lignin wastes would solve the issues related to the reduction of environmental impacts of the paper-making process and other delignification processes on the environmental burden. To date, many researches have focused on the production of high-value-added chemicals and development of lignin-derived functional materials, catalyst support, and carbon-based catalysts. In this dissertation work, a kind of zeolite-based catalyst was found to be effectively catalytic upgrading of lignin-derived bio-oils, and meanwhile, the lignosulfonate lignin was successfully applied as a precursor to prepare high-performance catalysts for hydrogen production from decomposition of formic acid and weak-acid carbon-based catalysts for the hydrolysis of cellulose and woody biomass as well as for the cyclization citronellal to produce p-menthane-3,8-diol. It includes 6 Chapters.</p> <p>Firstly, <i>in-situ</i> catalytic upgrading of bio-oil during the fast pyrolysis of lignin over five types of high aluminum zeolites, i.e., H-Ferrierite, H-Mordenite, H-ZSM-5, H-Beta and H-USY zeolites, were performed. It is found that the channel structure, pore sizes and acidity of zeolite had great effect on the product distribution, coke formation, and deoxygenation. The highest yield of light oil was obtained by using H-ZSM-5 zeolite and the highest selectivity toward monoaromatic hydrocarbons was achieved by H-Beta zeolite. This study could provide a guidance for the selection of suitable zeolite for the <i>in-situ</i> catalytic deoxygenation of bio-oil derived from fast pyrolysis of lignin.</p> <p>Secondly, based on the high char product produces in fast pyrolysis of lignin (52.2 wt%), dealkaline lignin (DAL) was used as a carbon and sulfur source to prepare MoS₂/Mo₂C based catalysts (Mo-DAL) with a facile impregnation-pyrolysis two-step process for the hydrogen production from the formic acid decomposition. Comparison of the catalytic performance of the Mo-DAL catalyst with the carbon black-based one (Mo₂C-CB) revealed that the Mo-DAL catalyst exhibited superior activity to the Mo₂C-CB catalyst. When 20 wt% of Mo was loaded on DAL, the catalyst produced hydrogen quite selectively (99.2%) with almost complete conversion of formic acid (97.4%) at 220 °C. In addition, the catalyst showed stable activity for at least 50 hours in these conditions. These catalytic activity and hydrogen selectivity are superior to the other reported non-precious metal catalysts. Since DAL contains not only carbon but also sodium and sulfur species, multiple kinds of active sites such as Na-intercalated MoS₂, MoS₂, and β-Mo₂C were formed on the Mo-DAL catalysts. Investigation of additional effects of sulfur and</p>			

sodium species on the Mo-CB catalyst revealed that both activity and selectivity for H₂ production was improved by adding those elements. Thus, this study provides a new viewpoint to utilize waste dealkaline lignin as a precursor of sustainable and selective precious metal-free hydrogen production catalysts for formic acid decomposition.

Thirdly, since the original structure of neutralized lignosulfonate lignin (alkaline lignin, pH 10) contains the phenolic hydroxyl groups, carboxyl groups, and SO₃H groups. Alkaline lignin (AL) can be utilized as low-cost and sustainable weak-acid carbon catalysts which is prepared by pyrolysis of AL followed by an acid solution treatment process, and applied for the hydrolysis of cellulose and woody biomass. The effect of pyrolysis temperature on the acidity of the final carbon catalyst was investigated. It is found that the AL-derived carbon catalysts at the pyrolysis temperature of 450 °C (denoted as AL-Py-450) exhibited the highest activity in the hydrolysis of ball-milled cellulose with a cellulose conversion of 70.8% and a glucose yield of 46.3% in a neat water reaction system. Furthermore, with the addition of 0.012 wt% hydrochloric acid (HCl) in the above reaction system, the cellulose conversion was increased to 96.1% with a glucose yield of 69.8%. In the same reaction conditions, the AL-Py-450 carbon catalyst also exhibited good catalytic activity for the hydrolysis of lignocellulosic biomass, i.e., Japanese cedar wood, with yields of glucose and xylose of 47.1% and 40.3%, respectively. Therefore, this study could provide a new perspective to utilize the wasted alkaline lignin as a source for the preparation of sustainable weak-acid carbon catalysts for the hydrolysis of cellulose and lignocellulosic biomass.

Finally, the AL-derived carbon catalysts were also applied for cyclization citronellal to produce p-menthane-3,8-diol(PMD), which is a natural mosquito repellent with lower toxicity than the widely-used *N,N*-diethyl *m*-toluamide (DEET). Especially, the carbon catalysts obtained by pyrolysis at 500 °C showed 97 % high conversion of (±) citronellal with a 86 % high PMD yield. In addition, it is found that the citronellal cyclization-hydration reaction via carbocation-hydration pathway rather than isopulegol hydration route over such an AL-derived carbon catalyst.