ABSTRACT

Gao, Danni. Ph.D., Purdue University, December 2014. Catalytic Hydrodeoxygenation of Guaiacol over Noble Metal Catalysts. Major Professor: Arvind Varma.

Pyrolysis of biomass is a promising technology to convert solid biomass into liquid bio-oils. However, bio-oils have high water and oxygen content which subsequently lowers their energy density relative to conventional hydrocarbons. For these reasons, an upgrading process is required. Catalytic hydrodeoxygenation (HDO) is a rapidly developing technology for oxygen removal from pyrolysis bio-oils and noble metal catalysts have shown promising activities, especially as compared to the traditional hydrodesulphurization catalysts (e.g. $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$). However, further understanding and development of the catalysts through improving robustness, increasing the oil yield and reducing the hydrogen consumption are still required. In this work, guaiacol, a phenol derived compound produced by the thermal degradation of lignin, was selected as a model compound to study the HDO process. Guaiacol is selected because it is among the major components of pyrolysis bio-oils, but it is thermally unstable and leads to catalyst deactivation.

In this study, four noble metals (Pt, Pd, Rh and Ru) and three catalyst supports (activated carbon, alumina and silica) were selected to investigate the activity of different metals and the effects of catalyst support. The screening criteria were as follows: (1) High degree of deoxygenation, (2) Low hydrogen consumption, (3) High carbon recovery in liquid phase, and (4) Long catalyst lifetime. The screening was performed systematically in a fixed-bed reactor at atmospheric pressure. The results show that among all the tested catalysts, Pt/C catalyst has the highest activity and stability. Additionally, the operating temperature for the Pt/C catalyst was optimized and 300 ^{o}C was found to be optimum.

For Pt/C catalyzed guaiacol HDO reaction, three major liquid products were observed (i.e. phenol, catechol and cyclopentanone). Based on the experiments performed under various space velocities and feed compositions, a reaction network including 5 sub-reactions was proposed. Furthermore, kinetic studies were conducted under integral conditions. The power-law model was found to describe the system well and the corresponding rate constants and activation energies for the 5 sub-reactions were obtained. In addition, the formation of cyclopentanone from guaiacol was investigated via density functional theory (DFT) calculations and a thermodynamically feasible pathway was proposed based on the results.

Finally, since Pt/C showed negligible deactivation during the 5 h testing period while Ru/C had significant deactivation, the catalyst deactivation mechanisms were investigated using Pt/C and Ru/C catalysts. Two possible causes for deactivation (thermal degradation and coking) were investigated. The results from catalyst characterization (SEM and TEM images, BET surface area measurements, TGA experiments and dichloromethane dissolution) showed that polyaromatic deposits, especially the condensed ring compounds, were the most likely cause for catalyst deactivation.