HYDROGENATION OF BIOMASS DERIVED OXYGENATES

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Biomass, which is abundant, renewable, and carbon-neutral, can be used for the manufacture of many valuable chemicals and biofuels as an alternative carbon source. However, biomass derivatives naturally contain high oxygen concentration, which lowers the energy density of the molecules, and thus are not feasible for direct use. Therefore, the development of catalytic processes for the removal of ‘excess’ oxygen from biomass-derived molecules is essential. On the other hand, shale gas production has increased rapidly since 2007 in the U.S. due to the new technologies such as hydraulic fracturing and horizontal drilling. As a clean, inexpensive, and abundant resource, methane has attracted scientists all over the world to devote efforts in the C1 chemistry. This dissertation focuses on the development of catalytic processes for biomass-derived oxygenates upgrading and natural gas conversion. Three types of heterogeneous catalysts have been investigated: catalysts for the hydrodeoxygenation of furfural, catalysts for the selective hydrogenation of aliphatic carboxylic acids to aldehydes, and for the non-oxidative coupling of methane.

The selective hydrodeoxygenation of furfural to 2-methylfuran was investigated over iron-promoted copper catalyst as the first part of the thesis. Iron was added as a promoter to the silica supported copper catalyst and the roles of the iron plays in this reaction were identified with various characterization methods. In
addition, the selectivity of this reaction was investigated under different pre-treatment and reaction conditions.

The selective hydrogenation of carboxylic acids to the corresponding aldehydes was carried out on chromium containing catalyst. Different types of chromium oxide catalysts from different synthetic methods were evaluated with a series of fatty acids of propionic acid (C3) to hexanoic acid (C6). The active phase of the catalyst was characterized and the reaction mechanism was studied further. Finally, a few kinetic studies were performed to validate the reaction rate expression derived from the proposed mechanism.

As a study for natural gas utilization, the methane coupling reaction to ethylene under oxidant-free condition was investigated with Mo$_2$C/ZSM-5 catalyst. The effect of zeolite acidity was investigated in this reaction to control the products selectivity. A boron containing zeolite was synthesized and the zeolite structure was investigated through the reaction. The active molybdenum species were characterized with surface and bulk techniques to find out the surface reaction with methane.