Catalysis of Carbon-Carbon Coupling Reactions for the Formation of Liquid Hydrocarbon Fuels from Biomass and Shale Gas Resources

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Biomass and shale gas have been proposed as alternate sources of liquid hydrocarbon fuels. Traditional petroleum refining, however, is not capable of directly converting either the highly oxygenated molecular structure of lignocellulosic biomass or the low molecular weight alkanes of shale gas into liquid fuels. In this work, we investigate two processes to generate fuels by upgrading low molecular weight species present in biomass pyrolysis vapors and in shale gas via carbon-carbon coupling reactions of low molecular weight species present in biomass pyrolysis vapors and shale gas.

In the first process, fast pyrolysis and hydrodeoxygenation are used to convert woody biomass into hydrocarbons. However, 22% of the carbon in this process forms C_1-C_3 species which are unsuitable for use as liquid fuels. Aldol condensation has been proposed as a means of leveraging carbonyl groups present in the pyrolysis product distribution prior to hydrodeoxygenation in order to couple low molecular weight species such as glycolaldehyde to transform the C_1-C_3 fraction into C_{4+} species. We demonstrate that aldol condensation of fast pyrolysis vapors results in a large (10%) reduction in carbon yield to C_6 species and only a small (5%) reduction in carbon yield to C_1-C_3 species to form C_{7+} products, suggesting that higher molecular weight species undergo significant reaction over the aldol condensation catalyst. We demonstrate a pathway by which levoglucosan can be converted into levoglucosenone, which then forms C_{7+} species through self-aldol condensation and condensation with light oxygenates.

In the second process, light olefins in shale gas, consisting primarily of ethane and propane, are dehydrogenated and oligomerized into higher molecular weight species. Ni cation sites exchanged onto microporous materials catalyze ethene oligomerization to butenes and heavier oligomers, but also undergo rapid deactivation. The use of mesoporous supports has been reported in the literature to alleviate deactivation in regimes of high ethene pressures and low temperatures that cause capillary condensation of ethene within mesoporous voids. Here, we reproduce prior literature findings on mesoporous Ni-MCM-41 and report that, in sharp contrast, reaction conditions that nominally correspond to ethene capillary condensation in microporous Ni-Beta or

Ni-FAU zeolites do not mitigate deactivation, likely because confinement within microporous voids restricts the formation of condensed phases of ethene that are effective at solvating and desorbing heavier intermediates that are precursors to deactivation. Deactivation rates are found to transition from a first-order to a second-order dependence on Ni site density in Ni-FAU zeolites with increasing ethene pressure, suggesting a transition in the dominant deactivation mechanism involving a single Ni site to one involving two Ni sites, reminiscent of the effects of increasing H_2 pressure on changing the kinetic order of deactivation in our prior work on Ni-Beta zeolites.