Pyrolysis-based processing of biomass and shale gas resources for the production of chemicals and fuels

Abhijit Talpade, Davidson School of Chemical Engineering, Purdue University
Advisors: Fabio H. Ribeiro and W. Nicholas Delgass

Thermochemical processing using fast-pyrolysis technology has been used to upgrade feedstocks like biomass and natural gas and has been recently studied for plastic recycling. This work aims to improve the selectivity to desired products through better catalysts and reactor designs.

Fast-pyrolysis of biomass to fuels is considered a promising technology due to the higher yields to liquid fuel products. However, the process suffers from carbon efficiency issues due to carbon losses to bio-char, accounting for 25-40 wt.% of the product stream depending on the biomass type. Using a combination of model compounds, biomass pretreatments and mass spectrometric analysis coupled with lab-scale reactors, the char contribution from the lignocellulosic components (cellulose, hemicellulose, and lignin) and mineral content was investigated. The lignocellulosic components were found to follow the order: Lignin > Hemicellulose > Cellulose. Addition of inorganic salts (K, Na and Ca) to cellobiose, a model compound for cellulose, was found to catalyze additional dehydration reactions on primary pyrolysis products (e.g., levoglucosan) to yield secondary products (e.g., 5-HMF), and produce more char. This knowledge of char formation contributors can enable optimization of the bio-refining process sequencing using process system engineering tools and thus achieve higher carbon efficiency for biomass conversion.

While biomass has been viewed as a future energy source, there is a need for a transition fuel with the lowest possible greenhouse gas footprint. Shale gas, consisting primarily of methane, is a candidate due to its large availability and high hydrogen to carbon ratio. Recently, single-atom catalysts have shown promise as stable and non-coking catalysts for non-oxidative coupling of methane (NOCM) to higher hydrocarbons. However, lack of post reaction catalyst characterization and kinetic results have raised questions on the stability of these materials. Our work uses homogenous (Chemkin simulations, gas phase kinetics) and heterogeneous reaction kinetics coupled with microscopy and surface characterization tools to understand the role of the solid materials during NOCM. Transmission electron microscopy (TEM) analysis on the spent samples (CH_4 treated at 975 ^{0}C for 3 hours) reveals that materials containing Pt (Pt single atoms (SA) and Pt nanoparticles (NP)) are found to sinter to particles approximately 5-7 nm in size. Ethylene hydrogenation experiments, a kinetic probe, on the fresh single atom catalyst (Pt/CeO_2), shows initial ethane formation rates that are four orders of magnitude lower on the isolated Pt^{+2} sites, found on Pt SAs, when compared to the rates obtained if all the surface Pt were assumed to be metallic. These results suggest that single atoms are not the active sites. However, the ethylene formation rates (in mol h^{-1}) on the solid materials are 2-7 times higher than the empty tube rates. All the solid materials, irrespective of the type of material (alpha Al_2O_3, Davisil SiO_2, 1 wt.% Pt/CeO_2, Graphene, Graphite, etc.), deactivate to a similar graphite-like surface under steady state conditions, evidenced by Raman spectroscopy. In fact, the ethylene formation rate on all the spent solid materials (tested under same reaction conditions) is proportional to the amount of spent surface area of the material, indicating that the surface is always covered by the same type of carbon deposits irrespective of the underlying material.