The Department of Chemical Engineering and Materials Science
Michigan State University
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The Gas-Phase Conversion of Bio-Derived 5-Methylfurfural to 2,5-Dimethylfuran
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*Concern over global warming and limited oil reserves has resulted in an increased interest in the production of fuels and chemicals from biomass. Currently there is considerable interest in a class of bio-derived molecules referred to as furans. Furans contain an aromatic heterocyclic ring that consists of four carbon atoms and one oxygen atom. The focus of this work is on the development of heterogeneous catalysts for the selective gas-phase hydrogenolysis and hydrogenation of 5-methylfurfural (5MF) to 2,5-dimethylfuran (DMF), which has the potential to be used as a liquid fuel as well as being a precursor for the production of bio-plastics.

The hydrogenolysis of C-O bonds is an important reaction in the processing of bio-renewables. Copper metal catalysts are known to cleave C-O bonds without significant cleavage of C-C bonds or hydrogenation of the furan ring. The primary focus of this work is on the study of copper chromite and promoted copper chromite catalyst systems; Cu/ SiO2 and Pd/C catalysts are shown to produce excessive ring opening and decarbonylation reactions, respectively.

The effect of adding Mg, Ca, Sr, Ba, and Mn to copper chromite is discussed. The active catalytic sites (e.g., Cu2+, Cu+, Cu0) in copper chromite has been debated in the literature for years. By comparing the results of the 5MF to DMF reaction over copper chromite systems with those obtained over Raney copper, it is shown that Cu0 is the primary active site. Surface area (BET) measurements before and after reaction indicate that deactivation is accompanied by significant decrease in BET surface area which can partially be recovered upon calcination of the used catalyst.

Over these catalysts in a co-current down-flow fixed-bed reactor at 225Â°C and 1 atm of H2 pressure 5MF is initially completely converted to DMF in yields Ɛf90% of theoretical with Ɛ,10% yield of the intermediate 5-methyl-2-furfuryl alcohol. Unfortunately, the conversion and yield of 5MF and DMF decrease with time on stream. At a 5MF weight hourly space velocity of 4.5 h-1 complete deactivation of Raney copper is observed over a period of 4-270h depending on the concentration of catalyst poisons remaining from the synthesis of 5MF. In addition to the catalyst composition feed impurities and feed pre-treatment procedures
are shown to significantly affect catalyst activity.

5MF is produced from six carbon carbohydrates in a multistep process that starts with the digestion of biomass in concentrated HCl which is determined by GC/MS to introduce organochlorine compounds. The organochlorine impurity is found in high purity 5MF obtained from multiple commercial sources. Chlorine compounds are known to be virulent copper catalyst poisons, and it is shown that a significant reduction in catalyst deactivation can be achieved by pretreating the 5MF over a guard-bed of activated copper catalysts. After guard-bed treatment GC/MS shows the removal of the organochlorine and energy-dispersive X-ray spectroscopy shows the accumulation of chlorine on the catalyst surface.*

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