

# Catalytic Conversion of Biomass Platform Molecules to Useful Products

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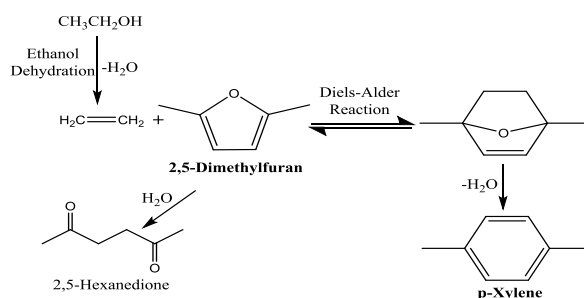
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## Abstract

In this conference, we will report a number of new catalytic conversions of biomass-derived molecules to useful fuels and chemicals over some of novel catalysts. They may offer hints to develop key catalytic technologies to enable the replacement of non-renewable sources for our fuels and chemicals in future. We will particularly demonstrate the uses of the start-of-the-art characterization techniques including synchrotron radiation, STEM and NMR to facilitate the mechanisms elucidation of these new catalysts.

## Introduction

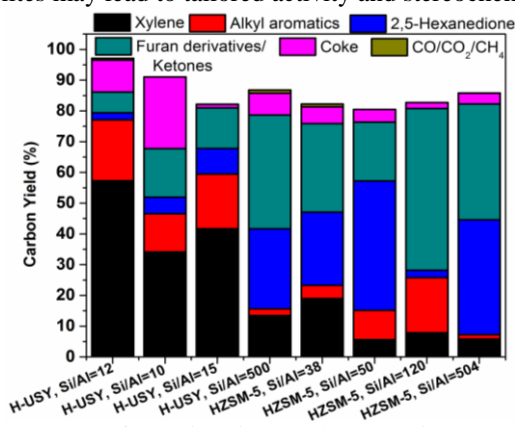
Over the past century our society has become heavily dependent on fossil fuel sources such as coal, gas and oil to produce our daily needed energy and chemicals. [1-3] The carbon dioxide produced by these non-renewable carbon sources has been significantly altering the climate on Earth [2] and our heavy reliance make them more expensive and less abundant. [1-3] Conversion of lignocellulosic biomass to renewable fuels and chemicals has attracted significant attention as a key technology to enable the replacement of petroleum. [4] Lignocellulosic biomass is the most promising renewable carbon energy source, as it is widely available around the world at a relatively low cost. It is composed of three main fractions: cellulose, hemicellulose, and lignin. [4] Although it is the most abundant plant material resource, its exploitation has been limited by its composite nature and rigid structure. In view of these facts, the conversion of biomass feedstocks into valuable products has been investigated, usually in multistep processes using platform molecules as intermediates. Bio-derived molecules, such as gamma-valerolactone (GVL) and 2,5-dimethylfuran (DMF), are important platform molecules that can be produced from biomass at good yields.[4] It has recently been demonstrated that these platform molecules can be converted into aromatics (particularly p-xylene) over acidic zeolite. [5] We have recently studied their catalytic conversions to useful fuels and chemicals over some of novel catalysts [6-11].



**Scheme 1.** A one-pot synthesis for p-xylene from 2,5-dimethylfuran (DMF) and ethanol over zeolite.

For example, the typical conversion for the synthesis of for p-xylene production from 2,5-dimethylfuran (DMF) and ethanol over zeolite is shown in Scheme 1. Fig. 1 shows a nearly complete conversion of DMF after it is mixed with liquid ethanol at 1:1 mole ratio over all zeolites. The condensable products include the desirable product, p-xylene from the DA and dehydration reactions (scheme 1), alkylated aromatics (i.e. acid-catalyzed substitution of p-xylene), 2,5-hexanedione (hydrolysis of DMF) and furan-derived products and coke (condensation of 2,5 hexanedione, etc). This type of product distribution is similar to the one originating from the DMF reacting with ethylene strongly suggesting that the *in-situ* production of ethylene from ethanol is coupled with the DA cycloaddition to DMF. Interestingly, the catalytic performance appears to be greatly influenced by the nature of zeolite and the acidic content used (Fig. 1). The zeolite HUSY-12 with intermediate acidic content (Si/Al=12) gives

the best carbon yield for aromatics compared with other Si/Al ratios. This HUSY also shows much higher yield than HZSM-5 of Si/Al= 38 or 50 with comparable Brønsted acid concentrations, suggesting HUSY has a preferred pore structure. Under comparable conditions, using ethylene as the co-reactant, our HUSY-12 sample (Si/Al = 12) with the same HY structure, but with partially destructed zeolite cavities and larger average pore sizes (~2.1 nm), appears to give higher p-xylene selectivity (77%) and total aromatics of 82%, further enhancing the fraction of useful products. When compared with ethanol as the source of dienophile, over the same HUSY-12, the ethanol pathway exhibits even higher conversion. Despite the fact that a slightly lower selectivity to p-xylene (67%) is obtained than that of using ethylene, the use of ethanol produces more alkylated aromatics (23% against 5% in ethylene reaction) over the HUSY-12 (Si/Al = 12), resulting to higher overall selectivity in the production of aromatics (90%). Apart from the alkylated xylene products (for example, 1-ethyl-2,5-dimethylbenzene as ethyl substituted p-xylene) as in the case of ethylene, the use of ethanol also produces a very small quantity of aromatics with oxygen-containing substituent groups. We will show in this conference that by combining high quality SXRD data and Rietveld refinement analysis with detailed kinetic measurements and high-level first principles calculations, ethanol can act as a dienophile source for furan cycloaddition exhibiting substantial higher rates and lower reaction barriers than that of ethylene. It is believed that the realization of higher production rates of aromatics in zeolites using bio-ethanol can underpin the rational design of zeolite catalysts and the employment of other co-substrates for this new improved process. The [4 + 2]-cycloaddition with different furans and dienophiles derived from biomass, including alkynes and alkenes in spatially defined zeolites may lead to tailored activity and stereochemistry [6,9].



**Figure 1.** Carbon yield for DMF transformation into xylene (mainly p-xylene) and alkylaromatics catalyzed by different zeolites. Reaction conditions: temperature 300 °C, molar ratio ethanol/DMF 1:1 for 12 h in 100mL reactor.

In this conference, we will also present catalytic conversions of biomass molecules into useful products over oxide interfaces. Reactions were carried out in either continuous or batch reactor under industrial applicable conditions. We will discuss the importance of hydro-deoxygenation step in biomass activation over catalytic surfaces [10,11].

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