Lewis Acid-Catalyzed Conversion of Biomass-Derived Dimethylfuran to p-Xylene

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Introduction
Increasing exploitation of fossil fuel feedstocks for the production of energy and materials has led to an increase in the price of crude oil as well as increasing levels of CO2 in the atmosphere. Therefore, there has been an accelerated research effort directed towards the conversion of renewable biomass feedstocks into fuels and chemicals. Lignocellulosic biomasses, which are comprised of up to 70 wt% of cellulose and hemicellulose, is considered one promising renewable biomass feedstock. Saccharification of lignocellulosic biomasses yields five and six carbon sugars (e.g., Xylose and glucose). These sugars are considered to be the primary feedstock for a renewable chemical industry.

A renewable route to p-Xylene from biomass-derived dimethylfuran and ethylene is investigated with zeolite catalysts. This conversion consists of two steps: a Diels-Alder cycloaddition of ethylene to dimethylfuran followed by dehydration of the oxabicyclic intermediate to p-Xylene (Figure 1). The capability of extra-framework cations in the zeolite framework—such as Na, Li, K, Ag, and Cu—in faujasites Y (Si/Al=40), Y (Si/Al=2.55) and X (Si/Al=1.25) to catalyze this reaction was investigated at low conversion (XDMF~10%).

Materials and Methods
NaY (Si/Al=2.55) and NaX (Si/Al=1.25) commercial zeolite catalysts from Zeolyst International were utilized as the starting materials for zeolite preparation. NaY (Si/Al=40 and Si/Al=2.55) and NaX were ion exchanged into Li, Ag, K, and Cu faujasites using nitrate or chloride salts of the cations. The zeolites were then characterized by X-ray diffraction, N2 adsorption, and Energy dispersive X-ray diffraction (EDX) to verify their crystallinity, micropore volumes, and degree of cation exchange. The reaction was carried out in a 45 mL-closed Parr reactor at 493 K and 1050 psig of ethylene for 6 hrs. Product identification was performed using gas chromatography (GC).

Results and Discussion
AgX zeolite was the most active catalyst for the formation of p-Xylene at 493 K (1.80 moles of p-Xylene/ (mole cation*hr)) (Figure 2). NaX (Si/Al=1.25) was the most selective catalyst for the formation of p-Xylene at these conditions (75.5%) (Figure 3). Competitive side reactions include hydrolysis of DMF to 2,5-hexanedione, alkylation of p-Xylene, and polymerization of 2,5-hexanedione. The observed trends may be explained by three main effects: the inherent Lewis acid strength of the cation, the site-distribution of cations in the zeolite framework, and the shielding effects associated with interaction between the cations and the zeolite framework.

Figure 1. Reaction Scheme

Figure 2. Rate of p-Xylene production per mole of cation.

Figure 3. p-Xylene Selectivity.

Significance
This catalytic system introduces a new chemical pathway to convert biomass-derived furans to high-value aromatic feedstocks.

References