

## Design of Solid Acid Catalysts for Cycloaddition of Dimethylfuran and Ethylene to Produce p-Xylene

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Diels–Alder cycloaddition between biomass–derived dimethylfuran (DMF) and ethylene and subsequent dehydrative aromatization have recently been proposed as a renewable route to produce p-xylene. Since p-xylene is a platform chemical in the production of polyethylene terephthalate (PET), the proposed process has received increasing attention. In this study, the Diels–Alder cycloaddition of dimethylfuran was investigated with different types of solid acid catalysts to develop the structure–activity relationships of this reaction. We have prepared and tested a series of well-characterized acid catalysts, including HZSM-5, HY, HBEA, Zr-P, sulfated zirconia, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> aerogels (SAA), WOX/ZrO<sub>2</sub>, sulfated graphene oxide, and AlCl<sub>3</sub>. Among the tested solid acid catalysts, the SAA with Si/Al=1 had the highest conversion and selectivity to p-xylene (67%). Acidity characterization of the catalysts with ammonia-TPD and solid state NMR revealed that the ratio of Bronsted to Lewis acid sites has a crucial role in the selective production of p-xylene.