

Renewable *p*-xylene from 2,5-dimethyl furan and ethylene using phosphorus-containing zeolite catalysts

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Introduction

p-Xylene is a major commodity chemical and precursor in the production of the most widely used polyester, polyethylene terephthalate (PET). Due to the rapid growth in the global market of PET (6-8% per year), its replacement with a renewable feedstock is highly desirable, and there are ongoing research and development efforts to produce *p*-xylene from biomass feedstocks [1]. Diels–Alder reactions of biomass-derived furans with subsequent dehydration have demonstrated the potential for producing renewable *p*-xylene and other aromatic derivatives with high stereospecificity [2]. To date, the most selective catalysts reported are acidic zeolites with large micropores (7.5 Å), which primarily catalyze the dehydration reaction. However, they also catalyze the formation of alkylated and oligomerized byproducts (Figure 1). Due to these side reactions, the highest yield to *p*-xylene previously achieved was 75%. Here, we report that phosphorous-containing siliceous zeolites are highly selective and stable catalysts for this reaction with an unprecedented *p*-xylene yield of 97%.

Materials and Methods

Two phosphorus-containing zeolites (P-BEA and P-SPP) were prepared in this study. P-BEA was synthesized by impregnation of phosphoric acid with dealuminated BEA obtained from dealumination of Al-BEA. Phosphorus-containing self-pillared pentasil zeolite, P-SPP, was synthesized following previous literature [3]. For comparison, Zr-BEA was prepared by earlier literature [4]. Al-BEA (CP814E, Si/Al=12.5) was supplied from Zeolyst.

Results and Discussion

Table 1 shows the properties of various catalysts for the 2,5-dimethylfuran (DMF) reaction with 62 bar of ethylene at a temperature of 250°C. P-BEA and P-SPP exhibited 97% yields of *p*-xylene at full conversion of (DMF). In contrast, homogeneous H₃PO₄ gave only 41% *p*-xylene yield at similar conversion. This indicates that supported phosphoric acid is fundamentally different from the homogeneous acid. Control experiments with Si-BEA and Si-SPP showed very low conversion, revealing that phosphorus on the P-zeolites is the catalytically active sites for the reaction. Table 1 also shows that Lewis acid Zr-BEA and Brønsted acid Al-BEA zeolites led to lower yields of *p*-xylene, 72% and 64%, respectively, at ~99% DMF conversion. These materials catalyze side reactions such as alkylation and oligomerization (Figure 1), thereby significantly decreasing the *p*-xylene selectivity. Pyridine FT-IR spectra and isopropylamine temperature program desorption (IPA-TPA) suggested that the P containing zeolite catalysts are different from commercial solid phosphoric acid catalysts. The outstanding performances of P-BEA and P-SPP can be attributed to unique acid properties

that can catalyze the cycloadduct dehydration without catalyzing the side reactions. This behavior is distinct from that of Al-containing zeolites and establishes a commercially attractive process for renewable *p*-xylene production.

Table 1. Comparison of catalytic activities for DMF reaction with ethylene in this study^a

Catalyst	DMF/P (mol/mol)	Production rate of <i>p</i> -xylene ^b (mM/h)	DMF conv. at 24 h (%)	<i>p</i> -xylene yield at 24 h (%)	<i>p</i> -xylene selectivity at 24 h (%)
P-BEA	100	411 (± 21)	99 (± 0.7)	97 (± 1.1)	98
P-SPP	100	357 (± 20)	100 (± 0.3)	97 (± 1.3)	97
H ₃ PO ₄	100	67	96	41	43
Zr-BEA	4 mM ^c	249	99	72	73
Al-BEA	4 mM ^c	214	98	64	65

^aReaction conditions: 1.35 M DMF in *n*-heptane; 250 °C; 62 bar ethylene. ^bReaction time: 30 min. ^cConcentration of Brønsted acid sites on Al-BEA, and that of Lewis acid sites on Zr-BEA.

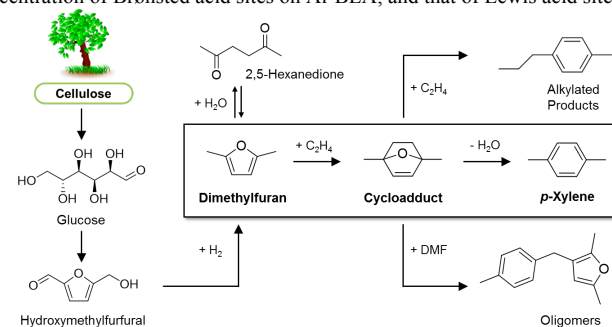


Figure 1. Production of renewable *p*-xylene from the reaction of 2,5-dimethylfuran (DMF) with ethylene.

Significance

Renewable *p*-xylene obtained from the reaction of DMF with ethylene is an attractive reaction pathway for its production from biomass feedstocks. We report that novel phosphorous-containing zeolite catalysts, P-BEA and P-SPP, are an active, stable and selective catalyst for this reaction with an unprecedented *p*-xylene yield of 97%.

References

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