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Renewable *p*-Xylene from 2,5-Dimethylfuran and Ethylene Using Phosphorus-containing Zeolite Catalysts

Hong Je Cho, Limin Ren, Vivek Vattipalli, Yu-Hao Yeh, Nicholas Gould, Bingjun Xu, Raymond J. Gorte, Raul Lobo, Paul J. Dauenhauer, Michael Tsapatsis, and Wei Fan*

Abstract: *p*-Xylene is a major commodity chemical used for the production of polyethylene terephthalate (PET), a polymer with applications in polyester fibers, films, and bottles. Diels-Alder cycloaddition of 2,5-dimethylfuran (DMF) and ethylene with subsequent dehydration of the cycloadduct intermediate to produce renewable *p*-xylene is an attractive reaction pathway for its production from biomass feedstocks. However, the highest yields presently reported do not exceed 75%. We report that phosphorous-containing zeolite Beta (P-BEA) is an active, stable and selective catalyst for this reaction with an unprecedented *p*-xylene yield of 97%. It can selectively catalyze the dehydration reaction from the furan-ethylene cycloadduct to *p*-xylene, without catalyzing reactions producing alkylated and oligomerized products. This behavior is distinct from that of Al-containing zeolites and other solid phosphoric acid catalysts and establishes a commercially attractive process for renewable *p*-xylene production.

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),[1] its replacement with a renewable feedstock is a highly desired goal,[2] and there are ongoing research and development efforts to produce *p*-xylene from biomass feedstocks.[3] 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.[3a-e] 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 (Scheme 1).[4] Due to these side reactions, the highest yield to *p*-xylene previously achieved was 75%.[4-5] 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%.

Scheme 1 depicts a reaction pathway for the production of *p*-xylene from cellulose[6]. Here glucose is produced by the depolymerization and hydrolysis of cellulose, the isomerization of glucose to fructose is then performed using enzymes or thermochemical catalysts such as base or Lewis acid heterogeneous catalysts, e.g., zeolite Sn-BEA.[7] Fructose is then converted to 5-hydroxymethylfurfural (HMF),[8] and further hydrodeoxygenated to form 2,5-dimethylfuran (DMF).[9] These steps have been demonstrated individually in high efficiency with the highest selectivity to HMF of 80% and DMF of 98%.[8-9] The last step to generate *p*-xylene is the Diels–Alder cycloaddition of DMF and ethylene, followed, in the same reactor, by the dehydration of the cycloadduct intermediate. This reaction offers a completely renewable pathway for *p*-xylene production since both DMF and ethylene can be obtained from glucose.[10] Increasing the efficiency of the reaction from DMF and ethylene to *p*-xylene is critical for ensuring the economic and technical feasibility for the entire process. As suggested by a techno-economic analysis on the process of Scheme 1, an increase in the yield substantially improves the economics of renewable *p*-xylene.[11]

Conversion of DMF with ethylene to *p*-xylene in n-heptane has been demonstrated using acidic zeolite catalysts, including zeolite Y and Al-BEA.[3c, 4] There are three competing side reactions: (a) hydrolysis of DMF to form 2,5-hexanedione, (b) multiple additions of ethylene to form alkylated aromatic species, and (c) dimerization of the furan feedstock and/or aromatic products to form oligomers (Scheme 1). Density functional theory (DFT) calculations have emphasized the role of Brønsted acids catalyzing the main reaction pathway and enhancing the yield of *p*-xylene by reducing the cycloadduct dehydration barrier from ~60 kcal mol^{-1} to ~10-20 kcal mol^{-1}.[3c, 12] However, these Brønsted acid zeolites also catalyze the alkylation and isomerization reactions, which not only reduce *p*-xylene yield but also lead to fast catalyst deactivation.[5] Lewis acid zeolites (*e.g.*, Zr-BEA and Sn-BEA) also catalyze the production of *p*-xylene from DMF with an initial formation rate of *p*-xylene comparable to that of Brønsted acid zeolite, Al-BEA[3a, 3b, 5]. In particular, Zr-BEA exhibited the highest reported *p*-xylene yield (75%) with much slower deactivation rates. The properties of Zr-BEA were ascribed to the weaker adsorption of DMF and reduced formation of by-products compared with Al-BEA.[5]

To improve *p*-xylene yield further, we tested two phosphorous-containing siliceous zeolites, zeolite Beta (BEA) and self-pillared pentasil (SPP) zeolite, which were known to us to be inactive for alkylation and oligomerization reactions. The P-containing zeolites are not only excellent catalysts for *p*-xylene production but also highly selective, leading to unprecedented high yields.

P-containing zeolite Beta (P-BEA) was prepared using a post-synthetic route, by which P was incorporated within the

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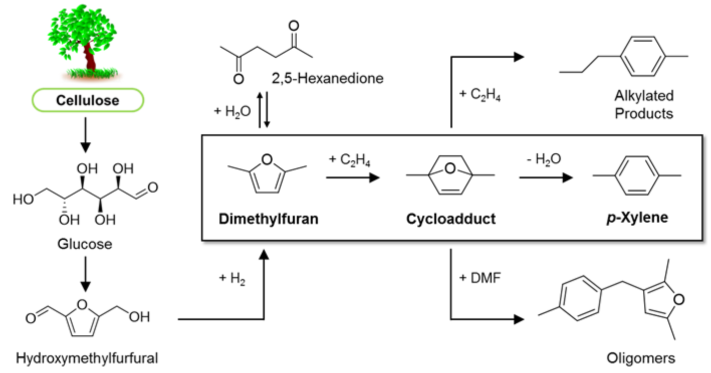

***Scheme 1.* Production of renewable *p*-xylene**. The pathway for the synthesis of *p*-xylene from the reaction of DMF with ethylene including major intermediates and by-products is indicated in the highlighted block. The renewable route for the production of DMF from cellulose is also indicated. Renewable ethylene can be commercially produced from ethanol dehydration. It can also be obtained from natural gas or other non-renewable sources.

dealuminated BEA micropores by calcining a phosphoric acid (H_3PO_4) impregnated sample. The synthesis procedure includes first the dealumination of Al-BEA (Zeolyst, CP814E, Si/Al = 12.5) using nitric acid, and second, the impregnation of the dealuminated zeolite BEA with H_3PO_4, followed by the incorporation of P within the zeolite by calcination. The crystal structure and morphology of the zeolite BEA were preserved after the incorporation of P, as revealed by the XRD patterns of the initial and treated samples (Figure S1) and by the SEM/TEM images (Figure S2). The micropore volume and BET specific surface area of the zeolite suggest that the high surface area and microporous structure were retained during the P modification step (Figure S3 and Table S1).

A second P-containing zeolite investigated is a hierarchical MFI zeolite called self-pillared pentasil (SPP).[13] P-containing self-pillared pentasil (P-SPP) was synthesized by a direct synthesis method using tetrabutylphosponium hydroxide (TBPOH) as an organic structure-directing agent (OSDA).[13] After crystallization, the formed SPP zeolite containing the OSDA was calcined, resulting in the decomposition of the OSDA and incorporation of P within the zeolite (Table S1). In contrast, the use of tetrabutylammonium hydroxide (TBAOH) as the OSDA or extensive washing of TBPOH-synthesized SPP with water results in a SPP zeolite free of phosphorous active sites. The crystallinity and morphology of P-SPP are the same as those of pure silica SPP displaying orthogonally connected single-unit cell lamellae of MFI,[13] as indicated by the XRD patterns, TEM images and Ar adsorption isotherms (Figures S1-S3). For further comparison, a commonly used P-based catalyst, P-Celite, was also examined. It is a solid phosphoric acid (SPA) catalyst synthesized by impregnation of H_3PO_4 on Celite (diatomaceous silica), a commercially available amorphous silica material (Figures S1-S3 and Table S1).[14]

Figure 1 shows the results from reacting DMF with ethylene over the P-containing solid catalysts, other Brønsted and Lewis acid zeolites and a homogeneous acid catalyst, H_3PO_4, under the same acid concentration (4.0 mM for both Brønsted and Lewis acid sites) or the same DMF/P molar ratio = 100 at 250 °C. All P-containing materials catalyze the reaction to some extent producing *p*-xylene (Figure 1a). In the absence of P, the same zeolites (siliceous zeolites; Si-SPP made using TBAOH, and Si-BEA) did not exhibit detectable catalysis (Figure S4). Among the catalysts, P-BEA (Si/P = 27) and P-SPP (Si/P = 27) exhibited superior performance with an excellent yield (97%) of *p*-xylene at 99% DMF conversion (Figure 1a). The superior properties of P-BEA and P-SPP could be attributed to the large micropore of P-BEA and the highly branched hierarchical micro-/meso-porous structure of P-SPP, respectively, which provide efficient dispersion of the active sites and facile transport of reactants and products.[3c, 5] The non-zeolitic P-based solid catalyst, P-Celite (Si/P = 5.0), showed a high *p*-xylene yield (about 90%), but lower than those obtained

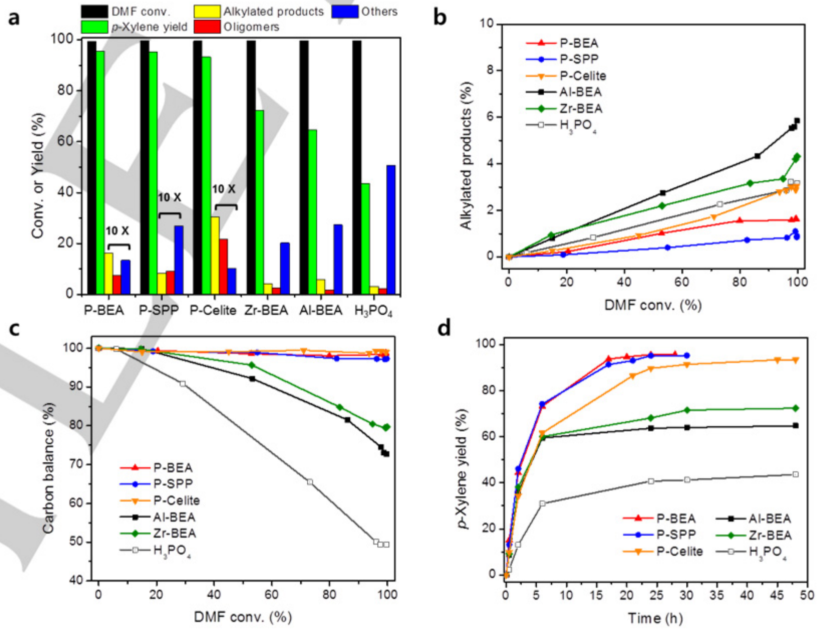

***Figure 1.* Catalytic performance of various catalysts for the *p*-xylene production from the reaction of DMF with ethylene.** (a) Overall product distributions. (b) Yield of alkylated by-products. (c) Carbon balance versus DMF conversion. (d) Yield of *p*-xylene versus reaction time. Reaction conditions are as follows: 1.35 M DMF in n-heptane; 250 °C; 62 bar ethylene; DMF/P (mol mol^{-1}) = 100 for P-BEA, P-SPP, P-Celite and H_3PO_4; 4.0 mM acid for Al-BEA and Zr-BEA. Reaction times in (a) for all catalysts were 48 hours, except 24 hours for P-BEA and P-SPP.

from P-BEA and P-SPP. The yields of *p*-xylene from Brønsted acid Al-BEA and Lewis acid Zr-BEA were significantly lower (i.e., 65% and 72% at 99% DMF conversion, respectively). Homogeneous H_3PO_4 also catalyzed the reaction but with a much lower yield to *p*-xylene (i.e., 39% at 99% DMF conversion). A control experiment conducted over P-containing Al-BEA prepared by impregnation of P on Al-BEA using the same post-synthetic method as P-BEA showed a low yield to *p*-xylene, suggesting that the use of siliceous zeolites as P supports is essential for the high-yield production of *p*-xylene (Figure S5).

The yield of alkylated by-products and carbon balance versus DMF conversion (Figure 1b and c), respectively, and the yield to *p*-xylene with reaction time (Figure 1d) illustrate the excellent catalytic properties of the P-containing microporous silicas for this reaction. Outstanding performance of the P-containing catalysts is due to the lower rate of formation of by-products, such as alkylated aromatics and other unidentified products formed during the reaction. Al-BEA, Zr-BEA and H_3PO_4, however, produced more alkylated and oligomerized by-products with rapid reduction of quantified carbon (i.e., lower carbon balance) (Figure 1b and c, Figure S6). Although DMF can be fully converted over Al-BEA, Zr-BEA and H_3PO_4, the *p*-xylene yield did not increase after six hours of reaction time (Figure 1d and Figure S6a); this is likely due to coke formation and blockage of the active sites. Compared to the Brønsted acidity of Al-OH-Si sites in Al-BEA, the active sites on the P-containing catalysts still catalyze the dehydration reaction to produce *p*-xylene, but only catalyze the side reactions at very slow rates.

Catalyst removal and recycle tests were conducted to verify that the reactions are heterogeneously catalyzed and not catalyzed due to leaching of phosphorous into the reaction mixture. In the catalyst removal test, the reaction of DMF was performed after separating the spent P-BEA catalyst from the reaction mixture. Upon removal of the catalyst the reaction showed almost the same reaction rate as a control experiment without a catalyst, that is, the catalytic activity observed was fully attributed to the solid catalyst (Figure S7). In Figure 2a, the reusability of the P-BEA catalyst was tested showing high selectivity to *p*-xylene (94%) at 98% conversion of DMF after the third recycling test. There were no significant changes in structure of P-BEA catalyst during the recycling test, as determined by SEM and XRD measurement (Figure S8). However, *p*-xylene yield from P-SPP was considerably reduced after sequential catalyst recycling (Figure 2b). By the third recycle, DMF conversion decreased to 76% with a *p*-xylene yield of only 65% (Figure 2c).

^{31}P solid state MAS NMR provided insights into the chemical interaction of P with the silicate frameworks of the P-containing catalysts. As displayed in Figure 2d, P-BEA and P-SPP showed three main signals at 0 (Q^0), -11 (Q^1) and -24 (Q^2) ppm that could be assigned to free H_3PO_4 not chemically bonded to silicate matrices, to $O=P(OSi$ or $OP)(OH)_2$ and to $O=P(OSi$ or $OP)_2(OH)$, respectively.[15] The relative peak area for the P-BEA was 35% for Q^0, 46% of Q^1 and 19% of Q^2 while P-SPP exhibited 68% for Q^0, 26% of Q^1 and 6% of Q^2. These spectra indicate that P binds more effectively in the micropores of the dealuminated BEA than with Si-SPP. P-Celite presented two main resonance peaks at -45 (Q^4) and -54 ppm, corresponding to PO_4 tetrahedra (oligomers of P) and silicon pyrophosphate (SiP_2O_7), respectively, in agreement with previous reports on phosphosilicate materials.[16] Although all the three P-containing materials catalyze the *p*-xylene production, P speciation detected by the MAS NMR is distinctly different. The enhanced catalytic performance of P-BEA and P-SPP (Table S2) could arise from the presence of isolated P sites, which are not dominant in the conventional solid phosphoric acid catalyst (i.e., P-Celite).

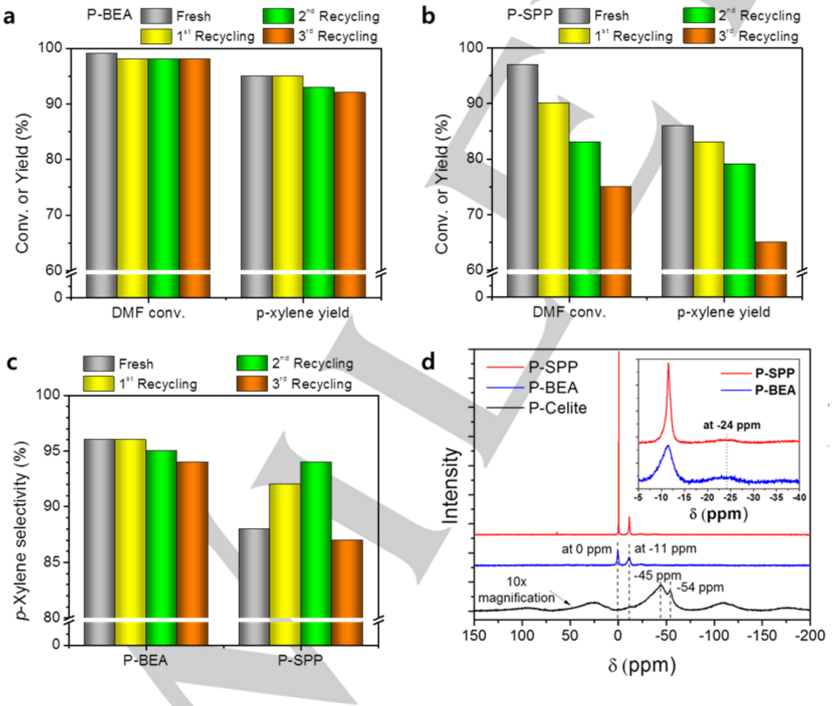

Figure 2. **Catalyst reusability and ^{31}P solid state MAS NMR spectra of P-containing catalysts.** (a,b) DMF conversion and *p*-xylene yield over P-BEA and P-SPP during catalyst recycling. (c) *p*-xylene selectivity over P-BEA and P-SPP during catalyst recycling. Reaction conditions are as follows: 50 mL of 1.35 M DMF in n-heptane; 250 °C; 62 bar ethylene; DMF/P (mol mol^{-1}) = 498 for P-BEA and P-SPP; 24 hours. For catalyst reusability, the spent catalyst was washed with n-heptane, dried and calcined at 550 °C for 12 hours. (d) ^{31}P solid state MAS NMR spectra of P-BEA, P-SPP and P-Celite.

Temperature-programmed desorption coupled with thermogravimetric analysis (TPD-TGA) of 2-propanamine was used to characterize the active sites on the P-containing solid catalysts. 2-Propanamine molecules that are protonated by Brønsted sites react via the Hoffman-elimination to form ammonia and propene, allowing easy quantification of Brønsted-site density.[17] By this measurement, Brønsted acid sites detected on P-BEA is not significant, which is consistent with the pyridine FT-IR measurement on the P-BEA sample (Figure S9), while P-Celite showed Brønsted-site density of 150 μmol g^{-1} (Figure S10). A demonstration that the P-containing zeolites have catalytic sites was shown by the ability of P-BEA to catalyze dehydration of 2,5-hexanedione during the TPD-TGA measurement. The dehydration of 2,5-hexanedione into DMF and water occurred at moderate temperatures (around 180 °C), without catalyzing the oligomerization of DMF (Figure S11). Previous work has shown that the Brønsted acid sites in Al-BEA catalyze the dehydration of 2,5-hexanedione at low temperatures; however, the Brønsted acid sites also catalyzed the oligomerization of DMF during desorption.[18] This result suggests that the phosphorous-containing zeolites exhibit a unique catalytic property for the selective dehydration reaction involved in the production of p-xylene from DMF and ethylene.

In summary, phosphorous-containing zeolite with Beta topology, P-BEA, and hierarhical self-pillared pentasil, P-SPP, exhibited an unprecedented *p*-xylene yield of 97% in the Diels-Alder cycloaddition and dehydration of DMF with ethylene, and establishes a commercially attractive process for renewable *p*-xylene production. The outstanding catalytic performance is due to their abilitity to selectively catalyze the dehydration reaction from the furan-ethylene cycloadduct to *p*-xylene, without performing side reactions including alkylation and oligomerization. This catalytic behavior is distinct from that of Al-containing zeolites and other solid phosphoric acid catalysts. The results presented here demonstrate that P-containing zeolite materials have intrinsically new catalytic properties and are a novel class of acidic zeolite catalysts, worthy of further investigation for other dehydration and acid catalyzed reactions.

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Keywords: *p*-xylene • phosphorous-containing zeolite • cycloaddition • dehydration • acid catalyst

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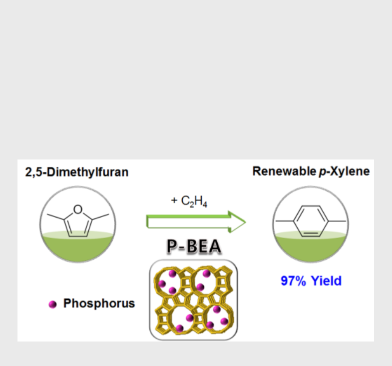
Renewable *p*-Xylene from 2,5-Dimethylfuran and Ethylene Using Phosphorus-containing Zeolite Catalysts



Phosphorous-containing zeolite with Beta topology, P-BEA, and hierarchical self-pillared pentasil, P-SPP, exhibited an unprecedented *p*-xylene yield of 97% in the Diels-Alder cycloaddition and dehydration of DMF with ethylene, and establishes a commercially attractive process for renewable *p*-xylene production.