



Selective *p*-xylene production from biomass-derived dimethylfuran and ethylene over zeolite beta nanosponge catalysts



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ABSTRACT

p-Xylene can be synthesized via a renewable route from biomass-derived 2,5-dimethylfuran (DMF) and ethylene with zeolite catalysts. Here, we propose mesoporous beta zeolite with a nanosponge-like morphology (NSP-BEA) as a highly efficient catalyst for the cycloaddition of DMF with ethylene. The NSP-BEA zeolite was synthesized through a hydrothermal synthesis route using multi-ammonium surfactants as a meso-micro dual structure-directing agent. From structural analyses and measurements of the surface acidity, the NSP-BEA was found to be composed of ultrathin zeolitic nanocrystals with intercrystalline mesopores (~4.5 nm). It also possessed a large number of Brønsted acid sites on its external surfaces and in its internal micropores. This NSP-BEA catalyst exhibited high catalytic performance upon a cycloaddition of DMF with ethylene as compared to the commercial beta zeolite, alumina, and silica-alumina catalysts reported previously.

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1. Introduction

p-Xylene (PX), an important large-volume commodity chemical in the petrochemical industry, is mainly used to produce terephthalic acid (TPA) [1,2], which is the co-monomer in a condensation with monoethylene glycol (MEG) for the manufacturing of polyethylene terephthalate (PET) [2,3]. Over 50 million tons of PET are globally produced per year [4], and PET is widely used in common applications to create plastics, films, and synthetic fibers. Due to the continuous growth of the global economy, the global PET market is also expected to grow by approximately 8% per year consistently [5–7]. Such large growth of the global PET market makes PX an important chemical as well as a key target with regard to the development of new technologies using renewable resources due to current situations such as the continuing unstable oil price, the depletion of petroleum, efforts to reduce greenhouse gas emissions, and the increasing requirement of the use of renewable feedstocks [2,4,8–10].

At present, the dominant technology for the production of PX is the petroleum-derived naphtha cracking process, where PX is obtained as a co-product. However, PX should be separated from mixtures of aromatics such as benzene and toluene as well as *o*-, *m*-, and *p*-xylenes because the production of PET requires high-purity PX. Thus, to purify PX, the aromatic mixture is treated with several separation technologies such as distillation, crystallization, and adsorption [11–13]. In contrast, the naphtha cracking process, a catalytically direct and selective PX production process involving the use of petroleum-based feedstock, remains not fully developed. The catalytic production of PX from petroleum-derived toluene has been reported by several researchers [14–20]. However, long-term shortages of aromatic chemicals are expected to results from the availability of the considerable quantities of natural gas caused by the recent American shale-gas revolution. Natural gas is going to displace naphtha as a primary feedstock in the petrochemical industry, which has motivated a push toward the development of alternative technologies for PX production from renewable, and non-petroleum resources [2,4,9,10,21].

Recently, companies and researchers have proposed an alternative route for the production of PX from renewable feedstocks. Virent developed a technology which converts C₅/C₆ sugars to

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a mixture of benzene, toluene, and xylenes (BTX) by means of aqueous-phase reforming and dehydrocyclization (BioForming[®] process) [22,23]. The resultant aromatic mixtures can serve as a drop-in feedstock in typical PX separation/purification processes, but the high cost of mixed xylene purification is not avoided. Anelotech and Prof. George W. Huber developed catalytic fast pyrolysis technology for the production of a drop-in BTX stream from lignocellulosic biomass in a single reaction. Biomass is rapidly heated under an anaerobic condition, and the resulting gases immediately are converted to aromatics by a zeolite catalyst [24,25]. In addition to producing a drop-in BTX mixture from renewable sources, Gevo developed a process which directly produces PX from isobutanol without a separation process. They produce isobutanol from starch and cellulose through a fermentation process in the presence of a microorganism which they developed. The isobutanol can be finally converted to PX via a series of chemical processes (dehydration, oligomerization, and dehydrocyclization) [26,27]. However, this technology involves complicated reaction processes and results in a low product yield during the fermentation process. It also consumes a considerable amount of energy during the removal of a large quantity of water.

The other potential route for the direct and selective production of bio-based PX is the Diels–Alder (DA) cycloaddition of biomass-derived 2,5-dimethylfuran (DMF) and ethylene followed by the dehydration of an intermediate (Scheme 1) [28–33]. This process is based on the concept of the production of 5-hydroxymethylfurfural (HMF) from cellulose as a raw material. HMF is one of the most promising biomass-derived intermediates [34], and it can be converted to DMF via hydrogenolysis with a high yield [35]. UOP has patented the catalytic conversion process of DMF to PX via the DA cycloaddition of ethylene to DMF using activated carbon, zeolites, and other porous solids [29]. The PX yield for the best-performing activated carbon catalyst in a batch reactor is as high as 78% of the total weight of all converted materials, and the one-pass conversion of DMF to PX is approximately 30% in a continuous fixed-bed reactor. Toray has also disclosed a PX production process via a DA cycloaddition reaction of DMF with ethylene using a composite oxide containing a silica-alumina in a patent [33]. Silica-alumina with titanium metal salt is used as a DA catalyst, and the PX yield is 96 wt% of the remaining organic materials in the reaction ampoule. Recently, researchers at the University of Massachusetts Amherst and at the University of Delaware reported the catalytic conversion of DMF and ethylene to PX with good selectivity through a combination of DA cycloaddition and dehydration reactions over zeolite catalysts [28]. They achieved PX selectivity of approximately 75% and DMF conversion of nearly 95% with H-Y zeolite using *n*-heptane as a solvent in a batch reactor. The DA cycloaddition of DMF and ethylene is promoted by confinement within the uniform micropores of zeolite catalysts. They also suggested possible reaction pathways and energetics of the reaction via the identification of the reaction products, and through a DFT study [30,31]. Wang et al. demonstrated that the acidic solid catalyst WO_x-ZrO₂ shows significant PX production via the DA cycloaddition of DMF and ethylene [36]. They concluded that Brønsted acid sites in the solid acid catalyst are active for PX production, with microporosity of the zeolite catalysts not required. More recently, the same group at the university of Massachusetts Amherst achieved PX selectivity and yields which both exceeded 90% in a DA cycloaddition reaction of DMF and ethylene with H-BEA zeolite in *n*-heptane [32]. H-BEA zeolite was assumed to suppress side reactions, which results in superior activity of H-BEA relative to those of other solid acids.

Despite showing excellent catalytic activity with good PX selectivity, H-BEA zeolite would show insufficient activity with fast catalytic deactivation, which is similar to other reactions using zeolitic microporous catalysts due to coke formation in the micropores. From the GC–MS and 2D-NMR analytic techniques, the DA

reaction of DMF and ethylene using a zeolite catalyst produces many bulky byproducts such as dimers, oligomers, and alkylated aromatics [31]. These bulky byproducts would be trapped in the small channels of the zeolite catalyst, leading to coke formation in the micropores, after which the zeolite catalyst would be deactivated. Moreover, the microporous properties of the zeolite materials cause significant pore resistance for the transportation of a liquid-phase reactant (DMF) to the catalytic active sites. The pore resistance may also affect the catalytic activity in this reactions. Therefore, it is very important to investigate the structural properties of zeolite catalyst that can reduce catalytic deactivation by means of coke formation and pore resistance.

In 2011, Ryoo and co-workers reported the direct synthesis of a hierarchically mesoporous zeolite using multi-ammonium surfactants as a meso–micro dual-structure-directing agent (SDA) [37–45]. Multi-ammonium surfactants are specially designed in a combination of cationic moieties and long alkyl chains for the formation of a microporous zeolitic framework (e.g., MFI, MTW, MRE, and Beta) and a hexagonally ordered or disordered mesostructure (e.g., nanosheet- or nanosponge-like morphologies), respectively. Typically, beta zeolite with a nanosponge-like morphology (NSP-BEA in short) was synthesized using [C₂₂H₄₅-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-CH₂-(C₆H₄)-CH₂-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-CH₂-(C₆H₄)-CH₂-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-C₂₂H₄₅(Br⁻)₂(Cl⁻)₄]. The NSP-BEA was assembled in irregular 3D networks of zeolitic nanocrystals to possess the intercrystalline mesopores with uniform diameters (~4.5 nm). This NSP-BEA zeolite exhibited superior catalytic activity and a long lifetime during the acid-catalyzed liquid-phase Friedel–Craft alkylation of benzene with benzyl alcohol [41] and the acylation of bulky aromatic compounds [45] as well as gas-phase benzene isopropylation to cumene reaction [38]. This result was explained in consideration of the large number of strong Brønsted acid sites on the external surfaces and the facile diffusion of molecules through the mesopores. Nevertheless, such effects of the mesostructure of the NSP-BEA zeolite on the catalytic performances have not been applied in liquid-phase DMF to the PX process.

In this regard, we investigated the performance of NSP-BEA as a catalyst during the DA cycloaddition of DMF and ethylene. We performed the DA reaction over NSP-BEA with different SiO₂/Al₂O₃ ratios (30 and 50) under various reaction conditions (i.e., various reaction temperatures, pressures, amounts of catalyst, and amounts of DMF in *n*-heptane). These results are discussed in comparison with the catalytic performances of commercial beta zeolite, γ -alumina, and silica-alumina.

2. Experimental

2.1. Preparation of catalysts

The NSP-BEA zeolite was hydrothermally synthesized using [C₂₂H₄₅-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-CH₂-(C₆H₄)-CH₂-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-CH₂-(C₆H₄)-CH₂-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-C₂₂H₄₅(Br⁻)₂(Cl⁻)₄] (in short, “C₂₂-6N”) as a SDA, as described in the literature [41]. In brief, tetraethylorthosilicate (TEOS, 95%, Junsei) was added to a NaOH solution containing both sodium aluminate (53 wt%, Sigma–Aldrich) and C₂₂-6N. The synthesis gel had a composition of 30 SiO₂: *a* Al₂O₃: 1 C₂₂-6N: 6.66 Na₂O: 1500 H₂O, where *a* = 0.6 and 1.0. The mixture was stirred at 60 °C for 6 h, and then heated for 3 days at 140 °C in a Teflon-lined autoclave, for zeolite crystallization. The zeolite products were collected after filtration, washing with water, and dried at 100 °C for 12 h. The obtained zeolites were calcined at 580 °C in air. The zeolite was then ion-exchanged three times with a 1 M NH₄NO₃ solution and subsequently calcined again at 580 °C for its full conversion to the

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