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Lewis acid zeolites for tandem Diels–Alder cycloaddition and dehydration of biomass-derived dimethylfuran and ethylene to renewable *p*-xylene†

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Lewis acid zeolites including Zr-, Sn-, and Ti-BEA were examined for tandem [4 + 2] Diels–Alder cycloaddition of 2,5-dimethylfuran (DMF) and ethylene to oxanorbornene with subsequent dehydration to produce biorenewable *p*-xylene. Zr-BEA (Si/Zr = 168) exhibited superior performance with improved recalcitrance to deactivation, which was attributed to its low activity for the hydrolysis of DMF to 2,5-hexanedione and subsequent condensation. Zr-BEA also achieved the highest selectivity to *p*-xylene of 90% at 99% conversion of DMF. For low catalyst loading within a three-phase reactor, the reaction rate to form *p*-xylene was linearly proportional to the number of Lewis acid sites, while high catalyst loading exhibited zero order dependence on Lewis acid sites. A maximum achievable reaction rate was shown to be consistent with a transition in rate-limiting reactions from dehydration of oxanorbornene, the Diels–Alder product, to the Diels–Alder cycloaddition of DMF and ethylene.

Introduction

p-Xylene is an important commodity chemical for the synthesis of terephthalic acid, which is a monomer for the manufacture of polyethylene terephthalate (PET). PET has been widely utilized to commercially manufacture synthetic fibers and plastic bottles due to its outstanding mechanical and chemical properties.[1–3] As the third largest chemical by volume in the world produced from petroleum (catalytic reforming of naphtha) with increasing demand (6–8% per year),[4] there are now ongoing efforts worldwide for developing alternative routes to produce *p*-xylene from renewable biomass resources.[5–14] For example, Lyons *et al.* demonstrated that *p*-xylene can be synthesized from ethylene (from dehydration of bio-ethanol) by a multi-step reaction pathway including trimerization of ethylene, the Diels–Alder reaction of 2,4-hexadiene with ethylene and dehydrogenation of 3,6-dimethylcyclohexene; Shiramizu and Toste also reported that *p*-xylene can be selectively produced from 2,5-dimethylfuran (DMF, from hydrogenolysis of cellulosic biomass-derived 5-hydroxymethylfurfural (HMF)) and acrolein (from glycerol, a biodiesel byproduct).[10,12]

In previous studies, we have reported a renewable reaction pathway to produce *p*-xylene from lignocellulosic biomass over solid Brønsted acid catalysts. The Diels–Alder dehydration reaction includes the cycloaddition of biomass-derived dimethylfuran (DMF) with ethylene, and subsequent dehydration of the formed Diels–Alder adduct to *p*-xylene (Scheme 1).[7,8,15–17] Competing reactions include hydrolysis of DMF to 2,5-hexanedione and reactions between the cycloadduct, DMF (oligomers) and ethylene (alkylated products).[16] The proposed process to produce *p*-xylene can be completely based on biomass resources. DMF can be produced from the hydrolysis of cellulose followed by dehydration of glucose or fructose to HMF, and hydrodeoxygenation of HMF to DMF.[18] Ethylene can be produced from dehydration of bioethanol.[19,20] We have demonstrated that 90% selectivity to *p*-xylene can be achieved by conducting the tandem Diels–Alder/

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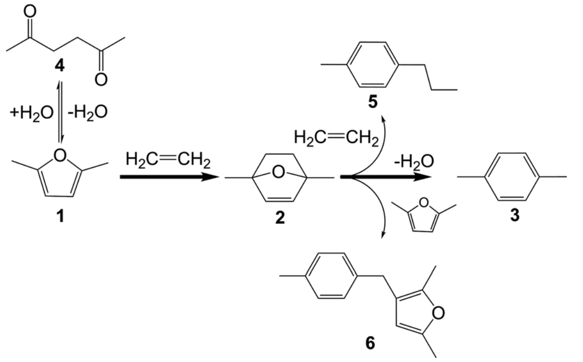
† Electronic supplementary information (ESI) available: XRD patterns and diethyl ether TPD data for Lewis acid zeolites, reaction kinetics from metal oxides, GC/MS data for the cycloadduct of DMF and ethylene, data for dehydration of cyclohexanol, and DMF and byproduct distribution of 2,5-hexanedione added reactions for Zr-BEA and Al-BEA. See DOI: 10.1039/c5gc02164b



Scheme 1 Simplified reaction scheme for synthesis of *p*-xylene from DMF and ethylene. **1**: DMF; **2**: cycloadduct; **3**: *p*-xylene; **4**: 2,5-hexanedione; **5**: representative alkylated product; **6**: representative oligomer.

dehydration reactions over Brønsted acid zeolite catalysts (*i.e.* Al-BEA zeolite, Si/Al = 12.5) in *n*-heptane solvent.[7] Toluene and benzene can also be produced with similar chemistry by starting with 2-methylfuran and furan, respectively.[21] The computational studies including density functional theory (DFT) and quantum mechanics/molecular mechanics (QM/MM) revealed that the formation of the oxanorbornene cycloadduct intermediate by the addition of ethylene to DMF is likely not catalyzed by Brønsted acid sites within zeolite catalysts.[8,22,23] However, Brønsted acids can effectively catalyze the dehydration of the cycloadduct intermediate and decrease the activation energy from 58–60 kcal mol^{-1} to 14–19 kcal mol^{-1}, leading to a significantly increased overall reaction rate.[8,15,22]

Although Brønsted acid zeolite catalysts exhibit promising performance, the overall reaction rate is limited due to the uncatalyzed Diels–Alder reaction. There are thus persistent needs for improving the overall reaction rate by developing catalysts which can promote the Diels–Alder reaction and more selectively dehydrate to reduce side product formation. Previous studies have suggested that Lewis acids can coordinate with dienes to catalyze the Diels–Alder reaction.[10,24–27] DFT studies of the production of *p*-xylene from DMF have also suggested that Lewis acids can coordinate with ethylene to catalyze the Diels–Alder reaction to form the cycloadduct intermediate, oxanorbornene.[15,28] In addition, experimental and theoretical studies have shown that solid Lewis acid catalysts are capable of catalyzing the dehydration of the cycloadduct intermediate and other alcohols.[15,28–30] Using a Fe^{3+}-exchanged montmorillonite K10 clay as a Lewis acid catalyst for the aromatization of oxabicyclic derivatives has also been reported.[27,31] Lewis acid zeolite catalysts, in particular Sn-BEA and Zr-BEA, have also shown catalytic activity for the synthesis of terephthalic acid *via* Diels–Alder reactions with oxidized variants of 5-hydroxymethylfurfural.[3]

Motivated by the existing experimental and theoretical studies, Lewis acid catalysts were employed in this work for producing *p*-xylene from DMF and ethylene through the tandem Diels–Alder/dehydration reaction pathway. We demonstrate that Lewis acid zeolite catalysts are active for producing *p*-xylene. The Zr-BEA catalyst, in particular, exhibited a high selectivity of 90% to *p*-xylene and slower deactivation due to the low hydrolysis rate for the by-product, 2,5-hexanedione. It was also evidenced that Zr-BEA can moderately enhance the formation of the cycloadduct from DMF and ethylene, resulting in the highest measured *p*-xylene production rate.

Experimental

Preparation of catalysts

Solid Lewis acid zeolite catalysts employed in this study were prepared according to the literature and our previous report based on a seeded growth method developed for Sn-BEA.[32–34]. The detailed procedure for the preparation of seed suspension is available in our previous study.[33]

Preparation of Zr-BEA. Typically, 23.72 g of tetraethylorthosilicate (TEOS, 99%, Alfa Aesar) was added to 27.39 g of tetraethylammonium hydroxide solution (TEAOH, 35 wt%, SACHEM) and magnetically stirred in a plastic beaker. After a homogeneous solution was obtained (about one hour), 0.3 g of zirconium(IV) oxychloride octahydrate ($ZrOCl_2·8H_2O$, Sigma-Aldrich) was dissolved in 1.92 g water and added dropwise into the silicate solution. The mixture was kept stirring in a fumed hood until the desired amount of water and ethanol (generated from hydrolysis of TEOS) was evaporated. To this solution, 1.712 mL of dealuminated zeolite BEA seed suspension (0.163 g of seed crystal per mL; corresponding to 4.0 wt% seed with respect to silica) was added and mixed with a plastic spatula. Finally, 2.36 mL of hydrofluoric acid (49%, Alfa Aesar) was added and mixed with a plastic spatula, and a hard gel was formed. The final composition of the gel was $SiO_2 : 0.008 ZrO_2 : 0.56TEAOH : 0.56HF : 7.5H_2O$. The hard gel was transferred to a Teflon lined stainless steel autoclave and heated in a preheated convection oven at 140 °C for four days with 2.0 rpm rotation. The solids were washed with 1.0 L of deionized water by filtration and dried in an 80 °C oven overnight. The organic template was removed by calcining the as-made catalyst at 550 °C with a ramping rate of 1.0 °C min^{-1} for 12 h under flowing dry air (Grade 0.1, Middlesex Gases & Technologies, Inc.).

Preparation of Sn-BEA. Typically, 20.94 g of TEOS was added to 23.02 g of TEAOH solution and magnetically stirred in a plastic beaker. After a homogeneous solution was obtained (about one hour), 0.3 g of tin(IV) chloride hydrate ($SnCl_4·xH_2O$, 34.4 wt% of tin) was dissolved in 1.96 g water and added dropwise into the silicate solution. The mixture was kept stirring in a fumed hood until the desired amount of water and ethanol was evaporated. To this solution, 1.541 mL of dealuminated zeolite BEA seed suspension (corresponding to 4.0 wt% seed with respect to silica) was added and mixed with a plastic spatula. Finally, 1.941 mL of hydrofluoric acid (49%, Alfa Aesar) was added and mixed with a plastic spatula, and a hard gel was formed. The final composition of the gel was $SiO_2 : 0.008SnO_2 : 0.54TEAOH : 0.54HF : 7.5H_2O$. The hard gel was transferred to a Teflon lined stainless steel autoclave and heated in a preheated convection oven at 140 °C for four days with 2.0 rpm rotation. The solids were washed with 1.0 L of deionized water by filtration and dried in an 80 °C oven overnight. The organic template was removed by calcining the as-made catalyst at 550 °C with a ramping rate of 1.0 °C min^{-1} for 12 h under flowing dry air.

Preparation of Ti-BEA. Typically, 24.66 g of TEOS was added to a mixture of 26.76 g of TEAOH solution and 4.24 g of hydrogen peroxide solution (H_2O_2, 30%, Fisher) and magnetically stirred in a plastic beaker. After a homogeneous solution was obtained (about one hour), 0.45 g of titanium(IV) ethoxide (Aldrich) was added dropwise into the silicate solution. The mixture was kept stirring in a fumed hood until the desired amount of water and ethanol was evaporated. To this yellow clear solution, 1.708 mL of dealuminated zeolite BEA seed suspension (corresponding to 4.0 wt% seed with respect to silica) was added and mixed with a plastic spatula. Finally, 2.306 mL of hydrofluoric acid (49%, Alfa Aesar) was added and mixed with a plastic spatula, and a hard gel was formed. The final composition of the gel was $SiO_2 : 0.008TiO_2 : 0.54TEAOH : 0.54 HF : 7.5H_2O$. The hard gel was transferred to a Teflon lined stainless steel autoclave and heated in a preheated convection oven at 140 °C for eight days with 2.0 rpm rotation. The solids were washed with 1.0 L of deionized water by filtration and dried in an 80 °C oven overnight. The organic template was removed by calcining the as-made catalyst at 550 °C with a ramping rate of 1.0 °C min^{-1} for 12 h under flowing dry air.

Preparation of Al-BEA. Aluminosilicate zeolite BEA (CP814E, Si/Al = 12.5) was obtained from Zeolyst. The catalyst was calcined at 550 °C with a ramping rate of 1.0 °C min^{-1} for 12 h under flowing dry air prior to the reaction.

Characterization of the catalysts

The crystalline phase of the Lewis acid catalysts was examined by powder X-ray diffraction (PXRD) on a diffractometer (X'Pert Pro, PANalytical) operated at a voltage of 40 kV and a current of 45 mA with an X'cellerator detector scanning from 4° to 40°. The quantity of Lewis acid sites within the zeolites was determined by diethyl ether temperature programmed desorption coupled with thermogravimetric analysis (TPD–TGA), with the exception of Ti-BEA. Ti-BEA interacted weakly with the probe molecules, and did not provide characterization of Lewis acid sites. Temperature Programmed Desorption (TPD) and Thermogravimetric Analysis (TGA) experiments were carried out using a CAHN 2000 microbalance mounted within a vacuum chamber that could be evacuated with a diffusion pump.[35] Prior to exposing them to a few hundred Pa of the diethyl ether, the samples were heated in a vacuum to 500 °C and then cooled to room temperature *in vacuo*. During TPD–TGA measurements, the sample weights were recorded continuously using the microbalance and the desorbing species were monitored using an SRI quadrupole mass spectrometer (RGA100) at a ramping rate of 10 °C min^{-1}. Elemental analyses were carried out in Analytical Geochemistry Lab, Department of Earth Sciences in the University of Minnesota using ICP-OES (iCAP 6500 Duo View, Thermo Scientific).

Reaction experiments

The reactor system schematic is available in our previous work.[8] In typical reactions with DMF (Alfa Aesar), 100 mL of 1.35 M of DMF in *n*-heptane (Alfa Aesar) with 0.08 M *n*-tridecane (Alfa Aesar) was enclosed in a 160 mL bench-top reactor (Parr), and the reaction vessel was purged with nitrogen. The catalyst acid concentration present in the system was defined as the total number of acid sites of the catalyst divided by the reactant volume. The mixture was then stirred at 1000 rpm with a gas entrainment impeller to ensure facile mass transfer. The system was heated to 250 °C and controlled with a 4848 control unit (Parr). The reactor was then pressurized with 38 bar (partial pressure) of ethylene gas (Airgas), and the total pressure of the system was maintained at 62 bar over the reaction period. Liquid was withdrawn by using a double block sampling system at designated reaction times. The composition of the sample was then analyzed with an Agilent 6890A gas chromatograph with a Rtx-VMS (Restek) column equipped with a flame ionization detector. The products (DMF, *p*-xylene, 2,5-hexanedione) were identified by comparing the retention times with standard chemicals. Based on the reaction scheme,[16] the concentration of the alkylated products was estimated by using the response factor (RF) for 1-methyl-4-propylbenzene, and the concentration of the oligomers was estimated using the additive RF of *p*-xylene and DMF. The oxanorbornene cycloadduct of DMF and ethylene was identified with a GC-MS system (5890 GC/5972 series mass selective detector, HP) and by comparing the electron ionization spectrum with the literature.[16] The concentration of the cycloadduct was estimated using the RF for *p*-xylene. The conversion of DMF and selectivity to products were defined as follows:

$$X_{\mathrm{DMF}}(\%) = 100 \times \frac{C_{\mathrm{DMF},t_0} - C_{\mathrm{DMF},t}}{C_{\mathrm{DMF},t_0}} \tag{1}$$

$$\mathrm{Selectivity}_i(\%) = 100 \times \frac{C_i - C_{i,t_0}}{\sum_i (C_i - C_{i,t_0})} \tag{2}$$

$$\mathrm{Yield}_i(\%) = 100 \times \frac{C_i}{C_{\mathrm{DMF},t_0}} \tag{3}$$

where t is the duration of time after ethylene was added to the reactor, and C_i is the concentration of the reactant and products, i. For a reaction carried out with 2,5-hexanedione, 0.2 M 2,5-hexanedione (Alfa Aesar) was added with 1.35 M DMF solution in *n*-heptane. The reactor was purged with N_2, heated to 250 °C and held at 250 °C for one hour prior to addition of ethylene (62 bar).

Results and discussion

To demonstrate the catalytic activity of solid Lewis acid catalysts for the Diels–Alder dehydration reaction, siliceous zeolite BEA with substituted metal atoms (Zr-, Sn-, and Ti-BEA) at framework positions were prepared according to the methods reported in the literature and applied in the reaction of DMF and ethylene. Other conventional metal oxide catalysts including ZrO_2, SnO_2, and TiO_2 were also tested in the reaction for comparison. The corresponding XRD patterns for the Lewis acid zeolites used in this study are shown in Fig. S1.† Typical diffraction peaks for zeolite BEA were observed for all samples, and no impurity phase (*i.e.*, metal oxides) was detected, indicating that high-quality crystals were obtained. Acid site concentrations of the Lewis acid zeolites were determined by the Si/M ratio obtained from elemental analysis measurement (ICP-OES), and further confirmed by diethyl ether TPD–TGA measurement (Table 1). It has been shown that diethyl ether forms a 1 : 1 complex pair with Lewis acid sites (Sn center) in the Sn-BEA catalyst, and it desorbs from the Sn site at the temperatures from 350 K to 450 K. Measuring the weight change between the temperatures can provide the quantity of Lewis acid sites in the sample.[29] The diethyl ether TPD–TGA results obtained from Sn-BEA, Zr-BEA and Ti-BEA catalysts are shown in Fig. S2.† As listed in Table 1, the TPD–TGA measurements for Sn- and Zr-BEA indicate good agreement with the elemental analysis, while the measurement for Ti-BEA shows a lower acid site density than the Ti concentration in the sample determined by elemental analysis (40 μmol g^{-1} *vs.* 129 μmol g^{-1}). This may be due to the weak interaction between diethyl ether and the Ti site in the Ti-BEA sample, resulting in desorption of the probe molecule from the sample *in vacuo* prior to heating. For Al-BEA, isopropylamine TPD–TGA was utilized to obtain the Brønsted acid site concentration.[21] The quantity of Brønsted acid sites in Al-BEA (620 μmol g^{-1}) was lower than the Al concentration (1230 μmol g^{-1}), indicating the presence of an extra framework Al species in the sample. Contribution from the extra framework Al species was neglected due to low activity from Al_2O_3 according to our previous report.[7] For reaction rate calculations, the acid site concentrations determined by TPD–TGA analysis were used. Due to weak adsorption of diethyl ether on Ti-BEA, the Ti concentration determined by elemental analysis was used in the reaction rate calculations.

Table 1 Acid site density of the zeolites

Catalyst	Si/T ICP	Acid site density (μmol g^{-1}) ICP	Chemical TPD[b]
Zr-BEA	168	98	95
Sn-BEA	126	130	120
Ti-BEA	128	129	40
Al-BEA	12.5[a]	1230	620[c]

[a] Zeolyst. [b] Diethyl ether TPD except as otherwise noted. [c] Isopropylamine TPD for Brønsted acid sites.

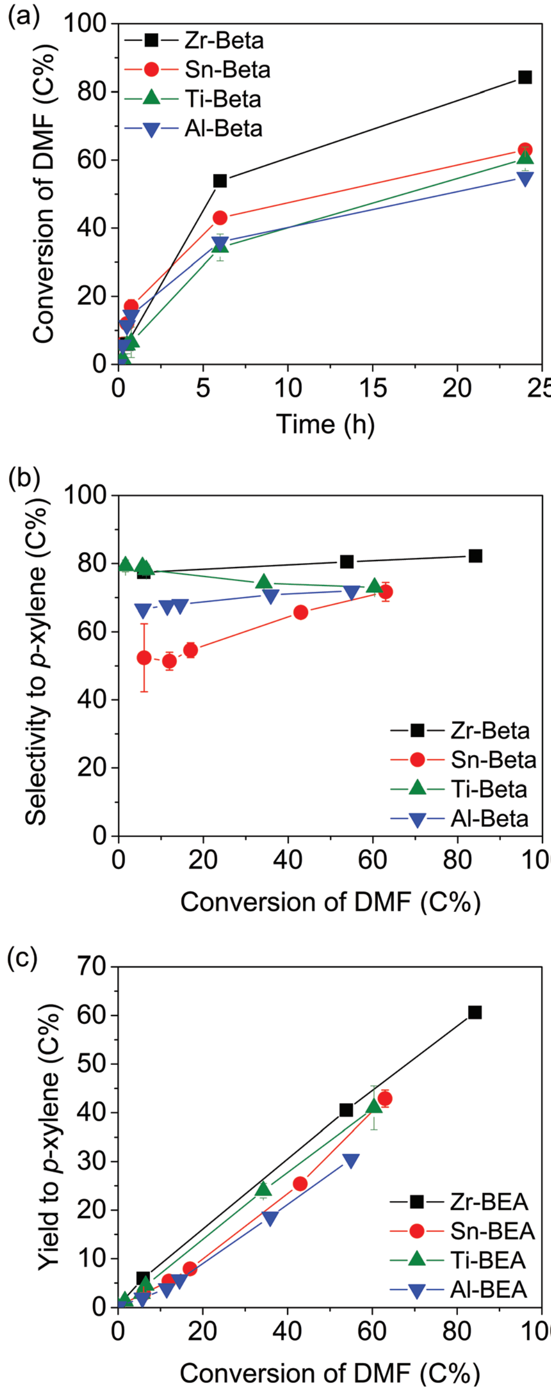


Fig. 1 (a) Kinetics of DMF conversion at 250 °C. (b) Selectivity and (c) yield to *p*-xylene as a function of DMF conversion for the reaction of DMF and ethylene at 1.0 mM acid loading of Sn-BEA, Zr-BEA, Ti-BEA, and Al-BEA.

Fig. 1 depicts the temporal profiles of yield and selectivity in the reaction to *p*-xylene with respect to DMF conversion over different catalysts at the same acid site concentration (1.0 mM) in the reaction system (1.35 M DMF in *n*-heptane and 62 bar of ethylene) at 250 °C. Surprisingly, all considered Lewis acid zeolites are capable of catalyzing the reaction to produce *p*-xylene. This activity was attributed to Lewis acidity from the isolated metal atoms located in the zeolite frameworks, as metal oxides (ZrO_2, SnO_2, and TiO_2) and pure siliceous BEA did not show significant catalytic activity (Fig. S3†).[8] Among the tested catalysts, Zr-BEA exhibited superior performance with 80% selectivity to *p*-xylene at 80% conversion of DMF (Fig. 1b) in 24 h. Sn-, Ti-, and Al-BEA, however, deactivated noticeably faster, and only achieved about 60% DMF conversion after 24 hours of reaction with lower selectivity to *p*-xylene. Furthermore, Zr-BEA yielded ∼33% more *p*-xylene than Al-BEA at 60% conversion (Fig. 1c). It is worth noting that the activity of Sn-MFI was considerably lower (8 mM h^{-1}; Table 2) under identical conditions, as it converted less than 20% of DMF after 24 h of reaction, which highlights the uniqueness of the zeolite BEA structure for this reaction. The result is consistent with our previous report which suggested that the small micropore structure of ZSM-5, an aluminum analog of Sn-MFI, is not favorable for the reaction.[7] This implies that either the Diels–Alder reaction could not be catalyzed within the framework or the formed cycloadduct intermediate could not easily diffuse within the micropore structure of the MFI zeolite.

To further understand the high selectivity to *p*-xylene over Zr-BEA, the byproduct distributions for the reaction of DMF and ethylene over Lewis acid zeolite catalysts and Al-BEA were measured and are shown in Fig. 2. Sn-BEA preferentially catalyzes the side reactions and produces a more hydrolysis product, 2,5-hexanedione, and oligomers at lower conversion, which explains the low selectivity to *p*-xylene for Sn-BEA. Zr-BEA, however, is able to minimize the hydrolysis of DMF, with low 2,5-hexanedione yield at all extents of conversion (Fig. 2a). Zr-BEA also minimizes the formation of oligomers (Fig. 2b) but promotes the reaction between cycloadduct and ethylene, giving the highest yield of alkylated products (Fig. 2c). Al-BEA, on the other hand, produces only small amounts of oligomeric products and more 2,5-hexanedione and alkylated products. At low conversion of DMF, strong Brønsted acidity of Al-BEA can effectively catalyze the hydrolysis reaction of DMF, which explains the even lower *p*-xylene selectivity at high catalyst loading shown later (Fig. 3). All results suggest that using Zr-BEA is moderately beneficial for the production of *p*-xylene compared with Al-BEA due to its low activity for catalyzing side reaction of the hydrolysis of DMF. The reaction results reveal that the characteristics of the acid type can manipulate the product distributions by affecting the reaction rates between the competing reaction pathways, while the selectivity towards *p*-xylene for all catalysts is not significantly different at high conversion of DMF.

Table 2 Summary of the reaction results for the catalysts[a]

Catalyst	Rate of *p*-xylene production (mM h^{-1})	DMF conversion after 24 h	*p*-Xylene yield after 24 h
Al-BEA	122 ± 11.0	55 ± 3.7	30 ± 0.5
Sn-BEA	113 ± 6.8	63 ± 0.1	43 ± 1.8
Zr-BEA	121 ± 4.9	83 ± 1.6	61 ± 1.5
Ti-BEA	65 ± 11.2	60 ± 3.5	41 ± 4.5
Sn-MFI	8	27	17
SnO_2	0.6	2	0.3
ZrO_2	0.7	2	0.5
TiO_2	1.1	3	1.4

[a] Reaction conditions: 1.0 mM acid (0.8 g for metal oxides), 1.35 M DMF in *n*-heptane, 62 bar ethylene, at 250 °C.

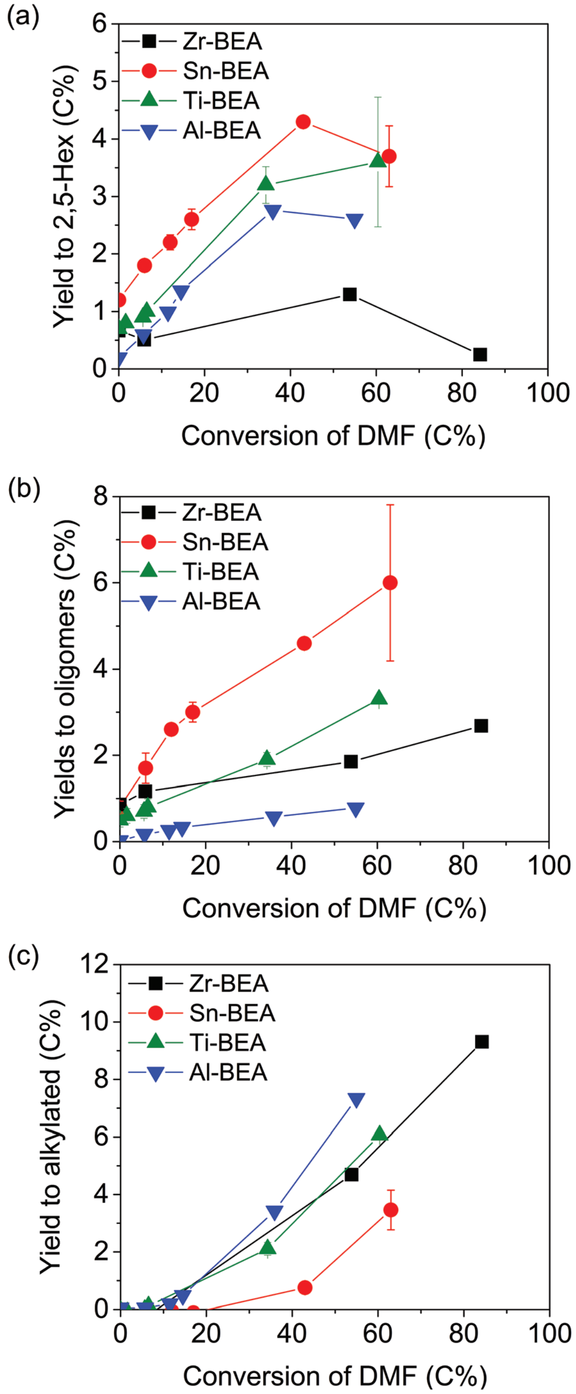


Fig. 2 Yield of (a) 2,5-hexanedione, (b) oligomers and (c) alkylated side products as a function of DMF conversion for the reaction of DMF in heptane with ethylene (62 bar) at 250 °C with Sn-BEA, Zr-BEA, and Ti-BEA as well as Al-BEA catalysts at 1.0 mM acid concentration.

To understand the effect of the active site concentration, Zr-BEA and Al-BEA catalysts were compared at high catalyst loading (acid site concentration of 3.5 and 3.1 mM, respectively). As shown in Fig. 3, it was found that the kinetics of DMF conversion and overall *p*-xylene yield were similar between Zr-BEA and Al-BEA, but the selectivity to *p*-xylene for

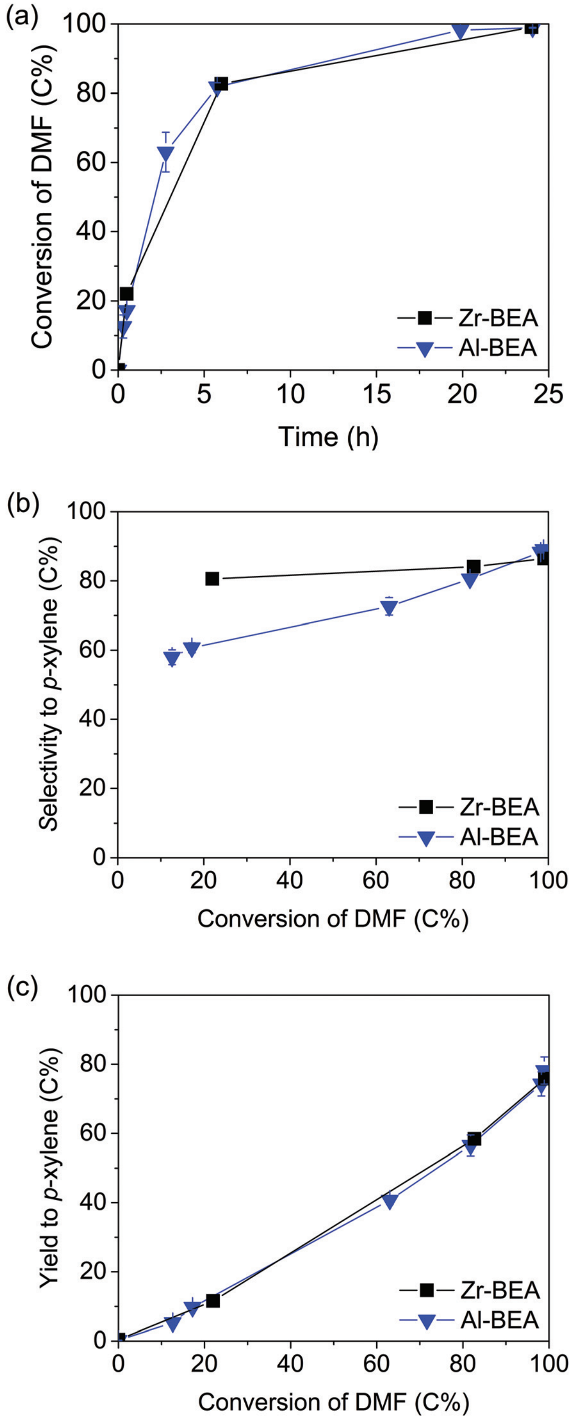


Fig. 3 (a) Kinetics of conversion of DMF, (b) selectivity, and (c) yield to *p*-xylene as a function of DMF conversion for the reaction of 1.35 M DMF in heptane and 62 bar of ethylene at 250 °C with high acid loading of Zr-BEA (3.5 mM) and Al-BEA (3.1 mM).

Zr-BEA was significantly higher at low conversion (80% *vs.* 60%). Differences in selectivity to *p*-xylene were larger when compared at low acid site loading (acid site concentration of 1.0 mM), which appears due to the low activity of Zr-BEA for catalyzing the hydrolysis reaction of DMF. Zr-BEA exhibited the highest selectivity to *p*-xylene (~90%) at full conversion of DMF at the acid site concentration of 3.5 mM, which was similar to the previously reported selectivity to *p*-xylene achieved with Al-BEA.[7]

Fig. 4 shows the rate of production of *p*-xylene *versus* the acid site concentration for different catalysts. The reaction rates were deliberately presented on a volumetric basis of mM h^{-1} (rather than TOF), due to the previous work which indicated that the overall reaction was limited by either Diels–Alder cycloaddition or dehydration depending on the active site concentration.[7,8,22] At a low acid site concentration, it was found that the rate of *p*-xylene production is proportional to the acid concentration and reaches a maximum when the acid site concentration is higher than ~2.5 mM for both Brønsted acid, Al-BEA, and Lewis acid zeolites, Sn-BEA and Zr-BEA. This is consistent with our recent report on the kinetic study for the same system using a Brønsted acid zeolite, zeolite Y.[22] The kinetic behavior and rate dependence on the acid site concentration can be interpreted as a transition in the rate controlling reaction. The overall reaction from DMF and ethylene to *p*-xylene is a sequence of Diels–Alder cycloaddition of ethylene and DMF followed by dehydration of the cycloadduct. Similar to the Brønsted acid zeolite catalysts, at low Lewis acid site concentrations, the overall rate might be controlled by the dehydration reaction due to insufficient quantity of catalytic sites; at high Lewis acid site loadings, the reaction could be limited by the cycloaddition reaction, which results in the plateau (*i.e.* a maximum reaction rate) of *p*-xylene production.

The activity of the catalysts was compared using the turnover frequencies (TOF) calculated within the dehydration-limited region (linear dependent region, <2.5 mM acid sites in Fig. 4) using the production rate of *p*-xylene normalized to the amount of acid sites of the catalysts (only Brønsted acid sites were considered for Al-BEA). Interestingly, Zr-BEA exhibited

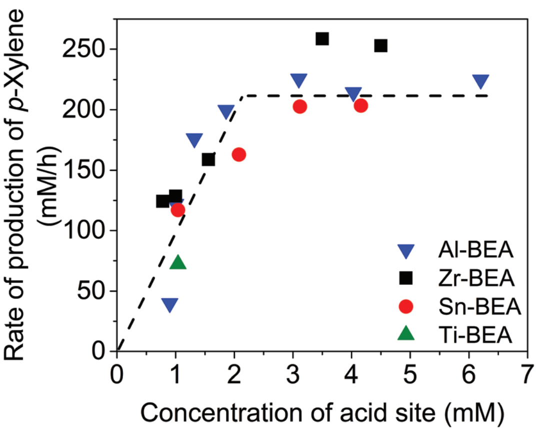


Fig. 4 *p*-Xylene production rate *versus* the active site concentration in *n*-heptane for Zr-BEA, Sn-BEA, Ti-BEA and Al-BEA for the reaction of DMF with ethylene (62 bar) at 250 °C. Initial catalytic rates were calculated at <20% conversion of DMF. The dashed line is provided as a guide to the eyes.

higher TOF (121 ± 4.9 h^{-1}) than Sn-BEA (113 ± 6.8 h^{-1}) and Ti-BEA (65 ± 11 h^{-1}), and was similar to Al-BEA (122 ± 11 h^{-1}) as shown in Table 2. The results suggest that Zr-BEA is an efficient catalyst for the sequential reaction to produce *p*-xylene. The result was unexpected since it has been known that Lewis acid zeolites are not efficient dehydration catalysts for several alcohols compared with Brønsted acid zeolites.[35]

Our control experiment for dehydration of cyclohexanol to cyclohexene using Al-BEA and Zr-BEA also indicates that Al-BEA is generally superior for dehydration reactions (Fig. S4†). A further study on the catalytic activity of Zr-BEA for the dehydration of the cycloadduct to *p*-xylene is necessary in order to further improve the catalytic system.

Despite significant catalytic differences under dehydration-controlling reaction conditions, only subtle differences were observed between Lewis acid catalysts and Brønsted acid zeolites within the "plateau region" (catalyst independent region, >2.5 mM acid sites in Fig. 4) where the Diels–Alder reaction controls the overall rate. Comparing the formation rates of *p*-xylene, Zr-BEA exhibited about 10–20% higher production rate than Sn-BEA and Al-BEA, which might indicate a slight enhancement in catalysis of the Diels–Alder reaction. However, the enhancement of the overall reaction with Lewis acids is minor; variation of the Lewis acid site concentration for either Sn-BEA or Zr-BEA (3.5–5.0 mM acid sites in Fig. 3) did not result in measurable differences in the overall rate.

To confirm the limited catalytic activity of Zr-BEA for the Diels–Alder reaction, the concentration of the cycloadduct produced from the Diels–Alder reaction during the reaction was monitored at low catalyst loadings. The formation of the DMF/ethylene cycloadduct was confirmed by GC/MS (Fig. S5†). As shown in Fig. 5, the Lewis acid zeolites are moderately more active to catalyze the Diels–Alder reaction compared to Al-BEA, and they produce a slightly higher cycloadduct intermediate concentration during the tandem reaction than Al-BEA. In particular, Zr-BEA produced the most cycloadduct intermediate throughout the reaction while exhibiting the same initial production rate of *p*-xylene as Al-BEA (Fig. 3). The results suggest that the Zr center is moderately effective for the cycloaddition reaction and less efficient for the dehydration reaction compared to Al-BEA.

In addition to the moderately improved production rate of *p*-xylene, Zr-BEA also exhibited slower deactivation compared to other Lewis acid zeolites and Al-BEA as shown in Fig. 1a. In the plot of selectivity to *p*-xylene (Fig. 1b), it was observed that both Lewis and Brønsted acid zeolite catalysts exhibit counter-intuitive behavior of increasing selectivity to *p*-xylene with DMF conversion. With the Zr-BEA catalyst, the selectivity to *p*-xylene at the DMF conversion of 20% is slightly lower than 80%, while it increases to 80% at higher conversion. This phenomenon has been observed with the Brønsted acid zeolite, Al-BEA, and was attributed to the equilibrium-driven formation of DMF from its hydrolysis byproduct, 2,5-hexanedione, followed by the formation of the thermodynamically stable final product, *p*-xylene.[7] It has been suggested by Do *et al.* that 2,5-hexanedione formed from the hydrolysis of DMF can cause catalyst deactivation by forming insoluble surface condensates *via* acid catalyzed aldol-type reactions.[16] In order to further understand the effects of 2,5-hexanedione on the deactivation of zeolite catalysts in the reaction, 2,5-hexanedione (0.2 M) was intentionally added in the reaction mixture as a reactant with Zr-BEA and Al-BEA catalysts (at 1.0 mM acid site concentration). The reaction mixture was well mixed and heated at 250 °C under nitrogen for one hour prior to the addition of ethylene. The changes in the concentration of 2,5-hexanedione and *p*-xylene with the reaction time are shown in Fig. 6. It was found that with increasing temperature, the

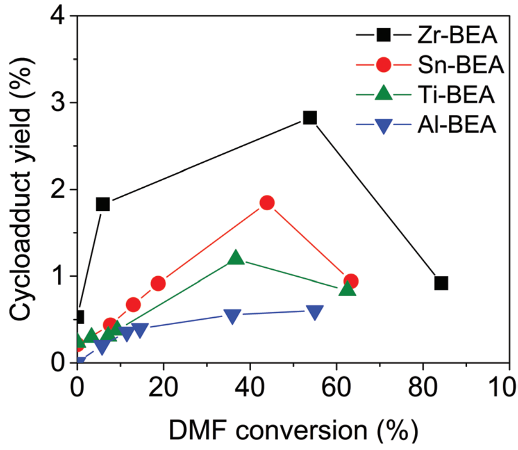


Fig. 5 Yield of cycloadduct *versus* DMF conversion (1.35 M DMF in heptane, 250 °C, 62 bar ethylene). The concentration of the cycloadduct was estimated by using the response factor of *p*-xylene. The acid concentration is 1.0 mM for all.

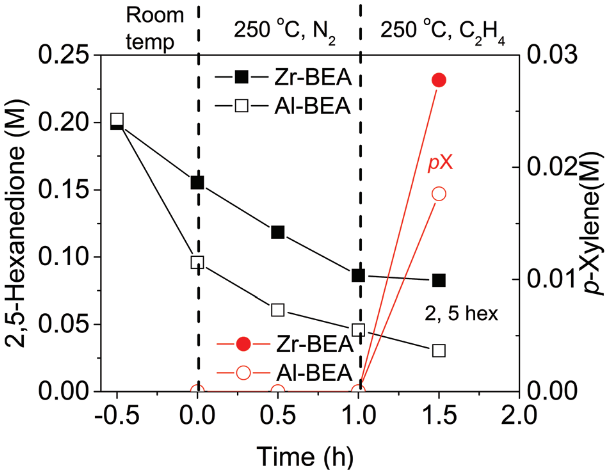


Fig. 6 The concentration evolution of 2,5 hexanedione (2,5-hex) and *p*-xylene with time for the deactivation-simulated reaction with 2,5 hexanedione added with DMF as the reactant for Al-BEA and Zr-BEA. The reaction mixture was heated at 250 °C under N_2 for 1 h before ethylene (62 bar of total pressure) was introduced into the reactor. The acid concentration is 1 mM in the system.

concentration of 2,5-hexanedione quickly decreased over both Zr-BEA and Al-BEA catalysts. After one hour at 250 °C, the concentration of 2,5-hexanedione was 0.05 M for the Al-BEA catalyst and 0.1 M for the Zr-BEA catalyst, indicating a faster reaction rate of 2,5-hexanedione over the Brønsted acid zeolite catalyst. One hour after the introduction of ethylene into the experiment, *p*-xylene was produced by both catalysts with Zr-BEA exhibiting a significantly higher *p*-xylene formation rate than Al-BEA (56 mM h^{-1} *vs.* 35 mM h^{-1}). However, the production rates of *p*-xylene were significantly lower than the rate achieved without adding 2,5-hexanedione at the beginning of the reaction (120 mM h^{-1}). In addition, it was observed that during the reaction the concentration of DMF does not increase with the decrease of 2,5-hexanedione, which indicates that 2,5-hexanedione did not undergo dehydration to form DMF under the reaction conditions (Fig. S6a†).

The results clearly suggest that the addition of 2,5-hexanedione did indeed cause catalyst deactivation, in particular for the Brønsted acid zeolite catalyst, Al-BEA. Zr-BEA, however, deactivated slower under the same conditions, which could be due to weaker acid sites on Zr-BEA compared to Al-BEA that are not efficient at catalyzing the condensation reactions of 2,5-hexanedione. The longer catalyst life (slower deactivation) of Zr-BEA may therefore be attributed to: (1) a slower production rate of 2,5-hexanedione (Fig. 2a), and (2) weaker acid sites that are not efficient for catalyzing condensation reactions of 2,5-hexanedione (Fig. 6).

The cycloaddition/dehydrative aromatization chemistry can be extended to 2-methylfuran (MF) and furan to produce toluene and benzene.[7,17,21] Due to the lack of protecting methyl groups on the furan α-carbon, the yields of toluene and benzene were generally lower than the reaction for producing *p*-xylene from DMF. As shown in Fig. 7, the conversion of MF and yield of toluene achieved over the Zr-BEA catalyst were slightly higher than Al-BEA after a 24 hour reaction. However, the selectivity to toluene was similar, which indicates that Zr-BEA can prevent fast catalyst deactivation but does not significantly enhance the production rate of toluene (70 *vs.* 68 mM h^{-1} toluene production rate for Zr-BEA and Al-BEA, respectively). In the reaction with furan, Zr-BEA only produced ~5% of benzene after the 24 h reaction (~70% conversion), revealing that the Lewis acid zeolite (Zr-BEA) is not effective in improving the yield of benzene. Overall, the performance of Zr-BEA was slightly better in furan and MF reactions in terms of catalyst life, but they exhibited no significant difference with regard to selectivity to benzene and toluene when compared with Al-BEA.

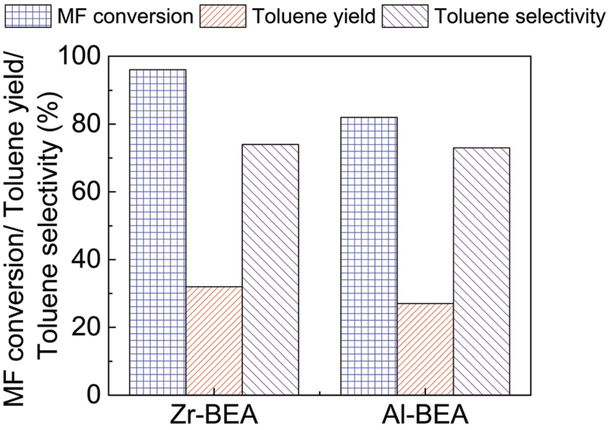


Fig. 7 MF conversion, toluene yield, and toluene selectivity for the reaction of MF and ethylene with Zr-BEA and Al-BEA after a 24 h reaction. The reaction involves 1.35 M of MF in *n*-heptane with 62 bar of ethylene at 250 °C. The acid concentration for both catalysts is 0.8 mM.

Conclusions

Solid Lewis acid zeolites including Zr-, Sn-, and Ti-BEA were evaluated in *p*-xylene production from DMF and ethylene. Lewis acid zeolites were shown to catalyze the Diels–Alder addition/dehydration reactions. It was also found that Lewis acid zeolites exhibit longer lifetime than Al-BEA, in particular Zr-BEA shows the best performance with higher turnover frequency and slower deactivation, which could be attributed to its low selectivity to the hydrolysis product, 2,5-hexanedione, and weak acid site nature which prevents the polymerization of 2,5-hexanedione. It was also demonstrated that the production rate of *p*-xylene was dependent on the total amount of the Lewis acid catalyst at low loading and independent at high loading due to the nature of the tandem reaction, which was similar to the behavior of Brønsted acid zeolite catalysts. Finally, it was revealed that Zr-BEA moderately promoted the Diels–Alder cycloaddition reaction by producing more oxanorbornene while being a less efficient dehydration catalyst; this resulted in a mild enhancement of *p*-xylene production by ~10–20% compared to Al-BEA. The current findings can serve as a guide to design efficient and long-lasting catalysts for the tandem Diels–Alder cycloaddition/dehydration reactions.

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