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Adsorption and Reaction Properties of SnBEA, ZrBEA, and H-BEA for Formation of p-Xylene from DMF and Ethylene

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Abstract. The adsorption and reaction properties of H-BEA, SnBEA, ZrBEA, and siliceous BEA were examined to understand the reaction of 2,5-dimethylfuran (DMF) with ethylene to form p-xylene. Temperature-programmed desorption (TPD) of diethyl ether, DMF, 2,5-hexanedione, and p-xylene on each of the zeolites demonstrated that the Brønsted sites in H-BEA are more reactive than the Lewis sites in SnBEA and ZrBEA and tend to promote oligomerization of DMF and 2,5-hexanedione, even at 295 K; however, adsorbed 2,5-hexanedione is converted to DMF at both Lewis- and Brønsted-acid sites. H-BEA, SnBEA, and ZrBEA all catalyzed the reaction to p-xylene with high selectivity in a continuous flow reactor, with all three catalysts showing rates that were first-order in both DMF and ethylene. H-BEA was found to deactivate rapidly due to coking, while ZrBEA and SnBEA were both stable. The implications of these results for practical applications are discussed.

1. Introduction

The reaction of 2,5-dimethylfuran (DMF) and ethylene to p-xylene is of significant interest, because it offers the possibility of producing an important commodity chemical from lignocellulosic biomass [1]. Yields above 90% have been achieved for this reaction, which proceeds via two separate steps, a Diels-Alder addition and subsequent dehydration. The reaction requires a catalyst and most work has been performed with zeolites that have Brønsted acidity [2]. Rates with these zeolites have been shown to depend on acid-site concentrations. For example, in a study using H-Y zeolites, two kinetic regimes were observed [3]. At low site concentrations, rates increased linearly with the number of sites and the activation energy was 45 ± 8.8 kJ/mol. Theoretical calculations indicated that the reaction under these conditions was limited by the catalyzed dehydration of the Diels-Alder cycloadduct. At high site concentrations, the overall rates were proposed to be limited by homogeneous Diels-Alder reaction. The rates in this regime were independent of site concentration and showed an activation energy of 84 kJ/mol.

Most recently, it was demonstrated that BEA zeolites that have only Lewis-acid sites, formed by either framework Zr, Sn, or Ti, are also active catalysts for this reaction [4–7]. Interestingly, the specific rates and product selectivities were similar for materials that had Brønsted acids formed by framework Al and for materials that had only Lewis sites. Given that past adsorption studies on zeolites with framework Sn showed very different characteristics from what is observed on Brønsted-acid sites [8], this similarity in rates is surprising. For example, Temperature-Programmed Desorption (TPD) studies clearly show alcohol dehydration, a reaction similar to the dehydration of the Diels-Alder cycloadduct, is much more facile on Brønsted sites compared to Sn sites. Furthermore, in the formation of p-xylene, competition for the acid sites by other reactant and product molecules will affect the observed chemistry. Therefore, one goal of the present study was to compare the adsorption properties of Lewis-acid (SnBEA and ZrBEA) and Brønsted-acid (H-BEA) zeolites for DMF, p-xylene, and other molecules similar to those that could form during reaction in order to gain additional insights into the reaction mechanism.

The second part of the present study involved rate measurements on SnBEA, ZrBEA, and H-BEA for the formation of p-xylene from DMF and ethylene using a continuous-flow, tubular reactor similar to that used in studies of hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) [9,10]. Because the reaction of DMF with ethylene must be carried out at high pressures and with long residence times, most of the previously published work has been performed in semi-batch reactors [1–4,11–14]. However, continuous-flow reactors more closely simulate industrial performance. Furthermore, because continuous-flow reactors can operate at steady state, it is easier to monitor catalyst deactivation.

The present work shows that even though the Lewis-acid and Brønsted-acid BEA zeolites exhibit different adsorption properties, rates for the formation of p-xylene on SnBEA, ZrBEA, and H-BEA are similar and can be described by a simple rate over a wide range of pressures and temperatures. One major difference between the zeolites is that deactivation due strong adsorption and oligomerization of reactants is a problem on H-BEA, while the Lewis-acid zeolites appear to be stable.

2. Experimental Methods:

Four BEA zeolites were used in this study. The H-BEA sample was prepared from NH_4-BEA, obtained from Zeolyst (CP814C ($Si/Al_2 = 38$)), by calcination at 823 K in flowing air for four hours. SiBEA (siliceous form of zeolite BEA) was synthesized according to the method of Camblor et al. [15]. First, 8.47 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, 98%) was added into the mixture of 8.08 g of tetraethylammonium hydroxide (TEAOH, 40 wt% Sigma Aldrich) and 1.44 g of DI water. After stirring the solution at room temperature for 6.5 h, 0.915 g of HF (48 wt%, Sigma Aldrich, fresh) was added. This solution with a final composition of 0.54 TEAOH: 0.54 HF: 1 SiO_2: 7.5 H_2O, was then transferred into a Teflon-lined, stainless steel autoclave (Parr) and heated in a convection oven at 413 K for 14 days, with rotation (~ 40 rpm). The solid that was produced in this process was filtered, washed with DI water, and calcined in dry flowing air at 830 K for eight hours using a temperature ramp of 1 K min^{-1}. X-Ray Diffraction (XRD) indicated that this material had the BEA structure. The Si/Al ratio was determined to be greater than 80,000 by atomic absorption and solid-state ^{29}Si MAS NMR spectroscopy indicated a low concentration of defects [15].

SnBEA and ZrBEA with Si/Sn and Si/Zr ratios of 126 and 168 (determined by ICP-MS) were synthesized by a seeded-growth method [4]. Using the synthesis of SnBEA to demonstrate the preparation procedures, 20.94 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, 99%) were added to 23.02g of tetraethylammonium hydroxide (TEAOH, 35% SACHEM) and stirred in a plastic beaker for 1 h. A solution containing 0.3 g of tin chloride hydrate ($SnCl_4 \bullet xH_2O$, 34.4 wt%

of tin) in 1.96 g of water was then added dropwise into the silicate solution. After removing some of the water and ethanol by evaporation, 1.541 mL of a seed suspension (corresponding to 4.0 wt% dealuminated BEA seed with respect to silica) was added into this solution. Next, 1.941 mL of HF (49%, Alfa Aesar) was added to the solution, which caused formation of a hard gel with a composition of 1 SiO_2: 0.08 SnO_2: 0.54 TEAOH: 0.54 HF: 7.5 H_2O. The hard gel was then transferred to a stainless steel autoclave and heated to 310 K for four days with rotation (~ 2.0 rpm). The resulting solids were washed with DI water, filtered, dried overnight at 350 K, and calcined at 830 K for overnight using a ramping rate of 1 K min^{-1} under flowing dry air. More details on the properties of the SnBEA and ZrBEA prepared in this way are given elsewhere [4]. Crystal diameters of H-BEA, SnBEA and ZrBEA were 1.3 μm, 1.1 μm, and 1.8 μm, respectively.

Temperature Programmed Desorption (TPD) and Thermogravimetric Analysis (TGA) experiments were performed using equipment described elsewhere[16]. The system consists of a CAHN 2000 microbalance mounted within a vacuum chamber that could be evacuated with a diffusion pump to a base pressure of approximately 10^{-5} Pa. The partial pressures during evacuation could be monitored using an SRI quadrupole mass spectrometer (RGA100). Prior to performing adsorption experiments, the 50 mg samples were heated in vacuum to 833 K. The samples could then be saturated with adsorbates of interest by exposure to the vapors above the liquids or they could be exposed to smaller, controlled doses of an adsorbate by expansion of a given volume of vapor into the chamber. Probe molecules of interest for this study were 2,5-dimethylfuran (DMF, 99%, Acros Organic), p-xylene (99%, Acros Organic), diethyl ether (99.9%, Fisher Scientific), 2-propanamine (99%, Alfa Aesar) and 2,5-hexanedione (97%, Acros Organic). For this study, the samples were exposed to the room-temperature vapor pressures of each adsorbate for 1 min prior to evacuation. The heating rate for the TPD-TGA experiments was 10 K min^{-1}.

The reaction of DMF with ethylene was examined in a continuous-flow reactor similar to that used in previous hydrodeoxygenation studies[9]. Approximately 0.1 g of catalyst was packed in the middle of a 4.6-mm ID, stainless-steel tube, 20-cm long. The catalyst was held in place using glass wool, and a 4.5-mm stainless-steel rod was inserted downstream from the catalyst to reduce the empty volume of the reactor. Liquid reactants, typically 2.0 g DMF in 100 mL of n-heptane (99%, Acros Organic), were fed into the reactor using an HPLC pump (Series III, Scientific System), which could be used to control the liquids flow rate and measure the pressure in the reactor. The pressure was controlled using a back-pressure regulator (KPB series, Swagelok) placed downstream from the reactor. Ethylene (C_2H_4, UHP grade, Praxair Inc) was introduced into the reactor from a high-pressure regulator, through 7 ft of 0.002 in. ID capillary tubing (Valco Instruments), and the gas flow rate was controlled using the pressure drop across the capillary tubing.

In the reaction studies, it was not possible for us to completely duplicate the reaction conditions used in previous semi-batch reaction studies [2,3]. First, the HPLC pump would not reliably operate with DMF concentrations higher than 0.2 M, because higher concentrations led to phase separation. Second, because the lowest rate that we could reliably measure in our system in its present configuration was 0.1 $\mathrm{mmol \bullet gcat^{-1}\ h^{-1}}$, it was necessary for us to work at higher temperatures than used in earlier studies. Using the rate expressions reported by Patet, et al [3] for the high acid-site regime, the minimum temperature at which we expect to see conversion of DMF on H-BEA is approximately 573 K. Because this is above the critical temperature of n-heptane, 540 K, there may be differences in the rate expressions derived in our studies compared to those obtained previously.

3. Results:

A summary of some key properties for the catalysts used in this study is shown in Table 1. For H-BEA, the acid-site density is the Brønsted-site density determined by TPD-TGA of 2-propanamine. Because alkyl-ammonium ions formed by adsorption of the amine on Brønsted sites undergo Hoffman elimination to propene and ammonia between 575 and 650 K, the Brønsted site density can be obtained by measuring the amount of 2-propanamine which reacts in this temperature range[17]. The Brønsted site density on the H-BEA sample, 500 μmol/g, is somewhat lower than the bulk Al density, 1140 μmol/g, possibly in part due to the presence of non-framework Al, but probably also due to steric crowding of amine molecules at adjacent sites for zeolites with relatively low Si/Al ratios [18]. Because there were no Brønsted sites on the SnBEA and ZrBEA samples, there was no reaction of 2-propanamine in TPD-TGA measurements. The Lewis-site densities for SnBEA and ZrBEA, 140 and 100 μmol/g respectively, were assumed to be that of the bulk Sn and Zr compositions. Pore volumes were determined by gravimetric uptakes for n-hexane on H-BEA and 1-hexene on SnBEA and ZrBEA at 0.01 bar at room temperature, assuming that the n-hexane or 1-hexene molecules pack the pores with its liquid density.

3.1 Adsorption Studies

The adsorption of diethyl ether was chosen to be a surrogate for the Diels-Alder cycloaddition product, 1,4-dimethyl-7-oxabicyclo[2.2.1]hept-2-ene. Fig 1 shows the TPD-TGA results for diethylether on H-BEA, SnBEA, and ZrBEA following a saturation exposure and one hour evacuation; as discussed elsewhere, diethyl ether was completely removed from the SiBEA following 1-h evacuation. On H-BEA (Fig 1a), the initial coverage of diethylether after evacuation corresponded to 620 μmol/g, a value slightly above the Brønsted-site density of this sample. Because diethyl ether desorbs completely from siliceous BEA, some of the diethyl ether may be adsorbed on Lewis sites associated with the Al in the H-BEA that is in excess of the Brønsted sites. During TPD, roughly half of the ether molecules desorbed unreacted (m/e = 31, 28) below 450 K, with the remaining molecules desorbing as ethylene (m/e = 28) and water (m/e = 18) in a sharp feature centered at 490 K. The presence of two desorption features does not indicate the presence of two types of sites since reaction and desorption are likely parallel processes. Rather, we suggest that those molecules remaining at Brønsted sites to 450 K in a normal desorption profile simply decompose when the reaction temperature is reached. Water and ethylene desorb simultaneously, because they are formed above their normal desorption temperatures. The TPD-TGA data for SnBEA and ZrBEA, reported in Figs. 1b and 1c respectively, demonstrate that diethyl ether desorbs intact from the framework Sn and Zr sites, with most desorption occurring below 450 K. The fact that the initial coverages are slightly lower than or equal to the metal site densities indicates that molecules adsorbed at the Lewis sites can be removed by evacuation over time.

TPD-TGA results obtained on each of the four zeolites following a brief, saturation exposure of DMF, followed by 1-h of evacuation, are shown in Fig. 2. The data in Fig. 2a indicate that 1-h evacuation is sufficient to remove essentially all of the DMF from SiBEA. Most of the very small apparent weight change observed in TGA could be due to the physical effects of heating a siliceous sample in vacuum, as demonstrated by the fact that little DMF is observed leaving the sample by mass spectrometry. The initial DMF coverages on SnBEA and ZrBEA, shown in Figs. 2b and 2c, were only slightly higher, about 50 μmol/g, but well-defined DMF peaks (m/e = 41, 96) were observed between 300 and 400 K. That the initial DMF coverages were below the Sn and Zr site densities shows that DMF is so weakly held that even molecules present at the Lewis sites can be removed by evacuation at room temperature. These results on the Lewis acids are in sharp contrast to what is observed with H-BEA, Fig. 2d. The weight change on H-BEA following exposure to DMF corresponded to more than two molecules per Brønsted site. Some DMF desorbed in a peak centered at 420 K but coverage at 500 K remains above one per Brønsted site. Some of the remaining molecules desorb as olefin products (propene and most olefins exhibit a peak at m/e = 41)[19] ; but the sample weight did not return to its initial value, even after heating to 800 K, implying that some of the DMF was converted to coke.

Previous mechanistic studies have shown that 2,5-hexanedione is a side product in the reaction of DMF to p-xylene and likely at least partially responsible for inhibiting isomerization of p-xylene[11]. TPD-TGA results on SiBEA and H-BEA following a saturation exposure to 2,5-hexanedione and 1-h evacuation are reported in Fig. 3. Even on SiBEA, Fig. 3a, the initial coverage was high, more than 1100 μmol/g; but all of the 2,5-hexanedione (m/e = 99) desorbed intact below 500 K. The adsorption should probably be classified as physical but fairly strong. The initial coverage on H-BEA, Fig. 3b, was similar but the products in TPD very different. Hexanedione was not observed in the desorbing products. Nearly 600 μmol/g of the 2,5-hexanedione was converted to DMF (m/e = 96, 41) and water in a peak centered at about 375 K. Additional water was formed between 370 and 550 K, leaving unidentified products at the acid sites, some of which desorbed as olefins near 600 K and some of which remained on the sample. Because the TPD-TGA data in Fig. 3b are so similar to those in Fig. 2d, the results suggest that 2,5-hexanedione was rapidly converted to DMF and water at low temperatures, consistent with reports that 2,5-hexanedione and DMF are essentially in equilibrium with each other under reaction conditions.

The high initial coverages observed in the results from both zeolites in Fig. 3 make it difficult to follow the initial chemistry that occurs on the acid sites. Therefore, additional experiments were performed in which the three acidic zeolites were exposed to controlled doses of 2,5-hexanedione corresponding to initial coverages of approximately 200 μmol/g. TPD-TGA following the controlled exposures are shown in Fig. 4. The results on H-BEA, Fig. 4a, were qualitatively similar to those obtained following saturation exposures. Again, DMF and water were observed leaving the sample below 450 K, olefin products were observed above 550 K, and some of the products remained in the sample. The data is consistent with conversion of 2,5-

hexanedione to DMF and water at low temperatures, followed by oligomerization during the desorption process. That oligomerization would occur, even with the low initial coverage and desorption into high vacuum, implies that 2,5-hexanedione is very reactive at Brønsted sites. The TPD-TGA data on SnBEA and ZrBEA, Figs. 4b and c, were similar to each other but different from that on H-BEA. Some 2,5-hexanedione was observed in the TPD in peaks centered near 430 K; however, there was also reaction to DMF and water near 480 K. All of the adsorbates were removed after heating to high temperatures. What the data indicate is that the Lewis sites formed by framework Sn and Zr were able to catalyze the dehydration of 2,5-hexanedione to DMF and water at moderate temperatures but that the Lewis sites do not further oligomerize and further react the DMF.

Finally, TPD-TGA data for all four zeolites samples following a saturation exposure to p-xylene and 1-h evacuation are shown in Fig. 5. A small amount (220 µmol/g, Fig. 5a) of p-xylene remained in the SiBEA sample, but all of this desorbed by 470 K. The initial coverages on the three acidic zeolites, shown in Figs. 5b-d, were higher, between 600 and 800 µmol/g. The TPD on the acidic zeolites also seemed to show two peaks, suggesting that there may be an additional interaction between p-xylene and the Brønsted sites in H-BEA and the Lewis sites in SnBEA and ZrBEA. This interaction must be weak, however, since all of the p-xylene could be removed from each of the samples by 500 K.

Reaction Measurements

In order to better understand the relationship between adsorption and catalytic properties, the reaction between DMF and ethylene was examined on all four zeolites used in the adsorption studies. Initial reaction experiments were performed using a total pressure of 55 bar and an ethylene:DMF mole ratio of 50 in the feed stream. In a demonstration that reliable rates could be obtained in our system, we first examined the reaction over the SnBEA catalyst as a function of space time at 700 K, with the results shown in Table 2. The conversions were found to increase almost linearly with space time for conversions ranging from 7.5% to 35%, resulting in Turnover Frequencies (TOF) in the range of 11.7 to 12.5 h^{-1}. The selectivity to p-xylene decreased with conversion, from 94% at 7.5% conversion to 74% at 35% conversion. By contrast, the conversion of DMF was negligible on SiBEA for all conditions studied, including for temperatures as high as 723 K.

The reaction kinetics on SnBEA were investigated more carefully by varying the catalyst loading in the reactor, the total feed flow rate, the ethylene:DMF ratio in the feed, the total pressure, the temperature, and DMF concentration, all under conditions of differential conversions. Because the conversions were low, the selectivities to p-xylene, were typically above 90%. The raw data from experiments conducted at 650 K are shown in the Supplemental Information section, Table S1. What the data show is that the rates can be described by a single rate expression of the form given in Eqn (1).

$$\mathrm{r} = k\mathrm{c}(\mathrm{DMF}) \cdot \mathrm{c}(\mathrm{C_2H_4}) \qquad (1)$$

This is demonstrated by plotting the data from Table S1 in Fig. 6. The line in this plot, which extends from the origin, shows that there is an excellent fit to this rate expression for a wide range of compositions. Similar results were observed at other temperatures.

Reaction rates over SnBEA and ZrBEA were stable and did not change with time over days of testing; however, this was not observed with H-BEA. Initial rates on H-BEA were high and the selectivities were typically above 50%, but there was rapid deactivation under all conditions. The change of TOF over H-BEA at 625 K with time and the comparison with SnBEA and ZrBEA at 650 K is shown in Fig. 7, using an ethylene:DMF ratio of 50 and a total pressure of 55 bar. The first data point for H-BEA in this experiment was taken 1 h after the catalyst was exposed to the feed stream, and the initial rates may have been even higher than those shown here. After four hours, the catalyst had almost completely deactivated. Furthermore, the H-BEA catalysts were visually black when taken out of the reactor, while SnBEA and ZrBEA remained their original light-gray color after 4-h reaction. Because of the rapid deactivation, all of the rates for H-BEA reported in this paper were taken within one hour of introducing the feed and fresh catalyst was used for each rate measurement. On the other hand, activities of SnBEA or ZrBEA did not change over the same period of time at all.

It is interesting to compare our measured rates to those reported in previous studies. At the reaction conditions of Fig. 7, the rate expression reported by Patet, et al.[3] for the linear acid-site regime where the reaction is limited by dehydration reaction would give a TOF of 1.15 h^{-1} using an activation energy of 45 kJ/mol, compared to our initial rate of 1.5 h^{-1}. Because the extrapolation from low temperature would not take the deactivation of catalysts into consideration, these results suggest that the mechanism in batch reactor or flow reactor were similar.

Using data obtained 1 h after introducing the feed, rates on both H-BEA and ZrBEA were found to again fit the rate expression in Eqn 1. This is shown in Fig. 8, using raw data from Table S2, where we have again plotted the TOF versus the product of ethylene and DMF concentrations. For ZrBEA, data is plotted for measurements at 650 and 700 K. For H-BEA, the measurements were performed at 625 K in an attempt to minimize the deactivation rate. Again, fits of the data by lines that extend through the origin were excellent.

The rate constants determined for the three acidic zeolites were plotted as a function of inverse temperature in Figure 9, from data shown in Table S3. First, it is apparent that the rate constants decreased in the order of ZrBEA ~ SnBEA > H-BEA. Because the site densities varied in the opposite direction, the overall volumetric rates on the three zeolites were similar. The activation energy on H-BEA was 50 kJ/mol, which is close to 45 kJ/mol, the activation energy reported by Patet, et al[3] for the regime in which reaction is limited by dehydration of the Diels-Alder cycloadduct. However, because deactivation may be worse at high temperatures, it is possible that our apparent activation energy on H-BEA was affected by this. The activation energies on SnBEA and ZrBEA, ~68 kJ/mol, should be considered more reliable, but data does not exist for comparison. Based on the lower reactivity of Lewis sites for performing the dehydration reaction, it is reasonable that the activation energy would be higher.

4. Discussion

The comparison of adsorption and reaction properties on SnBEA, ZrBEA, and H-BEA reveal important information about the reaction of ethylene and DMF to form p-xylene. At first glance, it is surprising that materials with such dramatically different adsorption properties for the reactants would give similar reaction rates. However, this is consistent with the mechanism presented by Patet, et al.[3], where it was proposed that the reaction occurs in two steps, an uncatalyzed Diels-Alder reaction to form the oxanorbornene intermediate, followed by its acid-catalyzed dehydration to p-xylene. Since both Brønsted- and Lewis-acid sites are able to carry out dehydration reactions at the reaction temperatures[8], both are effective in catalyzing the reaction. Indeed, similarities found in the conversion of 2,5-hexanedione to DMF in the TPD results on all three acidic zeolites tends to confirm this.

It is important to notice that the Diels-Alder adduct was not observed on SiBEA, even though catalytic sites are not required for this part of the reaction. The fact that the oxanorbornene intermediate was not observed implies either that its formation is reversible upon cooling or that it is present in low concentrations within the zeolite cavities.

The rapid deactivation observed on H-BEA is almost certainly related to the strong adsorption and oligomerization observed following adsorption of DMF and 2,5-hexanedione. The fact that Lewis sites are not able to catalyze this oligomerization is critically important. Practical implementation of this technology will require stable catalysts and the Lewis-acidic materials appear to be better suited for this than Brønsted-acidic materials. The Lewis-acid zeolites have an additional advantage in that they are not expected to catalyze the isomerization of p-xylene to the ortho- and meta-isomers. High selectivities are achieved in H-BEA because strong adsorption of DMF and 2,5-hexanedione on the Brønsted sites limits access of the p-xylene to those sites, but SnBEA and ZrBEA should be intrinsically more selective.

There is still much to learn about the reaction of DMF with ethylene and the use of zeolites to catalyze it. We believe that the combination of adsorption and reaction studies advances those goals.

5. Conclusion:

SnBEA, ZrBEA, and H-BEA all catalyze the formation of p-xylene from DMF and ethylene effectively, even though their adsorption properties for the reactants are significantly different. The key property required of the Lewis- and Brønsted-acid sites for this reaction is the ability of the sites to catalyze the dehydration of the oxanorbornene intermediate. Because the Brønsted sites in H-BEA tend to oligomerize DMF and 2-5 hexanedione, H-BEA is found to be less stable than the Lewis-acid zeolites, SnBEA and ZrBEA.

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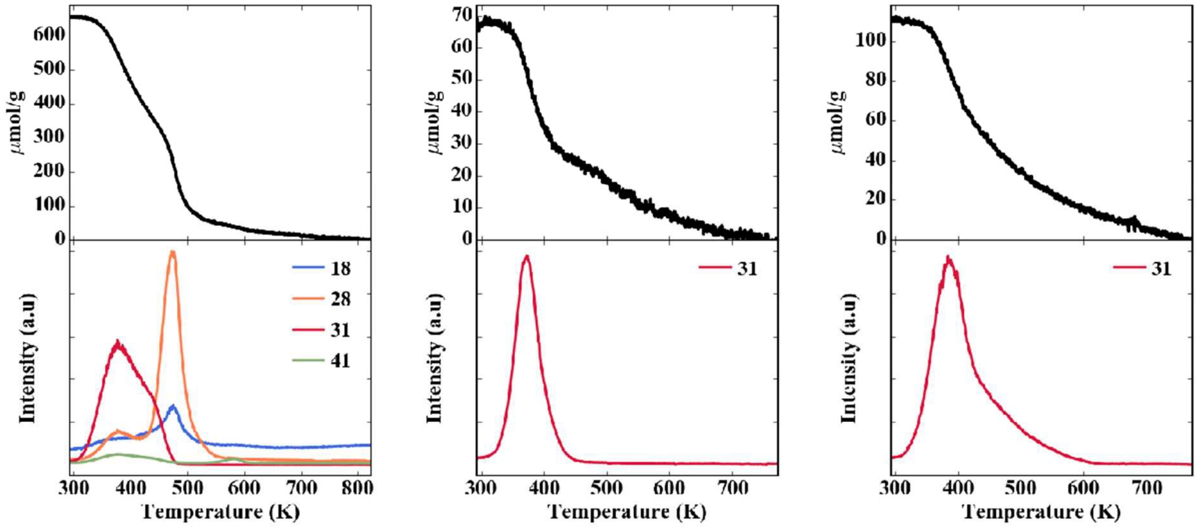
Table 1. Brønsted- and Lewis-acid site densities for the three acidic zeolite catalysts used in this study. The Pore volumes were determined by gravimetric uptakes of n-hexane on H-BEA and 1-hexene on SnBEA and ZrBEA at 0.01 bar and room temperature.

Catalyst	H-BEA	SnBEA	ZrBEA
Site density	500 μmol/g	140 μmol/g	100 μmol/g
Pore Volume	0.22 cm^3/g	0.20cm^3/g	0.21cm^3/g

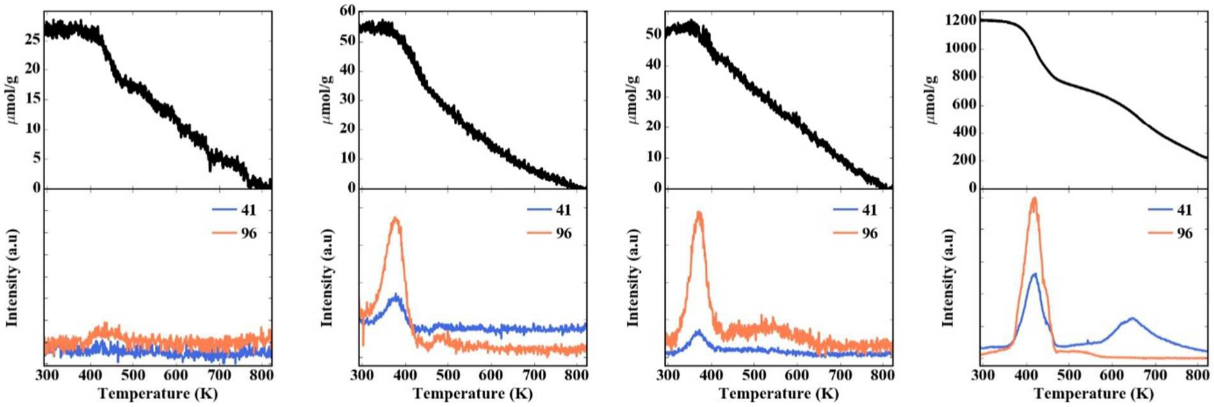
Table 2 Rates for 2-wt% 2,5-dimethylfuran in heptane with ethylene as a function of space time at 700 K.

Catalyst loading (g)	**Total mol flow rate ($*10^{-3}$mol/min)**	**Space time W/F ($*10^{-3}$ g.min/g)**	**Temperature (K)**	**Conversion**	**Selectivity**	**Turn Over Frequency (h^{-1})**
0.1	3.4	1.7	700	7.5%	94%	12.5
0.1	1.7	3.4	700	16%	85%	12.2
0.1	0.9	6.8	700	35%	74%	11.7



(a) (b) (c)

Figure 1 TPD-TGA of diethylether on (a) H-BEA, (b) SnBEA, and (c) ZrBEA. The peaks correspond to diethylether (m/e=28, 31), ethene (m/e=28), water (m/e=18), and oligomers (m/e=41).



(a) (b) (c) (d)

Figure 2. TPD-TGA of 2,5-dimethylfuran on (a) SiBEA, (b) SnBEA, (c) ZrBEA, and (d) H-BEA. Peaks correspond to 2,5-dimethylfuran (m/e=41, 96) and oligomers (m/e=41).

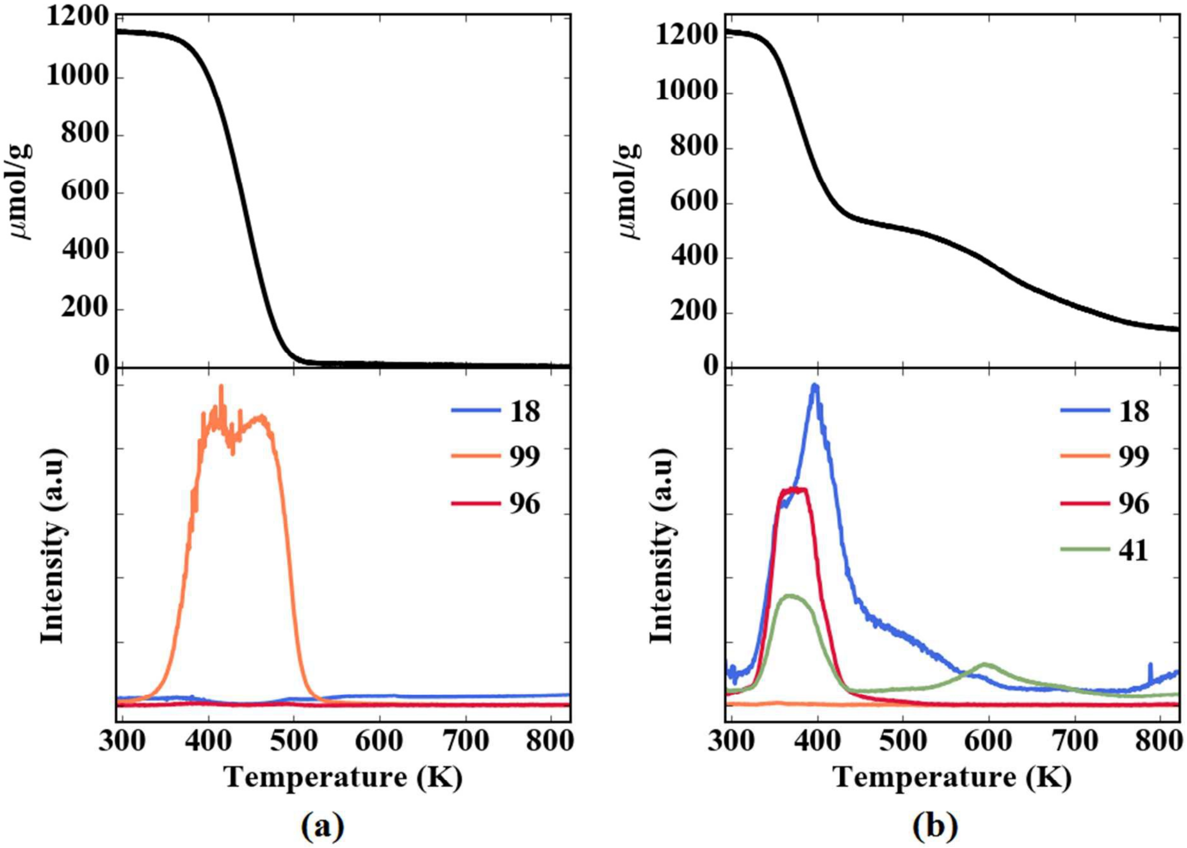
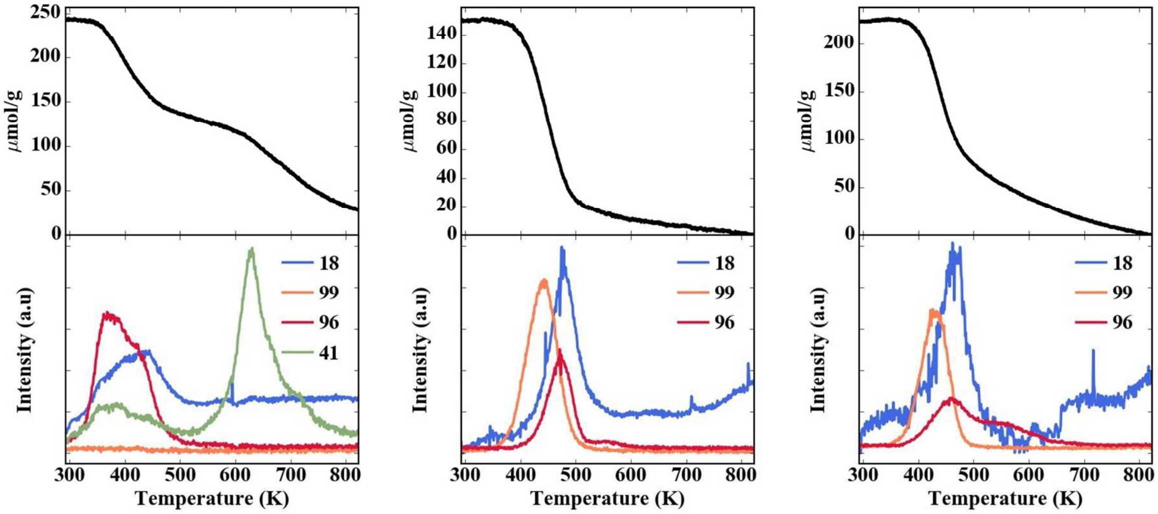


Figure 3 TPD-TGA of 2,5-hexanedione at high coverage on (a) SiBEA and (b) H-BEA. Peaks correspond to 2,5-hexanedione (m/e=99), 2,5-dimethylfuran (m/z=96), water (m/e=18) and oligomers (m/e=41).



(a) (b) (c)

Figure 4 TPD-TGA of 2,5-hexanedione at low coverage on (a) H-BEA, (b) SnBEA, and (c) ZrBEA. Peaks correspond to 2,5-hexanedione (m/e=99), 2,5-dimethylfuran (m/e=96), water (m/e=18), and oligomers (m/e=41).

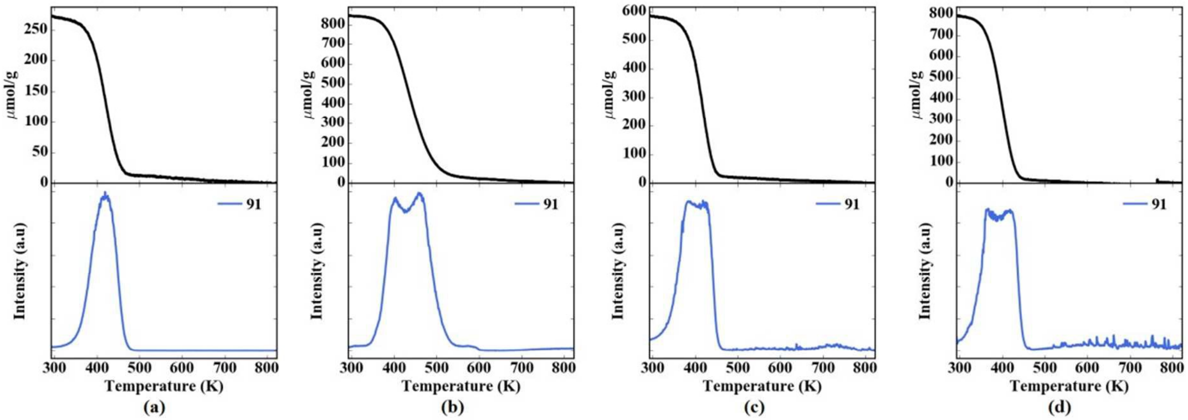


Figure 5 TPD-TGA of p-xylene on (a) SiBEA, (b) H-BEA, (c) SnBEA, and (d) ZrBEA.

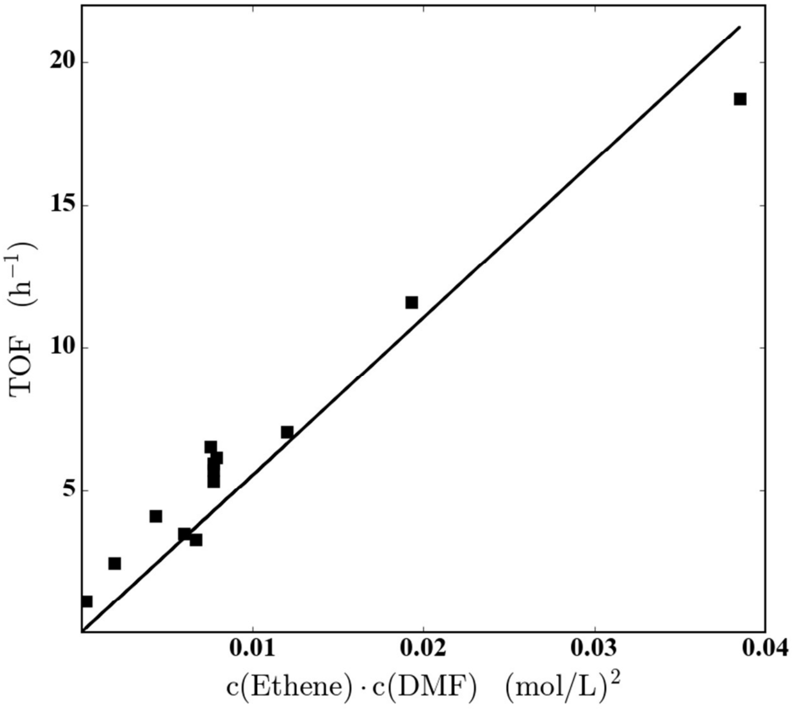


Figure 6 Turn over frequency versus the product of c(C_2H_4) and c(DMF) on Sn-BEA at 650 K

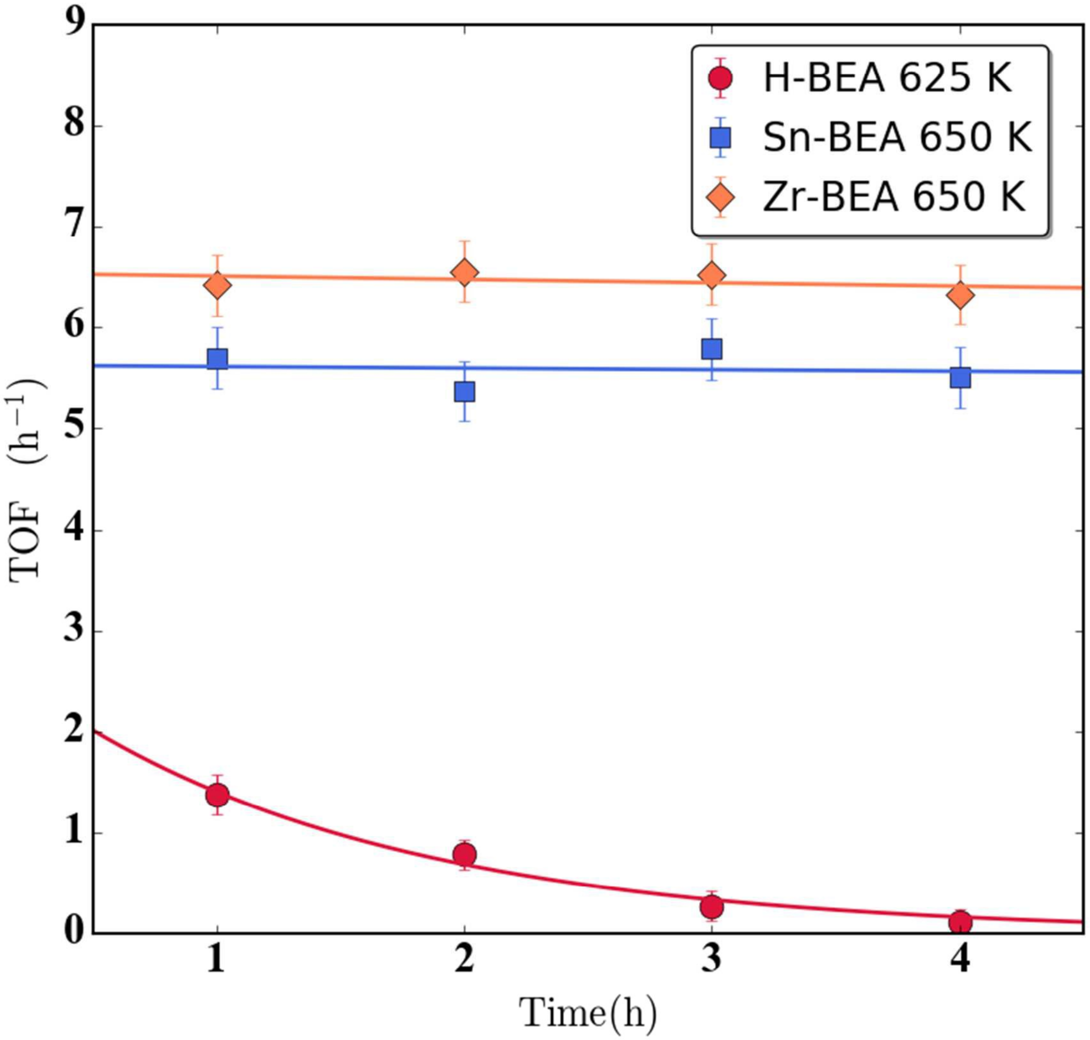


Figure 7 Turn over frequency vs time on 0.1 g H-BEA at 625 K, on 0.1g ZrBEA at 650 K, and on SnBEA at 650 K. The total pressure was 55 bar.

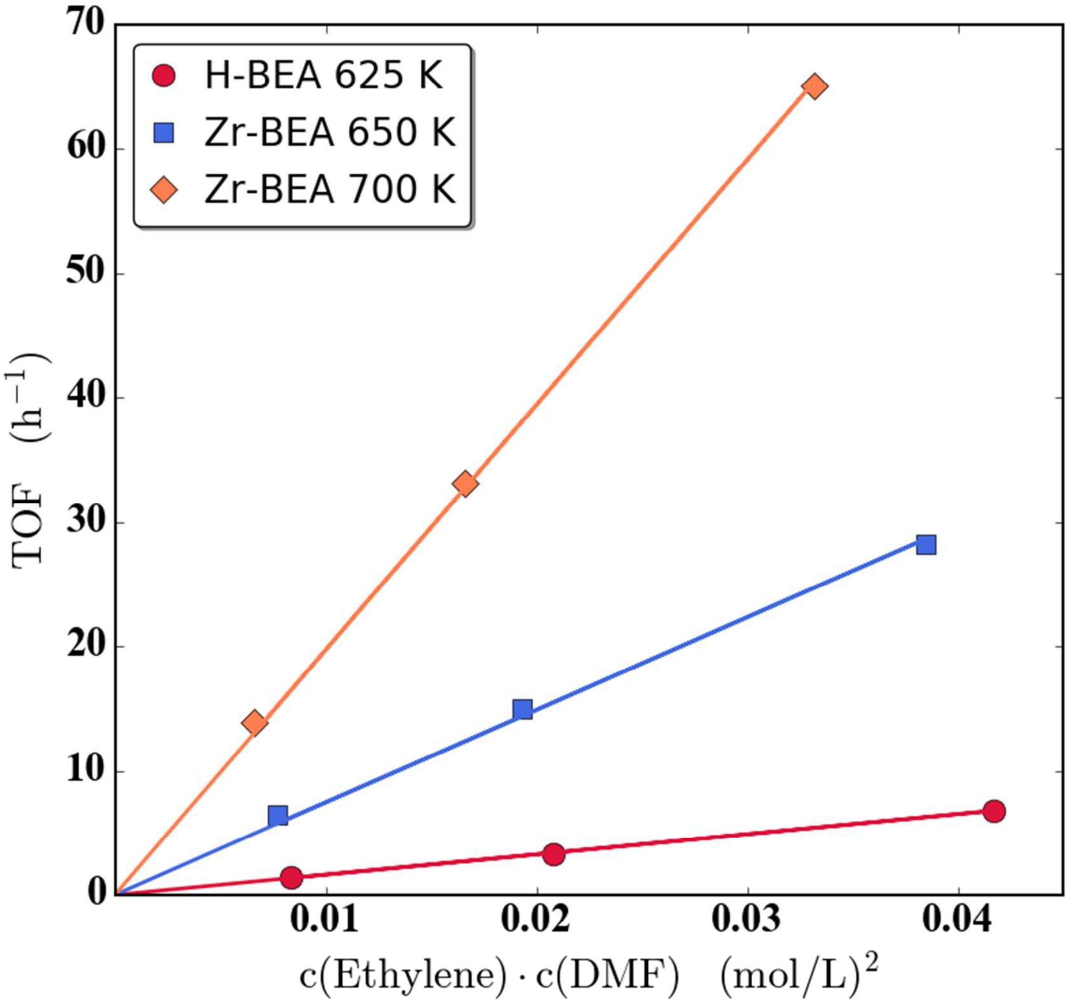


Figure 8 Turn over frequency vs the product of c(C_2H_4) and c(DMF), for 0.1 g H-BEA and ZrBEA at 55 bar

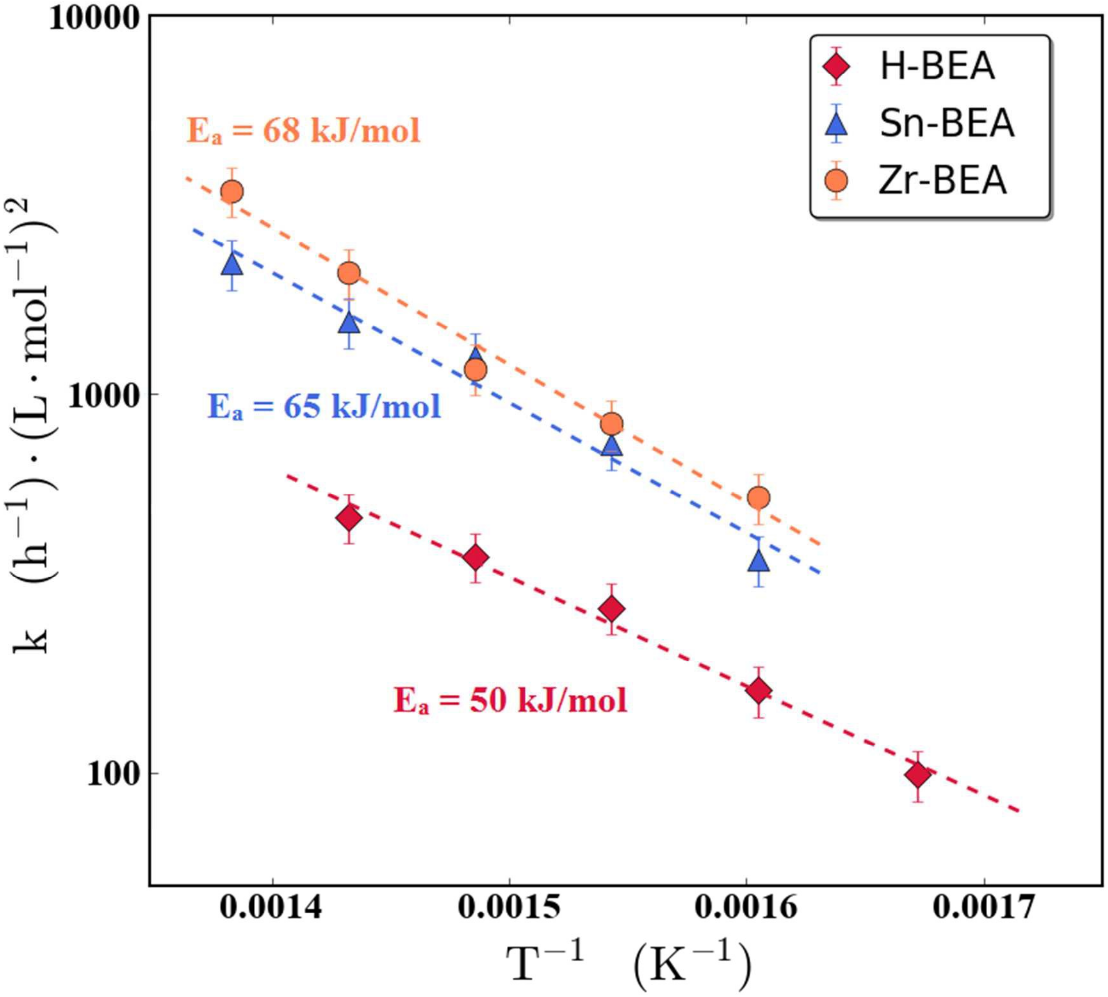
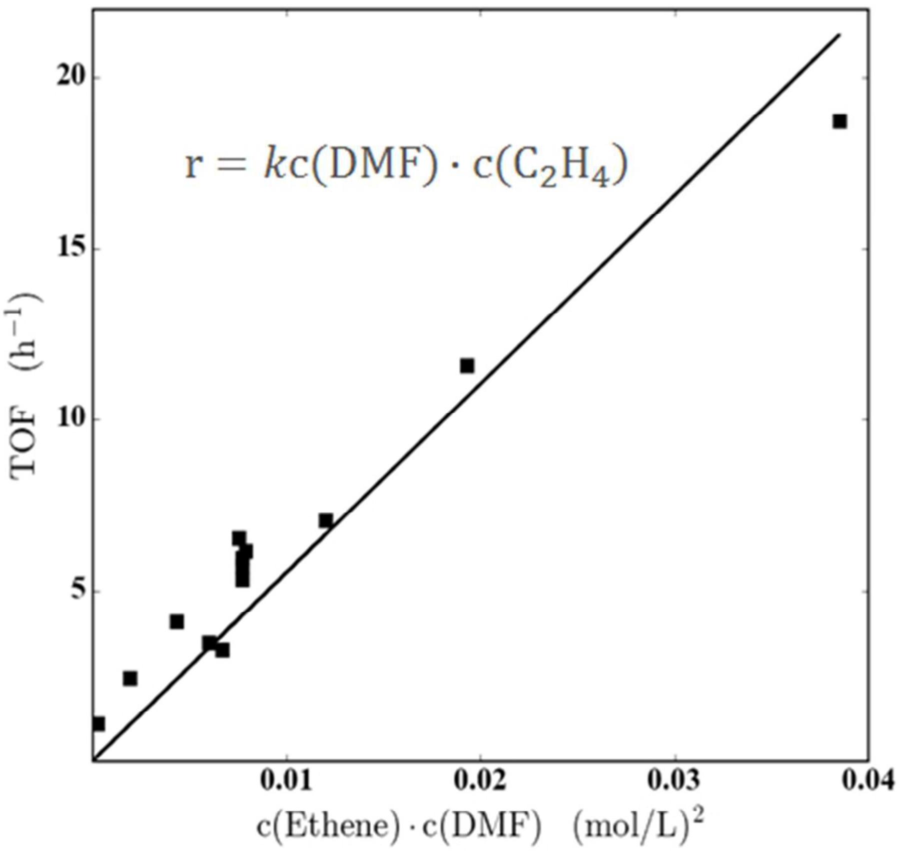


Figure 9 Reaction rate coefficient (k) versus inverse temperature (1/T) for H-BEA, Sn-BEA and ZrBEA


$r = kc(\mathrm{DMF}) \cdot c(\mathrm{C_2H_4})$
TOF (h^{-1})
20
15
10
5
0.01
0.02
0.03
0.04
$c(\mathrm{Ethene}) \cdot c(\mathrm{DMF})$ $(\mathrm{mol/L})^2$