1 Tandem Lewis acid/Brønsted acid-catalyzed
2 conversion of carbohydrates to 5-
3 hydroxymethylfurfural using zeolite beta

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13 **ABSTRACT**

14 We conduct a combined experimental and computational study to reveal the kinetics of tandem
15 glucose isomerization and fructose dehydration to 5-hydroxymethylfurfural (HMF) over a

bifunctional zeolite H-BEA-25 in water. The model accounts for multicomponent adsorption, homogeneous Brønsted acid catalyzed chemistry of fructose, and intrinsic heterogeneous Lewis acid catalyzed isomerization and Brønsted acid catalyzed fructose dehydration, HMF rehydration, and humin formation chemistry. The octahedrally coordinated extra-framework Al sites catalyze glucose to fructose isomerization effectively. The activation energy for the isomerization in H-BEA-25 is between those reported for Ti-BEA and Sn-BEA. We reveal that tandem reactions exhibit multiple kinetic regimes. When a bifunctional catalyst with a fixed total number of acid sites is used (e.g., aluminosilicate zeolites), the HMF formation rate exhibits a volcano type curve vs. the Lewis to Brønsted acid site ratio. On the other hand, when the two types of sites are varied independently (e.g., in Sn-BEA and HCl), the HMF formation rate increases and then approaches a plateau with increasing Brønsted acid site density. These appear to be generic features of tandem reactions catalyzed by multiple or multifunctional catalysts. We show that materials with stronger sugar adsorption would produce HMF in significantly higher yields and higher rate than H-BEA. When HMF degradation reactions are suppressed, a ratio of Lewis to Brønsted acid sites of ~ 0.3 maximizes the HMF rate produced from glucose and the HMF yield (which is predicted to be $\sim 60\%$ at $130\text{ }^{\circ}\text{C}$). These predictions provide a framework for understanding and improving tandem reactions catalyzed by heterogeneous catalysts.

33

34 1. INTRODUCTION

35 Furans, such as furfural and 5-(hydroxymethyl)furfural (HMF), derived from lignocellulosic
36 carbohydrates, are excellent platform-chemicals for the production of fuel additives,[1] alkylated
37 aromatics,[2] and organic solvents.[3] While furfural has been produced industrially from
38 pentose sugars since 1921,[4] HMF production has not yet been commercialized at large scale[5]
39 in part due to side reactions that render economics less attractive.[6]

40 HMF is typically produced by dehydrating fructose using a homogeneous Brønsted acid
41 catalyst.[7] Identifying suitable heterogeneous catalysts has attracted attention due to simplified
42 downstream separations. Many solid catalysts have been considered, including acidic carbons,[8]
43 silicoaluminophosphates,[9] sulfonated carbonaceous TiO₂,[10] and zeolites.[11, 12] However,
44 understanding of the underlying chemistry is poor because heterogeneous catalytic systems are
45 more complicated than their homogeneous counterparts. Kruger et al. studied fructose
46 dehydration in H-BEA-18 and identified several factors contributing to the dehydration
47 chemistry that are absent from homogeneous catalysts, including the adsorption strength and the
48 type of acid site, i.e., Brønsted or Lewis.[13]

49 While selectively converting fructose to HMF is an important scientific problem, glucose is far
50 more naturally abundant than fructose, making it a more desirable substrate. However, the direct
51 dehydration of glucose to HMF is slow and gives low yields (see Yang et al.[14] for recent work
52 and literature therein). Following the pioneering work of Davis and co-workers, it is now well
53 established that Lewis acid zeolites, such as Sn-beta,[15] catalyze the isomerization of glucose to
54 fructose. Additionally, Sn-beta can be combined with Brønsted acid catalysts for single pot
55 conversion of glucose to HMF via the formation of fructose as an intermediate.[16] Similarly,

Mazzota et al. found that a sulfonated carbon catalyst combined with Lewis-acidic TiO_2 can improve HMF yield from glucose.[10]

Tandem reactions in a single pot reactor have opened up new opportunities for the conversion of sugars, as recently reviewed in Caratzoulas et al.[17] Even though bifunctional solid catalysts, which contain both Lewis and Brønsted acid sites in a single material, can enable the direct conversion of glucose to HMF, the development and identification of optimal properties of such materials has not received much attention. Gallo et al. found recently that the H-BEA isomerizes xylose to xylulose and dehydrates xylulose to furfural, **an indication of a bifunctional material**.[18] Otomo et al. demonstrated that calcining H-BEA over 700 °C or in steam over 500 °C can increase the number of Lewis sites and ultimately lead to improved HMF yields from glucose.[19] **Kruger et al. studied fructose dehydration on H-BEA and found that when the zeolite was washed with HCl to remove the octahedrally coordinated Al atoms, no glucose formation was observed. They concluded that the extra framework Al was an active Lewis acid site for isomerization.**[13] **Aside from the lack of understanding of how bifunctional materials operate,** comparison of bifunctional catalysts to a physical mixture of Lewis and Brønsted solid acid catalysts or Lewis solid acid and homogeneous Brønsted acid catalysts is lacking.

Tandem reactions requiring different catalyst types have been of growing interest in biomass processing but their kinetics is generally poorly understood. In the first of its kind study, the kinetics of para-xylene formation via tandem Lewis-acid catalyzed cyclo-addition of dimethyl furan and ethylene followed by the Brønsted acid catalyzed dehydration of the resulting cycloadduct was recently explored.[20] We showed that the former reaction is catalyzed homogeneously and the latter heterogeneously. When the density of Brønsted acid sites was varied (at fixed solution volume and thus at fixed Lewis acid ‘site density’), two kinetic regimes

were discovered: a linear regime, where the rate of para-xylene formation increases almost linearly with increasing Brønsted acid site concentration, followed by a plateau at high Brønsted acid site concentrations. The linear regime was unexpected given that the Lewis acid chemistry has a higher reaction barrier and is expected to be rate-controlling. Sensitivity analysis showed that the lack of sufficient Brønsted acid sites limits the rate of the overall tandem reactions and underscores that the rates of tandem reactions catalyzed by different catalysts or multifunctional catalysts is controlled by intrinsic rate constants, concentrations of participating species, and active site concentrations. We hypothesized that this may be a generic kinetic behavior of tandem reactions, though this has not yet been addressed. In addition, since most of reactants and products in this chemistry have negligible vapor pressure at reaction temperatures and stability issues at higher temperatures, the use of solvent is necessary. The significant effect of solvents on isomerization and dehydration chemistry has been well documented.[21, 22] In water, which is the solvent used in this work, a small fraction of the zeolite dissolves into aluminosilicate species that catalyzed fructose dehydration to HMF homogeneously. Details of this homogeneous chemistry are described in our previous work.[23]

The selective production of HMF from glucose requires detailed understanding of the reaction kinetics of isomerization and dehydration reactions within the zeolite to identify optimal materials properties. The aim of the present work is to fill in this scientific gap. First, we present experimental adsorption and kinetic data in H-BEA-25. Next we build a model that (1) distinguishes homogeneous from heterogeneous (inside the zeolite) Brønsted acid catalyzed dehydration chemistry and includes Lewis acid catalyzed glucose isomerization and (2) accounts for the adsorption of multiple compounds inside the zeolite. To the best of our knowledge, this is the first kinetic model that explicitly considers the bifunctionality of Brønsted and Lewis acid

sites in a zeolite for the conversion of glucose to HMF. We predict and contrast for the first time the kinetic regimes of both bifunctional Lewis/Brønsted solid acid catalysts, which is the main focus of this work, and physical mixtures of Lewis and Brønsted solid acid catalysts for tandem reactions and provide insights into the properties of catalysts that maximize the yield and the production rate of HMF. Comparison to hybrid heterogeneous Lewis acid/homogeneous Brønsted acid catalysts is also performed. Finally, we predict the optimal yield of HMF from glucose as an upper performance-bound and identify the factors controlling this yield.

2. EXPERIMENTAL METHODS

2.1 Materials

Fructose 99% (Sigma Aldrich), HMF 98% (Sigma Aldrich), levulinic acid (LA) 98% (Sigma Aldrich liquid form), formic acid (FA) 88% (Fisher Scientific), hydrochloric acid 1 M (Sigma Aldrich), potassium chloride 98% (Merck) and distilled water were used for solution preparation. Commercial BEA zeolite from Zeolyst with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 25 in ammonium form (NH_4 -BEA-25) was calcined to generate the protonated form of the zeolite (H-BEA-25). The calcination program entailed heating the sample at 2 °C/min to 90 °C, holding for 1 h, heating at 2 °C/min to 450 °C, holding for 8 h, and cooling to room temperature.

Typical calcination introduces both Lewis and Brønsted acid sites.[24] For select experiments, the Lewis acidic octahedral aluminum sites were removed from H-BEA-25 using the method described by Hey et al.[25] 1 g of H-BEA-25 was added to a 20 ml glass vial containing 10 g of DI water, stirred at medium speed on a stir plate. The pH of the mixture was monitored using a glass electrode pH meter as 500 μL aliquots of 1.0 N HCl were added in 15 min intervals. Once the pH of the mixture reached between 0.97 and 1.03 and remained stable for at least 15 min, the

vial was sealed and stirred for 16 hours. The solid was then filtered and rinsed with 60 mL of DI water four times to remove the free acid from the zeolite.

The zeolite micropore volume was estimated from the N₂ adsorption isotherms using t-plot method and was found equal to 0.172 mL/g. The N₂ physisorption experiment was carried out with a Micromeritics ASAP 2020 instrument at 77 K.

2.2 Reaction kinetics

All reactions were performed in 20-mL glass vials. Each vial contained 2 mL of 10 wt% fructose or glucose in DI water or 2 wt% HMF in DI water and 0.25 g of H-BEA-25. Vials were weighed before and after the reaction to ensure that they did not leak during reaction. The vials were placed in a hot oil bath set to temperature, and a timer started immediately. The vials generally reached reaction temperature in less than 2 min after being placed in the oil bath. After reaction, vials were removed from the oil bath and quenched with cold water. Reaction times were chosen to achieve at least 10% conversion by the end of the reaction. Reaction solutions were analyzed using a Waters 2695 HPLC system with 2414 Refractive Index and 2998 Photodiode Array (UV) Detectors after filtering through a 0.22 µm syringe filter and diluting to a ratio of 0.3 g filtered solution to 0.7 g DI water. Analytes were separated on a BioRad Aminex HPX-87H column at 65 °C with 0.005 M H₂SO₄ mobile phase at 0.65 mL/min. Different temperatures between 110-140 °C were investigated for each composition for a total of 11 different experimental conditions. The concentration profiles as a function of time for all experiments are shown in the Supporting Information (see figures S3-S6). Errors were estimated based on experiments performed for the HCl-washed H-BEA-25. The standard deviation for replicated experiments was 5-10% at most, and typically far lower for most of the data.

2.3 Adsorption isotherms

The procedure for measuring solute adsorption isotherms from aqueous solutions was the same as that described by Leon et al.[26] Ten different concentrations of fructose, HMF, LA, and FA were prepared in single solute aqueous solutions. The adsorption experiments were done in batch mode. 0.2 g of H-BEA-25 zeolite was suspended in 1 mL of solution in a thermostatic water bath at the desired temperature for 5 hours to ensure that equilibrium was reached. The solution was then filtered with a 0.2 μm nylon membrane filter to obtain a clear liquid. The filtrate was analyzed using HPLC similarly to the reaction kinetics experiments. Each adsorption experiment was performed in triplicate.

2.4 Brønsted site density measurements

The Brønsted acid site density of H-BEA-25 zeolite was determined using the procedure of Kresnawahjuesa et al.[27] In summary, the total amount of propene formed from isopropylamine decomposition in the zeolite was determined. Isopropylamine decomposition is a Hoffman-elimination catalyzed by the Brønsted acid sites of the zeolite. Previous studies determined that a well-defined adsorption complex of one molecule of isopropylamine per Brønsted acid site precedes isopropylamine decomposition.[28] The amount of propene formed after complete isopropylamine decomposition is therefore equal to the number of Brønsted sites. A tubular flow reactor setup in conjunction with on-line gas chromatography (GC) analysis (Hewlett Packard 589 Series II equipped with dual FID/TCD detector) was used for these measurements. 2 mg of the zeolite was cleaned in the reactor furnace with helium flow at 500 °C for 30 min, then cooled down to 100 °C where the temperature was held constant for 30 min. During the 30 minute hold at 100 °C, a helium stream saturated with isopropylamine was fed through the reactor in order to saturate the Brønsted acid sites. The feed was switched to pure helium and the reactor

temperature was then increased to 200 °C and held for 90 min to remove isopropylamine that had not formed a complex with an adsorption site. Finally, the temperature was ramped up to 500 °C to desorb the decomposition products. During the desorption process, all gas products were trapped into liquid nitrogen cooled sampling loop. The amount of propene in the sample was then determined from the analysis of the gas chromatograph. The Brønsted acid site density, measured based on the amount of propene eluted, was 0.61 mmol/g.

2.5. Measurements of the ratio of Brønsted to Lewis acid site density

To estimate the ratio of Brønsted to Lewis acid site density we analyzed solid state ^{27}Al NMR spectroscopy and in situ FTIR pyridine adsorption data. Solid state ^{27}Al NMR spectra of the uncalcined NH_4 -BEA-25 zeolite and the protonated H-BEA-25 zeolite were measured using a Bruker AVIII 500 MHz spectrometer in single-pulse mode with a 4 mm HX MAS probe, 10 kHz spinning rate, 4096 scans, 1 second recycle delay time, and 1.5 μs pulse width. The spectrum of NH_4 -BEA-25 showed only one dominant peak at $\delta = 60$ ppm, which can be assigned to tetrahedral Al (Figure S1).[29] On the other hand, the spectrum of H-BEA-25 contains an additional peak at $\delta = 0$ ppm, indicative of Al atoms with octahedral coordination, which are formed during calcination.[24] It has been shown the tetrahedral Al acts as Brønsted acid site while the octahedral Al is likely the Lewis acid site responsible for glucose isomerization.[13] Therefore, we assume that the ratio of the integral peak area of octahedral Al to tetrahedral Al is equal to the relative amount of Lewis to Brønsted acid sites in the H-BEA-25 zeolite catalyst (Table S1, entry 1).

In situ FTIR spectrum of the pyridine adsorption measurement on H-BEA-25 zeolite was obtained using the same experimental setup as Murphy et al.[30] The zeolite wafer was degassed

at 450 °C under vacuum for two hours. After the sample cooled down to 200 °C, about 100 Torr of pyridine was introduced to the system and the IR spectrum was recorded as shown in Figure S2. The absorption bands at wavenumbers of 1543 cm^{-1} , which is the characteristic band of pyridinium cations, formed by pyridine interacting with Brønsted acid site.[31] There are also two other bands in the spectrum at wavenumbers of 1453 cm^{-1} and 1490 cm^{-1} , which according to literature can be assigned to pyridine interacting with the Lewis acid sites, and with combination of Lewis and Brønsted acid sites respectively.[32] We applied the extinction coefficients estimated from Take et al.[33] to the integrated absorbance of 1543 cm^{-1} and 1453 cm^{-1} peaks in order to determine the ratio of Brønsted to Lewis acid density in the zeolite sample (Table S1, entry 2).

The determination of different acid sites is the subject of debate. Specifically, in pyridine adsorption experiment, the characteristic absorption band of Lewis acid site at wavenumber of 1453 cm^{-1} could arise from silanol groups, impurity alkali cations, or “true” Lewis acid sites as discussed in van Santen’s book.[34] Therefore, the measured Lewis acid density from pyridine adsorption can be different from the number of octahedral coordinated Al, which we assigned to be the active site for glucose isomerization. In addition, the Lewis to Brønsted acid ratio is determined through extinction coefficients for each of the adsorbed sites and can slightly change with different experimental instrument setups. Due to the controversy of the accuracy of using pyridine adsorption experiments to measure the ratio of Lewis to Brønsted acid site, we employ the results from the aforementioned ^{27}Al NMR measurements to determine the L:B ratio in the H-BEA-25 zeolite and found to be 0.3.

3. COMPUTATIONAL METHODS

3.1 Adsorption

The numerical procedure for determining the parameters of the single-solute isotherms was outlined for H-BEA-18 elsewhere[26, 35] and here for H-BEA-25. Based on our previous findings, the adsorption isotherms of glucose and fructose in H-BEA are very similar.[26] Data and model performance are included in the SI (Figure S3). The temperature dependent isotherm parameters, K and b , were fit to the van't Hoff equation as shown in eqs 1 and 2. These relationships sufficiently describe the change in equilibrium adsorption loading with temperature (see Figure S4).

$$K = K_{298K} \cdot \exp \left[\frac{\delta H_K}{R} \left(\frac{1}{298K} - \frac{1}{T} \right) \right] \quad (1)$$

$$b = b_{298K} \cdot \exp \left[\frac{\delta H_b}{R} \left(\frac{1}{298K} - \frac{1}{T} \right) \right] \quad (2)$$

In eqs 1 and 2, K_{298K} is the Henry constant at room temperature, δH_K is the heat of adsorption, R is the universal gas constant, T is the temperature, b_{298K} is the second isotherm parameter with a corresponding δH_b enthalpy change. The reactions produce a multicomponent mixture that contains fructose, glucose, HMF, FA and LA. To minimize the experimental effort on massive data collection of multicomponent systems, we proposed to model multicomponent adsorption using the ideal adsorbed solution theory (IAST), originally developed for adsorption of multicomponent gases[36] and then extended to liquid mixtures,[37] using single-component experimental data.[26] The mathematical models have been outlined elsewhere.[37, 38] Analytical expressions for determining the spreading pressure by integrating the isotherm equations were used whenever possible. Otherwise, numerical integration was performed.

3.2 Continuity equations

We assumed that the rate for reaching adsorption equilibrium is much faster than that of the reactions. As a result, the system can be modeled using a system of differential-algebraic eqs 3 and 4. The species continuity in eq 3 includes reaction in both aqueous and adsorbed phases, while the adsorption isotherm relates the concentrations in both phases. Although including the activity coefficients in rate expressions would be more rigorous, we use concentrations because reagents are fairly dilute (at most 0.55 M of solute at 10 wt% glucose) and computing activities within zeolite pores is a generally an unsolved problem. This approach has been adopted in other studies of this system.[34, 39] The aqueous volume greatly exceeds the pore volume of the zeolite, so the aqueous volume is not expected to change with time.

$$\frac{dC_i}{dt} + \frac{m_{ads}}{V_{aq}} \frac{dq_i}{dt} = \frac{m_{ads}}{V_{aq}} r_i^{BEA} + r_i^{aq} \quad (3)$$

Here C_i is the moles of component i per liter of aqueous phase, t is time, m_{ads} is the mass of zeolite in the reactor, V_{aq} is the volume of the aqueous phase, q_i is the moles of component i in the zeolite per gram of zeolite, r_i^{BEA} is the rate of consumption of component i in the zeolite (heterogeneous contribution), and r_i^{aq} is the rate of consumption of component i in the aqueous phase (homogeneous contribution). The adsorption loading is given by eq 4:

$$q_i = f(C_{glu}, C_{fructose}, C_{HMF}, C_{LA}, C_{FA}) \quad (4)$$

The function f in eq 4 is evaluated using Newton's method to solve the IAST equations.

Kruger et al. have previously investigated the effect of interactions of water with the zeolite crystals and have shown that the catalytic performance of H-BEA-18 in aqueous solution does not change significantly after three uses.[13, 40] Therefore, in this work we assume constant

catalytic activity, while acknowledging that some loss of catalytic activity may occur at long times.

3.2.1 Homogeneous reaction network

The pH of the aqueous phase of the zeolite suspension is lower than that of water due to the dissociation of the zeolite surface silanol groups. This homogeneous acidity may catalyze chemistry, which is accounted for using the rate laws and parameters outlined by Swift et al.[41, 42] These reactions include: fructose dehydration to HMF, fructose degradation to humins, HMF rehydration to FA/LA, HMF degradation to humins, and a second fructose degradation reaction that produces both humins and FA. The rates of these reactions are described by eqs 5-8.

$$r_{fru}^{aq} = - \left(\frac{k_1^{aq} \phi_f}{C_{H_2O}} + k_2^{aq} + k_5^{aq} \right) C_{fru} C_{H^+} \quad (5)$$

$$r_{HMF}^{aq} = k_1^{aq} \phi_f \left(\frac{C_{fru} C_{H^+}}{C_{H_2O}} \right) - (k_3^{aq} + k_4^{aq}) C_{HMF} C_{H^+} \quad (6)$$

$$r_{LA}^{aq} = k_3^{aq} C_{HMF} C_{H^+} \quad (7)$$

$$r_{FA}^{aq} = k_5^{aq} C_{fru} C_{H^+} + k_4^{aq} C_{HMF} C_{H^+} \quad (8)$$

Here k_j^{aq} is the rate constant of reaction j in the aqueous phase and ϕ_f is the fraction of fructose in the furanose form. The proton concentration in solution was fixed (pH = 3.46) based on the measured pH using mass titration at room temperature using the method of Noh and Schwartz[43] (see Table S1).

3.2.2 Heterogeneous reaction network

Scheme 1. Reaction network inside H-BEA-25. Solid (dashed) lines indicate Brønsted (Lewis)-acid catalyzed reactions.

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274 The reaction network considered inside H-BEA is given in Scheme 1. This network was
 275 postulated given the observed reaction products (glucose or fructose depending on substrate,
 276 HMF, FA, and LA). The formation of glucose from fructose and the converse arises from
 277 octahedrally coordinated Al acting as a Lewis acid site. Indeed, when these Lewis sites are
 278 removed from the catalyst, no glucose is observed (see also below).[13] Minor products,
 279 including glyceraldehyde, lactic acid, mannose, and furfural were observed in less than 1% of the
 280 overall carbon balance and were not explicitly considered in the reaction network. The rate
 281 equations for reactions within the zeolite are given in eqs 9-13:

$$282 \quad r_{fru}^{BEA} = \frac{n_{Al}}{(1 + \phi_{Al_8:Al_4})} \cdot \left[- \left(\frac{k_1}{q_{H_2O}} + k_4 + \phi_{Al_8:Al_4} \cdot \frac{k_5}{K_{FG}} \right) \cdot q_{fru} + \phi_{Al_8:Al_4} \cdot k_5 \cdot q_{Glu} \right] \quad (9)$$

$$283 \quad r_{HMF}^{BEA} = \frac{n_{Al}}{1 + \phi_{Al_8:Al_4}} \cdot \frac{k_1}{q_{H_2O}} \cdot q_{fru} - \frac{n_{Al}}{1 + \phi_{Al_8:Al_4}} \cdot (k_2 + k_3) \cdot q_{HMF} \quad (10)$$

$$r_{LA}^{BEA} = \frac{n_{Al}}{1 + \phi_{Al_8:Al_4}} \cdot k_2 \cdot q_{HMF} \quad (11)$$

$$r_{FA}^{BEA} = \frac{n_{Al}}{1 + \phi_{Al_8:Al_4}} \cdot k_4 \cdot q_{fru} + \frac{n_{Al}}{1 + \phi_{Al_8:Al_4}} \cdot k_2 \cdot q_{HMF} \quad (12)$$

$$r_{Glu}^{BEA} = n_{Al} \cdot \frac{\phi_{Al_8:Al_4}}{1 + \phi_{Al_8:Al_4}} \cdot \frac{k_5}{K_{FG}} \cdot q_{Fru} - n_{Al} \cdot \frac{\phi_{Al_8:Al_4}}{1 + \phi_{Al_8:Al_4}} \cdot k_5 \cdot q_{Glu} \quad (13)$$

Here n_{Al} is the moles of **active** aluminum sites per gram of catalyst (mol/g) , $\phi_{Al_8:Al_4}$ is the ratio of Lewis acid sites to Brønsted acid sites (**L:B**), i.e., the ratio of octahedral to tetrahedral Al, k_j is the intrinsic rate constant of reaction j in the zeolite (either g/mol/min or 1/min), q_j is the real adsorption loading (mol/g), and K_{FG} is the equilibrium constant for glucose isomerization to fructose, calculated using the parameters in Rajabbeigi et al.[44] **The estimated adsorption corresponds to the total uptake in the zeolite pores and not specifically to chemisorption to the active sites. Hydrophobic zeolites, which lack active sites, still adsorb HMF in significant quantities primarily through van der Waals interactions within the pore and entropic contributions due to the re-arrangements of the solvation cell. Since we cannot distinguish adsorption on individual sites, we adopt within the pore what is known in the reaction engineering literature as, the pseudo-homogeneous modeling approach.[45]**

The complexity of this system necessitated simplifications regarding the reaction network (Scheme 1), the pH variation during the course of reaction, and transport limitations. These have been assessed using sensitivity analysis, and it was found that the trends and model parameters presented below are robust to various model alterations (Figure S5, Figure S6 and Figure S7).

3.2.3 Experimental data treatment

The vials used in reaction kinetic measurements were brought from reaction temperature to room temperature before concentrations were measured. As these vials cool, we expect the zeolite and solution to re-equilibrate as the adsorption isotherms are temperature-sensitive. We accounted for this lack of concentration measurements at reaction temperature by translating the aqueous concentration, measured at room temperature, to expected aqueous concentrations at the reaction temperature using mass conservation and the isotherms, as shown in eq

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$$C_i(T = 25^\circ C) + \frac{m_{ads}}{V_{aq}} q_i(T = 25^\circ C) = C_i(T = T_{rxn}) + \frac{m_{ads}}{V_{aq}} q_i(T = T_{rxn}) \quad (14)$$

3.2.4 Parameter estimation procedure

Eqs 3 and 4 were solved using the Matlab *ode15s* differential-algebraic equation (DAE) solver. The experimental initial concentrations were used. The rate constants were fit using two adjustable parameters per rate constant, corresponding to the log of the rate constant at a reference temperature and the dimensionless activation energy. The parameterization is the same as for HCl-catalyzed fructose dehydration.[42] Finally, the sum of the squares of the differences between measured and predicted concentrations form the objective function that was minimized by using **lsqnonlin** in Matlab R2013b, which uses a trust region reflective algorithm.

4. RESULTS AND DISCUSSION

4.1 Single-component isotherms

The estimated parameters for single-component adsorption isotherms are shown in Table 1. Experimental data and model predictions are included in the SI (Figure S3). Interpretation of adsorption from solution is much more complicated than understanding adsorption from gas phase due to the interaction of solvent and solute with the solid phase, as well as the solvation

effect on the solute. For example, a recent computational study of glucose transferring from aqueous solution to BEA zeolite showed that the enthalpic effect is unfavorable and was compensated with a large entropic effect. The positive entropic contribution was attributed to the reconfiguration of the first coordination shell of water around glucose as it leaves the solvent.[40] The magnitude of these effects is expected to be different for each solute. Due to this complexity, the adsorption isotherms in our study were determined empirically. Accordingly, glucose and fructose adsorption followed the Henry isotherm since the adsorption loading showed linear dependence on the solute's concentration at low uptake. Redlich-Peterson (for HMF and LA) and Freundlich (for FA) isotherms described the experimental adsorption data better than the Langmuir isotherm. The estimated enthalpy changes of adsorption for the components ranged from 8.4 kJ/mol to 32.3 kJ/mol. These values are in the expected range and similar values have been observed by Leon et al.[26] The low apparent enthalpy change is the difference between the true heat of adsorption and the enthalpy of water solvation.[46] Independent molecular simulations illustrate these points and the contributions to the net adsorption enthalpies.[46, 47]

Adsorption loadings in H-BEA-25 are higher than those previously reported in H-BEA-18.[26] This is expected since H-BEA-25 has a higher Si:Al ratio, corresponding to more hydrophobic pores than in H-BEA-18. We have performed adsorption isotherms of HMF in zeolite BEA with different Si : Al ratio. Decreasing Al content (increasing hydrophobicity of the zeolite) increases HMF saturation loading, without a pronounced effect on the enthalpy of adsorption.[48] The trend in adsorption loading is: HMF ~ LA > FA >> Fructose ~ Glucose. The strong adsorption of HMF implies that HMF displaces fructose from the zeolite pores, highlighting the need for considering competitive adsorption.

Table 1. Fitted adsorption isotherm parameters for solutes in H-BEA-25.

Solute	Isotherm equation	Fitted value
Fructose	$q=K\bullet C$	$K_{298K}=0.2557\text{ L/g}$
Glucose*		$\delta H=-20.14\text{ kJ/mol}$
		$K_{298K}=226.866\text{ L/g}$
		$\delta HK=-32.21\text{ kJ/mol}$
HMF	$q=K\bullet C^1+b\bullet C^n$	$b_{298K}=197.85\text{ L/g}$
		$\delta Hb=-29.97\text{ kJ/mol}$
		$n=0.8412$
		$K_{298K}=139.07\text{ L/g}$
		$\delta HK=-29.09\text{ kJ/mol}$
LA	$q=K\bullet C^1+b\bullet C^n$	$b_{298K}=107.05\text{ L/g}$
		$\delta Hb=-27.20\text{ kJ/mol}$
		$n=0.8145$
		$K_{298K}=0.4664\text{ L/g}$
FA	$q=K\bullet C^n$	$\delta H=-8.38\text{ kJ/mol}$
		$n=0.7840$

* Glucose and fructose adsorption isotherms fall on the same line, as shown in Figure S3.

4.2 Model assessment

Model predictions compared to experimental data for representative kinetic experiments in Figure 1 and a parity plot of all experimental data (Figure S8) indicate that the model describes experimental trends at various conditions. The model can also predict glucose conversion and

fructose yield at different catalyst loadings (Figure S9). Experiments using H-BEA-25 without any octahedral Al-sites were conducted to assess the predictive ability of the model. The octahedral Al sites were removed from the zeolite framework by washing with HCl while preserving the zeolite Brønsted acidity.[13, 25] As shown in Figure 1b, no glucose forms in these experiments, and the predicted concentration profiles (dashed lines) are in agreement with the experimental data (open symbols). This good agreement provides support that the model can describe the effects of altering the relative ratio of acid sites on performance discussed below.

Figure 1. Comparison between model (solid lines) and experimental (closed symbols) concentration profiles of glucose, fructose, and HMF for experiments starting with 10 wt% glucose (a) or fructose (b) at 130 °C with an H-BEA-25 loading of 125 g/l. Open symbols and dashed lines in (b) indicate experimental and predicted concentrations, respectively, for 10 wt% fructose dehydration using 125 g/L HCl-washed H-BEA-25. No glucose is formed in this case.

Next we turn into comparing model predictions to literature data in single phase and biphasic systems. The predicted selectivity of fructose dehydration to HMF is ~43% at 140 °C, qualitatively consistent with the 30% reported experimentally by Ordonsky et al.[12] Removing HMF from the reactive phase using an organic extractant can reduce HMF loss.[39] Kruger et al. found an HMF selectivity from fructose of ~35% when an organic extracting phase is added to a mixture of H-BEA-18 and water at 130 °C.[13] This finding is in qualitative agreement with simulations we performed here in a biphasic system (albeit H-BEA-25 was used here). When the Lewis sites of H-BEA-18 were experimentally removed, the selectivity of HMF from fructose increased to ~50%.[13] The corresponding model prediction of 59% is again in good agreement with the data.

4.3 Species partitioning between solution and zeolite phases and contribution of homogeneous chemistry

Here we address two topics that are hard to study via experiments alone. Simulations indicate that only a small fraction (up to 10%) of the chemistry proceeds homogeneously (Figure S10) under these conditions. The high zeolite loading used in our experiments (125 g/l) maximizes the contribution of the heterogeneous reactions to the overall reaction rate. This contribution is expected to vary with amounts of zeolite and solution, e.g., the less the zeolite, the more the contribution of the homogeneous chemistry.

A challenge in analyzing these experiments is the fact that significant portions of species remain adsorbed in the zeolite and that the adsorbed amounts are hard to measure experimentally during reaction. Adsorption isotherms can relate the adsorbed concentrations to measurable

concentrations in the aqueous phase to provide the overall concentration of each species in the system.

Typical experimentally measured (at room temperature) aqueous concentrations starting from fructose are shown in Figure 2 (closed symbols). We use adsorption isotherms to estimate the corresponding total concentration (adsorbed plus solution) profile of each component (open symbols in Figure 2). The total and solution concentrations of fructose and FA are very similar since they adsorb weakly in the zeolite; these compounds are primarily in the aqueous phase. On the other hand, very little HMF and LA are in solution due to their strong adsorption in the zeolite.

Recent work with homogeneous acids has shown that FA can be produced directly from fructose degradation[42] probably via a retro-aldol reaction.[14] As a result, the molar ratio of FA and LA was higher than 1 at low fructose conversions and then gradually decreased at higher conversions once the fraction of the HMF-derived FA becomes dominant. The data in Figure 2b show that FA is in excess of LA indicating that, as in homogeneous catalyzed reactions, the zeolite also catalyzes the direct conversion of fructose to FA.

Representative concentration profiles of the experiments using HMF as a substrate are shown in Figure 3. As expected, HMF rehydration produces equimolar amounts of FA and LA. However, an abrupt decrease in the HMF concentration in solution between the initial value and the one recorded at the first data point (10 min) is observed in Figure 3a, followed by a more gradual decrease thereafter. The total HMF concentration (open symbols in Figure 3a) does not exhibit the same rapid decrease, indicating that the initial drop is primarily an effect of HMF adsorption. This conclusion is further corroborated by the absence of significant fractions of FA and LA at early reaction times. Since the HMF and LA are mainly adsorbed in the zeolite, the

measured concentrations in solution are a poor indicator of their overall amount in the system and for estimating reaction rates. It is then not surprising that data in different labs cannot easily be reconciled. For example, differences in the amount of zeolites and/or solution-phase volume would result in different contributions of homogeneous and heterogeneous kinetics to the overall rates.

Figure 2. Measured concentration profiles in solution (closed symbols) and estimated total concentration (including aqueous and zeolite phase concentrations - see text; open symbols) starting with 10 wt% fructose at 140 °C with 125 g/l of H-BEA-25. Accounting for the adsorbed amounts, especially for HMF and LA, is important for correct description of kinetics.

Figure 3. Aqueous species concentrations (closed symbols) and estimated total concentration (including aqueous and zeolite phase concentrations; open symbols) starting with 2 wt% HMF at 140 °C with 125 g/l of H-BEA-25.

4.4 Kinetic parameters and comparison to other catalysts

Several prior studies have explored the reaction kinetics of zeolite catalyzed conversion of sugars to furans.[12, 49-51] Typically models describe rates as a function of solution concentrations[49] rather than those in the zeolite pores.[11] This approach lumps contributions from adsorption and homogeneously catalyzed reactions with heterogeneous catalysis, limiting the insights gained. One exception entails the work of Lourvanij and Rorrer who used a Langmuir-Hinshelwood model to estimate simultaneously adsorption and kinetics of glucose dehydration in H-Y, MCM-20, and MCM-41 catalysts.[52] Our work is the first to take input from single solute experimentally determined adsorption data for the construction of multicomponent isotherms and use this thermodynamic model to decouple homogeneous and heterogeneous reaction contributions using intrinsic (inside the zeolite) rather than bulk (solution) concentrations.

The experimental concentration profiles of reactants and products in reactions used for parameter estimation are shown in Figure S11-S14. The estimated activation energies, rate constants at a reference temperature, and corresponding Arrhenius pre-exponentials are shown in Table 2. The activation energy of fructose dehydration (142 kJ/mol) is close to that in homogeneous catalysts (values between 130 and 160 kJ/mol[41, 53, 54]), but lower than that reported by Lourvanij and Rorrer (205 kJ/mol) for H-Y zeolite.[52] This is not unexpected, as a different zeolite framework (faujasite vs. beta) and a different temperature range (130-190 °C vs. 110-140 °C) were considered and a rather limited number of data was employed in published work increasing the uncertainty in estimated parameters.

Table 2. Estimated parameters for the intrinsic reaction rates in zeolite beta.

Reaction	E_a , kJ/mol	$\ln(k_{398K})^a$	$\log 10A O^a$
Fructose $\rightarrow$ HMF	142 $\pm$ 8	2.65 $\pm$ 0.10 ^b	19.75 ^b
HMF $\rightarrow$ FA+LA	111 $\pm$ 6	2.92 $\pm$ 0.03	15.78
HMF $\rightarrow$ Humins	145 $\pm$ 18	1.43 $\pm$ 0.35	19.63
Fructose $\rightarrow$ FA + Humins	79 $\pm$ 8	3.44 $\pm$ 0.16	11.88
Glucose $\rightarrow$ Fructose	113 $\pm$ 8	5.01 $\pm$ 0.06	17.06

^a gmin•mol unless noted otherwise , ^b 7min

Glucose adsorbs weakly in the zeolite so the apparent activation energy obtained from an Arrhenius graph of initial rates (see Figure S15; 117 kJ/mol) is close to the intrinsic activation energy in Table 2 and in between those observed for Sn-BEA (~89 kJ/mol) and Ti-BEA (~155 kJ/mol),[55] as shown in Figure 4, indicating that octahedral Al sites catalyze the isomerization reaction effectively. While direct dehydration of glucose to HMF is slow[14], the rate constant of isomerization is larger than that of fructose dehydration by more than one order of magnitude

(Table 2), i.e., octahedral Al sites are efficient for isomerization, rationalizing why the concept of tandem reactions in a single pot works.

Figure 4. Apparent activation energy for glucose-fructose isomerization in Sn-BEA[55], Ti-BEA[55], homogeneous CrCl₃[56] and H-BEA (present work) based on glucose consumption at 110-130 °C.

The zeolite catalyzed HMF degradation reactions have higher activation energies (111-145 kJ/mol) than the HCl catalyzed counterparts (60-110 kJ/mol),[41, 57] suggesting that confinement within the zeolite changes the energetics of HMF degradation. While the activation energies are high, so are the pre-exponential factors resulting in high rate constants, that eventually lead to significant HMF degradation. Furthermore, strong HMF adsorption accelerates its degradation in the zeolite.

The ‘per-site’ reactivity of HCl and H-BEA-25 can be compared directly by examining the rates of HMF and fructose consumption using the turnover frequency (TOF) of the catalysts (Figure 5). HCl converts nearly an order of magnitude more fructose per ‘acid site in the reactor’ per unit time than the zeolite. The number of ‘active centers’ is also different. In a 10 wt% fructose solution at 140 °C, fructose loading in H-BEA-25 is 0.23 mmol/g. This is less than half the Brønsted site density in the zeolite measured experimentally (0.61 mmol/g). Under typical conditions of homogeneously catalyzed fructose dehydration, the concentration of the acid (i.e., HCl) is lower than that of fructose at those same conditions (i.e., 10 wt% fructose dehydration at pH~1 corresponds to 0.55 M fructose and 0.08 M HCl). Given that apparent kinetics in heterogeneous catalysis often combines various rate constants and that the number of active sites in various literature studies can differ, comparison between heterogeneous and homogeneous catalysts in this system should therefore be done with care, and intrinsic rate constants should be the preferred method.

Figure 5. Turnover frequency (TOF), determined from experimental data after 30 min, of 10 wt% fructose (a) and 5 wt% HMF (b) in HCl (pH = 1.1) and H-BEA-25 (125 g/l) at 140 °C.

4.5 Kinetic regimes

The tandem reactions of isomerization and dehydration require a balance between multiple rates to optimize HMF rate and yield. The rates are determined from intrinsic rate constants, the local concentrations around the active site, and the number of active sites. It has been demonstrated that by varying the post-synthesis calcination procedure,[19] the ratio of Lewis to Brønsted acid sites can be adjusted. By adjusting this ratio, the relative rates of glucose isomerization to fructose and fructose dehydration to HMF can be altered. Therefore, it is interesting to study the effect of changing L:B ratio on the kinetic regimes. We have found that the HMF's enthalpy of adsorption remains fairly constant on BEA zeolites with different Si/Al ratio. Therefore, we believe that the largest contribution to the measured enthalpies of adsorption originates from the interaction with the zeolite pore rather than with the active sites.[48] As a result, the adsorption in the zeolite can be assumed as constant when changing the Lewis to Brønsted acid ratio. Herein, we explore the effect of L:B ratio on the kinetics of tandem reactions and the behavior of bifunctional materials, which are currently unknown.

Figure 6(a-d) shows the predicted concentration profiles of glucose, fructose, HMF, and LA as a function of time for different Lewis to Brønsted acid site ratios in a single phase. Figure 6(e-f) shows the corresponding net reaction rates. The concentration of glucose decreases monotonically whereas those of fructose and HMF go through a maximum as a result of the competition between formation and consumption reactions. Initially, glucose is consumed faster with increasing L:B ratio since glucose isomerization is Lewis-acid catalyzed. Interestingly, for times past the maximum in fructose concentration (but not too long), the net rate of consumption of glucose is lower for higher densities of Lewis acid sites. This rather counterintuitive finding results from the fact that at high L:B ratios, there is an insufficient number of Brønsted acid sites

to dehydrate fructose, and fructose accumulates in the reactor. As a consequence, the reverse isomerization reaction (fructose to glucose) becomes significant, reducing the net rate of glucose consumption to zero. Simple kinetic analysis[58] indicates that the ratio of concentrations of glucose and fructose is in quasi-steady state and at high L:B ratios, the isomerization reaction is close to equilibrium.

At low L:B ratios, the fructose production rate is low due to slow isomerization and fast dehydration due to having excess of Brønsted acid sites. Low L:B ratios limit fructose accumulation in the reactor and, consequently, the reverse isomerization reaction. Eventually, fructose is consumed via dehydration nearly as fast as it is produced leading to a low net rate (Figure 6f) and a slowly varying, low concentration (Figure 6b). As L:B increases, the glucose isomerization rate increases eventually leading to accumulation of fructose in the reactor. The high fructose concentration leads to faster rates of reverse isomerization (fructose to glucose) as well as dehydration to HMF and degradation to humins. These degradation reactions eventually become faster than the production of fructose from glucose isomerization despite the slower intrinsic kinetics (see rate constants in Table 2), causing fructose concentration to decrease rapidly.

Figure 6c shows that the maximum HMF concentration increases with increasing L:B ratio. This is attributed to the decreasing number of Brønsted acid sites that catalyze HMF degradation (Figure 6f). Unlike fructose, whose concentration reaches a maximum at about the same time for various L:B ratios, the HMF concentration peaks at considerably longer times as L:B increases because HMF consumption reactions are limited by the lack of Brønsted acid sites. Finally, Figure 6d,h shows the concentration and net rate of LA, respectively, vs. time. As expected, over

523 typical time scales both the concentration and the rate of LA are optimized for intermediate L:B
524 ratios.
525

Figure 6. Predicted concentration profiles (a-d) and net reaction rates (e-h) of (a, e) glucose, (b, f) fructose, (c, g) HMF, and (d, h) LA at different L:B ratios. Conditions: 130 °C, 125 g/L H-BEA-25, 0.79 mmol/g total sites, 10 wt% glucose.

The net rate of HMF production in Figure 6 is masked by dominant HMF degradation reactions. This is in contrast to our previous study where para-xylene does not readily degrade. In order to draw a closer analogy to the para-xylene work, we consider the formation rate of HMF, rather than its net rate. As we show below, this case is relevant in biphasic systems. Figure 7a shows the formation rate of HMF as a function of the L:B ratio at different times. In all cases the HMF production rate exhibits a volcano relationship with an optimum L:B ratio, which indicates that at this L:B ratio, there is a balance between the rates of glucose isomerization to fructose and fructose dehydration to HMF. At 6 and 12 hours, the maximum HMF production rate is obtained at L:B ratio of 0.36 and 0.32, respectively. These L:B values are very closed to the L:B ratio of 0.3 of the H-BEA-25 catalyst in our experiments. At longer times the optimum L:B ratio is slightly lower (but does not change as sharply over a range of L:B ratios) since as the reaction proceeds further, the isomerization approaches equilibrium and more Brønsted acid is desirable to speed up dehydration. In order to rationalize the volcano relationship in Figure 7a, the normalized sensitivity coefficient (NSC) of HMF production rate with respect to the rate constants, defined as $(d \ln r_{HMF} / d \ln k_i)$, was computed for different L:B ratios (Figure 8). On the left of the volcano curve, both isomerization and dehydration control the overall rate with isomerization being more kinetically relevant. As L:B increases, the importance of isomerization decreases and eventually the Brønsted acid-catalyzed dehydration reaction becomes rate-determining step. At longer times, the rate of HMF formation becomes generally less sensitive to isomerization, because the reverse isomerization (fructose to glucose) becomes more prevalent. As the reverse isomerization becomes more important, the net rate of glucose consumption

approaches zero (Figure 6e), even though the concentration of glucose in the aqueous phase is significant (Figure 6a).

The bifunctional H-BEA system is different from that studied in the para-xylene work by Patet et al.[20] Here the total number of acid sites is fixed rather than varying. Furthermore, the first reaction (glucose isomerization) is heterogeneous rather than homogeneous. A system with closer resemblance to that studied in ref.[20] is a physical mixture of Lewis and Brønsted acid catalysts with properties those of the corresponding sites of H-BEA zeolite. When we simulated such a system and varied the Brønsted acid concentration alone (Figure 7b), a linear and a plateau regime are observed, as happens in the para-xylene chemistry. Thus, the multiple kinetics regimes appear to be a generic feature of tandem reactions catalyzed by multiple catalysts or multifunctional catalysts, as is the case here, and the shape depends on whether one can vary one site at the time or not.

Figure 7. Predicted rate of HMF formation (forward) as a function of (a) Lewis to Brønsted acid site ratio (holding the total number of sites constant at 0.79 mmol/g) after 6, 12, and 24 hours and (b) Brønsted site density with Lewis site density held constant at 0.3, 0.6, and 1.2 mmol/g after 6 hours. Reaction starts with 10 wt% glucose at 130 °C with 125 g/l of H-BEA.

Figure 8. Normalized sensitivity coefficient of the forward HMF production rate ($d\ln r_{HMF}/d\ln k_i$) for different L:B ratios after (a) 6 hours, (b) 12 hours, and (c) 24 hours. Conditions: 130 °C, 125 g/L H-BEA-25, 0.79 mmol/g total sites, 10 wt% glucose.

4.6 Optimizing HMF yield in single phase and biphasic systems

Next we turn to the yield that is an economically important quantity. Figure 9a shows the HMF yield vs. L:B ratio at three different reaction times. Overall, the HMF yield is low. The highest HMF yield occurs at high L:B ratios and longer times because isomerization is fast leading to accumulation of fructose but the degradation reactions of fructose and HMF are slow due to unavailability of enough Brønsted acid sites. This is further corroborated in the sensitivity of HMF yield with respect to rate constants shown in Figure 9b. Accelerating the isomerization and dehydration increases the HMF yield. Conversely, humin formation from fructose and HMF and HMF rehydration have a negative impact on HMF yield and their control is key to improving

HMF yield. Otomo et al. observed higher HMF yields from glucose when more Lewis sites were present in their H-BEA, in support of our findings.[19]

Figure 9. (a) HMF yield as a function of Lewis to Brønsted acid sites (L:B) ratio after 6, 12, and 24 hours and (b) corresponding normalized sensitivity coefficient of HMF yield for L:B = 0.3. Conditions: 130 °C, 125 g/L H-BEA-25, 0.79 mmol/g total sites, 10 wt% glucose.

A common approach used experimentally to increase the HMF yield is to add an organic extractant that selectively removes HMF before it reacts.[59] Therefore, it is important to be able to predict the HMF yield and rate of formation in biphasic systems. Since we have previously developed models for reactive extraction, the predictions should be reasonable. We simulate this in Figure 10 by considering extraction using a realistic organic solvent (partition coefficient = 2, $V_{org}/V_{aq}=5$, similar to those used in previous work [60]) and an ideal solvent that is immiscible with water and extracts all HMF as it is being produced. The ideal solvent provides the optimal HMF yield, whose value is controlled from the humins formed from sugars. As it is well-known, our simulations indicate that extraction can considerably increase the HMF yield. Realistic

extractors, such as those used in typical laboratory experiments, can lead only to moderate yields, whereas the ideal extractor can lead to (molar) yields approaching 60%. This indicates that developing a better separation scheme, e.g., by finding better extractants,[61] has the greatest potential for improving the HMF yield. This is extremely important in the case of Brønsted acid zeolites since the typical use of inorganic salts for enhancing the partition coefficient[60] employed using HCl Brønsted acid is not a practical alternative (due to ion exchange reactions). In the actual biphasic system, higher yields occur for higher L:B ratios because HMF forms slowly and is extracted as soon as is formed, rather than being consumed by side reactions. Interestingly, the time for the optimal yield increases with increasing L:B ratio due to the low rate of dehydration of fructose. In the ideal extractor case, on the other hand, the same optimal yield is obtained at very long times (not shown) for all L:B ratios but intermediate L:B ratios give higher yields at shorter times and should be preferred.

Figure 10. Predicted HMF yield in (a) aqueous single-phase solution, (b) a biphasic reactor (partition coefficient = 2, $V_{org}/V_{aq}=5$), and (c) an ideal biphasic reactor (all HMF extracted) at

different L:B ratios. Conditions: 130 °C, 125 g/L H-BEA-25, 0.79 mmol/g total acid sites, 10 wt% glucose.

4.7 Identification of key materials' properties

The HMF yield shown in the biphasic reactor using the bifunctional H-BEA catalyst (Figure 10b) is lower compared to systems consisting of physical mixtures of catalysts, primarily when homogeneous HCl is involved as a Brønsted acid catalyst. For example, Nikolla et al. obtain a 53% molar yield of HMF in an experimental biphasic reactor with Sn-BEA and HCl at 180 °C.[16] Our results above indicate that the Lewis sites of Sn-BEA are more effective than those of H-BEA[44] (see also Figure 4), and HCl converts fructose to HMF faster than H-BEA (Figure 5). These findings along with the sensitivity analysis in Figure 9b provide insights into why H-BEA is not as an effective catalyst. In order to achieve high HMF yields, one needs to increase the rate of glucose isomerization and fructose dehydration, and thus the rate of HMF production, while reducing the rates of HMF degradation reactions. To better rationalize the differences among catalysts, we conduct 'numerical' experiments. Figure 11 shows the predicted maximum yield (with respect to time) of HMF from glucose in hypothetical catalysts in both a single-phase (Figure 11a) and a biphasic (Figure 11b) system. Rajabbeigi et al. recently published kinetic parameters for glucose-fructose isomerization in Sn-BEA based on aqueous concentrations.[44] The rate constants reported are between 11 and 7 times higher than those of the present study, depending on temperature. Since their study differs from ours in several important respects (temperature range, catalyst, adsorption), we considered an increased isomerization rate constant by a factor of 10 to qualitatively capture differences in reactivity between Sn-BEA and H-BEA-25 (this does not imply that the two studies are directly comparable). The HMF yield from a hypothesized zeolite BEA that could enhance the rate of isomerization of H-BEA by 10 times

(BEA-L10) only marginally improved as shown in Figure 11. This is consistent with strong adsorption of HMF in H-BEA causing low HMF yields. Increasing HMF yield may be achieved either by reducing HMF adsorption strength, which would reduce its side-reactions or by increasing the strength of carbohydrate adsorption, which would promote the desirable glucose isomerization and fructose dehydration reactions. Indeed, when the adsorption properties of H-BEA are modified so that HMF adsorbs as weakly as glucose/fructose or the glucose/fructose adsorb as strongly as HMF or both, the HMF yield increases considerably (the time needed to achieve maximum HMF yields varies as shown). Increasing sugar adsorption increases the rate of HMF production and yield, whereas weakening the HMF adsorption decreases the side reactions of HMF and thus improves the HMF selectivity. A mixture of zeolite with enhanced Lewis acid (BEA-L10) and HCl converts glucose to HMF faster and avoids the strong adsorption of HMF, leading to high yields, qualitatively consistent with experimental data.[16] Putting all these findings together, the bifunctional H-BEA is not as good a catalyst because it converts sugars slower due to being (1) a weaker Lewis acid catalyst than Sn-BEA and (2) a weaker Brønsted acid catalyst than HCl and (3) at the same time a strongly HMF-adsorbing material that promotes HMF side reactions. Identification of bifunctional materials (i.e., pore size, hydrophobicity) and/or a solvent that can promote sugar adsorption over HMF can make them viable. On the other hand, the H-BEA catalyst would be more suitable for converting glucose to levulinic acid directly, as this process would benefit from strong HMF adsorption and rehydration.

Figure 11. Predicted maximum HMF yield from glucose in (a) single phase and (b) biphasic (partition coefficient = 2, $V_{org}/V_{aq}=5$) systems along with the time to reach that yield. Catalysts include the actual H-BEA, H-BEA with modified adsorption (H-BEA' has low HMF loadings, H-BEA'' has high glucose/fructose loadings, and H-BEA''' has increased glucose/fructose loading and lower HMF loadings), BEA-L10 combined with H-BEA or HCl.

5. CONCLUSIONS

The use of aluminosilicate zeolite BEA as a bifunctional catalyst for the conversion of glucose to HMF using tandem reactions has been investigated. We developed a model that accounts for multicomponent adsorption effects, homogeneous Brønsted acid catalyzed chemistry of fructose, and intrinsic heterogeneous Lewis acid catalyzed isomerization and Brønsted acid catalyzed fructose dehydration, HMF rehydration, and humin formation chemistry, the parameters of which were fitted to experimental data of this work. We show that the intrinsic reaction kinetics of fructose dehydration in H-BEA favor HMF formation. However, the relative strength of

carbohydrate vs. HMF adsorption, rather than intrinsic kinetics, causes slow fructose dehydration relative to homogeneous catalysts and low overall HMF yields due to strong HMF adsorption leading to side reactions. Using sensitivity analysis we show that strengthening fructose adsorption could increase HMF yield significantly, and HMF yields approaching those obtained using a combination of Sn-BEA and HCl can potentially be achieved. As far as H-BEA is concerned, despite its performance been modest in a single phase, it may be possible to attain high HMF yield using much better extractants.

We reveal that glucose conversion to HMF using tandem reactions exhibits two types of multiple kinetic regimes and this appears to be a generic feature of tandem reactions catalyzed by multiple or multifunctional catalysts. When a bifunctional catalyst with a fixed total number of acid sites is used (as in the case of aluminosilicate zeolites), the (forward) production HMF rate exhibits a volcano curve with increasing Lewis:Brønsted acid site ratio. In contrast, when the Brønsted and Lewis acid concentrations vary independently, a linear kinetic regime followed by a plateau form as the Brønsted acid concentration increases at fixed Lewis acid concentration.

Model predictions provide insights about the optimum catalyst properties under different reactor configurations. The HMF yield in a single aqueous phase is maximized when a catalyst with a high L:B ratio is used. When an ideal extracting phase is considered, then the maximum HMF yield approaches 60% at L:B ratio of ~ 0.3 and relatively short times. The exact value of L:B ratio would probably depend on the material. What is important is the concept of an optimum L:B ratio.

ASSOCIATED CONTENT

Supporting Information. Experimental data, parity plots, and sensitivity analysis.

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Graphical Abstract

Tandem reaction kinetic model of glucose conversion to 5-hydroxymethyl furfural by H-BEA-25 zeolite.