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Inert Competitive Adsorption for the Inhibition of Oligomerization of Alkenes During Alcohol Dehydration

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Abstract. Inhibition of secondary chemistries in a linear series of reactions remains a catalytic challenge, particularly when targeting the selective synthesis of intermediate chemicals. In this work, the inhibition of cyclohexene oligomerization following cyclohexanol dehydration with H-BEA zeolite catalyst was achieved with the addition of 2,5-dimethylfuran (DMF). Suppression of undesired olefin oligomerization occurred with the competitive adsorption of the hydrolysis product of DMF, 2,5-hexanedione, thereby preventing cyclohexene adsorption onto Brønsted acid sites. Activation energies were measured for cyclohexanol dehydration both with and without DMF and were found to be the same within experimental error, suggesting that DMF does not alter the catalytic mechanism of cyclohexanol dehydration. Adsorption models were generated to investigate the general case of adding inert chemicals to inhibit product side reactions. Allowable differences in free energies of adsorption between reactant, product, and inert necessary to promote inhibition of product adsorption, while allowing for reactant surface saturation, were quantitatively determined. Reactions that might benefit from the addition of inert chemicals were proposed including linear alcohol dehydration and benzyl acylation and alkylation.

1.0 Introduction

The availability of biomass resources of approximately one billion tons annual surplus in the United States has made renewably-sourced alcohols an intriguing bio-derived chemical intermediate for the production of green energy and chemicals.^{1–4} Traditionally, renewable alcohols produced by biomass fermentation, such as ethanol and butanol, have been considered primarily for their potential as liquid fuels. However, there exists potential for alcohols to be used as feedstocks in the chemicals industry. Alcohol dehydration produces alkenes, which are normally synthesized from fossil fuels and used for the production of chemicals and polymers^{5,6}. For example, ethylene, the unimolecular dehydration product of ethanol, is an important chemical for the production of plastics polymers, such as polyethylene (PE), polyvinyl chloride (PVC), and polystyrene (PS).⁷

Alcohol dehydration to alkenes has been thoroughly investigated, but difficulties remain achieving high selectivity to some alkenes at high reactor conversion. Strong solid acid catalysts, such as Brønsted acid zeolites, are desirable for dehydration chemistries due to their enhanced rates of reaction. However, stronger acids also readily catalyze undesired side reactions.⁸ The presence of strong acid sites, even at temperatures below 423 K (150 °C), can promote isomerization and oligomerization as well as catalyst deactivation, thereby decreasing the overall selectivity towards dehydration products.^{9–11} Specifically, butene isomerization occurs readily during *n*-butanol dehydration over aluminosilicate zeolites,^{12,13} and notably at full conversion.^{14,15} To address this issue, dehydration can be conducted with Lewis acidic catalysts, such as γ -alumina.^{8,16,17} However, weaker acids tend to decrease the rate of reaction. This necessitates a search for processes and catalysts that can simultaneously achieve high activity *and* selectivity to targeted chemical products.

We have previously demonstrated that aromatic chemicals can be produced via solid acid catalyzed dehydration at high conversion while simultaneously inhibiting subsequent isomerization and disproportionation reactions.¹⁸ Xylene isomerization should occur readily at temperatures of 573 K (300 °C), the condition used in previous studies, in the presence of Brønsted acid zeolites.^{19–21} However, in the selective production of *p*-xylene from ethylene and 2,5-dimethylfuran (DMF) with H-BEA and H-Y catalysts, negligible isomerization of *p*-xylene to *m*- and *o*-xylene was encountered.^{22–25} It was concluded that suppression of aromatic isomerization

resulted from the presence of 2,5-hexanedione, the hydrolysis product of the reactant, dimethylfuran.¹⁸ At high conversion, the Brønsted acid sites were populated by stronger adsorbing 2,5-hexanedione and the DMF-ethylene cycloadduct intermediate, while the weaker adsorbing *p*-xylene was unable to adsorb and react.

Similar surface coverage phenomena have been noted in other catalytic reaction networks. In the case of acetylation of anisole with acetic anhydride to form *p*-methoxyacetophenone (*p*-MOAP) and acetic acid, Derouane et al observed lower reaction rates in batch processes at longer times.^{26,27} This was attributed to the product, *p*-MOAP, accumulating on active sites of H-BEA, blocking the adsorption of the reactants (i.e. product inhibition). Derouane further investigated the ability of competitive adsorption to influence reaction rates and yields, considering zeolites to be ‘solid solvents’, where the zeolite adsorbates leave the solution and enter the zeolite phase.²⁸ He also discussed the capability for products and solvents to adsorb preferentially for inhibition, thereby controlling the extent of conversion of complex reaction networks.

In this paper, we extend the work of Derouane et al by the addition of inert chemical species to influence zeolite surface coverage and direct overall reaction networks. The competitive adsorption of reactant, inert, and product onto Brønsted acid sites present a unique catalytic challenge. In series reactions of reactant, A, forming desired product, B, the undesired reaction of B to form byproduct, C, will proceed when the barriers of the two reactions are similar; choice of acid catalyst will likely not affect this. One strategy that emerges in this scenario is surface species coverage manipulation. In the condition that A adsorbs significantly more strongly than the product B, high surface coverage of A will suppress the conversion of B at low overall conversion of A. However, at high conversions of A, an extra-reaction inert chemical must be added that preferentially adsorbs on acid sites to prevent even low surface coverage of component B, and therefore reaction of B. Design of an effective catalytic system to implement this strategy requires proper selection of catalyst, temperature, reaction concentrations, and identification of an inert chemical with appropriate adsorption characteristics.

To demonstrate the usefulness of competitive adsorption with added inert compounds, we examine the dehydration of cyclohexanol to cyclohexene using 2,5-dimethylfuran (DMF), and subsequently 2,5-hexanedione, as the inert compound in the presence of H-BEA (Scheme 1). The ability of DMF/hexanedione to inhibit oligomerization of cyclohexene produced from the dehydration of cyclohexanol will be examined. Specifically, the inert will be evaluated by

characterizing its effect on the yield and kinetics of cyclohexanol dehydration; these will be compared with and without added inert compound. We further propose a general strategy with quantitative parameters for employing competitive adsorption for other chemistries by examining the relative adsorption energies of reactants, products and potential inert additives.

2.0 Methods and Materials

2.1 Batch Reaction Procedures. Reactions were conducted in Parr 4560 series reactors equipped with 4848 controllers and gas entrainment impellers. Chemicals used in these experiments included: 2,5-dimethylfuran (inert, Alfa Aesar 98+%), *n*-heptane (solvent, Alfa Aesar 99+%), *n*-tridecane (internal standard, Sigma-Aldrich 98+%), cyclohexanol (reactant, Sigma-Aldrich 99%) and cyclohexene (product/reactant, Sigma-Aldrich >99%). An ammonium-form BEA catalyst (Zeolyst CP814E) was calcined at 550 °C for 12 hours in flowing air to produce the corresponding H-BEA zeolite (Si/Al 12.5) with an acid site density of 0.618 mmol/g, measured by alkylamine decomposition by reactive gas chromatography.²⁹ To minimize adsorbed water, the catalyst was stored in a desiccator and dried in a furnace at 200 °C prior to use.

A Parr reactor vessel was filled with 0.5 M cyclohexanol, 82 mL (or 90 mL without DMF added) heptane, 2.0 mL tridecane, 8.0 mL 2,5-dimethylfuran, and 1.8 mM H-BEA catalyst, then purged with nitrogen gas and heated. Once reaction temperature was reached, 13.6 atm (200 psi) nitrogen gas was introduced to the system and the first sample was taken. Pressures were held constant for the reactions and were re-pressurized with nitrogen after sampling.

Reaction temperatures were varied from 135 °C to 160 °C for experiments conducted in order to determine the apparent activation energy of cyclohexanol dehydration. Cyclohexanol conversion for these experiments was maintained at less than 10%. For all other experiments, the reaction temperature was 160 °C. Lower temperatures were selected to ensure only minimal conversion of cyclohexanol occurred upon heating of the reactor to the designated reaction temperature.

2.2 Chemical Analysis. Chemical analysis of the reaction solution was conducted with an Agilent 6890 gas chromatograph equipped with a G1513A autosampler, an HP-Innowax column, and a flame ionization detector (FID). Samples were collected from the Parr reactors using a double block sampling system, which allowed for safe sampling at high pressures and temperature without opening the vessel directly to the atmosphere.

3.0 Results and Discussion

3.1 Cyclohexanol Dehydration

The model reaction, cyclohexanol dehydration to cyclohexene, is depicted in Scheme 1. Cyclohexanol dehydration was selected due to similarities with the dehydration of oxanorbornene, the cycloadduct of *p*-xylene and ethylene; in both cases, 2,5-hexanedione adsorbs stronger than the dehydration products (cyclohexene and *p*-xylene) without displacing the reactants (cyclohexanol and oxanorbornene).

The effect of DMF/hexanedione on alcohol dehydration with H-BEA was examined via experimental cyclohexanol dehydration (Fig. 1). As shown in Figure 1A, cyclohexanol reacts to form cyclohexene (red circles), with the cyclohexene concentration reaching a maximum concentration within the first two hours of reaction before decreasing due to sequential reactions of cyclohexene. In contrast, the addition of 2,5-dimethylfuran enhances the rate of cyclohexene formation (black squares) and prevents the concentration of cyclohexene from decreasing between two hours and the end of the experiment, six hours later. The data demonstrates that DMF/hexanedione stabilizes the concentration cyclohexene and prevents oligomerization and other acid catalyzed reactions of cyclohexene.

In a separate experiment, the reaction of cyclohexene to oligomers and other products was evaluated (Fig. 1B). The conversion of cyclohexene over H-BEA (Si/Al 12.5) at 160 °C (red circles) occurs readily with >25% conversion after eight hours. In contrast, the reaction of cyclohexene at the same conditions with the addition of DMF/hexanedione (black squares) exhibited only negligible conversion (~4%). This suggests that DMF/hexanedione competes with cyclohexene for acid sites and inhibits further reaction. Though water is not in excess in the cyclohexene experiments of Figure 1B as it is not a product of a dehydration reaction, there is still a possibility for 2,5-hexanedione to form through hydrolysis of DMF. Water adsorbed on the zeolite during loading within the reactor will facilitate hydrolysis to form 2,5-hexanedione from DMF; we have previously observed that even low loadings of 2,5-hexanedione are able to prevent side reactions such as *p*-xylene isomerization¹⁸.

To further examine the influence of DMF/hexanedione on cyclohexanol dehydration, we examined the initial rates of cyclohexanol consumption both with and without the addition of dimethylfuran/hexanedione. These experiments specifically address the issue of whether

hexanedione competes with cyclohexanol for surface sites. As depicted in Figure 2, the rates of conversion of cyclohexanol from 135-160 °C were within experimental error both with and without dimethylfuran/hexanedione. For the reaction including DMF, the barrier of dehydration was found to be 52.0 ± 12.5 kJ/mol versus 44.8 ± 7.1 kJ/mol when excluding DMF. As the two activation energies are within error, it is likely that cyclohexanol dehydration is unaffected by the presence of DMF/hexanedione; cyclohexanol and hexanedione do not substantially compete for active sites. It is also apparent from Figure 2 that the cyclohexanol dehydration rate at each temperature is the same within experimental error. It can be interpreted that the adsorption energy of hexanedione exists between that of cyclohexanol and cyclohexene, allowing for the inhibition of alkene reactions while also not impeding dehydration.

3.2 Further Investigation into Competitive Adsorption of Alcohols

Dehydration of a broad range of alcohols may also be enhanced with a competitive surface adsorbant (e.g. 2,5-hexanedione). With alkenes formed from asymmetric alcohols, both oligomerization and migration of the double bond must be considered. To evaluate the potential for suppressing double bond migration, we have conducted an experiment with 1-dodecene and H-BEA with and without added DMF, as shown in Figure S1 of the Supporting Information. In the presence of H-BEA at 200 °C, 1-dodecene achieves 99.2% conversion after two hours. However, with the addition of 2,5-dimethylfuran (DMF) and under the same conditions, only 1.5% conversion of 1-dodecene was observed, signifying the ability for DMF/hexanedione to preferentially adsorb relative to dodecene and prevent reaction.

Extension of the strategy of competitive adsorption to many types of alcohol dehydration reactions also requires consideration of the free energy of adsorption (ΔG_{ads}) on Brønsted acid sites in aluminosilicate zeolites. Difficulty exists obtaining reliable free energies of adsorption derived from experiment or computation, primarily due to the lack of accurate entropies of adsorption (ΔS_{ads}).^{30,31} Instead, heats of adsorption (ΔH_{ads}) on USY, BEA, and ZSM-5 are examined from a combination of microcalorimetry data and computational results (Fig. 3).^{18,32–35} As shown in Figure 3, alkenes such as ethylene and 1-butene have the least negative heats of adsorption ($30 < -\Delta H_{\text{ads}} < 75$ kJ/mol), while amines such as isopropylamine, pyridine, and *n*-butylamine have the most negative heats of adsorption ($200 < -\Delta H_{\text{ads}} < 225$ kJ/mol). A clear distinction between alkenes

(red in Fig. 3) and alcohols (black) indicates that alcohols should outcompete alkenes for acid sites, particularly at low alcohol dehydration conversions, which is supported by previous studies^{36,37}.

Interestingly, the enthalpies of adsorption of 2,5-hexanedione and acetone, both ketones, are found between alkene and alcohol groups in Figure 3. This can potentially explain why 2,5-hexanedione inhibits cyclohexene conversion but allows for unimpeded cyclohexanol dehydration. Other ketones may be considered for other alcohol dehydration chemistries if 2,5-hexanedione / DMF cannot be used, provided these ketones are inert under the reaction conditions.

3.3 Modeling Ideal Conditions for Competitive Adsorption

Further application of competitive adsorption for inhibition necessitates the elucidation of reaction selection criteria. First, the selected inert must be unreactive under experimental conditions. Second, the reaction needs to achieve high conversion; under all but high conversion, this method is unnecessary as the surface will be fully saturated with reactant, inhibiting adsorption and reaction of the product. This seems limiting; however, many industrial processes would greatly benefit from the ability to operate at full reactor conversion due to difficulty and cost in separation and recycling of reactant material.

Third, the relative free energies of adsorption of the reactant, inert, and product must be significantly different (Fig. 4); the reactant, A, should have the highest free energy of adsorption, then the inert, I, followed by the product, B. The extent of those differences in free energy of adsorption can be determined using Langmuir adsorption equations. Here, we assume two scenarios: (1) high conversion of A, where A barely dominates the surface coverage relative to I, and (2) full conversion, where I dominates the surface over B. Two equations can be derived as follows for each instance:

$$\theta_{A1} = \frac{K_{A1}C_{A1}}{1+K_{A1}C_{A1}+K_I C_I} \quad (1)$$

$$\theta_{I2} = \frac{K_{B2}C_{B2}}{1+K_{B2}C_{B2}+K_I C_I} \quad (2)$$

Then equilibrium constants are then solved for A and B:

$$K_{A1} = \frac{\theta_{A1}(1 + C_I K_I)}{(1 - \theta_{A1})C_{A1}} \quad (3)$$

$$K_{B2} = \frac{(1 - \theta_{I2})K_I C_I - \theta_{I2}}{\theta_{I2} C_{B2}} \quad (4)$$

The minimum differences in free energy can then be determined for each scenario, describing the minimum differences in free energy needed between A and I as well as I and B for the reaction of A and the inhibition of reaction of B. These values can also be combined to express the minimum total difference in free energy needed between A and B:

$$\Delta\Delta G_{A,min} = \Delta G_I - \Delta G_{A1} = -RT \ln K_I + RT \ln \left(\frac{\theta_{A1}(1 + C_I K_I)}{(1 - \theta_{A1})C_{A1}} \right) \quad (5)$$

$$\Delta\Delta G_{B,min} = \Delta G_{B2} - \Delta G_I = -RT \ln \left(\frac{(1 - \theta_{I2})K_I C_I - \theta_{I2}}{\theta_{I2} C_{B2}} \right) + RT \ln K_I \quad (6)$$

$$\Delta\Delta G_{A,min} = \Delta\Delta G_{A,min} + \Delta\Delta G_{B,min} \quad (7)$$

When A, I, and B meet the criteria of $\Delta\Delta G_{A,min}$ and $\Delta\Delta G_{B,min}$, the intended inhibition through competitive adsorption occurs (Fig. 5A). If $\Delta\Delta G_{B,min}$ is met but $\Delta\Delta G_{A,min}$ is not, then the inert will dominate the surface, impeding the reaction of A and B if formed. If $\Delta\Delta G_{A,min}$ is met but $\Delta\Delta G_{B,min}$ is not, then both A and B will react and the inert will serve no purpose.

Assumptions were made regarding the model, which are described in detail in the Supporting Information. Calculation of $\Delta\Delta G_{A,min}$ and $\Delta\Delta G_{B,min}$ in Equations 5 and 6 necessitated the assignment of the following values of reaction parameters. Though important to make an initial guess, the absolute value of K_I does not need to be known, as the equations solve for a relative value ($\Delta\Delta G$) rather than an absolute value (ΔG). Instead, an approximation will suffice; this is particularly true since the value of this guess does not significantly alter the $\Delta\Delta G$ values. The temperature and C_I , the concentration of the inert normalized by initial reactant concentration, were treated as independent variables. However, the remaining parameters needed to be assigned including surface coverages (θ) and extent of conversion (χ). The values were chosen by identifying the transition at which these parameters drastically change $\Delta\Delta G_{A,min}$ and $\Delta\Delta G_{B,min}$.

From this analysis outlined in the Supporting Information, values of 99.8% have been assigned to χ_{A1} , θ_{A1} , θ_{I2} parameters.

With the use of these model assumptions, $\Delta\Delta G_{A,\min}$ and $\Delta\Delta G_{B,\min}$ can be plotted as functions of the normalized concentration of inert and temperature (Figure 5B, 5C, 5D). Figure 5B describes $\Delta\Delta G_{A,\min}$ and $\Delta\Delta G_{B,\min}$ at 160 °C as a function of inert concentration. These curves are mirrors of each other. As inert concentration increases, $\Delta\Delta G_{A,\min}$ increases as it is more difficult for A to compete with I for active sites. However, $\Delta\Delta G_{B,\min}$ decreases since it is easier for I to compete with B for sites. Each of these values are minima; $\Delta\Delta G$ s above these values will also allow for inhibition via competitive adsorption to occur. Figures 5C and 5D add a second independent variable of temperature to describe $\Delta\Delta G_{A,\min}$ and $\Delta\Delta G_{B,\min}$, respectively. Here, a general trend is shown; as temperature increases, the minimum necessary differences of free energies of adsorption also increase. For example, $\Delta\Delta G_{A,\min}$ at equimolar C_I to C_{A0} is 37 kJ/mol at 373 K and increases to 57 kJ/mol at 573 K.

The final variable, $\Delta\Delta G_{T,\min}$, describes the total free energy difference between reactant, A, and product, B. The derived model requires this value to be at least ~65 kJ/mol at 160 °C, the featured temperature of cyclohexanol dehydration in this work, and does not depend on inert concentration. Again, this is a minimum value, and the adsorption model predicts that all $\Delta\Delta G_T$ values over 65 kJ/mol will meet the requirement for inhibition through competitive adsorption. However, since $\Delta\Delta G_T$ is a constant set by selection of the reaction chemistry, it is important to determine this quantity with high accuracy.

Here, we calculate expected $\Delta\Delta G_{\text{ads}}$ ($\Delta\Delta G_T$) for alcohol dehydration with a combination of ΔH_{ads} values from literature and ΔS_{ads} calculated from statistical mechanics assuming loss of three degrees of translational freedom (Supplementary Information). $\Delta\Delta G_{\text{ads}}$ obtained include 92.5 kJ/mol and 74.5 kJ/mol for ethanol-to-ethylene and 1-butanol-to-1-butene, respectively (Table 1). These values are significantly above the model-derived requirement of ~65 kJ/mol, consistent with our data from this work.

3.4 Extending the Use of Inert Adsorbants to New Chemistries

Inert adsorbants can be used to control reaction networks in other classes of chemistries. For each chemistry, $\Delta\Delta G_T$ is set by the selected reaction and changes only with the identities of the reactant(s) and product(s). Design variables include the selection of inert adsorbant,

concentration of the inert, and reaction temperature. Each variable can significantly affect the capability of selective reaction inhibition and should be tuned to maximally inhibit side reactions using the metrics of Section 2.3.

The choice of inert chemical will primarily influence the $\Delta\Delta G_A$ and $\Delta\Delta G_B$ values of a particular reactant-inert-product combination. Identity of inert is largely related to the experiment reaction conditions since it is necessary to be unreactive at these conditions. We demonstrate that some ketones are suitable inerts for alcohol dehydration; however, acetone reacts even at lower temperatures in the presence of acid catalysts to form mesityl oxide and eventually isobutene.^{38–40} It is necessary to identify inert molecules (under acidic conditions) over a wide range of free energies of adsorption for broader application.

Another challenge for selection of an inert adsorbant is the lack of accurate free energies and enthalpies of adsorption for many molecules, leading to the use of proton affinity as an alternative descriptor. Proton affinity can linearly relate to heats of adsorption, but it is not a perfect replacement for the free energy. Adsorption enthalpies are a function of parameters other than proton affinity including deprotonation energy and interaction energies and can widely vary from proton affinity trends, especially when considering the solution phase.^{41,42} A list of possible reactants, inerts, and products and their proton affinities have been included (Table 2). Stable nitrogen- and oxygen-containing species dominate this list including amines, ethers and ketones, but this also contains benzene, which should adsorb more strongly than alkene products.

As previously discussed, extension of this method to other unimolecular alcohol dehydration reactions may be applicable. Primary focus should be applied to the mitigation of double bond propagation in primary alkenes. This necessitates identification of new inerts if 2,5-hexanedione no longer satisfies the requirements for competitive adsorption with new chemistries. Other diketones or even benzene may be able to inhibit isomerization of the alkene product while not interfering with alcohol dehydration. A similar type of reaction is alkylamine decomposition to an alkene and ammonia. Though many inerts included in the table would be useful, it is believed that the ammonia formed in the reaction would serve as an inert adsorbant and inhibit the alkenes from adsorbing and reacting.

Another group of impactful and applicable chemistries include aromatic alkylation and acylation. An industrial example, toluene alkylation, involves the acid-catalyzed reaction of toluene and methanol to form *p*-xylene. Methanol is introduced in lower concentrations to limit

the formation of dimethyl ether (a precursor to ethylene) that can lead to coke formation and deactivation.^{43,44} Introduction of an inert, such as 2,5-hexanedione, may be able to populate active sites, preventing unfavorable xylene isomerization and disproportionation reactions. This is, however, contingent on the first step being methanol adsorption; if it is necessary for toluene to adsorb first, then addition of an inert will also inhibit the alkylation reaction. Proposed toluene alkylation mechanisms begin with methanol adsorption,^{45,46} indicating that toluene alkylation might be a good candidate for inhibition of isomerization through competitive adsorption. Similarly, other alkylation and acylation reactions may be applicable for this method.

The results described in this work present a potential tool for controlling a specific class of sequential chemical reactions. The ability to operate processes at full conversion and prevent the side reaction of products can reduce operating costs associated with separation while also reducing the cost associated with feedstock converted to byproducts. For this approach to function, the selection of an added inert adsorbant requires accurate data of the enthalpy and entropy of adsorption in zeolites. For example, Gorte et al. have conducted microcalorimetry studies of adsorption in zeolites of amines and alcohols.^{33,34,47} More encompassing data on relative adsorption on acid sites in zeolites of additional classes of organic molecules will bring us closer to increasing reaction selectivity through use of competitive adsorption.

4.0 Conclusion

In this paper, we have demonstrated high selectivity to cyclohexene during cyclohexanol dehydration at high cyclohexanol conversion through the use of an inert, 2,5-dimethylfuran (DMF), and its ring opened product 2,5-hexanedione. Hexanedione outcompeted cyclohexene for active sites, preventing cyclohexene oligomerization. Reaction rate data has also suggested that cyclohexanol dehydration is unaffected by the presence of DMF / hexanedione, indicating cyclohexanol can achieve high surface coverage of active sites when in solution. We extend to other chemistries the ability to inhibit product reaction at full conversion through the use of competitive adsorption with an inert by developing a model for competitive adsorption. The model predicts a minimum total difference in free energies of adsorption necessary at 433 K ($\Delta\Delta G_{T,min} = \sim 65$ kJ/mol). The free energy of adsorption of the inert, described relatively in the model by $\Delta\Delta G_{A,min}$ and $\Delta\Delta G_{B,min}$, must exist between the free energies of adsorption of the reactant and product and depends on inert concentration and temperature. Reactions that may benefit from the

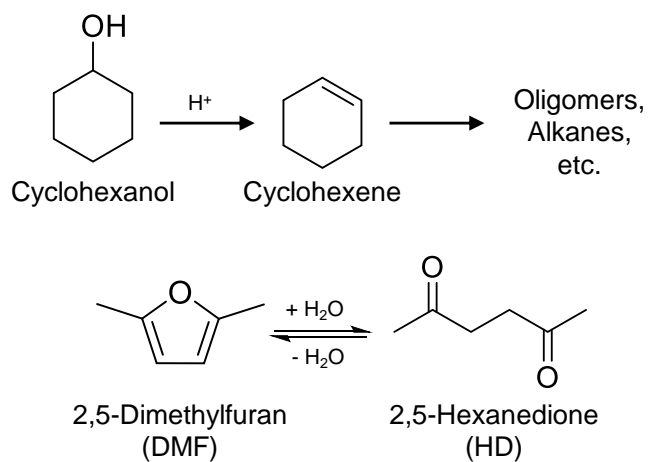
use of this method include primary alcohol dehydration, toluene alkylation, benzyl acylation, and other chemistries with strong differences in surface adsorption strength common to biomass applications.

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Scheme 1. Cyclohexanol Dehydration and 2,5-Dimethylfuran Network. Acid catalyzed dehydration of cyclohexanol to cyclohexene. Cyclohexene can undergo oligomerization and other side reactions under these conditions. The inert, 2,5-dimethylfuran, can undergo hydrolysis in the presence of water to form 2,5-hexanedione.

Table 1. Difference in Free Energy of Adsorption for Alcohol Dehydration. Differences in entropies, enthalpies and free energies of adsorption of alcohols and their dehydration products at 433 K. Entropies were derived using statistical mechanics equations, assuming three degrees of translational freedom lost during adsorption. Enthalpies were found in literature and are either experimentally determined with microcalorimetry or computationally derived with Density Functional Theory (DFT).^{18,32,34,48}

Reactant / Product	$\Delta\Delta S_{\text{ads}}$ (J/mol K)	$\Delta\Delta H_{\text{ads}}$ (kJ/mol)	$\Delta\Delta G_{\text{ads}}$ (kJ/mol)
Ethanol / Ethylene	-6.2	89.8	92.5
1-Butanol / 1-Butene	-3.5	73.0	74.5

Table 2. Proton Affinities of Organic Molecules.^{18,34–37,47–49}

Chemical	Proton Affinity (kJ/mol)
Ethylene	681.6
Water	691.0
Propene	722.5
1-Butene	747.0
Benzene	750.5
Methanol	754.3
Toluene	784.0
Cyclohexene	784.1
Butanol	789.2
<i>p</i> -Xylene	794.4
Ethanol	796.2
Propanol	800.8
Cyclohexanol	810.1
Diethyl Ether	828.4
Ammonia	857.7
2,5-Dimethylfuran	865.9
Aniline	882.5
2,5-Hexanedione	892.0
Ethylamine	909.0
<i>n</i> -Butylamine	916.3
Isopropylamine	918.6
Pyridine	922.2

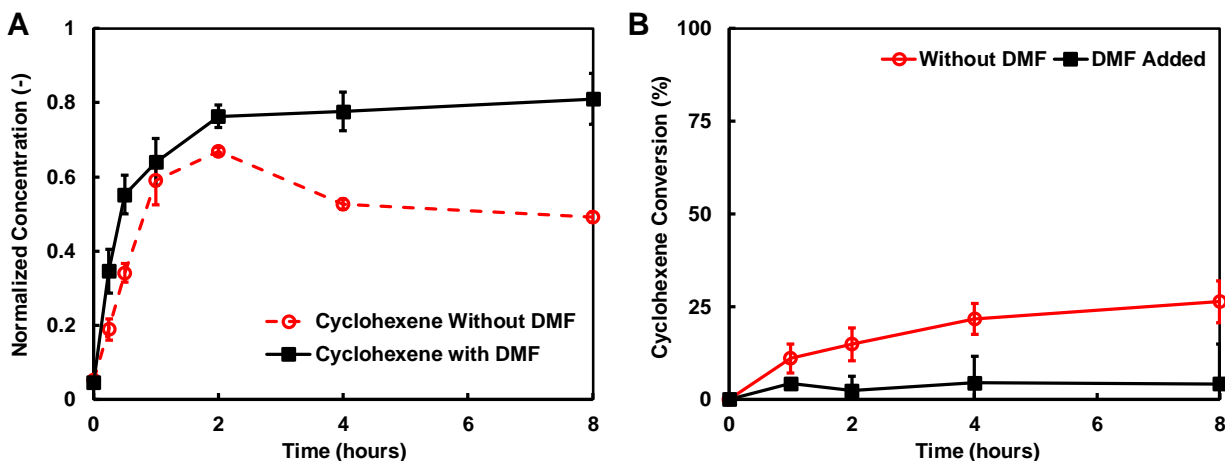


Figure 1. Cyclohexanol Dehydration and Reaction of Cyclohexene. (A) Cyclohexene normalized concentration versus time (hours) during cyclohexanol dehydration with H-BEA catalyst (Si/Al 12.5) over 8 hours at 433 K (160 °C). In experiments, 100 mL reaction solutions contained 0.5 M cyclohexanol and 1.8 mM H-BEA (0.74 M 2,5-dimethylfuran when added). Once reaction temperature was reached, the reactor was pressurized with 13.6 atm (200 psi) of nitrogen gas. (B) Cyclohexene conversion was calculated at 433 K (160 °C) for reaction solution both containing and devoid of 2,5-dimethylfuran (DMF). In both sets of experiments, reaction solutions were 100 mL in size and contained 0.5 M cyclohexene and 1.8 mM H-BEA (Si/Al 12.5) and 0.74 M 2,5-dimethylfuran, when added, and were pressurized with 13.6 atm (200 psi) of nitrogen gas.

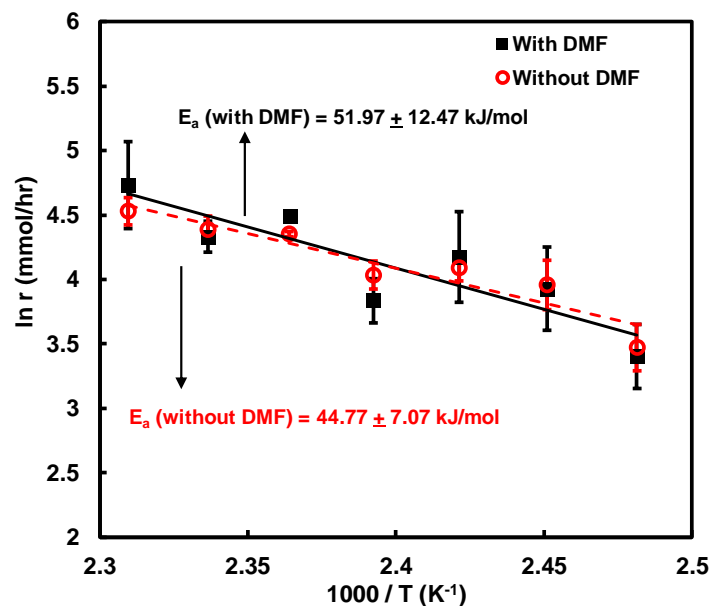


Figure 2. Arrhenius Plot of Cyclohexanol Dehydration. Reaction rates were calculated for cyclohexanol dehydration to cyclohexanol between the temperatures of 408 – 433 K (135 – 160 °C) for reaction solution both containing and devoid of 2,5-dimethylfuran (DMF). In both sets of experiments, reaction solutions were 100 mL in size and contained 0.5 M cyclohexanol and 1.8 mM H-BEA (Si/Al 12.5) and 0.74 M when DMF was added and were pressurized with 13.6 atm (200 psi) of nitrogen gas.

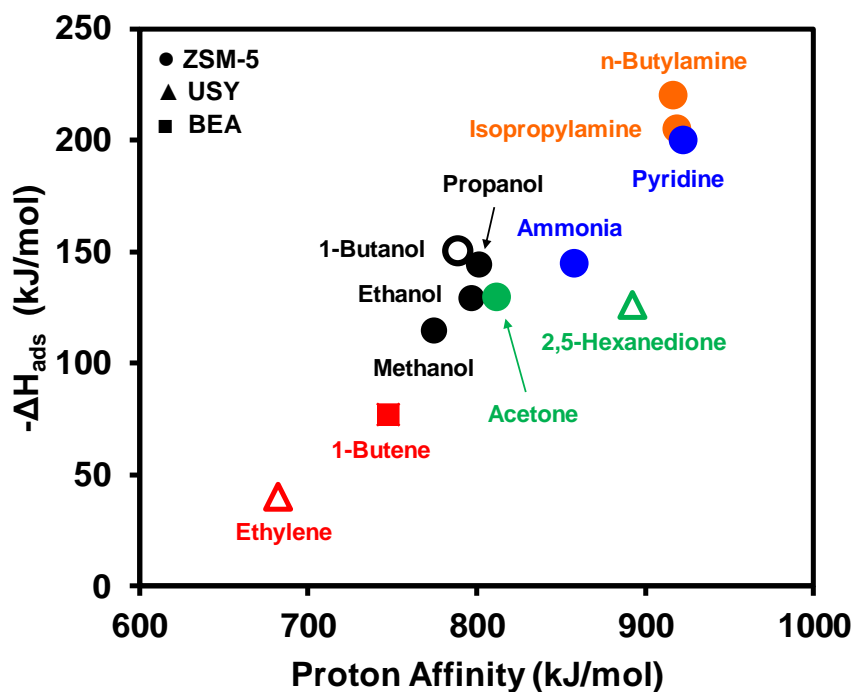


Figure 3. Enthalpy of Adsorption and Proton Affinities of Relevant Organic Molecules. Enthalpies of adsorption are presented versus proton affinities for many organic molecules found in literature.^{18,32–34,47,48} Alkenes are presented in red, alcohols in black, ketones in green, ammonia and pyridine in blue, and primary amines in orange. The shape of the point corresponds to the zeolite: USY (▲), ZSM-5 (●), and BEA (■). Filled shapes correspond to experimentally derived heats of adsorption, while unfilled represents computational results.

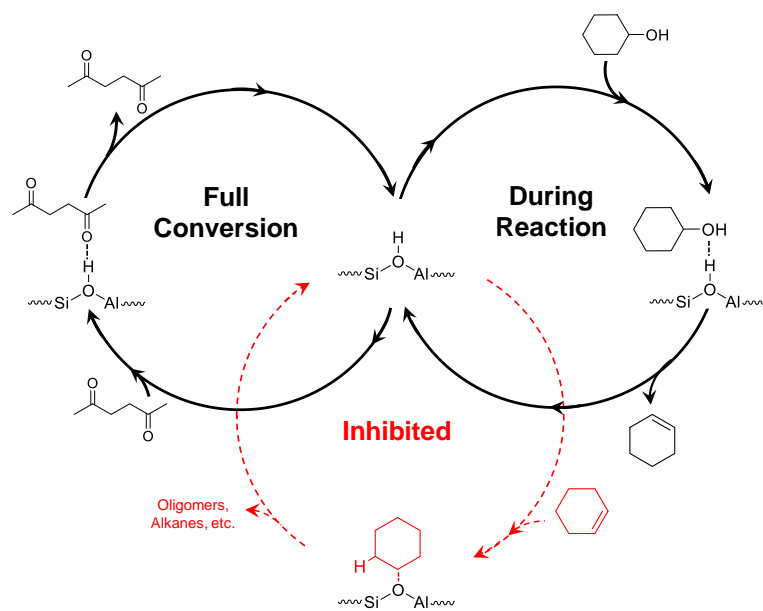


Figure 4. Adsorption Diagram of Cyclohexanol Dehydration with the Addition of Inert Inhibitor. Diagram describes three adsorption scenarios: (1) adsorption and dehydration of cyclohexanol, (2) surface domination and adsorption of 2,5-hexanedione, and (3) inhibited cyclohexene reaction and adsorption. The first adsorption/reaction occurs at all but full conversion of cyclohexanol; cyclohexanol dominates the surface. The second occurs after full conversion in which 2,5-hexanedione dominates the surface, blocking cyclohexene. The third is inhibited at all points due to stronger adsorbents, cyclohexanol and 2,5-hexanedione.

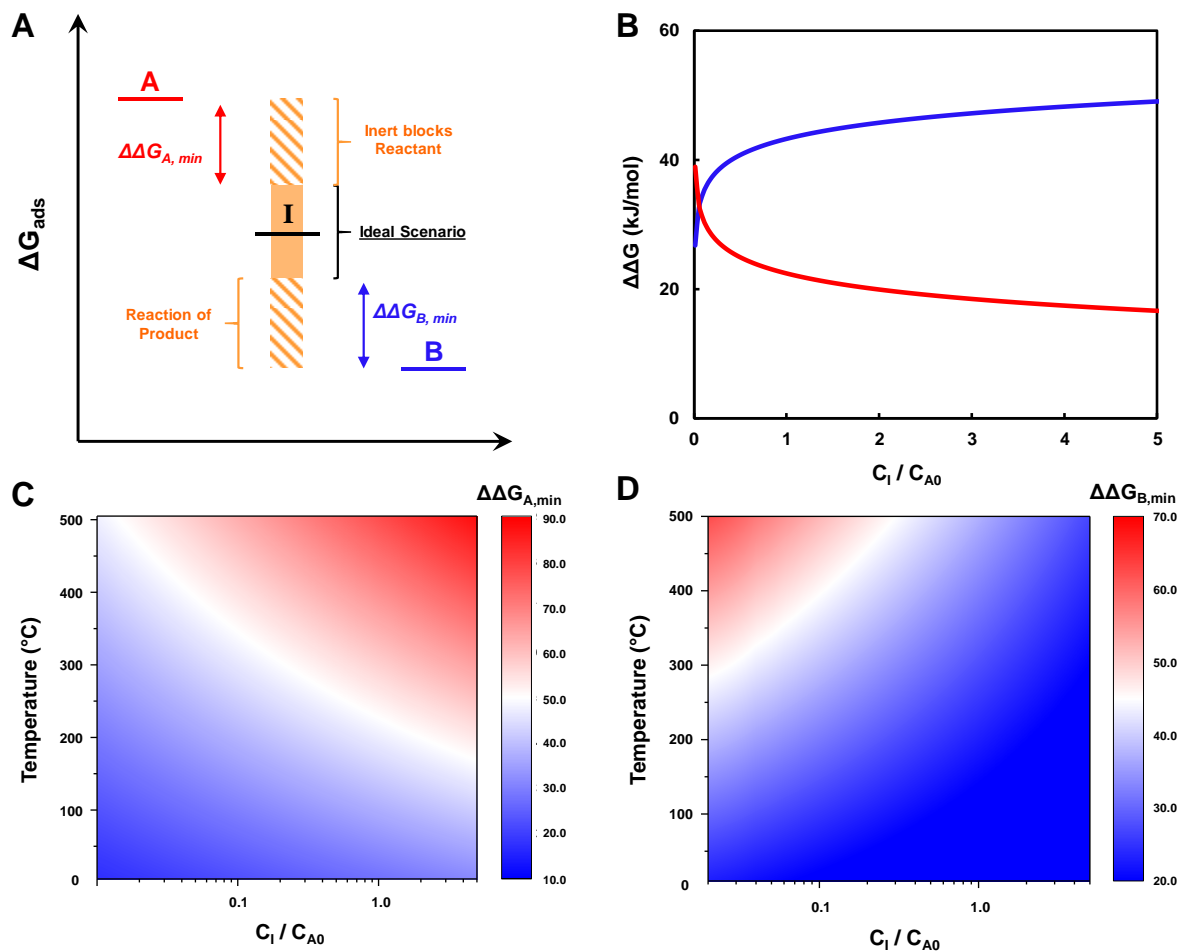
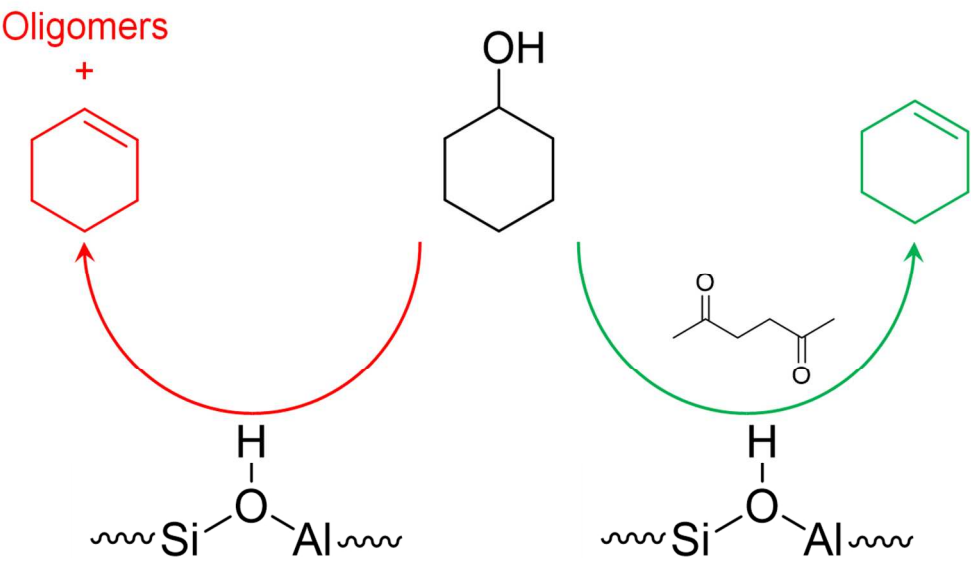


Figure 5. Model for Inhibition through Competitive Adsorption. (A) Diagram describes range of ΔG_{ads} of inert to block reaction of product, but not prevent reactant adsorption. This is represented by terms $\Delta\Delta G_{A, \min}$, $\Delta\Delta G_{B, \min}$. (B) Model showing $\Delta\Delta G_{A, \min}$ and $\Delta\Delta G_{B, \min}$ necessary to allow for successful competitive adsorption of inert over range of inert concentrations at 433 K (160 $^{\circ}\text{C}$). (C) Contour plot of $\Delta\Delta G_{A, \min}$ (kJ/mol) versus temperature ($^{\circ}\text{C}$) and normalized inert concentration. (D) Contour plot of $\Delta\Delta G_{B, \min}$ (kJ/mol) versus temperature ($^{\circ}\text{C}$) and normalized inert concentration.



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