

Supplementary Information:
**Inert Competitive Adsorption for the Inhibition of
Oligomerization of Alkenes During Alcohol Dehydration**

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S1. Inhibition of 1-Dodecene Conversion

S2. Competitive Adsorption Model for Inhibition in Series Reactions

S3. Free Energies of Adsorption

S1. Inhibition of 1-Dodecene Conversion

The inhibition of primary alkene isomerization on zeolite acid catalysts has the ability to improve overall yield of alkenes during alcohol dehydration. Though this work has shown the inhibition of cyclohexene conversion during cyclohexanol dehydration with the use of an inert, 2,5-dimethylfuran (DMF) and its hydrolysis product 2,5-hexanedione, cyclohexene is neither a primary alkene, nor is it able to isomerize.

To demonstrate the application of co-fed inerts towards inhibiting isomerization, the reaction of 1-dodecene over an H-BEA zeolite catalyst is considered (Fig. S1).

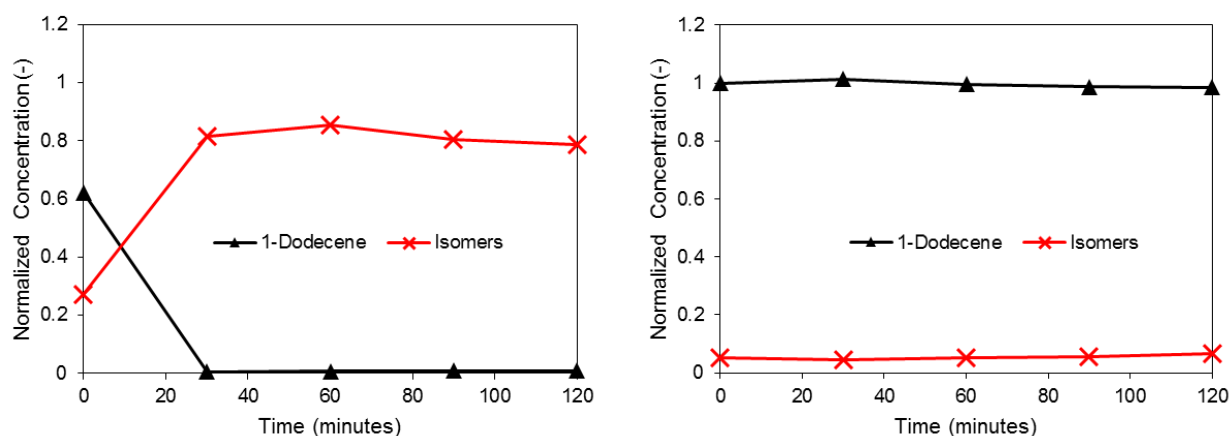


Figure S1. Inhibition of 1-Dodecene Isomerization. (A) 1-Dodecene conversion (99.2%) to isomers after two hours at 200 °C with H-BEA catalyst. 0.45M 1-Dodecene in 100 mL solution with heptane solvent, 1.8 mM H-BEA, 2 mL tridecane internal standard. (B) 1-Dodecene inhibition to isomers with 2,5-dimethylfuran in solution (1.5% conversion) after two hours at 200 °C with H-BEA catalyst. 0.45M 1-Dodecene in 100 mL solution, heptane solvent, 1.8 mM H-BEA, 8 mL 2,5-dimethylfuran, and 2 mL tridecane internal standard.

Over two hours, 99.2% conversion of 1-dodecene was achieved, compared to the same experiment with the introduction of 2,5-dimethylfuran, which yielded 1.5% conversion of 1-dodecene. The conversion of 1-dodecene occurred quickly and during the heating of the reactor (time zero sample is taken as the reactor reaches 200 °C). The results suggest that DMF/hexanedione is able to adsorb preferentially on the acid sites, blocking 1-dodecene isomerization.

S2. Competitive Adsorption Model for Inhibition in Series Reactions

An adsorption model was developed to estimate the differences in free energies of adsorption between reactant, inert and product needed for inhibition through competitive adsorption. Assumptions were made in this model and our methodology. Justification of these assumptions are as follows:

The model describes a series reaction of $A \rightarrow B \rightarrow C$ in which we attempt to inhibit the second reaction to form C. It is most applicable in the cases where the activation energies of each reaction are similar or the second reaction has a lower activation energy. This ensures a scenario in which the selectivity cannot be easily controlled by tuning acid site strength.

The method attempts to use relative adsorption strengths of the reactant, A, product, B, and an inert, I, to our advantage. In the ideal case, the reactant adsorbs strongest, followed by the inert, and finally the product ($A > I > B$) with a sizable separation between each. The purpose of the model is to determine the separation needed for high selectivities of B, and which variables can be manipulated to help in this goal.

The surface is assumed to be fully populated by the reactant until either very high or full conversion, at which the surface will be populated by the inert. This method is therefore only relevant in processes operated at high conversion. Though we have performed experiments with liquid batch reactors, this model is not phase or reactor specific and should be widely applicable.

Two scenarios of Langmuir adsorption are considered: (1) very high conversion; the last point at which surface is dominated by the reactant and (2) full conversion; the surface is dominated by the inert. These scenarios are described by the following equations:

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

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

Numerical subscripts describe the scenario (high or full conversion). Alphabetical subscripts describe the species (reactant, product or inert). Θ denotes surface coverages, K denotes the equilibrium constant, and C denotes the concentration of the species. The concentration of A in the first scenario is a function of the conversion of the reaction at that point in time. The concentration of B in the second scenario is assumed to be C_{A0} (initial concentration of A), as full conversion and no reaction of B is assumed.

The equations can be manipulated to solve for the equilibrium constants:

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

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

and finally converted to differences in free energies of adsorption:

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

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

Where $\Delta\Delta G_{A,min}$ is the absolute value of the difference between the free energies of adsorption of the inert and the reactant and $\Delta\Delta G_{B,min}$ is the same, but for the inert and the product. These values depict the lowest differences in free energies needed for inhibition through competitive adsorption.

It is important to discuss the need for initial guesses for either K_I , or K_A/K_B . As we have written Equations 5 & 6, K_A and K_B are functions of K_I , but we can consider this in reverse as well. In all cases, one of these values must have an initial guess. However, since the final value is a difference in free energies of adsorption, the initial guess is not binding and must only be an educated approximation. This is apparent when we change the initial guess in the calculation by hundreds of kJ/mol, and no difference is seen in the results of the model. Considering the values for alcohols and alkenes from a combination of microcalorimetry and statistical mechanics calculations found in Tables S2 and S3, we have chosen a respectable -150 kJ/mol for ΔG_I in our model to try to be as consistent with actual values as possible.

Next, a few key assumptions of values must be made. The first, is the value of C_{A1} or the conversion of A in the first scenario. The conversion of the reactant must be very high at this point as the surface is about to be dominated by the inert. However, it is difficult to choose an exact value with real significance. Instead, we decide to solve the model for $\Delta\Delta G_{A,min}$, keeping C_I and coverages constant and changing the reactant's conversion (Fig. S2).

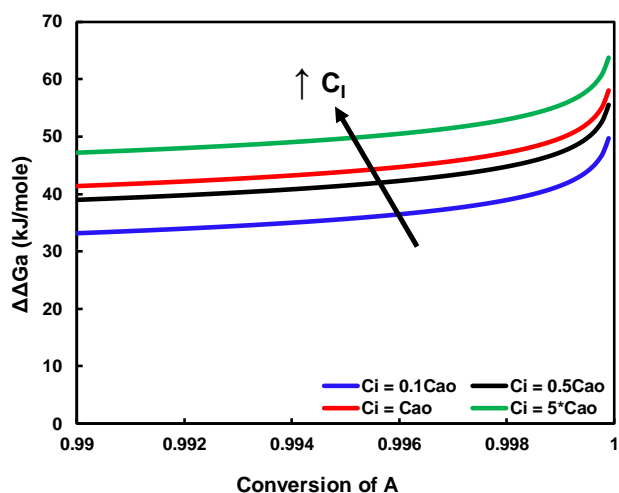


Figure S2. Difference in Free Energies of Adsorption by Changing Conversion in the First Scenario. $\Delta\Delta G_{A,min}$ is plotted versus conversion of reactant for multiple ranging values of C_I . A drastic change in the slope begins to occur at a conversion of about 99.8%.

As a significant change in the slope begins at about 99.8% conversion, we choose this as the model's value of conversion, as it is the transition point for the model.

We can perform the same exercise for surface coverages. An assumption that the surface coverage in the first scenario for A is the same as the surface coverage of I in the second scenario, is made. Also, the surface is assumed to be only dominated by two species in each scenario: (1) $\theta_{A1} + \theta_{I1} = 1$; (2) $\theta_{I2} + \theta_{B2} = 1$. The minimum differences in free energies of adsorption were plotted when changing surface coverages of the dominate species (Fig. S3).

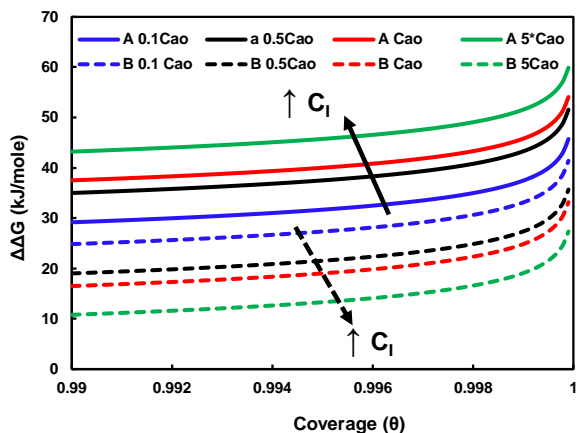


Figure S3. Differences in Free Energies of Adsorption by Changing Surface Coverages. $\Delta\Delta G_{A,\min}$ (solid lines) and $\Delta\Delta G_{B,\min}$ (dashed lines) are plotted versus site coverages for A in scenario 1 and I in scenario 2 for multiple ranging values of C_I . A drastic change in the slope begins to occur at coverages of about 99.8%.

As a change in the slope begins at about 99.8% conversion, we choose this as the model's value of coverages, as it is the transition point for the model.

To justify our choices, the model was solved for an independent variable of the minimum total difference of free energies of adsorption, differences between reactant (A) and product (B). This is referred to as $\Delta\Delta G_{T,\min}$. Here, we take one value of C_I , as equal to C_{A0} , and assume the same conversion as before and that the coverages are equal in each scenario. Coverage and derivative of the coverage are plotted versus $\Delta\Delta G_{T,\min}$ (Fig. S4).

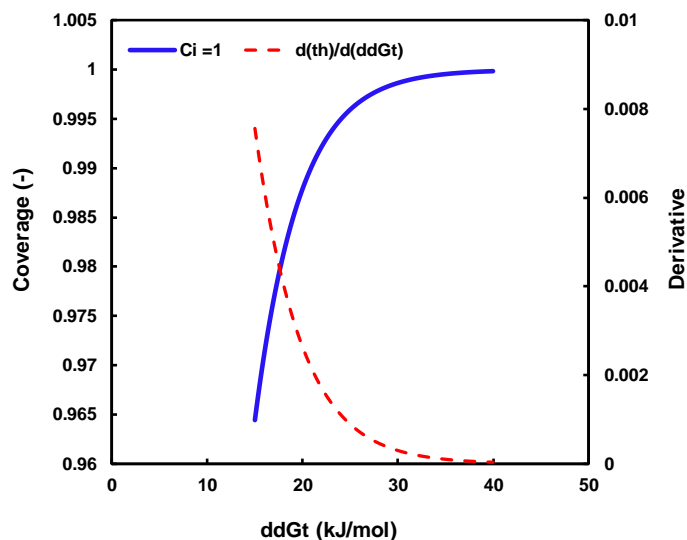


Figure S4. Coverage and Derivative as a Function of $\Delta\Delta G_{T,\min}$. Coverage (θ_{A1} , θ_{I2}) and derivative of coverage plotted versus $\Delta\Delta G_{T,\min}$. Transition in slope found at coverages of ~99.8%, corresponding to $\Delta\Delta G_{T,\min}$ of less than 30 kJ/mol.

A strong transition is seen at about 30 kJ/mol $\Delta\Delta G_{T,\min}$ and ~99.8% coverage. The shows much lower coverages are needed to give lower $\Delta\Delta G_{T,\min}$ values. Anything below this transition point show coverages unreasonable to allow for inhibition of product reaction. Above this point, we see a drastic sensitivity of $\Delta\Delta G_{T,\min}$ with respect to coverage. The derivative of the coverage underlines the transition of the slope. This analysis provides more confidence in our choices of constants values (Table S1). The model depicted in the manuscript are based on these choices.

Table S1. Model Constant Values. Choices of constant values chosen for coverages and concentrations for both model scenarios.

Constant	Value
Θ_{A1}	0.998
Θ_{I1}	0.002
Θ_{I2}	0.998
Θ_{B2}	0.002
C_{A1}	$0.998 * C_{A0}$
C_{B2}	C_{A0}

S3. Free Energies of Adsorption

Differences in free energy of adsorption of alcohols and alkenes were determined by a combination of experimental data, computational results, and calculations. Enthalpies were mainly found by microcalorimetry¹⁻³, but also by computational methods.⁴⁻⁶

Entropies of adsorption were calculated by statistical mechanics equations, assuming adsorption involves the loss of three degrees of translational freedom⁷:

$$\Delta S_{ads} = -R \left[18.6 + \ln \left(\left(\frac{MW_i}{40} \right)^{1.5} \left(\frac{T}{298.15} \right)^{2.5} \right) \right] \quad (S1)$$

Free energies of adsorption were determined with the following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \quad (S2)$$

The differences of free energies, entropies and enthalpies were taken as the absolute values of the differences from alcohol to corresponding alkene. Temperature was chosen as 433 K to be more realistic to actual alcohol dehydration conditions. Tables S2 and S3 contain these values for ethanol and 1-butanol dehydration.

Table S2. Difference in Free Energy of Adsorption for 1-Butanol Dehydration. Entropies, enthalpies and free energies of adsorption of 1-butanol and 1-butene 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).^{5,6}

Species	ΔS_{ads} (J/mol K)	ΔH_{ads} (kJ/mol)	ΔG_{ads} (kJ/mol)
Ethanol	164.2	-130.0	-201.1
Ethylene	158.0	-40.2	-108.6
$\Delta\Delta$	-6.2	89.8	92.5

Table S3. Difference in Free Energy of Adsorption for Ethanol Dehydration. Entropies, enthalpies and free energies of adsorption of ethanol and ethylene 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).^{1,4}

Species	ΔS_{ads} (J/mol K)	ΔH_{ads} (kJ/mol)	ΔG_{ads} (kJ/mol)
1-Butanol	170.1	-150.0	-223.7
1-Butene	166.6	-77.0	-149.1
$\Delta\Delta$	-3.5	73.0	74.5

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