Density Functional Theory Study of Mixed Aldol Condensation Catalyzed by Acidic Zeolites HZSM-5 and HY

Angela N. Migues,[†] S. Vaitheeswaran,^{$\dagger,\ddagger}$ and Scott M. Auerbach^{$*,\dagger,\ddagger}$ </sup></sup>

[†]Department of Chemistry and [‡]Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States

Supporting Information

ABSTRACT: We applied density functional theory to investigate the mixed aldol condensation of acetone and formaldehyde in acid zeolites HZSM-5 and HY, as a prototypical bond-forming reaction in biofuel production. We modeled the acid-catalyzed reaction in HZSM-5 and HY in two steps: keto– enol tautomerization of acetone and bimolecular condensation between formaldehyde and the acetone enol. For both acid zeolites, the keto–enol tautomerization of acetone was found to be the rate-determining step, consistent with the accepted mechanism in homogeneous acid-catalysis. Convergence studies of the activation energy for keto–enol tautomerization, with respect to cluster sizes of HZSM-5 and HY, exhibit rather different convergence properties for the two zeolites. The keto–enol activation energy was found to converge in HY to ~20 kcal/mol for a cluster with 11 tetrahedral atoms (11T cluster), which does not complete the HY supercage. In contrast, the activation energy for HZSM-5 reaches an initial plateau at a value of ~28



kcal/mol for clusters smaller than 20T and then converges to \sim 20 kcal/mol for clusters of size 26T or greater, well beyond the completion of the HZSM-5 pore. As such, completing a zeolite pore surrounding a Brønsted acid site may be insufficient to converge activation energies; instead, we recommend an approach based on converging active-site charge.

1. INTRODUCTION

The dependence of the global economy on petroleum, partnered with limited supply and environmental concerns, has increased the urgency for developing cellulosic biofuels as a renewable, carbon-neutral fuel source.¹ Biomass refinement often begins with conversion of a cellulosic biomass source to oxygenated intermediates, which can then be catalytically processed to yield biofuels or biomass-based chemicals.²⁻⁴ Although progress has been made in streamlining these processes, many production methods remain too inefficient or environmentally unfriendly for wide-scale substitution of petroleum. The mixed aldol condensation represents an example of such a process for upgrading biomass-derived species. This reaction forms a new carbon-carbon bond between, e.g., acetone and formaldehyde (Figure 1), hence converting smaller oxygenates to larger feedstocks suitable for producing fuels and chemicals. The acid-catalyzed, solutionphase aldol condensation occurs in two steps: keto-enol tautomerization as the rate-determining step followed by condensation to form the new carbon–carbon bond.^{1,4}



Figure 1. Acid-catalyzed aldol reaction between acetone and formaldehyde (HA is a general acid catalyst).

Homogeneous liquid-phase catalysis, using corrosive solutions, lacks product selectivity and produces environmentally hazardous chemical waste. Running aldol condensations in nanoporous catalysts such as acidic zeolites can mitigate the costs and environmental impacts of large-scale acidic or caustic processing^{1,4} and may confer new and useful selectivities over product formation.^{5–7} However, it remains unclear whether confinement in zeolite nanopores alters the conventional mechanism of aldol condensation. In this article, we investigate this question through quantum calculations via density functional theory (DFT) applied to cluster models of zeolites.

Zeolites are microporous, alumino-silicates composed of TO_4 (T = Si or Al) subunits, which form larger 3-dimensional structures consisting of channels, intersections, and cages.⁸ Several properties of zeolites distinguish them from other solid catalysts; these include the molecular-sized dimensions of the pores, strong Brønsted acid sites, and hydrothermal stabilities allowing relatively facile catalyst regeneration.^{8,9} Confinement of guest molecules within zeolite pores can perturb guest electronic structures and constrain reactive geometries, hence influencing (increasing or decreasing) rates for reaction paths that occur outside the zeolite.^{5,7,9,10} In the context of aldol chemistry, it remains unclear whether the second step of acid-

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catalyzed aldol condensation, the bimolecular combination step, can proceed rapidly in the confined spaces of zeolite nanopores. Here we investigate the energetics underlying aldol condensation for medium- and large-pore zeolites HZSM-5 and HY, respectively, to determine if pore size alters the conventional mechanism of aldol condensation.

Relatively few computational studies of zeolite catalysis have investigated aldol chemistry, and these have focused on the tautomerization step.^{11,12} For example, computational work by Boekfa et al.¹¹ on acetone tautomerization in acid zeolites HFER, HZSM-5, and HMCM-22 suggests that relative strengths of host-guest hydrogen-bonding interactions with Brønsted acid sites at reactant (adsorbed acetone) and transition state are critical for determining activation energies. Tautomerization activation energies and endothermic reaction energies were found to increase with decreasing zeolite pore size, as smaller pores perturb host-guest hydrogen bonding. However, in the study by Boekfa et al., the condensation step was not investigated and only a few zeolite atoms were allowed to relax. Also, though Boekfa et al. performed calculations on relatively large ("34T") zeolite clusters, there was no study of convergence with respect to system size, leaving open the question of an optimal cluster size for future calculations. In the present work we address this question of convergence with cluster size for HY and HZSM-5, finding different convergence properties for the two zeolites.

In the present study we applied clusters to model the aldol condensation of acetone and formaldehyde (Figure 1) catalyzed by zeolites HZSM-5 and HY, important examples of mediumand large-pore zeolites. Although biomass-derived aldehydes such as furfural are more industrially relevant,⁵ our study of formaldehyde condensation with acetone establishes key methodological parameters for a future computational study of furfural condensation. Our calculations below on both zeolites corroborate the homogeneous-phase mechanism, involving slow keto-enol tautomerization and fast condensation. We thus seek to converge the keto-enol activation energy for both acid zeolites with respect to cluster size. We note that such convergence is possible despite the presence of long-range contributions to host-guest interactions. This is because when computing activation energies, the energy differences between nearby configurations, the slowly varying, long-range contributions essentially cancel for large enough but finite cluster sizes.¹³ The question remains whether HY and HZSM-5 ketoenol barriers converge at similar cluster sizes. We address this below, finding that HY barriers converge faster than those of HZSM-5. The system-size study of barriers in HZSM-5 reported below suggests two regimes: a small-to-medium cluster regime, possibly mimicking catalysis at Brønsted acid sites on external surfaces of an HZSM-5 crystallite, and a medium-to-large cluster regime capturing intracrystalline catalysis. This intracrystalline regime was found to emerge only after Brønsted acid-site partial charges reach plateau values, suggesting a new approach for establishing convergence with respect to zeolite cluster size.

The remainder of this article is organized as follows: Section 2 describes the cluster models and computational methods employed; Section 3 provides results and their discussion; and Section 4 offers a summary and concluding remarks.

2. METHODS

2.1. Zeolite Models. In this study, we used cluster methods to model the acid-catalyzed aldol condensation between

acetone and formaldehyde in HZSM-5 and HY clusters of various sizes. In general, we specify cluster size by indicating the number of tetrahedral atoms (Si or Al) in a given cluster. For example, an "11T" cluster contains one Al atom and ten Si atoms (in addition to several oxygens and hydrogens). The designation 11T does not give the precise atom count, connectivity, or three-dimensional structure of a cluster (these are given in the Supporting Information for selected, key clusters studied below). Rather, the notation 11T gives a rough sense of cluster size compared to, e.g., 20T or 37T.

We do not use QM/MM embedded cluster methods below because of numerical instabilities we have encountered during transition-state searches with such embedded clusters. Nor do we use periodic plane wave approaches because of the very large unit cells in HZSM-5 ("MFI" structure type) and HY ("FAU" structure type) zeolites.¹⁴ Instead, we apply the medium-sized clusters shown in Figure 2A (HZSM-5) and



Figure 2. (A) HZSM-5 zeolite cluster and (B) HY zeolite cluster, where the 11T cluster is shown as ball and stick with the extended framework as wire mesh; the 11T cluster used is shown as an inset, where oxygen numbers are defined for consistency with those in HY. For comparison between active sites in HY and HZSM-5, we denote the two active oxygens as O1 and O2 in both structures; these are not the crystallographically sanctioned labels in HZSM-5.

Figure 2B (HY) to efficiently investigate the relative energetics of the tautomerization and condensation kinetics in both zeolites. Such clusters capture approximately half the HZSM-5 pore intersection and the HY supercage and may be viewed as providing rough models of Brønsted acid-site catalysis on external zeolite surfaces. We performed a cluster-size convergence study using clusters in the 3T-37T range for both zeolites. Such a study allows comparison of system-size convergence between HY and HZSM-5 and investigation of the role of "completing a pore" versus converging electronic properties such as acid-site charge.

Zeolite clusters used in this study were extracted from the Xray crystallographic data of Czjzek et al.¹⁵ for HY and of van Koningsveld et al.¹⁶ for HZSM-5. Here we employ the common nomenclature that zeolite rings with *n* T atoms are denoted *n*-rings. The HY framework structure is composed of a tetrahedral network of roughly spherical cages, each connected to four adjacent cages through 12-ring windows of nominal diameter ~7.4 Å¹⁴. In contrast, HZSM-5 features 10-ring channels running along the crystallographic *b*-axis, which intersect with 10-ring sinusoidal channels running along the

a-axis, all of which exhibit a diameter of about 5.5 Å¹⁴. The cluster models of HZSM-5 were all constructed at the intersection of the 10-ring straight and sinusoidal channels and were built around the Brønsted acid site between Si(2) and Si(8), centered on O(13) (see Figure 2A).¹⁷ Because of its proximity to the intersection, O(13) is a catalytically relevant site.¹⁷ The HY cluster models were centered on O(1) in the 12-ring window with the Brønsted acid site pointed directly into the supercage (see Figure 2B). The applicability of the O(1) site as the Brønsted acid site was previously determined to be a catalytically relevant position.¹⁷ We note in Figure 2A,B that the two active oxygens, O(13) and O(1) in HZSM-5 and HY, respectively, are denoted as O1 in both structures for ease of comparison between active sites in HY and HZSM-5; these are not the crystallographically sanctioned labels.

In general, we seek to terminate all zeolite clusters with fixed OH groups to mimic the electronic environment of zeolites. However, doing so may introduce strong steric effects between capping hydrogens. We found such steric overlaps, e.g., in the 11T HZSM-5 cluster shown in Figure 2A. The 11T HZSM-5 cluster model shown in Figure 2A was thus terminated at silicon atoms with capping hydrogens placed along the vector toward nearest-neighbor oxygens at a Si-H bond distance of 1.4 Å and subsequently frozen. In the 11T HY cluster, shown in Figure 2B, terminal framework oxygens were capped with hydrogens, placed in the location of the next framework silicon atom at an O-H bond distance of 0.9 Å, and subsequently frozen. In HY, the two silicon atoms at the top of the 12-ring window were "capped" with hydrogens instead of hydroxyl subunits to minimize spurious hydrogen bonding at the edge of the cluster. Restraining terminal atoms mimics the covalent footprint of the zeolite framework structures.

Our cluster convergence study involved the following cluster sizes for HZSM-5 and HY:

- HZSM-5 (11 clusters): 3T, 5T, 9T, 11T, 15T, 20T, 20T', 21T, 26T, 30T, 37T
- HY (9 clusters): 3T, 5T, 7T, 9T, 11T, 13T, 15T, 20T, 30T.

We note that three similarly sized cluster models of HZSM-5, shown in Figure 3, have been expanded differently around the same Brønsted acid site. In the first cluster model (denoted I), the 10-ring window belonging to the straight channel has been completed and parts of the extended straight channel are included, comprising 20T total size. In the second (II), the 10ring from the sinusoidal channel has been completed and augmented further with three 5-rings, giving a total size of 21T. The third cluster (III) represents the intersection of straight and sinusoidal channels, in which both 10-ring windows are completed to comprise a 20T cluster size. These three clusters turn out to play an important role in the transition of keto enol barriers from a small-to-medium plateau regime to a medium-to-large intracrystalline regime.

2.2. Computational Details. The B3LYP hybrid density functional was used with the 6-311G(d,p) basis set as implemented with the Gaussian09¹⁹ suite in all calculations presented herein.^{20,21} This model chemistry has been shown by Fermann et al.¹³ to capture ~90% of activation barriers for proton transfer processes in zeolites. We thus expect similar performance in describing acid-catalyzed aldol chemistry. Dispersion corrections using the Grimme²² approach, as implemented in the Jaguar²³ computational chemistry software suite, were applied to all structures (reported in the Supporting



Figure 3. Three HZSM-5 cluster models of similar size: (A) cluster I is a 20T model of the 10-ring straight channel; (B) cluster II is a 21T model of the 10-ring sinusoidal channel with added pentasil rings; (C) cluster III is a 20T construction of two 10-rings at the intersection of straight and sinusoidal channels (looking down straight channel); and (D) side view of cluster III. Images were rendered using Maestro.¹⁸

Information); these were not found to qualitatively influence the computed trends, likely because of the importance of sitespecific hydrogen bonding in zeolite-catalyzed aldol chemistry. Atomic charges were calculated using the Merz–Kollman procedure to reproduce the electrostatic potential.^{24,25} During the optimization of geometries and searches for transition states, all atoms in the zeolite clusters were allowed to relax except for terminal "capping" hydrogens on either silicon (HZSM-5) or oxygen (HY) atoms, which were fixed.

To reduce computational cost, a semiempirical, PM6 approach was used to quickly explore plausible transitionstate conformations. Before all all transition states were located, a constrained optimization was performed, in which atoms thought to be involved in the reaction coordinate were frozen, allowing the remaining atoms to relax. Previous computational work on keto-enol acetone tautomerization¹¹ suggested likely reaction coordinates for this step. In particular, the zeolite protonates the acetone carbonyl while the methyl group donates a proton. As such the acetone carbonyl oxygen, methyl carbon, the two involved protons, and the zeolite O1 and O2 atoms (see Figure 2 for oxygen labels) were frozen at various configurations along a likely reaction coordinate, yielding different initial conditions for full transition-state searches. For the second step, our previous experience and chemical intuition suggested that the enol would react with the adsorbed formaldehyde at a carbon-carbon distance of about ~2.6 Å, forming the new carbon-carbon bond while simultaneously donating a proton (from acetone to the zeolite) and accepting a proton (from the zeolite to the formaldehyde carbonyl).

These constrained optimizations were followed by unconstrained transition-state searches. All transition states were located using the Berny optimization algorithm,²⁶ confirmed as first-order saddle points by normal-mode analysis (NMA), and by steepest-descent calculations to confirm that transition states connect with desired reactant and product minima. NMA was performed on all minima to confirm that they are true minima

with all real vibrational frequencies. Confirmed transition states were then used as initial transition-state geometries in higherlevel calculations using B3LYP. Once found in a given smaller cluster, the corresponding transition-state structures were then used as initial geometries in larger cluster sizes. All energies reported are bare potential energies. Energetics corrected by zero-point vibrational energy and free-energy corrections are provided in the Supporting Information; these corrections were not found to change any of the computed trends.

3. RESULTS AND DISCUSSION

Here we report our results for the mixed aldol condensation reaction between acetone and formaldehyde in three parts. In Section 3.1, we report the stepwise, gas-phase (uncatalyzed) mixed aldol condensation. Section 3.2 details the acid zeolitecatalyzed mixed aldol condensation in 11T models of HZSM-5 and HY. Section 3.3 describes the convergence of keto—enol tautomerization barriers with respect to cluster size, with analysis of acid-site atomic charges to rationalize the cluster-size dependence of activation energies.

3.1. Gas-Phase, Uncatalyzed Mixed Aldol Condensation. The complete aldol condensation actually consists of three steps: (*i*) keto-enol tautomerization, (*ii*) condensation between the enol and aldehyde, and (*iii*) elimination of water to yield an olefin.^{11,12,27} Below we refer to the first step as "tautomerization" and the second as "condensation". We do not consider the third step in the present study. The reaction including steps one and two is referred to below as the mixed aldol condensation.

The gas-phase tautomerization of acetone, having been previously investigated computationally,¹¹ is used herein to establish the applicability of our model chemistry and to provide a baseline for understanding the catalytic chemistry. A concerted mechanism for enol formation has been previously established^{11,28–34} and hypothesized to be the rate-determining step in the overall reaction.¹²

Figure 4 shows the potential energy diagram for the gasphase tautomerization of acetone. The B3LYP/6-311G(d,p)



Figure 4. Bare electronic energy profile (kilocalories per mole) and molecular structures of the gas-phase, uncatalyzed tautomerization of acetone. Reactant state (acetone), transition state, and product state (acetone enol) are illustrated.

activation energy is 68.2 kcal/mol and the reaction energy is 12.7 kcal/mol. These results agree well with the previously calculated activation and reaction energies computed by Boekfa et al. of 68.0 and 9.9 kcal/mol, respectively, using the M06-2X functional.¹¹ Our results also agree well with energies computed using second-order Möller–Plesset perturbation theory with 6- $31G^{**}//cc$ -pvtz and 6- $31G^{**}$ basis sets,^{33,34} which give

activation energies of 64.0 and 69.2 kcal/mol, respectively, and reaction energies of 11.6 and 13.1 kcal/mol. Moreover, the calculated reaction energy is in reasonable agreement with the experimental gas-phase enthalpy of 10 ± 2 kcal/mol, measured by gas-phase ionization of suitable precursors.^{33,34}

Figure 5 shows the potential energy diagram for the gasphase condensation between the acetone enol and form-



Figure 5. Bare electronic energy profile (kilocalories per mole) and molecular structures of the gas-phase, uncatalyzed condensation between acetone enol and formaldehyde. Reactant state (acetone enol and formaldehyde), transition state, and product state (aldol) are illustrated.

aldehyde. The activation energy is calculated to be 15.0 kcal/mol, with a reaction energy of -22.0 kcal/mol. The gas-phase barrier for condensation is significantly less than that for tautomerization, consistent with the notion that tautomerization is the rate-determining step in the gas phase.

3.2. Mixed Aldol Condensation Catalyzed by Acid Zeolites. Next we discuss the mixed aldol condensation catalyzed by acid zeolites HZSM-5 and HY in 11T cluster models. In both zeolites mixed aldol condensation begins with the adsorption and subsequent tautomerization of acetone at the Brønsted acid site. Boekfa et al. previously modeled acetone tautomerization in HZSM-5 using cluster methods.¹¹

3.2.1. Tautomerization Catalyzed by HZSM-5 and HY. Panels A and B in Figure 6 show potential energy diagrams for the tautomerization of acetone in HZSM-5 and HY, respectively. The activation energies in 11T cluster models of HZSM-5 and HY are 28.1 and 19.3 kcal/mol, respectively. These results are consistent with the trend found by Boekfa et al. of decreasing activation energy with increasing pore size.¹¹ However, our computed activation energy in the 11T cluster model of HZSM-5 is significantly higher than the value of 20.5 kcal/mol calculated by Boekfa et al. using a 34T cluster.¹¹ The convergence of activation energies with respect to cluster size will be discussed in detail in the next section.

We wish to be careful not to overinterpret geometrical details of these 11T calculations because of the relatively small size of these clusters. However, in the cluster convergence study detailed in the next section, we find that the 11T HY cluster is essentially converged with respect to system size, while the 11T HZSM-5 cluster is characteristic of a plateau regime that may mimic catalysis on external HZSM-5 surfaces. As such, we seek to understand key differences in HY and HZSM-5 geometric and electronic structures in these 11T clusters.

The tautomerization barriers from our 11T cluster models are controlled by relative strengths of hydrogen bonding at the Brønsted acid site. In HY, the barrier is lower than in HZSM-5 because of stronger hydrogen bonding at the Brønsted acid site



Figure 6. Bare electronic energy profile (kilocalories per mole) and molecular structures of the tautomerization of acetone in an 11T cluster model of (A) HZSM-5 and (B) HY obtained at the B3LYP/6-311G(d,p) model chemistry. Reactant state (acetone), transition state, and product state (acetone enol) are shown in both A and B.



Figure 7. Bare electronic energy profile (kilocalories per mole) and molecular structures for condensation between the acetone enol and formaldehyde in 11T cluster models of (A) HZSM-5 and (B) HY obtained at the B3LYP/6-311G(d,p) model chemistry. Reactant pair (acetone enol and formaldehyde), transition state, and product state (aldol) are shown in both A and B.

in the HY transition state. To understand the origin of this hydrogen bonding difference, we consider distances, angles, and charges. In particular, the intermolecular $O(3)H_2 \cdots O(1)$ distances (see Figure 6 for atom labels) at the transition states are similar in both HY and HZSM-5, whereas the O(3)-H₂... O(1) complex is slightly more linear in the 11T model of HY (168.3°) than it is in HZSM-5 (163.2°) . As such, the HY $O(3)H_z \cdots O(1)$ hydrogen bond may be somewhat less sterically hindered than it is in HZSM-5. Perhaps more important is the acid-site charge, which correlates with hydrogen-bonding strength. We have computed acid-site charge in the bare zeolite 11T cluster models by summing the ESP charges from $O2-Al-O1-H_z$ atoms (see labels in Figure 2), finding activesite charges of +0.17 in HZSM-5 and +0.34 in HY, correlating with a lower barrier in HY. In the next section we expand our analysis of active-site charge as it relates to convergence with respect to cluster size.

The data in Figure 6A,B also show that the tautomerization reaction is less endothermic in the 11T model of HY compared to the 11T HZSM-5 cluster because of stronger hydrogen bonding of the adsorbed enol in HY. The enol in HY exhibits an $O(1)\cdots$ H_z distance of 1.78 Å (see Figure 6 for atom labels) and an $O(1)\cdots$ H_z-O(3) angle of 164.9°, as compared to 2.55 Å and 128.5° in HZSM-5. These findings suggest that subtle differences in zeolite cluster models can produce significant differences in host–guest hydrogen-bonding properties.

3.2.2. Condensation Catalyzed by HZSM-5 and HY. After acetone tautomerization produces the activated enol, a new carbon-carbon bond forms in the condensation reaction with formaldehyde. The zeolite-catalyzed reaction begins with coadsorption of the reactant pair in the zeolite framework.

The potential energy diagrams for condensation catalyzed by HZSM-5 and HY are shown in panels A and B of Figure 7, respectively.

The activation energies in these 11T cluster models of HZSM-5 and HY are 2.0 and 0.4 kcal/mol, respectively. The condensation barriers in HZSM-5 and HY are thus significantly lower than those for the uncatalyzed, gas-phase condensation and also substantially smaller than the barriers for zeolitecatalyzed tautomerization. These 11T cluster models suggest that acetone tautomerization remains the rate-determining step of acetone/formaldehyde mixed aldol condensation even in zeolite pores. Because of the substantial difference in these tautomerization and condensation barriers, we find it extremely unlikely that this conclusion will change for larger clusters. We note that considering zeolite catalysis of mixed aldol condensation between larger guest molecules such as the more industrially relevant acetone/furfural may change this mechanistic picture; we will report on this in a forthcoming publication. We now proceed to study the convergence of acetone tautomerization barriers with respect to cluster size.

3.3. Cluster Size Convergence of Acetone Tautomerization in HZSM-5 and HY. Conventional wisdom in zeolite cluster modeling suggests that completing a pore surrounding a given active site is sufficient to capture the effect of guest molecule confinement. To test this assumption, we investigate the dependence of acetone tautomerization barriers on HZSM-5 and HY cluster sizes. The previously computed acetone tautomerization barrier in HZSM-5 of 20.5 kcal/mol, obtained by Boekfa et al. with a relatively large cluster model (34T), serves as a comparison point for our HZSM-5 study.¹¹ Figure 8 shows the dependence of the acetone tautomerization barriers



Figure 8. Dependence of keto–enol tautomerization bare electronic activation energy with respect to system size in both HZSM-5 and HY zeolites. Two distinct regimes in HZSM-5 are labeled A and B.

with respect to increasing cluster size in both HZSM-5 and HY zeolites. The activation energies in HZSM-5 and HY exhibit different dependencies on system size. In particular, convergence in HY is achieved at smaller system sizes (9T-11T) compared to HZSM-5 (26T), where larger clusters were found to be necessary to establish convergence.

In HY activation energies converge rapidly to ~19 kcal/mol for cluster sizes in the 9T-11T range. To our knowledge, activation energies for acetone tautomerization in HY have not been determined, neither experimentally nor theoretically. However, our computed activation energy compares well to the value obtained in zeolite MCM-22,¹¹⁷ which contains 12rings as does HY. In contrast, for HZSM-5 we found two distinct regimes in Figure 8, involving clusters larger or smaller than ~20T. For HZSM-5 clusters larger than 20T, acetone tautomerization barriers converge to 20.5 kcal/mol, which agrees essentially perfectly with the previously determined value from Boekfa et al.¹¹ For HZSM-5 clusters smaller than 20T, we observe in Figure 8 a broad plateau of barriers at the significantly higher value of ~ 27 kcal/mol. The stability of this broad plateau region suggests the possibility that this regime is chemically relevant, e.g., to catalysis on HZSM-5 external surfaces. We will investigate this possibility in future work.

Figure 8 also shows that there are three similarly sized HZSM-5 clusters connecting these two regimes, with activation energies spanning the range of $\sim 20-28$ kcal/mol. Although these clusters are similar in size, they are structurally distinct in that each has been expanded about the Brønsted acid site in a different manner (see Figure 3). We recall that cluster I includes a 10-ring from the straight channel; cluster II comprises a 10-ring from the sinusoidal channel with additional pentasil rings; and cluster III involves the intersection of the two 10-rings.

The activation energy from cluster I agrees with the 11T cluster model, demonstrating that completion of a 10-ring surrounding an active site in HZSM-5 may be insufficient to converge reaction barriers. The barrier from cluster III agrees well with those from larger clusters such as 30T and 37T, making cluster III the smallest cluster representing the intracrystalline regime. These results beg the following question: which system property governs barriers in cluster

models of zeolites? Our analysis of the 11T clusters above suggests that active-site charge is a key property to consider.

Figure 9 shows the dependence of total active-site charge with respect to (A) system size and (B) activation energies, in



Figure 9. Dependence of active-site charge with respect to (A) system size and (B) bare electronic activation energy in both HZSM-5 and HY, where I, II, and III denote similarly sized cluster models of HZSM-5 (defined previously in Section 2.1). The dashed line and circles appearing in panels A and B were added to serve as a visual aid.

both HZSM-5 and HY. The total charge was obtained by summing ESP charges of individual atoms in the active sites $(O2-Al-O1-H_z)$ of the bare zeolites without guest molecules. In HZSM-5, the total charge on the active site becomes increasingly positive with respect to increasing cluster size (Figure 9A), with a step increase for the critical clusters I, II, and III discussed above. Figure 9 also shows that as positive charge accumulates on the HZSM-5 active site, activation energies decrease (Figure 9B) because of increasing host–guest hydrogen-bond strength. That is, the charge of the active site is directly related to its acidity and thus to the strength of hydrogen bonding between the guest and Brønsted acid site. In HY, a different trend is observed; active-site charge very weakly decreases with increasing cluster size (Figure 9A), with no discernible correlation to activation barriers (Figure 9B).

These results suggest that sheer zeolite cluster size may be an insufficient criterion for converging barriers with respect to system size. The correlation between active-site charge in bare zeolite clusters, and resulting activation energy, suggests a new criterion for converging barriers with respect to zeolite cluster size. This approach is especially promising considering that determining active-site charges in bare zeolites does not require transition-state searches, which can be computationally

expensive. The question remains why the trends in HY and HZSM-5 are so different; we will consider this in future work.

4. SUMMARY AND CONCLUSIONS

We have applied density functional theory to model the mixed aldol condensation reaction between acetone and formaldehvde in HY and HZSM-5 acid zeolites. This reaction is an important prototypical carbon-carbon bond-forming reaction, requiring study to optimize biofuel and biomass-based chemical production processes. We have applied the B3LYP/6-311G-(d,p) model chemistry and have computed all relevant energy corrections, i.e., Grimme dispersion, zero-point vibrational energy, enthalpy, and free-energy corrections. We have studied this mixed aldol condensation in two steps, tautomerization and condensation, and have shown that both HY and HZSM-5 greatly reduce the activation energies of both steps relative to the gas-phase barriers through extensive zeolite-guest hydrogen bonding. Using cluster models with 11 tetrahedral atoms ("11T" clusters) for both zeolites, we have found that acetone keto-enol tautomerization remains the rate-determining step of this mixed aldol condensation in zeolites, consistent with the mechanism in homogeneous acid catalysis.

We have examined the convergence of acetone tautomerization barriers with respect to cluster size for both HY and HZSM-5 zeolites. We considered cluster sizes 3T-30T for H, and 3T-37T for HZSM-5. For HY, this barrier was found to converge relatively rapidly to ~20 kcal/mol for a cluster of size 11T, which does not complete the HY supercage. In contrast, the tautomerization barrier in HZSM-5 was found to reach an initial plateau value of ~28 kcal/mol for clusters in the broad range of 3T-20T. For HZSM-5 clusters larger than 20T, well beyond the completion of an HZSM-5 10-ring, the acetone tautomerization barrier converges to ~ 20 kcal/mol. The smallest HZSM-5 cluster that produces the converged barrier includes 10-rings from both straight and sinusoidal HZSM-5 channels. We speculate that the breadth and stability of the 3T-20T plateau for HZSM-5 may indicate chemical relevance for this higher activation energy, pertaining possibly to zeolite catalysis on Brønsted acid sites on external surfaces of HZSM-5. Further study is required to investigate this idea.

Our results show that completing a zeolite pore surrounding a Brønsted acid site may be insufficient to converge activation energies, especially for HZSM-5. We found instead a strong correlation between active-site charge, summing ESP charges over $O2-Al-O1-H_z$ atoms in bare zeolites, and the corresponding acetone tautomerization barrier, especially for HZSM-5. The active-site charge convergence criterion is especially promising because determining active-site charges in bare zeolites does not require transition-state searches. More research is required to determine why the dependence of active-site charge on cluster size is different for different zeolite frameworks.

ASSOCIATED CONTENT

Supporting Information

Gaussian 09 citation; thermodynamic energy corrections; energy corrections for all HZSM-5 and HY clusters; energy corrections for gas-phase, uncatalyzed reaction; optimized structures for keto-enol tautomerization in 11T HZSM-5 and in 11T HY; optimized structures for condensation in 11T HZSM-5 and in 11T HY; additional optimized structures for keto-enol tautomerization in HY and in HZSM-5; and

references. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: auerbach@chem.umass.edu.

Notes

The authors declare no competing financial interest.

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