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Selective ketonization of acetic acid over HZSM-5: The importance of acyl species and the influence of water



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1. Introduction

Bio-oil derived from the fast pyrolysis of biomass is a complex mixture of oxygenated compounds typically containing furanics, phenolics, carboxylic acids, and other small oxygenates [1–13]. In recent years, upgrading bio-oil has been the subject of significant interest due to its potential as an alternative energy source and for mitigating environmental challenges. Two very significant challenges are associated with the upgrading of bio-oil to fuels and chemicals. The first is the fact that it is thermally unstable, with compounds condensing to solids upon aging at room temperature. The second challenge is due to the large amounts of light C_2 – C_3 oxygenates that are converted to low-value light gases after conventional upgrading via hydrotreating, limiting the potential for incorporation of the biomass-derived species into the gaso-line/diesel fuel range [14].

Acetic acid is largely responsible for both of these challenges. It is the most abundant single compound in bio-oil [3,15], and its acidity is known to present corrosion problems and promote polymerization of other species present in the mixture. The resulting solids are not readily upgraded and they accelerate catalyst deactivation, which is a major concern for upgrading of pyrolysis oils [1–13]. In addition, the fact that acetic acid contains only

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ABSTRACT

The ketonization of acetic acid over HZSM-5 is investigated via a combination of temperature-programmed techniques (TP), IR, and reaction kinetics. TP experiments demonstrate the generation of stable acyl intermediates that require higher temperatures to facilitate C–C coupling with a second acetic acid molecule. Near-exclusive selectivities for the ketonization reaction devoid of significant sequential aldol condensation are observed at temperatures ranging from 270 to 330 °C. The rate-determining step is proposed to involve the interaction of an acyl group with a second acid, with an apparent reaction order of 1.6. This order can be explained by a second-order rate-determining step that is reduced as a result of acid-derived surface species. Isotope labeling experiments reveal that the rate-determining step is the formation of the C–C bond rather than the activation of the second acid. The ketonization reaction exhibits a -0.46 order with respect to water, but this loss in activity is accompanied by a significant increase in catalyst stability.

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two carbon atoms in its backbone means that conversion via hydrotreating will yield low-value C_1 and C_2 hydrocarbons.

The conversion of acetic acid to a stable, nonacidic molecule with a longer C–C backbone is highly desirable. The ketonization reaction is a well-known and effective method of carboxylic acid upgrading, as it converts two organic acids to a ketone while removing oxygen in the form of water and CO_2 [16–25]. This reaction is very appealing, as the stable ketones formed can be further converted to produce longer-chain hydrocarbons via aldol condensation/hydrogenation [21–25].

The ketonization of carboxylic acids via the decomposition of salts [13,26–28], as well as over basic and reducible oxides, has been extensively studied. While several reactive surface intermediates have been proposed over high-lattice reducible oxides involving ketenes, ketene-like species, carboxylates, and even anhydrides [16-25], consensus is slowly growing on the importance of a β-ketoacid intermediate. In contrast, the reactive intermediates responsible for this transformation over acidic zeolites remain unexplored, while some similar species such as ketenes have been reported over Brønsted zeolites [29]. Despite the fact that ketones have been observed as products from the transformation of acetic acid over zeolites since the early 1980s, specific details of the reaction mechanism still remain elusive [30-34]. While ketones are reported in several cases, conditions that yield high selectivity to acetone while minimizing sequential aldol condensation reactions have yet to be identified. In addition to uncertainty surrounding







the mechanism, the critical role of water, which is present in significant quantities in virtually all streams that contain acetic acid, has not been investigated for this reaction. Zeolites, especially MFI framework zeolites, are among the most promising and commonly employed catalysts for the conversion of bio-oil to fuels and chemicals. The fact that so little is known about the mechanism of conversion of the most abundant species in bio-oil over this catalyst is surprising, and warrants further investigation.

The few studies investigating the ketonization reaction over zeolites have operated under conditions that also involve a variety of secondary reactions such as aldol condensation and aromatization [34], making it difficult to come to mechanistic conclusions. In addition to these sequential and parallel products, the intrinsic ability of a zeolite to activate various oxygenated species, such as acetic acid, can be nullified by the rapid deactivation that is associated with the subsequent conversion of reaction products such as acetone, as has been illustrated by Kresnawahiuesa et al. [35]. As early as 1983, Chang et al. [32] offered the suggestion that the ketonization reaction over zeolites may occur via a nucleophilic attack of an acylium ion on an acetate. Due to the rapid deactivation observed over zeolites, they proposed that these acetate species were formed from the decomposition of acylium species by dehydroxylation of the zeolite, leading to an inherent irreversible deactivation of the catalyst. Martens et al. [31] proposed a similar mechanism involving a surface acyl intermediate similar to that in Chang et al. Rather than forming an activated acetate via dehydroxylation of the zeolite, they speculated that a second acid could interact directly with the basic site on the zeolite generated via the formation of a surface acyl group to dissociate the O-H bond on the carboxylic acid, regenerate the Brønsted site, and form a carboxylate anion. The location of the surface acyl species during this process is not specified. They proposed that this carboxylate anion subsequently interacts with the positively charged acyl cation to form the ketone

Other types of reactive intermediates have been proposed for reactions involving acvl species and acvlium ions. Of particular relevance to this reaction are ketenes. Surface acvl species are in equilibrium with acylium ions, as well as gas phase ketenes in low abundance. Ketenes are often proposed as important reactive intermediates for reactions involving carboxylic acids and acyl groups [29]. Specifically, for the ketonization reaction, it has been shown that over oxides such as TiO₂, gas phase ketenes are parallel side products that do not lead to ketone formation, as discussed in depth in a recent review of the topic [21]. Martinez et al. argued against a sequential ketene-based mechanism, using a monolith reactor while varying the contact time [11]. Similarly, Pestman et al. [19] used ¹³C-labeled acids to perform cross ketonization reactions between a carboxylic acid capable of forming a ketene and another carboxylic acid lacking an alpha hydrogen and thus incapable of forming a gas phase ketene. They showed by labeling the carbonyl carbons of carboxylic acids that gas phase ketenes are not responsible for the ketonization reaction over TiO₂.

Surface-bound acyl species and their corresponding acylium ions have long been proposed as intermediates for similar C–C coupling reactions as well, such as acylation reactions with aromatics over zeolites [36–41]. Corma et al. [42] proposed that surface acyl species and acylium ions are important intermediates involved in aromatic acylation reactions. This claim was later challenged by Bonati et al. [43,44], who, upon observing ketenes at trace levels, argued that ketenes were responsible for these reactions. Deuterium labeling studies by the same group later showed that while ketenes are produced in parallel to acyl groups and acylium ions, they are not intermediates in the acylation reaction [45], but rather side products that contribute to catalyst deactivation via coke formation. In this contribution, we report the ketonization of acetic acid over HZSM-5 under conditions that selectively yield acetone. A systematic variation of temperature gives insight into the mechanism of acetone production and the resulting changes in selectivity. Temperature-programmed desorption and IR studies combined with reaction kinetics are used to investigate the reaction pathway and the possible reaction intermediates. The role of water in the ketonization mechanism and its impact on catalyst deactivation, competitive adsorption, and interaction with intermediate surface species are also discussed.

2. Experimental

2.1. Catalyst preparation

ZSM-5 (CBV-8014) with SiO₂/Al₂O₃ purchased from Zeolyst International in the ammonium form was calcined at 600 °C for 5 h in dry air to obtain the protonated HZSM-5 by thermal decomposition of NH₄⁺ to NH₃ and H⁺. Silicalite-1 was hydrothermally synthesized from the gel composition of tetrapropylammonium hydroxide (TPAOH):SiO₂:H₂O:EtOH = 9:25:477:100 by following the procedure outlined in Ref. [46]. Reagents used for the synthesis include tetraethyl orthosilicate (TEOS, Sigma Aldrich, reagent grade, 98%), tetrapropylammonium hydroxide (TPAOH, Alfa Aesar, 40% w/w ag. soln.), and deionized water. The gel was stirred at ambient temperature for 24 h and then hydrothermally treated for 24 h at 80 °C in an autoclave. The synthesized sample was washed and filtered by centrifugation, followed by drying overnight (12 h) at 80 °C. The dried sample was then calcined at 600 °C for 5 h to remove the template. Both catalysts were pelletized after calcination and subsequently crushed and sieved to particles with sizes ranging from 90 to 250 µm.

Na⁺ exchange was conducted on the samples to titrate a portion of the Brønsted sites and test for diffusion limitations. A fraction of the Brønsted acid sites were poisoned with sodium dosing as reported in the literature [47]. Three different samples (referred to as samples 1, 2, and 3) were prepared by varying the amount of sodium loading using 0.5 M NaNO₃ solution as the sodium source. Double-distilled water and commercial NaNO₃ (Sigma Aldrich, ReagentPlus, \geq 99.0%) were used to prepare 0.5 M NaNO₃ solution. All samples were characterized by IPA-TPD to quantify the resulting Brønsted acid site density.

2.2. Catalyst characterization

The crystallinity of the samples was investigated by X-Ray diffraction using a Rigaku automatic diffractor (Model D-MAX A) with a curved crystal monochromator. It had Cu K-alpha as the radiation source and was operated at 40 kV and 35 mA in the angle range 5–55°. For analysis, a well-ground catalyst sample was placed on a plastic slide and spread evenly to obtain a flat surface.

Scanning electron microscopy (SEM) measurements of the samples were performed by a Zeiss-NEON FEG-SEM instrument to estimate the particle diameter. To prepare SEM samples, a small amount of the zeolite aqueous suspension was placed on carbon tape and dried for 1 h.

Isopropylamine (IPA) temperature-programmed desorption (TPD) experiments were conducted on the zeolites used in this study to investigate the concentration of Brønsted acid sites. A portion of 50 mg of catalyst was taken in a quartz reactor (1/4'' OD) and flushed at 300 °C for 1 h with helium as a carrier gas at a flow rate of 20 ml/min. After pretreatment, the temperature was reduced to 100 °C and 2 µL pulses of IPA were injected into the reactor through a septum using a syringe. To ensure saturation of all the acid sites in the catalyst bed with IPA, the mass-to-charge

ratios (m/z) of 44 and 58 were tracked at the exit of the reactor with an MKS Cirrus 200 quadrupole mass spectrometer (MS). IPA pulses were continued until constant peak heights corresponding to m/z = 44 and 58 were observed as sequential pulses were injected. After adsorption of IPA onto the catalyst bed, helium carrier gas was flushed over the bed at a rate of 20 ml/min at 100 °C for 4 h to remove physically adsorbed IPA, after which the temperature was ramped from 100 to 600 °C at a rate of 10 °C/min. The products desorbing from the reactor during the temperature ramp were tracked via MS. Products were quantified through calibration of the MS signal using standards and a sample loop.

2.3. Continuous-flow reactions

Flow reaction studies were performed in a quartz tube reactor (1/4" OD) at atmospheric pressure and temperatures varying from 250 to 340 °C. The catalyst sample was packed into the reactor between quartz wool and the reactor was filled with acidwashed glass beads with a diameter of 1 mm from the inlet of the reactor to the catalyst bed. The inlet of the reactor was heated to create a vaporization zone and the outlet stream of the reactor, which was connected to a six-port valve for sampling, was heated to 250 °C to prevent condensation. The temperature of the catalyst bed was controlled by a thermocouple attached to the outer wall of the reactor. The catalyst was preheated and flushed with helium flowing at 50 ml/min for 1 h at 300 °C before acetic acid (Sigma Aldrich, ACS reagent, \geq 99.7%) was introduced via a syringe pump. The results and product distribution at the desired time on stream (TOS) were analyzed using a Hewlett Packard 6890 gas chromatograph equipped with a flame ionization detector and an Innowax column of dimensions 30 m and 0.25 µm. The vapors downstream of the six-port valve were condensed in a sample bubbler using ice and water as a coolant medium.

External mass transfer limitations in the flow reactions were tested at 300 °C by varying the helium carrier gas flow rate from 50 to 125 ml/min. It is important to mention that the W/F (weight of catalyst in g/feed flow rate in g/h) and the partial pressure of acetic acid were held constant during this study. When measured rates are controlled by external mass transport limitations, the rate increases linearly with increasing (carrier gas flow/particle diameter (dp))^{0.5} [48]. This test was used to ensure that data used to obtain kinetic parameters were not corrupted by diffusion limitations.

The kinetic isotope effect on ketonization of acetic acid over HZSM-5 was studied in this flow reactor at a reaction temperature of 300 °C under atmospheric pressure. Two different isotopically labeled acetic acid probe molecules were tested, acetic acid-d (Aldrich, 99 at.% D) and acetic acid-d₄ (Aldrich, 99.5 at.% D). As with the previous runs, the catalyst bed was preheated and flushed with helium at 300 °C for 1 h before the feeding of the reactant. Acetic acid was fed to the reactor through a syringe pump with a rate of 0.0000728 mol/min at a reactant partial pressure of 10.67 Torr. A catalyst weight of 0.025 g was used for these experiments. Products at the desired time on stream (TOS) were analyzed using the Hewlett Packard 6890 gas chromatograph described above.

2.4. Acetic acid TPRx experiments

The temperature-programmed reaction of acetic acid over Brønsted acid sites of CBV8014 was studied in a reactor setup similar to that used for IPA TPD, explained in Section 2.2. A portion of 50 mg of catalyst was packed into a quartz reactor (1/4" OD) and flushed at 300 °C for 1 h with helium at a flow rate of 50 ml/min. It is important to mention that a moisture trap was installed in the helium line to avoid the introduction of moisture with the gas stream. It was ensured that the catalyst bed was completely dried after flushing with dry helium by tracking water (m/z = 18) at the exit of the reactor via MS. After pretreatment, the temperature was reduced to 100 °C and glacial acetic acid was pulsed using a syringe in 2 µL increments. The catalyst bed was saturated with acetic acid, as confirmed by analyzing exit gases from the reactor using MS. m/z = 60 was tracked for acetic acid to ensure a constant signal per pulse in the exit stream of the reactor. After adsorption of acetic acid, the catalyst bed was flushed at 100 °C with dry helium at a flow rate of 50 ml/min for 4 h, after which the temperature was ramped from 100 to 600 °C at 10 °C/minute. The products desorbing from the reactor during the temperature ramp were tracked by MS and were quantified by injecting standards.

2.5. IR experiments

Infrared spectroscopic study of acetic acid over CBV8014 was conducted in a PerkinElmer Spectrum 100 FT-IR Spectrometer equipped with a Harrick Praying Mantis chamber. After CBV8014 was pretreated at 300 °C in helium flow of 50 ml/min for 1 h, the temperature was reduced to 50 °C and a blank spectrum of the zeolite surface was taken as a reference. Acetic acid was then adsorbed onto the surface for 30 min at 50 °C through a sample bubbler maintained at $-7 \,^{\circ}$ C while helium was flowed at a rate of 50 ml/ min. This was followed by flushing for 2 h at 50 °C under a flow of 50 ml/min to remove physically adsorbed acetic acid. After flushing, the spectrum of the CBV8014 surface adsorbed with acetic acid was collected at 50 °C and then the temperature was raised at a steady rate of 10 °C/min. Analysis at each desired temperature was conducted by stopping the ramp, holding at the desired temperature, and performing 64 scans to obtain the spectrum prior to continuing the temperature ramp.

3. Results and discussion

3.1. Reaction mechanism and evidence for stable acyl species

A simple analysis of the Brønsted acid sites post-reaction provides insight into the nature of activation of the carboxylic acids before the ketonization reaction. Fig. 1 shows that the Brønsted sites are clearly recovered after desorption of acetic acid and produce ketones at 300 °C, demonstrating that irreversible dehydroxylation of the zeolite is not a prerequisite for activation of the acids for this reaction. The peak at 3605 cm⁻¹ corresponding to Brønsted acid sites disappears after acetic acid is adsorbed. A subsequent temperature ramp to 300 °C is sufficient to desorb the ketones that were produced. The reappearance of the Brønsted sites indicates the absence of zeolite dehydroxylation to form an acetate as a necessary step for the ketonization reaction. A similar reappearance of IR bands corresponding to Brønsted sites was reported by Martens



Fig. 1. Acetic acid IR on CBV8014 shows the regeneration of Brønsted acid sites.

et al. upon exposure of HT zeolite to butyric acid followed by evacuation at 300 °C [31].

A temperature-programmed desorption (TPD) experiment with acetic acid over CBV8014 was conducted to probe the reaction mechanism. Water (m/z = 18), CO₂ (m/z = 44), acetone (m/z = 58), and m/z = 43 (a fragment of both acetic acid and acetone) correspond to the most abundant species produced in this experiment. This profile, shown in Fig. 2, clearly indicates that an initial dehydration step occurs on the reaction pathway. This would likely result in the formation of an acyl intermediate, as had been speculated in previous studies [30–32]. It is important to note that CO₂ has a lower heat of adsorption on HZSM-5 as compared with that of water [49], so readsorption or bed effects could not explain the evolution of water prior to CO₂. Quantification of the water produced during the dehydration step amounts to 16.75 µmoles, which corresponds to the dehydration of an acid on >82% of the 20.3 µmoles of Brønsted acid sites present in the catalyst bed.

FTIR analysis of the catalyst after exposure to acetic acid and subsequent heating provides better understanding of the surface species formed during the course of the reaction. The IR spectrum of the catalyst surface after pretreatment is shown in Fig. 3. After acetic acid is introduced to the catalyst at 50 °C via a saturated vapor stream, a significant peak is observed at $\sim 1720 \text{ cm}^{-1}$, as indicated by the solid vertical line. This peak is associated with surface-adsorbed acetic acid [50-52]. After the temperature is ramped to 150 °C at a steady rate, the peak at \sim 1720 cm⁻¹ shifts to lower wavenumber along with another peak appearing at 1755 cm^{-1} , as indicated by the two dashed lines, which have been attributed to acetyl species [53]. It is important to note that the Brønsted acid sites are not recovered in this temperature range, as indicated by the lack of reappearance of the band at 3605 cm⁻¹ after heating to 150 °C, as can be seen in Fig. S3 in the Supplemental Information. This indicates that the acyl species remain bound to the zeolites under these conditions.

The IR results presented in Fig. 3 support the presence of a stable acyl intermediate, and the TPD results in Fig. 2 suggest that the dehydration step is not the rate-determining step for the overall coupling reaction. A reaction mechanism can be proposed as shown in Fig. 4. The coupling step on the left may be a combination of several steps in series. Dashed bonds are not meant to represent a proposed transition state, but simply to illustrate the bonds involved in a possible route to the formation of a β -keto acid, which can subsequently decompose to form acetone. A rate-determining step involving a surface acyl group and another acid will yield a second-order kinetic dependence with respect to acetic acid, as will be discussed in Section 3.4. This is true if the rate-determining step involves (a) the tautomerization or activation of



Fig. 2. Acetic acid TPD on CBV8014, showing an initial dehydration step involved in the reaction pathway followed by the decomposition of the intermediate to acetone and CO₂.



Fig. 3. Acetic acid IR on CBV8014 after adsorption of acetic acid at 50 °C and subsequent heating to 150 °C. The IR spectra are offset for clarity.



Fig. 4. Acetic acid TPD on CBV8014 showing an initial dehydration step involved in the reaction pathway followed the decomposition of the intermediate to acetone and CO₂.

the second acid or (b) the formation of a C–C bond with the acyl. Further insight may be obtained through kinetic fitting to determine the reaction order and deduce a rate-determining step.

3.2. Identification of a selective ketonization regime under continuous flow

Subsequent aldol condensation and aromatization of acetone often complicates the kinetic analysis of the ketonization reaction. The conversion of acetic acid in a flow reactor over CBV8014 at 300 °C yields nearly 100% selectivity to acetone and CO₂ as shown in Fig. 5. After the CO₂ generated during the ketonization reaction for each mole of acetone produced is accounted for [16–25,30–34], over a 95% carbon balance was observed for each reaction unless otherwise noted. The fact that most studies report a variety of subsequent aldol condensation products can clearly be mitigated by operating at milder temperatures under the conditions used in this study.

The ketonization reaction over zeolites is surprisingly selective over a broad range of temperatures. Fig. 6 shows the flow reaction of acetic acid on CBV8014 at various temperatures, with W/F being constant for all of the runs. These experiments were performed at temperatures ranging from 270 to 340 °C and, as expected, the yield of acetone increased with increasing temperature. High carbon balances were observed only up to a temperature of 330 °C, beyond which a significant amount of carbon was lost due to the formation of heavier species that do not desorb from the catalyst. Vervecken et al. [30] and later Martens et al. [30,31] reported a similar effect, with higher yields to aldol condensation products at elevated temperatures. Though no condensation products were observed in our study, the drop in carbon balance at 330 °C indicates their formation. Higher temperatures may be required to desorb these species from the active site so that they leave the catalyst particle at a rate higher than subsequent condensation reactions that ultimately lead to coke formation. The lack of aldol condensation products observed at lower temperatures could be due to a combination of the reduced rate for this reaction and a lower population of vacant sites for acetone readsorption at lower reaction temperatures.

Figs. 5 and 6 show that stable conversion may be achieved under more moderate conditions, with deactivation resulting from consecutive reactions, as well as potentially through parallel reactions involving ketene species. This loss of activity as a function of time on stream (TOS) can be recovered by a simple calcination. Fig. S4 in the Supplemental Information highlights the reaction rate as a function of TOS across both the fresh and regenerated catalyst. After the catalyst has been exposed to acetone at 300 °C for 105 min, the carbonaceous deposits are removed by temperature-programmed oxidation. The catalyst is then placed back in the reactor and the initial catalyst activity is recovered. This provides further support for the result that irreversible dehydroxylation of the zeolite does not occur significantly under these conditions.

3.3. Effect of water on catalyst deactivation rates

Most streams that contain acetic acid are also accompanied by large amounts of water. Bio-oil produced from the pyrolysis of lignocellulosic biomass contains approximately 60% water by weight; thus understanding the role of water in the ketonization reaction is critical for any practical application utilizing these renewable streams. The mechanism outlined in Fig. 4 implies that water may inhibit the formation of acylium species. However, a second-order step may be rate-determining, as will be discussed in more detail below. The role of water in this reaction can be twofold, interacting with surface acyl species or desorbed ketenes to reform acids and by competing for adsorption sites.

Fig. 7 shows a flow reaction conducted at 300 °C during which water co-fed at a 1:1 molar ratio with acetic acid is introduced after a TOS of 100 min. A sudden drop in conversion is observed upon the introduction of water. When water co-feeding is stopped, the activity is recovered to a level equal to that observed prior to



Fig. 5. Flow reaction studies of acetic acid on CBV8014 at 300 $^{\circ}$ C showing very high selectivity to acetone and CO₂. The flow rate of acetic acid is maintained at 0.0000728 mol/min with a catalyst weight of 25 mg.



Fig. 6. Flow reaction studies of acetic acid on CBV8014 showing yields of acetone and carbon balance as a function of temperature. The acetic acid partial pressure was maintained at 10.67 Torr. Rates at each temperature were taken at 30 min TOS.



Fig. 7. Acetic acid flow reactions at 300 and 320 °C, showing a sudden drop in conversion when water is introduced. Catalyst weights 0.025 and 0.014 g were used for reactions at 300 and 320 °C, respectively, to match the initial rates, with an acetic acid flow of 7.28 \times 10⁻⁵ mol/min at a partial pressure acetic acid of 10.8 Torr. Water was introduced at a 1:1 molar ratio.

water introduction into the system, showing no measureable irreversible effect of water on the catalyst. The drop in the activity with water co-feeding could be due to either (i) the reversible reaction of acylium formation, i.e., the surface acyl interacting with water to form acetic acid, or (ii) competition between water and acetic acid for the active sites on the catalyst. The same experiment is repeated at a higher temperature of 320 °C with a reduced W/F to maintain the same conversion levels as those observed at 300 °C. When water is added at the higher temperature, the impact of water on the rate of ketonization is less pronounced.

Any influence of competitive adsorption for active sites will become less pronounced at higher temperatures; thus the role of water in competition for active sites cannot be ruled out. Similarly, if the dehydration step to form an surface acyl species is endothermic, as was shown to be the case by Boronat et al. [54] studying the Koch reaction over H-MOR zeolites, higher temperatures will favor a greater equilibrium concentration of acyl groups on the surface. A more detailed analysis of water partial pressure's effect on the reaction rate is presented in the next section.

The rate of acetone formation after the catalyst has been exposed to water co-feeding, shown in Fig. 7, indicates that water inhibits deactivation of the catalyst. While water decreases the rate of the reaction, the stability of the catalyst may actually be improved. The positive influence of water on inhibition of the deactivation rate is more pronounced when the reaction order with respect to water is evaluated as a function of time on stream.

Fig. 8 shows that the reaction order increases when measured at later TOS values. This indicates that, in extrapolation to 0 TOS, the -0.46 order with respect to water is a measure of the true impact that water has on the reaction rate. At later TOS, as the catalyst begins to deactivate, the overall order is shifted by the influence that water has on the catalyst decay rate, with the apparent order approaching -0.2. This can be observed more directly by evaluating the exponential dependence of the rate as a function of time. By considering the exponential dependence of rate in terms of a deactivation coefficient, k_{d} , it can clearly be observed that water inclusion positively impacts the catalyst stability. The rates fit the decay curves; the deactivation coefficients as a function of water partial pressure can be found in the Supplemental Information in Fig. S8. This positive influence of water on catalyst stability has very promising practical implications for real renewable streams, which are often accompanied by significant amounts of water.

3.4. Reaction kinetics and identification of the rate-determining step

Tests were conducted to ensure that the kinetic data are not limited by mass transfer. The reaction rate at 310 °C as a function of helium carrier gas flow rate is shown in Fig. 9. At low flow rates, the rate increases with increasing carrier gas flow, indicating that the rate is controlled by external mass transport to the catalyst surface. This effect disappears above 100 ml/min of gas flow, suggesting that the reaction is devoid of external diffusion corruptions above this flow rate. All kinetic experiments were therefore conducted with a carrier gas flow rate of 125 ml/min. This includes the experiments reporting reaction orders vs. TOS as described in the previous section.

The necessity of Brønsted acid sites for this reaction to proceed was confirmed by passing acetic acid over silicalite-1 at 300 °C, with no measurable conversion observed over silicalite-1, as shown in Fig. S5. This was further confirmed by Na⁺ exchange of the HZSM-5 (samples 1, 2, 3 in Table S1 in the Supplemental Information). The activity dropped in proportion to the concentration of Brønsted sites passivated by Na⁺, as shown in Fig. 10, with a constant TOF of $1.03 \pm 0.09 \text{ min}^{-1}$ per Brønsted site over all of the catalysts tested. This confirms that the measured rates are not limited by internal or external mass transfer under these conditions. This result also demonstrates that any Lewis acidity introduced by the incorporation of Na cations does not accelerate the rate-determining step.

By varying the concentration of acetic acid fed, we observe that the order of the ketonization reaction is greater than one. Rates were found by extrapolating the conversion to initial TOS values



Fig. 8. Order of reaction rate with respect to water as measured at varying TOS values. Conditions are vs. water concentration over CBV8014 at 300 °C, 0.025 g catalyst, with initial rates extrapolated to 0 min TOS. Error bars represent ± 1 standard error value of the reaction order coefficient.



Fig. 9. Dependence of acetic acid reaction rate over carrier gas flow rate at constant W/F = 0.095 h and reactant concentration over CBV8014 at 310 °C and 30 min TOS.



Fig. 10. Rate of acetic acid conversion as a function of the density of Brønsted acid sites at a constant W/F = 0.095 h over CBV8014 at 300 °C and 30 min TOS. The concentration of Brønsted acid sites was varied via Na⁺ exchange of CBV8014.



Fig. 11. Natural logarithm of the rate of reaction vs. acetic acid concentration over CBV8014 at $300 \degree$ C, $0.025 \degree$ g catalyst, with rates extrapolated to $0 \min$ TOS. Conditions are identical to those in Fig. 8.

to eliminate effects of catalyst deactivation, as described in the previous section. The fact that the reaction appears to be greater than first order, as shown in Fig. 11 implies a rate-determining step involving two acid-derived species. The reason for an observed order less than two with respect to acetic acid could be due to the coverage of acetic acid and acid-derived surface species. This behavior is very similar to that observed when the apparent

reaction order is measured for coupling of acids over reducible oxides, where the second-order coupling exhibits a fractional apparent order [21,22].

Combining the observance of water evolution in Fig. 2 with the observation of acyl surface species at 150 °C in Fig. 3 implies that the dehydration of an acetic acid molecule to form a surface acylium species is not the rate-determining step. The further observance of CO₂ (m/z = 44) and acetone (m/z = 43) evolution at 250 °C in Fig. 2 indicates that an acylium ion and an activated carboxylic acid can couple to form an intermediate and subsequently decompose to yield CO₂ and acetone. The kinetic order greater than one further supports a second-order rate-determining step. This second-order dependence, which is manifested as an apparent 1.6-order rate dependence on acetic acid partial pressure, can be explained by examination of a rate law derived assuming that an adsorbed acid and an adsorbed acvl interact during the ratedetermining step to form a β -keto acid that rapidly decomposes to yield acetone and CO₂. The left hand side of Eq. (1) represents an acetic acid molecule in the proximity of an acyl group with the right hand side representing a β -keto acid. The nature of the transition state of the rate determining step could involve either the activation of the second acetic acid or C-C bond formation as discussed in section 3.1. We will investigate the kinetic relevance of these two possibilities later in this section.

$$\operatorname{RCOOH}/\operatorname{RCO}^+ \xrightarrow{\kappa} [\operatorname{RCORCOOH}]^+$$
(1)

An expression highlighting the second-order dependence of this rate-determining step is derived in the Supplemental Information, resulting in equation (2) below:

Further insight may be gained by investigating the dependence of water on the rate expression. By varying the water partial pressure and extrapolating data to initial TOS values, the rate of acetone production exhibits a -0.46 order with respect to water as shown in Fig. 12. Based on rate Eq. (2), competitive adsorption of water alone would not be able to account for the -0.46 order observed. Further simplification of expression (2), where the surface is completely saturated with adsorbed water species, would yield

$$rate = \frac{kK_{Com}K_{equilibrium}K_{Acid}P_{Acid}^2}{\left(K_{H_2O}P_{H_2O}^2\right)}.$$
(3)

Rate Eq. (3) does not agree with the observed experimental rate. Lower coverage of water, without considering the possibility of surface acyl species, would yield an order with respect to water that varies from -1 to -2, as discussed in the Supplemental Information. Similarly, if the surface were completely saturated with surface acyl and acid/acyl species, the order with respect to acetic acid indicates that sites are not all occupied by acyl groups or acyl/acid complexes, but clearly a significant fraction of the sites must be occupied by these species to justify an order with respect to water that is between 0 and -1.

Ison and Gorte [49] measured a heat of adsorption of water over HZSM-5 as 51 kJ/mol at low coverage, while Kresnawahjuesa et al. of the same group [55] later reported the heat of adsorption of acetic acid over HZSM-5 as 139 kJ/mol. This indicates that while water could potentially compete for adsorption sites at high enough concentrations, excluding entropic contributions, water is

$$rate = \frac{kK_{\text{Com}}K_{\text{equilibrium}}K_{\text{Acid}}P_{\text{Acid}}}{P_{\text{H}_2\text{O}}(1 + K_{\text{Acid}}P_{\text{Acid}} + \frac{K_{\text{equilibrium}}K_{\text{Acid}}P_{\text{Acid}}}{P_{\text{H}_2\text{O}}} + \frac{K_{\text{Com}}K_{\text{equilibrium}}K_{\text{Acid}}P_{\text{Acid}}^2}{P_{\text{H}_2\text{O}}} + K_{\text{Ketone}}P_{\text{Ketone}} + K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}} + K_{\text{CO}_2}P_{\text{CO}_2})}$$
(2)

Several scenarios depicting variants of most abundant surface intermediates (MASI) are highlighted in the Supplemental Information. One can clearly see by inspection of (2) that a fractional order of 1.6 with respect to acetic acid can be attributed to contributions to the rate equation by a combination of surface acetic acid, acetic acid/acyl complex, and surface acyl groups (corresponding to the three terms in the denominator that increase with the partial pressure of acetic acid).



Fig. 12. Natural logarithm of the rate of reaction vs. water concentration over CBV8014 at 300 $^{\circ}$ C, 0.025 g catalyst, with initial rates extrapolated to 0 min TOS. Acetic acid partial pressure is maintained at 10.8 Torr.

not expected to occupy the majority of Brønsted sites under these conditions. While we cannot exclude the possibility that a significant portion of the negative order attributed to water in the reaction rate is due to competition for active sites, it is a reasonable assumption that a greater proportion of Brønsted sites are occupied by acyl species than by water under these conditions, based on the proposed rate expression. While we have eliminated the influence of water on catalyst deactivation rates with this analysis, the possibility of water interacting with transition states and facilitating proton transfer has not been investigated. If, for example, the tautomerization of the carboxylic acid in proximity to an acyl



Fig. 13. TOF values for acetic acid and its deuterated counterparts in the OD position (D1) and fully deuterated (D4). Reaction conditions are described in Section 2.3.

group is a limiting step in this reaction, water could play yet another positive role in this reaction.

The kinetic consequences of a rate-determining step involving the activation of the alpha hydrogen, either through direct abstraction or through tautomerization, may be probed by examining the variation in reaction rate with deuterated acid feed molecules. It should be noted that these rates are not limited by internal or external diffusion, as illustrated by Fig. 10. A rate-determining step that involves the direct cleavage of an OH or a CH bond will exhibit a primary KIE of approximately 3.2 or 2.6 at the reaction temperature, respectively [56,57]. The absence of a primary KIE, based on the insignificant shift in TOF when acetic acid is replaced with either OD or fully deuterated acetic acid, shows that activation of the alpha hydrogen is not the rate-determining step (see Fig. 13). This, coupled with the second-order dependence of the rate on acetic acid, demonstrates that the rate-determining step is the formation of the C–C bond between an acyl and an activated acid.

4. Conclusions

Conditions necessary to convert acetic acid to acetone over HZSM-5 in the gas phase with nearly 100% selectivity to the ketonization reaction have been identified. Significant sequential condensation of acetone was observed at a temperature beyond 300 °C, as indicated by a decrease in the carbon balance. An initial dehydration step is involved in the reaction pathway to yield a surface acyl species in equilibrium with an acylium ion. This acylium ion couples with a second acid, with a step involving two acetic acid-derived species serving as the rate-determining step as supported by IR, TPD, and kinetic data. The lack of a primary KIE upon introducing deuterated reactants reveals that the rate-determining step is the formation of the C–C bond. Water inhibits the reaction, exhibiting a -0.46 order in the reaction rate, but also has a positive influence on the catalyst stability under the conditions reported here.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.04.017.

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