Elucidating the Cooperative Roles of Water and Lewis Acid–Base Pairs in Cascade C–C Coupling and Self-Deoxygenation Reactions

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1. INTRODUCTION

C–C coupling coupled with oxygen elimination is one of the most promising ways to produce valuable chemicals and fuels from biomass-derived oxygenates (e.g., alcohol, ketone, carboxylic acids),1–3 e.g., diacetone alcohol (DAA) and mesityl oxide (MSO) from acetone. Since McAllister et al. first reported on DAA and MSO conversion to isobutene,4 extensive studies have been conducted on the direct acetone-to-isobutene conversion (ATIB).4–11 This ATIB cascade reaction, including enolization, C–C coupling (aldol-addition), dehydration, C–C bond scission, and ketonization, may occur depending on the type of active sites (i.e., Bronsted acid–base pairs8,12). Over zeolites with Bronsted acid sites, the cascade ATIB via aldol condensation of acetone followed by deoxygenation have been widely accepted.10,11 Recent mechanistic insights reveal that the ATIB over Bronsted acid sites5,6,9,11 generally starts with the protonation of acetone followed by C–C coupling to form acetone dimers (e.g., DAA, MSO, isomesityl oxide, etc.); the formed dimers then undergo facile β-scission to produce isobutene (Scheme 1).5,13 Other than the β-scission, there are also competing pathways, which results in the formation of large oligomers and rapid deactivation of the catalyst as well as cracking and isomerization of isobutene, especially at higher reaction temperatures (i.e., >643 K).5,11 In addition to this, zeolites are less hydrothermally stable because of the facile leaching of aluminum cations as compared with metal oxides.

Over Lewis acid–base pairs, although acetone aldolization has been well studied and understood,3,4,11–16 reports on ATIB (i.e., C–C coupling followed by self-deoxygenation) are still scarce.7,8,12 A spectroscopic study by Zaki et al. showed that the formation of isobutene arises from C–C bond cleavage of acetone oligomers, i.e., MSO. By comparing the IR spectra of acetone/MSO on SiO2, Al2O3, SiO2/Al2O3, K2SiO4/Al2O3, and Py-SiO2/Al2O3, it was found that MSO coordinates to Lewis acid–base pairs and can be converted into surface acetate species and gas-phase isobutene at high temperatures (573–673 K),17 due to the nucleophilic attack of basic OH groups in their proximity.18 We reported that Zn/ZrO2 catalysts with
balanced Lewis acid–base pairs are active in the ATIB reaction in the presence of water. It was also found that the diacetone alcohol-to-isobutene step is a kinetically relevant one in cascade ATIB reactions. Rorrer et al. recently confirmed that isobutene is generated from DAA decomposition and the kinetic relevant step is the C-β bond cleavage of DAA. They further postulated that surface hydroxyls and Brønsted acidic protons are generated by water dissociation, leading to the attack of protonated DAA by a hydroxyl species, but no evidence of Brønsted acidity was provided.

Although water has been found critical in many reactions including ATIB, its intrinsic roles are yet to be clarified. In the cascade ATIB reaction over zeolite catalysts, it was found that cofed water could mitigate the deactivation of the catalyst. It was proposed that cofed water could prevent the poisoning of bridging hydroxyls by coke components (e.g., large oligomers etc.) and thus suppressing the deactivation in acetone aldol condensation over zeolites. The content of water also affects the surface properties, which further influences the catalyst performance (e.g., stability, selectivity). For example, during the conversion of ethanol to C3–C4 olefins in a zeolite-based catalyst, an appropriate amount of cofed water improves the formation of light olefins and the catalyst stability, which was attributed to (a) weakened surface acidic sites and thus an attenuation of the side cracking reactions; (b) a mitigated oligomerization, which subsequently prevents coke formation. On the other hand, a high water content coupled with high reaction temperatures could lead to the deactivation of the catalyst due to the dealumination and the deconstruction of microporous structures. It was also speculated that the production of isobutene is favored in the presence of cofed water, because water prevents the dehydration of DAA as well as further aldolization, although reasons behind this phenomenon were not discussed. Recent studies conducted by Herrmann et al. confirmed that water could slow down the deactivation of aluminosilicate catalysts in the ATIB reaction. They also discovered two β-scission pathways, the anhydrous and H2O-mediated pathways, to produce isobutene. In the absence of water, dehydrated dimers are the only direct precursor of isobutene (anhydrous β-scission). However, when water is cofed with acetone, both DAA and dehydrated dimers are direct precursors of isobutene and the β-scission of DAA is H2O-mediated. So far, the critical role of water in the Lewis acid–base pairs (i.e., Zn2ZrO2) catalyzed ATIB reaction remains elusive. In this contribution, we combine in situ DRIFTS-pyridine, in situ 1H NMR, reaction kinetics, DRIFTS-MS, isotopic labeling, and density functional theory (DFT) to elucidate the cooperative roles of Lewis acid–base pairs and cofed water, as well as the detailed reaction mechanism in ATIB on Zn2ZrO2 catalysts. 

2. EXPERIMENTAL METHODS

2.1. Catalyst and Materials

Zn2ZrO2 was synthesized with Zn(NO3)2·6H2O (Sigma-Aldrich, reactant grade, 98%) and Zr(OH)4 (MEL, ZX0631/01) by the incipient wetness impregnation method. The details of synthesis and characterization could be found elsewhere. Acetone (J.T. Baker, 99.8%), H218O (Sigma-Aldrich, 97 atom % 18O), pyridine (J.T. Baker, 100%), diacetone alcohol (Sigma-Aldrich, 99%), and phorone_A (2,6-dimethyl-2,5-heptadien-4-one, Oakwood Chemical, 99.93%) were used as purchased.

2.2. Catalyst Characterization

2.2.1. Diffuse Reflectance Infrared Fourier Transform Spectroscopy Analysis of Adsorbed Pyridine (DRIFTS-Py) and Acetone (DRIFTS-acetone). Infrared spectra of pyridine on the dehydrated and the hydrated sample were obtained at a resolution of 4 cm⁻¹ between 4000 and 600 cm⁻¹ using a Bruker Tensor 27 FTIR spectrometer. Inert gas (5%Ar/He) was flowed through a 50 mL Pyrex bottle to introduce gas phase pyridine into the DRIFTS in situ cell. About 20 mg of the catalyst was loaded and pretreated at 723 K for 30 min in inert gas (5%Ar/He) flow (50 SCCM). After pretreatment, the sample was cooled to 323 K, followed by the collection of background spectrum and pyridine adsorption (ca. 2.5 kPa, 10 min) to obtain the pyridine spectra of the sample without water treatment. For the pyridine spectra of the hydrated sample, after pretreatment, water was pulsed in (ca. 3.2 × 10⁻⁸ mol H2O/pulse, 3 pulses in total) at 523 K followed by 30 min of purging with the same inert gas to remove any physisorbed water. The treated sample was then cooled to 323 K followed by the same procedure to obtain the pyridine spectra of the hydrated sample. Other details of the procedure can be found elsewhere.

2.2.2. Solid-State Proton Nuclear Magnetic Resonance (1H-SSNMR). Solid-state proton nuclear magnetic resonance (1H-SSNMR) of the samples was performed with a DRIFTS-MS set up. Ca. 20 mg Zn1Zr10O2O4 was loaded into DRIFTS in situ cell followed by pretreatment at 723 K in 5%Ar/He (50 SCCM) for 30 min. The gas phase water-acetone mixture (acetone H2O) was introduced by slowly flowing (10 SCCM) 5%Ar/He through the bubbler at room temperature. The system was then purged with 5%Ar/He for 40 min before introducing “Acetone H218O” mixture. In the isotopic experiment (“Acetone H218O”), partial pressure of gas phase acetone was 1.4 kPa which was calculated by Henry’s Law. We assume that the water pressure in the gas phase is the vapor pressure of water at 298 K (3.2 kPa) because the effects of acetone to water evaporation were negligible, as the water to acetone molar ratio is large (>50). To remove impurities (i.e., oxygen, CO2 etc.), the bubbler containing water–acetone solution (“Acetone H2O” or “Acetone H218O”) was first purged in 5%Ar/He for 1 h before introducing to the cell. MS was used to monitor gas phase species for the entire process.

2.2.3. Solid-State Proton Nuclear Magnetic Resonance (1H-SSNMR). Solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were conducted using a Varian Inova wide-bore 300 MHz NMR spectrometer equipped with a 7.5 mm commercial ceramic probe. The samples were activated in a stream of N2 at 723 K and then transferred to a dry glovebox, where the samples were loaded into a custom-made 7.5 mm sealable rotor. Water was introduced to the sample via micro syringe prior to sealing the sample cell followed by 10 min before introducing “Acetone H218O” mixture. In the isotopic experiment (“Acetone H218O”), partial pressure of gas phase acetone was 1.4 kPa which was calculated by Henry’s Law. We assume that the water pressure in the gas phase is the vapor pressure of water at 298 K (3.2 kPa) because the effects of acetone to water evaporation were negligible, as the water to acetone molar ratio is large (>50). To remove impurities (i.e., oxygen, CO2 etc.), the bubbler containing water–acetone solution (“Acetone H2O” or “Acetone H218O”) was first purged in 5%Ar/He for 1 h before introducing to the cell. MS was used to monitor gas phase species for the entire process.
was conducted in situ via a heating stack externally calibrated with an ethylene glycol thermometer. The Larmor frequency was 299.969 MHz and a π/4 pulse width of 3.5 with a 5 s recycle delay was employed to collect 128 repetitions.

2.3. Catalytic Evaluation

The measurements were performed in a home-built test unit which was described in our previous work. Specifically, a given amount of catalyst (i.e., 2.5–5 mg) diluted with SiC (500 mg in total) was loaded into a microtubular fixed-bed reactor (i.d. five mm). The catalyst was heated to 723 K under N₂ flow at 50 SCCM (hold at 723 K for 30 min) to remove surface impurities prior to the evaluation of the catalyst. Steady-state isobutene formation rates were measured at 0.5–1.4 kPa acetone and 4–17 kPa H₂O at 723 K. The acetone–water solution, with different ratios (i.e., P₁₃≡P₆ₓc = 6.5–17), was evaporated and mixed with N₂ in an evaporator, which was set at different temperatures (303–383 K) for a stable mixed flow. The flow rate of the mixed feed and the amount of catalyst loaded were adjusted to ensure the rate measurements under different reactor conditions (conversion <7%). A customized Shimadzu GC-2014 gas chromatograph (GC) with HP-Plot Q column (30 m, 0.53 µm, 40 µm), flame ionization detector (FID), and thermal conductivity detector (TCD) were used to analyze the products. The turnover rate (µ) was calculated as follows: the total amount of catalytically relevant Lewis acid base pairs (low/medium strength) calculated from NH₃-TPD; the most prevalent coordination environment of Zn²⁺ was the monoclinic ZrO₂(m-ZrO₂) phase. Thus, the monoclinic ZrO₂ (m-ZrO₂) was chosen as a starting point. The bulk phase lattice constants of the monoclinic phase were optimized using a Monkhorst–Pack (14 × 14 × 14) k-point mesh. The optimized m-ZrO₂ cell parameters are a = 5.14 Å, b = 5.24 Å, c = 5.31 Å, α = γ = 90°, and β = 99.26° from the DFT simulations, which agree very well with the X-ray experimental values of a = 5.17 Å, b = 5.23 Å, c = 5.34 Å, α = γ = 90°, and β = 99.15° at 293 K. Thus, the DFT approach describes the crystal structure very well.

The (111) surface of m-ZrO₂ was modeled as it was identified as the most stable facet of m-ZrO₂. The basic structure was modeled as a p(2 × 3) m-ZrO₂ (111) slab with three stoichiometric layers. The unit cell of the slab consists of 48 Zr and 96 O atoms and has a surface area of 13.54 × 13.16 Å². In all geometry optimization calculations, the bottom two layers were fixed at their optimized bulk positions while the top layer was allowed to fully relax. A vacuum layer of 15 Å and a dipole correction along the z-direction were incorporated for eliminating interactions between periodic images of the system. A Monkhorst–Pack (2 × 2 × 1) k-point mesh was used and all calculations were spin-polarized.

The clean Zn₆Zr₄O₁₄ surface was modeled by replacing a Z₄⁺ to a Zn²⁺ at the terminal layer of the surface, forming a stoichiometric Zn₆Zr₄O₁₄ catalyst. In addition, the Zn²⁺ cation was charge balanced by two protons which were placed at their most energetically favorable positions. Distinct substitution positions for Zn²⁺ were then scanned to obtain the final model shown in Figure 1A. The hydrated surface was modeled by adding one extra water molecule on the dehydrated surface. On the basis of the previous DFT results in the literature, water easily dissociates on the m-ZrO₂(111) surface with a low activation barrier of 5.6 kJ/mol. Thus, we have systematically determined the most favorable coadsorption sites of OH and H on the model. Considering the complexity of the water cofacial surface, two candidates were considered herein as shown in Figure 1B, C, labeled as Hydrated Surface Type 1 and Hydrated Surface Type 2, respectively, based on their underlying energetics. A comparison of all other dehydrated and hydrated surface models with respect to the most energetically favorable structures are displayed in Figures S1–S4.

The adsorption sites of DAA were evaluated by calculating the adsorption energy of the DAA complex. This was calculated as

\[
E_{\text{ads}} = E_{\text{surface}} + E_{\text{molecule}} - E_{\text{adsorbate}} 
\]

(1)

where \(E_{\text{surface}}\) and \(E_{\text{molecule}}\) is the total energy of the DAA adsorbed on Zn₆Zr₄O₁₄, \(E_{\text{adsorbate}}\) is the total energy of the clean Zn₆Zr₄O₁₄, and \(E_{\text{adsorbate}}\) is the isolated energy of DAA in gas phase.
Another method for evaluating the strength of the interaction between the adsorbate and the surface is through the distortion energy, since the molecule will become distorted from its free gas geometry when it chemisorbs. The surface–adsorbate interaction will increase as its distortion energy increases. The energy that the adsorbate gains due to its geometric distortion from the interaction with the catalyst surface is quantified by evaluating:

\[
E_{\text{distortion}} = E_{\text{distorted geometry}} - E_{\text{free gas geometry}}
\]

which is the energy of distorted DAA in the gas phase, and \(E_{\text{molecule}}\) is the energy of the optimized DAA molecule in the gas phase. The electronic interactions between molecule and catalyst surface were also quantified through the differential charge density, which illustrates the movement of electrons in the system as the molecule adsorbs onto the surface. The differential charge density is calculated according to

\[
\Delta \rho(\vec{r}) = \rho_{\text{total}}(\vec{r}) - \rho_{\text{molecule}}(\vec{r}) - \rho_{\text{surface}}(\vec{r})
\]

where \(\rho_{\text{total}}(\vec{r})\), \(\rho_{\text{molecule}}(\vec{r})\), and \(\rho_{\text{surface}}(\vec{r})\) are the charge distribution for the whole system, the gas phase molecule and the catalyst surface, respectively. On the basis of the differential charge of electron density, we then integrated over the unit cell to give us the mean absolute charge transferred between the adsorbate and the surface (Q):

\[
Q = \frac{1}{2} \int \Delta \rho(\vec{r})
\]

3. RESULTS AND DISCUSSIONS
3.1. Distinct Role of Water in ATIB
3.1.1. Effects of Water on Surface Acidity and Proton Formation. A detailed structural study of Zn,Zr,O has been previously reported.\textsuperscript{24} Herein, a comparison of fresh and spent (24 h time on stream, \(P_{\text{H}_2O}/P_{\text{Ace}} = 10.7 \text{ kPa}/1 \text{ kPa},\) space velocity = 0.03 molAce/(gcat h)) Zn,Zr, catalysts was carried out to examine the effect of water on the surface structure of the catalysts under the conditions studied, as shown in Figure S5. From DRIFTS analysis of surface hydroxyl groups (Figure S5A), the stable surface monoclinic ZrO\textsubscript{2} structure was observed that Brønsted acid sites do not exist on a Zn,Zr catalyst. As compared to the dehydrated sample (black curve in Figure 2), a lower \(\nu_{\text{OH}}\) intensity ratio was observed in the hydrated sample while the band shape and position barely changed. The increased intensity of the \(\nu_{\text{OH}}\) mode relative to the \(\nu_{\text{OH}}\) mode (\(I_{\text{OH}}/I_{\text{OH}}\)) suggests that water treatment leads to an increased ratio of HPy-to-LPy.\textsuperscript{42} This increased ratio is due to the water adsorption and dissociation occupying a portion of the surface Lewis acid sites, which decreases the number of Lewis acid sites for LPy and increases surface hydroxyls for HPy.

From the DRIFTS-Py result, Zn,Zr, shows only Lewis acidity even in the presence of dissociated water on the catalyst’s surface; however, the nature of surface protons in hydroxyl groups generated from the dissociated water may be different on the Lewis acid–base pairs. SSNMR is a powerful method to characterize the acidity of solid catalysts\textsuperscript{45,46} and \(^1\)H-SSNMR measurements were performed to further explore the effects of water on the properties of surface acidity. Figure 3 depicts the spectra of the dehydrated and rehydrated Zn,Zr, samples at 298 and 473 K. The spectra of dehydrated samples at 298 and 473 K show two similar major peaks at 2.5 ppm (full width at half-maximum, fwhm = 841 Hz; broad peak) and 1.8 ppm (fwhm = 60 Hz; sharp peak) which can be ascribed to surface bridged (OH\textsubscript{b}) and terminal hydroxyl groups (OH\textsubscript{t}), respectively, similar to other metal oxide species.\textsuperscript{37–49} Such OH\textsubscript{b} species have also been assigned to Zr–OH species that are in proximity to the Lewis acid Zr\textsuperscript{4+} site.\textsuperscript{50} In either case, ammonia adsorption does not lead to a protonated NH\textsubscript{4} cation, demonstrating that OH\textsubscript{b} species are not acidic to an extent sufficient to catalyze this reaction.\textsuperscript{51} As compared to the OH\textsubscript{b} resonance, sharper OH\textsubscript{t} signals were observed that might be ascribed to a greater homogeneity of the local nuclear environment instigated by the enhanced

![Figure 2. In situ DRIFTS-Py of pretreated (50 SCCM N\textsubscript{2}, 30 min at 723 K) Zn,Zr, (black) after water pulsing at 323 K (blue) and 523 K (red).](https://doi.org/10.1021/jacsau.1c00218)
mobility of OHT at elevated temperatures because of their relatively free nature. Further, such species are likely related to the interaction of ZnO with ZrO2 at the surface of the catalyst, as ZrO2 does not exhibit such features.\textsuperscript{49,50} Other minor peaks at <1.5 ppm are likely due to the weak or nonacidic OHT on Zn\textsubscript{1}Zr\textsubscript{10}O\textsubscript{z}.\textsuperscript{50} The absence of signals at >4.5 ppm suggests that Brønsted acidic hydroxyl groups are not present on these mixed metal oxides.\textsuperscript{49,50} Similar spectra were observed on both dehydrated and hydrated samples except for the appearance of a relatively broad resonance centered at 1.7 ppm on the hydrated samples. In addition, OHB downfield shifting occurred after high temperature activation on the hydrated sample (Figure 3B, 473 K). The new peak at 1.7 ppm likely results from the formation of protons possessing unique Lewis basic oxygen sites during the rehydration process. It should be noted that such a sharp feature does not exist on ZrO2 materials,\textsuperscript{49} suggesting that these terminal sites may arise due to the incorporation of Zn. These protons are relatively weakly bonded, evidenced by the enhanced apparent nuclear symmetry and downfield shift of nearly 0.2 ppm at elevated temperatures. At 473 K, the decreased peak width of OH\textsubscript{T} at ca. 1.7–1.9 ppm concomitant with a downfield shift (2.6 ppm to 3.2 ppm) of OH\textsubscript{T} is discerned, implying a more uniform OH\textsubscript{T} local environment and potentially suggesting an elongated O–H bond of OH\textsubscript{T} over a hydrated Zn\textsubscript{1}Zr\textsubscript{10}O\textsubscript{2} catalyst after high temperature activation. Given this, they may be hydroxyls that were more easily removed during the dehydration process. This would be consistent with our DRIFTS observations in which a reduction of Lewis sites is accompanied with an increase in surface hydroxyls. The downfield shifting of the OH\textsubscript{T} peak might be also due to H exchanging between water and surface hydroxyl groups which matches the facile H-D exchange previously reported over Zn\textsubscript{1}Zr\textsubscript{10}O\textsubscript{2}.\textsuperscript{8} More importantly, the lack of peaks in the downfield range (i.e., >4.5 ppm) further confirms that no Bronsted acid sites are generated on the hydrated sample, consistent with the DRIFTS-Py result.

Comparing both the dehydrated sample and hydrated sample, the water treatment introduces new surface protons that likely result from the presence of oxygen vacancies, which could dissociate H\textsubscript{2}O through the transfer of one proton to a nearby site (e.g., oxygen atom or hydroxyl groups).\textsuperscript{52} A more uniform local environment and an improved mobility were obtained at a high temperature (i.e., 473 K) as evidenced by the decreased fwhm of OH\textsubscript{T} and downfield shifting of OH\textsubscript{T} (Figure 3B). Cofed water does not induce Bronsted acid sites, although surface hydroxyl groups (especially OH\textsubscript{T}) with greater mobility on Zn\textsubscript{1}Zr\textsubscript{10}O\textsubscript{2} are achieved. In contrast to the reported ATIB on Bronsted acid sites (proton donors),\textsuperscript{5,10} the unique nature of Lewis acid–base pairs (electron pair acceptors/donors) on the Zn\textsubscript{1}Zr\textsubscript{10}O\textsubscript{2} leads to a different acetone reaction pathway, which will be further discussed in the following sections.

### 3.1.2. Effects of Water on the ATIB Reaction Pathway

Previously, it has been proposed that direct decomposition of DAA to isobutene is a rate limiting step in the ATIB reaction.\textsuperscript{8} Water is not required assuming that DAA could be directly decomposed to isobutene based on the stoichiometry of the equation (DAA $\rightarrow$ isobutene + CH$_3$COOH), and it is reasonable to infer that water is also not required in the acetone aldol addition as well as the subsequent ketonization.

To further explore the role of water in the DAA-to-isobutene reaction, we compared the reaction of key intermediate, i.e., DAA, on the Zn\textsubscript{1}Zr\textsubscript{10}O\textsubscript{2} with and without cofeeding water. As shown in Figure 4, the reaction was very stable, with ca. 94.5%
of acetone and 4.9% isobutene being formed, when water was co-fed during the reaction. This result suggests that both the DAA-to-isobutene forward reaction and the DAA-to-acetone reaction occur, and the DAA-to-acetone reaction is much faster than the DAA-to-isobutene conversion. When water was not co-fed in the feed, a doubled initial isobutene selectivity (i.e., 11.2%) was observed with the concurrent decrease of acetone selectivity (87.5%). Note that ca. 0.5% of MSO was also detected. With time-on-stream, however, the selectivity to isobutene rapidly decreased and disappeared after 100 min of time-on-stream. Meanwhile, the selectivity to MSO first increased then decreased and disappeared. These observations imply that, though it inhibited the forward DAA-to-isobutene reactivity, water helped maintaining active sites for the DAA-to-isobutene forward

Scheme 2. (A) Proposed Reaction Mechanism (acetone-phorone_A-isobutene) of the ATIB Cascade Reaction over Zn$_1$Zr$_{10}$O$_z$; (B) Sequential Reaction Steps (acetone-phorone_A-isobutene) of the ATIB Cascade Reaction over Zn$_1$Zr$_{10}$O$_z$

Scheme 3. Oxygen Resource of Different Acetone Surface Reactions over Zn$_1$Zr$_{10}$O$_z$$^{a}$

$^{a}$O (orange) and O (dark red) represent $^{16}$O (orange) and $^{18}$O (black).
reaction likely via suppressed formation of MSO, a culprit that can readily poison/coke the acid sites. This comparison between the DAA reaction pathways with and without cofed water reveals that water plays an essential role in influencing the reaction pathway in the ATIB cascade reaction.

From our previous DRIFTS-MS experiments, the secondary MSO enolization followed by aldolization could only occur on balanced Lewis acid–base pairs (e.g., Zn1Zr10O16). Leading to the formation of 2,6-dimethyl-2,5-heptadien-4-one (phorone_A) on the surface, another possible key intermediate to isobutene. Isobutene could be produced from phorone_A at low temperature (e.g., 373 K). Otherwise, secondary MSO side reactions toward isophorone and other oligomers were observed on ZrO2 with weaker Lewis basicity which eventually blocked the active sites (i.e., Lewis acid–base pairs). Therefore, another possible reaction pathway of ATIB is proposed (Scheme 2): isobutene is produced from phorone_A, followed by the water-assisted decomposition of carbonate (surface residues after C–C cleavage of phorone_A) releasing the active sites. Gorte and co-workers and Coenen et al. have demonstrated that water can enhance the decomposition of carbonate. In the DRIFTS-MS study of the acetone surface reaction, the carboxylate species dominate on the Zn1Zr10O16 surface in the absence of cofed water even at high temperatures. Our separate DRIFTS experiment also confirmed that the presence of water is beneficial to partially eliminate the strongly adsorbed surface carbonate on the Zn1Zr10O16 catalysts (Figure S6).

3.1.3. Possible Involvement of H2O in the ATIB Reaction. As mentioned above, two possible reaction pathways have been proposed where cofed water is involved in the reaction cycle (Scheme 3A, B). To further confirm that cofed water is indeed involved in reaction cycle, a DRIFTS-MS study of 18O-labeled water was utilized to examine the ATIB conversion.

Prior to the experiments, the possible oxygen distribution of the 18O labeled water corresponding to each reaction pathway is proposed as shown in Scheme 3. When DAA is proposed as the direct precursor of isobutene, Bronsted acidic protons and surface hydroxyl groups (via water dissociation) promote the DAA decomposition to isobutene and acetic acid (as Rorrer et al. proposed, Scheme 3A), CO2 should be produced by a facile acetic acid ketonization, where C16O216O (MS signal: 46) is generated. If the reaction proceeds through the acetone-phorone_A-isobutene pathway (Scheme 3B), carbonate will be produced via surface hydroxyl groups attacking the phorone_A. Coenen et al. reported that bidentate carbonate is stable at high temperatures (i.e., > 673 K) and desorbed CO2 includes C=O in carbonate based on the carbonate decomposition mechanism proposed by Burch. Thus, the decomposition of surface carbonate generated from phorone-A will also create C16O216O. Moreover, C16O216O likely be produced via acetone decomposition pathway, whereas acetone steam reforming will lead to both C16O218O and C18O2 as exhibited in Scheme 3.

Figure S5 depicts the evolving percentage of C16O2/C16O18O/C16O16O18O signal and DRIFTS spectra of surface hydroxyls in isotopic experiments. The reaction performance under similar isotopic experimental conditions is shown in Figure S7. No obvious deactivation was observed, and the selectivities barely changed. Because of the extremely low natural abundance of H218O (<0.3%), 18O-containing CO2 was not detected in the Acetone H218O reaction (Figure 5A). Upon switching to

Acetone H218O, however, C16O2 was still dominant (64%) with only 21% C16O18O and 15% C16O2 being observed in the CO2 (Figure 5A). From Scheme 3, C16O18O can be produced via water-involved ATIB pathways (Scheme 3A, B), aceton steam reforming (Scheme 3C), and acetone decomposition (Scheme 3D), whereas C16O2 should only result from acetone steam reforming (Scheme 3C). Based on the reaction stoichiometry (Scheme 3C, D), 7.5% C16O16O should be obtained from the acetone steam reforming reaction (calculated by the detected 15% C18O2), and 0.5% C18O16O should be from acetone decomposition (calculated by the ca. 1% methane derived from the flow reactor under similar conditions). Upon subtraction of the C18O16O contribution from acetone steam reforming and acetone decomposition, ca. 13% of the obtained C18O16O was contributed by the “water-involved” ATIB reaction pathways (Scheme 3A, B). In addition, a red shift of peaks ascribed to hydroxyls was observed after H218O was replaced with H216O (Figure SB) suggesting that water dissociates on the surface of catalyst. In Figure 4, the simultaneous disappearance of MSO and stable generation of isobutene likely be a result of the enhanced MSO-to-isobutene reaction in the presence of water. Note that, water must be involved in the reaction cycle if MSO is consumed to produce isobutene. However, the observation of minor C18O16O is contradictory to this assumption. The fact that a majority of C16O2 was detected in the Acetone H218O
reaction points to an alternative pathway, which will be further discussed in the following sections.

As above-mentioned, based on the CO₂ associated with the ATIB reaction (64% C¹⁶O₂ + 13% C¹⁶O¹⁸O), one can conclude that the majority of ATIB reactions (i.e., 83%, 64%/ (64% + 13%)) do not involve water. Therefore, we propose and confirm in the next section another possible reaction pathway to form isobutene and surface acetic acid/acetate via an intramolecular rearrangement of DAA (Scheme 4A). As CO₂ is generated by the subsequent ketonization of DAA to form isobutene and surface acetic acid/acetate, this unique reaction pathway leads to the exclusive production of C¹⁶O₂ in the steady-state "Acetone + H₂O" reactions (Scheme 4A). On the other hand, concurrent MSO production and deactivation was observed in the absence of water while robust ATIB was achieved in the presence of water (Figure 4). Scheme 4 describes the possible pathways proposed for the two scenarios. Regardless of cofed water, the density of water (Figure 4). Scheme 4 describes the possible pathways proposed for the two scenarios. Regardless of cofed water, acetone aldol addition is facile, leading to the formation of DAA. Without cofed water, we postulate the density of surface oxygen vacancies or Lewis acid sites is high, and the formed surface DAA exposed to the vicinal acid sites or oxygen vacancies tends to dehydrate to form MSO, which eventually leads to surface polymerization/coking (Scheme 4B). With cofed water, because the majority of water is not involved in the catalytic reaction cycle as proposed in Scheme 4A, we hypothesize that the adsorbed water significantly reduces the density of surface oxygen vacancies or Lewis acid sites creating an environment around DAA which mediates its early transition state to form isobutene instead of MSO. On the basis of the NMR and DRIFTS results, water dissociation readily occurs, leading to the formation of newly generated hydroxyl groups and thus highly mobile protons on the catalyst surface, although the deprotonation energy of those protons are not low enough to show Brønsted acidity (section 3.1.1). The fact that DAA decomposition to isobutene was observed instead of DAA dehydration in the presence of cofed water further confirms the less-acidic nature of the protons. Rapid proton exchange between surface bridging hydroxyls and adsorbed molecules have been reported on both Zn₂Zr₁₀O₁₈ and TiO₂. We postulate that the newly generated mobile protons in bridged hydroxyls over Zn₂Zr₁₀O₁₈ facilitate the rearrangement of DAA, where C−O bond cleaves and O−C(=O) bond forms simultaneously to form surface acetate and C−C bond cleaves to release gas phase isobutene.

3.2. Nature of Active Sites and Kinetic Analysis of ATIB Reaction Over Zn₂Zr₁₀O₁₈

In Section 3.1, we demonstrated that cofed water could not generate Brønsted acidity but creates more mobile protons via water dissociation on the Lewis acid sites of Zn₂Zr₁₀O₁₈. Rather than being directly involved in the acetone-DAA-isobutene reaction cycle (Figure 4), cofed water prevents the DAA dehydration to MSO, a culprit causing the catalyst deactivation, and promotes a facile DAA decomposition to isobutene and surface acetic acid/acetate via a proposed intramolecular rearrangement pathway. To further elucidate the role of water, in this section, we combine the DRIFTS and kinetic analysis to explore the nature of binding sites and reaction mechanism for the ATIB reaction catalyzed by the balanced Lewis acid-base pairs on the Zn₂Zr₁₀O₁₈. Although titration experiments are beneficial to elucidate the active sites on the surface, finding a suitable titrant that can survive under the current reaction conditions (i.e., high temperature, existence of water) is still challenging.

3.2.1. DRIFTS Study of Acetone Adsorption on ZnO, ZrO₂, and Zn₂Zr₁₀O₁₈

A series of DRIFTS measurements were performed to explore the nature of binding sites for acetone adsorption and activation. Figure 6 displays the acetone adsorption on ZnO, ZrO₂, and Zn₂Zr₁₀O₁₈. Negative peaks in the ν(OH) region implies that surface OH groups were perturbed by acetone adsorption. As compared to the Zn₂Zr₁₀O₁₈ spectrum, a much higher consumption of the terminal OH band at 3768 cm⁻¹ was detected in the ZrO₂ spectrum. Additionally, a blue shift of the bridged OH peak on Zn₂Zr₁₀O₁₈ (3700 cm⁻¹) relative to ZrO₂ (3687 cm⁻¹) was observed, likely due to perturbation of Zn⁺ in the ZrO₂ framework as reported in our previous work. A peak consumption at 3621 cm⁻¹ was also discerned on ZnO.
which can be attributed to OH groups related to oxygen vacancies on the ZnO oxide.63,64 This peak, however, was not observed on the Zn1Zr10O sample, further confirming the incorporation of Zn2+ in the ZrO2 framework.24

The structure of Zn1Zr10O mixed metal oxides has been studied, and it is found that incorporation of Zn2+ into the ZrO2 framework creates Zn−O−Zr moieties.24 Given the comparable surface areas of ZrO2 and Zn1Zr10O,8,24 a lower consumption of terminal hydroxyls on Zn1Zr10O relative to that on ZrO2 (Figure 6) indicates less adsorption of acetone on Zr cations associated with terminal hydroxyl groups over the former catalyst. Instead, our DRIFTS results and reaction data demonstrate an enhanced acetone enolization as well as C−C coupling over Zn1Zr10O, a strong indication that the ATIB reaction occurs on the Zn−O−Zr Lewis acid−base pair.8,25 Together with the dominant consumption of the blue-shifted peak at 3700 cm−1 on Zn1Zr10O (vs the dominant one at 3768 cm−1 on ZrO2), we propose that acetone predominantly adsorbs and is activated on the cationic sites (i.e., Zrσ+) in proximity to Zn2+ on Zn1Zr10O, namely, the Zrσ+−Oα−Zn Lewis acid−base pairs. The formation of the balanced Zrσ+−Oσ−Zn site pairs not only enhance the aldol-addition of acetone to DAA, but also provides the required synergy for the subsequent DAA decomposition to isobutene on the Zn1Zr10O catalysts in the presence of cofed water. The details regarding the concerted reaction pathway will be further discussed in the following section.

3.2.2. Kinetic Study of Acetone-DAA-Isobutene Over Zn1Zr10O. To further probe mechanism details, a kinetic study was conducted under differential conditions (conversion

Figure 7. Steady-state TOFIB (723 K) as a function of (A) acetone and (B) water partial pressure.

Scheme 5. (A) Proposed Reaction Mechanism (acetone-DAA-isobutene) of ATIB Cascade Reaction over Zn1Zr10O; (B) Sequential Reaction Steps (acetone-DAA-isobutene) of ATIB Cascade Reaction over Zn1Zr10O.
between acetone (or acetone evolved surface species) and reaction order of water reveals the competitive adsorption that the reaction mechanism and surface dominant species at room temperature.25 Given that the dehydration of DAA is a two-step process, DAA is formed via a facile acetone aldol addition via intramolecular rearrangement. Scheme 5 depicts the hypothesized reaction pathway where C=C bond cleavage and C=O bond formation occur (Scheme 5A). Surface protons with greater mobility as evidenced by 1H NMR may help facilitate the subsequent conversion of the DAA intermediate, producing isobutene and surface acetate via a concerted step. Our separate acetic acid experiments also revealed a much faster ketonization kinetics relative to that of the acetone to isobutene reaction (Figure S11). Additionally, the acetone-d8/D2O results suggest that α-H abstraction and water dissociation are not kinetic relevant. Therefore, we propose the rate-determining-step (r.d.s.) of ATIB is the DAA decomposition. Assuming water and acetone are surface prevalent species, the isobutene formation rate can be described as eq 5 (detailed derivation is in Section S2 in the Supporting Information):

$$r_{IB} = \frac{k_{decom}K_{C6}K_{ads,Ace}P_{Ace}^2}{(1 + K_{ads,Ace}P_{Ace} + K_{ads,H2O}P_{H2O})^2}$$

In eq 5, $K_{ads,Ace}$, $K_{ads,H2O}$ and $K_C$ represent the equilibrium constants of acetone adsorption, water adsorption, and acetone dimerization, respectively, whereas $k_{decom}$ is the rate constant for isobutene generation. The kinetic measurements at different water and acetone partial pressures is illustrated in Figure 8. The R-square of 0.96 indicates that the proposed kinetic model reasonably describes the measured isobutene formation rates.

![Figure 8. TOFIB as a function of $P_{H2O}$ and $P_{Ace}$ over Zn1Zr10Oy (acetone-DAA-isobutene, 723 K, conversion <7%).](https://doi.org/10.1021/jacsau.1c00218)

It is important to note that, despite the minor contribution of the “water-involved” pathway to the isobutene formation, this reaction pathway (Scheme 3A, B) includes both phorone-A secondary intermediate decomposition evidenced by our DRIFTS-MS7 and the surface hydroxyl-assisted DAA decomposition pathways proposed by Rorrer and co-workers. In principle, the measured rates can be fitted to the corresponding rate equation if the contribution of one pathway is negligible. However, if two “water-involved” reaction pathways are comparable and compromise each other, developing and testing of two “water-involved” pathways could be very complicated and thus is not attempted in this study.

To further confirm that water promotes the DAA intramolecular rearrangement, $Zn_xZr_{10-x}O_y$ in the presence/absence of water was also evaluated, particularly focusing on how the water affects the apparent activation energy in the isobutene formation as shown in Figure 9. The calculated apparent activation barrier is 98.9 kJ mol$^{-1}$ in the absence of water, which decreased to 88.2 kJ mol$^{-1}$ at $P_{H2O} = 0.4$ kPa. Because DAA is also the precursor of MSO (dehydration product), the fact that no MSO was observed even at $P_{H2O} = 0.4$ kPa
indicates that the cofed water must have affected the dehydration activation barrier. As described in eq 6, assuming the surface coverage of adsorbed water can be ignored under both conditions (details in Figure S12, Figure S13), the formation rate ratio between isobutene and MSO exclusively reflects the differences in stability between two transition states of DAA decomposition and dehydration.

\[
k_{\text{DAA-isobutene}} = \frac{k_{\text{DAA-isobutene}}}{k_{\text{DAA-MSO}}} = \frac{A_{\text{DAA-isobutene}}}{A_{\text{DAA-MSO}}} \times \exp\left(-\frac{E_{\text{DAA-isobutene}} - E_{\text{DAA-MSO}}}{RT}\right)
\]

\(k, A, \text{and } E\) represent rate constant, pre-exponential factor, and apparent activation barrier of DAA-to-isobutene or DAA-to-MSO. Note that the pre-exponential factor reflects the activation entropy. In the absence of water, the product distribution (Figure S13A) indicates that apparent activation barriers are comparable for the transition states of isobutene and MSO. However, in the presence of 0.4 kPa water (Figure S13B), almost 10-fold difference between the normalized selectivity to isobutene and MSO suggests \(r_{\text{DAA-isobutene}} \gg r_{\text{DAA-MSO}}\). The decreased apparent activation barrier for DAA-isobutene in the presence of water is likely a result of water altering the transition state. The slight decrease in \(E_{\text{DAA-isobutene}}\) would result in the improved production of isobutene assuming water does not affect the MSO formation. However, the fact that a higher partial pressure of water significantly hinders the MSO formation suggests that water must have also increased \(E_{\text{DAA-MSO}}\) or affect the activation entropy (i.e., \(A_{\text{DAA-isobutene}}/A_{\text{DAA-MSO}}\) ratio), leading to the favorable DAA-isobutene pathway.

To conclude this section, acetone-DAA-isobutene was confirmed as the dominant reaction pathway where the r.d.s. is the decomposition of an eight-membered DAA-derived transition intermediate. The transition state is likely to be stabilized by two Lewis acid centers that complement each other through a unique local environment resulting from the co-adsorption of H₂O/OH. We also demonstrated the multifaceted effects of water in the ATIB reaction in the following ways: (1) an appropriate amount of water is necessary to prevent the formation of MSO, a precursor to eventually form coke in the ATIB catalyzed by Lewis acid–base pairs; (2) surface protons with greater mobility on hydrated Zn₁Zr₁₀O₃ create a favorable environment, which likely stabilize the transition state of an eight-membered ring intermediate enabling a robust ATIB reaction.

### 3.3. Density Functional Theory Simulations

#### 3.3.1. DAA Adsorption on a Zn₁Zr₁₁O₁₂(111) Surface.

To study the adsorption of DAA on the dehydrated Zn₁Zr₁₁O₁₂ (111) surface (Figure 1A), the plausible adsorption sites were systematically scanned with the DAA molecule both with horizontal and vertical configurations with its functional groups (FGs) pointing toward the surface. The corresponding site numbers and a top view of the corresponding configurations are shown in Figures S14, S17, and S18. To evaluate the strength of the interactions of DAA and the surfaces, the adsorption energy was calculated based on eq 1. These energies of 24 distinct sites are plotted in Figure 10A. A strong average adsorption energy of \(-2.91\,\text{eV}\) was found. To understand this, the adsorption configurations at Site 10 was taken as an example by performing a corresponding charge density difference analysis and calculating the mean absolute charge transfer according to eqs 3 and 4. Both the hydroxyl and the carbonyl FGs were found to strongly interact with the surface. There is an electron gain that is predominantly localized within the oxygen FGs, leading to major electron losses from the surface Zr⁺⁺⁺ cations. A minor charge transfer was observed from the molecule’s carbon atoms to the adjacent hydrogen atoms near the FGs, inducing weaker dipole–dipole interactions with the surface. As a result, the strong attraction coming from an approximate charge transfer of 2.04 electrons (Figure 10B) leads to the strong adsorption...
Thus, the DAA molecule most favorably interacts with the Zn$_x$Zr$_y$O$_z$ surface through its two FGs because the FGs facilitate direct charge transfer to the surface. In addition, for comparison, the corresponding adsorption energies of DAA when its FGs point away from the surface were also determined, as shown in Figures S15, S16, and S19. Little charge transfer leads to the weak dipole–dipole interactions between C, H and the surface ions, indicating that the DAA molecule is unlikely to adsorb in this configuration on a Zn$_x$Zr$_y$O$_z$ surface.

### 3.3.2. Role of Water

To understand the influence of water on the adsorption of DAA, a water molecule was adsorbed on the dehydrated Zn$_x$Zr$_y$O$_z$ surface. The water molecule was assumed to decompose and form two hydroxyl groups. The hydrated surface models previously shown in Figure 1B (Hydrated Surface Type 1) and Figure 1C (Hydrated Surface Type 2) were used to model their interaction with the adsorption of DAA. The adsorption energies at 30 distinct possible adsorption sites on these two model surfaces were systematically compared. The corresponding site numbers and the top view of these configurations are shown in Figures S14–S23. The calculated average adsorption energies of DAA are $-2.07$ and $-2.20$ eV on the Hydrated Surface Type 1 (Figure 11A) and Type 2 (Figure 11B), respectively, which are both weaker than those on the dehydrated surface, where DAA’s average adsorption energy is $-2.91$ eV. Therefore, water likely plays an important role toward affecting the adsorption strength of DAA.

Our experimental results indicate that co-fed water enhances the production of isobutene and hindering the formation of MSO and its polymerization/coking reactions. Also, it is hypothesized that isobutene is produced by facilitating the attack of the DAA’s hydroxyl toward the carbon atom of the carbonyl FG (illustrated in Figure 12A). The bond distance...
between the C of the carbonyl FG and the O of the hydroxyl FG was calculated to understand the role of water toward distorting the DAA adsorbate and facilitating the formation of isobutene. The average C–OH distances are labeled in Figure 12 were bond lengths larger than 3.0 Å occur when the DAA molecule adsorbs on sites that are outside the vicinity of adsorbed water fragments (3.01 Å on the Hydrated Surface Type 1 in Figure 12D; 3.07 Å on the Hydrated Surface Type 2 in Figure 12F; and 3.07 Å on the dehydrated surface in Figure 12B). However, this average decreases to ~2.88 Å within the vicinity of the water fragments (2.90 Å on the Hydrated Surface Type 1 in Figure 12C; 2.86 Å on the Hydrated Surface Type 2 in Figure 12E). Thus, the adsorbed water fragments likely tend to repel the FGs from the surface, bend the hydroxyl FG toward the carbonyl FG, which may facilitate DAA’s further intramolecular arrangement to form isobutene.

To explain how the adsorbed water fragments affect the adsorption strength and deformation severity of DAA on the Zn1Zr11O12 surface, we compared several related adsorption sites of the DAA on Hydrated Surface 1 and Hydrated Surface 2 to the dehydrated surface. Figures 13A−D show four sites

![Image](image.png)

Figure 13. Top and side views of DAA (A–D) at sites within the vicinity of an adsorbed OH group on a hydrated surface type 1 and (E–H) at the corresponding sites on the dehydrated Surface. Zr, Zn, C, O, and H atoms or ions are represented by green, gray, black, red, and white spheres, respectively. Surface-adsorbed O and H atoms are represented by blue and orange spheres in the top views, respectively, for better illustration. Partial charge densities are presented by yellow isosurfaces for electron gains and by blue isosurfaces for electron losses with an isosurface value of 0.002 electrons/Bohr3.

where DAA adsorbs near the surface water OH fragments on Hydrated Surface 1 (“within the vicinity of surface OH”), whereas Figure 13E–H show four corresponding sites where DAA adsorbs on dehydrated Surface (“outside the vicinity of surface OH”). The detailed adsorption energy, distortion energy (based on eq 2), number of transferred electrons, and the C–OH bond distances as illustrated in Figure 13 and are tabulated in Table 1 whose average values are shown in Figure 14.

Interestingly, the average adsorption energy when DAA adsorbs within the vicinity of a surface OH is −1.48 ± 0.06 eV, which is substantially weaker than when it is outside the vicinity of surface OH, with a mean adsorption energy of −3.81 ± 0.63 eV. Such energy differences are clearly reflected in the differential charge analysis shown in Figure 13. As shown

![Image](image.png)

Figure 14. Comparison of average number of transferred electrons, adsorption energy, distortion energy, and carbonyl-bonded carbon—hydroxyl distance for systems in Figure 13

Table 1. Adsorption Energy, Distortion Energy, Number of Transferred Electrons, and Carbonyl-Bonded Carbon—Hydroxyl Distance for Systems in Figure 13

| site | A | B | C | D |
|------|---|---|---|---|
| adsorption energy (eV) | −1.60 | −1.58 | −1.40 | −1.35 |
| distortion energy (eV) | 0.34 | 0.36 | 0.36 | 0.40 |
| transferred electron no. | 1.43 | 1.25 | 0.91 | 1.34 |
| C−O distance (Å) | 3.00 | 2.84 | 2.85 | 2.97 |
| site | E | F | G | H |
| adsorption energy (eV) | −4.17 | −5.13 | −3.83 | −2.10 |
| distortion energy (eV) | 4.10 | 5.81 | 4.90 | 0.80 |
| transferred electron no. | 1.61 | 2.04 | 1.85 | 1.46 |
| C−O distance (Å) | 3.09 | 3.11 | 2.83 | 3.17 |

in the side view of Figure 13E−H, when DAA is far from a surface OH, both FGs strongly bind with the surface. The strong adsorption coming from the high average charge transfer value of 1.74 ± 0.13 electrons between the adsorbate and the surface ions. In contrast, when DAA adsorbs in the vicinity of the surface OH, as shown in Figure 13A−D, the average charge transfer decreases to 1.23 ± 0.10 electrons. Taking Figure 13C as an example, one can see why this is the case. Indeed, although DAA’s hydroxyl FG directly interacts with the surface metal ions, the flexible surface proton coordinates with the O of DAA’s carbonyl FG, which physically hinders the direct contact of the carbonyl FG and the surface cations. This weak proton-carbonyl dipole–dipole interaction correlates with the low charge transfer value of 0.91 electrons, a ~2 Å bond length between the carbonyl FG with the surface proton, and DAA’s low adsorption energy value of −1.40 eV. Thus, it is the coordination and repellency of the surface proton to the carbonyl FG that are responsible for the reduced average adsorption energy of 2.33 eV and a decreased average electron transfer value of 0.51 electrons. In addition, the surface proton, resulting from dissociation of the water molecule, plays a similar role as the adsorbed surface OH, as shown in Figure S24 and Table S1.

Furthermore, the adsorption configuration of DAA can determine the extent of bond weakening. When DAA is outside of the surface–OH vicinity, a strong interaction occurs
between its FGs and surface ions leading to a dramatic deformation of DAA with a severe distortion of the hydroxyl (Figure 13E, F) and the carbonyl (Figure 13H) FGs, stretching the bond distance between the O, from the DAA hydroxyl FG, and the C, from the DAA carbonyl FG, to a C–O bond length value of ~3.10 ± 0.04 Å. A smaller C–O bond distance of 2.83 Å occurs in the configuration shown in Figure 13G, due to the distorted carbon chain. We speculate that dehydration reactions would be more likely to occur on areas of the surface where no surface hydroxyl groups are present. In such a case, our DFT-based model indicates that the O–H bond of the DAA hydroxyl FG could dissociate upon its adsorption to the surface, as shown in Figure 13F. C–H bond dissociation could also occur from the methyl FG of DAA upon its structural distortion, as the methyl group interacts strongly with the surface (Figure 13G). Significant structural changes have led to a high average distortion energy of ~3.90 ± 1.09 eV, which may explain why coking is more likely to occur. These results support the hypothesis that without coveted water, the formed surface DAA is more likely to dehydrate, which eventually leads to surface polymerization/coking (Scheme 4B). In contrast, within the vicinity of the surface OH, DAA’s deformation is significantly limited without an apparent distortion of the FGs or the carbon chain, and its integrity is preserved, which hinders further dehydration reactions. This is because the surface OH inhibits the strong interaction of one of the FGs’ with the surface, leading to a much lower distortion energy of ~0.36 ± 0.01 eV. In such a case, the distance between DAA’s hydroxyl FG and carbon of the carbonyl group decreases to ~2.90 ± 0.04 Å (Figure 13A–D). Thus, the surface proton plays a significant role in protecting the integrity of DAA’s hydroxyl FG from severe distortion or dehydration reactions, and slightly bends the O of the hydroxyl FG toward the carbon of the carbonyl FG, which likely makes the formation of the isobutene possible. A summary of these results is given in Figure 14.

4. CONCLUSIONS

In this work, we demonstrated that the reaction mechanism of ATIB over a Lewis acid–base pair differs from the widely accepted one proposed on Brønsted acid sites. The distinct roles of water in the ATIB cascade reaction catalyzed by Lewis acid–base pairs (e.g., Zn,ZrO2) are also extensively elucidated. The reaction follows the acetone-DAA-isobutene mechanism in which DAA decomposition is the r.d.s. (Scheme 5). The rigorous mechanistic interpretation, kinetic evaluations, isotopic study, and DRIFTS-MS analysis confirm that majority of isobutene is directly formed from DAA via an intramolecular reaction with OH attacking to carbonyl FG of a formed eight-membered ring intermediate. Water is required to competitively adsorb on Lewis acid base pairs, which hinders the formation of MSO as well as provides an appropriate environment (mobile surface protons) to facilitate the transition from DAA to isobutene.

Our DFT-based model suggests that OH and H resulting from the decomposition of adsorbed water on the Zn,ZrO2 surface play important roles in protecting DAA from coking because the decomposed H is predicted to coordinate with the O of the carbonyl FG, physically hindering the energetic trapping of DAA. Consequently, the adsorbed DAA shows limited distortion when it is adsorbed within the vicinity of the decomposed water. Additionally, the adsorbed OH tends to repel against the hydroxyl FG, pushing it toward the carbon of the carbonyl FG, which promotes the intramolecular rearrangement of DAA to form isobutene. In contrast, when DAA absorbs outside of the vicinity of adsorbed water fragment, its adsorption is much stronger, evidenced by the large amount of transferred electrons between the O of the carbonyl FG, the hydroxyl FG, and the Zr4+ ions of the catalyst surface. The strong interactions between the FGs and the surface result in DAA’s dramatic structural distortion, which likely cause subsequent dehydration reactions. Thus, our theoretical calculations demonstrate how the exposure of water to the surface of the catalyst can prevent the energetic trapping of DAA and help facilitate the formation of isobutene.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00218.

Figure S1, top view of the possible configurations of the dehydrated Zn,Zr11O12 surface; Figure S2, relative energy comparisons and top view of the most favorable Zn,Zr11O12 surfaces; Figure S3, top view of the possible configurations of a hydrated Zn,Zr11O12 surface; Figure S4, relative adsorption energies for the dissociative adsorption of water and top view of the two most favorable configurations on a hydrated Zn,Zr11O12 surface; Figure S5: DRIFTS–OH and XRD of fresh and spent (24 h time on stream, Phto/PAdo=10.7 kPa/1 kPa, space velocity=0.03 molAce/gcat/h) Zn,Zr10O12; Figure S6, DRIFTS of acetone adsorption; Figure S7, conversion and selectivities as a function of time-on-stream; Figure S8, acetone conversion and isobutene selectivity as a function of inverse flow rate during steady-state ATIB reaction; Figure S9, ATIB reaction stability over Zn,Zr10O2 at different conditions; Figure S10, catalyst evaluation of fresh sample and 10-time-regenerated sample; Figure S11, comparison of acetone to isobutene reaction and acetic acid ketonization; Figure S12, measured TOF; Figure S13, selectivity and conversion; Figure S14, distinct position and corresponding number of each site; Figures S15–18, top views for vertical and horizontal configurations of DAA adsorbed at plausible positions pointing different directions; Figure S19, adsorption energies of possible adsorption sites for the DAA molecule with its FGs pointing away from a dehydrated Zn,Zr11O12 (T11) surface and top and side view for the adsorption of DAA at site 10; Figures S20–S23, top view for the horizontal and vertical configurations of DAA adsorbed at plausible positions on Hydrated Surfaces 1 and 2; Figure S24, top and side view of DAA at the sites within the vicinity of the adsorbed H on Hydrated Surface 2 and at the corresponding sites on the dehydrated Zn,Zr11O21 surface; Table S1, adsorption energy, distortion energy, and number of transferred electrons for systems in Figure S23; Section S2, derivation of the rate equation for the acetone-DAA-isobutene kinetic model (PDF)

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Notes

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