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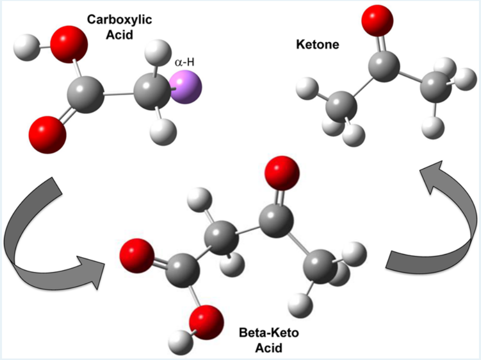
Ketonization of Carboxylic Acids: Mechanisms, Catalysts, and Implications for Biomass Conversion

Tu N. Pham, Tawan Sooknoi, Steven P. Crossley, and Daniel E. Resasco*

School of Chemical, Biological and Materials Engineering, and Center for Interfacial Reaction Engineering (CIRE), University of Oklahoma, Norman, Oklahoma 73019, United States



ABSTRACT: Ketonization is a reaction in which two carboxylic acids convert into a ketone, carbon dioxide, and water. While this reaction once found its industrial application for acetone production, it is regaining interest for its value in the upgrading of biomass-derived oxygenates, for example, bio-oils obtained from the fast pyrolysis of biomass. Namely, ketonization is crucial to reduce the detrimental effects of carboxylic acids in bio-oil. This review addresses reaction mechanisms, families of materials that catalyze the reaction (metal oxides and zeolites), and current applications of ketonization in the upgrading of biomass-derived oxygenates. A variety of mechanisms have been proposed to explain the ketonization reaction, and these proposals are critically discussed. The role of the *α*-hydrogen has been proven as a critical requirement for ketonization over catalysts that are active for surface ketonization and serves as the initial basis for the discussion. The role of crucial reaction intermediates such as ketene, beta-keto-acids, carboxylates, and acyl carbonium ions is critically evaluated. Finally, the importance of amphoteric properties of metal oxides on the ketonization reaction is explained. This analysis also explains the positive influence of additives, as well as prereduction treatments, on catalytic performance.

KEYWORDS: *carboxylic acid, ketonization, metal oxides, zeolites, ketene, β-ketoacid, α-hydrogen, bio-oil upgrading*

1. INTRODUCTION

With increasing demand for fossil fuels and growing concerns on climate change, biomass-derived hydrocarbon fuels have gained significant attention as alternative energy sources. Two important routes for the conversion of biomass into liquid hydrocarbon fuels and chemicals are fast pyrolysis and hydrolysis.[1−10] Fast pyrolysis converts solid biomass into liquid oil with yields near 80%. The bio-oil thus derived is a complex mixture of oxygenated compounds that varies widely with different biomass sources and process variables, and it typically contains furanics, phenolics, carboxylic acids, and other small oxygenates, which must be further upgraded to obtain gasoline, diesel, or chemical platforms.[1−3] The second option involves the aqueous phase hydrolysis of biomass to produce mainly sugars that can be dehydrated and further hydrolyzed to levulinic and formic acids.[8] In both approaches, the conversion of carboxylic acids is one of the first required upgrading steps. Ketonization (or ketonic decarboxylation) is a reaction that converts two carboxylic acid molecules into a ketone, carbon dioxide, and water, as follows:

$$R_1COOH + R_2COOH \rightarrow R_1COR_2 + CO_2 + H_2O$$

Therefore, ketonization can play a crucial role in many biomass conversion processes since it can remove the highly reactive carboxylic functional groups while increasing the size of the carbon chain. The result is a more stable product with higher energy content. In addition, the ketones produced are building blocks that can undergo further aldol condensation to expand the fraction of molecules that fall in the gasoline/diesel molecular size range. Therefore, in the next hydrodeoxygenation step, the smaller molecules are not eliminated in the form of light gases, but can be retained in the liquid product. The specific applications of ketonization in biofuel production will be further discussed in the last section of this review.

The first example of ketonization was reported in 1858 by Friedel,[11] who produced acetone by decomposition of calcium acetate. Following the same approach, other low-lattice-energy alkali and alkaline earth oxides were later found to be effective for producing acetone from acetic acid via the decomposition of the corresponding acetate. Later developments have shown that high-lattice-energy metal oxides such as TiO_2, CeO_2, ZrO_2, and MnO_2,[12−24] as well as zeolites[25] and heteropoly acid catalysts[26] do not follow the decomposition path, but can act as surface catalysts for the ketonization reaction.

Industrial applications of ketonization appeared before WWI, when acetone was commercially produced by dry distillation of calcium acetate, obtained from lime neutralization of wood distillates.[27] More recent cost-effective petrochemical routes of acetone production, such as the cumene process,[28] made ketonization less commercially appealing. However, ketonization has regained attention in recent years because of its potential applications in biomass conversion.

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A few comprehensive reviews on ketonization have been published in the past.[29−31] However, in view of the rapid development in this area during the past decade, an updated summary is appropriate. This review intends to provide a critical description of the mechanistic theories as well as the different catalysts that can be used for ketonization. In addition, process concepts for the application of ketonization in biofuel production will be delineated, together with research areas that require further efforts.

2. KETONIZATION MECHANISMS

Extensive research efforts on ketonization during the past 30 years have resulted in a variety of mechanistic explanations, with some of them not exempt of controversy. First, it is important to differentiate between bulk ketonization, which occurs via decomposition of the corresponding carboxylate salts, and surface ketonization, which is catalyzed by solid surfaces. For the bulk ketonization it is necessary to determine what oxides are able to form bulk carboxylates, which decompose releasing ketones. For the surface ketonization, it is crucial to understand the involvement of α-hydrogen and a number of various surface intermediates including ketene, β-ketoacids, adsorbed carboxylates, acyl carbonium ions, and acid anhydrides.

2.1. Bulk and Surface Ketonization. Yakerson et al.[32,33] were the first to point out the two entirely different phenomena that can lead to the formation of acetone from acetic acid. They noticed that oxides with low lattice energies (or very high basicity) such as alkali and alkali earth oxides, including MgO, CaO, BaO, SrO, and CdO, interact very strongly with acetic acid. This interaction results in the formation of bulk carboxylate salts, which decompose upon thermal treatment, generating acetone, water, and CO_2. This reaction has also been observed over highly basic rare earth oxides such as La_2O_3, Pr_6O_{11}, and Nd_2O_3.[34] In contrast, on oxides with high lattice energies such as TiO_2, CeO_2, ZrO_2, SnO_2, and so forth, the reaction proceeds via a completely different pathway, which is confined to the catalyst surface. This distinction was later emphasized by Ponec et al.[14−16,35] in a series of papers covering several oxides, such as TiO_2, Al_2O_3, ZrO_2, and Cr_2O_3 that are catalytically active to convert acetic acid to acetone. In the presence of H_2 and high enough temperatures, some of them are also active for the deoxygenation of acetic acid to acetaldehyde. They noticed that, in contrast, low-lattice-energy oxides transformed to acetate salts and only decomposed to acetone, even in the presence of H_2. They tested a number of oxides for ketonization of acetic acid in the vapor phase using H_2 as carrier gas.[14] Periodic sampling was performed during a temperature ramp, and the reactant/product concentrations were plotted against temperature to identify the mechanistic pathway. It was shown that for oxides with high lattice energy, the appearance of acetone, water, and CO_2 occurred simultaneously with the disappearance of acetic acid. In contrast, in the case of MgO, PbO, Bi_2O_3, the decrease in acid concentration occurred significantly before the formation of products. This observation led the authors to support the conclusion of the existence of two separate phenomena, as identified by Yakerson et al.[32,33] It is possible that in some cases, both mechanisms may be simultaneously operative on a given solid, and, depending on the reaction conditions, one of them can prevail. For instance, Kuriacose and Jewur[36] studied the ketonization of acetic acid over iron oxides in the presence of H_2 and found that the activation energy changed at 400 °C signaling a potential change in mechanistic pathway. They proposed that, below 400 °C, ketonization proceeds on the catalyst surface by interaction of two adsorbed molecules of acetic acid. By contrast, at higher temperatures, the reaction takes place through the bulk acetate decomposition. More recently, Snell and Shanks[20] have reported similar observations for the case of CeO_2, which has been typically considered a surface ketonization catalyst. They conclude that CeO_2 can promote the ketonization reaction through either the bulk or the surface mode, depending on reaction temperatures. However, opposite to the early study on Fe_2O_3,[36] CeO_2 seems to undergo bulk transformation in the low-temperature range (150−300 °C), whereas above 300 °C, the reaction only occurs on the catalyst surface. Clearly, different oxides may exhibit different behavior regarding formation/decomposition of bulk carboxylates, and the low/high lattice energy description may need refinement, which will require further research. In spite of many different mechanisms proposed to explain the bulk carboxylate decomposition pathway, there is an agreement in the necessity of two intermediate species, which serve as the source of alkyl and acyl (or carbonyl) fragments to form the ketone product.[15,49] Much of the research conducted on the thermal decomposition of aliphatic and aromatic carboxylate salts suggests that the formation of alkyl and acyl fragments are due to radical-like decomposition at elevated temperatures.[37,38] Such a mechanism does not require the presence of α-hydrogen atoms in the acids, which will be discussed in more detail in section 2.2 below. On the other hand, many studies on various carboxylic acids reveal an important effect of α-hydrogen for the surface-catalyzed ketonization. Furthermore, as discussed below, the mechanism and intermediate species formed during the surface catalyzed reaction are subject to debate. For this reason, in the subsequent part of this review, we focus on the role of α-hydrogen, mechanistic pathways, and intermediate structures together with catalyst requirements for the surface-catalyzed ketonization.

2.2. Role of α-Hydrogen. One characteristic element that consistently appears in all surface-catalyzed ketonization studies is the need for an α-hydrogen in at least one of the carboxylic acids participating in the reaction. α-Hydrogen is defined as the hydrogen bonded to a carbon atom in the α position relative to a carbonyl group. This atom displays relatively higher acidity in comparison to other alkyl hydrogens. For instance, while the pK_a values for alkyl C−H bond dissociation is typically on the order of 40−50, those for the α-hydrogen atoms are usually in the range of 19−20.[39] The critical role of the α-hydrogen in the ketonization of carboxylic acids has been well documented, mostly by H/D exchange studies and the strong dependence of ketonization activity on the number of α-hydrogens present on carboxylic acids.

Neunhoeffer and Paschke[40] were the first to point out that only those carboxylic acids that possess an α-hydrogen can undergo ketonization, that is, intramolecular ketonization of the dicarboxylic adipic acid to produce cyclopentanone.

As illustrated in Figure 1, their proposed mechanism starts with the abstraction of an α-hydrogen by a basic site of the catalyst surface, which leads to the formation of a nucleophile that can readily attack another carboxylic acid to form a ketone. In a more detailed study, Ponec et al.[14] showed a clear trend of increasing ketone formation rate with the greater number of α-hydrogen atoms on the carboxylic acid. This trend indicates that the presence of α-hydrogen atoms is essential for

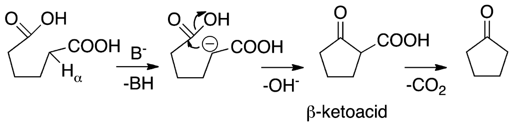


Figure 1. Ketonization mechanism of adipic acid proposed by Neunhoeffer and Paschke.[40]

ketonization. The role of α-hydrogen was also emphasized in a study by Nagashima et al.,[41] whose results are summarized in Table 1.

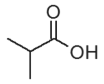
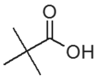
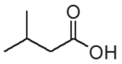
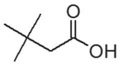
Here, again, it is seen that the formation of ketones in the reaction of propanoic acid with other α-substituted carboxylic acids depends on the presence of α-hydrogen atoms in the reactants. That is, the self-ketonization of propanoic acid, which has two α-hydrogen atoms, proceeds 10 times faster than that of 2-methylpropanoic acid, which only has one α-hydrogen atom. Finally, with the 2,2-dimethylpropanoic acid, which has no α-hydrogen, the self-ketonization activity cannot proceed. A similar conclusion is reached when the relative rates of cross-ketonization between propanoic acid and other carboxylic acids are considered. For example, the rate of cross-ketonization of propanoic acid and 2-methylpropanoic acid is much higher than the rate of 2,2-dimethyl-3-pentanone formation from propanoic acid and 2,2-dimethylpropanoic acid. Thus, while the reactivity trend seems to follow the number of α-hydrogen atoms in the molecule (i.e., 2,2-dimethylpropanoic acid < 2-methylpropanoic acid < propanoic acid), one must note that to vary the number of α-hydrogen atoms in this study, methyl groups have been incorporated. This substitution opens the discussion on steric hindrance, the second important aspect in determining ketonization activity. In fact, Table 1 shows that not only the number of α-hydrogen atoms but also the number of substituents at the β position influences the reactivity. This is clearly demonstrated in the comparison between 3-methylbutanoic and 3,3-dimethylbutanoic acids. Both, cross- and self-ketonization are greatly lowered with the increase in the number of methyl groups at the β position. Therefore, both the number of α-hydrogens and their steric accessibility are crucial elements to determine ketonization activity.

Among the several studies that illustrate the important role of the α-hydrogen in ketonization, Pulido et al.[42] investigated a mixture of two C5 carboxylic acids, namely valeric and pivalic acids, over a ZrO_2 catalyst. As displayed in Figure 2, valeric acid, with two α-hydrogens, and pivalic acid, with no α-hydrogen, show clear differences in activity. Valeric acid can be completely converted with 89% selectivity to self-ketonization and 4% selectivity to the cross-ketonization with pivalic acid, whereas the symmetric ketone of pivalic acid was not obtained. The results lend further support for the requirement of the α-hydrogen in at least one of the carboxylic acids.

Experiments with isotopically labeled compounds have also corroborated the crucial role of α-hydrogen in ketonization reactions. Ponec et al.[14−16] found that α-D was present in the acetone product formed by acetic acid ketonization on a predeuterated TiO_2 surface, whereas when feeding acetone, no H/D exchange occurred with the deuterated surface. This result clearly suggests that the intermediate for the formation of acetone interacts with the catalyst surface through its methyl group, resulting in α-hydrogen abstraction and exchange. Similar observations were previously reported by Jayamani and Pillai[43] and Munuera et al.,[44] who found that D in the α-position of ketones formed when unlabeled acid vapors were reacted over deuterated oxide surfaces.

Theoretical modeling was employed to study the activation energy of α-hydrogen abstraction of carboxylic acids, which may help to ascertain the feasibility of this step during ketonization. Ignatchenko[45] calculated the heat of adsorption and α-hydrogen abstraction energy barrier of various acids on a zirconia surface, using periodic density functional theory (DFT) calculations. It was found that the lattice oxygen on

Table 1. Molar Composition of Effluent Flow in the Reaction of 1:1 Molar Ratio of Propanoic Acid with Carboxylic Acid at 375 °C Using CeO_2−Mn_2O_3 at the Mn Content of 60 mol %[41]

Propionic acid (P)+ Carboxylic acid (CA)		3-pentanone (2P)	Asymmetric ketone (CA:P)	Symmetric ketone (2CA)	Unreacted propanoic acid	Unreacted counter acid	Others
2-Methylpropanoic acid		1.00	0.97[a]	0.10[b]	0.09	1.30	0.12
2,2-Dimethylpropanoic acid		1.00	0.03[c]	0.00[d]	0.34	2.16	0.09
3-Methylbutanoic acid		1.00	1.58[e]	0.25[f]	0.11	1.58	0.34
3,3-Dimethylbutanoic acid		1.00	0.26[g]	0.00[h]	0.30	2.10	0.14

[a] :2-methyl-3-pentanone

[b] :2,4-dimethyl-3-pentanone

[c] :2,2-dimethyl-3-pentanone

[d] :2,2,4,4-tetramethyl-3-pentanone

[e] :5-methyl-3-hexanone

[f] :2,6-dimethyl-4-heptanone

[g] :5,5-dimethyl-3-hexanone

[h] :2,2,6,6-tetramethyl-4-heptanone

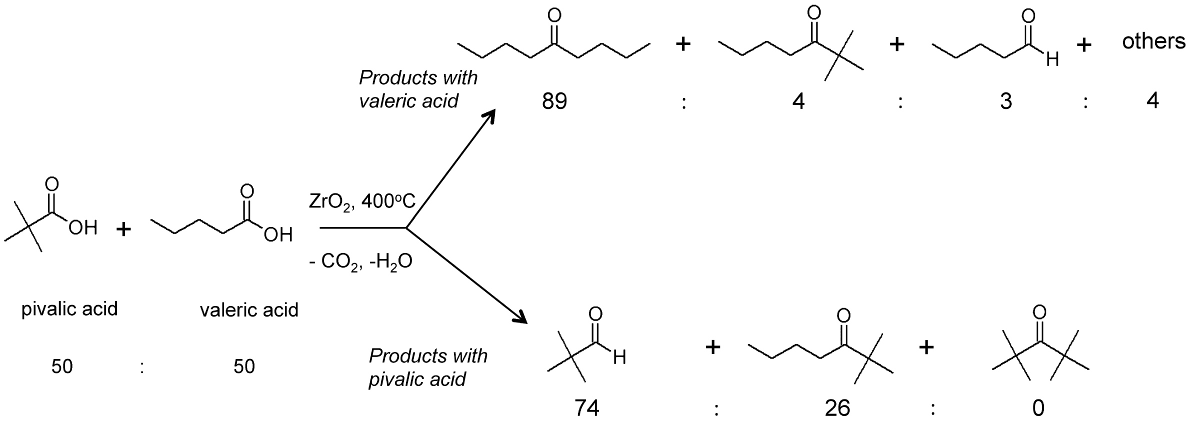


Figure 2. Conversion and product selectivity for ketonization of a mix of valeric and pivalic acid (1:1 molar ratio).[42]

the (111) ZrO_2 plane could readily abstract the H atom from the α position relative to the carboxylic group, as shown in Figure 3.[45]

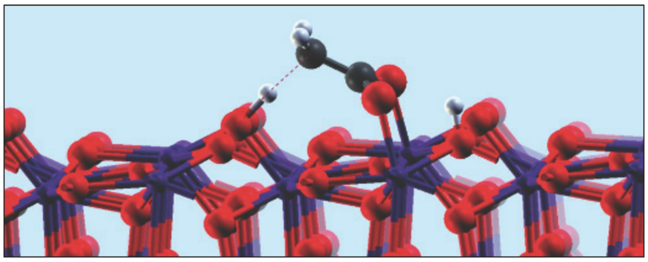


Figure 3. Dianion acetate species on the surface of ZrO_2.[45]

Three carboxylic acids, including acetic, propionic, and isobutyric acids with a varying number of α-hydrogens were investigated in this study. These calculations indicated that the energy barrier for the abstraction of the α-hydrogen that produces a dianion species appears to be 120−159 kJ/mol on the (111) ZrO_2 plane, depending on acid branching. In another theoretical DFT study that also used a periodic slab model of ZrO_2,[42] the reaction pathway involving an α-hydrogen abstraction step was compared to a concerted mechanism that does not involve α-hydrogen abstraction. The calculations indicated that the mechanism involving the α-hydrogen abstraction is kinetically favorable with a much lower activation energy, mainly because of the formation of a reactive nucleophilic center formed upon the α-hydrogen abstraction that can easily couple with another adsorbed molecule to produce a β-ketoacid intermediate, which then undergoes decarboxylation to produce the ketone. Details of this pathway will be further discussed in section 2.4. It is also significant that the reverse reaction, that is, protonation of the dianion, was reported to have a much lower energy barrier than the abstraction of α-hydrogen to form the dianion. Therefore, a competition between dianion protonation and β-ketoacid intermediate formation, which has a comparable activation energy, can exist.

An alternative route involving the required participation of the α-hydrogen for ketonization, but without the direct abstraction onto the surface to form a dianion species, has been recently considered.[22] In this case, the participation of the α-hydrogen would not be via direct abstraction by the surface but following a keto−enol tautomerization step, by which an intramolecular transfer produces a surface enolate, as illustrated in Figure 4.

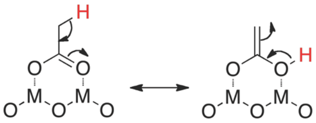


Figure 4. Keto−enol tautomerization step that converts the surface carboxylate into a surface enolate via intramolecular transfer of the α-hydrogen.

One might expect that this route is energetically more favorable than the direct abstraction of the α-hydrogen by the surface from an adsorbate that has already lost a proton. The resulting singly negative charged enolate species is more electronically stable than the dianion that would result from the deprotonation of the surface carboxylate. Theoretical calculations, comparing these two routes, have not been attempted yet, but they would be useful to shed more light on this important step in the mechanism.

In summary, a large part of the published ketonization studies seem to agree on the required participation of α-hydrogen. However, the exact details on how the α-hydrogen is involved in the reaction pathway are still debatable. Nevertheless, the recognition of the central role of the α-hydrogen has served as the basis for the development of several mechanisms, including the formation and participation of different intermediates, such as ketene and β-ketoacid, which are reviewed below in sections 2.3 and 2.4, respectively.

2.3. Ketene Based Mechanism. A ketene ($R_2C{=}C{=}O$) is formed by dehydration of a carboxylic acid containing at least one α-hydrogen atom.[46] Therefore, because of the connection with the requirement of an α-hydrogen, ketene has been frequently considered as a ketonization intermediate. A mechanism involving the coupling of an adsorbed ketene with a carboxylate was suggested in 1978 by Munuera et al.[44] and later further supported by Dooley et al.[18,19,47] In this mechanism, a carboxylate intermediate is first formed on a coordinatively unsaturated metal site and then dehydrated to a surface ketene intermediate. This adsorbed intermediate then couples with the alkyl group of an adsorbed carboxylate species to form the ketone. In this mechanism, the acyl group in the ketone originates from the ketene and not from the carboxylate. The suggested mechanism is illustrated in Figure 5.

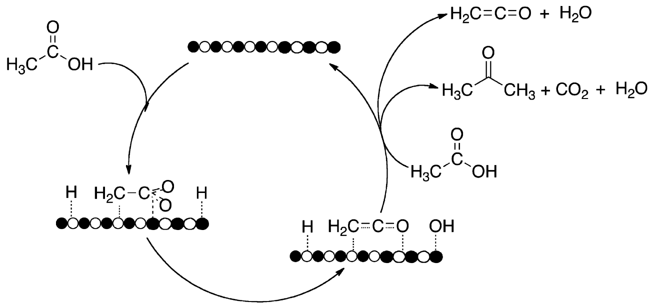


Figure 5. Ketene-based mechanism of acetic acid ketonization.

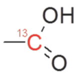
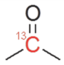
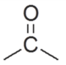
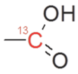
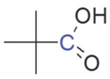
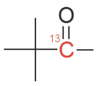
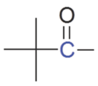
While the ketene mechanism is attractive because of its correlation with a central role of an α-hydrogen, the details on how a ketene and carboxylate couple to form a ketone on the surface are missing since this process should involve more than one elementary step.[31] While some evidence that supports the ketene based mechanism is given in the literature, as highlighted below, the common requirement of an α-hydrogen participation for both ketonization and ketene formation is perhaps the only solid argument in favor of the ketene mechanism.

Using a TiO_2 (anatase) catalyst, Munuera et al.[44] studied the ketonization of acetic acid combined with FT-IR analysis and isotopic labeling. Specifically, FT-IR was employed to examine the nature of various adsorbed species formed on the surface under different conditions. The similarity between the observed absorption bands with those corresponding to vapor phase ketene (3005 and 1730 cm^{-1}) was taken as an evidence for the existence of ketene on the surface after exposure to acetic acid. Furthermore, acetone was observed to evolve at around 200−350 °C during temperature programmed desorption (TPD) following exposure to acetic acid. This is about the same temperature range over which disappearance of the bands associated with the ketene occurred. This correspondence was used to conclude that ketene is the most likely ketonization intermediate. In addition, products from the reaction between unlabeled acetic acid with a catalyst surface pretreated with deuterated acetic acid were analyzed by mass spectrometry. Formation of all possible deuterated acetone products was observed. This outcome demonstrates that the reaction involves deuterated species from the surface. However, it is unclear whether they necessarily were deuterated ketene intermediates. It has also been proposed that the rate-determining step is the rate of ketene formation from the adsorbed acetate. The driving force for this step would be the electronic saturation of Ti^{4+} sites with the two surface species formed, −OH and CH_2CO.[44]

Likewise, Dooley et al.[18,19,47] supported the ketene mechanism by a series of studies that included isotopic labeling experiments on various supported CeO_2 catalysts. For example, they conducted the ketonization of acetic acid and cyclopropane carboxylic acid (CCA) on a 10 wt % CeO_2/TiO_2 catalyst to produce acetone and methylcyclopropylketone. Using a 3:1:1 mixture of CD_3COOH:H_2O:CCA as a feed, the authors compared the experimentally observed distribution of labeled products with the binomial distribution that one might expect from either the ketene or the direct concerted mechanism. The former should show D-exchange since the acetic acid only contains D atoms at the α-position. By contrast, the latter would result in no D-exchange, producing only CD_3COCD_3 and $CD_3COC_3H_5$. The experimental results showed that the most abundant products were of the type CHD_2COCD_3 and $CHD_2COC_3H_5$, demonstrating both the participation of only one α-hydrogen and the lack of any other exchange with the surface. While these results strongly support the participation of α-hydrogen in the reaction and provide indisputable evidence against the direct concerted mechanism, they are not conclusive about the participation of ketene as a kinetically significant reaction intermediate.

In fact, other authors have expressed opposing views to the participation of ketene as a crucial reaction intermediate. They have offered convincing evidence that seems to demonstrate that ketene may be a side product formed in parallel to the ketonization pathway rather than being a kinetically significant intermediate. Perhaps the strongest evidence against the ketene mechanism comes from the work of Ponec et al.[15] on a TiO_2 catalyst. They carried out reactions with mixtures of ^{13}C (^{13}C=O) labeled acetic acid and unlabeled pivalic acid, containing no α-hydrogen. As shown in Table 2, their results indicate that the cross ketonization product 2,2-dimethyl-3-butanone (pinacoline) does not contain any ^{13}C, which could only come from the ^{13}C-labeled acetic acid. At the same time, all of the side-product CO_2 was ^{13}C-labeled.

Table 2. Distribution of Labeled and Unlabeled Ketones Products in the Reaction of $CH_3\,{}^{13}COOH$ and $(CH_3)_3COOH$ over TiO_2 Catalyst at 350 °C[16]

Reactants	Products: Labeled	Products: Unlabeled
	 100%	 0%
 	 + CO_2 0%	 + $^{13}CO_2$ 100%

This unambiguous outcome indicates that the carbonyl group remaining on the ketone product has originated from pivalic acid, while CO_2 was produced from acetic acid. However, without an α-hydrogen, pivalic acid cannot form a ketene, while only acetic acid can. This is a strong argument against the involvement of a ketene as an intermediate for ketonization. If acetic acid forms the ketene (CH_2=C=O), which serves as the carbonyl group in the cross ketonization product between acetic and pivalic acid, it then could not generate CO_2. That is, the ketene might be a side product that is in equilibrium with the intermediate adsorbed species on the surface but not an intermediate directly linked to the ketonization reaction.

Similar conclusions can be drawn from a study reported by Martinez and Barteau.[13] They conducted the ketonization of various carboxylic acids at short contact times over titania-functionalized monoliths in the temperature range 533−680 K. Both, ketene and ketones were detected as products. However, the acetone selectivity of the bimolecular ketonization reaction on the titania-functionalized monolith was not affected when varying the conversion from 3 to 100%. The observed value of acetone carbon selectivity of approximately 75% agrees with the values given by the stoichiometry of the ketonization reaction (3C:1C in $(CH_3)_2{=}CO{:}CO_2$). If the reaction were sequential, one would expect to observe significantly lower selectivity at low conversions. These results provide another piece of evidence against the ketene-intermediate pathway and are consistent with previous surface science studies by Barteau's group,[12] in which the formation of both ketene and acetone from surface acetates on TiO_2 were indicated as parallel, rather than sequential pathways. In those studies, TPD was employed to investigate carboxylic acid decomposition on single crystal TiO_2 (rutile). Acetate species were shown to be stable intermediates formed by carboxylic acid adsorption on the various TiO_2 surfaces investigated. It was shown that the surface carboxylates can decompose at high temperatures via two parallel pathways, depending on the surface structure and composition. The (011) faceted surface, containing 5-fold O-coordinated Ti cations, was shown to decompose surface acetates exclusively via monomolecular dehydration to ketenes. By contrast, the (114) faceted surface catalyzed the bimolecular ketonization to acetone. These contrasting results indicate that, at high acetate coverage and when adjacent sites are present, the α-hydrogen activation results in ketonization, while isolated acetate species dehydrate to ketene. Clearly, these are parallel, rather than sequential reactions.

2.4. β-Ketoacid Intermediate. In addition to the crucial role of the α-hydrogen in the initial activation, another important component is the coupling of the two species on the surface, with the formation of an intermediate able to decompose with evolution of CO_2 and water. A species that fulfills these requirements is a β-ketoacid, which can be formed by coupling an enolate (enolized carboxylate) (alkyl fragment) and a carboxylate or an acylium (carbonyl or acyl fragment). These β-keto acids (or 3-oxocarboxylic acids) are organic compounds that contain a ketone group at the second carbon (or β position) from the carboxylic acid group. This type of compound can undergo decarboxylation to produce a ketone and CO_2 quite readily upon mild thermal treatment. It is generally accepted that the mechanism for decarboxylation of β-ketoacids involves redistribution of six electrons in a six-membered cyclic transition state to give an enol that can be rapidly tautomerized to form the corresponding ketone, as shown in Figure 6. It is important to note that the easiness of decarboxylation is a unique characteristic of β-ketoacids.[48]

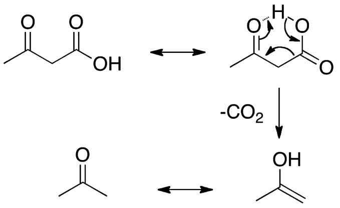


Figure 6. Decarboxylation mechanism of β-ketoacid.

The participation of this intermediate in the mechanism is, in fact, in line with the original proposal of Neunhoeffer and Paschke[40] who recognized the role of a β-keto acid in the formation of cyclopentanone from adipic acid, as already shown in Figure 1, above. Of course, in that case, it was a monomolecular step, while in the case of acetic acid ketonization, it necessarily implies the participation of two adsorbed molecules. There have been a number of studies that support the path involving a β-ketoacid as an intermediate in the ketonization reaction, even though a β-ketoacid has never been detected during ketonization. The rapid decomposition mentioned above makes the detection practically impossible. Among the various studies proposing β-ketoacid-mediated mechanisms, the one by Nagashima et al.[41] is illustrated in Figure 7.

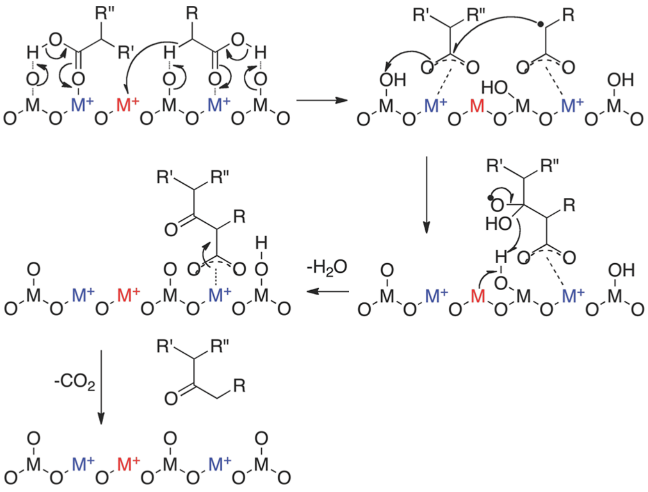


Figure 7. Proposed β-ketoacid based mechanism for vapor phase ketonization of carboxylic acid over $CeO_2{-}Mn_2O_3$ catalyst.[41]

As mentioned above, the formation of surface carboxylates is the first step. Subsequent abstraction of an α-hydrogen atom from the carboxylate results in an anionic radical that attacks another carboxylate and forms the β-ketoacid intermediate, which, as mentioned above, can readily decarboxylate to form the ketone product. This mechanism involves consecutive reduction–oxidation cycles of the catalyst, a process for which redox oxides such as CeO_2 are particularly effective.

Our group[22] has also suggested a ketonization pathway through a β-ketoacid intermediate as shown in Figure 8. However, instead of considering the direct abstraction of an α-hydrogen by the surface, we proposed that the adsorbed carboxylic acid could be enolized, which might be energetically more favorable than a second deprotonation. The enolized carboxylate species can readily undergo nucleophilic attack to another adjacent carboxylate to yield the β-ketoacid, which can then readily decompose to form a ketone and CO_2. This proposed mechanism takes into account the demonstrated need for the involvement of an α-hydrogen since, to form the β-ketoacid, a nucleophilic center at the α-carbon must be formed. Hence, removal of the α-hydrogen must occur either via surface abstraction or, as proposed here, through an enolization step.

This mechanism is also consistent with the isotopic labeling studies by Ponec et al.,[15] which reported that CO_2 was produced from the molecule in which the α-hydrogen was activated. As seen in the β-ketoacid reaction pathway, the carboxylate species that has undergone enolization/α-hydrogen abstraction, is the one that gets decarboxylated.

In the two mechanisms described above, the β-ketoacid is proposed to be formed from two adjacent surface carboxylates. An alternative path has been suggested by Renz. et al.[42] and Ignatchenko et al.[49] who propose that the β-ketoacid results

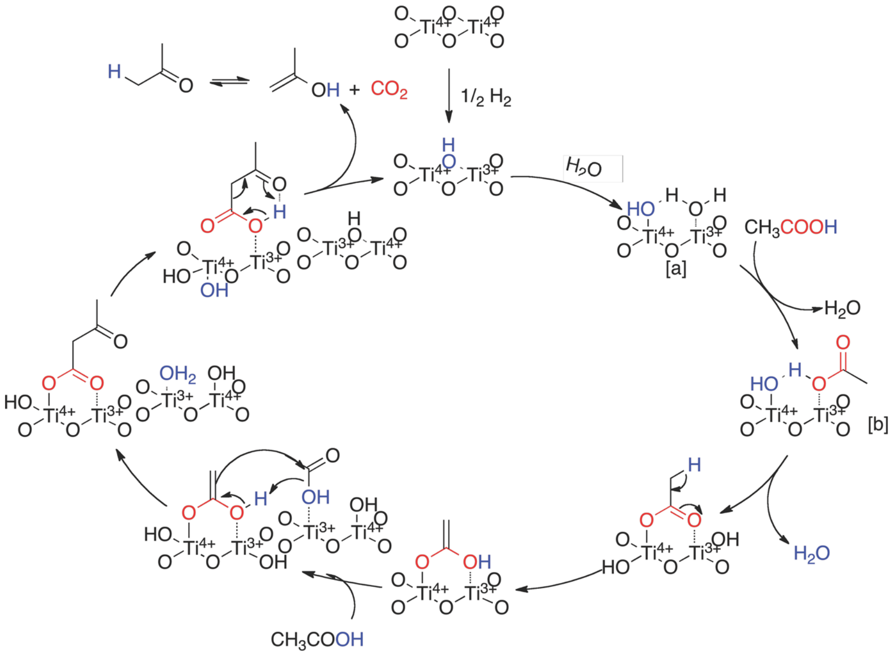


Figure 8. Proposed β-ketoacid based mechanism for liquid phase ketonization of carboxylic acid over TiO_2 catalyst.[22]

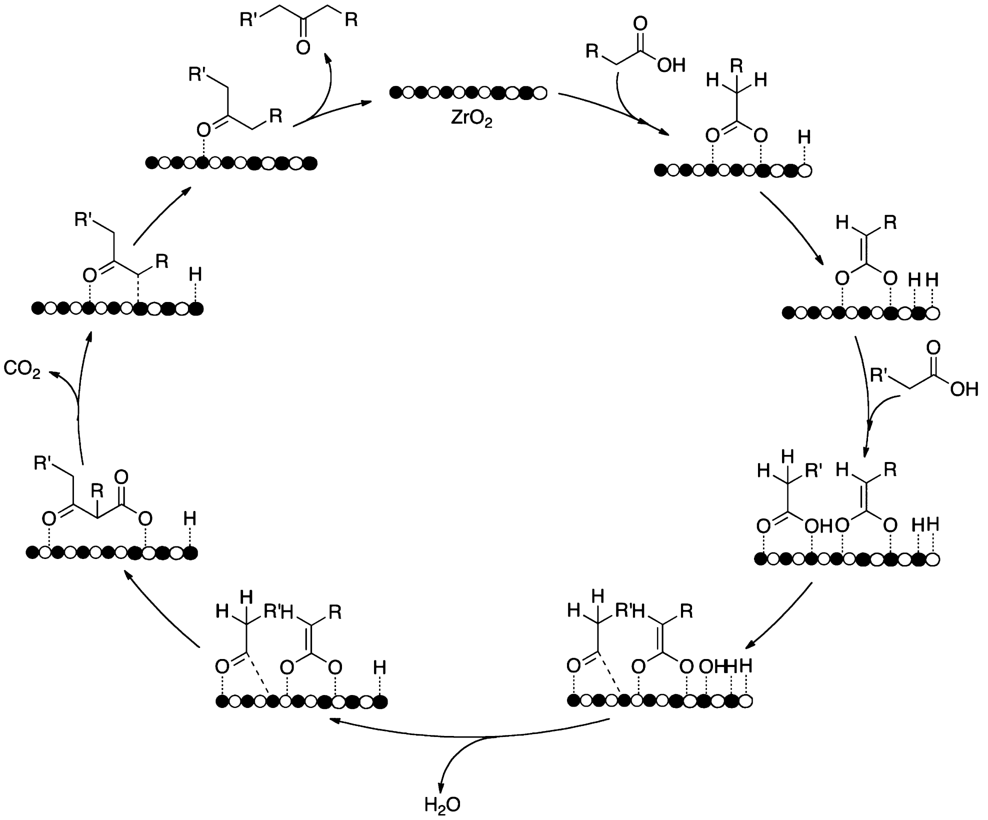


Figure 9. Proposed mechanism for ketonization of carboxylic acid over ZrO_2 catalyst via β-ketoacid formed by an acyl and an enolized carboxylate on the surface.[42]

from the coupling of a surface enolate with an acylium ion. The former species is formed by typical deprotonation and α-hydrogen abstraction of a carboxylic acid while the latter is formed by dissociation of OH on the surface, as proposed by Kuriacose et al.[81,36] The mechanistic pathway put forward by Renz et al. is summarized in Figure 9.

As will be discussed in section 3, acyl species have been detected on the surface of zeolite catalysts.[50−52] However, on reducible oxides, it is hard to differentiate between an acyl and a carboxylate since an acyl can be converted to a carboxylate by nucleophilic addition of lattice oxygen. In fact, surface science studies of carboxylic acids on reducible oxides have only given evidence for the presence of carboxylate species.[61,71]

The energy barriers calculated in the DFT study of Pulido et al.[42] show that the ketonization via the β-ketoacid route would require a much lower activation energy (108 kJ/mol) than the direct concerted pathway (154 kJ/mol), which is in agreement with the experimental results described above. Unfortunately, the calculations become less convincing when they indicate that the β-ketoacid decarboxylation step that forms the ketone and CO_2 is rate limiting. It is well-known that this step is relatively easy and may occur by simple thermal heating, which makes it unlikely as a rate limiting step.

2.5. Other Mechanisms. Other mechanisms have also been suggested for the ketonization of carboxylic acids. From their detailed isotopic labeling investigations, Ponec et al.[16] concluded that an α-hydrogen is necessary for the ketonization reaction to proceed and that the rate determinant intermediate is in equilibrium with the ketene. They arrived at this conclusion after inferring that the ketene is not kinetically significant, but its concentration followed very closely the inverse of acetone concentration. The proposed mechanism is displayed in Figure 10.

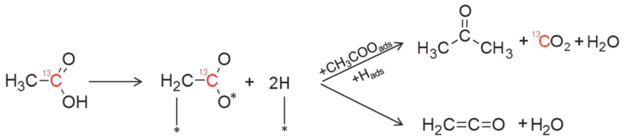


Figure 10. Proposed mechanism for ketonization of carboxylic acid over TiO_2 catalyst by Ponec et al.[16]

In this mechanism, after the initial adsorption of a ^{13}C-labeled acid molecule that forms a surface carboxylate, a second hydrogen abstraction occurs, leading to a multiply bonded surface intermediate that ends up parallel to the surface. This configuration allows for the dissociation of the C−^{13}C bond to form a methylene species. This adsorbed species is suggested to be in equilibrium with the gaseous ketene. In this proposal, the methylene species is the crucial intermediate that reacts with a carboxylate in the immediate vicinity to form the ketone product. This mechanism, however, has been questioned by Nagashima et al.[41] They argue that if such methylene species were present during the reaction, methanol should have been produced in measurable amounts by interaction with water, which is present under the ketonization reaction conditions. This is a valid argument against this mechanism.

Bamberger[53] suggested the formation of intermediate acid anhydrides, which decarboxylate to give a ketone. This was based on the observation that over MnO_2, carboxylic acids yielded both acid anhydrides and ketones. In line with the ketene mechanism, acid anhydride may be formed by the reaction of a ketene and another carboxylic acid. However, it is still unclear that the decomposition of acid anhydride yields a ketone and CO_2. As ketonization is often observed along with decarbonylation/decarboxylation, one may expect that a similar mechanism may well lead to the formation of ketone. For example, over a Pd catalyst,[54] it was proposed that an acid anhydride complex decomposed to acyl and a carboxylic acid as shown in Figure 11.

The decarbonylation of the acyl complex results in a surface alkyl with a redox cycle of Pd^{2+} and Pd^0. In this case, the alkyl on the surface dehydrogenates to an alkene while water is formed as side product. However, such surface alkyl species may also react with adjacent acyl species to form a ketone. Alternatively, the decomposition of such acid anhydride complex in a redox cycle may lead to coupling of the acyl-M-R complex as shown in Figure 12.

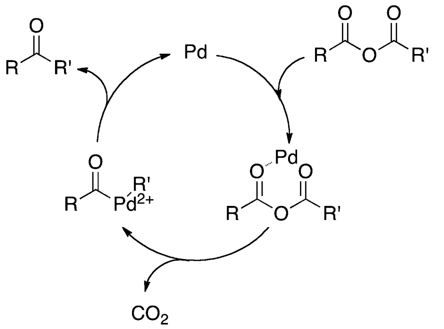


Figure 12. Possible ketone formation mechanism from acid anhydride.

3. CATALYSTS

Over the past thirty years, a large number of catalysts, including metal oxides and zeolites, have been found to be active for the ketonization of carboxylic acids. Many studies on different types of catalysts have been devoted to find answers to fundamental questions related to the nature of the active sites and structure of the kinetically significant intermediates on the different catalysts. Various techniques and approaches have been employed toward this goal. In this section, we attempt to offer a comprehensive description of the adsorption behavior of carboxylic acids and the required catalytically active sites for ketonization.

3.1. Metal Oxides. A variety of basic, acidic, and amphoteric oxide catalysts have been investigated in the literature for ketonization of different carboxylic acids under various reaction conditions. Glinski et al.[55] demonstrated that

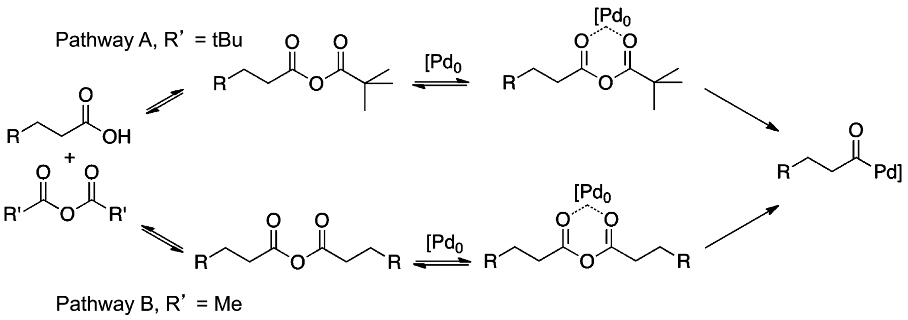


Figure 11. Proposed decomposition pathways of acid anhydride.[54]

ketonization can be catalyzed by many different oxides. To show this, they carried out ketonization on 20 different metal oxides supported on silica. The results are listed in Table 3.[55]

Table 3. Activity of 10 wt % MO_x/SiO_2 Catalysts in Ketonization of Acetic Acid[a]

	yield of acetone	
catalyst	648 K	673 K
B_2O_3	2	3
MoO_3	4	5
WO_3	6	5
P_2O_5	10	12
V_2O_5	9	21
Bi_2O_3	11	18
NiO	31	
Al_2O_3	15	37
CuO	29	39
ZnO	19	33
PbO	36	76
Cr_2O_3	48	39
Fe_2O_3	66	59
CoO	50	63
MgO	53	59
Nd_2O_3	22	61
La_2O_3	50	87
MnO_2	72	96
CdO	76	94
CeO_2	96	97

[a] Data taken from ref 55.

One can see that amphoteric oxides (CeO_2, MnO_2, La_2O_3) appear to be better catalysts than pure acidic or basic oxides. Subsequent investigations[12−23,56,57] have led to the same conclusion. That is, amphoteric reducible oxides possess good ketonization activity and selectivity. A generalized description of the adsorption behavior of carboxylic acids on typical amphoteric metal oxides can be derived from surface science studies. As reviewed in the following section, these studies reveal the nature of the key properties that determine ketonization activity, in good agreement with the proposed reaction mechanisms described above. Therefore, an effective oxide catalyst for surface ketonization should be able to dissociatively adsorb the carboxylic acid forming surface carboxylates and have adjacent coordinately unsaturated cation sites to allow the adsorbate−adsorbate interaction that leads to the formation of the crucial intermediate (i.e., a *β*-keto-acid). Some authors have described this behavior in terms of acid−base or redox properties, as summarized below. However, these are different manifestations of the same fundamental phenomena.

3.1.1. Interaction of Carboxylic Acids with Oxide Surfaces.

The adsorption geometry and chemistry of carboxylic acids, including formic acid, acetic acid, propanoic acid, and higher carboxylic acids on various metal oxides have been thoroughly investigated both theoretically and experimentally. Investigations on the amphoteric oxides TiO_2 and CeO_2 will be specifically discussed as case studies. The adsorption of carboxylic acids on anatase and rutile TiO_2 has been thoroughly investigated for years, particularly on the most stable planes, that is, (110) rutile and (101) anatase. Several excellent reviews on the surface science of TiO_2 single crystals have been written by Diebold[58,59] and Barteau et al.[60,61] Carboxylic acids adsorb dissociatively on both surfaces, producing surface carboxylates ($RCOO^-$) and hydroxyl groups (OH^-) associated to surface cations.[62−66] One can visualize this as a simple proton abstraction of a carboxylic acid by a basic oxygen on the metal oxide surface. Several studies calculated energies for dissociative and nondissociative adsorption modes of various carboxylic acids. The results of these investigations clearly indicated that dissociative adsorption is more energetically favorable. The carboxylates ($RCOO^-$) can bind by one or two oxygen atoms binding to the metal cations with three possible coordination structures, namely, monodentate, bridging, and chelating bidentate, as shown in Figure 13.

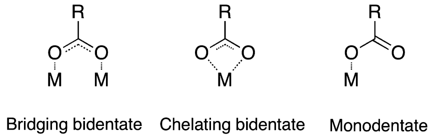


Figure 13. Different adsorption configuration of carboxylates on catalyst surfaces.

It is widely established that the most stable carboxylates bind to two surface cations in a bridging bidentate configuration,[67] as evidenced by scanning tunneling microscopy,[68] FTIR, X-ray photoelectron diffraction[69] as well as by ab initio slab and cluster calculations.[70] However, if there exists an oxygen vacancy on the surface, an alternative geometry involving the filling of an oxygen vacancy site by one of the carboxyl oxygen atoms with the other bound to a Ti atom has also been observed. A near edge absorption fine structure spectroscopy (NEXAFS) study of formate, acetate, and propionate supported the existence of minority adsorption sites involving oxygen vacancies.[64]

Numerous efforts have been aimed at understanding the participation of the adsorbed carboxylates in the catalytic reaction. For example, Pei and Ponec[71] examined the adsorption and surface reaction of acetic acid on TiO_2 using FT-IR. When acetic acid was dosed at room temperature, new strong bands appeared associated with carboxylates in monodentate and bidentate configurations. However, upon heating to 100−300 °C, the monodentate band gradually disappeared, leaving only the bands associated to strongly bound bidentate carboxylates. Since only bidentate carboxylates can be observed at 300 °C, which is a typical temperature for ketonization activity in a vapor phase flow reactor, these studies suggest that bidentates are species of crucial importance in the catalytic process.

In a surface science study, Kim and Barteau[12] used TPD to explore the decomposition pathway of surface acetates on single crystals at high temperatures. On the TiO_2 (114) plane, where two acetates are bound to the same Ti, acetone evolved at 580 K as a product of ketonization. An equivalent result was observed for propanoic acid, which produced pentanone. However, on the TiO_2 (011) plane, which can only bind one acetate group per Ti center, monomolecular dehydration to ketene was the major pathway. It is noteworthy that in contrast to the well-known bidentate adsorption configuration observed in FT-IR investigation by Pei and Ponec,[71] the two acetate species involved in ketonization should be monodentate coordinated to the same Ti on the (114) rutile surface. This suggests the possibility that carboxylate species can bind with metal cations in a number of different conformations during the course of ketonization. The change in binding type might play an important role in determining the ease at which the transition state is formed. For instance, the bidentate, as the most stable adsorbed species, could form initially on the surface. However, during the catalytic cycle this species could undergo a transformation to the less restricted adsorption configuration such as monodentate that can readily undergo the attack from another species to form the ketone with a lower energy barrier.

These results provide strong support for the participation of carboxylates rather than ketene species in the ketonization reaction. In addition, it also sheds some light on the site requirements of metal oxides for ketonization activity. The authors concluded that for ketonization to occur, a surface containing doubly unsaturated cations must be present.[12] These single crystal studies have helped to identify as an important requirement the creation of coordinatively unsaturated vacancies on the catalyst surface. While this study indicates that the cations need to retain their 4+ oxidation state, one might anticipate that reduction could be a way to create such coordinatively unsaturated sites on high surface area powder catalysts and thus improve catalytic activity.

Studies of the interaction of carboxylic acids with CeO_2 allow to draw some conclusions about the similarities and differences with those observed with TiO_2. For example, the reaction of acetic acid on the CeO_2 surface has been investigated by employing FT-IR. Zaki et al.[72] showed that the adsorption behavior of acetic acid on CeO_2 is essentially similar to the adsorption on TiO_2. Specifically, adsorption bands due to bidentate acetate surface species appeared over the full range of scanned temperature of 200−400 °C, and a strong shoulder was observed above 300 °C, suggesting the occurrence of acetone condensation into mesityl oxide surface species. In another study, Stubenrauch et al.[73] studied the adsorption and reaction of acetic acid on CeO_2 (111) and (100) single crystal faces using TPD and HREELS techniques. Dissociation (deprotonation) of the acid and formation of surface carboxylates was observed on both surfaces, similar to the situation observed with TiO_2. However, the specific morphology of the adsorbate on CeO_2 and its relationship with the surface topology are less clearly understood than in the case of TiO_2. During the heating ramp, the acetates were found to decompose and form ketene and acetone on CeO_2 (111), while only ketene was observed on CeO_2 (100).[73]

In summary, adsorption of carboxylic acids gives rise to similar carboxylate species on different oxide surfaces. Upon increasing the temperature, conversion of the adsorbed carboxylate to ketones occurs on certain surfaces, which is entirely consistent with the picture of a bidentate carboxylate as an initial reaction intermediate. More importantly, the surface science studies are useful in providing concrete insight concerning the nature of the surface properties that dictate the ketonization reaction. Two important requirements for ketonization active sites are the following: (i) coordinatively unsaturated surface metal cations/oxygen anions for the initial deprotonation of carboxylic acids; (ii) surface cation sites that can bind mutiple carboxylates or pairs of adjacent exposed cations for coupling pairs of carboxylates to produce ketones. These surface coordination features, from a catalytic chemistry perspective, are viewed and discussed in terms of acid−base and/or redox properties, as illustrated by the following examples.

3.1.2. Acid−Base Properties. Amphoteric reducible metal oxides, such as CeO_2, TiO_2, and ZrO_2, have been reported to be the most active catalysts for ketonization. Therefore, acid−base properties or exposed surface cations/anions with coordination vacancies have been proposed to play a crucial role in their superior ketonization activity. Different characterization techniques including TPD of CO_2 and NH_3 and FTIR of adsorbed acetone/pyridine[74,75] demonstrate the amphoteric character of CeO_2, TiO_2, and ZrO_2. Adsorption of a basic molecule, such as pyridine, shows evidence of Lewis acid sites on three types of oxides. Based on the frequency of pyridine coordinated to Lewis acid sites, the Lewis acid strength of the various metal oxides follows the order $TiO_2 > ZrO_2 > CeO_2$.[74,76] On the basis of CO_2 adsorption studies, Martin and Duprez[77] compared the density of basic sites on several oxides and concluded that CeO_2 possesses the highest basic site density (3.23 μmol CO_2 m^{-2}), followed by MgO (1.77 μmol CO_2 m^{-2}), and ZrO_2 (1.45 μmol CO_2 m^{-2}). However, in terms of strength, CeO_2 and ZrO_2 both have weaker basic sites than MgO. By contrast, while CO_2 adsorbs on TiO_2, it desorbs upon evacuation at room temperature, indicating a much weaker basicity than that of ZrO_2 and CeO_2.[78] It is important to note here that CO_2 in the presence of reducible oxides may adsorb in defects on the catalyst surface, and may not be an accurate representation of the number or strength of basic sites.

Exposed metal cations generally act as Lewis acid sites while oxygen anions are Lewis base sites. However, the coordination of oxo oxygen (e.g., ketones, carboxylic groups) to oxophilic coordinatively unsaturated cations or oxygen vacancies is not necessarily due to the acidity of the site. At the same time, for the formation of surface carboxylates discussed above, the oxygen anions must act as Brønsted basic sites rather than Lewis basic sites. Therefore, the ketonization activity of amphoteric oxide catalysts may not necessarily relate to their acid/base character.

As mentioned above, there is ample experimental evidence that links the observed ketonization activity with the presence of surface acid and base sites or, in light of our ongoing discussion, of exposed coordinatively unsaturated metal cations and oxygen anions. At the same time, since CO_2 and acetone have affinity for surface Lewis base and acid sites, they are expected to act as inhibitors of the ketonization reaction as they compete with acid molecules for the coordination sites, that is, exposed cations and anions.[79] In fact, this inhibition has been verified experimentally.[80] It is worth noting here that the extent of CO_2 adsorption is not only a measurement of Lewis basicity, but also the density of uncoordinated cations, which are more relevant for formation of surface carboxylates.

Gaertner et al.[81] studied the conversion of hexanoic acid over ceria-zirconia and reported that the catalytic activity decreased to approximately 30% of its initial value when cofeeding CO_2. More importantly, activity was not regained after the CO_2 flow was stopped. This result not only demonstrates the competitive adsorption of CO_2 with the carboxylic acids, but also an irreversible loss of active sites by permanent coordination of CO_2 to the exposed cations (or oxygen vacancies). At the same time, inhibition by acetone has been observed on Zr−Cr−Fe mixed oxides.[82] Acetone significantly suppressed the reaction rate of acetic acid, suggesting the blocking of required exposed cations for the reaction. In another study, the inhibition of dehydration and dehydrogenation rates of isopropyl alcohol and cyclohexanol by the presence of acetic and propanoic acids has been quantified.[83] It was reported that acetic and propanoic acids suppressed both dehydration and dehydrogenation rates, which take place on acid and base sites of metal oxides, respectively.[84,85] A correlation between ketonization rates and the extent to which they suppress the dehydration and dehydrogenation was established. These results suggest that carboxylic acids utilize both dehydration and dehydrogenation sites, implying the involvement of both acid and base sites for ketonization. In line with these results, our recent kinetic studies on the ketonization of acetic acid show negative reaction order with respect to the concentrations of CO_2, water, and acetone, all of which compete for coordinatively unsaturated cation sites.[80] We have also shown that while the ketonization activity increases with a reductive pretreatment of the TiO_2 catalyst,[22] it drops when the reduced catalyst is exposed to O_2 before reaction.[80]

3.1.3. Redox Properties. Together with acid−base properties, the redox capacity of the solid (i.e., how easily coordination vacancies can be formed) has been linked to its ketonization activity, especially in the case of CeO_2.[14,19] The exceptional redox properties of CeO_2 are well-known for its application in automotive catalytic converters, since this oxide is able to undergo fast and deep reduction/oxidation cycles (i.e., $CeO_2 \leftrightarrow CeO_{2-x} + O_x$). Therefore, it effectively stores and releases oxygen during the fuel-lean (excess O_2) and fuel-rich phases (no O_2), respectively.[86] In reference to ketonization, Nagashima et al.[41] proposed that the surface oxide may be reduced by α-hydrogen abstracted from the feed and reoxidized through the combination of its proton and hydroxyl group from the acid to form water as seen in Figure 7. In this sense, the redox cycle was considered key in maintaining the ketonization activity. While the bulk redox ability of ZrO_2 and TiO_2 is much lower than that of CeO_2,[87,88] they are still able to form oxygen vacancies and exposed surface cations with a high degree of unsaturation. Therefore, their ketonization activity may be more closely related to the capacity to form these sites than the bulk reducibility.

3.1.4. Effect of Dopants and Catalyst Pretreatments. The enhancement of ketonization activity by the addition of dopants such as transition metals and metal oxides and by prereduction treatments has been a matter of interest in various investigations. Doping or prereduction of the catalyst can presumably affect the density of several of the potential characteristics that can be linked to ketonization activity:

(a) oxygen vacancies
(b) coordinatively unsaturated cations
(c) acid sites
(d) basic sites
(e) redox properties.

These studies have shed some more light on our understanding of surface active sites for ketonization. Glinski et al.[55] examined the effects of oxide supports, including SiO_2, TiO_2, and Al_2O_3 on the ketonization activity of MnO_2 and CeO_2. The authors observed a significant enhancement in catalytic activity without a change in selectivity over MnO_2 and CeO_2 deposited on Al_2O_3 and TiO_2 supports in comparison with those on SiO_2 supports, despite their lower surface areas. It is reasonable to associate the observed changes in catalytic activity to the incorporation of the acidic function of the support to basic sites of the supported oxides at the interface. Teterycz et al.[89] in their study of conversion of *n*-butanol have observed significant changes in selectivity of the products upon the addition of MgO to ZrO_2. The selectivity toward *n*-butene and butyraldehyde was found to decrease whereas that of dipropylketone increased. The authors proposed that butyraldehyde was oxidized to butyric acid by picking up a lattice oxygen. The acid in turn would undergo ketonization to yield the observed ketone. The ease of oxygen vacancies formation on the mixed oxide surface was suggested to promote formation of the acid and its conversion to ketone.

The addition of ZrO_2 to CeO_2 to produce mixed oxides has also been found to enhance the ketonization activity. Several explanations have been proposed in the literature. The addition of ZrO_2 leads to the formation of a highly defective surface, higher Lewis acid content, and oxygen vacancies, indicated by X-ray photoelectron spectroscopy characterization. As a result, ketonization activity of $CeZrO_2$ has been found to be higher than that of pure CeO_2. On the other hand, the addition of ZrO_2 leads to a reduction of the bulk oxide at lower temperatures. The reduction temperature of the mixed oxide was found to be at 250 °C, as compared to 500 °C for CeO_2. This phenomenon results in a great enhancement of the redox properties of the mixed oxides, or as discussed above, a higher density of uncoordinated cations. As a result, the $CeZrO_2$ obtained improved oxidation−reduction cycling through high temperature reduction and a subsequent oxidation while pure CeO_2's redox abilities were significantly hindered.[90]

In addition to ZrO_2, other dopants have been investigated and found to promote ketonization activity. For example, a mixed $CeO_2-Al_2O_3$ catalyst was found to have similar redox properties to the mixed $CeZrO_2$ catalysts in the sense that the bulk CeO_2 was more easily reduced when supported on alumina.[91] In addition, the catalytic activity of $CeO_2-Al_2O_3$ and CeO_2-TiO_2 for ketonization was studied as a function of time on stream and number of regeneration cycles. It was reported that the catalyst performance of $CeO_2-Al_2O_3$ and CeO_2-TiO_2 improved with time on stream during the first 2−5 regeneration cycles. This activity enhancement was attributed to a higher dispersion of CeO_2 facilitated by consecutive reduction/oxidation cycles inherent to the reaction, causing gradual dispersion on the support.[18]

Likewise, addition of transition metals to CeO_2 also causes significant improvement in ketonization activity. For example, Dooley et al.[19] studied the effects of adding Co and Pd to alumina-supported CeO_2 particles in the vapor phase ketonization of isobutyric, acetic, and decanoic acids. Both the Pd- and Co-CeO_2/Al_2O_3 catalysts were shown to be more active for ketonization, as compared to the CeO_2/Al_2O_3 catalyst under the same conditions. XANES and EXAFS characterization showed a significant enhancement in the number of oxygen vacancies around each Ce atom upon the incorporation of small amounts of Pd and Co (both at 0.8%) when compared to the base CeO_2/Al_2O_3 catalyst.

Likewise, our group has shown that the incorporation of Ru into carbon-supported TiO_2 nearly doubled ketonization activity of acetic acid.[22] A TPR study showed a sharp distinction in the reduction behavior between TiO_2/C and Ru/TiO_2/C. While the former showed a broad hydrogen consumption only in the 500 °C−700 °C range, the latter showed multiple reduction peaks from 100 to 600 °C ascribed to reduction of both Ru oxide and TiO_2. Quantitative calculation revealed a significant reduction of TiO_2 on the Ru/TiO_2/C catalyst at temperatures below 500 °C, while no reduction was observed on the TiO_2/C catalyst in this temperature range. XPS characterization showed that the addition of Ru shifted the binding energy of Ti $2p_{3/2}$ from 459.5 eV for TiO_2/C to 458.2 eV, and down to 457.9 upon reduction, indicating a lower oxidation state of Ti^{4+} to Ti^{3+}. In another study, the TPD of CO_2 on fully oxidized and reduced TiO_2 was carried out. The results indicated an increase in CO_2 uptake with increasing amounts of Ti^{3+}.[92] As discussed in section 4, Ru/TiO_2 has been shown to be an effective catalyst to upgrade and stabilize full biomass pyrolysis vapors by reducing their acid content via ketonization.

The addition of alkali and alkali earth metals as promoters of metal oxide catalysts has been explored as well. In a study conducted by Parida,[93] all the alkali metals (Na, K, Cs), except Li were found to increase the ketonization activity of ZrO_2 at 623−698 K. A decrease in activity in the case of the Li-doped sample may have been due to the drastic decrease in surface area observed on this catalyst. Among all tested alkali metals, Na was the most effective for ketonization, followed by K and Cs. A 5 mol % Na doped ZrO_2 catalyst reached 99% conversion with 94% selectivity toward acetone at 623 K and a gas hourly space velocity (GHSV) of 160 mL $g^{-1}min^{-1}$. The authors claimed that Na favors the formation of surface carbonates and stabilizes the tetragonal phase of ZrO_2, resulting in the observed increase in ketonization activity. With respect to the requirement for acid−base properties mentioned earlier, the addition of alkali would incorporate a basic center to accompany the acidic ZrO_2. In contrast, it has been found that doping of alkali on CeO_2 catalysts only promotes the formation of heavy products by aldol/Michael condensations of the ketones produced. The excessive number of basic sites on the alkali-doped surface appears to be the main reason.

Direct H_2 reduction is another method that has been employed to improve ketonization activity. Zaytseva et al.[94] showed that ketonization of valeric acid gave higher conversion and comparable selectivity over CeO_2, ZrO_2, and CeO_2/ZrO_2 at 628 K in a H_2 environment, as compared to runs in inert gas. The increased amount of coordinatively unsaturated Lewis acid sites under H_2 flow, as observed in X-ray photoelectron spectroscopy analysis, was suggested to be responsible for the change in catalytic activity. Likewise, reduction also leads to a boost in ketonization activity over pure TiO_2 after a pretreatment in H_2 at 250 °C, as demonstrated by our own studies on unreduced and prereduced TiO_2 catalysts.[22]

The importance of surface reduction is not only limited to ketonization reactions. For example, Calaza et al.[95] examined adsorption and enolization of acetaldehyde for the aldol condensation reaction on a fully oxidized and a highly reduced thin film CeO_2 (111) by employing a combination of reflection absorption infrared spectroscopy and periodic DFT calculations. The mechanism of aldol condensation shares several mechanistic steps with ketonization. For instance, they both need an α-hydrogen to form an enolate that acts as a nucleophile to attack the electrophilic acyl C of another aldehyde. Acetaldehyde predominantly adsorbs weakly through its carbonyl oxygen on top of a Ce^{4+} cation on the fully oxidized CeO_2 (111) surface without any coupling reaction. The adsorption energy of this state was calculated to be weak, −0.21 and −0.09 eV at 1/4 and 1/2 monolayer coverage, respectively. The lack of reaction on the fully oxidized CeO_2 surface suggests that lattice Ce^{4+} cations evidently cannot stabilize the carbonyl O and form a stable electrophilic carbonyl C to be attacked by an enolate species. On the reduced surface containing about 60% Ce^{3+}, the carbonyl group is indicated to be strongly stabilized on coordinatively unsaturated Ce^{3+} sites (oxygen vacancies), resulting in stronger adsorption of acetaldehyde. This stable adsorption enables the formation of a strong electrophilic center on acyl C, thus enabling the coupling reaction.

Based on all these studies, it is reasonable to suggest that the presence of adjacent Lewis acid and Brønsted basic sites is the key for ketonization on most oxides. The coordination of primary intermediate species, adsorbed carboxylates, produced by dissociative adsorption of carboxylic requires the availability of Brønsted basic sites on the surface. More importantly, basic sites are required to perform α-hydrogen abstraction or keto/enol tautomerization to generate the enolate species with a nucleophile center at an α-carbon. An adjacent Lewis acid (or coordinatively unsaturated cation site) is needed to stabilize and activate another carboxylic acid for the coupling reaction. At the same time, the bulk redox ability of the oxide may also correlate well with the ketonization activity since the redox properties are strongly linked to the acid−base properties of the solid and the ability to expose surface cations.

3.2. Ketonization over Zeolites. Compared to the ample literature on ketonization of carboxylic acids on basic and reducible oxides, far fewer studies exist on ketonization over acidic zeolites. Despite their relatively good ketonization performance, only a few reports have analyzed the reaction mechanisms over zeolites with much detail. First, we must point out that it is immediately obvious that significantly different reaction mechanisms, reaction intermediates, and catalyst site requirements should be expected from those in reducible oxides, discussed in the previous sections.

We anticipate that the presence of the strongly acidic protons in zeolites should promote the formation of surface acyl species rather than carboxylates. However, the complex nature of secondary reactions that accompany ketonization over zeolites complicates the analysis and elucidation of the reaction mechanism, since it is hard to find conditions that result in high selectivity to the symmetrical ketone.[30,96,97] In one of the earlier studies on acidic zeolites, Chang et al.[98] proposed that the ketonization mechanism occurs via the nucleophilic attack of an acylium ion by a carboxylate species. It is important to note that this hypothesis was derived from the prevalent mechanism at the time over titania and chromia,[44,99] which as mentioned above is now a subject of debate.

This proposed mechanism is similar to the ketene intermediate pathways discussed above, although the acylium ion may in this case be formed directly through protonation of the acid and release of H_2O. Based on the results from Bielanski and Datka over HY,[100] the carboxylate species formed at temperatures in excess of 350 °C. It was initially claimed that the formation of carboxylate species, as the necessary first step, resulted in dehydroxylation of the zeolite, which would gradually destroy the crystallinity of the zeolite.[101] Chang et al.[97] mentioned that HZSM-5 was regenerable after coke removal, according to flow studies. To rationalize this regenerability, they concluded that the acylium species was a precursor to the acetate, leading to zeolite dehydroxylation, but the acylium ion could also be trapped with methanol forming an α-ketocarbenium ion that can subsequently decompose to acetone via hydride abstraction from a gas phase donor. No explanation was given, however, on why the zeolite was not irreversibly destroyed in the absence of methanol. We believe that zeolite dehydroxylation is not the mechanism of carboxylate formation, as will be discussed in more detail below.

Additional support for the nondestructive conversion of acetic acid to ketones is provided by recent results from our group. We have demonstrated stable conversion of acetic acid to acetone over HZSM-5 in a flow reactor. We have also shown by FTIR that the Brønsted sites are regenerated by desorption of the reaction products upon heating, which demonstrates that the zeolite is not irreversibly attacked during the interaction with the carboxylic acid.[102]

Likewise, Jacobs et al.[97] have also reported the reappearance of Brønsted acid sites via FTIR upon evacuation of adsorbed butyric acid HT zeolite and heating to 300 °C. They proposed that the ketonization reaction occurs through an acylium cation intermediate as well, but through a different reaction pathway. They proposed that the carboxylate was not formed through an acylium intermediate, but rather from a second acid molecule interacting directly on the negative framework charge of the zeolite that results after the formation of the initial acylium intermediate. It was speculated that an interaction of the adsorbed acylium with a nearby-adsorbed carboxylate[96] results in the ketone. Further details regarding the formation of a carboxylate-like species from the second acid, activation of the α-hydrogen, and the transition state are lacking in the literature. One possibility does exist, however, that the recombination of a surface acyl with a carboxylate could form a β-ketoacid that decomposes to yield the ketone through a similar route to that proposed by Pulido et al.[42] A detail that has yet to be explained is the mechanism responsible for the activation of the α-hydrogen in the adsorbed carboxylate prior to forming the β-ketoacid.

A critical point in both of these proposed mechanisms is that the carboxylic group that would ultimately end up in the ketone product is that of the acylium cation, and not the carboxylate. The similarities between the acylium cation and the ketene intermediate reactions proposed over oxides suggest that isotopic labeling studies similar to those conducted on TiO_2 by Ponec et al.[14] would be needed with zeolites. However, to our knowledge such studies have not yet been performed.

Jacobs et al.[96] observed a very interesting influence of acidity on the external surface of the zeolite on the conversion of butyric acid over H-T zeolite. The two major products observed were the symmetrical ketone, 4-hepthanone, and butyric anhydride. After removing the contribution from the external OH groups by poisoning with bulky triphenylchlorosilane, the selectivity toward production of the dehydration product, butyric anhydride, significantly decreased. They later observed that anhydride selectivity for a variety of cross ketonization reactions increases as the zeolite deactivates.[97] Interestingly, they propose that this is not a sequential pathway with a very reactive anhydride, but rather two different pathways that are somehow dependent on the nature of the environment of the various active sites. They proposed that the acylium ion could interact with a carboxylate in two ways to either form an anhydride, or acetone and CO_2.[97] While both authors propose a similar overall mechanism where an acylium cation and carboxylate are involved, many details have yet to be explained regarding the rate limiting step and the transition state responsible for ketone formation.[96−98]

The role of the anhydride has also been proposed as a possible intermediate that loses CO_2 to produce a ketone.[29,53,103] Anhydrides can also be produced via gas phase reaction of a ketene with acetic acid.[13] However, these proposals are based on the appearance of anhydride in the product at very low conversions, as opposed to theoretical or direct experimental evidence.

A reaction that has been widely studied concerning the interaction of carboxylic acids and acyl-forming species on Bronsted acid catalysts is Friedel−Craft acylation. This reaction involves the interaction of surface acyl species with aromatic compounds. Several reviews and books have been written on this subject,[104−106] so only those aspects that are relevant to the ketonization reaction over zeolites will be discussed here. It appears that the Friedel−Craft acylation reaction may be more closely related to ketonization on H zeolites than ketonization on reducible oxides. In fact, studies on acylation over zeolites provide important insight into the interaction of carboxylic acids and anhydrides over Brønsted acid sites. For example, Gorte et al.[50] studied the adsorption of acetic acid, acetic anhydride, and acetyl chloride on HZSM-5. They concluded that, based on the FTIR spectra of adsorbed of acetyl chloride, acetyl zeolite intermediates are formed at temperatures greater than 100 °C and contribute to the formation of ketones. In this study, C_3H_6 formation was observed at higher temperatures, and it was proposed that ketones may also be formed through the recombination of propylene and ketene species to produce acetone and acetylene. Acetylene was not observed, although it was speculated that it may be too reactive to be observed, if formed. What is rather unclear is how this reaction could yield such high selectivity to acetone at lower temperatures, since the recombination of ketenes would rapidly produce coke precursors and a variety of side-products. Any trace levels of water present in the system could lead to the formation of carboxylates and acids from acyl species as well, further complicating the analysis.

Acetic anhydride has been proposed to quickly decompose upon contact with Brønsted acids to produce an adsorbed acetyl species and acetic acid. Upon the adsorption of acetic anhydride over H-mordenite at 165 °C, Iglesia et al.[51] observed IR bands at similar wavenumbers to those observed by Gorte et al.[50] and attributed them to adsorbed acetyl species. Based on the IR data, Iglesia et al.[51] concluded that the anhydride quickly decomposes to the reactive acetyl surface species. They also supported their assignment by a rapid initial increase in conversion to reaction products upon interaction of the adsorbed species formed from anhydride decomposition with dimethyl ether and CO.

The reactive nature of adsorbed acetyl species has been debated for many years. Surface acetyl species covalently bound to the zeolite,[52] acylium ions,[107] and gas phase ketene species[108−110] have all been proposed to be active intermediates for the acylation reaction. In most of these studies, it was assumed that the highly reactive surface acylium ions may be too short-lived to be observed by NMR.[111−114]

While it is clear that even the nature of the reactive intermediate when active surface acetyl species are observed is debatable for several reactions, another concept that has not received much attention is the reversible nature of anhydride formation from acetic acid and surface acetyl groups. As mentioned above, Jacobs et al.[96,97] proposed that an anhydride can result from the interaction between acylium ions with adsorbed carboxylate species, since it is well-known that the reaction of a carboxylic acid with a ketene produces an anhydride.[13] Based on the acylation studies, in which acids or anhydrides are both used as feed, it has been proposed by multiple authors that anhydrides rapidly decompose to surface acetyl species and carboxylic acids upon contact with the zeolite.[50,51] In our own work, we demonstrated that at a moderate temperature of 300 °C and under atmospheric pressure ketones are produced from carboxylic acids on a protonated zeolite with a selectivity close to 100%. We believe that the interconversion of acetyl and anhydride species is a reversible reaction.[102] A possible path for this reversible process is the recombination of a surface acetyl with acetic acid (gas phase or adsorbed) to produce a surface-bound anhydride, which can quickly decompose back to the surface acetyl and acid. While it is likely that the reactive intermediate results through the combination of the acetyl or acylium ion with a carboxylate as proposed by Jacobs et al.,[96,97] it is important to recognize that many of these highly reactive species should be present on the catalyst surface. An outline of a possible mechanism for ketonization from acetic acid over zeolites is shown in Figure 14.

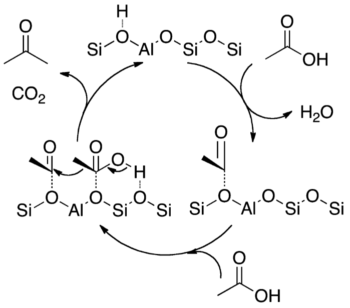


Figure 14. Proposed route for acetic acid conversion to acetone over acidic zeolites.

Both, the formation of anhydrides and surface acetyl groups will be inhibited by the presence of water, and an initial dehydration is necessary prior to acetone formation. The presence of water in the vapor phase, however, should not eliminate the ketonization reaction, but it may decrease the relative abundance of reactive surface acyl species or anhydrides by promoting the reverse reaction back to carboxylic acids. In temperature programmed reaction experiments, Bilbao et al.[115] observed significant yields of acetone and CO_2 over a wide range of temperatures under flow of acetic acid and water (50:50 vol.) over HZSM-5, indicating that ketonization over acidic zeolites can occur with moderate partial pressures of water present. It is logical to assume that the rate determining step for ketonization over acidic zeolites may be (i) the formation of a surface carboxylate from an acid, (ii) coupling of the acyl with adsorbed carboxylic acid, or (iii) the decomposition of the adsorbed anhydride. The rate-limiting step may shift with higher amounts of water present. It is apparent that detailed kinetic studies incorporating the activation entropy combined with theory might shed light on the nature of the reactive intermediates responsible for the selective ketonization of carboxylic acids over acidic zeolites. This would be an interesting study that has not yet been performed.

The investigation of the role of the α-hydrogen on the ketonization reaction has yet to be conducted on zeolites as well. One complication that does not arise in traditional oxides is the possibility of decomposition of acylium ions to more stable carbocations in the case of highly branched molecules. For example, Davis et al.[116] studied the acylation of biphenyl with pivalic acid (containing no α-hydrogen) over H-Beta. Instead of acylation as they expected, they observed alkylation of the isobutyl group directly to the aromatic ring, with no resulting ketone. They attributed this behavior to a higher stability of the t-butyl cation, as opposed to the corresponding trimethylacetyl group, that would alter the nature of the surface species. These side reactions must be taken into consideration when probing the role of the α-hydrogen on the ketonization reaction over acidic zeolites.

4. IMPLICATIONS OF KETONIZATION REACTION IN BIOMASS CONVERSION

As mentioned above, ketonization is a unique route to simultaneously remove acid functionality and achieve C−C coupling, leading to products with higher heating values and stability. Therefore, there have been a number of different processes involving ketonization as a key step in the upgrading of biofuels. A few examples of applications of ketonization to produce fuel-grade products from triglycerides or lignocellulosic biomass are discussed below.

The most common process to upgrade triglycerides to fuels or biodiesel is the transesterification to methyl esters. However, the less-than-optimal stability and cold flow properties in both triglycerides and methyl esters make further upgrading still a requirement. Problems with triglycerides originate from their long-chain lengths, olefin content, ester groups, and free fatty acids. Likewise, the presence of the oxygen-containing groups cause problems with water solubility, storage, and corrosion.[117] One promising upgrading option for free fatty acids would be catalytic ketonization that could remove oxygen and carboxylic acids. The resulting long chain ketones can be sent to the refinery unit for hydrocracking and isomerization to obtain diesel-like fuels. Several metal oxide catalysts have been explored and found to be active for the ketonization of fatty acids at various temperatures (250−400 °C) under a H_2-free or H_2-lean environment including TiO_2, Al_2O_3,[118] and ZrO_2.[119]

While the production and upgrading of the first generation biofuels has been extensively explored, current interest focuses more on the second generation of biofuels from lignocellulosic biomass. The upgrading of short carboxylic acids derived from biomass by pyrolysis or hydrolysis for the production of fuels and chemicals is an area in which ketonization holds significant promise.[120,121]

Fast pyrolysis of biomass to produce liquid bio-oil can yield up to 10% of small carboxylic acids, such as acetic and propionic acids.[122] Considerable amounts of carboxylic acids not only give rise to serious corrosion issues during storage and transport, but also catalyze unwanted reactions of gum formation. Therefore, acid removal is an important step in the upgrading of pyrolysis oil. Ketonization, as previously stated, offers great advantages for this process since it not only removes the highly reactive acidic carboxyl groups and reduces oxygen content in the liquid but also provides an efficient path to form carbon−carbon bonds between low-molecular-weight acids, so that they are not eliminated as light gases during the subsequent hydrodeoxygenation steps. Moreover, ketone products are highly desirable molecules since they can easily couple with other bio-oil products (via aldol condensation and hydrogenation/alkylation) to create longer chain molecules that fall into the fuel range.[131,137] Because of the remarkable advantages of ketonization in bio-oil upgrading, the number of publications has increased rapidly in the past few years.[20−23,123,124,141−143] Various technological approaches involving ketonization steps have been proposed for upgrading biomass pyrolysis products, both before and after the vapors condense.

The first application in which ketonization may play an important role is the so-called catalytic fast pyrolysis, a commonly proposed strategy for biomass conversion.[125] This process involves the incorporation of a catalyst in direct contact with the biomass under pyrolysis conditions ranging from 400 to 600 °C, where the pyrolysis vapors interact in situ with the catalyst prior to condensation.[126] The most typical catalyst employed in catalytic pyrolysis is HZSM-5[127] because of its high tolerance to sulfur poisoning and more importantly, low selectivity to coke compared with other less-confined zeolites and solid acid catalysts. As discussed in section 3.2, ketonization reactions followed by subsequent aldol condensation occur over acidic zeolites such as HZSM-5 under conditions close to those employed in catalytic pyrolysis in the presence of water.[122] During catalytic pyrolysis, the selectivity of carboxylic acids to form ketones as primary products depends heavily on the partial pressure of species such as water and phenolic species present in the bio oil vapors produced. Improved knowledge of the mechanism and kinetics responsible for ketonization reactions occurring with pyrolysis oil vapors will enable the development of catalytic strategies using zeolites to maximize the conversion of the corrosive acids to desirable products. In addition, the effects of alkali metals, such as sodium and potassium on activity and selectivity during catalytic pyrolysis possibly via their alteration to number of active acid sites on zeolite, is another important research area which requires further investigation. Another approach, direct vapor phase upgrading, can also be performed immediately after pyrolysis, but before the condensation step. This is accomplished by incorporating a catalyst bed at the outlet of the pyrolysis system to remove the acid functionality and improve the stability of condensed oil. To illustrate this concept, our group[128] presented the catalytic upgrading of real bio-oil vapors exiting a pyrolysis unit by using a bed of Ru/TiO_2 catalyst, which has been indicated as an effective ketonization catalyst for small acid compounds.[22] Table 4[128] displays the comparison of selected components and fractions of the product obtained from oak pyrolysis vapors with and without catalytic upgrading processed at 400 °C under and under H_2 flow at atmospheric pressure. As can be seen in the table, the concentration of acetic acid is significantly suppressed while acetone shows a sharp increase after the catalytic upgrading, clearly indicating the conversion of acetic acid via ketonization over Ru/TiO_2. It is also noteworthy that, unlike the results obtained with the model compounds, the increase in acetone concentration is less than the corresponding decrease in acetic acid, suggesting that acetone reacts further with other compounds present in bio-oil such as aldehydes and furanics to produce larger condensation products. In addition it was observed that ketonization, hydrodeoxygenation, and condensation took place simultaneously, evidenced by significant changes in not only acetic acid but also other oxygenates present in bio-oil. Together with the conversion of small oxygenates, phenolic compounds also underwent deoxygenation over Ru/TiO_2 as observed with model compounds.[129] For instance, no guaiacol was found in catalytic oil, while deoxygenated aromatic products like toluene increased from a negligible amount to 0.15% and a large amount of phenol was obtained. These results demonstrate that Ru/TiO_2 is a promising catalyst for upgrading small acid molecules as well as other oxygenates in bio-oil. Nevertheless, the complexity of the bio-oil and its notorious propensity to deactivate all catalysts require further investigations.

Table 4. Products of Oak Pyrolysis with and without Catalytic Vapor Upgrading[a]

	oak blank	Ru-TiO_2 1st run	Ru-TiO_2 3rd run
acetone	0.32 ± 0.09	1.62 ± 0.17	0.74 ± 0.15
butanone		0.82 ± 0.12	0.57 ± 0.10
acetic acid	6.26 ± 0.67	0.84 ± 0.11	2.42 ± 0.31
acetol	2.42 ± 0.29		0.64 ± 0.14
2-cyclopentene-1-one		1.51 ± 0.16	1.44 ± 0.14
phenol	0.81 ± 0.15	1.58 ± 0.17	1.27 ± 0.16
levoglucosan	1.75 ± 0.19	0.12 ± 0.04	1.46 ± 0.21
GC eluent time fraction			
0−15 min[b]	13.67 ± 1.55	7.89 ± 0.80	7.55 ± 0.78
15−30 min[c]	9.19 ± 1.00	5.66 ± 0.61	6.98 ± 0.69
30−45 min[d]	7.21 ± 0.70	8.60 ± 0.80	8.41 ± 0.75
45−60 min[e]	7.51 ± 0.77	5.00 ± 0.56	6.46 ± 0.60
> 60 min[f]	3.17 ± 0.60	0.80 ± 0.14	2.18 ± 0.22
total organic liquid	40.76 ± 1.68	27.95 ± 1.31	31.58 ± 1.52

[a]Data taken from ref 128. [b]0−15 min: small oxygenates fraction (acetic acid, acetol). [c]15−30 min: furan and pyran derivatives. [d]30−45 min: light phenolics with one hydroxyl group. [e]45−60 min: heavy phenolics with more than one hydroxyl group. [f]> 60 min: → heaviest volatile part (levoglucosan, other sugars, and some heavy phenolics).

In another example, Hakim et al.[130] studied the catalytic upgrading of acetic acid in the presence of other common bio-oil compounds including furfural, acetol, *p*-cresol, and levoglucosan over a bed of $CeZrO_2$ to investigate the effects of these compounds on ketonization. Known as a highly active catalyst for carboxylic acid ketonization, $CeZrO_2$ showed high stability for ketonization of 20 wt % acetic acid in water at 543 K for over 300 h on stream. However, the conversion of acetic acid dramatically decreased from 50% to below 5% within 40 h on stream when 10 wt % furfural was added to the feed. It was proposed that furfural adsorbs on the surface sites necessary for ketonization. In contrast, acetol did not cause a significant change in the deactivation profile and was found to exhibit high reactivity. It reached more than 80% conversion to form a mixture of C3−C6 ketones. Similar to acetol, *p*-cresol did not show any measurable inhibition on ketonization, and similar deactivation profiles were obtained with and without *p*-cresol. On the other hand, *p*-cresol caused reactor plugging at the entry of the reactor tube, a problem that was also observed with levoglucosan. This is probably due to thermal polymerization, or the low rate of vaporization and high viscosity of these compounds.

An alternative approach, which minimizes the detrimental effects of molecules like sugar-derived furanics, with high tendency for coke formation, is to conduct the upgrading in the liquid-phase. Our group[120] has proposed that prefractionation of bio-oil by multistage pyrolysis facilitates the subsequent catalytic upgrading. In this strategy, the light components obtained from decomposition of hemicellulose at low temperature (300 °C) mainly composed of acetic acid and water can undergo ketonization to produce acetone. To increase the molecular weight, acetone can couple with furans such as furfural, hydroxymethylfurfural (HMF) or with acetone itself via aldol condensation to elongate the carbon chain length by numerous active solid base catalysts.[131−136] It is also possible to convert the acetone to isopropanol, which can then dehydrate to form olefins that can subsequently alkylate phenolic components present in the bio-oil to produce diesel boiling range compounds.[137] The adducts from these processes can be hydrodeoxygenated to produce liquid hydrocarbons in the transportation fuel range.[119] This strategy can be achieved using consecutive reactors in a cascade system or using single biphasic reactors. The latter offer the potential of lower capital cost. A few examples using emulsions to perform consecutive reactions can be found in the literature.[131,138−140]

Together with fast pyrolysis, hydrolysis is another promising process for the conversion of lignocellulosic biomass to liquid fuels. It is well-known that cellulose and hemicellulose can be broken down in the liquid phase by using mineral acids or enzymes. In these process, sugar monomers containing mainly xylose and glucose are obtained.[1] Unfortunately, the sugar-derived monomers have undesirable properties such as low volatility, high water solubility, and exceptionally high oxygen content and functional groups, which make it very challenging to selectively increase the chain length through C−C coupling reactions. Direct hydrodeoxygenation is not favorable since the maximum carbon chain length of the alkane hydrogenation product is limited to the carbon number of the sugar or polyol feed, such as glucose (6) and xylose (5). For this reason, a promising strategy for the production of liquid transportation fuels from biomass is to start with controlled oxygen removal reactions to produce functional intermediates. These molecules can also be referred to as platform molecules, some examples of which include monofunctional species (such as alcohols, ketones, and carboxylic acids), levulinic acid, HMF, and furfural. These partially deoxygenated platforms are more stable compared to sugar molecules and, at the same time, have sufficient functionality to undergo C−C coupling reactions (via ketonization and aldol condensation) to enhance the molecular weight and C chain length.

Kunkes et al.[141] reported a process in which the aqueous solution rich in sugars (40 wt % glucose) and polyols (60 wt % sorbitol) can be efficiently converted to monofunctional compounds, including monocarboxylic acids, monoalcohols, ketones, and heterocyclic compounds by combination of reforming, hydrogenation, and dehydration reactions over Pt−Re catalysts at moderate temperatures (210−250 °C) and pressures (20−30 bar) in a single reactor. They reported that 80% of the initial oxygen in the feed can be removed by controlling decarboxylation and decarbonylation. Subsequently, the mixture of monofunctional species could be subjected to catalytic C−C coupling processes, including ketonization and aldol condensation to produce higher molecular weight species. The C−C coupling lead to the formation of C7−C12 linear and branched ketones, which can be further upgraded to hydrocarbons via dehydration/hydrogenation over bifunctional solid metal/acid catalysts.

To illustrate this upgrading strategy, the ketonization of hexanoic acid mixed with 1-pentanol and 2-butanone was investigated over $CeZrO_2$ at varied temperatures ranging from 170 to 350 °C.[80] Two parallel reactions were observed to take place under the testing condition: (i) ketonization of hexanoic acid to produce 6-undecanone, and (ii) reversible esterification of hexanoic acid and 1-pentanol to produced 1-pentylhexanoate. The esterification occurs more quickly than the ketonization at low temperature, while ketonization becomes dominant at elevated temperature. This trend is consistent with the higher activation energies for ketonization compared to esterification.[23] Therefore, one approach to maximize the selectivity to ketones would be to conduct the reaction at high temperatures (e.g., > 275 °C).

Levulinic acid is another useful functional intermediate, which can be selectively produced by direct hydrolysis of cellulose or decomposition of hydroxymethylfurfural using either solid or mineral acid catalysts with formic acid as a side product. Once formed, levulinic acid can be converted to γ-valerolactone through consecutive dehydration/hydrogenation reactions using metal catalysts in the presence of H_2, which can be generated in situ upon the decomposition of formic acid. A promising upgrading strategy for γ-valerolactone that has been well received is conversion over bifunctional metal/acid catalysts (Pd/Nb_2O_5) to form pentanoic acid, which is used to produce 5-nonanone by ketonization and subsequently hydrodeoxygenated to nonane.[142,143]

5. FUTURE OUTLOOK

Ketonization is foreseeably a feasible method for the upgrading of various biomass-derived products. While the everlasting quest for catalysts with low cost and high activity will remain the same as with any other fundamental reaction of industrial significance, there are specific challenges for ketonization in practice. For example, many oxygenates derived from biomass have a low vapor pressure, high solubility in water, and high reactivity. Low-temperature aqueous phase ketonization thus appears to be especially effective. Hydrothermal stability in liquid water is an important component that must be considered when choosing an effective catalyst. Several groups, including our own, have made significant progress in this aspect, but further investigations are required. Another important issue that must be addressed, as indicated by several examples, is the improvement of catalyst stability to minimize inhibition and deactivation of ketonization catalysts by other compounds in the liquid mixture (e.g., furanics). This may be accomplished either through advanced separation efforts, for example staged thermal conversion of biomass, or by introducing a metal function capable of converting strongly inhibiting species and cleaning the catalyst surface. These strategies could be highly advantageous with regard to catalyst performance. However, a detailed study of process design and control to optimize the separation as well as minimize the investment and operating cost would be needed.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: resasco@ou.edu.

Notes

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