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Experimental and theoretical assessment of the mechanism and site requirements for ketonization of carboxylic acids on oxides

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ABSTRACT

Ketonization of carboxylic acids removes O-atoms and forms new C—C bonds, thus providing routes from sustainable carbon feedstocks to fuels and chemicals. The elementary steps involved and their kinetic relevance, as well as the number and nature of the active sites on active TiO_2 and ZrO_2 catalysts, remain matters of active discourse. Here, site titrations demonstrate the requirement for coordinatively-unsaturated M-O-M sites (M = Ti, Zr) with specific geometry and intermediate acid-base strength. The measured site densities allow rigorous reactivity comparisons among catalysts based on turnover rates and activation free energies, as well as the benchmarking of mechanistic proposals against theoretical assessments. Kinetic, isotopic, spectroscopic, and theoretical methods show that C_2—C_4 acids react on anatase TiO_2 via kinetically-relevant C—C coupling between 1-hydroxy enolate species and coadsorbed acids bound at vicinal acid-base pairs saturated with active monodentate carboxylates. Smaller Ti—Ti distances on rutile TiO_2 lead to the prevalence of unreactive bidentate carboxylates and lead to its much lower ketonization reactivity than anatase. The prevalent dense monolayers of chemisorbed acid reactants reflect their strong binding at acid-base pairs and their stabilization by H-bonding interactions with surface OH groups derived from the dissociation of the carboxylic acids or the formation of 1-hydroxy enolates; these interactions also stabilize C—C coupling transition states preferentially over their carboxylate precursors; high coverages favor sequential dehydration routes of the α-hydroxy-γ-carboxy-alkoxide C—C coupling products over previously unrecognized concerted six-membered-ring transition states. Infrared spectra show that ubiquitous deactivation, which has precluded broader deployment of ketonization in practice and unequivocal mechanistic inquiries, reflects the gradual formation of inactive bidentate carboxylates. Their dehydration to ketene-like gaseous species is faster on anatase TiO_2 than on ZrO_2 and allows the effective scavenging of bidentate carboxylates via ketene hydrogenation to alkanals/alkanols on a Cu function present within diffusion distances. These strategies make anatase TiO_2, a more effective catalyst than ZrO_2, in spite of its slightly lower initial turnover rates. This study provides details about the mechanism of ketonization of C_2—C_4 carboxylic acids on TiO_2 and a rigorous analysis of the sites required and of active and inactive bound species on TiO_2 and ZrO_2. The preference for specific distances and for intermediate acid-base strength in M-O-M species is consistent with the structure and energy of the proposed transition states and intermediates; their relative stabilities illustrate how densely-covered surfaces, prevalent during ketonization catalysis, represent an essential requirement for the achievement of practical turnover rates.

1. Introduction

Carboxylic acids form new C—C bonds via bimolecular ketonization reactions to give alkanones, CO_2, and H_2O [1]:

$$R_1COOH + R_2COOH \rightarrow R_1C(=O)R_2 + CO_2 + H_2O \quad (R_1, R_2 = \text{alkyl}) \tag{1}$$

Such reactions remove three O-atoms and form a new C—C bond from two acid molecules, thus providing an attractive route for oxygen removal using the C-atoms within reactants, instead of added H_2, in upgrading biomass-derived feedstocks into fuels and chemicals [2–6]. The alkanone products can be used in subsequent aldol condensation reactions to increase their chain length and remove additional O-atoms [7,8].

Ketonization is catalyzed by metal oxides (e.g. MgO, BaO, MnO_2, CeO_2, ZrO_2, and TiO_2) [6–22], with ZrO_2 and TiO_2 among the most effective oxides [2,3]. Ketonization elementary steps and their

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kinetic relevance on oxides remain controversial subjects of inquiry, because of a dearth of detailed kinetic, isotopic, and spectroscopic data at conditions of strict kinetic control and also because of limited theoretical confirmation for the diverse types of pathways proposed [2,3,9,17,19].

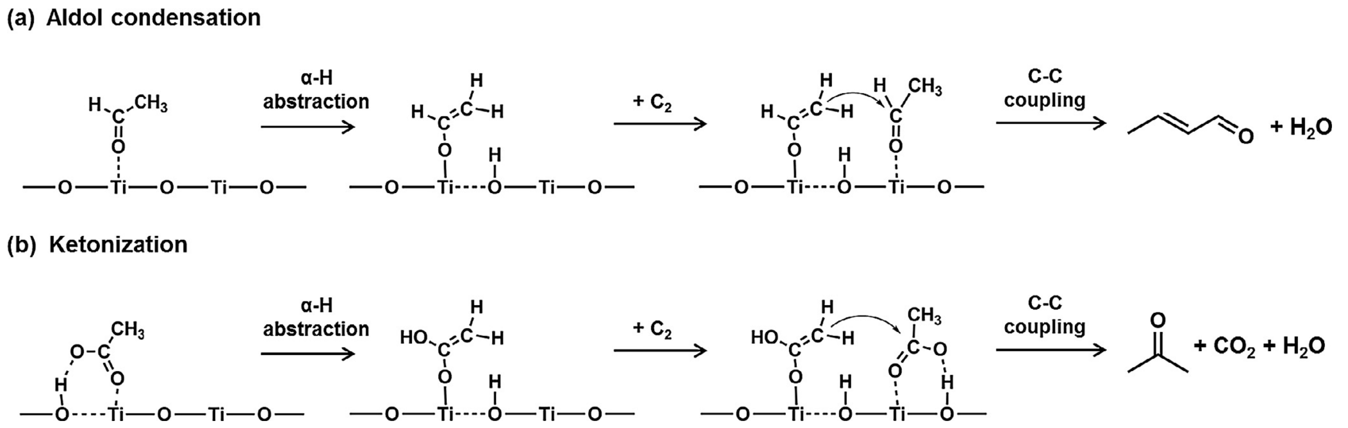
Ketonization requires the presence of a H-atom at an α-position with respect to the —COOH group in one of the acid reactants [2]. For instance, pivalic acid ($C(CH_3)_3COOH$), which lacks an α-H-atom, reacts with valeric acid ($CH_3(CH_2)_3COOH$, two α-H-atoms) to form 2,2-dimethyl heptan-3-one in cross-ketonization, but cannot undergo self-ketonization to form 2,2,4,4-tetramethyl pentan-3-one [19]. Similarly, aldol condensation reactions of carbonyl compounds require two α-H-atoms in one of the reactants, because such reactions involve enolate species formed by cleavage of α-C—H bonds and subsequent dehydration of aldols formed to α, β-unsaturated carbonyl compounds [23,24]. These C—H bonds exhibit lower heterolytic dissociation energies than those at other locations within the molecules; their cleavage is mediated by acid-base pairs of intermediate strength, which stabilize the transition states required for enolate formation [5,7,24]. The enolates formed from the carbonyl reactants then couple with another carbonyl species to form unstable aldols with a new C—C bond, which subsequently dehydrate to α,β-unsaturated carbonyl aldol condensation products (Scheme 1).

It seems plausible that the ketonization of carboxylic acids is also mediated by enolate-like species, in this case, in the form of 1-hydroxy enolates. The species formed from C—C bond formation via reactions of 1-hydroxy enolates with another acid reactant ultimately decompose via CO_2 and H_2O elimination, instead of the H_2O elimination route in condensation reactions, because neither dehydration nor decarboxylation steps alone can form stable products (Scheme 1). ^{13}C tracer studies show that the CO_2 molecule forms from the carboxyl group in the acid reactant that undergoes α-C—H bond cleavage and then nucleophilically attacks a coadsorbed acid reactant [10,25]; this is consistent with 1-hydroxy enolates as reaction intermediates, but excludes ketene-mediated routes, which would form CO_2 from the carboxyl group in the coadsorbed acid instead of that in the acid that undergoes α-C—H bond cleavage [2,9].

Here, we report turnover rates and selectivities for ketonization of C_2—C_4 carboxylic acids on anatase and rutile TiO_2 (TiO_2(a), TiO_2(r)) and on monoclinic and tetragonal ZrO_2 (ZrO_2(m), ZrO_2(t)). This study exploits the benefits of gaseous H_2 and a Cu function to confer unprecedented catalyst stability, thus allowing detailed mechanistic inquiries on stable catalysts. These mechanistic studies include kinetic, isotopic, spectroscopic, and theoretical methods, which are combined here to probe plausible ketonization elementary steps and their kinetic relevance on TiO_2(a), an active and stable catalyst for these reactions, and on TiO_2(r), the least active catalyst among those examined. A parallel examination of such ketonization pathways on ZrO_2 has confirmed the involvement of elementary steps similar to those reported here on TiO_2. Reactivities are reported here as ketonization turnover rates, using the number of acid-base M—O (M = Ti, Zr) pairs determined by titration with propanoic acid during catalysis; such rates allow comparisons of the intrinsic properties of acid-base pairs on different metal oxides and rigorous benchmarking of theoretical methods against experiments. These data provide compelling evidence for the involvement of acid-base pairs in ketonization steps and for the consequences of their acid-base properties and geometry on the intrinsic ketonization reactivity of metal oxide surfaces.

These experimental and theoretical methods show that acid-base pairs are saturated with monodentate carboxylates on TiO_2(a) and with bidentate carboxylates on TiO_2(r) during ketonization catalysis. Monodentate carboxylate structures form from dissociation of the carboxylic acid on a Ti—O pair via interactions of their two O-atoms with the Ti center and the abstracted proton bound at the O site, while bidentate configurations place the two O-atoms at Ti centers of two vicinal Ti—O pairs. Such near-saturation coverages by acid-derived species prevent the re-adsorption and secondary condensation of primary alkanone products along the catalyst bed, thus maintaining the high ketonization selectivities typical of TiO_2 (and ZrO_2) catalysts. Infrared spectra during catalysis show that monodentate carboxylates and molecularly adsorbed acids are reactive intermediates on TiO_2(a) and TiO_2(r) surfaces, respectively; bidentate carboxylates, in contrast, act as unreactive spectators on both surfaces. These bidentate carboxylates can be scavenged via hydrogenation of ketene, present as trace gaseous species in equilibrium with bidentate carboxylates; such reactions are mediated by a Cu function present within diffusion distances from TiO_2 surfaces, leading to much slower deactivation for TiO_2 (and ZrO_2) catalysts when H_2 and Cu are present.

The form of the measured rate equations for all carboxylic acids, the observed (H/D) kinetic isotope effect values near unity, the infrared evidence for near saturation coverages of monodentate or bidentate carboxylates, and the effects of alkyl substituents on ketonization turnover rates are consistent with C—C bond formation between a 1-hydroxy enolate and a coadsorbed acid as the sole kinetically-relevant step. These conclusions are confirmed by DFT treatments on densely-covered TiO_2(a) and TiO_2(r) surfaces, which lead to activation free energy barriers and kinetic isotope effects in excellent agreement with experiments, while also



Scheme 1. Analogous elementary steps involved in ethanal condensation and ethanoic acid ketonization on acid-base pairs (shown for TiO_2 catalysts as an illustrative example).