Enolization of Acetic Acid on Monoclinic Zirconia Surface

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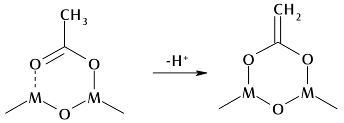
Introduction

The direction of a catalytic pathway for carboxylic acid decarboxylation on metal oxides depends on its acid-base function. In general, the presence of hydrogen and catalyst acidity help hydrocarbon formation and subsequent isomerization [1], while basic sites promote ketonic decarboxylation [2]. Both types of decarboxylation have important industrial applications, such as the production of biofuels from fatty acids [1] and preparation of various ketones [3]. Decarboxylative ketonization was discovered more than 150 years ago, and its speculative mechanisms have been extensively discussed in the literature for almost a century. However, unambiguous experimental support has not yet been provided. In the stepwise mechanism, the so-called "surface ketene" deserves attention as a likely and highly reactive intermediate. While the term "surface ketene" is chemically incorrect, it is intended to describe the structure derived by ketene reaction with metal oxide. The same structure may be formed by hydrogen abstraction from the alpha carbon of the adsorbed carboxylic acid, as depicted below.



In this work, the adsorption of acetic acid on the most stable surfaces of monoclinic zirconia and its subsequent enolization were studied by DFT method for periodic structures.

Computational Method

Crystal structures were built based on lattice parameters published for monoclinic zirconia [4] and adjusted by computing and minimizing their energy. Surfaces were cleaved to a depth of 10–15 Å, and the top two surface layers were allowed to relax, while the bottom layer was constrained. A vacuum slab 10 Å thick was built above the surface of the supercell constructed of 12 zirconium atoms and 24 oxygen atoms for monoclinic zirconia surfaces (Table 1). Energy minimization for the obtained supercell was performed by using the DNP basis set for a gradient-corrected potential PBE [5]. Core treatment included effective core potentials. Real space cutoff was 3.5 Å. SCF density convergence, optimization energy convergence, and gradient convergence were set to 0.00001, 0.00002, and 0.004 a.u., respectively. The same parameters were utilized for energy minimization with AcOH on the surface.

Results and Discussion

The preferred mode of AcOH adsorption was found to be the bidentate one, with O–H bond dissociation on all three surfaces of the monoclinic zirconia studied (Table 1). On some surfaces, C–OH bond dissociation is also possible. Bridging two Zr atoms by AcOH oxygen atoms is a more common mode than chelating the same Zr atom. On at least two surfaces of zirconia, a low-energy pathway for AcOH enolization was found via hydrogen abstraction by lattice oxygen. TS were optimized. The energy barriers 25.9 and 29.0 kcal/mol were found for AcOH enolization on $(\bar{1}11)$ and (111) surfaces, respectively. Modeling showed that binding two AcOH on the same Zr atom for subsequent ketonization via a concerted mechanism is energetically highly unfavorable.

Table 1. DFT-Computed Adsorption of AcOH on Metal Oxides

Entry	Surface	AcOH, nm^{-2}	Coverage, %	Adsorption Type	Adsorption Mode	Adsorption Energy, kcal/mol (eV)
1	$(\bar{1}11)$	2.19	25	Dissociative, AcO and H	Bidentate bridging	38.8 (1.68)
2	$(\bar{1}01)$	2.76	50	Dissociative, AcO and H	Bidentate chelating	45.5 (1.97)
3	$(\bar{1}01)$	2.76	50	Dissociative, Ac and OH	Bidentate chelating	44.6 (1.93)
4	(111)	1.97	25	Dissociative, AcO and H	Bidentate bridging	70.0 ((3.03)

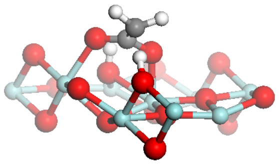


Figure 1. Optimized transition state for the enolization of acetic acid on $(\bar{1}11)$ surface of monoclinic zirconia. Zr – small light, O- large dark, C – medium dark, H – small white.

Significance

Computational results proved a relatively low energy barrier for the enolization of acetic acid on surfaces of monoclinic zirconia. The enolized form of acetate is a more reactive intermediate that could serve as the nucleophile in the mechanism of ketonic decarboxylation.

References

1. Koivusalmi, E., Jakkula, J., *U.S. Pat. Appl. Publ.* 20070135669 (2007).
2. Parida, K., Mishra, H.K., *J. Mol. Catal. A* 139, 73 (1999).
3. Renz, M., *Eur. J. Org. Chem.*, 6, 979-988 (2005).
4. McCullough, Y.D., Trueblood, K.N., *Acta Cryst.* 12, 951 (1959).
5. a) Perdew, J.P., Wang, Y., *Phys. Rev.* B45, 13244 (1992); b) Perdew, J.P., Burke, K., and Ernzerhof M., *Phys. Rev. Lett.* 77, 3865 (1996).