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# Acetic acid ketonization on tetragonal zirconia: Role of surface reduction ☆

Sergio Tosoni, Gianfranco Pacchioni *

*Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via Cozzi 55, 20125 Milano, Italy*

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ABSTRACT

The ketonization reaction of acetic acid on the (101) surface of tetragonal zirconia, a process relevant in the catalytic upgrade of cellulosic biomass has been studied by means of DFT+U calculations. The aim was to better understand the role of catalyst pre-reduction. Acetic acid adsorbs strongly on the zirconia surface, and deprotonation to acetate takes place easily. Then, a proton transfer from the methyl group of the acetate ion, $CH_3COO^-$, to the surface occurs to form an eno-species, $CH_2COO^{2-}$ (intermediate 1). In a parallel step, acetate ions convert into acyl fragments, $CH_3CO$, by oxygen extraction (intermediate 2). Once formed, the acyl intermediate 2 is able to attack the eno-species intermediate 1, to form a β-keto-acid. On stoichiometric zirconia, the formation of the intermediate 1, $CH_2COO^{2-}$, is unfavorable; oxygen vacancies on the reduced surface stabilize the reaction product and strongly reduce the activation energy. Reduced $Zr^{3+}$ centers are essential to stabilize the acyl intermediate 2. The present work shows at an atomistic level the beneficial role of O vacancies and reduced $Zr^{3+}$ centers for the ketonization process.

## 1. Introduction

In a general frame characterized by a growing demand of fuels derived from renewable sources, lignocellulosic biomasses represent a key-material for future development in fuel chemistry. A fundamental step in the biomass upgrading process consists in the elongation of the C-chain length and the reduction in the oxygen content of the raw material [1–3]. This can be achieved by pyrolysis of large volumes of biomasses [4] or, more efficiently, by promoting catalytically the condensation of short-chain carboxylic acids with elimination of water [1]. In pyrolytic processes, the dominant reaction to reduce the oxygen content of the biomass is the unimolecular decarboxylation [5]; for the case of acetic acid this results in the formation of $CH_4$ and $CO_2$. Differently, on heterogeneous catalysts such as oxide surfaces, several reactions take place, such as reduction of the carboxylic acids to aldehydes or ketonization [6,7]. Ketonization is a process where two carboxylic acids condense to form a ketone, eliminating $H_2O$ and $CO_2$. The mechanisms of the ketonization reaction and the role of the heterogeneous catalysts have been extensively reviewed [8,9]. On oxide surfaces, in particular, the important role of undercoordinated cations and the presence of reduced centers are assumed to have a strong influence on the reactivity toward carboxylic acids [10,11]. Particular attention is devoted in the literature to the role of zirconia surfaces in biomass upgrading [12–18]. In this context, zirconia has been shown to be more effective in ketonization compared to other oxides widely employed in heterogeneous catalysis, such as ceria, silica or alumina [15]. Usually, the oxide catalyst ($ZrO_2$, $TiO_2$, etc.) is prepared by pre-treatment in hydrogen, a process that was shown to increase considerably the activity [8,18–20].

As discussed by Pulido et al. [15], two mechanisms have been proposed in the literature for ketonization: a concerted mechanism [21,22], and a stepwise mechanism implying the formation of a β-keto-acid intermediate [23]. The β-keto-acid mechanism has been studied in detail also on oxide surfaces [6,15,19,20,24]. Starting from two acetic acid molecules, the concerted mechanism implies the simultaneous formation of a C—C bond and decarboxylation, forming acetone and $CO_2$. The elementary steps of the initial phases of the stepwise mechanism, α-hydrogen abstraction and C—C coupling, are depicted in Scheme 1. These are followed by C—C scission with $CO_2$ formation and enolate hydrogenation to form acetone (not shown). In step (a), an acetic acid molecule is adsorbed on zirconia, forming an acetate ion and a hydroxyl group grafted on the surface. The adsorbed acetate ion is further subjected to the enolization reaction (step b1), where a proton from the methyl group is transferred to the surface, forming a hydroxyl

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* Corresponding author.

*E-mail address:* gianfranco.pacchioni@mater.unimib.it (G. Pacchioni).

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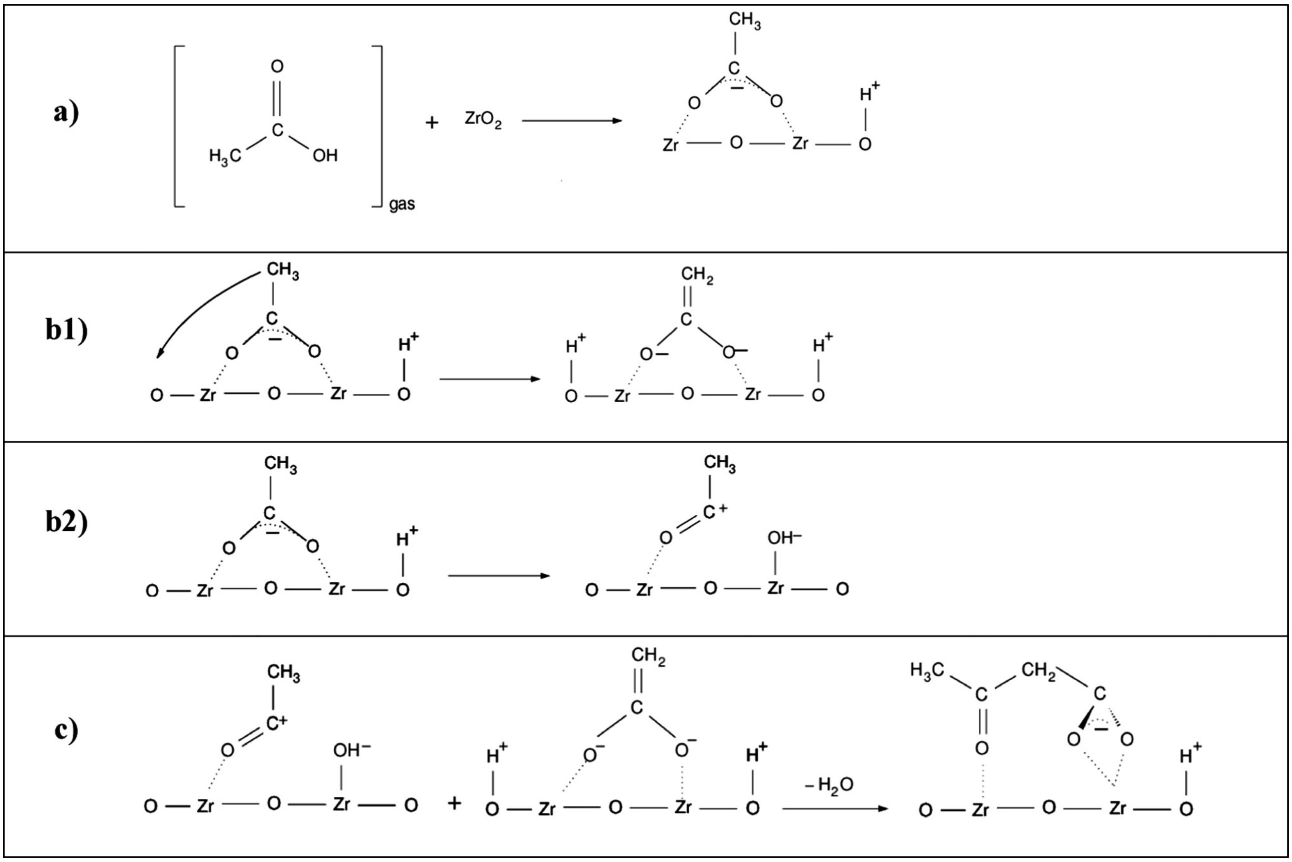

**Scheme 1.** Elementary steps of ketonization on the zirconia surface: (a) adsorption of acetic acid, (b1) formation of the enolate intermediate 1, (b2) formation of the acyl intermediate 2, (c) reaction of acyl and enolate to form the β-keto-acid.

and a 1,1-ene-diolate species (intermediate 1). Alternatively (step b2), the acetate molecule undergoes deoxygenation, forming an acyl species (intermediate 2) and an $OH^-$ group bound to a surface cation. The importance of the acyl intermediate in the reaction has been recently shown for the case of HZSM-5 [25]. In step c, the enolate and acyl intermediates 1 and 2, respectively, combine to form a β-keto-acid ion, namely the 3-oxo-butyrate in case of acetic acid reaction.

Of course, other reaction paths are also possible. For instance, the $CH_2COO^{2-}$ intermediate 1 may directly attack a carboxylate fragment, $CH_3COO^-$. In other words, while it is rather well established that $CH_2COO^{2-}$ is the key intermediate for C-C coupling, this is not necessarily the case for the $CH_3CO$ species.

According to DFT calculations on acetic acid ketonization on monoclinic zirconia (m-$ZrO_2$), the β-keto stepwise mechanism is kinetically favorable [15]. Moreover, experiments on the ketonization of isomeric pentanoic acids showed that the abundance ratio of the products could not be explained according to the concerted route, further supporting the β-keto mechanism [15]. Once the 3-oxo-butyrate is formed, a further reaction cleaves the C1—C2 bond with the hydrogenation of the methylene bridge, forming acetone and carbon dioxide. As shown by DFT calculations, this step is endothermic on m-$ZrO_2$ [15].

Thus, the catalytic activity of zirconia in biomass conversion has already been at the center of several investigations which have helped to elucidate the reaction mechanism. Looking at the elementary steps of the most plausible mechanism, it is clear that the capability of the support to act as an electron acceptor or donor is of paramount importance for three aspects: (i) the acid-base equilibrium regulating the adsorption and deprotonation of acetic acid; (ii) the charge transfer process in the acetate-enolate tautomeric equilibrium; and (iii) the deoxygenation reaction that forms the acyl species. What still has to be better understood, is the role of the chemical reduction of the catalyst in the whole process [9]. In particular, the presence of reduced centers on the zirconia support seems to have a very strong impact on its reactivity [18]. This is the goal of the present investigation.

Zirconium dioxide is a wide-gap insulator that displays a complicated polymorphism. At room temperature, the most stable phase is the monoclinic one. At 1480 K, a phase transition to the tetragonal (t-$ZrO_2$) structure is observed. The latter finally converts into the cubic polymorph at the temperature of 2650 K [26]. The adsorption and reactivity of carboxylic acids on the surface of the most stable monoclinic phase have been thoroughly studied by means of DFT calculations [8,15,27]. The stabilization of the cubic and tetragonal phases down to room temperature is obtained by incorporating a small amount of impurities, in particular divalent or trivalent cations [28–30]. Tetragonal $ZrO_2$ exhibits excellent thermal and mechanical properties [31,32] but it has been less studied both experimentally and theoretically in relation to ketonization compared to the monoclinic one. Experimentally, a comparison of the activity of m-$ZrO_2$ with t-$ZrO_2$ has been reported in a few studies [18,33,34], and there is some evidence that the monoclinic phase may be more active than the tetragonal one [18]. In some cases the reaction has been studied on mixed tetragonal and monoclinic phases [35]. On both m-$ZrO_2$ and t-$ZrO_2$ a positive effect on ketonization of carboxylic acids was observed when the amount of surface coordinatively unsaturated $Zr^{4+}$ cations is high and also when the catalysts are pre-treated with $H_2$. This has been justified with the appearance of $Zr^{3+}$ cations on the