Selectivity and mechanism shifts in the reactions of acetaldehyde on oxidized and reduced $TiO_2(001)$ surfaces

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Depending on the oxidation state of the $TiO_2(001)$ surface, acetaldehyde can form C_4 products by either aldol condensation or reductive coupling routes. Aldol condensation generates crotonaldehyde and crotyl alcohol, and is favored on oxidized, stoichiometric surfaces. Reductive coupling produces butene, and occurs only on reduced surfaces. The switch-over in selectivity with increasing extents of surface oxidation provides important insights into the active site requirements for each of these reactions.

Keywords: acetaldehyde; butene; crotonaldehyde; aldol condensation; reductive carbonyl coupling; titanium dioxide

1. Introduction

The chemistry of metal oxide surfaces often can be altered by variations of preparation methods and prior treatment conditions. Characterization of properties such as surface structure, surface acidity (or basicity), and surface cation oxidation states may lead to correlations with surface reactivity. However, one needs to recognize that these characteristics cannot always be varied independently of each other (i.e., changing one property very often results in changing others at the same time). For example, changing the surface structure not only affects the geometric relationships between surface sites which influence adsorption, dissociation, and reaction, but may also alter the degree of coordination of metal cations to oxygen, thus changing the accessibility and the local electron density of these sites. The latter characteristics may in turn affect activity for acid/base and/or oxidation/reduction reactions. On the other hand, changing cation oxidation state, which is often achieved by reducing metal oxide or oxidized metal surfaces, not only changes surface structure but also changes the population and characteristics of Lewis acid–base sites. On partially reduced oxide surfaces, oxygen vacancies play the role of strong Lewis acid sites (electron acceptors) and the partially reduced cations may act as Lewis base sites (electron donors).

Working on metal oxide single crystals or well-ordered thin films in UHV is perhaps the simplest way to study surface modifications and their effects on chemical reactions of these materials in a systematic, reproducible, and reversible manner. One of the most interesting model surfaces is $TiO_2(001)$, which has been studied extensively in the last decade, since it can carry out a wide variety of surface reactions, each associated with a specific surface state. Ion-sputtered (reduced) surfaces contain Ti suboxides (Ti^{1+}, Ti^{2+}, Ti^{3+}), the relative population of which can be altered by annealing at different temperatures [1]. Stoichiometric surfaces can be prepared which contain only Ti^{4+} cations, but with two different faceted arrangements: the {011}- and the {114}-faceted surfaces [2]. Previously it was observed that disordered suboxide surfaces can reduce carboxylic acids to aldehydes [2,3], aldehydes to alcohols [4], and alcohols to hydrocarbons [5]. This chemistry is not unique to reduced TiO_2; it has also been reported that partially reduced metal oxides such as Fe_3O_4 [6], Cu/ZnO [7], and $ZrO_2(100)$ [8] are active for the reduction of carboxylic acids to aldehydes, and reduced Cu/ZnO/Al_2O_3 [9] and CeO_2 [10], among others, are also active for the reduction of aldehydes to alcohols. In addition, these reduced TiO_2 surfaces exhibit activity for C–C bond formation by reductive coupling of aldehydes [11,12] and ketones [13,14]. The stoichiometric surfaces (obtained by annealing in UHV at 750 K or above) not only can dehydrate carboxylic acids into ketenes [2] but also, in the case of the {114}-faceted structure, can couple carboxylic acids into ketones [2] as well as couple alcohols into ethers [5]. Moreover, changing the faceting from {011} (where Ti^{4+} cations are all five-fold coordinated to oxygen) to 114 (where Ti^{4+} cations are 4, 5, and 6-fold coordinated to oxygen) [2], increases the disproportionation (Cannizzaro reaction) [4] and condensation (β-aldolization) [15] reactions of aldehydes.

Acetaldehyde (and aldehydes in general) are interesting reactants on all catalytic surfaces and, more particularly, on metal oxides. They appear in a wide variety of catalytic technologies, including condensation to higher unsaturated aldehydes and alcohols for polymer resins, etc. [16], they are proposed as intermediates in syngas conversion to alcohols [17], and have recently been observed to undergo reductive coupling to higher molecular weight olefins [11–14]. Moreover, they are intermediate in oxidation between alcohols and carboxylic acids and can be easily reduced to the former [18] or oxidized to the latter [19]. From a mechanistic stand-point it has been observed that their adsorption in an η^2 mode is associated with their reduction to alkoxides [20] while adsorption in an η^1 mode is associated with their oxidation to carboxylates [21]. While the η^2 mode is favored on metals [22,23] and partially reduced oxides [4,20], the η^1 mode is favored on stoichiometric oxides [24] as well as on oxygen-predosed metals [22,23]. Thus different selectivities arise on different surfaces.

This work presents the reactions of acetaldehyde (by temperature programmed desorption (TPD)) on the surfaces of a $TiO_2(001)$ single crystal. These surfaces included both oxidized and reduced surfaces, characteristics of which are discussed below. As will be shown, the principal reactions of acetaldehyde observed were: β-aldolization with dehydration

$$2CH_3CHO \rightarrow CH_3CH{=}CHCHO + H_2O$$

reductive carbonyl coupling

$$2CH_3CHO \rightarrow CH_3CH{=}CHCH_3 + 2O(ad)$$

along with some reduction of aldehydes to alcohols. The selectivities of these reactions depended strongly on the extent of surface reduction, and the principal reaction channel was observed to switch from reductive coupling on reduced surfaces to aldol condensation on oxidized surfaces, as shown herein.

2. Experimental

TPD experiments were conducted in a stainless steel, ion-pumped vacuum chamber (Physical Electronics model 548) equipped with four-grid LEED optics, single-pass cylindrical mirror analyzer for Auger, and a UTI 100 C quadrupole mass spectrometer, all described in detail elsewhere [2,4,15]. An IBM PC was used to multiplex the mass spectrometer and to control the heating rate (1.2 K/s), during TPD experiments. A typical TPD experiment consisted of dosing the surface with acetaldehyde (previously purified by freeze–pump–thaw cycles) to surface saturation (requiring a direct dose of ca. 1.5 L) then allowing the system to pump until a pressure of ca. 5×10^{10} Torr was reached. Up to 100 masses were monitored at an interval of 3–4 s for the complete cycle (up to 800 K); the complete TPD procedure was published elsewhere [7,15]. The $TiO_2(001)$ single crystal ($10 \times 9 \times 1.5$ mm^3) was aligned by the Laue method, cut, polished, mounted, and cleaned as described previously [4]. Detailed characterization studies of the sputtered, 550, 625, 750, and 850 K-annealed surfaces by AES [2], LEED [2], XPS [1] and UPS [25] have been reported previously. These surfaces in the order listed contain decreasing concentrations of Ti suboxides (Ti^{x+}, $x < 4$) from the sputtered (which contains ca. 75% Ti^{x+}) to the 750 and 850 K annealed surfaces (which are stoichiometric surfaces, i.e., they contain no detectable Ti^{x+} cations). Product identification relied on matching major peaks at various m/e values with pure component cracking patterns measured in the vacuum system (except for butene, for which published cracking patterns were used [26]). After product identification, the contributions of high molecular weight products to signals for lower molecular weight products were removed using the pure component cracking patterns. Relative carbon yields were calculated by multiplying the peak area of a given product by its mass spectrometer correction factor (following the method of Ko et al. [27]) and by its number of carbon atoms. The correction factors for the reaction products were: acetaldehyde (m/e 29): 3, ethanol (m/e 31): 2.1, butene (m/e 56): 3.8, crotonaldehyde (m/e 70): 5.6, and crotyl alcohol (m/e 72): 22. Previous comparisons between TPD and XPS results for other carbonyl compounds on TiO_2 surfaces have demonstrated good correspondence of coverage determinations by these methods, even on highly reduced surfaces [12].

3. Results

The reactions of acetaldehyde were investigated on surfaces of a $TiO_2(001)$ single crystal. These surfaces have the following characteristics:

(1) Sputtered $TiO_2(001)$: Disordered, contains Ti cations in 1+, 2+, and 3+ oxidation states representing about 75% of all Ti cations in the near surface region (the remainder are Ti^{4+}). This surface does not contain Ti metal [1,4,7].

(2) Surfaces annealed at 550 or 625 K (for 20 min each): Both are still in the suboxide form however, Ti^{x+} ($x < 4$) concentrations decrease with increasing annealing temperature to about 25% for the 625 K-annealed surface.

(3) Surfaces annealed at 750, 850, or 950 K: all are fully oxidized surfaces (only Ti^{4+} detectable by XPS). At 750 K the surface reconstructs to the {011}-faceted structure (with all Ti^{4+} cations five-fold coordinated to oxygen) and at 850 K the O to Ti ratio (from AES [2]) is slightly higher than that observed for the 750 K-annealed surface. After annealing at 950 K the surface reconstructs to the {114}-faceted structure (with Ti^{4+} cations four-, five-, and six-fold coordinated to oxygen) and the AES O to Ti ratio is higher than that of the 850 K-annealed surface [2].

The desorption products from acetaldehyde-TPD on sputtered $TiO_2(001)$ surfaces which had been annealed at different temperatures are presented in figs. 1–3 and table 1. Three principal reactions were observed:

(1) acetaldehyde reduction to form ethanol,

(2) acetaldehyde self-condensation to form crotonaldehyde (a portion of which is further reduced to crotyl alcohol), and

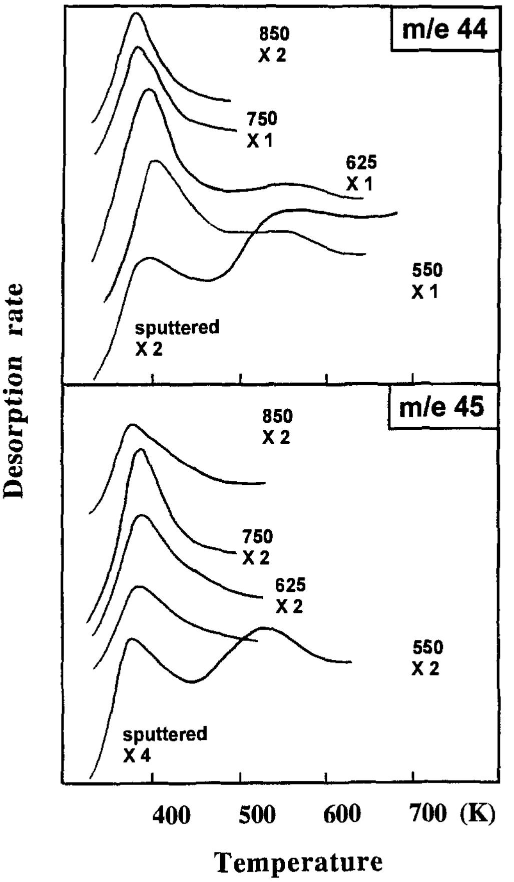

Fig. 1. Desorption of acetaldehyde (*m/e* 44) and ethanol (*m/e* 45) during acetaldehyde-TPD on the surfaces of a $TiO_2(001)$ single crystal, previously sputtered and annealed at the temperatures shown.

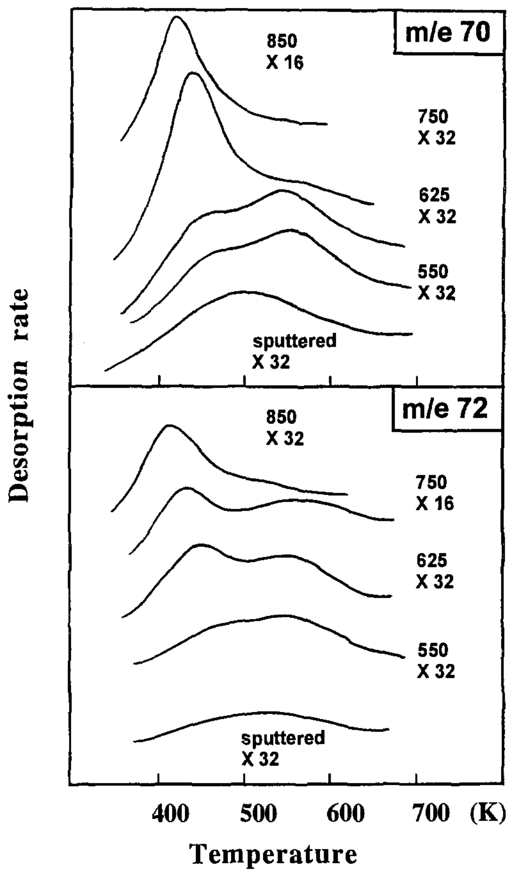

Fig. 3. Desorption of crotonaldehyde (*m/e* 70) and crotyl alcohol (*m/e* 72) during acetaldehyde-TPD on the surfaces of a $TiO_2(001)$ single crystal.

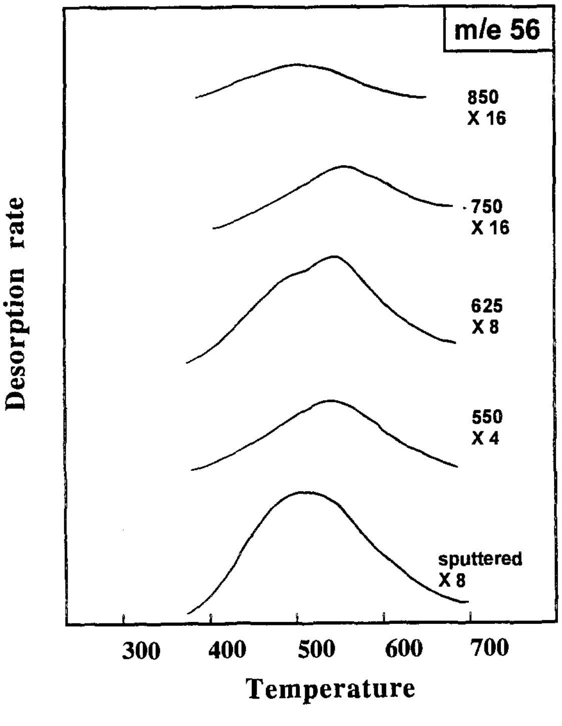

Fig. 2. Desorption of butene (*m/e* 56) during acetaldehyde-TPD on the surfaces of a $TiO_2(001)$ single crystal.

(3) acetaldehyde reductive coupling to form butene.

No evidence of total oxidation to CO_2 or of products evolved from decomposition to CO and CH_4 were observed (although minor contributions of these products to the mass spectrometer signals for $m/e = 28$, 16, and 15 cannot be ruled out). Also no desorption products related to ethyl acetate (*m/e* 88, 59, and 45) were detected, indicating that the Tischenko reaction does not occur on these surfaces of TiO_2. In addition aldol (i.e., the product resulting from self-condensation of acetaldehyde before dehydration to crotonaldehyde) was not detected.

Fig. 1 presents acetaldehyde (*m/e* 44) and ethanol (*m/e* 45) desorption spectra (*m/e* 44 arises exclusively from acetaldehyde in this case and not from CO_2 based on comparison with the fragmentation pattern of acetaldehyde). On the sputtered surfaces two desorption peaks were observed at 380 and 520 K for both acetaldehyde and ethanol with comparable magnitudes. The second desorption peak decreased dramatically with increasing annealing temperatures and disappeared totally on the fully oxidized surfaces, previously annealed at 750 and 850 K.

Fig. 2 presents the desorption of butene (*m/e* 56) during acetaldehyde TPD on TiO_2 surfaces. A wide peak

Table 1
Carbon selectivity of TPD products after acetaldehyde adsorption, at room temperature, on sputtered and annealed surfaces of a $TiO_2(001)$ single crystal

	Sputtered	Prior annealing temperature				
		550 K	625 K	750 K[a]	850 K	950 K[a]
acetaldehyde	33	49	50	30	31	39
ethanol	20	16	17	36	18	traces
butene	29	21	13	1	7	2
crotonaldehyde	6	5	5	19	17	20
crotyl alcohol	12	9	14	14	27	39

[a] From ref. [15].

centered at around 500 K (most likely resulting from two undeconvoluted peaks as shown in the case of the 625 K-annealed surface) was observed in all cases, but was clearly the largest on the sputtered surface (accounting for 29% of the total carbon yield, table 1). On the 750 K-annealed surface butene desorption decreased dramatically (to ca. 2%, table 1).

Fig. 3 presents the desorption of crotonaldehyde (*m/e* 70) and crotyl alcohol (*m/e* 72). On the sputtered surface each product was represented by one wide, but small, peak at ca. 500 K; each of these peaks evolved into two distinct peaks (at 410–450 K and 550–600 K) on the 550, 625, and 750 K surfaces. Suboxide surfaces were the least active (this is opposite to butene production); 18 and 14% yields of crotonaldehyde were observed (table 1), for the sputtered and the 550 K-prior-annealed surfaces, respectively. In contrast, the 950 K-annealed surface was the most active for aldol condensation; together both products (crotonaldehyde and crotyl alcohol) accounted for ca. 60% of the total carbon yield (table 1).

4. Discussion

Each of the three observed reactions is related to a specific surface state. Changing the surface of $TiO_2(001)$ from the disordered suboxide into an oxidized stoichiometric surface resulted in switching the reaction products of acetaldehyde as shown in fig. 4, which illustrates the carbon distribution among the reductive coupling (butene) and aldol condensation (crotonaldehyde and crotyl alcohol) products. The crossover of the principal reaction channel, from reductive coupling to aldol condensation as the surface is oxidized by annealing, is readily apparent.

The only other reaction channel of significance was the hydrogenation of acetaldehyde to form ethanol. On the suboxide surfaces, (those sputtered and annealed up to 625 K before acetaldehyde adsorption), as well as on the fully oxidized surfaces, ethanol is most likely formed via direct reduction of adsorbed acetaldehyde as follows:

$$CH_3CHO(g) \rightarrow CH_3CH{=}O(a)$$

$$CH_3CH{=}O(a) + 2H(a) \rightarrow CH_3CH_2OH(a)$$

$$CH_3CH_2OH(a) \rightarrow CH_3CH_2OH(g) \quad \text{at 380 and 520 K}.$$

Hydrogen required for the reduction is presumably evolved from trace total decomposition of adsorbed acetaldehyde or from implanted hydrogen diffusing from the bulk in the case of sputtered surfaces, as previously suggested in our studies of alkyne cyclization [28] based on reports of electron stimulated desorption of hydrogen from argon ion-bombarded TiO_2 surfaces [29]. The principal effect of such hydrogenations is to

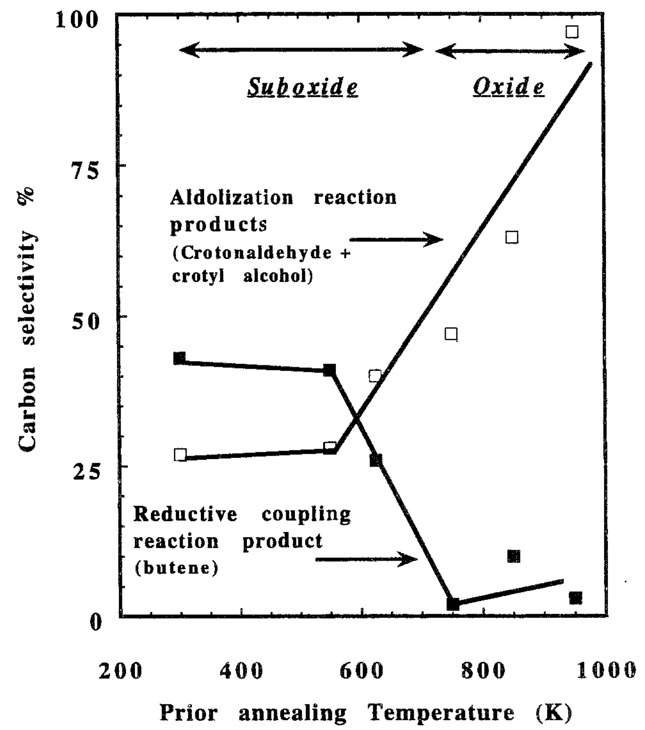

Fig. 4. Carbon selectivity (carbon yield of product i/{$\sum$ products carbon yield excluding unreacted acetaldehyde}) of butene (reductive coupling product) and crotonaldehyde and crotyl alcohol (condensation products), as a function of prior annealing temperatures of $TiO_2(001)$ single crystal.

reduce the pool of unsaturated reactants available for other (coupling) reactions . Although it is tempting to attribute the reduction on the suboxide surfaces to the presence of Ti^{x+} cations ($x < 4$), the fact that the ethanol yield was still significant on the fully oxidized surfaces (the 750 K, and 850 K-annealed surfaces) indicates that Ti^{4+} cations are also active for this reduction reaction if hydrogen is available. It is unlikely that another mechanism, such as a Cannizzaro-type disproportionation, takes place on the fully oxidized surfaces for two reasons. (1) Previous results indicated only traces of carboxylates (very small XPS C(1s) signal at 290.5 eV [4,15] when compared to the signal for alkoxide at 286.5 eV) showing that the Cannizzaro reaction is a minor reaction for acetaldehyde on TiO_2 surfaces. One would expect comparable intensities of alkoxide and carboxylate peaks if both were formed via the Cannizzaro reaction. (2) No CO_2 nor CH_4 desorption peaks were observed during TPD; these products together are often a finger print of acetate decomposition (ref. [2], and references therein). The dramatic decrease of ethanol production on the 950 K-annealed surface is most likely a consequence of the increase in selectivity in favor of the condensation reaction (see below).

Both crotonaldehyde and crotyl alcohol are formed via aldol condensation on these surfaces. Clearly this reaction, which requires either acid or base sites [30–32], is most important on the fully oxidized surface. It is unlikely that this reaction is related to surface faceting, since it is also observed (although with somewhat lower selectivity due to competition with other reactions) on reduced surfaces (fig. 4). It is most likely, in the case of $TiO_2(001)$, related to the available oxygen sites on the surface which act as bases to abstract the hydrogen in the α position from the carbonyl group of acetaldehyde as follows:

$$CH_3CHO(a) + O(l) \rightarrow -CH_2CHO(a) + OH(a)$$

$$-CH_2CHO(a) + CH_3CHO(a) \rightarrow CH_3CH{=}CHCHO(a) + OH(a)$$

$$2OH(a) \rightarrow H_2O + 2O(l)$$

$$CH_3CH{=}CHCHO(a) \rightarrow CH_3CH{=}CHCHO(g) \quad \text{at 380 and 520 K}$$

$$CH_3CH{=}CHCHO(a) + 2H(a) \rightarrow CH_3CH{=}CHCH_2OH(a)$$

$$CH_3CH{=}CHCH_2OH(a) \rightarrow CH_3CH{=}CHCH_2OH(g) \quad \text{at 380 and 520 K}$$

(O(l) denotes surface lattice oxygen atoms).

The consistent increase in the selectivity to crotonaldehyde and crotyl alcohol (together) as a function of increasing prior annealing temperatures clearly indicates that the condensation of acetaldehyde is sensitive to surface changes produced by annealing. The increase in this reaction (fig. 4) with annealing tracks the oxidation of the surface, as previously observed on these surfaces [2], reinforcing the conclusion that self-condensation of aldehydes on TiO_2 surfaces is governed by available base sites (surface oxide anions).

In contrast, reductive coupling of aldehydes and ketones occurs only on reduced surfaces. This reaction has been observed as a gas–solid reaction on reduced TiO_2 single crystals (in UHV) [11–14] as well as on reduced TiO_2, FeO(II, III), and CeO_2 powders (at 1 atm) [33]. This reaction was originally observed as a stoichiometric reaction in liquid slurries (in the presence of $TiCl_3$ and reducing agents) and is known as the McMurry reaction [34]. Its observation as a solid–gas reaction opens the possibility of making it catalytic. One can obtain by this reaction symmetric olefins [11,12] and polymers, among other products [13]. This reaction requires the suboxide form of the surface (partial reduction [12], but not necessarily total reduction as was previously thought [34]). It results in oxygen deposition to repair the surface oxygen deficit (or in other word to oxidize M^{x+} cations into their fully oxidized form). Fig. 4 clearly indicates that activity for this reaction tracks surface reduction. The highest carbon yield for butene was observed on the sputtered surface and the lowest on the fully oxidized ones. Two adsorbed acetaldehyde molecules react together giving one butene molecule and oxidizing the surface, as evidenced by Ti^{x+} oxidation to higher oxidation states, an increase in the Ti $2p_{3/2}$ lines corresponding to Ti^{4+} cations, and a decrease of those corresponding to Ti^{x+} upon adsorption of aldehydes [12] and ketones [13] at room temperature:

$$2CH_3CHO(a) + 2Ti{-}V_o \rightarrow 2CH_3CH(Ti)O(V)$$

where V_o denotes an oxygen vacancy,

$$2CH_3CH(Ti)O(V) \rightarrow CH_3CH(O{-}Ti)CH(O{-}Ti)CH_3$$

(The intermediate pinacolates have been observed on TiO_2 single crystals in UHV [35] during acetophenone TPD, and by IR in TiO_2 derived-slurries during acetone reaction [36].)

$$CH_3CH(O)CH(O)CH_3 \rightarrow CH_3CH{=}CHCH_3(a) + 2Ti{-}O$$

$$CH_3CH{=}CHCH_3(a) \rightarrow CH_3CH{=}CHCH_3(g) \quad \text{at ca. 500 K}.$$

One might argue that butene, instead of being formed by reductive coupling of two molecules of acetaldehyde, could result from further reactions of crotyl alcohol (successive dehydration and hydrogenation) on the reduced surfaces as follows:

$$CH_3CH{=}CHCH_2OH \xrightarrow{+[2H]} CH_3{-}CH{=}CH{-}CH_3 + H_2O$$

This route is, in fact, highly unlikely. Probably the most solid argument against it comes from the investigation of the reaction products from benzaldehyde-TPD on these same reduced surfaces of $TiO_2(001)$ [11,12]. Benzaldehyde does not contain hydrogen in the α position and thus cannot undergo β-aldolization like acetaldehyde. As a result there is no competition between the two reactions (β-aldolization and reductive coupling). Indeed, the selectivity of the reductive coupling product (stilbene) is very high (ca. 70%) on the reduced surfaces and decreases dramatically on the oxidized surfaces [12]. Thus aldolization activity is not necessary to produce reductive coupling. Likewise, the expected reductive coupling products of other carbonyl compounds cyclohexanone [14], cyclohexenone [14], *p*-benzoquinone [13], acetone [35,36], acetophenone [35] and acrolein [11] were observed on these same surfaces. It has also been reported that ethylene is formed, via reductive coupling, from formaldehyde on reduced $TiO_2(110)$ surfaces [37]; formaldehyde, like benzaldehyde, cannot undergo β-aldolization since it does not contain hydrogen in the α position. Finally, if one considers crotonaldehyde dehydration + dehydrogenation as a plausible route to butene, in spite of the number of successive reactions required by such a scheme on single crystal surfaces during TPD in UHV, one would need to explain the absence of butene in similar condensation reactions on TiO_2 powders at atmospheric pressure under steady state conditions [16]. For all these reasons it is clear that there are two distinct routes for C–C bond formation from aldehydes and ketones on the surfaces of TiO_2, the first via the reductive coupling to give symmetric olefins and the second via aldolization to give unsaturated higher aldehydes and alcohols.

5. Conclusions

The effects of surface modifications of $TiO_2(001)$ on the reactions of acetaldehyde have been studied by TPD. Three reactions were observed: reduction to ethanol, aldol condensation to crotonaldehyde (and crotyl alcohol), and coupling to butene. Acetaldehyde reduction to ethanol is not necessarily related to the presence of Ti suboxides since both reduced and fully oxidized surfaces showed considerable activity for this reaction. In contrast, condensation and coupling reactions exhibited important but opposite dependences on surface reduction. While reduced surfaces were active for the coupling of two molecules of acetaldehyde to one molecule of butene due to the presence of oxygen vacancies, oxidized (stoichiometric) surfaces were active for self-condensation of two moles of acetaldehyde to one mole of crotonaldehyde/crotyl alcohol due to the abundance of oxide anions (acting as Lewis base sites). In addition, aldol condensation reactions are not necessarily sensitive to surface reconstruction since the reduced surfaces also showed some activity for this chemistry.

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