



ETHANOL OXIDATION OVER Au/TiO₂ CATALYSTS

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ABSTRACT

The adsorption and reaction of ethanol over Au/TiO₂ catalysts was investigated using pulse flow reactor, DRIFTS, and TPD. The adsorption of ethanol over TiO₂ (P25) indicated a full monolayer adsorption of ethanol, with much of it in a dissociative state, forming ethoxy group on the cationic sites and hydroxyl group at anions. The ethoxy is relatively stable until 300°C, at which point dehydration to ethene occurs by a bimolecular surface reaction. As the concentration of ethoxy on the surface disappears, so the mechanism reverts to a decomposition pathway, producing methane, CO and hydrogen (~320°C) in TPD. However, the presence of gold on the catalysts prepared by deposition precipitation method indicates that the reaction is complete oxidation to CO₂ and water similar to Titania. The effect of the presence of low level of gold is marked with complete conversion of ethanol at low temperature (220°C) lower than Titania (240°C). Simultaneously, ethanol oxidation on Au/TiO₂ catalyst was followed by dehydration to ethene at 300°C (characteristic of TiO₂) and dehydrogenation to ethanal at high temperature. The pathway which gives ethene as seen on TiO₂ remains, but a new feature of the reaction is the evolution of CO₂ and H₂ (a peak is seen in TPD above 350°C) and appears to be due to the production of formate species on the surface of the catalysts. This formate species is mainly involved in the complete oxidation reaction of ethanol on the catalysts.

Keywords: Au catalysis, ethanol oxidation, ethanol catalytic combustion, TPD, DRIFTS

INTRODUCTION

The oxidation of ethanol has been extensively studied through different approach during the past two decades (Brust, *et al.* 1997), (Voronstov *et al.* 2004), (Sanchez *et al.* 2005), (Schmid *et al.* 2004) and (Daniel *et al.* 2000). The adsorption of ethanol over different metal oxides has been reported and indicate that the main products are ethanal, and diethyl ether. However, the presence of gold when highly dispersed over metal oxides (Fawcett *et al.* 2000) and (Gamal *et al.* 1991) such as TiO₂, the catalyst exhibit good stability and selectivity toward desired products under even milder conditions. Several other products have been reported in the literature for ethanol oxidation over TiO₂ (Yu *et al.* 2007), (Kecskes *et al.* 2004), and (Voronstov *et al.* 2004), and non reported the oxidation of ethanol over Au/TiO₂ catalyst.

MATERIALS AND METHODS

Catalyst preparation

The catalysts used in this study were prepared by incipient wetness impregnation method (Fawcett *et al.* 2000) and (Gamal *et al.* 1991). The pores of titania (TiO₂) treated in air at 500°C for 2 hours were impregnated with a suitable volume of an aqueous solution of HAuCl₄ (0.705 ml/gcat in this case) until incipient wetness was achieved. The sample was dried

in air for two hours and ground using a pestle and mortar. The catalyst sample was pressed in to a disc, crushed and then sieved between 850 μm and 600 μm particle aggregate size.

Ethanol oxidation

The reactivity of the catalyst was tested using a pulse flow reactor, which has been described in detail elsewhere (Bowker *et al.* 2007). 0.5g of the pressed catalyst was held vertically in a U- tube within the oven of the reactor. The gas (10% O₂/He gas) was allowed to flow at a rate of 30 ml per minutes. Ethanol was injected periodically (2 minutes intervals) in to the gas stream. At the beginning, the gas stream passed through the bypass until the mass spectrometer signal had settled. The gas stream was then switched to over the catalyst and the products of ethanol oxidation were observed using a quadrupole mass spectrometer.

RESULTS AND DISCUSSIONS

Temperature programmed reaction

The temperature programmed pulse flow reaction of ethanol oxidation over TiO₂ catalyst is shown in figure (1). Ethanol reaction over TiO₂ is complete oxidation to CO₂ and water.

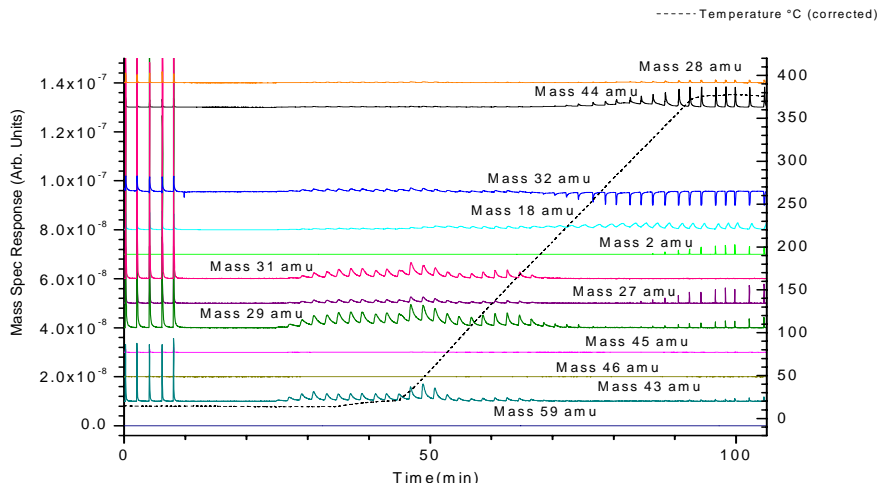


Figure (1): Temperature Programmed Pulse Flow Reaction for aerobic ethanol oxidation reaction in 10%O₂He gas flow over TiO₂ catalyst

The reaction was accompanied by dehydration of ethanol to ethene followed by deoxygenation to ethane as seen in figure (1). When the data in figure 1 was integrated and analyzed figure (2) was obtained, and shows that, 100% of ethanol was observed at relatively higher temperature

(250°C) than the Au/TiO₂ catalyst, with low selectivity to CO₂ being ~70% through out the experiment. Simultaneously, the selectivity to CO was also around 20%, with less than 10% selectivity to both ethene and ethanal.

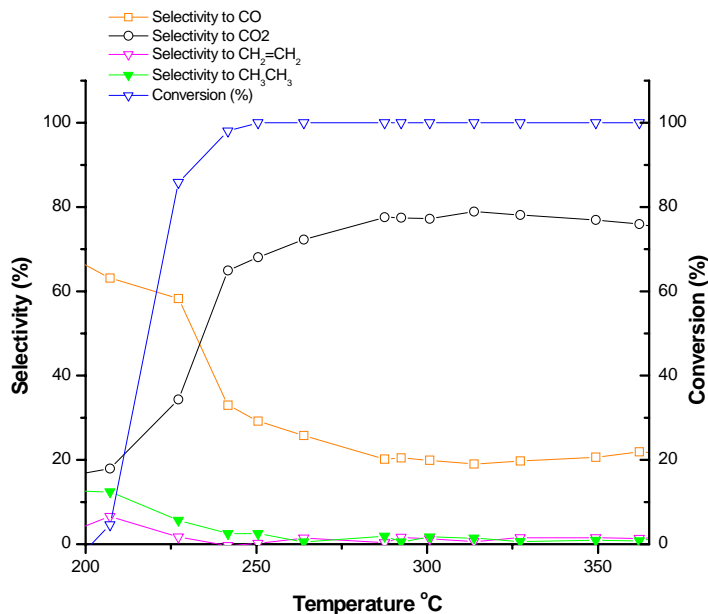


Figure (2): Selectivity and conversion with temperature for aerobic ethanol oxidation in 10%O₂/He flow over TiO₂ catalyst

Figure (3) shows the results of temperature programmed pulse flow reaction (aerobic) for ethanol oxidation over 1wt% Au/TiO₂ catalyst. The first five pulses of 1□l of ethanol injections were through the bypass. This gives the idea of the cracking pattern observed for ethanol. After the bypass, about 7□l of ethanol was used to saturate the surface (appearance of mass 31, 29 and 27 amu signals) and represent 100% of un- reacted ethanol, though the signal peaks are short and broad compared to the bypass peaks.

Similarly, when the peaks are integrated for injections through the bypass and over the catalyst, they are of the same intensity.

When the surface was saturated only ethanol broke through and no conversion of ethanol occurred, similarly, the uptake of ethanol has indicated to be 7□l corresponding with 1.44x 10²⁰ molecules g⁻¹ of catalyst. This in turn corresponds with about 2.88x 10¹⁹ molecules m⁻², if we assume a total surface atom density of 10¹⁹m⁻².

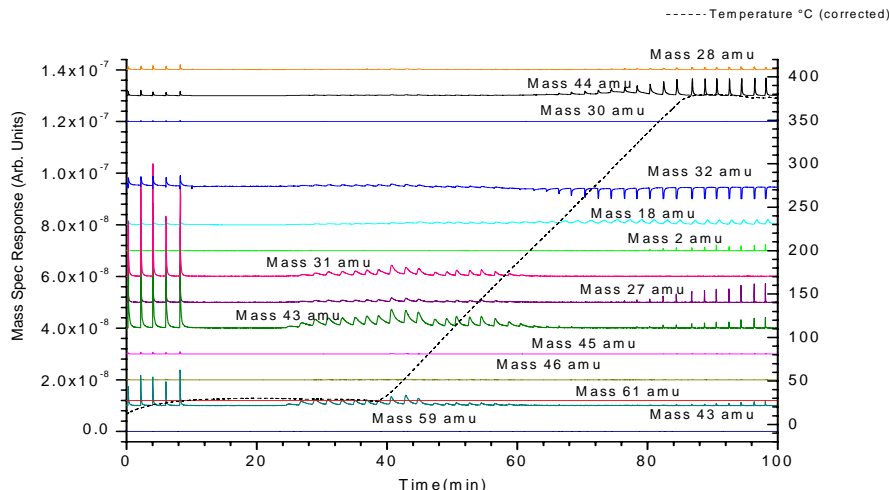


Figure (3): Temperature Programmed Pulse Flow Reaction for aerobic ethanol oxidation in 10%O₂/He gas flow over a 1wt% Au/ TiO₂ catalyst

However, as the temperature was increased to about 100°C, more ethanol observed, until the temperature reached 220°C, in which 100% conversion of ethanol was obtained (loss of mass 31,29 and 43 amu signals). CO₂ production occurred (from 75 minutes), with a short and wide signal peaks of CO₂ after each pulse injection and continued at a faster rate as the temperature increases, evident by the sharp peaks of CO₂ and the uptake of oxygen. The data obtained in figure 3 shows 1wt% Au/TiO₂ is a good combustor of ethanol to CO₂ and water as the main products. The oxidation reaction of ethanol was followed by dehydration to ethene at ~300°C and dehydrogenation to CH₃COH (ethanal) at high temperature. The result is in consistent with the reported literature (Masatake *et al.* 1997).

When the data in figure (3) was integrated and analyzed, figure (4) was obtained. The figure (4) shows as the conversion of ethanol was 50%, the temperature was 180°C and selectivity to CO₂ was 50% with CO selectivity being 25%. When the temperature was increased to 250°C, 100% conversion of ethanol was reached with CO₂ selectivity being ~90% and with selectivity to CO being >10%. Both selectivities (CO and CO₂) remained the same in a steady state. It was observed that the selectivity to CH₂CH₂ and CH₃COH was very small, with both selectivities being less than 10%

Temperature programmed reaction

Temperature programmed desorption was also carried out (figure 5). Low temperature desorption peaks at

approximately 80°C are due mostly to molecular ethanol weakly bound on the surface. As the temperature was increased to 250°C, diethyl ether (the appearance of masses 31, 59, 29 and 45 amu signals) and ethane (appearance of masses 28, 30, 27 and 29 amu signals) were observed due to dehydration and deoxygenation respectively.

When the temperature further increased to 300°C, more ethene (appearance of mass 28, 27, and 29 amu signals) and ethanal (appearance of mass 29, 44, 43, and 15 amu signals) was observed due to dehydration and dehydrogenation respectively, with desorption peaks of both centered at 320°C. Nevertheless, some methane was desorbed above 350°C due to decomposition of ethanol at that temperature with evolution of CO and hydrogen similar to the anaerobic reaction with ethanol.

Similarly, the TPD carried out of ethanol over 1wt% Au/TiO₂ catalyst (figure 6). As seen from figure 5-6 some water and ethanol desorbed at low temperature due to dehydration of ethanol to ethene (appearance of mass 28, 27, and 29 amu signals) and occurred at about 200°C with hydrogen being evolved.

The result indicates that the main Desorption products were due to dehydrogenation to ethanal (appearance of mass 29, 44, 43, 16 amu signals). When the temperature was increased further to 350°C, another hydrogen desorption peak was observed, followed by masses 16 and 15 amu, due to methane. This is also similar to the product pattern in the reactor, with main desorbed products which are due decomposition of ethanol to methane, CO and hydrogen.

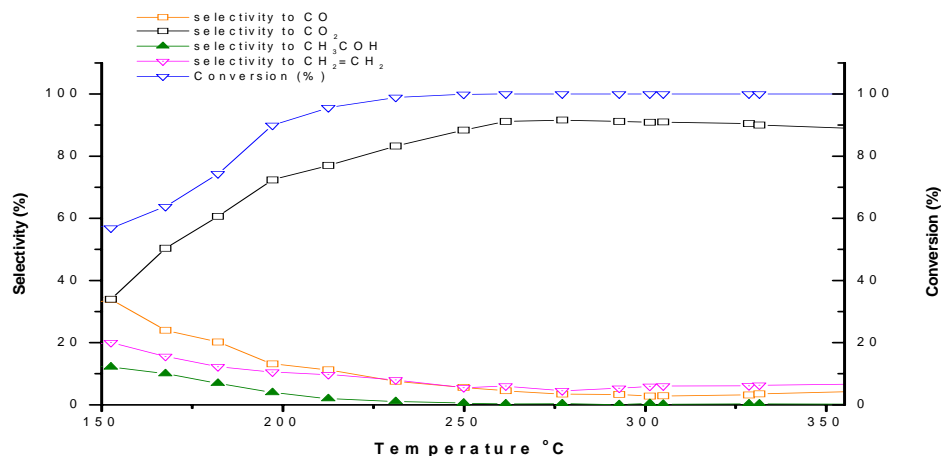


Figure (4): Selectivity and conversion with temperature for aerobic ethanol oxidation over a 1wt% Au/TiO₂ catalyst

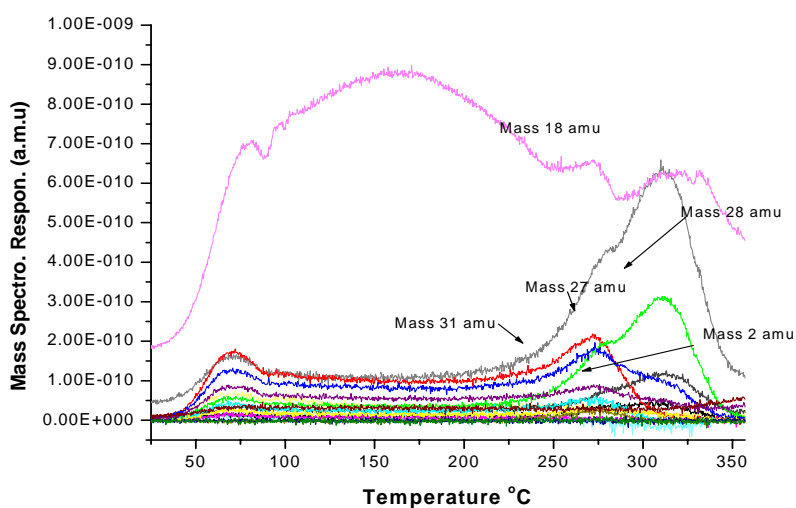


Figure (5): Temperature Programmed Desorption of TiO₂ catalyst saturated with ethanol at room temperature

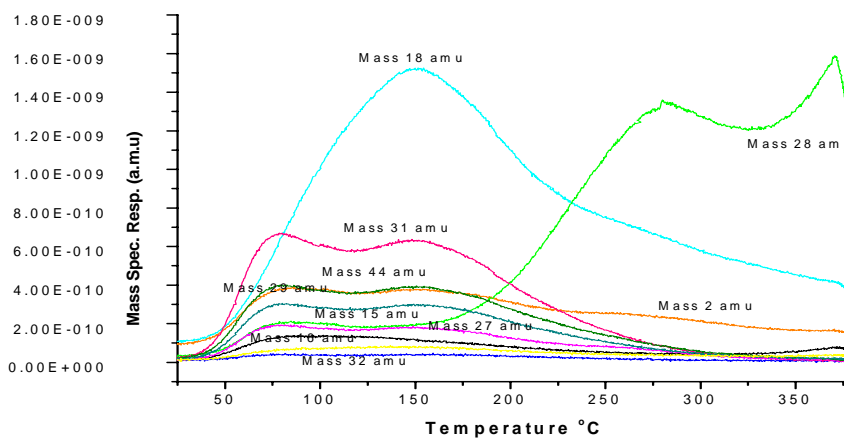


Figure (6): Temperature Programmed Desorption of a 1wt% Au/ TiO₂ catalyst saturated with ethanol at room temperature

Infra red spectrometry

Figure (7) shows the DRIFTS spectrum of ethanol introduced at room temperature on the Au/TiO₂ catalyst. Initially, the Au/TiO₂ catalyst was heated in O₂ for 1 hour at a temperature of 500°C and allowed to cool to room

temperature. Ethanol was introduced at room temperature and allowed to stabilize in pressure and then nitrogen was subsequently introduced to purge the gas phase species before the spectra were taken.

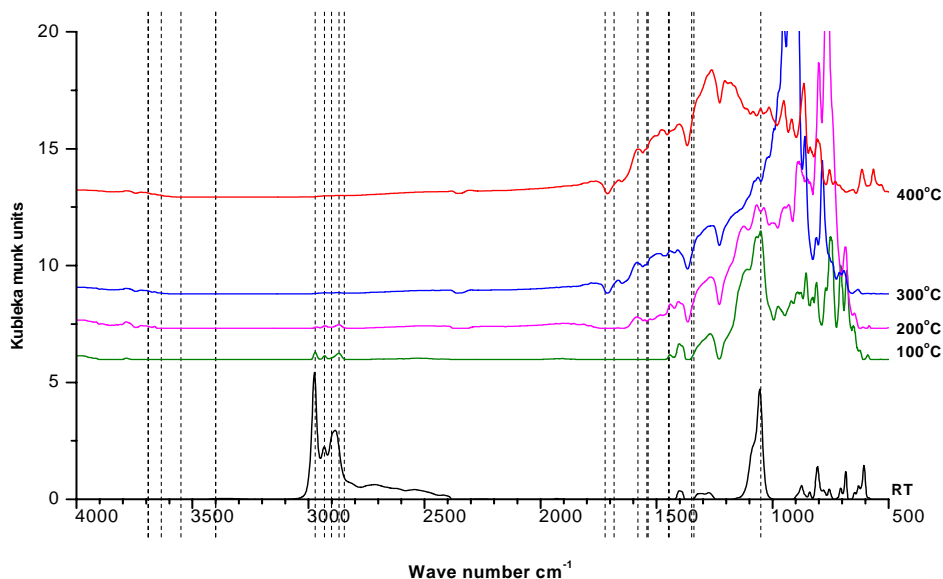


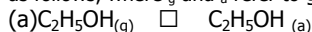
Figure (7): DRIFTS spectra from the adsorbed ethanol over a 20%wt Au/TiO₂ catalyst at different temperatures

Figure (7), shows spectra in the range 1000cm⁻¹ to 1750cm⁻¹ and in the range 2500cm⁻¹ to 4000cm⁻¹. The bands at 2971, 2931 2901and 1058 cm⁻¹ are assigned to ν_{as}(CH₃), ν_{as}(CH₂) and ν_s(C-O) of the adsorbed ethanol (C₂H₅OH_{ad}) respectively (Gamal *et al.* 1991) and (Kecsces *et al.* 2004). Similarly, the presence of the peaks at 1723cm⁻¹ was assigned by Yu *et*

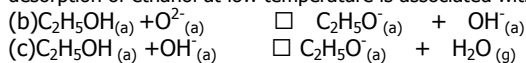
However, the bands at 2846 and 1350cm⁻¹ were assigned to the ν(CH₂) and ν_s(COO) for the adsorbed formate (HCOO⁻_{ad}) (Yu *et al.* 2007), (Gamal *et al.* 1991) and (Kecsces *et al.* 2004).The data obtained in figure 5-6 show that the band at 3690, 3550 and 3634cm⁻¹ are likely due to ν(OH) of the isolated OH (Gamal *et al.* 1991) and (Kecsces *et al.* 2004). The spectrum is similar to that for TiO₂ alone but with some small differences. Higher spectrum intensities are observed in the Au/TiO₂ catalyst than when TiO₂ was used alone. The high intensities may be due to more formate and acetate formation on the gold and reduced coverage of ethoxy species on the surface of the catalyst (Vorontsov *et al* 2004).

Mechanism of ethanol oxidation on Au/TiO₂ catalyst.

Based on the study and data gathered so far, the following mechanism may be proposed for the ethanol oxidation on Au/TiO₂ as follows, where g and a refer to gas phase and adsorbed species respectively:



From the temperature programmed desorption data (figure 5-6), ethanol is seen to be desorbed at low temperature. The uptake of ethanol (figure 5-6) was measured to be about half monolayer from the pulses taken up by the catalyst. The desorption of ethanol at low temperature is associated with a



The steps (b) and (c) are the most likely ways for the ethoxy formation, however, with (b) likely to be dominant at ambient temperature for titania. In this case, the anion vacancies are designated as Vo²⁻, although the electrons are likely to be associated with cation sites, as Ti³⁺ than the vacancy itself.

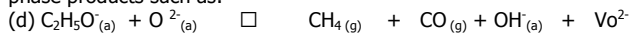
al.(2007) and (Idriss *et al.* 2004) as the ν(C=O) band due to adsorbed ethanal (CH₃CHO_{ad}). The bands observed at 1542, 1469 and 1340cm⁻¹ will also be assigned to ν_{as}(COO), δ_{as}(CH₃), and δ_s(CH₃) for adsorbed acetate (CH₃COO⁻_{ad}) respectively.

The result is similar to reduced coverage of methoxy due to high intensity of formate present due gold.

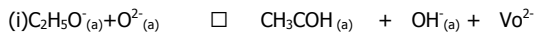
The spectrum shows similar bands to those observed when TiO₂ was used alone. The increase in the intensities at 2971, 2901 and 1058cm⁻¹, are likely due to more formate and acetate present in the catalyst. The disappearance of the pair of bands at 2971 and 2901cm⁻¹ upon heating may be correlated the CO,CO₂,CH₄ and hydrogen seen in the temperature programmed desorption (figure 6). The remaining bands are probably ethoxy-derived species and are related to titania, which are responsible for the dehydrogenation and dehydration.

weakly bound form of molecular ethanol on the surface, and the higher temperature desorption states are those involved with catalytic processes and involved the reaction of ethanol with the surface as follows:

The presence of the bands at 2971 2931 and 1450cm⁻¹ indicate that ethoxy species are formed according steps (b) and (c) above. The adsorbed ethoxy formed by the reaction in (b) and (c) are likely the main intermediate for the formation of gas phase products such as:



(e) The adsorbed ethoxy may also react with adsorbed oxygen on the surface and give hydrogen as seen as a product at high temperature from titania and even in the presence of gold. The appearance of the peaks at 1723cm⁻¹ indicated the presence of adsorbed acetaldehyde species,

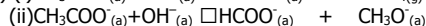
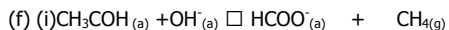


or

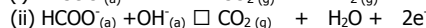
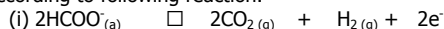


while the peaks at 2846 and 1350cm⁻¹ also indicated the presence of adsorbed acetate species respectively. The adsorbed acetate species may be formed by the following reaction.

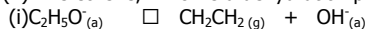
The bands observed at 2846 and 1350cm⁻¹ are associated with the presence of adsorbed formate species which are likely be formed either through adsorbed acetate or adsorbed acetaldehyde species according the following reaction.



(g) The formates adsorbed on gold may subsequently (i) decompose or (ii) react with the adsorbed surface hydroxide according to following reaction.



(h) The ethene, which is a dehydration product mainly on TiO₂, will be formed according to the following reaction:



From the data gathered and presented and the subsequent discussion of the results of ethanol oxidation over TiO₂ and Au/TiO₂ catalyst, it would be understood that ethanol oxidation over TiO₂ and Au/TiO₂ catalysts is selective oxidation. However, it would be observed that the ethanol is being adsorbed on the surface of TiO₂ by either one of the two ways as shown (figure 8a and b).

The surface of TiO₂ catalyst was made up of basic and acidic sites; when ethanol was adsorbed on the surface similar to methanol (figure 8a and b); it can be adsorbed leading to the formation of an ethyl group as shown in figure

(8a). The figure shows that, when ethanol was adsorbed on the surface the carbon atom was not substituted, a nucleophilic reagent can attack it - here a basic site (O), in a reaction similar to methanol as observed in a SN² mechanism. This produces a CH₃CH₂⁺ ion adsorbed at the basic site (O) and the OH⁻ ion, which is a strong base and can react on an even more weakly acidic site Ti. This type of attack should be easier if the C-OH bond is polarized by an interaction between acid centre and the OH group of the ethanol.

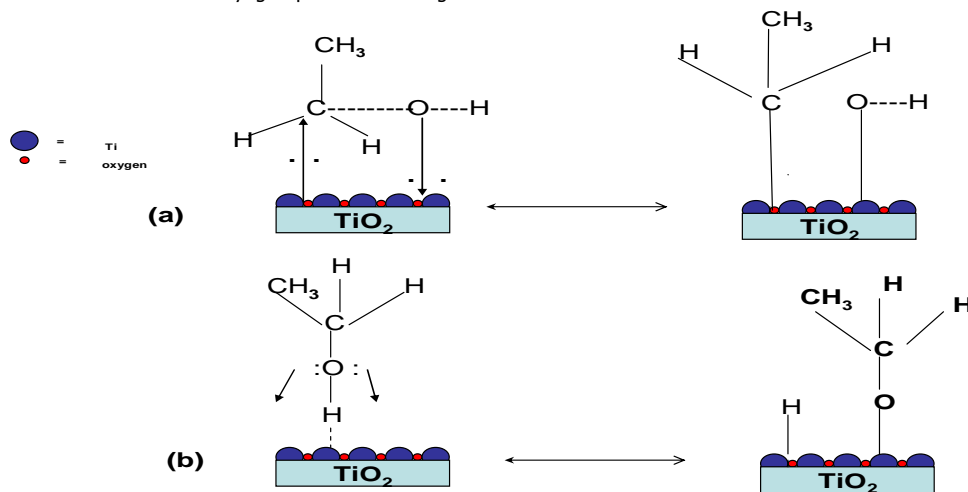


Figure (8): Ethanol adsorption over a TiO₂ catalyst surface

In the same figure (8b) indicates the ethanol adsorption, leading to a surface ethoxide which was identified by infra spectrometry. In this case, the basic site (O), extracts the hydroxyl hydrogen producing an ethoxylate ion, which is a strong base and can neutralize a weak acid centre Ti. In this case, if the acidic and basic sites are considered as charged centers there must be a mutual neutralization and the adsorbed species will be electrically neutral. However, the most probable adsorption step of ethanol was in figure (8b)

as shown by the infrared. However, even if gold was present, the ethanol adsorption was found to be with ethoxy being bonded with acidic site (Ti) and H⁺ on the basic site (O) of the surface of Au/TiO₂ catalyst as shown as in figure (9). The presence of adsorbed ethoxy is responsible for most of the ethanol surface reaction on TiO₂ and Au/TiO₂. The presence of adsorbed ethoxy is responsible for most of the ethanol surface reaction on TiO₂ and Au/TiO₂.

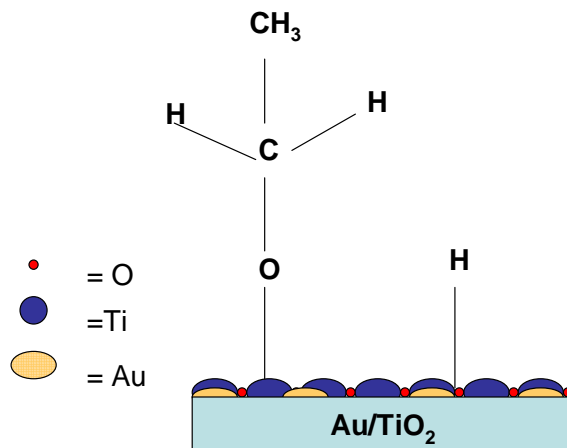


Figure (9): Ethanol adsorption over Au/TiO₂ catalyst surface

The ethanol surface reaction on TiO₂ confirmed that the principal products of aerobic oxidation reaction are mostly complete oxidation products (CO₂ and H₂O); associated with dehydration product ethene and deoxygenation product ethane. However, for anaerobic ethanol reaction, the products are partial oxidation to ethanal due to dehydrogenation, dehydration to ethene, deoxygenation to ethane, and decomposition to CO, hydrogen and methane.

The presence of gold shows that the aerobic ethanol oxidation reaction is also a complete oxidation to CO₂ and water, followed by dehydration to ethene and dehydrogenation to acetaldehyde at low temperature.

Conclusion

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