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Propan-1-ol Oxidation Reaction on Au/TiO_2 Catalysts

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ABSTRACT

Alcohols such as propanol and n- butanol have been oxidised to aldehydes by resin- supported gold in the liquid phase, and several other primary and secondary alcohols have been oxidised with very high selectivity in vapour phase over a 1wt% Au/SiO_2 catalyst between 373- 573K. In this work, the adsorption of propan-1-ol was carried over 1%Au/TiO_2 catalysts prepared by deposition precipitation method. This was further investigated using Pulse Flow reactor, TPFRP, TPD, and XRD,. The adsorption of propan-1-ol over TiO_2 (P25) indicated a full monolayer with much of it in a dissociated state, forming propoxy group on the cationic site and hydroxyl group at anions. The propoxy is relatively stable until about 250°C, at which dehydration to propene occurs by bimolecular surface reaction. As the concentration of propoxy on the surface disappear, so mechanism reverts to a decomposition pathway, producing CO_2 and H_2O. However, the presence of gold on the catalyst is marked with complete conversion of propan-1-ol at low temperature (230°C) lower than Titania (300°C). Similarly, propan-1-ol oxidation on Au/TiO_2 catalyst was followed by dehydration to propene at 300°C (Characteristic of TiO_2) and dehydrogenation to propanal at high temperature. The evolution of CO_2 and H_2 appear to be due to the production of formate species on the surface of the catalyst. This formate species is mainly involved in the complete oxidation reaction of propan-1-ol on the catalysts.

Keywords: Gold Catalysis, Propan-1-ol Oxidation, TPD, TPFRP, XRD

INTRODUCTION

The major industrial application of propylene oxide (about 65%) is as a monomer for the production of polyether polyols for use in making polyurethane plastics. Propyleneoxide is also used in the production of propylene glycol (using about 30% of propylene oxide) and propylene glycols ethers (about 5%).

Industrial production of propylene oxide is currently performed in three different processes, which are complex and have economic and environmental disadvantages (*Nijhuis et al., 2006*). The chlorohydrin method uses chlorine and propylene. The two other methods use hydroperoxide and a second chemical (iso-butene or benzene) which results in production of the coproducts styrene or tert-butyl alcohol. Using Enichem TS-1 technology (Tullo, 2004; Tullo and Short, 2006) DOW and BASF propylene is oxidized with hydrogen peroxide to propylene oxide and water. In this process no side products other than water are formed.

As the current production methods have disadvantages, much research is devoted to the development of new catalysts and new processes to improve the propylene oxide production. One of the methods under study is the use of gold-titania catalysts, which are potentially attractive since propylene oxide is produced out of propylene, hydrogen and oxygen in a single reactor under mild conditions. Unfortunately, however, the conversion levels (2%) are too low for industrial application (Sinha *et al.*, 2004).

Our recent results concerning the oxidation of ethanol on gold based catalysts, which show a high selectivity towards production of ethylene oxide (Lippits *et al*., 2009; Lippits and Nieuwenhuys, 2010) motivated us to investigate the possibility of converting 1-propanol and/or 2-propanol directly to propylene oxide sites (Kulkarni and Wachs, 2002).

In this exploratory study we investigated the performance of gold based catalysts in the dehydration and oxidation reactions of 1-propanol.

MATERIALS AND METHODS

Catalyst Preparation

The catalysts used in this study were prepared by incipient wetness impregnation (Haruta, 1997, Bowker *et al.*, 2007) of titania (P25) treated in air at 500°C for 2 hours, using a suitable volume of an aqueous solution of $HAuCl_4$ (0.705 ml $gcat^{-1}$). The sample was dried in air for two hours and ground using a pestle and mortar. The catalyst sample was passed in to a disc, crushed and then sieved between 850 μm and 600 μm particle aggregate size.

Propan-1-ol oxidation

The reactivity of the catalyst was tested using a pulse flow reactor, which has been described in detail elsewhere (Nuhu, 2009). 0.5g of the pressed catalyst was held vertically in a U- tube within the oven of the reactor. 10% O_2/He gas was flowed at a rate of 30 mL min^{-1}. Propan- o-l was then injected periodically (at 2 minutes intervals) in to the gas stream. Initially, the gas stream passed through the bypass until the mass spectrometer signal had stabilised, and then was switched to pass over the catalyst, and the products of Propan-1-ol oxidation were observed using a quadrupole mass spectrometer.

Activity test

In order to study the activity of the catalyst with respect to propan-1-ol oxidation over Au/TiO_2 catalyst, control experiments were carried out in order to get an insight and the role of gold on propan-1-ol oxidation over Au/TiO_2 catalysts. Hence, similar experiments were carried out on TiO_2 alone in the presence of 10% O_2/He. Figure 1 shows the temperature programme reaction for propan-1-ol over TiO_2 alone in the presence of 10% O_2/He flow of gas.

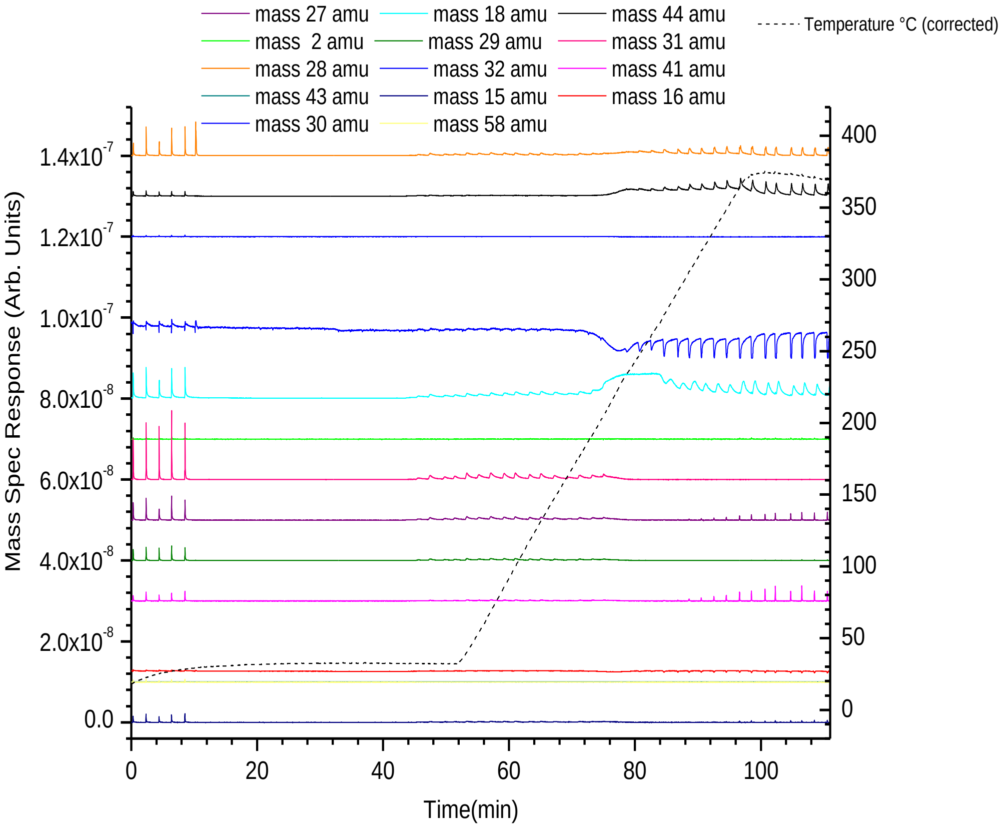

Figure 1: Temperature Programmed Pulse Flow Reaction for aerobic propan-1-ol oxidation in 10%O_2/He gas flow over TiO_2 catalyst

However, in each experiment, different masses were monitored for propan-1-ol oxidation over TiO_2 the Au/TiO_2 catalysts (Table 1). The aerobic propan- 1 -ol oxidation over TiO_2 catalyst is a complete oxidation. The lines of the flow gas were heated to 100°C and injections of propan-1-ol were done over the bypass and the catalyst. It is followed by the dehydration to propene (appearance of mass 41 and 27 amu signals) and dehydrogenation to propanal. When the data in Figure 1 was integrated, Figure 2 was obtained.

Table 1: Masses monitored for propan-1-ol oxidation over a 1wt% Au/ TiO_2 catalyst

SNO	MASS	PRODUCT NAME
1	2	Hydrogen (H_2)
2	15 and 16	Methane (CH_4)
3	18	Water (H_2O)
4	28	Carbon monoxide (CO),Ethene, Ethane, propane, propanal, and Nitrogen (N_2)
5	29	propanol, Ethene, Ethane, propanal, propanoic acid and propane
6	27	Propanol, Ethene (CH_2CH_2), propanal, and propene.
7	30	Ethane (CH_3CH_3)
8	31	Ethanol (CH_3CH_2OH) and Diisopropyl ether ($C_3H_7OC_3H_7$)
9	32	Oxygen (O_2)
10	43	Diisopropyl ether and propane
11	44	Carbon dioxide CO_2 and Ethanal(CH_3COH)
12	58	Propanal (CH_3CH_2CHO)
13	74	Propanoic acid (CH_3CH_2COOH)

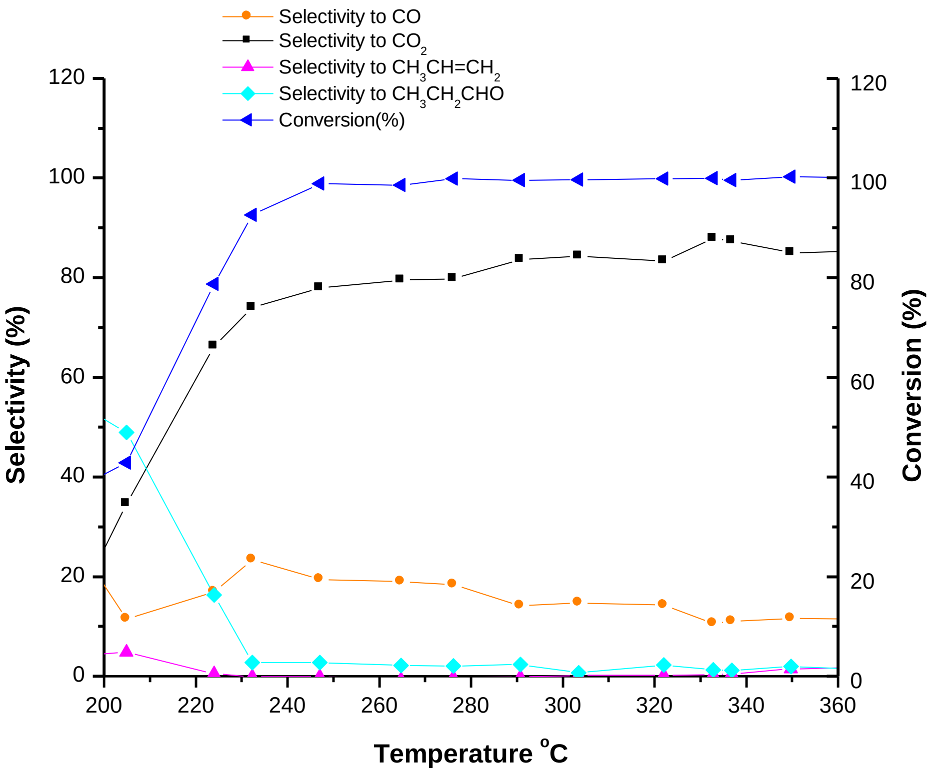

Figure 2: Selectivity and conversion with temperature for anaerobic propan-1-ol reaction in He flow over TiO_2 catalyst

As the conversion of propan- 1- ol is 40%, the selectivity to CO_2 begins to increase and continues as the temperature increases; when the temperature reached 250°C, CO_2 selectivity was about 85% with CO and propanal sharing the remaining 15%. However, as the temperature increases, the selectivities to CO and propanal decrease and CO_2 selectivity increase to almost 90% due to decomposition of propan-1- ol and continue in a steady state throughout the experiment.

Similarly, a freshly prepared 1wt% Au/TiO_2 calcined sample of the catalyst was calcined at 400°C in air. It was then loaded in a pulse flow reactor in the presence of 10% O_2/He flow of gas at rate of 30ml per minute.

RESULTS AND DISCUSSIONS

The masses monitored were chosen because propan -1-ol can be dehydrogenated to produce CH_3CH_2CHO in the presence of oxygen (oxidation) or it may be decomposed to produce CH_3CH_3, CO, H_2 and sometime CO_2 and water, similar to ethanol. Ethanol can be oxidised and dehydrogenated to acrolein (propenal). Similarly, propanal can also be oxidised to produce propanoic acid and simultaneously, can further react with propan-1-ol to produce isopropyl ester. However, propan-1-ol can also be deoxygenated to propane or dehydrated to propene Based on the study so far using temperature programmed pulse flow reaction in 10%O_2/He, the results for propan-1-ol oxidation over a 1wt% Au/TiO_2 catalyst (aerobic) were as shown in Figure 3

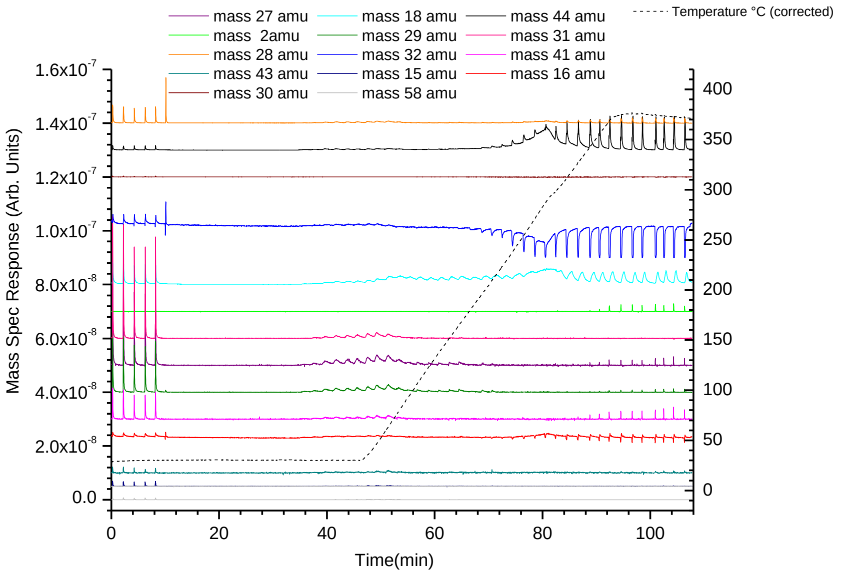

Figure 3: Temperature Programmed Pulse Flow Reaction for aerobic propan-1-ol oxidation in 10%/ He gas flow over a 1wt% Au/ TiO_2 catalyst

The first five pulses were observed for propan-1-ol injection over the bypass and this gave the cracking pattern observed for propan-1-ol.When the surface was saturated (after approximate 40 minutes), only propan-1-ol molecules broke through and no conversion of propan-1-ol occurred. The peak areas were much smaller and broader than those passing through the bypass and the integrals were similar to those through the bypass. The uptake of propan-1-ol was about 10µl, corresponding with $1.67x10^{20}$ molecules g^{-1} of catalyst. This in turn corresponds with 8.349 x 10^{19}molecules m^{-2}.

As the temperature increased to 120°C, 100% of propan-1-ol was obtained (loss of mass 31, 29, 27 and 28 amu signals), and two stages of CO_2 production occurred. In the first stage (70-80min), there was slow CO_2 evolution, together with slow uptake of oxygen after each pulse injection. When the temperature reached 250°C, the production of CO_2 and uptake of oxygen occurred at a faster rate as evident from the sharp peaks. At 300°C, the evolution of hydrogen (mass 2 amu signal) signifies the propanal evolution but its production is very minimal (absent of mass 58 amu signal); propane (mass 29, 28, 27, 44 and 43 amu signals), and propene (mass 41 and 27 amu signals) begin to emerge as the temperature increases.

The data obtained in figure 3 indicate that the main reactions seen for propan-1-ol oxidation over Au/TiO_2 catalyst are complete oxidation between 120-300°C, followed by dehydration to propene, deoxygenation to propane above 300°C and dehydrogenation to propanal but very minimal from 350°C

Figure 4 shows the integrated and analysed data of Figure 3. At a temperature of 100°C, propan-1-ol conversion was 60% and the catalyst was selective to CO_2, with a value being almost 50%. When the temperature was increased to 125°C, 100% conversion of propan-1-ol was observed. However, as the temperature increased above 250 °C, with selectivity increases towards CO_2, with a CO_2 selectivity observed to be almost 98% throughout the experiment, while CO, propanal, propene and propane selectivities being less than 2%.

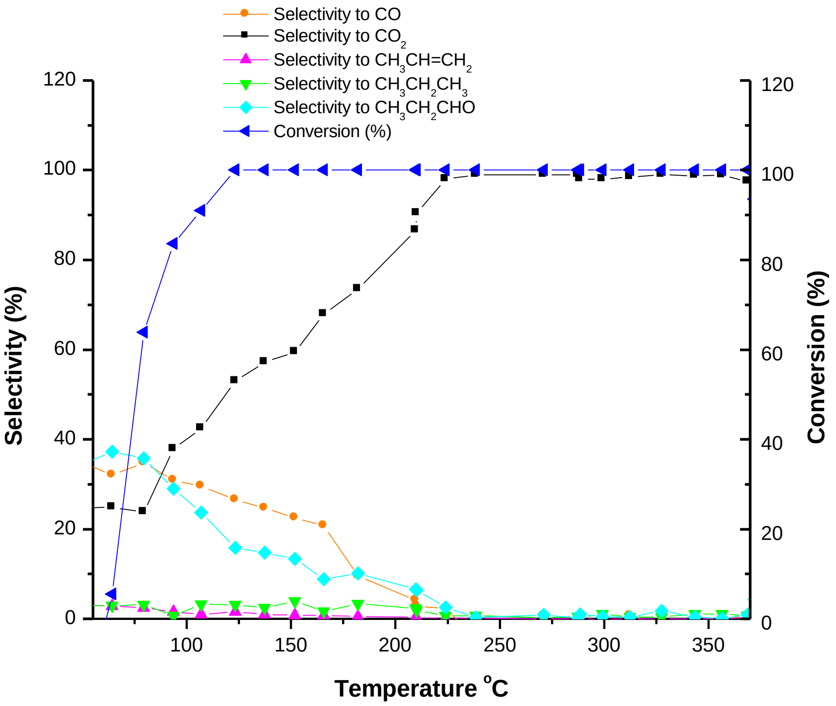

Figure 4: Selectivity and conversion with temperature for aerobic propan-1-ol oxidation in 10%O_2/He flow over a 1wt% Au/ TiO_2 catalyst

Temperature Programmed Desorption of propan-1-ol over Au/TiO_2 catalyst

Temperature programmed desorption was also conducted. The sample was dosed with pulses of propan-1-ol and the uptake corresponded to about one monolayer of propan-1-ol at saturation.

The temperature programmed desorption of propan-1-ol over TiO_2 catalyst is shown in Figure 5. Propan-1-ol was being desorbed at lower temperature, but as the temperature was increased to 250°C, the dehydrogenation indicates the presence of propanal and the appearance of mass 41, and 27 and 18 amu signals

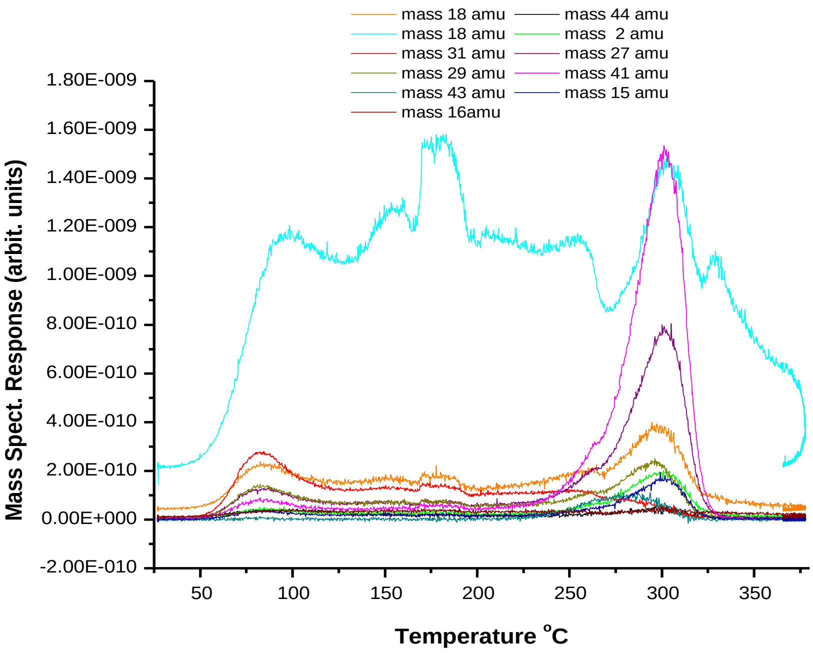

Figure 5: Temperature Programmed Desorption of TiO_2 catalyst saturated with propan-1-ol at room temperature

confirmed the dehydration of the adsorbed propan-1-ol to propene. Similarly, propane was also desorbed (the appearance of mass 29, 28, 27, 44, 43 and 15 amu signals).

However, the emergence and coincidence of CO_2 and H_2 in the propan-1-ol TPD on TiO_2 confirmed the presence of formate as adsorbed species present as in the case of Au/TiO_2 catalyst. The TPD also confirmed that the reaction involved for propan-1-ol on TiO_2 is mainly dehydration and deoxygenation as evident in figure 5 and is also due to high surface coverage of 1-propoxy species adsorbed on the catalyst.

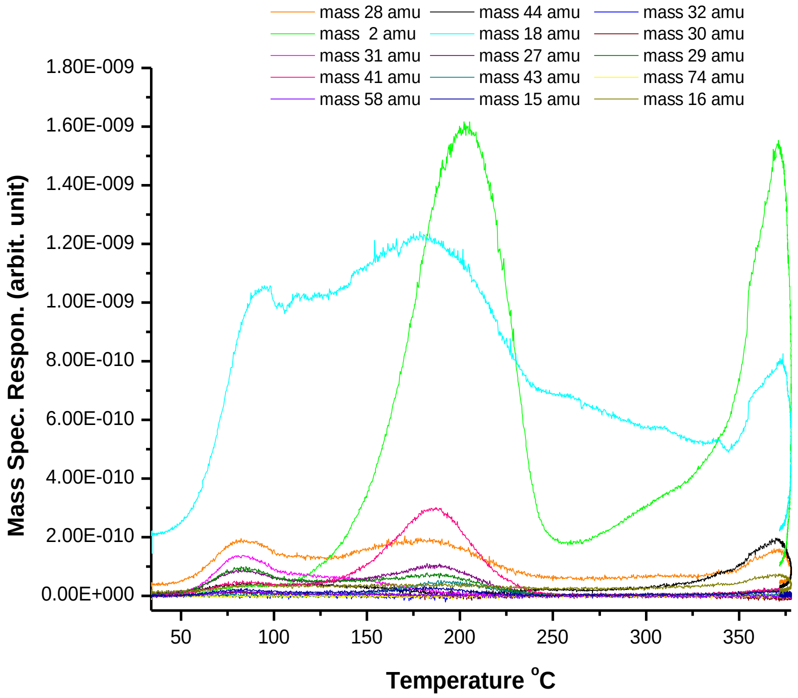

Figure 6: Temperature Programmed Desorption of a 1wt% Au/ TiO_2 catalyst saturated with propan-1-ol at room temperature

As depicted in Figure 6 shows the temperature programmed desorption of propan -1-ol over Au/TiO_2 catalyst, it indicates some water and propan-1-ol desorbed at lower temperature ~90^{o}C and as the temperature was increased to 180^{o}C, hydrogen, CO, propanal, propene and propane was evolved due to dehydrogenation of propan-1-ol, dehydration to propene and deoxygenation to propane. However, as the temperature further increased above 350^{o}C, hydrogen, water and CO_2 was evolved due to decomposition of propan-1-ol to CO_2 and water. The coincident appearance of CO_2 and hydrogen confirmed the presence of formate as adsorbed species on the Au/TiO_2 catalyst. The results are consistent with that reported by (Arana *et al*., 2005; Baile *et al.*, 1995).

X-ray Diffraction (XRD)

The pre- reaction XRD data information regarding TiO_2 and Au/TiO_2 catalyst has been fully presented in Figure 7. However, figure 7 indicates the X-ray diffraction of TiO_2 alone, with the peaks corresponding to a mixture of Anatase and Rutile (both tetragonal), but the Anatase phase has dominated the Rutile phase as expected. Weak XRD peaks of gold were observed. The low peaks of gold on the catalyst might be due to intense peaks of TiO_2, which merged, with gold peaks. In particular the $2\theta = 38.2^o$ is position very close to anatase peak $2\theta = 38.5^o$.Two main phases of P25 Degussa was observed before and after reactions of propan-1-ol oxidation over TiO_2 and Au/TiO_2 catalyst.

Another important characteristics peaks of gold (AuO as reported in the literature (Schubert *et al.*, 2001), particularly at $2\theta = 44.4^o$ and 64.5^o were not observed in the spectra. This may also be due to low or smaller size of gold, which is too small and very difficult to be detected by the X-ray diffraction machine.

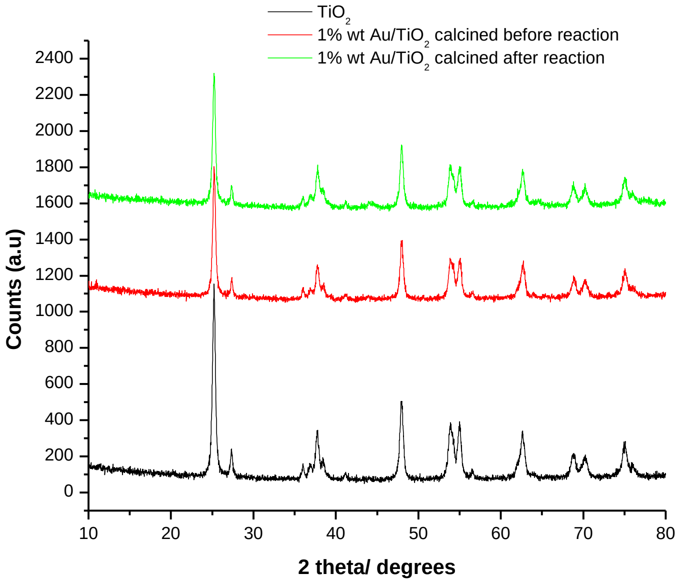

Figure 7: XRD patterns for propan-1-ol oxidation (in the flow of 10%O_2/ He) post reaction over TiO_2 and different weight loadings of calcined Au/TiO_2 catalyst

CONCLUSIONS

In this study, it was found that gold based catalysts are capable of dehydrogenation of propan-1-ol to propanal and ethanol and dehydration of propanal to propene. However, other products with very minimal selectivities were also found. Similarly, other experimental evidences are needed such as infrared spectroscopy and other anaerobic reactions in order to get clear insight into the mechanism of propanal oxidation to various products.

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