



METHANOL OXIDATION OVER Au/ γ -Al₂O₃ CATALYSTS

Abdullahi Nuhu

Kano State University of Science and Technology, Wudil, P. M.B 3244, Kano State, Nigeria

Email:abdullahinuhu@ymail.com

ABSTRACT

Methanol adsorption and reaction was investigated over Au/ γ -Al₂O₃ catalysts. The catalysts were prepared by deposition precipitation (DP) and incipient wetness impregnation methods. The catalysts were used to catalyze the oxidation of methanol and characterised using X-ray diffraction (XRD), temperature programmed desorption (TPD), temperature programmed pulse flow reaction, scanning electron microscopy (SEM), X-ray photoemission spectroscopy (XPS) and Energy dispersive x-ray analysis (EDAX). The adsorption of methanol over γ -Al₂O₃ indicated a monolayer adsorption of methanol, forming methoxy group on the surface. The methoxy is relatively stable until 120°C, at which point dehydration to dimethyl ether occurs by bimolecular surface reaction. As the concentration of methoxy diminishes, so the mechanism reverts to a decomposition pathway, producing methane, CO and hydrogen (~340°C) in TPD. The gold supported on γ -Al₂O₃ play a role on the performance of the catalyst with respect to methanol oxidation. The oxidation reaction of Au/ γ -Al₂O₃ catalysts prepared by deposition precipitation and incipient wetness impregnation both shows the reaction is complete oxidation to CO₂ and H₂O. However, it involved dehydration of methanol to dimethyl ether (DME) at about 150°C followed by decomposition of DME to CH₄, CO, and H₂. The main product from TPD is DME due to high surface coverage of methoxy species on the catalysts surface. The XPS, SEM, EDAX, indicated high dispersion of gold with complete methanol conversion attained at lower temperature compared to when γ -Al₂O₃ catalyst was used alone.

Key Words: Au catalysis, methanol oxidation, methanol catalytic combustion, TPD, XPS, SEM, and EDAX

INTRODUCTION

The adsorption and reactivity of methanol over metal oxides supports have been studied extensively by many researchers (Bowker *et al.* 1981) and (Ozkan *et al.* 1990). The reactions and experimental results indicate that a ZnO-Cr₂O₃/CeO₂-ZrO₂/Al₂O₃ catalyst is a promising catalyst for the hydrogen production from methanol oxidation reforming. There was no significant deactivation of the catalyst over 1000 hours of continuous operation. The oxidation of methanol over TiO₂ has been studied and the role of TiO₂ has been fully discussed and the main products are dehydrogenation and dehydration products (Gamal *et al.* 1991).

It has been agreed that when gold is present on the support, it plays an important role particularly, when it is in the dimension 1-5nm, exhibits unexpectedly activity and reactions to various products, properties which have not been revealed by bulk gold (Choudhary *et al.* 2002), (Haruta *et al.* 2002 and 2004), (Hutchings *et al.* 2005) and (Didier *et al.* 2005). The presence of gold leads to the formation of catalysts with a high activity and a high stability and play an important role in the process of methanol oxidation. In this paper, the Au catalysts with high activities and selectivities for methanol oxidation have been developed.

MATERIALS AND METHODS

Catalyst preparation

The catalysts used in this study were prepared by incipient wetness impregnation method (Choudhary *et al.* 2002) and (Bowker *et al.* 1981). The pores of Alumina (γ -Al₂O₃) (treated in air at 500°C for 2h) 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 grounded using a pestle and mortar. The catalyst sample was pressed in to a disc, crushed and then sieved between 850 μ m and 600 μ m particle aggregate size.

Methanol oxidation

The reactivity of the catalyst was tested using a pulse flow reactor, which has been described in detail elsewhere (Bowker *et al.* 1981). 0.5g of the pressed catalyst was held vertically in a U- tube within the oven of the reactor. 10% O₂/He gas was flowed at a rate of 30 ml per minutes. Methanol was injected periodically (2 minutes intervals) into 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 methanol oxidation were observed using a quadrupole mass spectrometer.

RESULTS AND DISCUSSION

Temperature programmed reaction

The γ - Al_2O_3 support was first calcined in-situ in 10% O_2 /He gas flow at a temperature of 400°C for 30 minutes, then cooled in the gas, and then temperature-programmed reaction with methanol was carried out, as shown in figure 1. The results in figure 1 indicate the saturation of methanol on the γ - Al_2O_3 surface (the appearance of mass 31 and 29 amu signals) at about 25

minutes. The amount of methanol used to saturate the surface was about 10 l. Similarly, as the temperature was raised and the injection was continued, the dehydration to dimethyl ether begins from 50 minutes (The appearance of mass 45 and 15 amu signals). Nevertheless, the dehydration continues up to 70 minutes while the oxidation begins with CO and CO_2 being the products of oxidation.

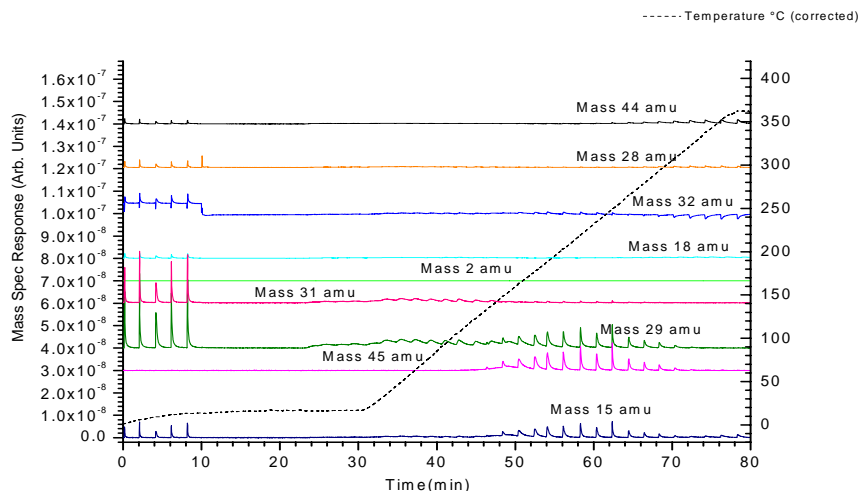


Figure 1: Temperature Programmed Pulse Flow Reaction for methanol oxidation over a γ - Al_2O_3 Catalyst

Figure 1 shows five pulses of methanol which by pass the catalyst, and this can give an idea of the cracking pattern observed for methanol. When the surface was saturated (at approximately 35 minutes) only methanol molecules broke through and no conversion of the methanol occurred. The peaks were much smaller than those passing through the bypass, but they were also broader, due to diffusive broadening through the bed, and the integrals were similar to those through the bypass. The methanol uptake was about 10ml corresponding to molecules 6.022×10^{20} molecules g^{-1} . This corresponding with about half monolayer, the Integrals were similar to those through the bypass. When the data in figure 1 was integrated figure 2 will be obtained.

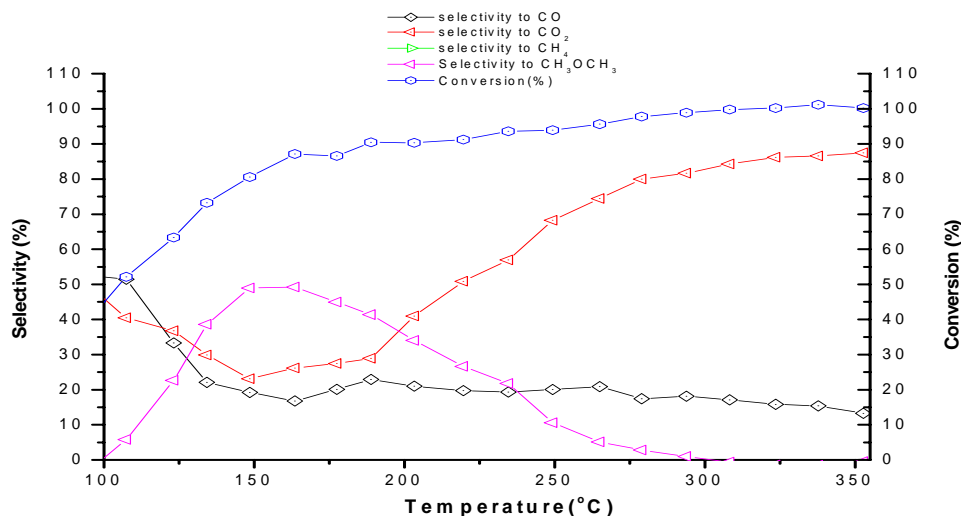


Figure 2: Selectivity and conversion for methanol oxidation over a γ - Al_2O_3 Catalyst

As the conversion of methanol reached 50%, dehydration and deoxygenation begin and the selectivity to dimethyl ether and methane begin to increase. High selectivities to

dimethyl ether (~35%) and methane (30%) were observed at 150°C and the conversion of methanol was 85%. However, when the temperature was increased,

dimethyl selectivity decreases as the temperature reached 300°C. Similarly, the CO₂ selectivity begin to increase as the temperature reached 180°C and continue until its selectivity was almost 89%. Simultaneously, the CO selectivity decreases at the same temperature (180°C) and continues in a steady state through out the course of the experiment. The dehydration observed from 100 to 300°C was due to high surface coverage and retention time of methoxy species at these temperatures. Methanol oxidation was carried out over Au/ γ -Al₂O₃ (figure 3). Low conversion of methanol was observed at relatively low temperature (the disappearance of mass 31

and 29 amu) and no sign of dimethyl ether production (mass 45 amu). The catalyst shows selectivity to CO, CO₂ and methane produced at high temperature. When the data was integrated and analyzed, figure (4) was obtained. It also shows that the catalyst activity was very much selective to CO₂ at temperature of 200°C with selectivity value being 70% and the conversion of methanol was only 50%. When the temperature was increased to 260°C, the conversion of methanol was 100%, the selectivity of CO₂ was 93% with CO selectivity being less than 5%.

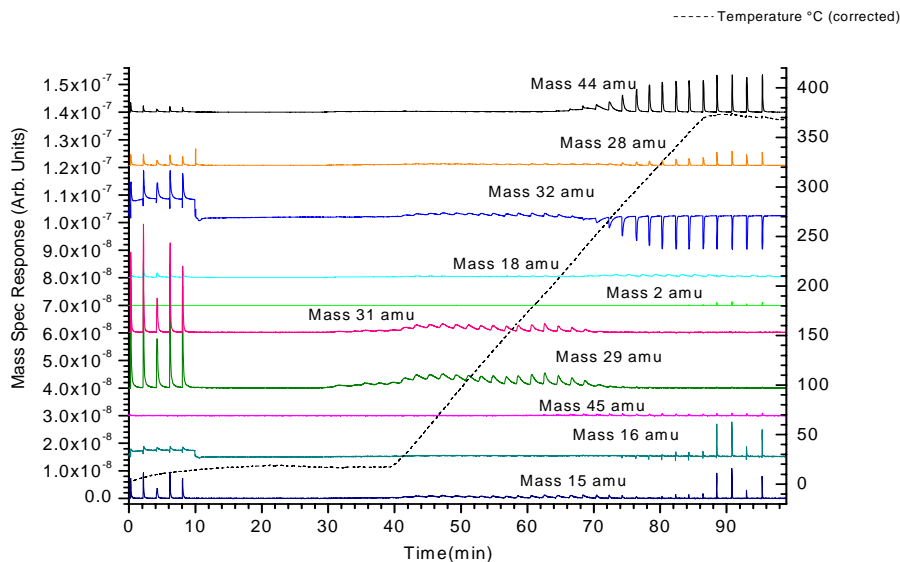


Figure 3: Temperature Programmed Pulse Flow Reaction for (aerobic) methanol oxidation over a 1wt% Au/ γ -Al₂O₃ catalyst prepared by IW

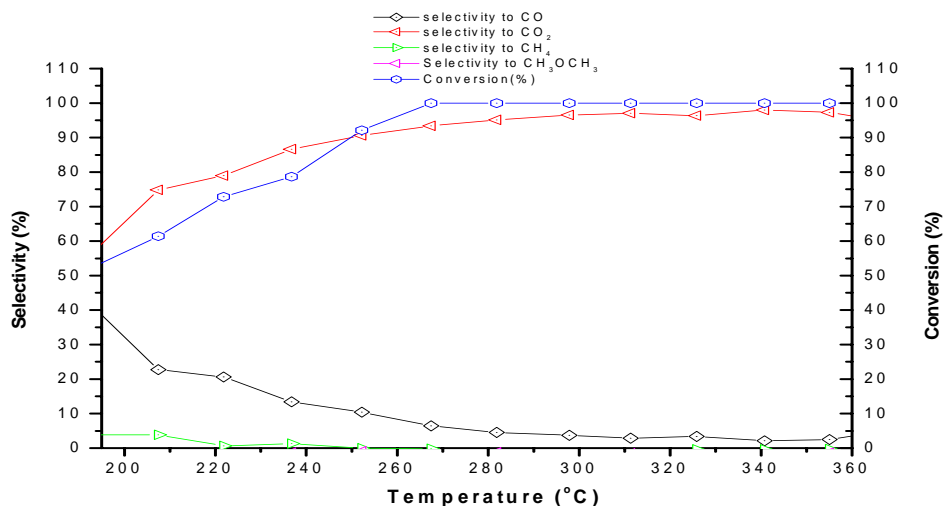


Figure 4: Selectivity and conversion with temperature for (aerobic) methanol oxidation over a 1wt% Au/ γ -Al₂O₃ catalyst prepared by IW

Temperature Programmed Desorption

The TPD carried out over Au/ γ -Al₂O₃ (figure 5) also indicates that molecular methanol was desorbed at a lower temperature with desorption peaks at 69°C, lower than the temperature when SiO₂ was used alone.

Therefore, this has confirmed to us that, the presence of Au lowers the activation energy of the methanol desorption, although the difference was not much significant.

Figure (5) shows the TPD of methanol over γ -Al₂O₃ alone, it indicates the desorption of methanol at lower

temperature (80°C). However, when the temperature was increased to 172°C, the desorption peak of dimethyl ether was observed. In the same manner, as the temperature reached 350°C, CO and methane desorption peaks were also observed. This implies that the γ -Al₂O₃

sample is selective to dehydration due to the high coverage of methoxy at low temperature and decomposition of dimethyl ether to CO, CH₄ and of methanol at high temperature.

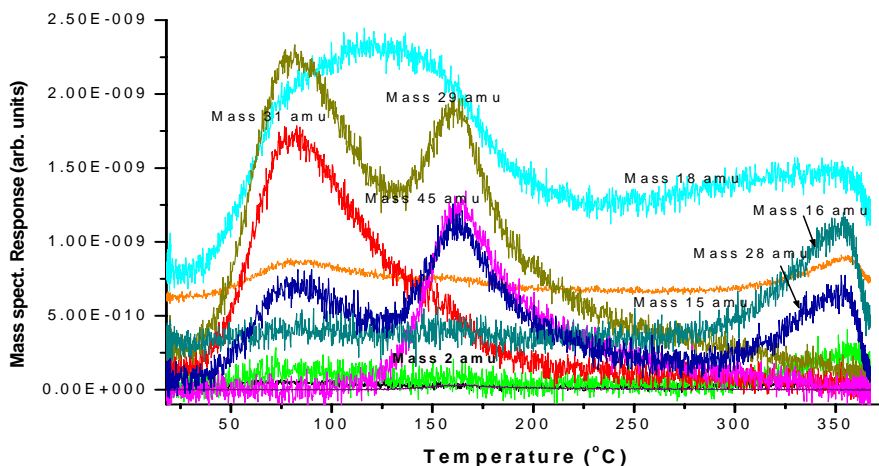


Figure 5: Temperature Programmed Desorption of a γ -Al₂O₃ saturated with methanol at room temperature

Similarly, a Temperature Programmed Desorption result for a 1wt% Au/ γ -Al₂O₃ catalyst is shown in figure (6). It shows methanol desorption at a low temperature of approximately 76°C. Dimethyl ether

desorbed at 168°C, lower than its desorption temperature when γ -Al₂O₃ was used alone. However, methane was also observed with a desorption peak centered at 347°C, lower than for γ -Al₂O₃ alone.

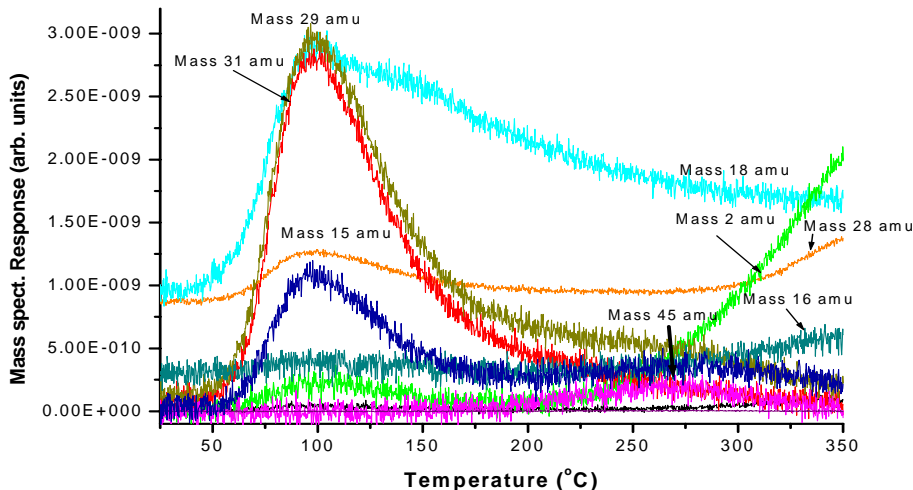


Figure 6: Temperature Programmed Desorption of 1wt% Au/ γ -Al₂O₃ catalyst saturated with methanol at room temperature

The Temperature Programmed Desorption of methanol over a 1wt% Au/ γ -Al₂O₃ catalyst was accompanied with high selectivity to dimethyl ether due to dehydration of methanol at lower temperature and subsequent decomposition to methane, hydrogen and CO at high temperature (figure 6). However, the presence of gold played an important role especially in lowering the activation energy of the reaction. The main products obtained are associated with high surface coverage and

longer residence time of methoxy species available on the catalyst surface. The XRD pattern for γ -Al₂O₃ and Au/ γ -Al₂O₃ catalysts are shown in figure (7), the figure shows the XRD pattern observed for all the catalysts mainly showed the presence of phase presence in the support (figure 7). The absence of gold species phase(s) can be attributed to the low loading of gold or a high dispersion of the gold species phase(s) on the surface of the support.

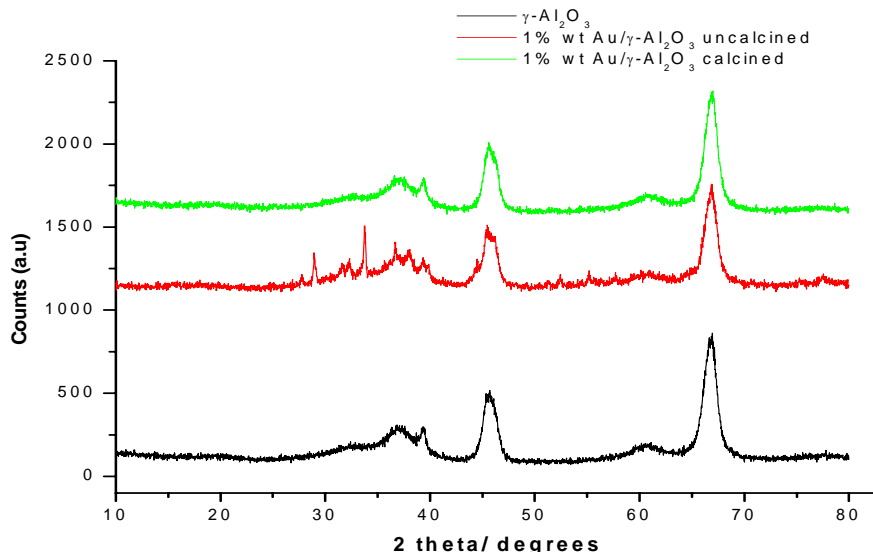


Figure 7 XRD patterns for $\gamma\text{-Al}_2\text{O}_3$ and 1wt%Au/ $\gamma\text{-Al}_2\text{O}_3$ (uncalcined and calcined) catalysts

Figure 8 shows the SEM images for $\gamma\text{-Al}_2\text{O}_3$ alone (a) and uncalcined 1wt% Au/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (c) dried at 120°C for 2h prepared by deposition precipitation. The figure shows the uncalcined 1wt% Au/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (shows a peculiar morphology (porous irregular gold particles of varying sizes < 104 to approximately 242.9 nm). These features indicate high dispersion and good size distribution of the gold particles on the catalyst surface. However, SEM images of the calcined 1wt% Au/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (b) dried at 400°C for 2h shows different morphology (porous irregular gold particles of varying sizes < 1.4 μm to approximately 2.4 μm). These features also indicate that large gold particles were distributed on the surface of the compared to the uncalcined catalyst.

The XPS data obtained for the catalyst of Au/ $\gamma\text{-Al}_2\text{O}_3$ prepared by deposition shows no detectable sign of gold on the catalyst. However, figure (9) shows the XPS spectrum of 1wt% Au/ $\gamma\text{-Al}_2\text{O}_3$ catalyst prepared by incipient wetness. The XPS spectrum shows that most of the Au 4f envelope is situated around 85 eV; these features indicate the existence of gold as Au⁺ oxidation state. The result is contrary to the data obtained in the case Au/TiO₂ prepared by deposition precipitation in which the oxidation state of gold was found to be Au³⁺ and Au⁰. Similarly, from the XPS data the nominal gold loading is within the expected values as depicted in table 1.

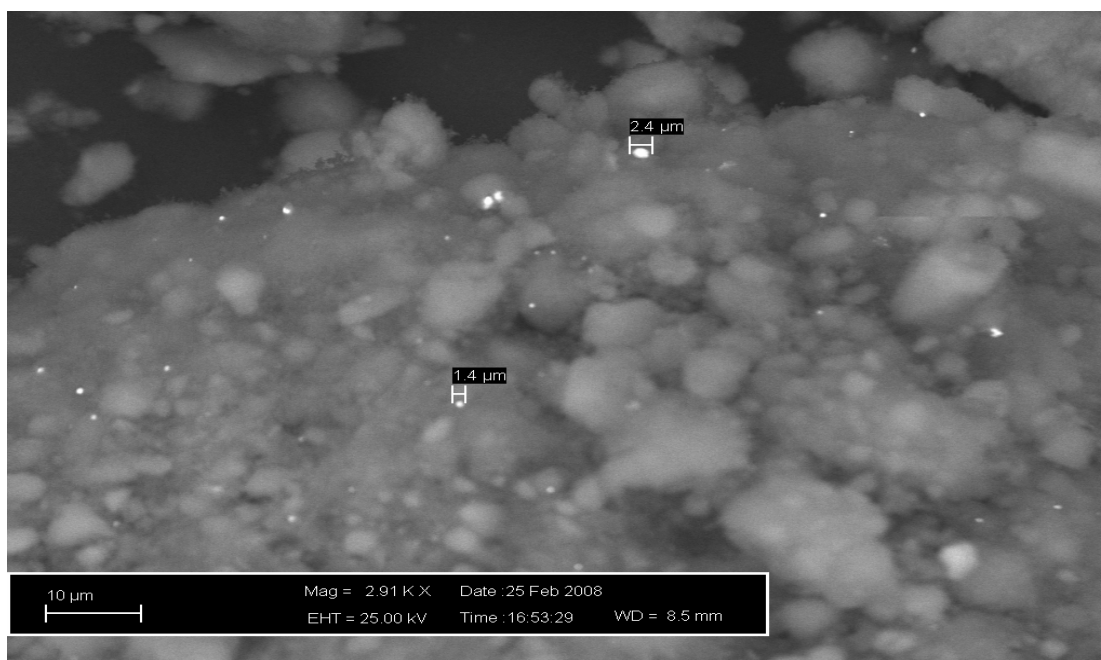


Figure 8: Scanning Electron Microscopy for a 1% wt Au / $\gamma\text{-Al}_2\text{O}_3$ catalyst (calcined) prepared by deposition precipitation

Table 1: Elemental composition for (a) 1wt% Au/ γ -Al₂O₃ (uncalcined), (b) 1wt% Au/ γ -Al₂O₃ (calcined) catalysts prepared by incipient wetness of impregnation

Sample	Atom %			Wt %
	Al	O	Au	Au
(a)	29.9	70.0	0.1	1.0
(b)	30.2	69.8	<0.1	<1.0

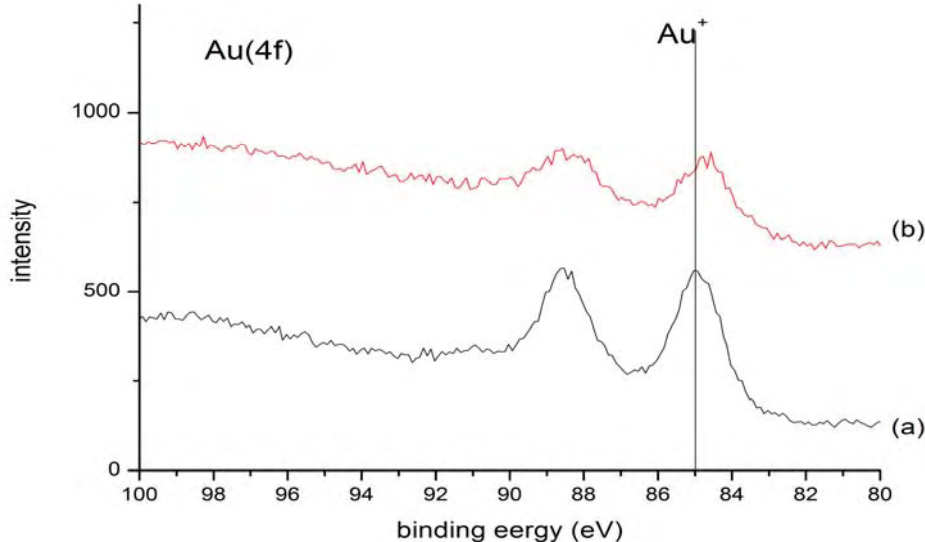


Figure 9: Au (4f) spectrum for (a) 1wt% Au/ γ -Al₂O₃ (uncalcined), (b) 1wt% Au/ γ -Al₂O₃ (calcined) catalysts prepared by incipient wetness of impregnation

The elemental analysis shown by EDAX confirmed that the 1wt% Au/ γ -Al₂O₃ catalyst prepared by incipient wetness impregnation method indicates that the Bulk of the catalyst contained about 56.2%, 6.0%, 37.4% and 0.4% of O, Na, Al, and Cl respectively. While the spot shows O, Na, Al, Cl, and Au with weight % of 43.3%, 3.8%, 51.1%, 0.7% and 1.2% respectively. The results show less contamination and free from sintering due to less Cl⁻ in the catalyst.

Conclusion

The main products of methanol oxidation are mostly dehydration products dimethyl ether due to high coverage of methoxy on the surface of γ -Al₂O₃. However, the presence of Au enhances the reactivity of the TiO₂ and the methanol oxidation over these metals was also complete oxidation. The Au/ γ -Al₂O₃ catalyst is an acidic catalyst because it involved dehydration products of methanol, which is dimethyl ether.

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