4.2.2 Catalyst activity for epoxidation of ethylene

Form the previous work, 13.18% Ag/Al_2O_3 loading and space velocity of 6,000 h^{-1} were identified as the optimum conditions. Therefore, the effect of gold was studied under these conditions. Gold was added in the range of 0.06, 0.27, 0.54, 0.63, and 0.93% wt, to the catalyst with optimal silver loading (13.18% Ag/Al_2O_3). An addition of gold can improve significantly ethylene oxide activity as shown in Figures 4.15-4.16. The highest ethylene oxide selectivity of 90% is obtained on the catalysts containing 0.63% wt Au, but the highest ethylene oxide yield is obtained on the sample with 0.54% wt Au at 240°C (Figure 4.17). It is interesting to note that the catalyst with the highest yield showed a significant shift of the XRD peak. The reason why adding gold gives good ethylene oxide selectivity can be explained that gold acts as a diluting agent on the silver surface and creates new single silver sites, which favor molecular oxygen adsorption (Kondarides and Verykios, 1996). This molecular oxygen reacts with ethylene into ethylene oxide according to the mechanism proposed by Campbell (Campbell, 1985) and in agree with the TPD results. For the blank Au/Al_2O_3, a small of desorbed O_2 was found by

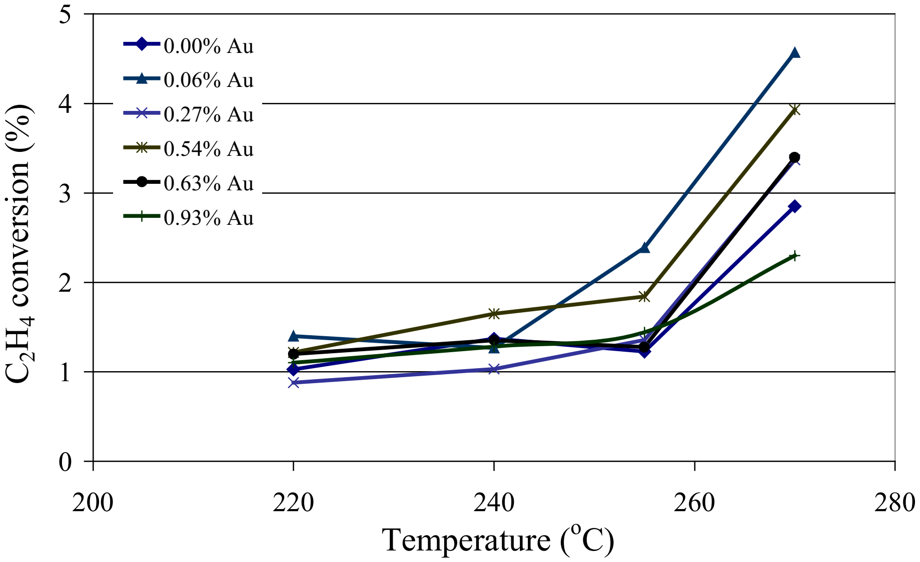

Figure 4.15 Ethylene conversion for 13.18% Ag/Al_2O_3 at various gold loadings at space velocity of 6,000 h^{-1}, P = 10 psig and 6% O_2 and 6% C_2H_4 balance with He.

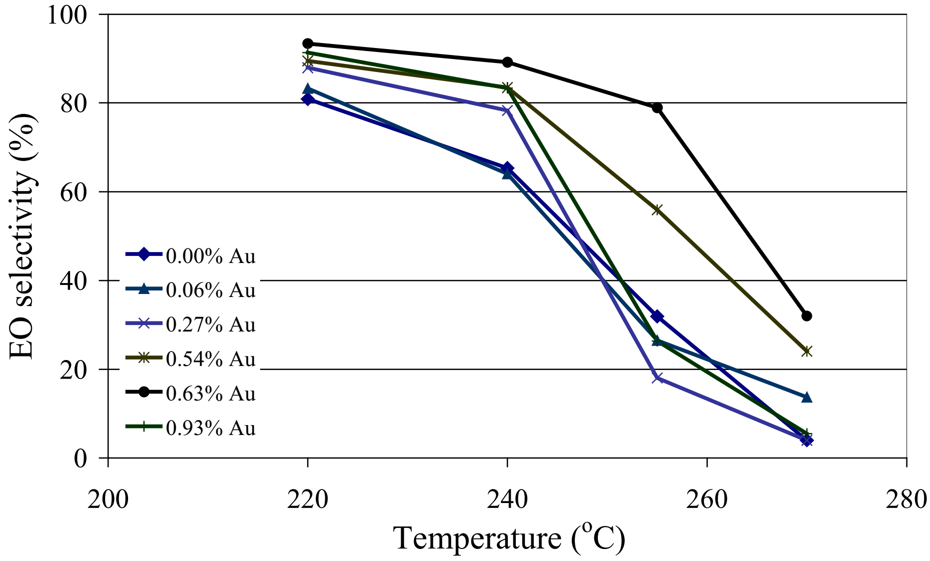

Figure 4.16 Ethylene oxide selectivity for 13.18%Ag/Al_2O_3 at various gold loadings at space velocity of 6,000 h^{-1}, P = 10 psig and 6% O_2 and 6% C_2H_4 balance with He.

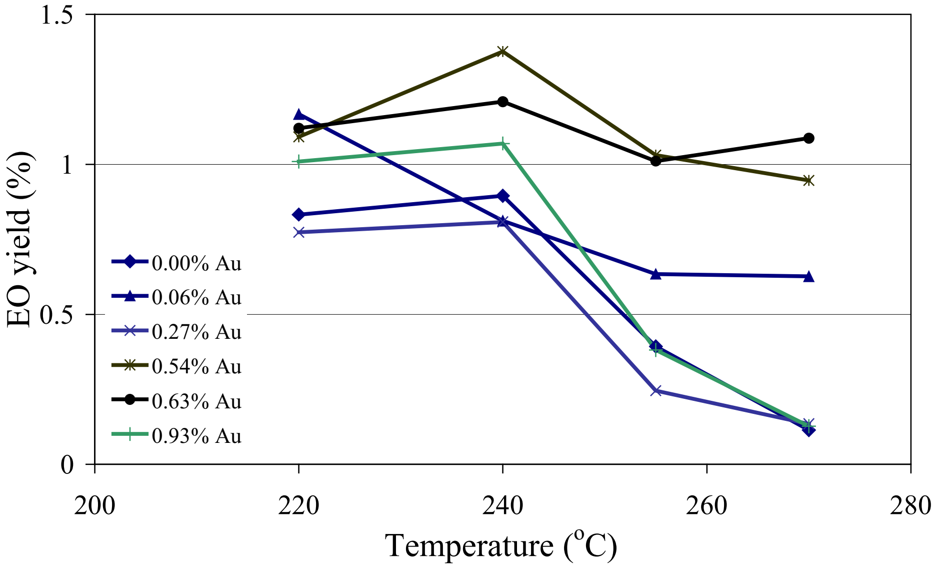

Figure 4.17 Ethylene oxide yield for 13.18% Ag/Al_2O_3 at various gold loadings at space velocity of 6,000 h^{-1}, P = 10 psig and 6% O_2 and 6% C_2H_4 balance with He.

TPD, However, no enhance of ethylene oxidation was observed on this catalysts. Therefore, one can neglect the effect of residual chorine from the use of auric acid in catalyst preparation, as the promoter effect of halogen is noticeable here. It is noteworthy that adding a small amount of Au to Ag supported on amorphous Al_2O_3 improves the ethylene oxide selectivity and yield. Therefore, Au represents a promising promoter for the epoxidation reaction of ethylene.

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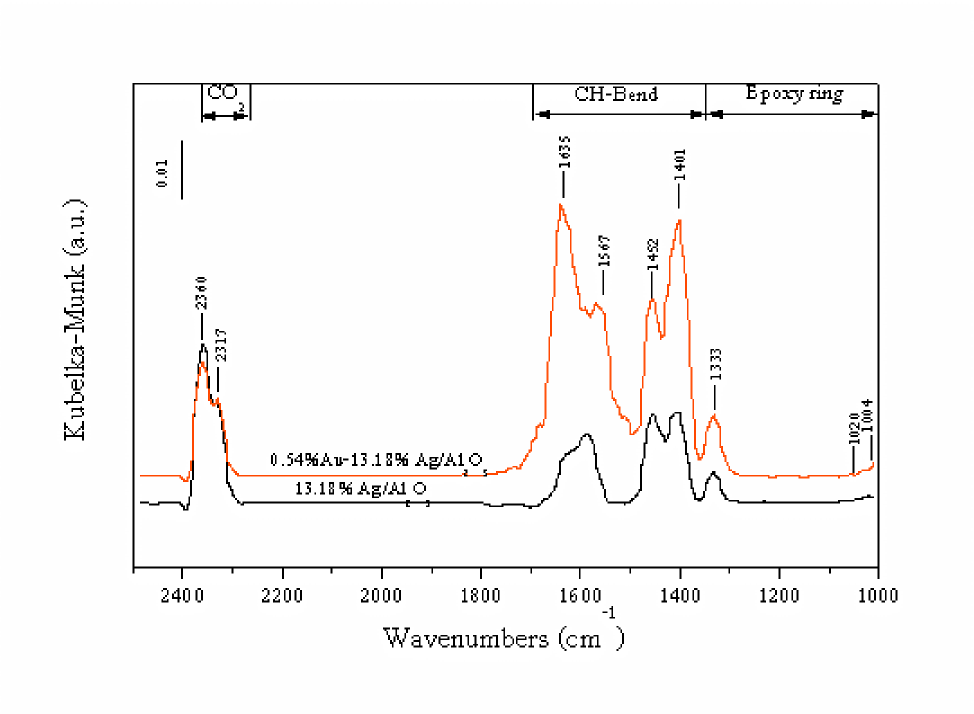

Figure 4.18 DRIFTS spectra of 0.54%Au-13.18% Ag/Al_2O_3 compare to13.18% Ag/Al_2O_3 samples recorded after 30 min exposure of gas mixture with concentration ratio of C_2H_4:O_2 = 2%:2%.

From the FT-IR results, it can be verified that ethylene oxide can be produced over these catalysts. Moreover, it was observed that bimetallic Au- Ag catalyst is more active than monometallic Ag catalyst as well as the activity study results. By the way, it is noteworthy that adding a small amount of Au to Ag support on amorphous Al_2O_3 improves the ethylene oxide selectivity and yield.

4.2.3 Conclusions

Based on the STEM-EDS results, it can be concluded that the gold-silver catalysts contain an inhomogeneous distribution of gold. Some particles are metallic silver and silver oxide, while some other particles contain both silver and gold. No evidence was found for separate gold particles. The mean particle size of the bimetallic silver-gold catalysts was around 180-186 Å compared with 180-190 Å for the monometallic Ag catalyst. Impregnation of the silver catalyst with gold did not appear to change the particle size. The TPD of oxygen showed a slight shift towards lower temperature with increasing gold loading. This indicates that there must be an interaction between Ag and Au causing a weakening of the adsorption bond strength between silver and oxygen. Within the range of gold loadings investigated, the catalyst containing 0.54 %wt Au on 13.18 %wt Ag/Al_2O_3 gave the highest activity and yield of ethylene oxide. In agreement with previous suggestions in the literature, the effect of gold is attributed to a geometric effect where the silver surface is diluted, creating single silver sites that favor molecular oxygen adsorption, which react with ethylene to produce ethylene oxide.

4.3 Ethylene epoxidation on TiO_2 supported Au catalysts

The study of well-known strong metal-support interaction (SMSIs) when the support is a reducible oxide has deserved an extensive attention. The migration of oxygen from reduced support particles onto metallic particles can induce formation of a suboxide of the support, the reduction being induced by the metallic particles (Holgado *et al.*, 1998). That group VIII noble metals supported on TiO_2 exhibits a strong metal-support interaction effect is well known. Schwank *et al.* (Shastri *et al.*, 1984) compared the behavior of gold supported on TiO_2 with other typical catalyst support materials. TiO_2 could stabilize as well as provide high dispersion of Au up to 700°C. It was suggested that this phenomenon did not appear to be due to the SMSI effect. Though a temperature of 700°C was sufficient to accomplish complete phase transformation of anatase to rutile in blank TiO_2, but no transformation occurred under identical conditions when TiO_2 impregnated was with Au. Au/TiO_2 is well known that it is good for low temperature, water-gas shift and propylene epoxidation; therefore, it should also be applicable for ethylene epoxidation.

4.3.1 Characterization results

TPD of oxygen experiments of Au/TiO_2 catalysts prepared by different methods were carried out with and without cooling step as described in previous results studying the effect of gold presence (chapter 4.2). As be seen from Figures 4.19-4.20, the desorption temperatures of oxygen with and without cooling step have the similar trend, Interestingly for three prepared catalysts and blank TiO_2, large desorption peaks were observed at around 400°C (with cooling step) and 460°C (without cooling step). These broad desorption peaks are assigned to desorbing of oxygen from TiO_2 support due to the removal of lattice oxygen from subsurface regions causing the creation of oxygen vacancies (Walton *et al.,* 1997). Typically, molecular oxygen desorbs from oxide surfaces between 27 to 127°C (Bielanski and Haber, 1991). As expected, 0.96% Au/TiO_2 sol gel gave the largest amount of desorption peak. The reason is that Au particle size of this catalyst is the smallest and better distribution on the support as compared to those with the other two preparation methods according to the TEM results. Therefore, there are more active sites that O_2 can be absorbed and the interaction between Au and O_2 is weak and oxygen can easily be desorbed (Hayashi *et al.,* 1998). In addition, it is noticeable that an addition of gold on TiO_2 support affected to shift oxygen desorption peaks to lower temperature for all preparation methods as compared to blank TiO_2. It can explain in term of electronic effect that there are electrons transfer between gold atom and TiO_2 support while adsorbed oxygen also requires transfer of electrons between TiO_2 support and oxygen. Therefore, it is expected that the electron deficiency due to the neighbor interaction between gold atom result in weakening of Ti-O bond.

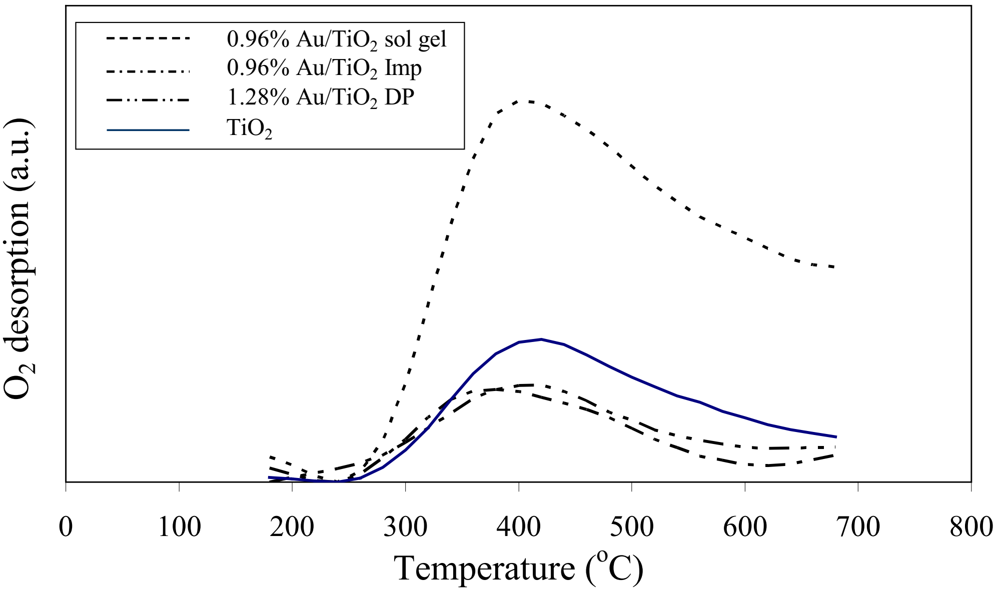

Figure 4.19 TPD profiles of O_2 with cooling step on Au/TiO_2 sample.

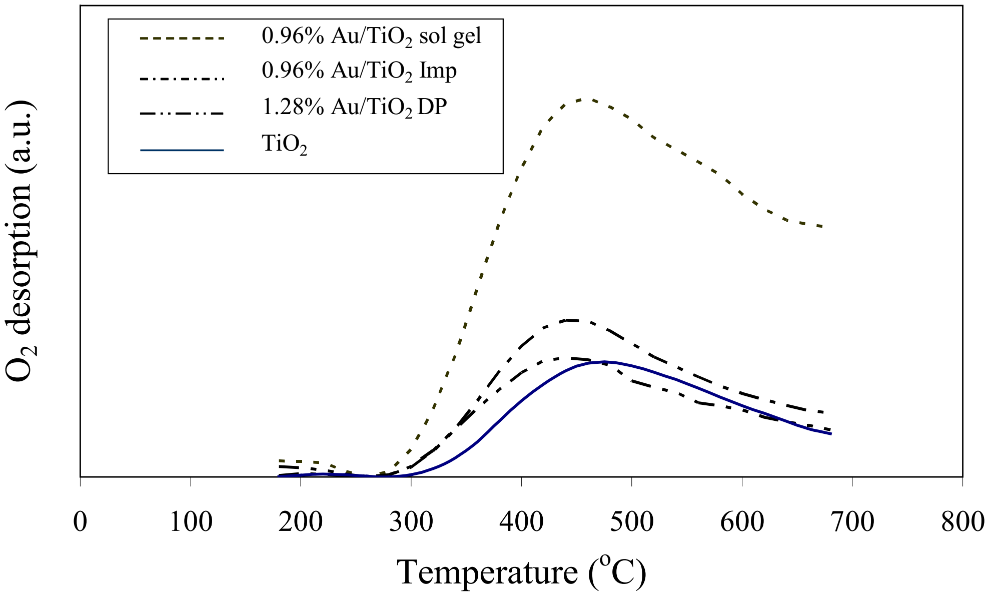

Figure 4.20 TPD profiles of O_2 without cooling step on Au/TiO_2 sample.

Figure 4.21 shows the oxygen desorption with and without cooling step of different Au/TiO_2 catalysts. It has been known that the oxygen desorption in the range 227-527°C may be ascribed to one or combination of the following effects; spill over oxygen (Bielanski and Haber, 1991), surface and sub-surface lattice oxygen (Komuro, 1975) and oxygen from Au sites (Walton *et al.*, 1998a). As can be seen from Figure 4.21, there is some oxygen desorption below 200°C due to the molecular oxygen on Au active site (Schwank, 1983). The highest desorption peaks at around 300-400°C are assigned to oxygen that adsorbs on the surface or subsurface on TiO_2. Furthermore, the oxygen desorption from the TiO_2 support is confirmed by using He as a exposure gas instead of O_2 as shown in Figure 4.22. The result insists that the oxygen desorbs out from the TiO_2 support at higher temperature range of 300-400°C. It is observed from the TPD results that oxygen desorption peak with He exposure gives higher amount of desorbed oxygen than that with O_2 exposure. It can be explained that TiO_2 is a nonstoichiometric material. There are two main defects for titania known as oxygen vacancies and interstitial Ti^{3+} ions. When the catalyst is exposed with O_2, it will anneal oxygen vacancies with oxygen absorption into the surface and sub-surface region of the lattice (Komuro, 1975 and

Walton *et al.*, 1998b). This results in higher stability of the lattice causing desorption of O_2 at higher temperature than exposure with He. When the catalyst is exposed to He at higher temperatures, it will produce the defect of lattice causing the unstable support. Therefore, the oxygen on the surface or sub-surface desorbs out more easily.

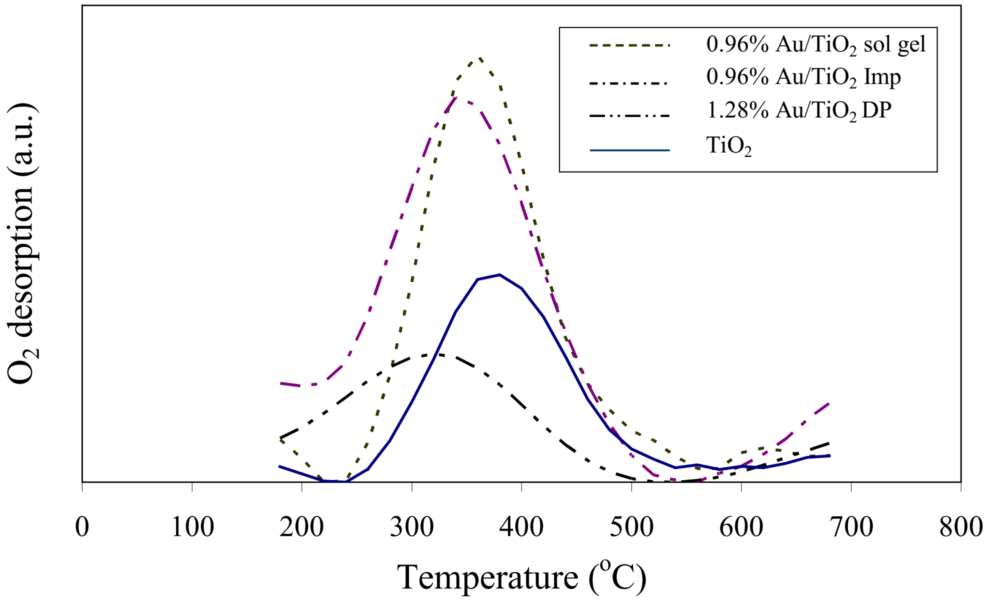

Figure 4.21 O_2 desorption difference between TPD runs with and without cooling step.

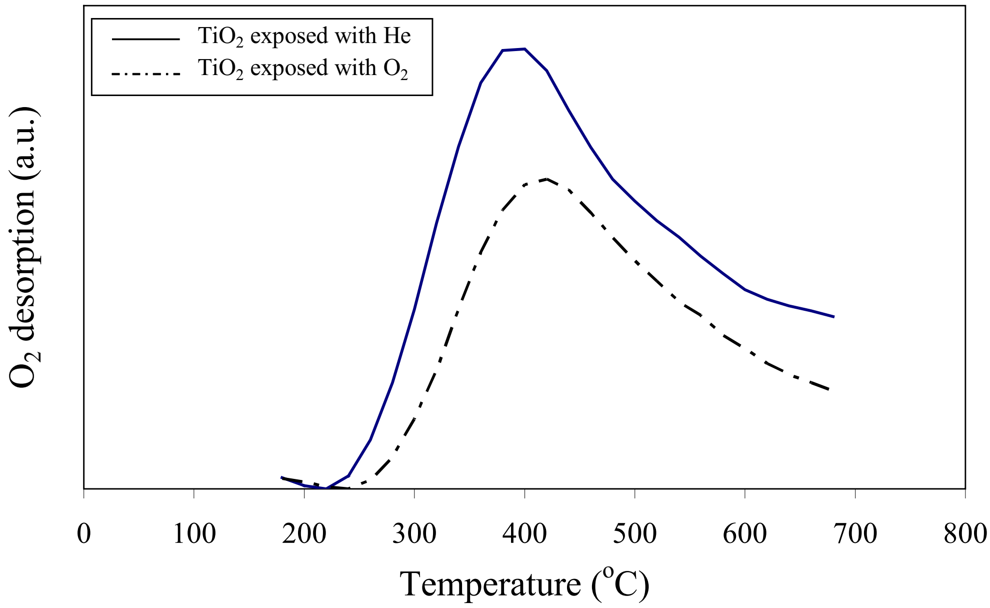

Figure 4.22 Comparison between TiO_2 (P25) exposed to He and O_2.

The XRD results of Au on TiO_2 catalyst prepared with different techniques are compared with pure TiO_2 and shown in Figure 4.23. The results show that 0.96% Au/TiO_2 with impregnation (Imp) and 1.28% Au/TiO_2 deposition-precipitation (DP), prepared by TiO_2 P25 from Degussa, are composed of both anatase (A) and rutile (R) phase but 0.96% Au/TiO_2 (sol gel) shows only anatase phase. All three catalysts have similar BET surface areas around 60 m^2/g.

As expected, the gold peaks are not clearly discernible from these XRD patterns, however very small peaks at 38.27°, 44.65° and 77.58° could be seen. The gold catalysts prepared have nanosize gold particles which are undetectable by XRD equipment. However, the average crystallite sizes of Au/TiO_2 catalyst prepared by impregnation, deposition-precipitation and sol gel were 23, 19 and 37 nm, respectively , calculated using the Scherer equation.

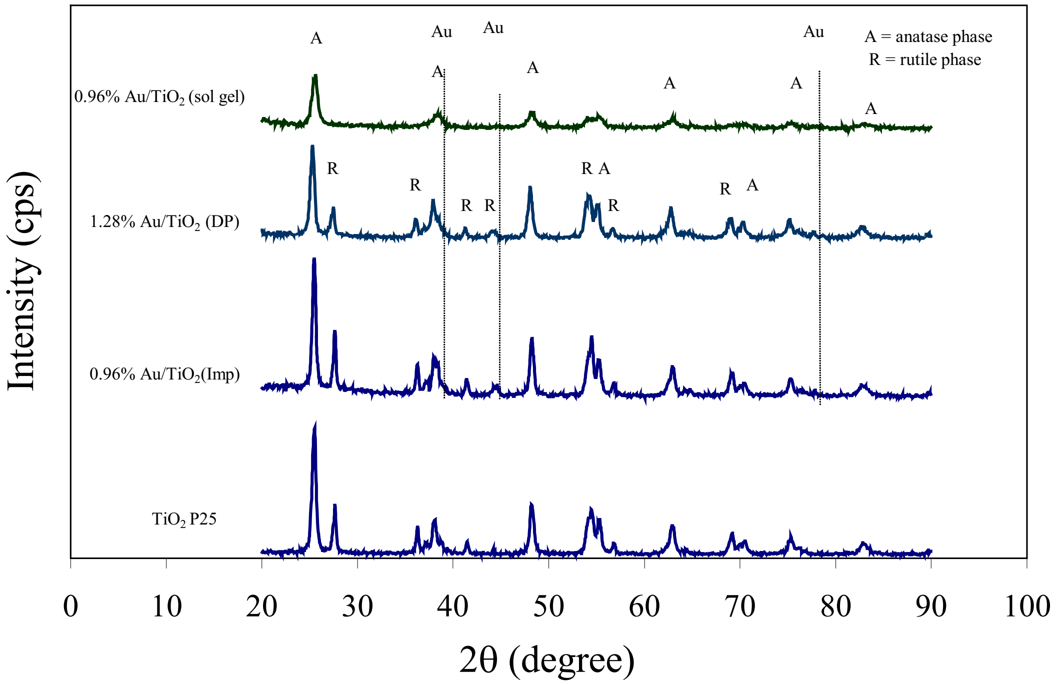

Figure 4.23 XRD patterns of Au/TiO_2 catalysts prepared with three different methods compared to XRD patterns for commercial TiO_2.

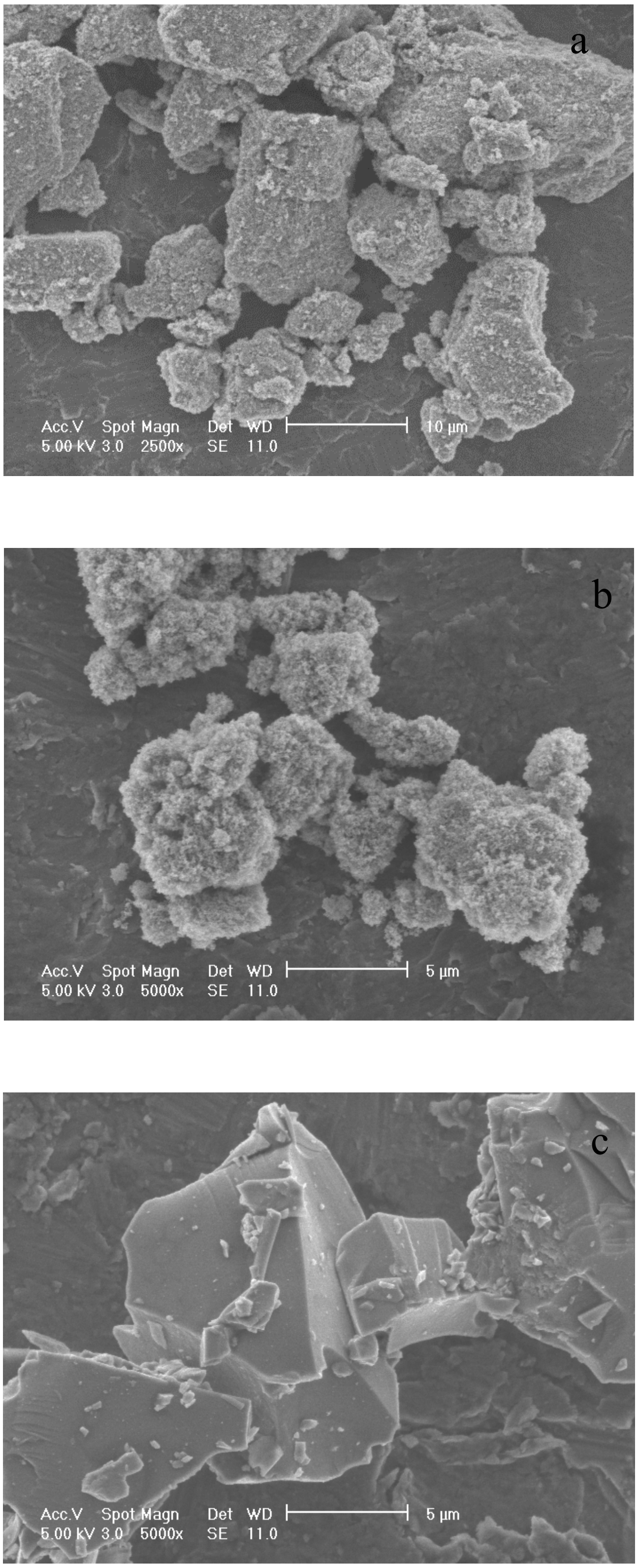

Figure 4.24 SEM surface morphology of gold catalysts prepared by different methods: (a) impregnation; (b) deposition-precipitation; (c) sol gel.

The SEM morphology of 0.96% Au/TiO_2 (Imp)(Figure 4.24 (a)) and 1.28% Au/TiO_2 (DP) (Figure 4.24 (b)) are found the deposition of gold atoms on the the surface supports, where as, 0.96% Au/TiO_2 (sol gel) has smooth clusters (Figure 4.24 (c)) because Au and Ti are formed into network structure.

The TEM micrographs shown in Figures 4.25-4.27 reveal the presence of the gold particles as dark spots in the catalyst clusters. The existence of gold particles on TiO_2 support was verified by using EDS focusing on the regions containing highly contrasting spots using transmission electron microscope. For 0.96% Au/TiO_2 (Imp), the gold particles are seen as highly contrasting spots with an average particle size of 3.2 ± 0.7 nm (Figure 4.25). Interestingly, the 1.28% Au/ TiO_2 (DP) catalyst apparently had a smaller Au particle size of 2.5 ± 0.6 nm (Figure 4.26). Figure 4.27 is a TEM micrograph of 0.96% Au/TiO_2 (sol gel) which reveal a better distribution of Au compare with those of the other two methods and the Au particle size is much smaller, 1.2 ± 0.3 nm. Therefore, Au deposited on TiO2 by the three preparative methods have nanoparticle sizes in the order sol gel <deposition-precipitation< impregnation.

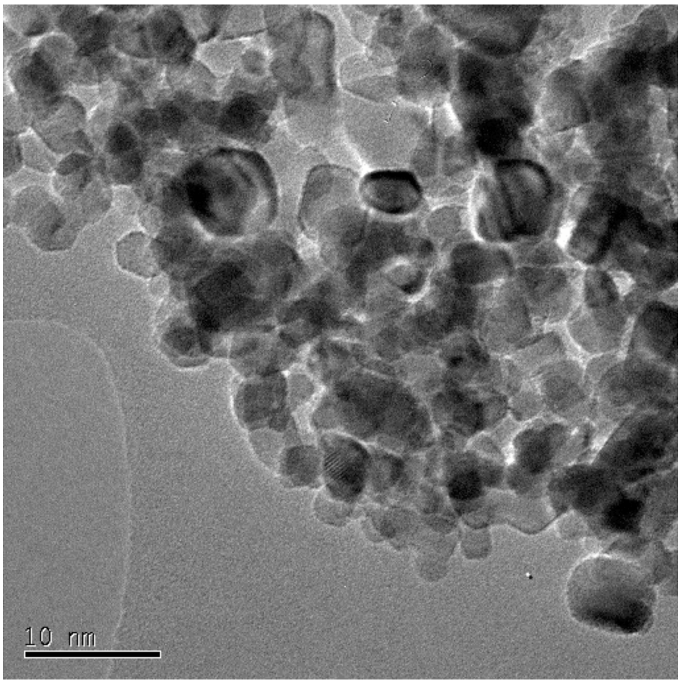

Figure 4.25 Gold particles (dark spots) on the TiO_2 surface for 0.96% Au/TiO_2 catalyst prepared by impregnation method.

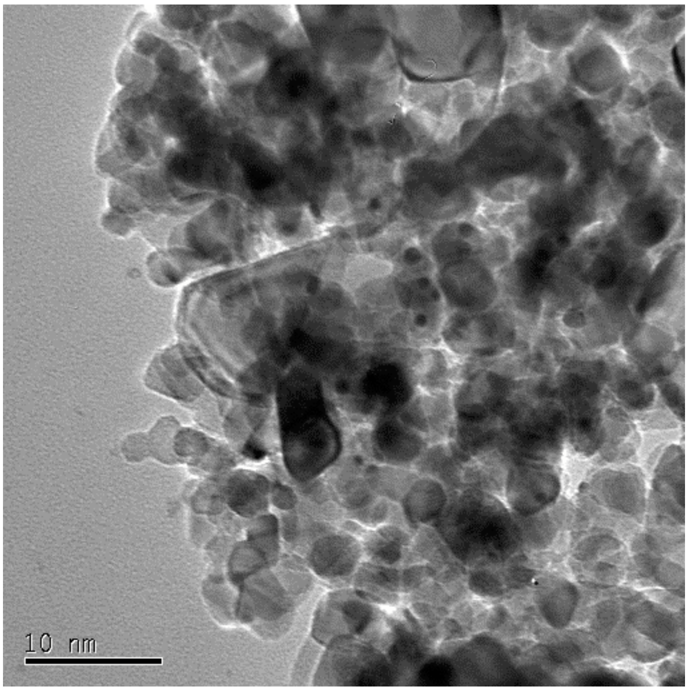

Figure 4.26 Gold particles (dark spots) on the TiO_2 surface for 1.28% Au/TiO_2 catalyst prepared by deposition-precipitate.

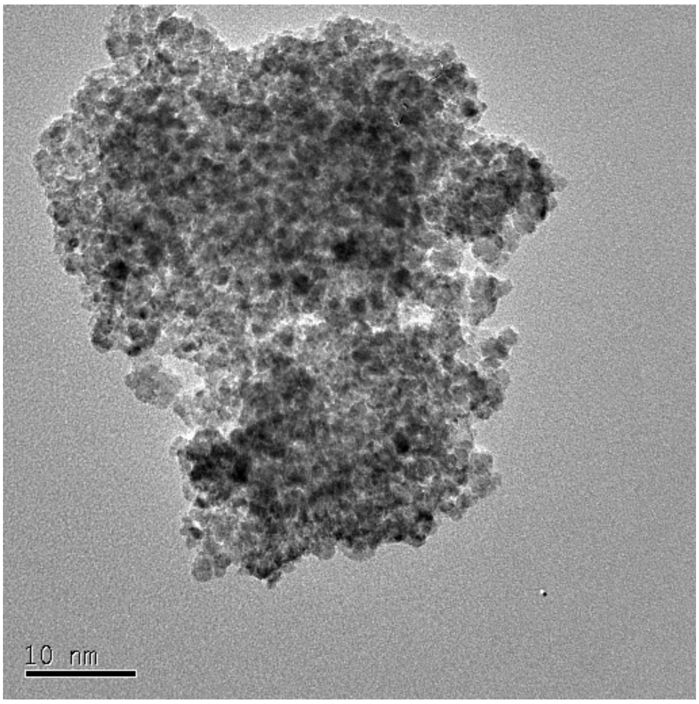

Figure 4.27 Gold particles (dark spots) on the TiO_2 surface for 0.96% Au/TiO_2 catalyst prepared by sol gel.

4.3.2 Catalyst activity of ethylene epoxidation

Figure 4.28 and 4.29 illustrates the effect of temperature on the ethylene epoxidation activity of Au/TiO_2 catalysts prepared by three different methods. For all studied catalysts, the ethylene conversion increased with increasing the reaction temperature, while the selectivity of ethylene oxide decreased with increasing reaction temperature, as a result of the two competitive reactions, partial oxidation and deep oxidation. For the deep oxidation reaction, both ethylene and ethylene oxide react with oxygen from the support to produce carbon dioxide and water. As is well known, a higher temperature leads to a higher rate of deep oxidation reaction resulting in lower ethylene oxide selectivity. Furthermore, 0.96% Au on TiO_2 prepared by impregnation gives a highest ethylene oxide selectivity and yield than the other two preparation methods of deposition-precipitation and sol gel (Figures 4.28-4.30). From the results of the present study, it is clearly seen that there is a good correlation between the particle size of gold and the ethylene epoxidation reaction. It has been reported that oxygen species are formed at the perimeter interface between the gold particles and the TiO_2 support when the particle size is greater than 2 nm (Hayashi *et al.,* 1998) . These oxygen species located at the perimeter interface are mostly molecular oxygen (Schwank, 1983 and Haruta and Date, 2001) which may react directly with ethylene in gas phase to produce the ethylene oxide. The results shows that the maximum yield is at 255°C somewhere in the region of 1% for 0.96% Au/TiO_2 with impregnation and around 0.8% for 1.28% Au/TiO_2 deposition-precipitation. On the other hand, 0.96% Au/ TiO_2 sol gel gives the maximum 0.6% ethylene oxide yield at 240°C. Moreover, the TPD results confirm that the interaction between oxygen molecule and Au are weak leading to the promotion on ethylene oxide. Regarding to the gold particle size, the impregnation method gives the largest gold particle size (~ 3 nm) compare to the other methods; therefore, ethylene oxide selectivity depended on the particle size of gold and the interaction between gold and support.

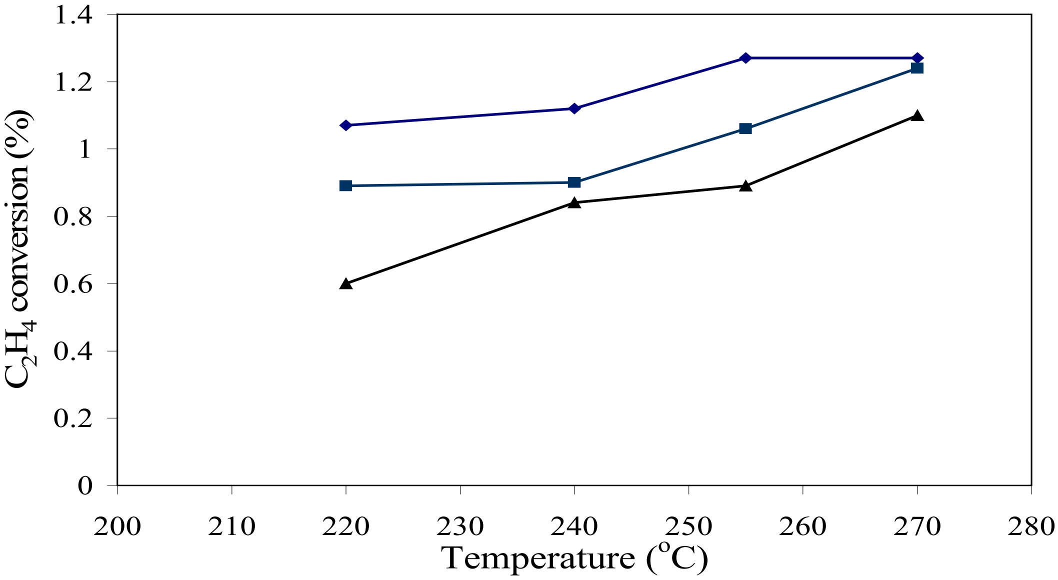

Figure 4.28 Ethylene conversion for different catalyst preparations at space velocity of 6,000 h^{-1}, P = 10 psig and 6% O_2 and 6% C_2H_4 balance with He: (◆) 0.96% Au/TiO_2 with impregnation; (■) 1.28% Au/TiO_2 deposition-precipitate; (▲) 0.96% Au/TiO_2 sol gel.

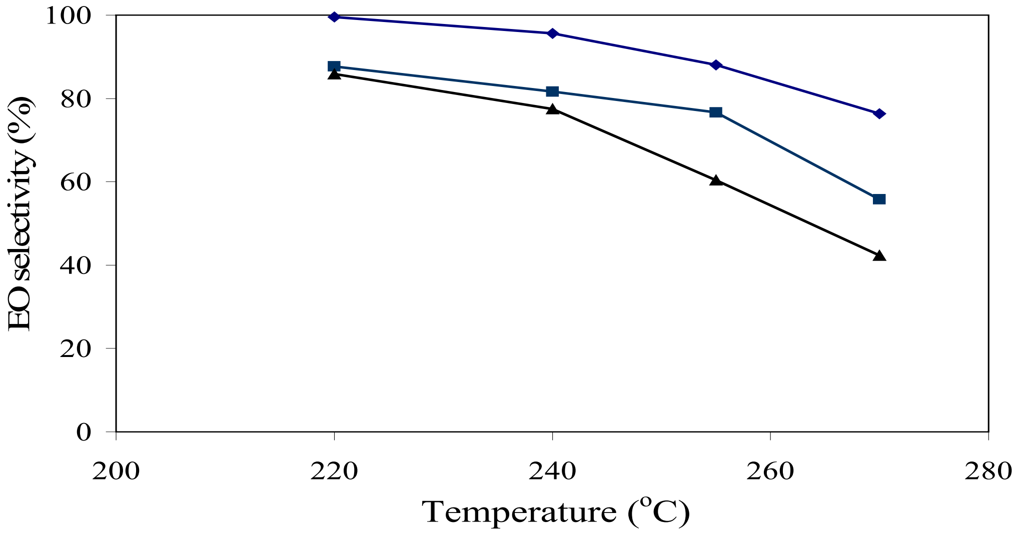

Figure 4.29 Ethylene oxide selectivity for different catalyst preparations at space velocity of 6,000 h^{-1}, P = 10 psig and 6% O_2 and 6% C_2H_4 balance with He: (◆) 0.96% Au/TiO_2 with impregnation; (■) 1.28%

Au/TiO$_2$ deposition-precipitate; (▲) 0.96% Au/TiO$_2$ sol gel.

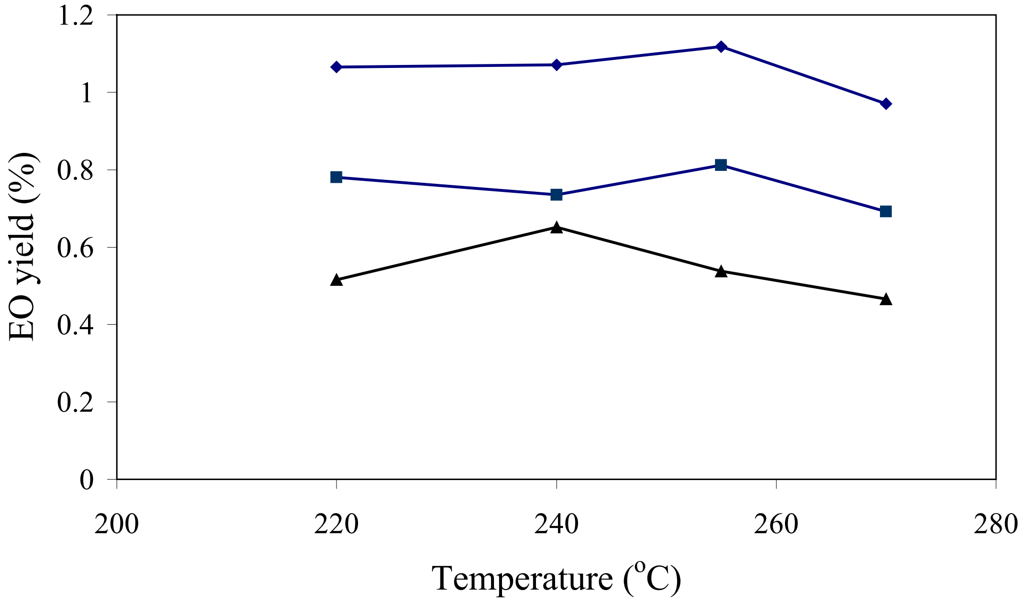

Figure 4.30 Ethylene oxide yield for different catalyst preparations at space velocity Of 6,000 h^{-1}, P = 10 psig and 6% O$_2$ and 6% C$_2$H$_4$ balance with He: (◆) 0.96% Au/TiO$_2$ with impregnation; (■) 1.28% Au/TiO$_2$ deposition-precipitate; (▲) 0.96% Au/TiO$_2$ sol gel.

The FT-IR results of the catalytic oxidation of ethylene are shown in the Figures 4.31-4.33, recorded at increasing exposure times at a reaction temperature of 220°C. The reaction was carried out at 220°C in the gas phase and the FT-IR spectra collected after 1, 5, 10, 15, 20, 25 and 30 min reaction times. These bands are compared with spectra containing CH-bending (1300-1700 cm^{-1}), epoxy functional groups (800-1300 cm^{-1}) and CO$_2$ functional groups (2300-2400 cm^{-1}). For 0.96% Au/TiO$_2$ (Imp), The dominant spectra of 1065, 1330, 1445 and 1717 cm^{-1} increase with increasing exposure time (Figure 4.31, curves b-g) compared with the curve of ethylene exposed for 30 min at 220°C (Figure 4.31, curve a). Figure 4.32 shows that for 1.28% Au/TiO$_2$ (DP) the intensity of bands (1015, 1347, 1445 and 1534 cm^{-1}) increases progressively with time. Similarly, the same behavior occurs for 0.96% Au/TiO$_2$ (sol gel) at spectra 1067, 1342, 1447 and 1530 cm^{-1} as shown in Figure 4.33, curves a-f. For the spectra of each catalyst the epoxy ring and CH-bending modes can be assigned (Skoog *et al.*, 1998). Thus, it was concluded that the reaction over each catalyst in DRIFTS was ethylene epoxidation. Moreover, a comparison of Figures 4.31-4.33 for FT-IR spectra of ethylene epoxidation over each catalyst shows that 1.23% Au/TiO_2 (DP) is the most activity than others. Incidentally, spectra bands for CO_2 at 2330 and 2360 cm^{-1} were observed for each catalyst (not shown on the figures). From the results, it can be stated that there is a good relation between the particle size of gold deposited and activity of ethylene epoxidation reaction. It has been reported that oxygen species are formed at the perimeter interface between the gold particles and the TiO_2 support when the particle size of gold is greater than 2 nm (Hayashi *et al.*, 1998). These oxygen species are mostly molecular oxygen (Schwank, 1983 and Haruta and Date, 2001) which is believed to be responsible for reacting directly with ethylene in the gas phase to produce ethylene oxide.

4.3.3 Conclusions

Au/TiO_2 is used as a catalyst not only for CO oxidation, but also for epoxidation as well. This gold on TiO_2 was previously used for propylene epoxidation and found that the particle size had a significant effect on the epoxidation activity. Based on results of present studies, it is suggested that the reaction of ethylene epoxidation depends on the size of gold which is governed by a catalyst preparation method. The optimum size of gold particles was approximately 3 nm for the epoxidation reaction of ethylene. If the particle size was less than 2 nm, the reaction was difficult to occur that why the ethylene oxide yield of Au/TiO_2 (sol gel) was found to be low (0.6%). Moreover, support also has effect on the reaction because oxygen on support directly promotes complete combustion noticeably from TPD. Nevertheless, these gold catalysts still give the lower activity comparing to Au-Ag/Al_2O_3 catalysts of the previous study(Roatluechai *et al.*, 2002).

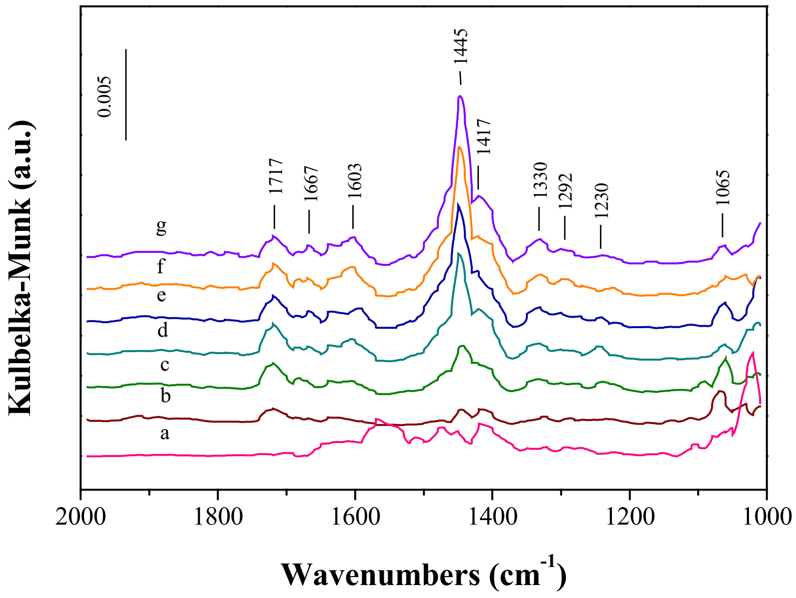

Figure 4.31 FT-IR spectra over Au/TiO$_2$ (Imp) of (a) ethylene and ethylene oxidation recorded after (b) 1 min; (c) 5 min; (d) 15 min; (e) 20 min; (f) 25 min; (g) 30 min.

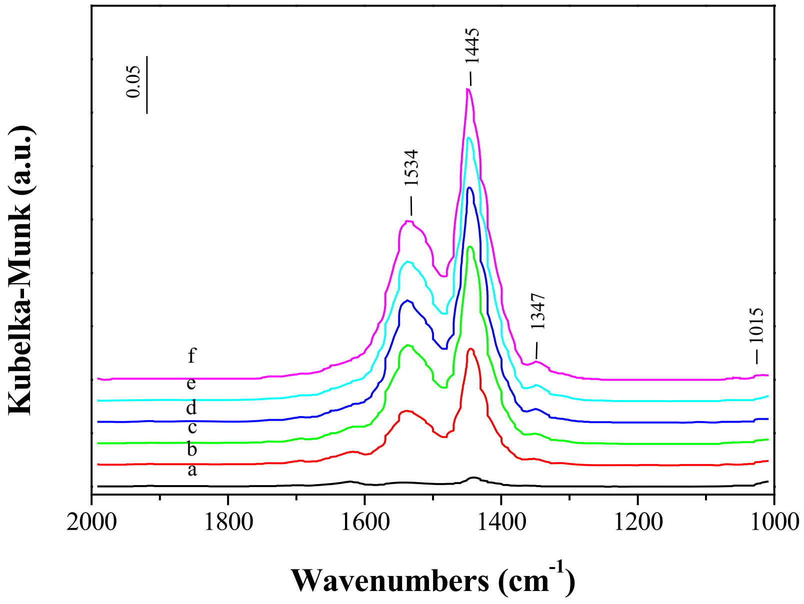

Figure 4.32 FT-IR spectra of ethylene oxidation over Au/TiO$_2$ (DP) recorded after (a) 1 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) 25 min; (f) 30 min.

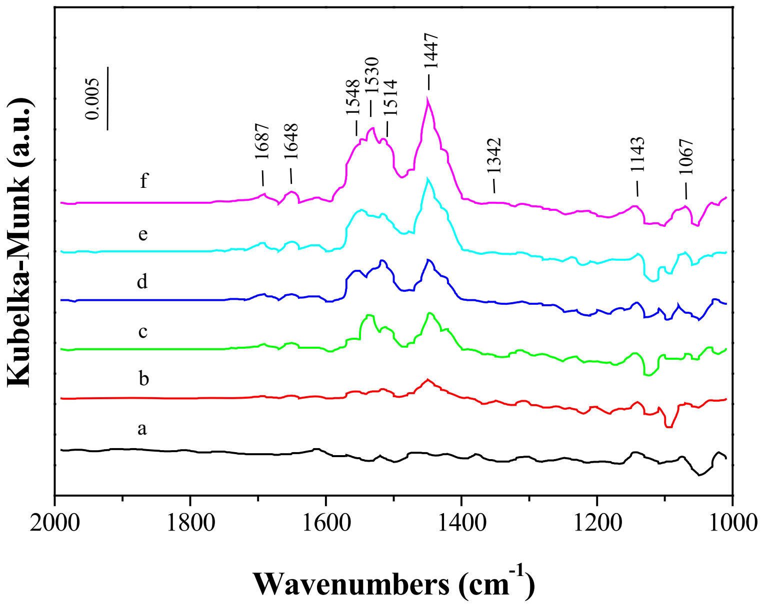

Figure 4.33 FT-IR spectra of ethylene oxidation over Au/TiO$_2$ (sol gel) recorded after (a) 1 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) 25 min; (f) 30 min.

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CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

Many researchers have claimed that only low surface area Al_2O_3 can enhance the ethylene epoxidation reaction. Several attempts were made unsuccessfully to use high surface area Al_2O_3 as support for Ag to produce ethylene oxide. In this research work, high surface area fumed Degussa C alumina support was investigated because of its non porous property that was believed to give large Ag particles and a good distribution of Ag particle sizes. It was found that this non porous support material could give large Ag particles, around 21 nm for metallic Ag, and 30 nm for silver oxide and could enhance the ethylene epoxidation reaction confirmed by DRIFTS experiment. Therefore, it can be stated that Ag on high surface area alumina can promote ethylene epoxidation provided that the Ag particle size is large. Moreover, high oxygen coverage on silver catalyst increases ethylene oxide activity.

Addition of gold as promoter enhanced the ethylene oxide selectivity. It is believed that gold can create single silver sites that favor molecular oxygen adsorption. In other words, gold can reduce the dissociation of molecular oxygen on Ag sites, lowering the concentration of atomic oxygen. In addition, the interaction between Ag and Au causes a weakening of the adsorption bond strength between silver and oxygen. In this work, 0.54% Au on 13.18% Ag/Al_2O_3 gave the highest ethylene epoxidation activity.

It has been known that gold catalyst is good for low temperature CO oxidation, propylene epoxidation and photocatalytic reaction. Thus, Au/TiO_2 with different methods of preparation were studied. From the results, the gold particle size of Au/TiO_2 influenced the ethylene epoxidation and the suitable gold particle was found to be around 4 nm. It is known that oxygen species located at the perimeter interface are mostly molecular oxygen which favors to ethylene epoxidation. If the particle size of Au was less than 2 nm, the epoxidation reaction would not occur. The different methods of catalyst preparation gave different gold particle sizes. Au/TiO_2 with impregnation gave the highest activity due to its optimum particle size.

The mechanism of adsorbed oxygen should be studied by using isotope O^{18} and O^{16}. Thus, the evidence of atomic and/or molecular oxygen adsorbed on this high surface area supports such as Al_2O_3 and TiO_2 can be verified. Moreover, the reaction mechanism of ethylene with the adsorbed oxygen species can be clarified.

Both Ag and Au particle sizes influence significantly on ethylene epoxidation. Therefore, catalysts with a wide range of particle sizes should be prepared by varying the calcination temperature. As is known, a high temperature can induce the agglomeration of the metal particle to form a bigger size.

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