

**CHAPTER IV**  
**RESULTS AND DISCUSSION**

**4.1 Catalysts Characterization**

This section shows the catalysts characterization results of only uncalcined support types which the catalysts were calcined at 473 K, 573 K and 773 K. The results were obtained from variety characterization techniques, including AAS, BET, XRD, TEM, TPD and TPR. The synthesized titania nanotubes were characterized and discussed in this section. Additionally, the characteristic of the catalysts in this part will be used to explain the catalytic activity of all catalysts in ethylene oxidation.

**4.1.1 Actual Gold Loading of Prepared Catalysts**

The actual amounts of Au loading in all prepared catalysts were determined by Atomic Absorption Spectroscopy as described earlier in Chapter III. Table 4.1 shows the comparison between the prepared values and the actual values of Au contents in all catalysts with two different supports prepared by impregnation method.

**Table 4.1** The actual amount of gold loading in all prepared catalysts

Support	Calcination temperature (K)	Wt% of gold content		
		Prepared Value	Actual value	Average actual value
TiO <sub>2</sub> P25	473	1	0.90	0.86
	573	1	0.81	
	773	1	0.87	
TiO <sub>2</sub> Nanotubes	473	1	0.84	0.90
	573	1	0.97	
	773	1	0.90	

In this study, the actual values of Au loading were approximately the same at 1%. It was found that the actual values of Au contents in all studied catalysts were a little lower than the prepared values because of the hygroscopic property of hydrogen tetrachloroaurate trihydrate, the Au precursor. It was due to during the weighing step, the Au precursor adsorbed water molecules rapidly from the atmosphere so the original values from weighing were higher than the actual values.

#### 4.1.2 The BET Surface Area of Prepared Catalysts

The BET surface area, pore volume, and pore diameter of the Au-doped oxide catalysts prepared at different calcination temperatures using impregnation method and two types of the titania support are shown in Table 4.2. The commercial TiO<sub>2</sub> P25 powder were known to be very fine with particles size of 25-30 nm and had the specific surface areas around 47 m<sup>2</sup>/g.

**Table 4.2** The BET surface areas of TiO<sub>2</sub> P25, 1 % Au/TiO<sub>2</sub> P25, titania nanotubes (TNT) and 1% Au/titania nanotubes (Au/TNT) catalysts prepared by impregnation method at different calcination temperatures

Sample	Calcination Temperature (K)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)	S <sub>BET</sub> (m <sup>2</sup> /g)
TiO <sub>2</sub> P25	dried	0.0595	6.60	47.00
Au/TiO <sub>2</sub>	473	0.1724	13.38	51.53
	573	0.1640	11.61	56.50
	773	0.1847	13.02	56.70
TNT	dried	0.9954	13.14	303.0
Au/TNT	473	0.7135	10.23	279.1
	573	0.6849	10.82	253.2
	773	0.7073	22.35	126.6

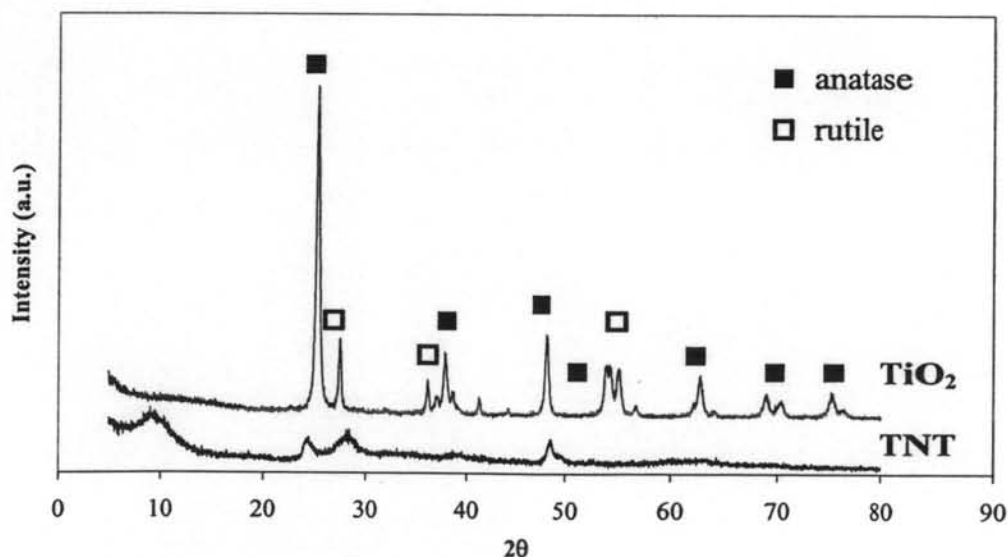
- dried at 383 K

After hydrothermal treatment at 423 K with 10 mol/L of NaOH aqueous solution, the surface area of the synthesized titania nanotubes from the commercial titania was greatly increased to  $303 \text{ m}^2/\text{g}$  as well as enhancing of pore volume and pore diameter.

As can be seen, there were no obviously different specific surface areas of different calcined Au/TiO<sub>2</sub> catalysts whereas, calcined Au/TNT catalysts at higher temperature decreased the specific surface area moderately. It caused from the agglomeration of titania nanotubes to irregular shape and the tubes broken to be shorter size which was confirmed in the TEM results. Therefore, the adsorption of nitrogen in BET surface area analysis was decreased and affected to the decreasing of specific surface area.

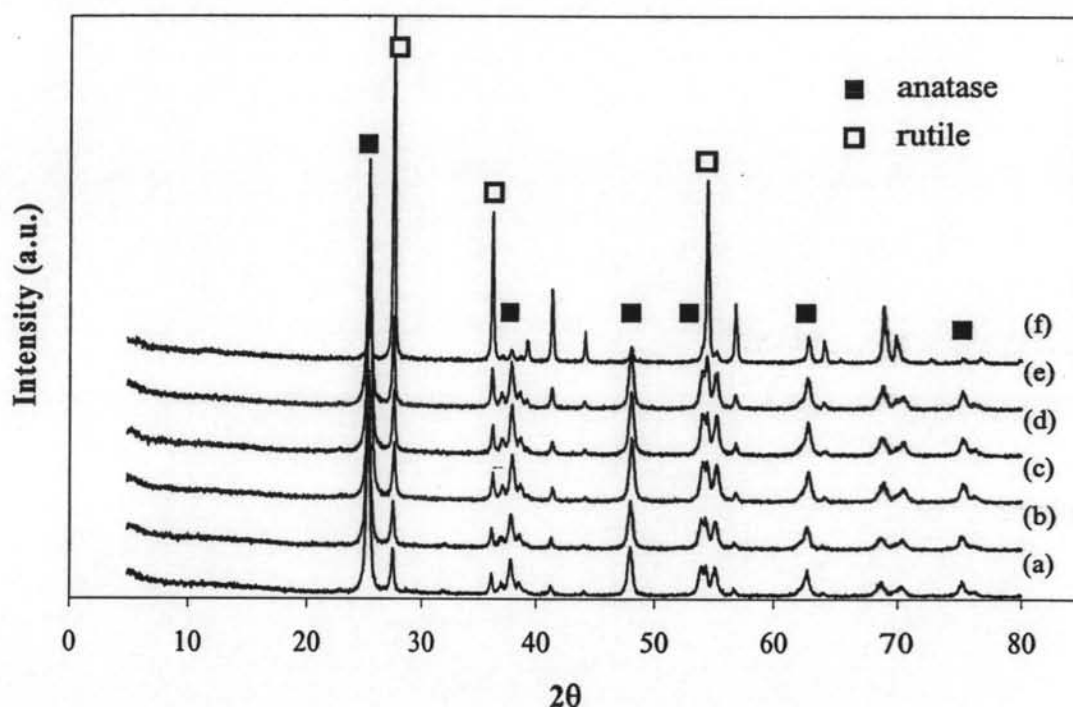
#### 4.1.3 X-ray Diffraction Patterns

X-ray diffraction analysis was carried out for all catalysts. The XRD patterns for the TiO<sub>2</sub> P25 used as the starting material and titania nanotubes (TNT) obtained from hydrothermal treatment in the temperature of 423 K are shown in Figure 4.1.



**Figure 4.1** XRD patterns of TiO<sub>2</sub> P25 and titania nanotubes (TNT) from hydrothermal treatment in the temperature of 423 K.

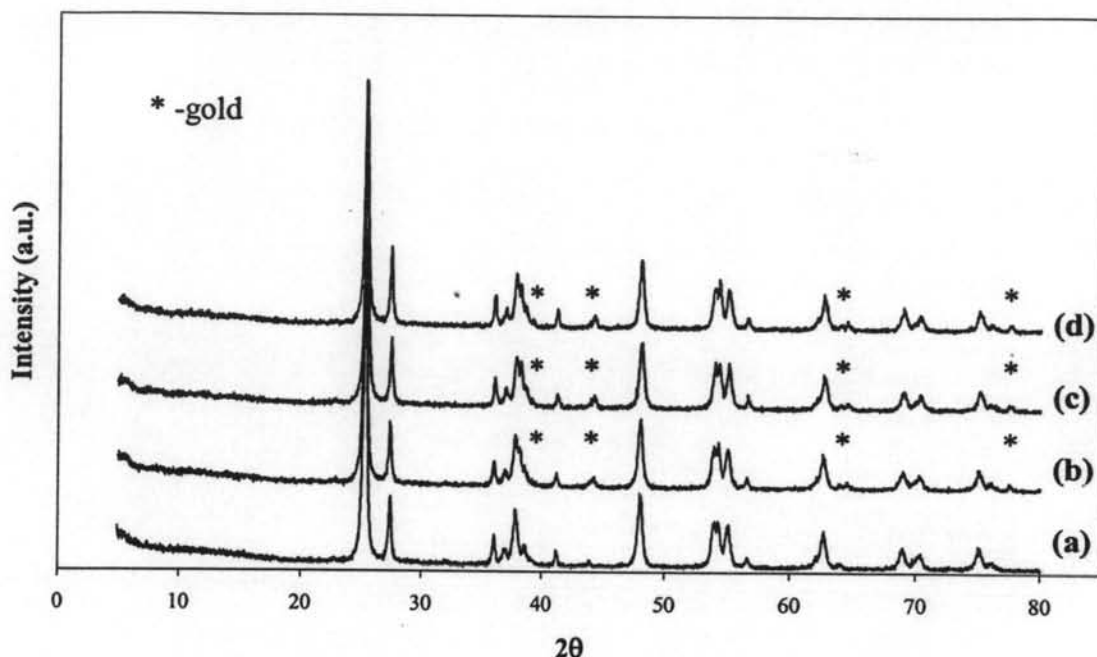
Figure 4.2 shows the XRD patterns of pure  $\text{TiO}_2$  at different calcination temperatures. It was been found that  $\text{TiO}_2$  transformed from anatase to rutile phase when increased the calcination temperature. In addition, it was reported that the rutile phase was an inactive form of  $\text{TiO}_2$  and had lower surface area than anatase phase. Therefore, the catalytic activity of calcined catalysts at higher temperature was decreased because the transformation to rutile phase.



**Figure 4.2** XRD pattern of  $\text{TiO}_2$  P25 at different calcination temperatures: (a) 473K, (b) 573 K, (c) 673 K, (d) 773 K, (e) 873 K, (f) 973 K.

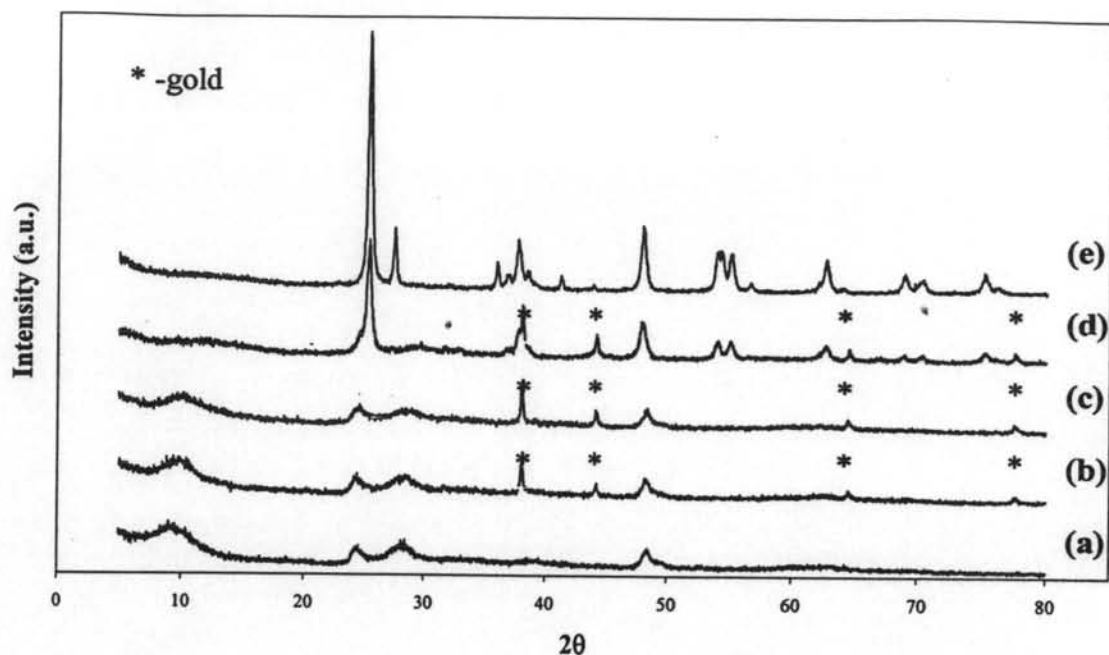
There were insignificant differences of the XRD patterns after doped Au on the samples by comparison with  $\text{TiO}_2$  as shown in the Figure 4.3. No serious changing for the Au-based catalysts calcined at different temperatures could also be noticed exception of increasing slightly of rutile phase. In contrast, the XRD patterns of titania nanotubes obtained from hydrothermal treatment at temperature 423 K after doped of Au followed by calcined at different temperatures showed a little different

pattern as illustrated in Figure 4.4. The crystallinity of the formed anatase phase increased as the calcination temperature increased.



**Figure 4.3** XRD patterns of the samples: (a)  $\text{TiO}_2$  P25 and 1%  $\text{Au/TiO}_2$  P25 calcined at different temperatures; (b) 473 K, (c) 573 K and (d) 773 K.

As expected, the gold peaks were not clearly discernible from these XRD patterns because the nanosize of gold particles on both titania supports were hardly to detect by XRD equipment, however very small peaks at  $38.2^\circ$ ,  $44.4^\circ$ ,  $64.6^\circ$  and  $77.58^\circ$  could be seen. Nevertheless, the typical lines of any Au signals in the gold containing for both supports, calcined at higher temperature were observed more clearly than in the samples at lower temperature. The average crystallite sizes of  $\text{Au/TiO}_2$  catalyst prepared by impregnation for commercial titania and synthesized titania nanotubes supports were 29 nm and 34 nm, respectively calculated using the Scherer equation.

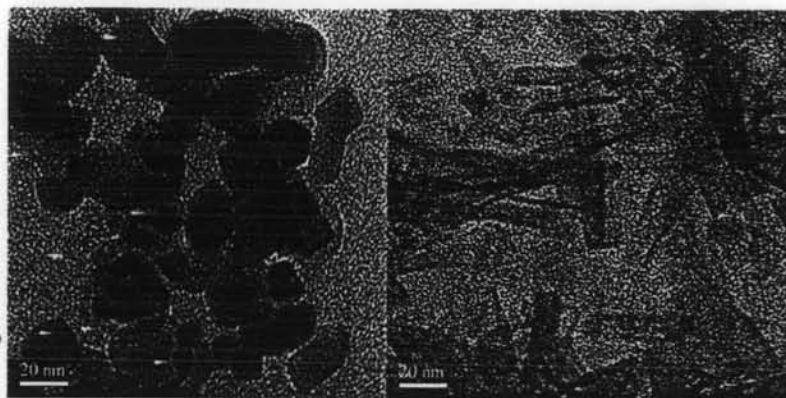


**Figure 4.4** XRD patterns of the samples: (a) dried titania nanotube (TNT), 1% Au/TNT calcined at different temperatures; (b) 473 K, (c) 573 K and (d) 773 K and (e) initial material (TiO<sub>2</sub> P25),

#### 4.1.4 Transmission Electron Microscope (TEM)

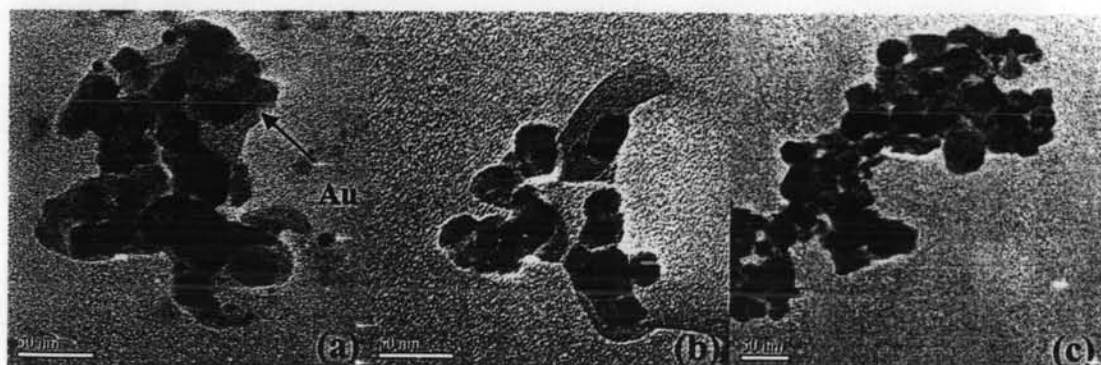
Figure 4.5 shows the TEM images of TiO<sub>2</sub> P25 nanoparticles and titania nanotubes (TNT) obtained from hydrothermal treatment at 423 K. The commercial TiO<sub>2</sub> P25 powder were known to be very fine with particles size of 25-30 nm. The synthesized TNT had an average diameter around 8 nm to 10 nm and several tens nanometer in length. These values were quite close to that observed by N<sub>2</sub> adsorption analysis.

Figure 4.6 shows TEM images of the three calcined Au/TiO<sub>2</sub> catalysts, (a) 473 K, (b) 573 K, and (c) 773 K. Gold particles were seen as dark contrasts on the surface of TiO<sub>2</sub> particles. It could be observed that the average diameters of the Au particles of calcined catalysts at 473 K, 573 K, and 773 K were 14 nm, 29 nm, 34 nm, respectively. In case of calcination 473 K, Au particles were well dispersed on TiO<sub>2</sub> keeping the size and the spherical shape of original colloidal particles. In addition, the Au particles were contacted on the TiO<sub>2</sub> surface.

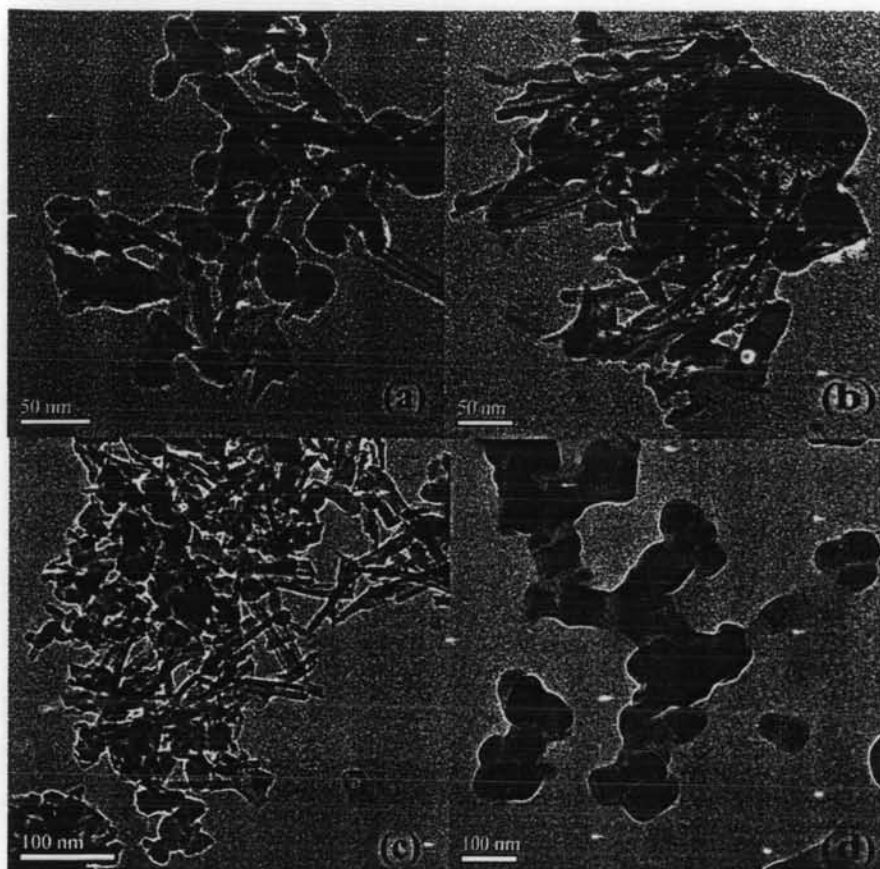


**Figure 4.5** TEM images; (a)  $\text{TiO}_2$  P25, (b) titania nanotubes (TNT) obtained from hydrothermal treatment at 423 K.

On the other hand, in the case of calcination at 773 K, Au particles became larger and were accompanied by changes in their shape from round to irregular facing. Moreover, the gold particles were encapsulated into the  $\text{TiO}_2$ . It caused the losing of parameter interface which acted as an active site. It could be imply that the large particles were formed after calcination at higher temperature by agglomeration of Au particles. In addition, the atomic structure of the Au- $\text{TiO}_2$  interface could not be observed, because Au particles were too big to clarify the interface structure with an atomic resolution.



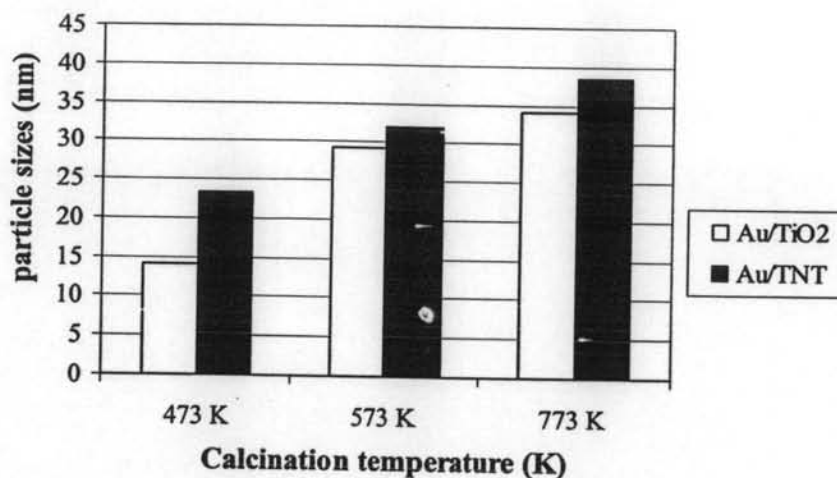
**Figure 4.6** TEM images of  $\text{Au/TiO}_2$  P25 catalysts calcined in air at different temperatures. Au loading is 1.0 wt%; (a) 473 K, (b) 573 K, (c) 773 K.



**Figure 4.7** TEM images of Au/TNT catalysts calcined in air at different temperatures. Au loading is 1.0 wt%; (a) 473 K, (b) 573 K, (c) and (d) 773 K.

Figure 4.7 shows the overall view of the three calcined Au/TNT catalysts, (a) 473 K, (b) 573 K, and (c),(d) 773 K. A dark contrasts which indicated the gold particles were larger than Au/TiO<sub>2</sub> as shown in the Figure 4.8 and seem to contact on the residue of TiO<sub>2</sub> P25 more than TNT. The average gold diameters were around 23 nm, 32 nm, 39 nm of calcined Au/TNT at 473 K, 573 K and 773 K, respectively. Moreover, when calcined at higher temperature the sample were slightly damaged to irregular shape having more defects and the gold particles were larger. In addition, calcined catalyts at 773 K, the gold particles were encapsulated with the support as shown in the Figure 4.6 (d).





**Figure 4.8** The comparison average diameter of gold particles at different calcination temperatures between Au/TiO<sub>2</sub> and Au/TNT.

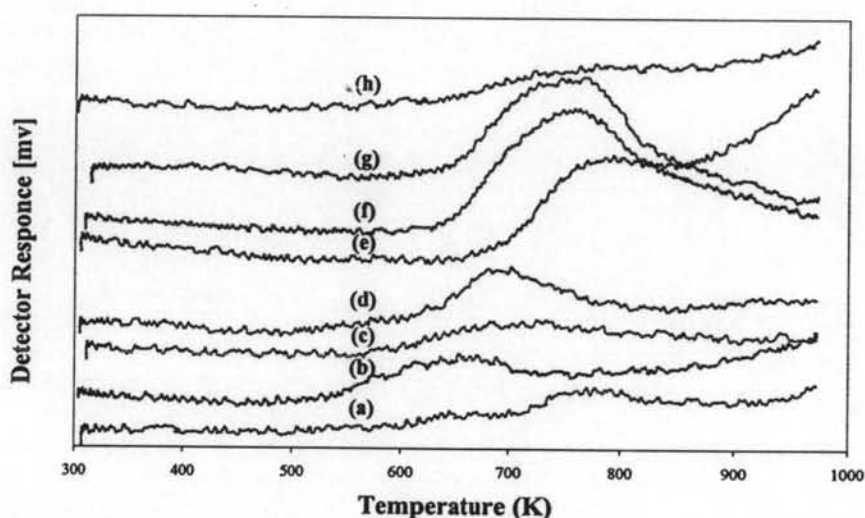
According to TEM, the decreasing catalytic activity at higher temperature of calcination which will be performed in the catalytic activity results can therefore be explained by an increasing size of the gold particles and encapsulated of gold particles by the support.

#### 4.1.5 Temperature Programmed Desorption (TPD)

Figure 4.9 shows the comparison of TPD profiles between TiO<sub>2</sub>, Au/TiO<sub>2</sub>, TNT and Au/TNT catalysts at different calcination temperatures. They demonstrated that the broad desorption peaks were proportional to the amount of desorbing oxygen from the catalysts surface. It was due to the removal of lattice oxygen from subsurface regions causing the creation of oxygen vacancies (Walton *et al.*, 1997).

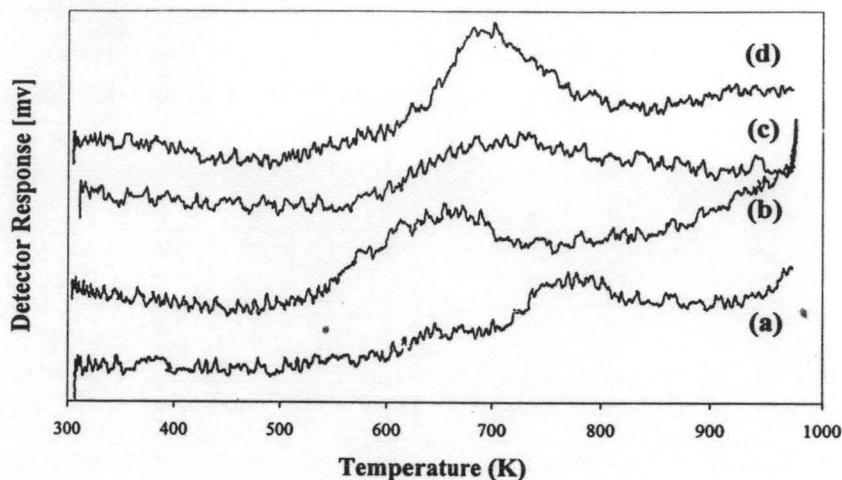
In case of TiO<sub>2</sub> support, it was noticeable that an addition of gold affected to shift oxygen desorption peaks to lower temperature (around 750 K) when compared with the blank TiO<sub>2</sub> (around 800 K). It could be explained in term of electronic effect that there were electrons transfer between gold atom and TiO<sub>2</sub> support while adsorbed oxygen also required transfer of electrons between TiO<sub>2</sub> support and oxygen. Therefore, it was expected that the electron deficiency due to

the neighbor interaction between gold atom resulted in weakening of Ti-O bond thus increasing the mobility of the lattice oxygen. In addition, when compared the TPD signals of different calcined catalysts, they showed that the TPD signals of Au/TiO<sub>2</sub> calcined at 473 K and 573 K were similarly while 773 K the desorption peak was very broad and low intensity. It can be implied that calcined catalysts at 473 K and 573 K had more interaction between gold and TiO<sub>2</sub> support than 773 K.



**Figure 4.9** TPD profiles of O<sub>2</sub> desorption on prepared Au/TiO<sub>2</sub> and Au/TNT catalysts at different calcination temperatures; (a) TNT; Au/TNT: (b) 473 K, (c) 573 K, (d) 773 K; (e) TiO<sub>2</sub>; (f) 473 K, (g) 573 K, (h) 773 K.

Figure 4.10 shows the magnification of TPD profiles of TNT and Au/TNT catalysts at different calcination temperatures. In case of TNT support, they gave the similarly results with TiO<sub>2</sub> support but the intensity of signals was lower and broader than TiO<sub>2</sub>. In addition, calcined Au/TNT catalysts at different temperatures did not improve the oxygen desorption which can be implied that there were very low interaction between gold atom and TNT support.



**Figure 4.10** The magnification of TPD profiles of O<sub>2</sub> desorption on prepared Au/TNT catalysts at different calcination temperatures; (a) uncalcined, (b) 473 K, (c) 573 K, (d) 773 K.

#### 4.1.6 Temperature Programmed Reduction (TPR)

Figure 4.11 shows the TPR spectra of TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts at different calcination temperatures. In the spectrum of commercial TiO<sub>2</sub>, a high temperature (HT) peak (above 800 K) due to TiO<sub>2</sub> reduction of bulk oxygen was detected. After doped gold on TiO<sub>2</sub>, they showed the new peak at low temperature (around 400 K). This LT peak was due to the reduction of oxygen species which caused from the formation of superoxide O<sup>2-</sup> bound to Ti<sup>4+</sup> and proposed that the presence of Au species made easy the formation of oxygen defected on titania surface at the boundary of gold particles (Liu *et al.*, 1999). Moreover, the HT peak was shifted to lower temperature in comparison with HT peak of pure TiO<sub>2</sub>. The shifting toward the low-temperature side indicated the formation of more easily reducible species. From the TPR spectra, it can be implied that calcined Au/TiO<sub>2</sub> catalyst at 573 K gave the strongest of metal support interaction because the LT peak shifted to the lowest temperature followed by 573 K and 773 K

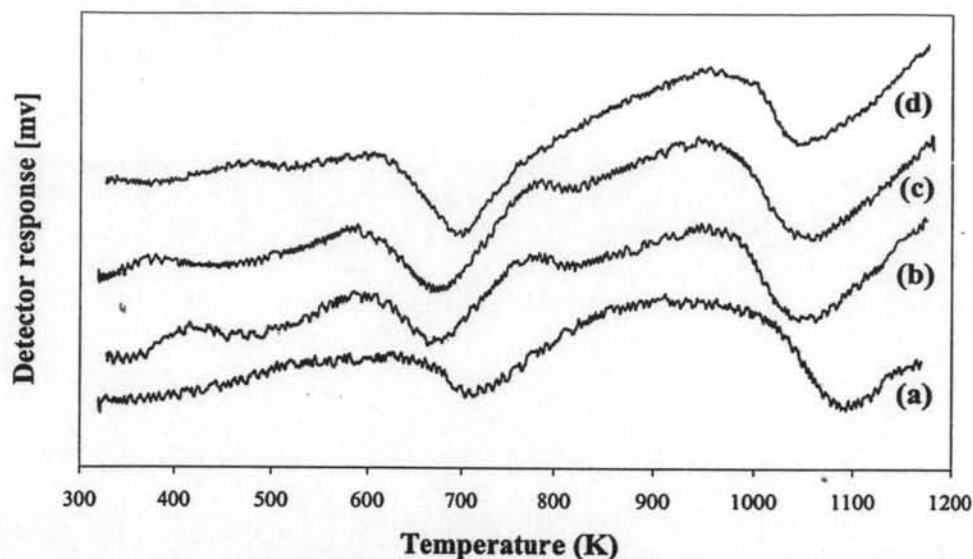


Figure 4.11 TPR spectra of Au/TiO<sub>2</sub> catalysts at different calcination temperatures.

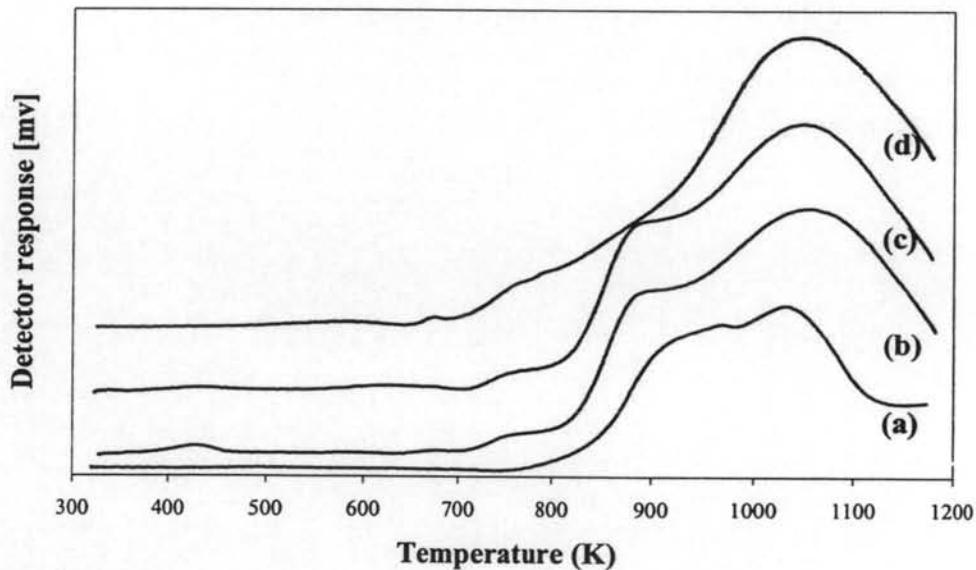


Figure 4.12 TPR spectra of Au/TNT catalysts at different calcination temperatures.

Figure 4.12 shows the TPR results of titania nanotubes (TNT) and Au/TNT at different calcination temperatures catalysts. In the spectrum of TNT, only a high temperature (HT) peak (above 900 K) due to TiO<sub>2</sub> reduction of bulk

oxygen was detected. In the spectrum of Au/TNT catalysts at different calcination temperatures showed only the high temperature peak also and shifted to the higher temperature when compared with the pure TNT. It can be implied that additional of gold did not improve the reducible property of TNT because of they were changed the electronic properties during hydrothermal treatment and provided very poor strong metal support interaction effect. In addition, there are no differences of reduction peak between Au/TNT catalysts at different calcination temperatures.

From the results, it can be implied that  $\text{TiO}_2$  was easier to be reduced at lower temperature than TNT although the intensity of TNT was extremely higher than  $\text{TiO}_2$ . It was because the high surface area and the transformation of TNT to poor crystalline phase effected to electronic properties of the support so amount of oxygen molecule can be reduced out higher than  $\text{TiO}_2$ .

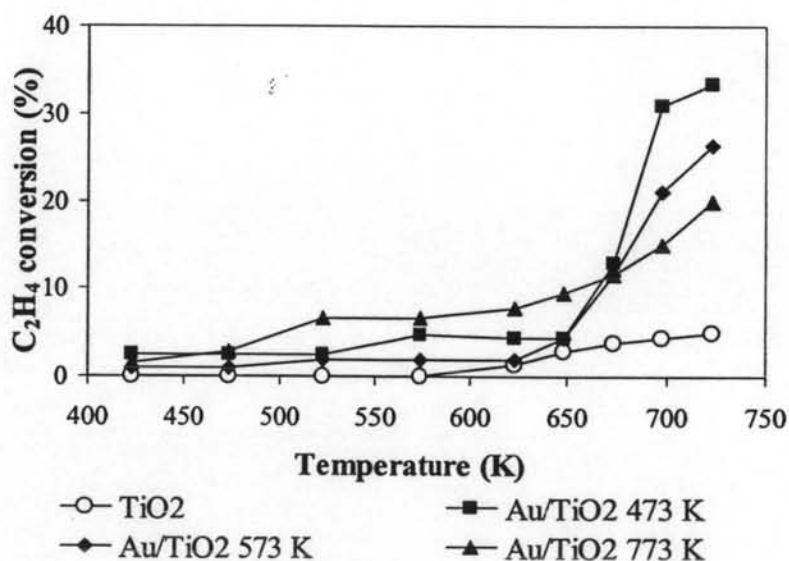
#### 4.2 Catalytic Activity of Prepared Gold Catalysts in Oxidation of Ethylene

The ethylene oxidation experiments were carried out at different temperatures and different amount of oxygen in the reaction. The Au-based catalyst samples were prepared by impregnation method at different calcination temperatures. For all studied catalysts, the ethylene conversion increased with increasing the reaction temperature. In oxidation of ethylene, it gave the two competitive reactions which were partial oxidation and total oxidation as shown in the following equation. For total oxidation reaction, ethylene reacted with oxygen from the support to produce carbon dioxide and water while partial oxidation, the main products were carbon monoxide and water.

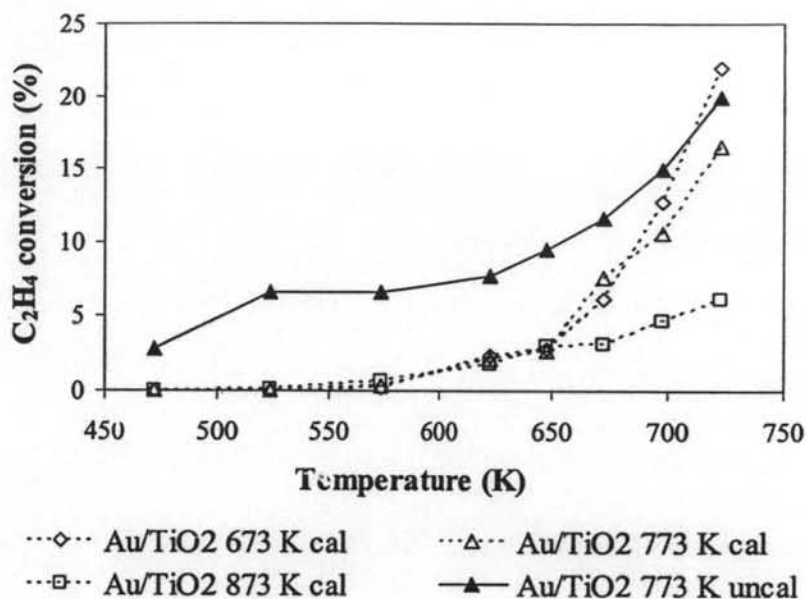


#### 4.2.1 Catalytic Activity and CO<sub>2</sub> Selectivity in Ethylene Oxidation under Deficient of Oxygen Conditon

Figure 4.13 and 4.14 illustrate the ethylene conversion of uncalcined and calcined support Au/TiO<sub>2</sub> catalysts, respectively under deficient of oxygen condition in oxidation of ethylene. It was shown that the ethylene conversion increased with increasing the reaction temperature. In case of uncalcined support, the catalytic activity results showed that the lowest calcination temperature 473 K of Au/TiO<sub>2</sub> catalysts exhibited the highest ethylene conversion around 33 % at temperature 725 K followed by 573 K and 773 K. In addition, the ethylene conversion decreased moderately when calcined the TiO<sub>2</sub> support before impregnated gold because of the transformation to the rutile phase which was an inactive form during the calcination. Anyway, calcined support catalysts demonstrated more stability than uncalcined support catalysts because they were not changing the structure during the reaction.

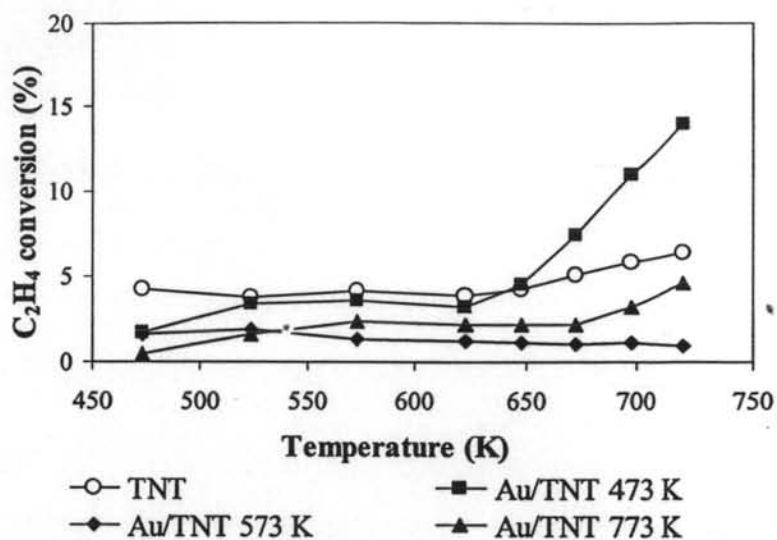


**Figure 4.13** Ethylene conversion of uncalcined support Au/TiO<sub>2</sub> P25 catalysts at different calcination temperatures. Starting reaction gas mixture in case of deficient of oxygen was 9% C<sub>2</sub>H<sub>4</sub> and 13.5% O<sub>2</sub> balance with He; SV 7500 h<sup>-1</sup>; 1 atm.

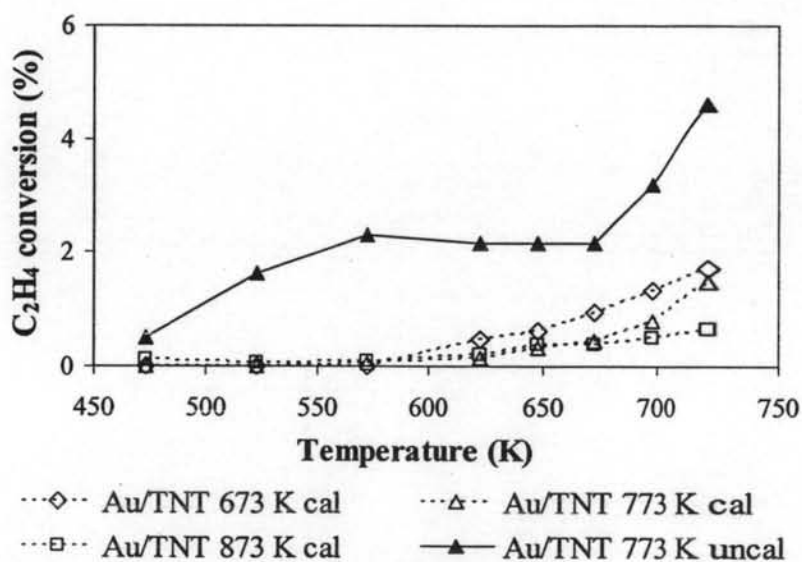


**Figure 4.14** Ethylene conversion of calcined support Au/TiO<sub>2</sub> P25 catalysts at different calcination temperatures. Starting reaction gas mixture in case of deficient of oxygen was 9% C<sub>2</sub>H<sub>4</sub> and 13.5% O<sub>2</sub> balance with He; SV 7500 h<sup>-1</sup>; 1 atm.

In contrast, uncalcined and calcined support Au/TNT catalysts exhibited the poor activity and low conversion of ethylene (<10%) when compared with pure TNT and Au/TiO<sub>2</sub> catalysts as shown in Figure 4.15 and Figure 4.16. In addition, there were no obviously different of catalytic activity between Au/TNT at different calcination temperatures. It was because the Au/TNT catalysts exhibited the poor reducible property when compared with the pure TNT from the TPR profiles and low oxygen desorption from the TPD results. In addition, the calcined support catalysts had the lower activity than uncalcined support which and can be explained in the same way with the Au/TiO<sub>2</sub> case because of the transformation of the support structure. Anyway, at high temperature (>650 K) calcined Au/TNT at 473 K demonstrated higher activity than pure TNT.



**Figure 4.15** Ethylene conversion of uncalcined Au/TNT catalysts at different calcination temperatures. Starting reaction gas mixture in case of deficient of oxygen was 9%  $C_2H_4$  and 13.5%  $O_2$  balance with He; SV  $7500\text{ h}^{-1}$ ; 1 atm.



**Figure 4.16** Ethylene conversion of calcined Au/TNT catalysts at different calcination temperatures. Starting reaction gas mixture in case of deficient of oxygen was 9%  $C_2H_4$  and 13.5%  $O_2$  balance with He; SV  $7500\text{ h}^{-1}$ ; 1 atm.



As was well known, the higher temperature led to a higher rate of deep oxidation reaction or gave the higher CO<sub>2</sub> selectivity. In case of uncalcined support, calcined Au/TiO<sub>2</sub> catalyst at 573 K showed the highest CO<sub>2</sub> selectivity and provided 100% of selectivity at temperature higher than 650 K. It was because calcined catalyst at 573 K exhibited the highest reducible property confirmed by TPR spectra and resulted the highest activity followed by 473 K and 773 K, respectively as shown in Figure 4.17. In case of calcined support Au/TiO<sub>2</sub> catalysts, the CO<sub>2</sub> selectivity was improved when compare with the uncalcined support catalysts. Calcined catalysts at 673 K exhibited the highest CO<sub>2</sub> selectivity and there were no insignificant different between the calcined catalysts at 773 K and 873 K as shown in Figure 4.18.

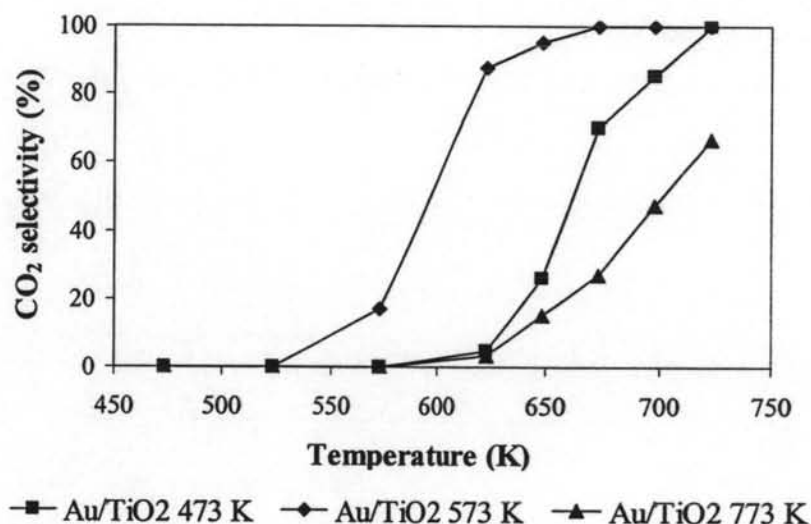
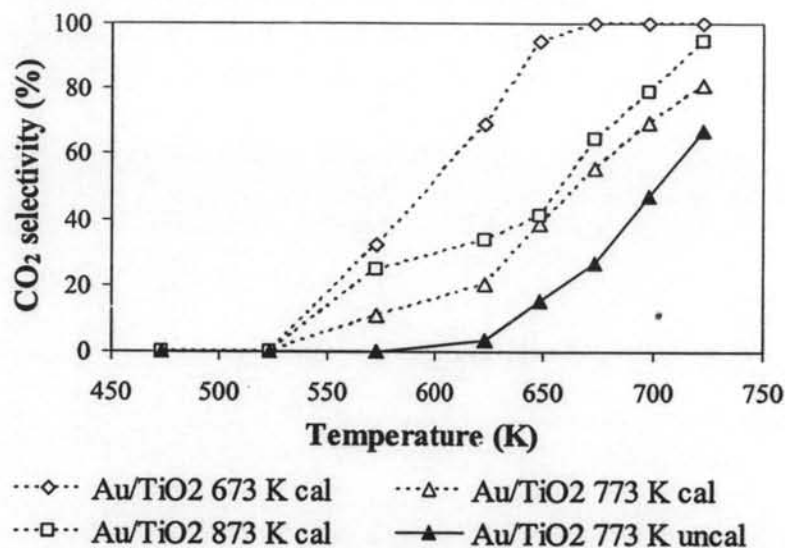


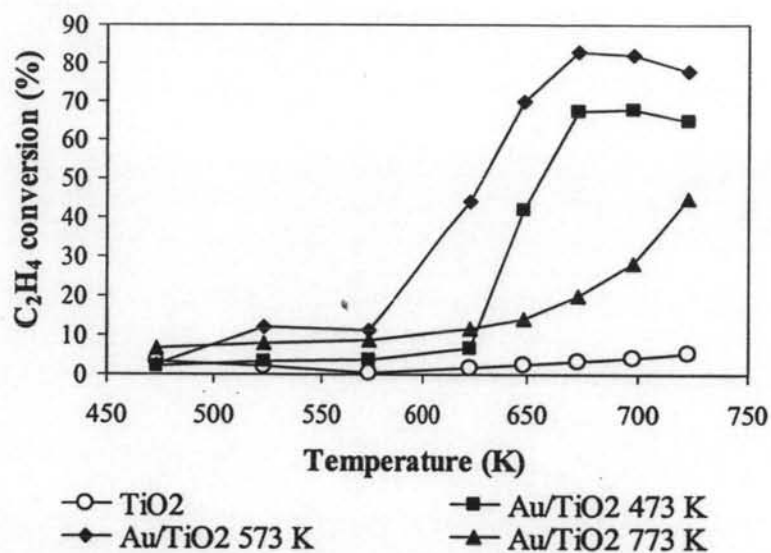
Figure 4.17 CO<sub>2</sub> selectivity in oxidation of ethylene of different calcination temperatures uncalcined support Au/TiO<sub>2</sub> catalysts under deficient of oxygen condition.



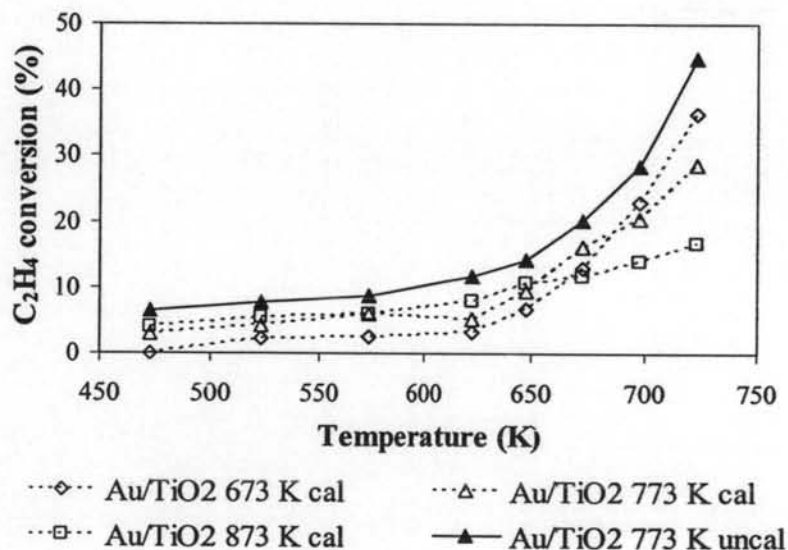
**Figure 4.18** CO<sub>2</sub> selectivity in oxidation of ethylene of different calcination temperatures calcined support Au/TiO<sub>2</sub> catalysts under deficient of oxygen condition.

#### 4.2.2 Catalytic Activity and CO<sub>2</sub> Selectivity in Ethylene Oxidation under Stoichiometry of Oxygen Condition

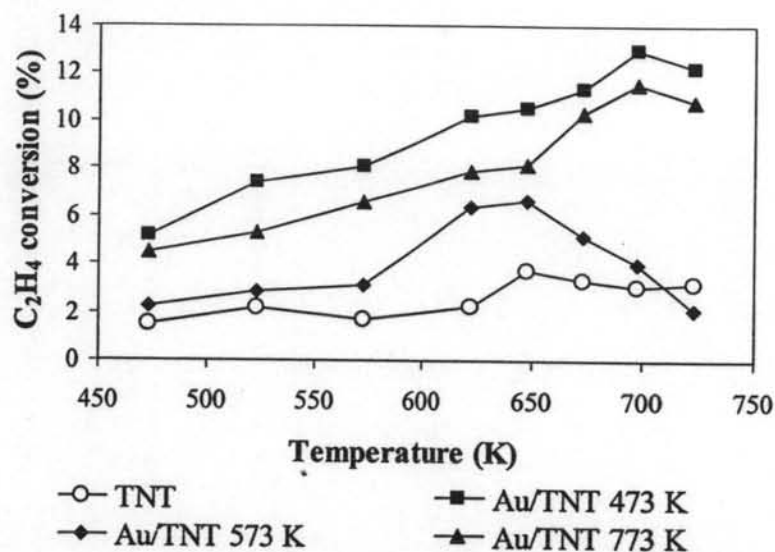
Under stoichiometry of oxygen condition, C<sub>2</sub>H<sub>4</sub> conversion of uncalcined and calcined support Au/TiO<sub>2</sub> catalysts are shown in the Figure 4.19 and 4.20, respectively. The addition of gold on commercial TiO<sub>2</sub> increased ethylene conversion substantially because increasing amount of oxygen can generate the opportunity of oxygen adsorption on the catalysts surface. In case of uncalcined support, calcined Au/TiO<sub>2</sub> catalysts at 473 K and 573 K created the highest ethylene conversion more than 65% and 80%, respectively at reaction temperature 670 K, while conversion of calcined at 773 K was lower (~ 40%). It caused from calcined catalyst at 773 K exhibited the lowest of oxygen desorption and worse of reducible property than the others from the TPD and TPR results. The optimum calcination temperature was around 573 K. In case of calcined support Au/TiO<sub>2</sub> catalysts exhibited lower catalytic activity than uncalcined form because of the transformation of TiO<sub>2</sub> structure.



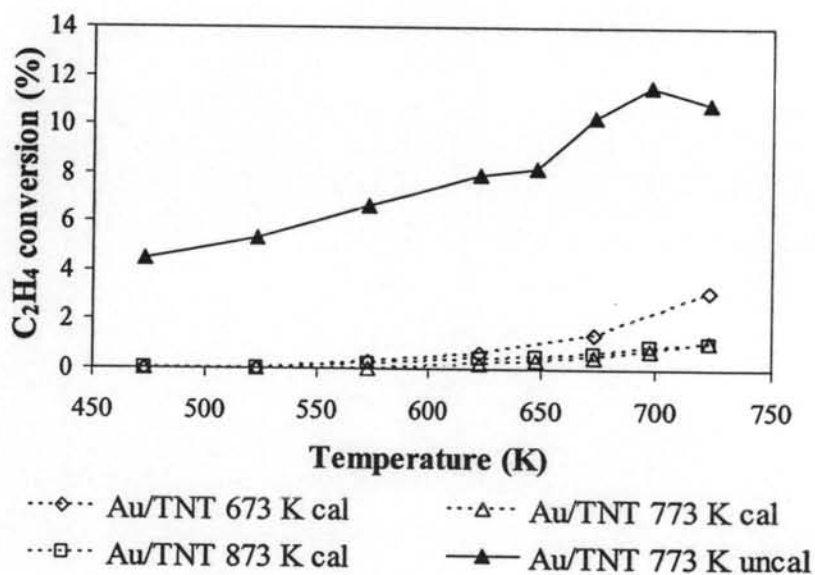
**Figure 4.19** Ethylene conversion of uncalcined support Au/TiO<sub>2</sub> P25 at different calcination temperature. Starting reaction gas mixture in case of stoichiometry of oxygen was 9% C<sub>2</sub>H<sub>4</sub> and 27% O<sub>2</sub> balance with He; SV 7500 h<sup>-1</sup>; 1 atm.



**Figure 4.20** Ethylene conversion of calcined support Au/TiO<sub>2</sub> P25 at different calcination temperature. Starting reaction gas mixture in case of stoichiometry of oxygen was 9% C<sub>2</sub>H<sub>4</sub> and 27% O<sub>2</sub> balance with He; SV 7500 h<sup>-1</sup>; 1 atm.



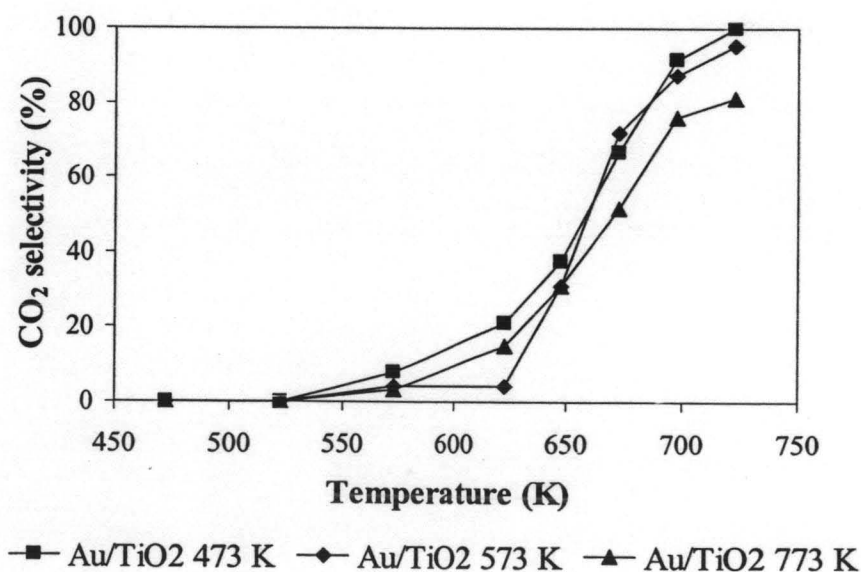
**Figure 4.21** Ethylene conversion of uncalcined Au/TNT at different calcination temperatures. Starting reaction gas mixture in case of stoichiometry of oxygen was 9%  $C_2H_4$  and 27%  $O_2$  balance with He; SV  $7500\ h^{-1}$ ; 1 atm.



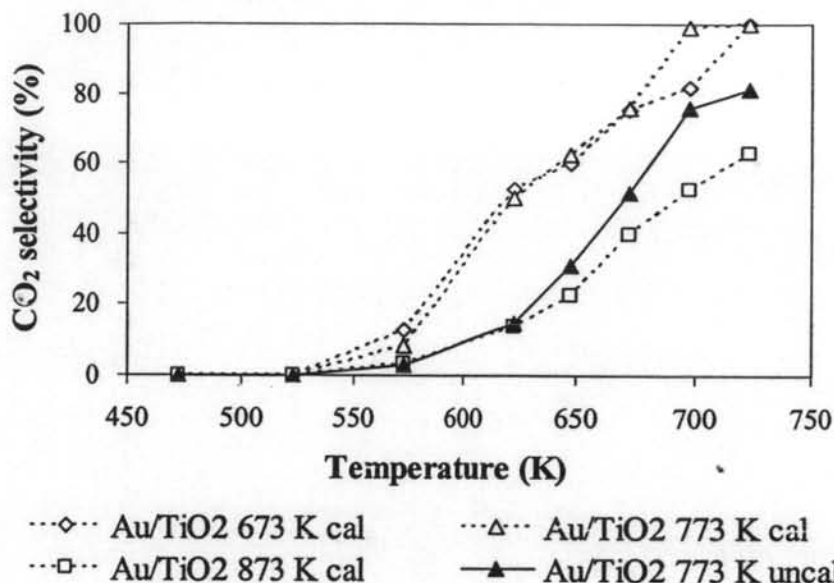
**Figure 4.22** Ethylene conversion of calcined Au/TNT at different calcination temperatures. Starting reaction gas mixture in case of stoichiometry of oxygen was 9%  $C_2H_4$  and 27%  $O_2$  balance with He; SV  $7500\ h^{-1}$ ; 1 atm.

Although increasing amount of oxygen can create the higher activity of Au/TiO<sub>2</sub> catalysts, the catalytic activity of Au/TNT catalysts was improved slightly and the ethylene conversion still remained low (<12%) as shown in Figure 4.21 and 4.22. Both of Au/TNT catalysts types did not noticeably differ of catalytic activity at different calcination temperature. They can explain in the similar way with the previous.

The CO<sub>2</sub> selectivity results of uncalcined support and calcined support Au/TiO<sub>2</sub> catalysts were shown in Figure 4.23 and 4.24, respectively. In case of uncalcined support catalysts, they exhibited a similar trend between calcined catalysts at different temperatures and gave 100% CO<sub>2</sub> selectivity at temperature 720 K for Au/TiO<sub>2</sub> 473 K. In contrast, the CO<sub>2</sub> selectivity of calcined support Au/TiO<sub>2</sub> catalysts was higher than the uncalcined support catalysts. It can be caused from more stability of calcined support catalysts. The optimum calcination temperature of calcined support Au/TiO<sub>2</sub> catalysts was 773 K because it gave the highest CO<sub>2</sub> selectivity and high ethylene conversion.



**Figure 4.23** CO<sub>2</sub> selectivity in oxidation of ethylene of different calcination temperatures uncalcined support Au/TiO<sub>2</sub> catalysts under stoichiometry of oxygen condition.

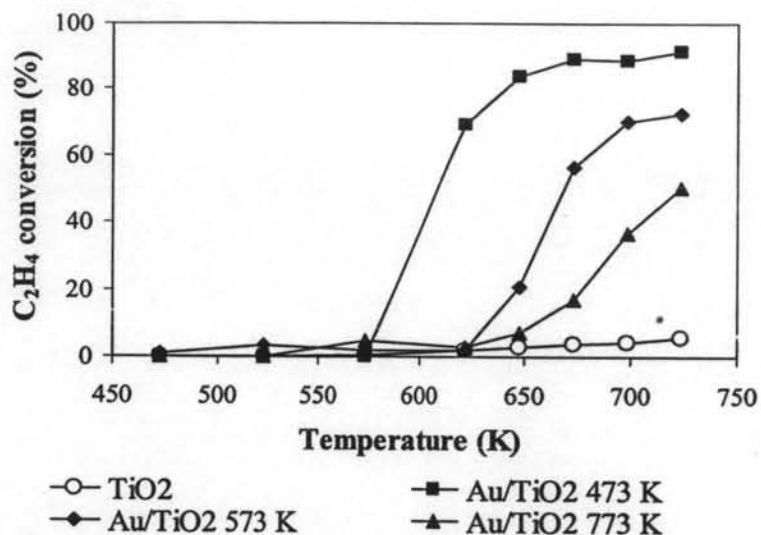


**Figure 4.24** CO<sub>2</sub> selectivity in oxidation of ethylene of different calcination temperatures calcined support Au/TiO<sub>2</sub> catalysts under stoichiometry of oxygen condition.

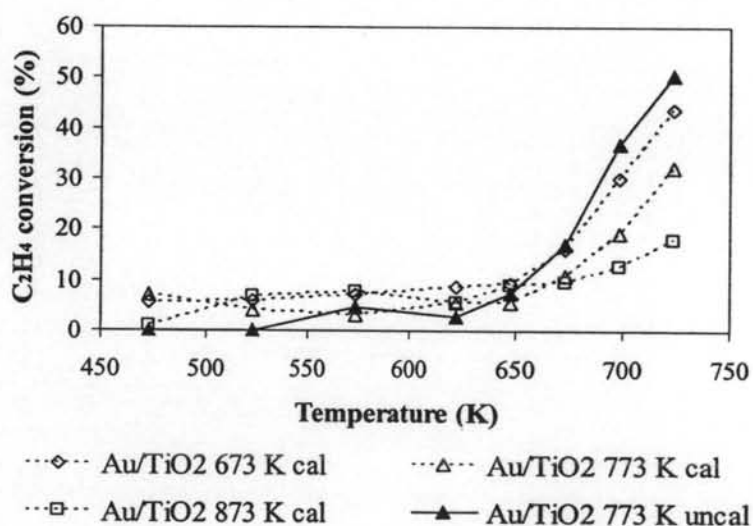
#### 4.2.3 Catalytic Activity and CO<sub>2</sub> Selectivity in Ethylene Oxidation Under Excess of Oxygen Condition

Under excess of oxygen condition, ethylene conversion of uncalcined and calcined support Au/TiO<sub>2</sub> catalysts shown in the Figure 4.25 and 4.26, respectively. In case of uncalcined support Au/TiO<sub>2</sub> catalysts, ethylene conversion increased dramatically around 90% and 70% for calcined catalysts at 473 K and 573 K, respectively at 725 K. The conversion was higher than stoichiometry of oxygen because the opportunity of oxygen adsorption on the catalysts surface increased as was mentioned before. In addition, the calcined support of Au/TiO<sub>2</sub> catalysts showed the same results with the first two cases which had the lower catalytic activity than the calcined support types.

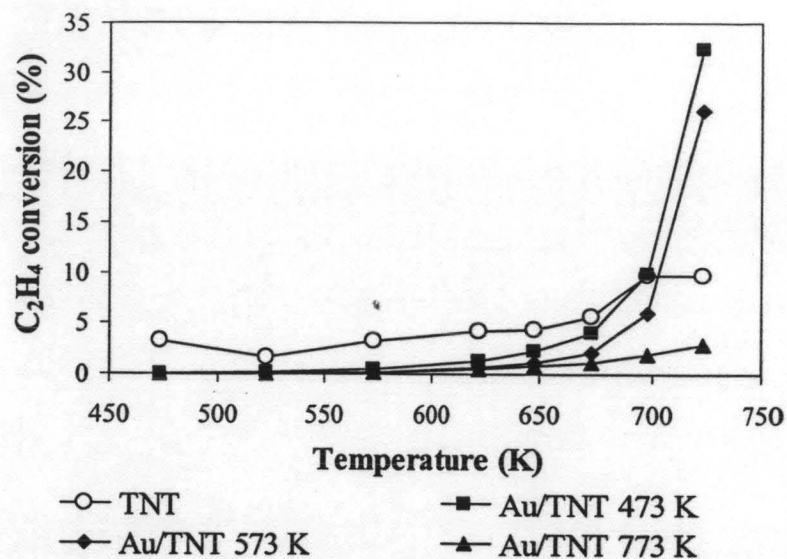
In case of Au/TiO<sub>2</sub> catalysts, both of the TiO<sub>2</sub> support types gave the same results with the first two cases which gold did not improve the catalytic activity and there were no obviously different catalytic activity with different calcination temperatures.



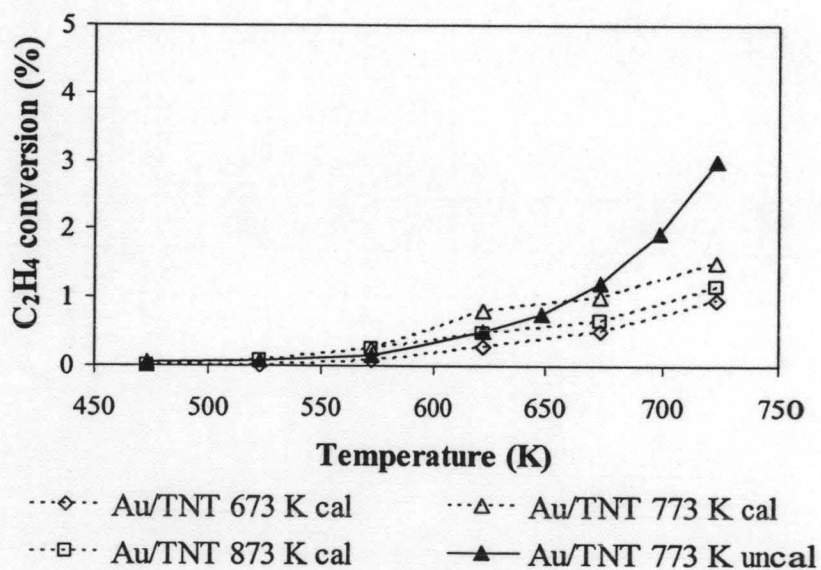
**Figure 4.25** Ethylene conversion of uncalcined support Au/TiO<sub>2</sub> P25 at different calcination temperature. Starting reaction gas mixture in case of excess of oxygen was 9% C<sub>2</sub>H<sub>4</sub> and 54% O<sub>2</sub> balance with He; SV 7500 h<sup>-1</sup>; 1 atm.



**Figure 4.26** Ethylene conversion of calcined support Au/TiO<sub>2</sub> P25 at different calcination temperature. Starting reaction gas mixture in case of excess of oxygen was 9% C<sub>2</sub>H<sub>4</sub> and 54% O<sub>2</sub> balance with He; SV 7500 h<sup>-1</sup>; 1 atm.



**Figure 4.27** Ethylene conversion of uncalcined support Au/TNT at different calcination temperatures. Starting reaction gas mixture in case of excess of oxygen was 9%  $C_2H_4$  and 54%  $O_2$  balance with He; SV  $7500\text{ h}^{-1}$ ; 1 atm.



**Figure 4.28** Ethylene conversion of calcined support Au/TNT at different calcination temperatures. Starting reaction gas mixture in case of excess of oxygen was 9%  $C_2H_4$  and 54%  $O_2$  balance with He; SV  $7500\text{ h}^{-1}$ ; 1 atm.



From the CO<sub>2</sub> selectivity results of uncalcined support Au/TiO<sub>2</sub> catalysts, all of calcined catalysts gave the dramatically increasing of CO<sub>2</sub> selectivity so the carbon monoxide production was very low. The optimum calcination temperature of Au/TiO<sub>2</sub> catalysts was 473 K which gave 100% CO<sub>2</sub> selectivity at 570 K as shown in Figure 4.219. When compare the CO<sub>2</sub> selectivity with the other two cases of oxygen condition, it was found that under excess oxygen condition gave the best CO<sub>2</sub> selectivity and ethylene conversion for Au/TiO<sub>2</sub> catalysts. However, the CO<sub>2</sub> selectivity of calcined support of Au/TiO<sub>2</sub> catalysts had the lower CO<sub>2</sub> selectivity than the uncalcined support but there were no obviously different between the different calcination temperature catalysts.

It is clearly demonstrated that the conversion of ethylene of Au/TiO<sub>2</sub> catalysts appeared to be higher than Au/TNT catalysts for all range of oxygen concentration in reaction which was confirm by TPD and TPR results. Furthermore, the calcined support catalysts exhibited higher catalytic activity than calcined support because the structure of calcined support was an inactive form in case of TiO<sub>2</sub> and the decreasing of surface area in case of TNT during the calcination. Additionally, they can be proposed that why TNT support was lower activity in total oxidation of ethylene. It can be caused from the changing of electronic properties of TNT support which resulted to the strong metal support interaction effect. It was an important factor of catalytic activity of gold catalysts. Moreover, all catalysts activated for the complete oxidation because the large size of gold particles prepared by incipient wetness impregnation method as shown in the TEM image favored for total oxidation which had also been confirmed by many research groups. In addition, CO<sub>2</sub> selectivity was increasing with reaction temperature as well as amount of oxygen in the reaction.

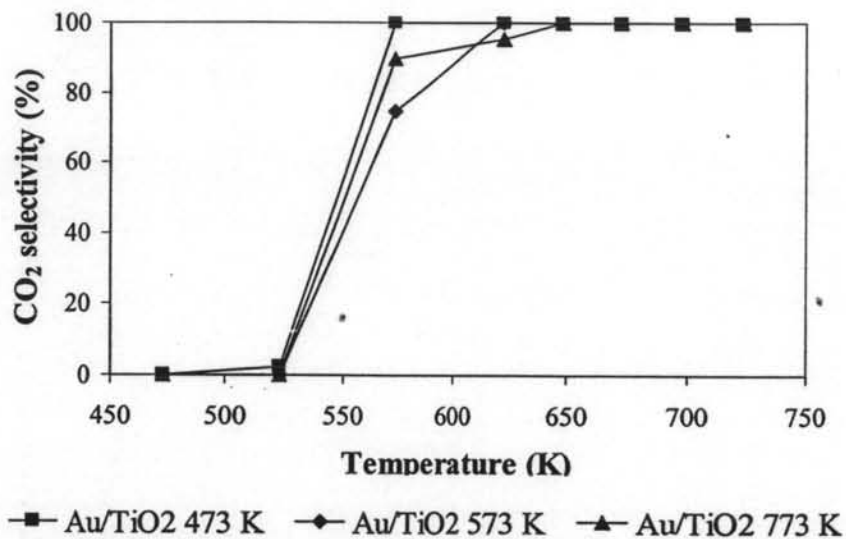


Figure 4.29 CO<sub>2</sub> selectivity in oxidation of ethylene of different calcination temperatures uncalcined Au/TiO<sub>2</sub> catalysts under excess of oxygen condition.

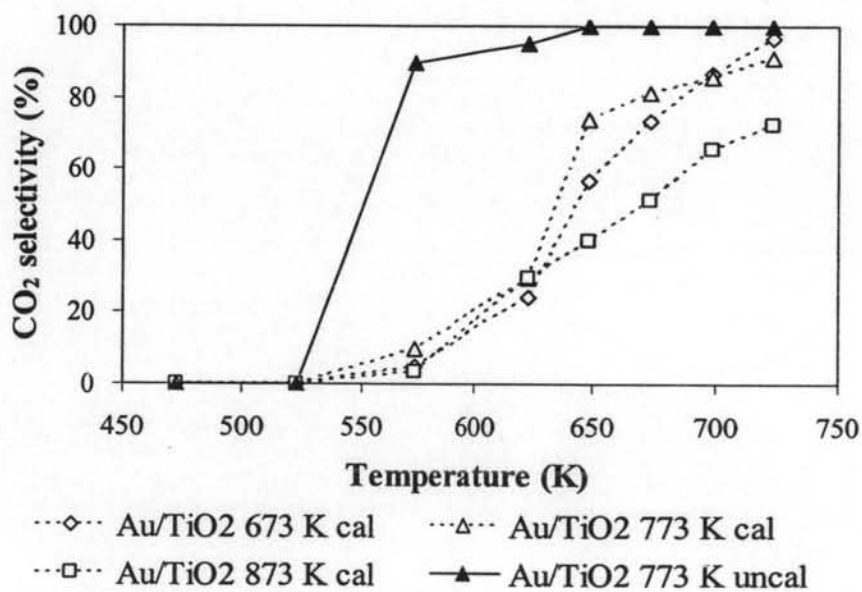


Figure 4.30 CO<sub>2</sub> selectivity in oxidation of ethylene of different calcination temperatures calcined Au/TiO<sub>2</sub> catalysts under excess of oxygen condition.