

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Catalyst Characterization

The catalysts were characterized by BET, XRD, and AAS to determine their surface area, surface composition, and percentage of metal loading.

4.1.1 Surface Area Measurement

The effects of percentage of gold loading and calcination temperature on surface area were investigated by five-point BET method using the surface area analyzer.

Table 4.1 shows the BET surface area Au/ZnO catalysts prepared by co-precipitation (CP) method. The surface area was strongly dependent on the initial surface area of the support. In addition, gold loading did not affect the surface area.

Table 4.1 Surface area of Au/ZnO catalysts prepared by CP method calcined at 400°C.

Catalyst	Surface area (m ² /g)
ZnO	46.12
0.2% Au/ZnO	44.36
0.5% Au/ZnO	38.81
1% Au/ZnO	36.75
2% Au/ZnO	35.81

Table 4.2 presents the BET surface area of gold supported on alumina catalysts prepared by sol-gel (SG) method. The surface area was slightly changed as the percentage of gold loading increased but there was no definite trend.

Table 4.2 Surface area of Au/Al₂O₃ catalysts prepared by SG method calcined at 400°C.

Catalyst	Surface area (m ² /g)
Al ₂ O ₃	355.7
0.5% Au/Al ₂ O ₃	424.7
1% Au/Al ₂ O ₃	496.2
2% Au/Al ₂ O ₃	466.3

Table 4.3 exhibits the BET surface area of gold supported on titania catalysts prepared by SG method. The surface area was depended on the initial surface area of the support. Otherwise, it also was depended on the percentage of gold loading and calcination temperature. The 1% Au/TiO₂ catalysts, calcined at 300°C and 500°C, showed lower surface area than that calcined at 400°C. At calcination temperature lower than 400°C resulted in the lower surface area due to the blockage of unremovable volatile organic compounds in the pores of the surfaces, while at the higher calcination temperature the structure of the support was sintered.

Table 4.3 Surface area of Au/TiO₂ catalysts prepared by SG method.

Catalyst	Calcination temperature (°C)	Surface area (m ² /g)
TiO ₂	400	90.5
0.2 Au/TiO ₂	400	60.88
1% Au/TiO ₂	400	89.74
2% Au/TiO ₂	400	75.89
1% Au/TiO ₂	300	62.74
1% Au/TiO ₂	400	89.67
1% Au/TiO ₂	500	38.24

Table 4.4 presents the BET surface area of gold supported on titania catalysts prepared by deposition-precipitation (DP) method. The stability of initial titania (Degussa P-25) support showed the important role in surface area even with different metal loadings. It shows a slight decrease with increasing in calcination temperature but was not significant.

Table 4.4 Surface area of Au/TiO₂ catalysts prepared by DP method.

Catalyst	Calcined temperature (°C)	Surface area (m ² /g)
TiO ₂	-	69.13
1% Au/TiO ₂	300	66.42
1% Au/TiO ₂	400	64.08
1% Au/TiO ₂	500	61.58



4.1.2 X-ray Diffraction Analysis

X-ray diffraction analysis was carried out for all gold catalysts. The patterns identified the kind of support structures and metal loading on the supports. Figure 4.1 illustrates the XRD patterns for all Au/ZnO catalysts prepared by CP method. It can be seen that at every percentage of gold loading, the XRD patterns were identical to the pure ZnO, which had crystalline structure. There was no evidence of gold in metallic form on the CP catalyst surfaces, even at 2% Au. This was due to the fact that gold was well dispersed on ZnO active surface.

Figure 4.2 shows the XRD patterns of Au/Al₂O₃ catalysts at different percentages of gold loading prepared by SG method. At every percentage of gold loading, the patterns exhibited peaks of metallic gold on the surface at even the percent gold loading as low as 0.2%. The attempt to make gold more dispersed by adding magnesium citrate into the catalyst preparation step as showed in Figure 4.3 was not successful*.

Figure 4.4 shows the XRD patterns of Au/TiO₂ prepared by the SG method at different percentages of gold loading at calcination temperature of 400°C. It shows no evidence of metallic gold on the titania surface. It may be assumed that gold was well dispersed on the support. The marked peaks represented the anatase structure of titania which was the active form.

Figure 4.5 shows XRD patterns for 1% Au/TiO₂ prepared by the SG method. At calcination temperature of 500°C or lower, the same patterns which had only anatase form of titania was found. However, both the anatase and rutile forms were found at calcination temperature of 600°C.

* Haruta et al. (1996) reported that Mg citrate might be prevented coagulation of gold particles during the calcination due to the blockage by citrate anions sticking on TiO₂ surface.

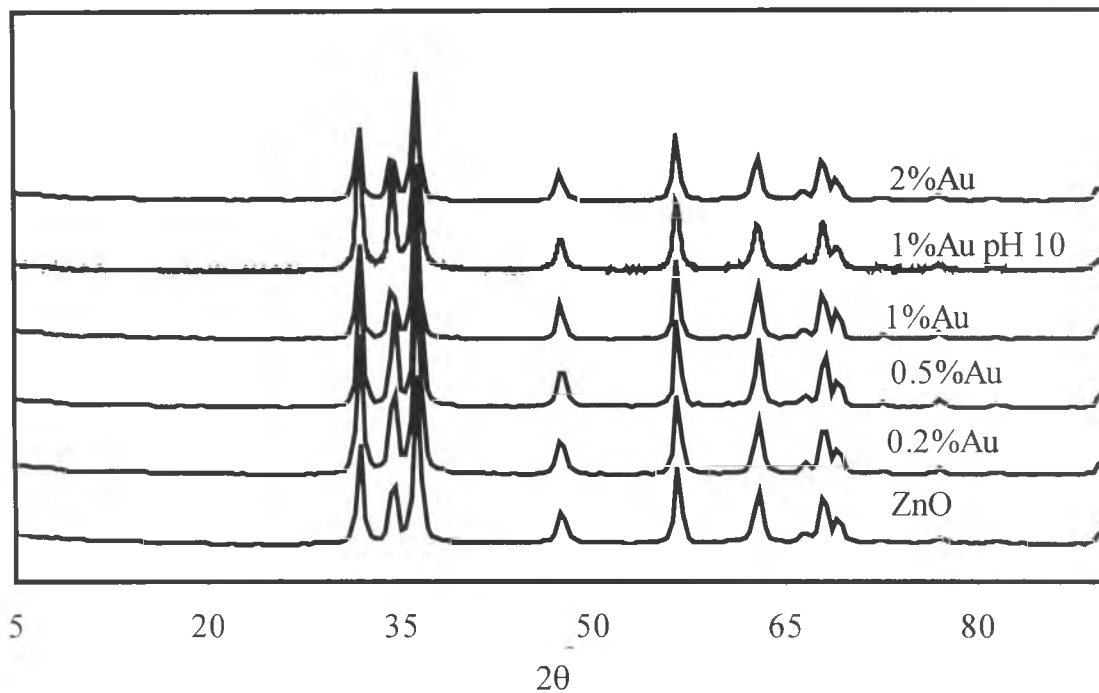


Figure 4.1 XRD patterns of Au/ZnO (CP) catalysts calcined at 400°C.

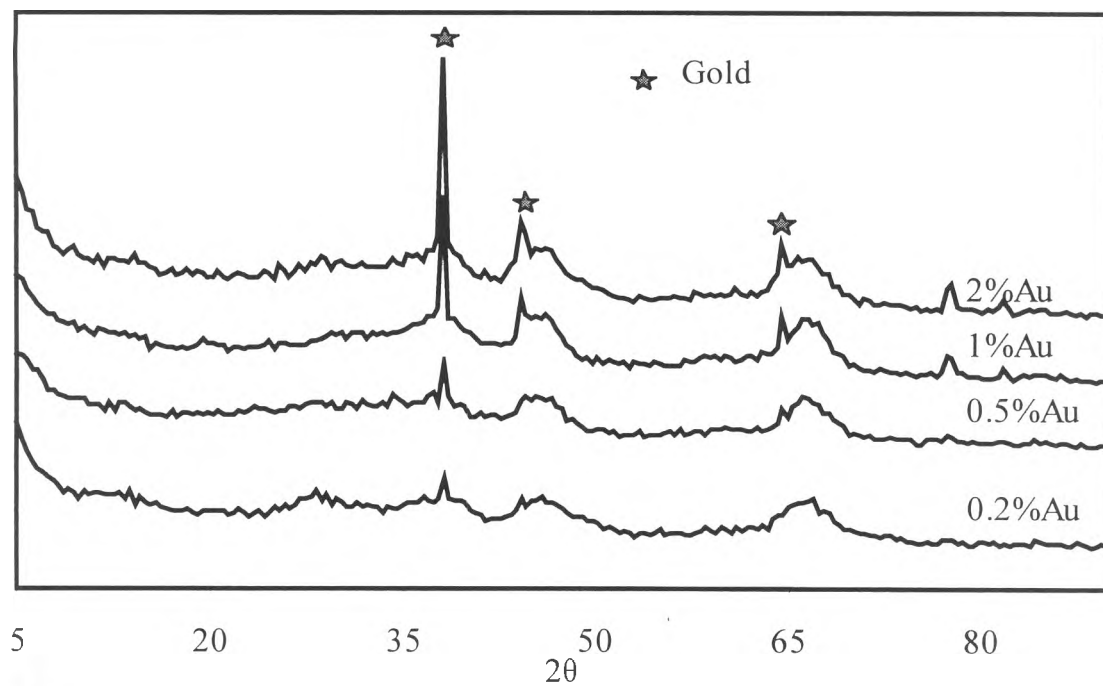


Figure 4.2 XRD patterns of Au/Al₂O₃ (SG) catalysts calcined at 400°C.

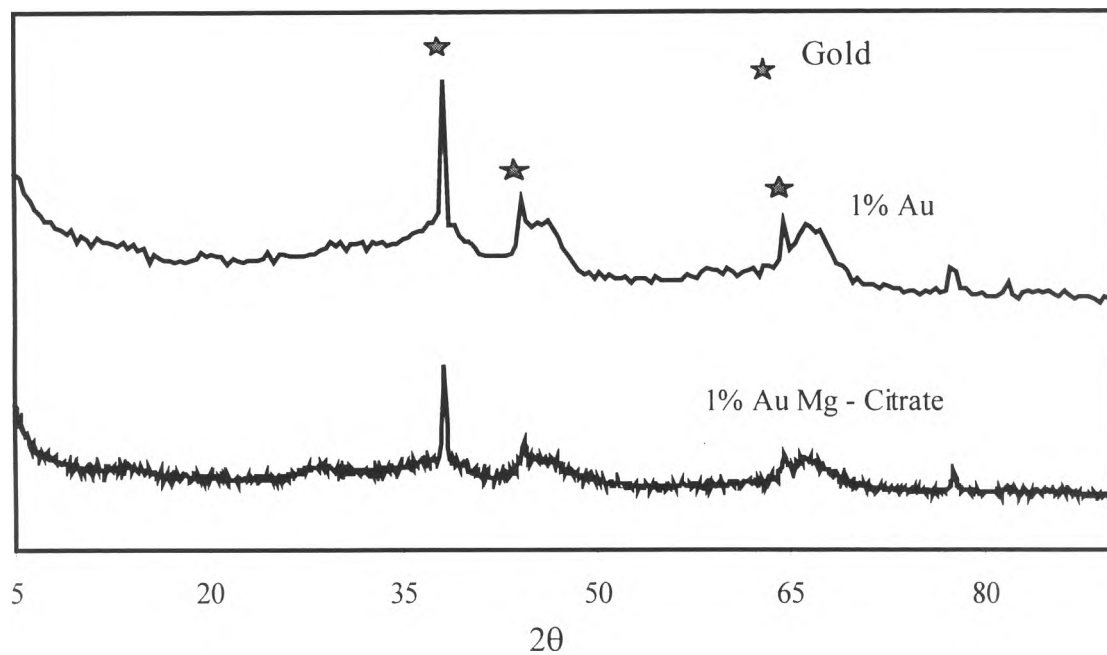


Figure 4.3 XRD patterns of Au/Al₂O₃ (SG) catalysts calcined at 400°C.

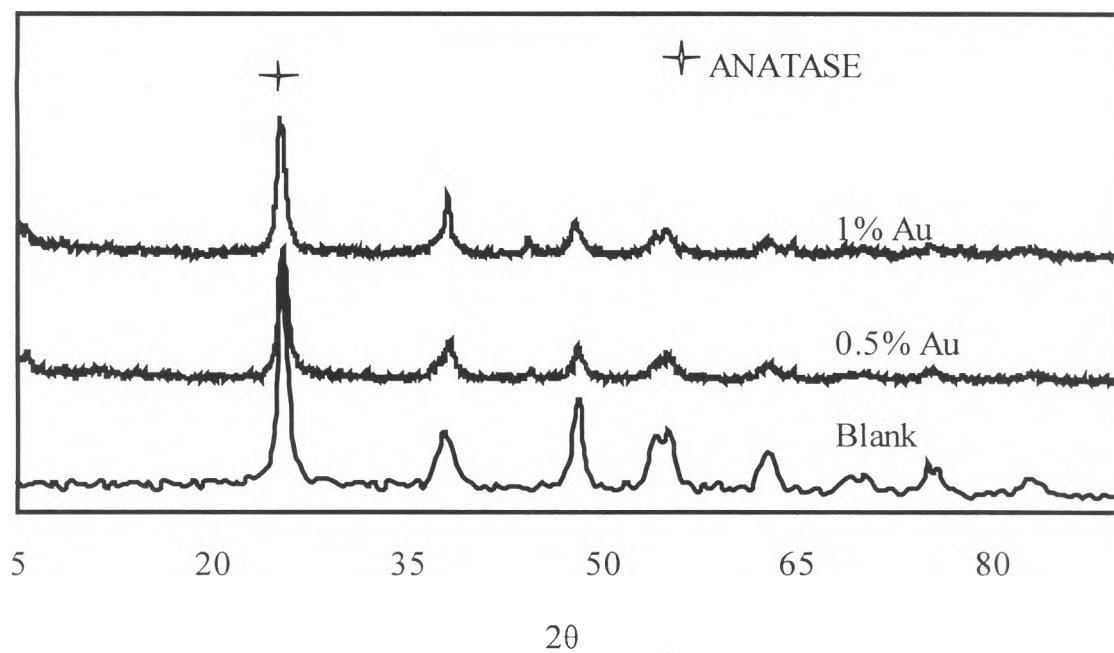


Figure 4.4 XRD patterns of Au/TiO₂ (SG) catalysts calcined at 400°C.

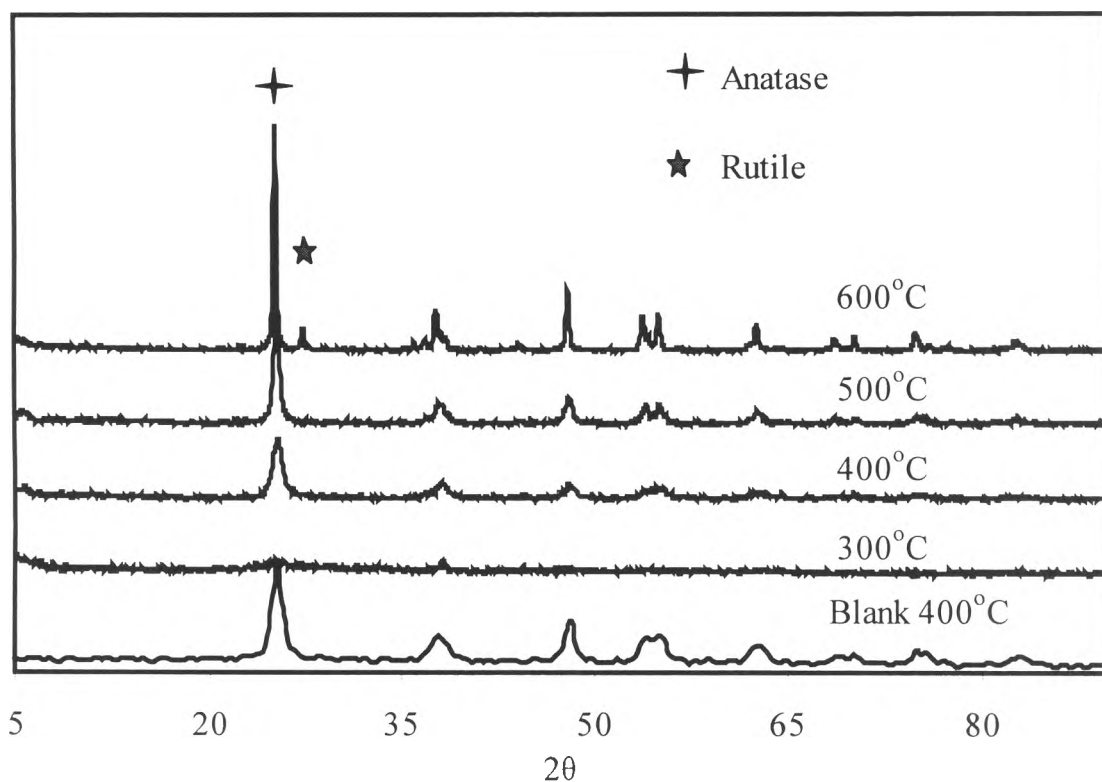


Figure 4.5 XRD patterns of 1% Au/TiO₂ (SG) catalysts at various calcination temperatures.

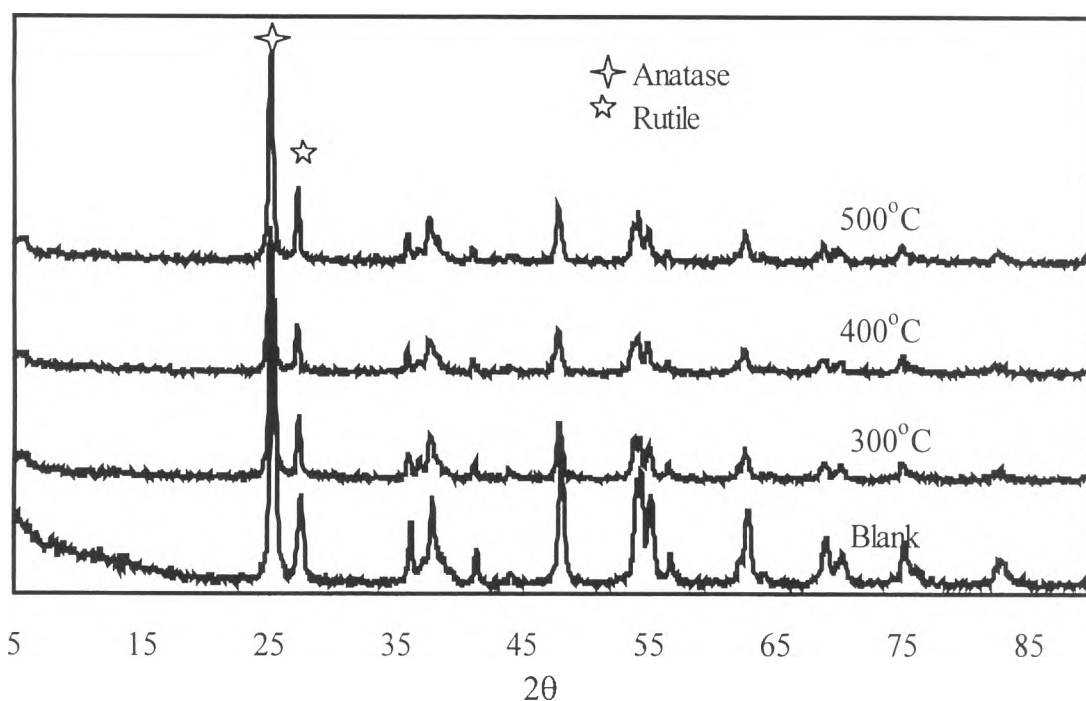


Figure 4.6 XRD patterns of 1% Au/TiO₂ (DP) catalysts at various calcination temperatures.

Figure 4.6 shows the XRD patterns of 1% Au/TiO₂ prepared by DP method and calcined at 300, 400, and 500°C. The anatase and rutile forms of titania were observed. The percentage of gold loading affected to the intensity of supports' peaks. The decreasing intensity of peaks of support was due to the well dispersed gold on the supports.

4.1.3 Percentage of Gold Loading

The AAS or Atomic absorption spectroscopy was used to analyze the concentration of active metal in catalysts. The results were shown in Table 4.5.

Table 4.5 Percentage of gold loading on supports.

Catalyst	Metal loading (%)
0.5% Au/ZnO (CP)	0.04
1% Au/ZnO (CP)	0.10
2% Au/ZnO (CP)	0.30
0.5% Au/Al ₂ O ₃ (SG)	0.40
1% Au/Al ₂ O ₃ (SG)	0.91
2% Au/Al ₂ O ₃ (SG)	1.30
1% Au/TiO ₂ (SG)	0.96
1% Au/TiO ₂ (DP)	0.40

4.2 Catalyst Activity Testing

The catalyst activity testing was divided into two parts. The first part was the study of the activity of Au/ZnO prepared by CP method, Au/Al₂O₃ and Au/TiO₂ prepared by SG method. Another part was activity testing and comparison of Au/TiO₂ SG catalyst to Au/TiO₂ DP catalyst.

4.2.1 Activity of Gold Catalysts on Various Supports

In order to test the catalyst activity, the feed composition was set at 10% propylene, 10% oxygen, and 10% hydrogen balanced in helium. The total flowrate of the reactant gas was kept constant at 70 ml/min, and the reaction temperature was varied from 40 to 200°C.

4.2.1.1 *Gold Supported on Zinc Oxide Catalysts (Au/ZnO)*

The gold loading was varied in the range of 0.5 to 2.0 wt% to clarify the effect of gold loading on zinc oxide catalysts prepared by CP method on the selective oxidation of propylene to PO. Table 4.6 shows the results at the reaction temperature of 80°C. It shows that the 0.5 and 1% Au/ZnO catalysts gave some activity and selectivity to propane only, while 2% Au/ZnO catalyst gave small amount of PO with very low selectivity of 0.91%.

Table 4.6 Effect of gold loading on Au/ZnO (CP) catalysts calcined at 400°C, at the reaction temperature of 80°C.

Catalyst	% CO ₂ yield	% C ₃ H ₈ yield	% PO yield	PO production rate*	% PO selectivity
0.5% Au/ZnO	0.0004	0.4719	-	-	-
1% Au/ZnO	-	0.1996	-	-	-
2% Au/ZnO	0.0008	0.1822	0.0194	0.0081	0.91

*PO production rate unit = mmol/h/g.cat

4.2.1.2 Gold Supported on Alumina Catalysts (Au/Al₂O₃)

The catalytic activity of Au/Al₂O₃ prepared by SG catalysts was investigated at different percentages of gold loading of 0.5 and 1%. As shown in Table 4.7, the 0.5% Au/Al₂O₃ catalyst gave low selectivity to PO of only 1.51% and produced propane as a major product with a small amount of CO₂.

The increase of gold loading from 0.5 to 1% could slightly enhance the selectivity to PO. The higher selectivity to PO of 2.58% was found with very low percent yield, which means that the catalyst was not active.

4.2.1.3 Gold Supported on Titania Catalysts (Au/TiO₂)

Table 4.8 shows the effect of Au/TiO₂ prepared by SG method. At 0.2, 0.5, and 1% gold loadings, the selectivities were 31.44, 95.38, and 85.00% respectively. The 1% catalyst gave highest PO production rate of 0.401 mmol/h/g.cat at the selectivity of 85%.

Table 4.7 Effect of gold loading on Au/Al₂O₃ (SG) catalysts calcined at 400°C, at the reaction temperature of 80°C.

Catalyst	% CO ₂ yield	% C ₃ H ₈ yield	% PO yield	PO production rate	% PO selectivity
0.5% Au/Al ₂ O ₃	0.0033	0.0510	0.0077	0.0024	1.51
1% Au/Al ₂ O ₃	-	0.0011	0.0094	0.0030	2.58

*PO production rate unit = mmol/h/g.cat

Table 4.8 Effect of gold loading on Au/TiO₂ (SG) catalysts calcined at 400°C, at the reaction temperature of 80°C.

Catalyst	% CO ₂ yield	% C ₃ H ₈ yield	% PO yield	PO production rate	% PO selectivity
0.2% Au/TiO ₂	0.0122	0.0125	0.2881	0.129	31.44
0.5% Au/TiO ₂	0.0024	0.0015	0.2567	0.055	95.38
1% Au/TiO ₂	0.0007	0.0102	0.8445	0.401	85.00

*PO production rate unit = mmol/h/g.cat

4.2.2 Comparison of Au/TiO₂ Catalysts Prepared by SG and DP Methods

Au/TiO₂ catalysts prepared by SG and DP methods were compared for their activities as functions of calcination temperature, H₂ and O₂ concentrations in the feed stream. The results are reported as follows.

4.2.2.1 *Calcination Temperature*

Figure 4.7 shows the PO production rate and selectivity to PO of 1% Au/TiO₂ catalysts prepared by SG and DP methods calcined at 300, 400, and 500°C.

For DP catalyst, the PO production rate reached maximum at calcination temperature of 400°C. There was no activity and selectivity to PO at the calcination temperature of 300°C. On the other hand, for the catalyst calcined at 500°C, it produced small amount of PO with very low selectivity.

The SG catalyst produced PO at production rate of higher than 0.15 mmol/h/g.cat at all calcined temperatures and gave the highest PO production rate and selectivity when calcined at 400°C.

The high PO production rate but low selectivity may be caused by the oligomerization or polymerization of C₃H₆ or C₃H₆O that are catalyst poisoning compounds (Nijhuis et al., 1999).

It can then be concluded that both catalysts should be calcined at 400°C for their best performance. The SG catalyst was more active than the DP catalyst.

4.2.2.2 *Hydrogen in Feed Stream*

To study the effect of H₂ in the reaction, the concentration of H₂ was varied from 7.5 to 12.5% while keeping C₃H₆ and O₂ concentrations constant at 10% each.

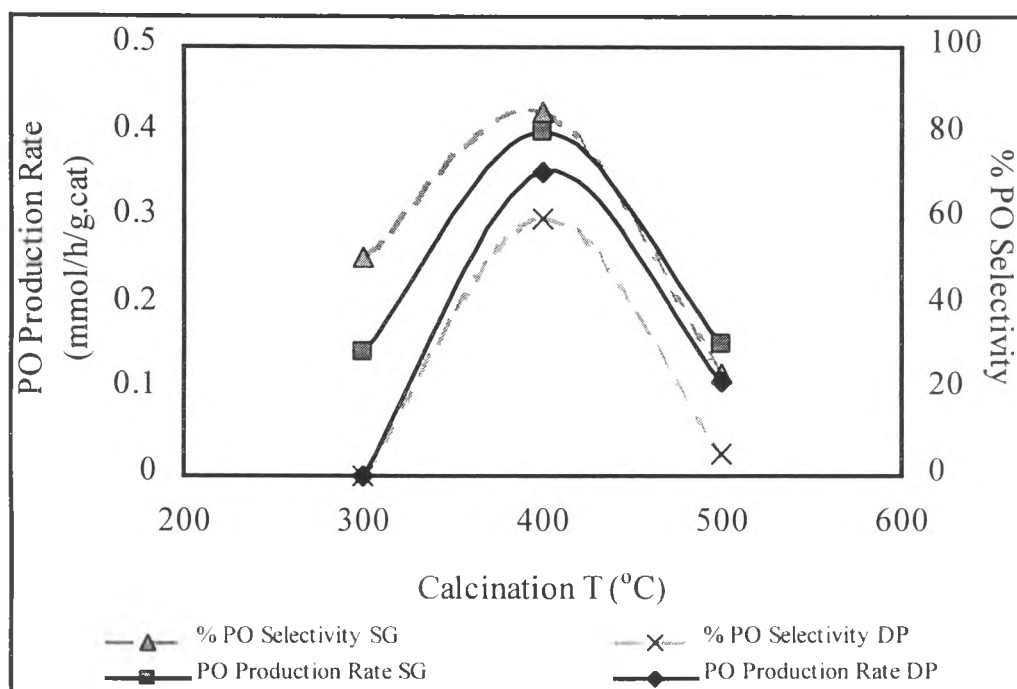


Figure 4.7 Effect of calcination temperature on selectivity to PO and PO production rate for 1% Au/TiO₂ (at 10% C₃H₆, 10% O₂, and 10% H₂).

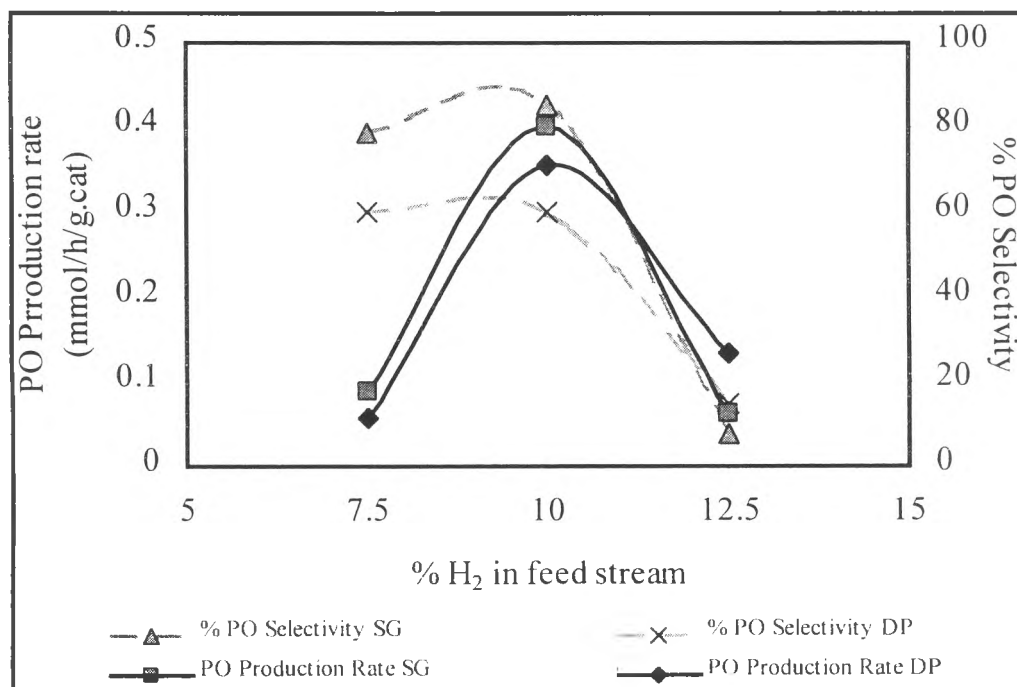


Figure 4.8 Effect of % hydrogen in feed stream on selectivity to PO and PO production rate for 1% Au/TiO₂ (at 10% C₃H₆ and 10% O₂).

The experiments were done at 80°C for 1% Au/TiO₂ catalysts prepared by SG and DP methods with the results shown in Figure 4.8. For both catalysts, the PO production rate reached maximum at 10% H₂. The SG catalyst yielded higher PO production rate than DP catalyst.

The selectivity of both SG and DP catalysts slightly changed while increasing the concentration of H₂ in the feed stream from 7.5 to 10% but decreased significantly when % H₂ was increased to 12.5%. It is then concluded that for SG and DP catalysts, 10% H₂ in feed stream should be used because it gave both high PO production rate and selectivity.

These phenomena may be caused by when the total amount of hydrogen was higher to make oxygen-radical more favorable to hydrogen atom. While the γ -hydrogen atoms of the PO reaction intermediate came across the surface from the location where the reaction with the first oxygen atom occurred. The distance between the different oxygen was close enough for the γ -hydrogen atoms to reach. The abstraction of one of these hydrogen atoms was favourable and the intermediate formed can only resulted in complete combustion of the molecule (Nijhuis, 1997).

4.2.2.3 Oxygen in Feed Stream

For the effect of O₂, similar experiments were performed by varying the concentration of O₂ in the feed stream from 5 to 15%, while keeping C₃H₆ and H₂ concentrations constant at 10% each. The results are shown in Figure 4.9.

It is clear from the Figure that 10% O₂ concentration in the feed stream gave the best result in terms of selectivity and PO production rate. Besides, the SG catalyst performed better than DP catalyst.

In summary, 1% Au/TiO₂ SG catalyst calcined at 400°C for 5 h with reactant mixture of 10% C₃H₆, 10% O₂, and 10% H₂ yielded the best result with selectivity of 85.00% and PO production rate of 0.401 at 80°C.

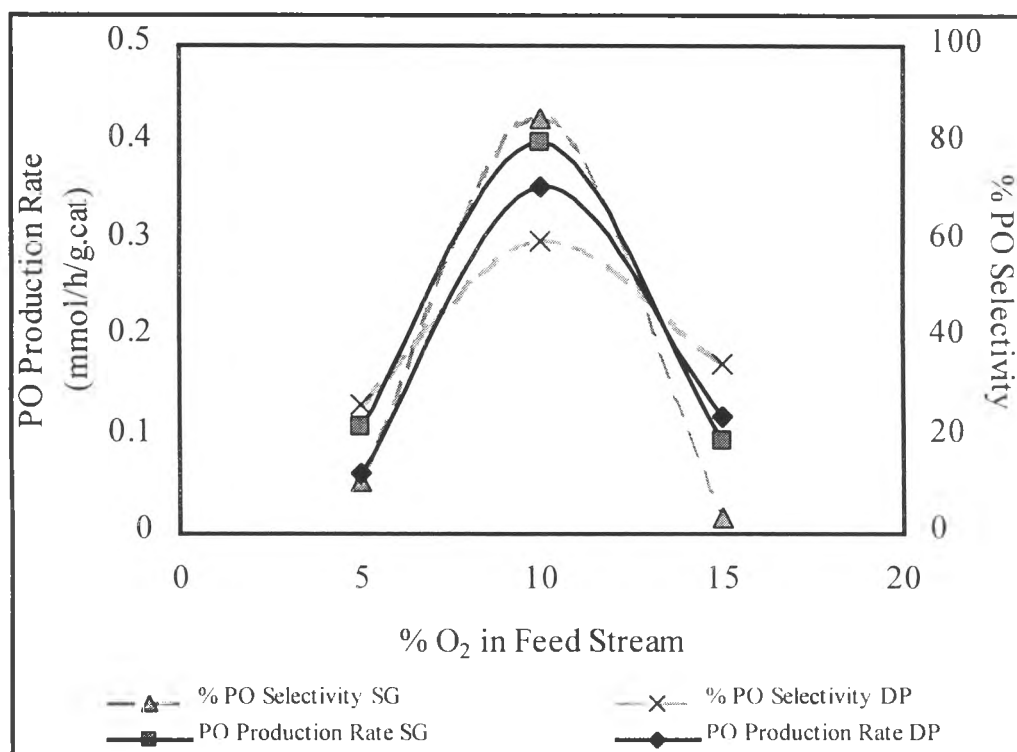


Figure 4.9 Effect of % oxygen in feed stream on selectivity to PO and PO production rate for 1% Au/TiO₂ (at 10% C₃H₆ and 10% H₂).

4.3 Comparison with Other Workers

Table 4.9 tabulates the best results of this work for both 1% Au/TiO₂ SG and DP catalysts in comparison to the works by Hayashi et al. (1998). All experiments were performed at similar operating conditions i.e. calcination temperature, calcination time, feed composition, reactant flowrate, and reaction temperature.

In this work, the 1% Au/TiO₂ SG catalyst gave both higher selectivity and PO production rate when compared to the one prepared by DP method. The 1% Au/TiO₂ SG catalyst gave lower selectivity but yielded twice higher PO production rate than that of Hayashi et al. The difference in % selectivity calculation method between this work and Hayashi's work were cited in the Table. This may cause the higher % selectivity obtained by Hayashi et al.

Table 4.9 Comparison with other workers for 1% Au/TiO₂ catalysts.

	This work		Hayashi (1998)
	SG	DP	DP
Preparation method	SG	DP	DP
Surface area (m ² /g)	90	60	50
Calcination temperature (°C)	400	400	500
Calcination time (h)	5	5	2
Catalyst weight (g)	0.4	0.4	0.5
Feed composition (mole%)			
C ₃ H ₆ /O ₂ /H ₂	10/10/10	10/10/10	10/10/10
Reactant flowrate (ml/min)	70	70	33.33
Reaction temperature (°C)	80	80	50
Propylene conversion (%)	0.99 ^a	1.26 ^a	1.10 ^b
Selectivity (%)	85.00 ^c	59.90 ^c	>99 ^d
PO production rate (mmol/h/g.cat)	0.401	0.355	0.200

^a by equation (3.1)

$${}^b \%C_3H_6 \text{ conversion} = \frac{\text{moles of } C_3H_6 \text{ detected by GC}}{\left[\frac{\text{moles of } C_3H_6 \text{ fed}}{\text{moles of } CO_2 \text{ formed} / 3} \right]} * 100$$

^c by equation (3.3)

$${}^d \%selectivity \text{ to PO} = \frac{\text{moles of PO detected by GC}}{\left[\frac{\sum \text{all products detected by GC}}{\text{moles of } CO_2 \text{ formed} / 3} \right]} * 100$$