# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Catalyst Characterization

The catalysts were characterized by BET and XRD measurements to determine their surface areas and surface compositions.

### 4.1.1 Surface Area Measurement

The effects of calcination temperature and silver loading on surface area were investigated. As shown in Table 4.1, the surface area is strongly affected by the calcination temperature, but is slightly affected by the amount loading of silver. The sol-gel method produced silver supported on alumina catalysts with surface areas in the range of 320-490 $m^2/g$. Sol-gel preparation is a low temperature process, which produced catalysts with large surface areas and high porosity in mesopore and macropore ranges (Livage, 1998). Surface area of sol-gel catalyst depended on thermal treatment. The BET surface area decreased with an increase in calcination temperature. At 600°C which was the highest calcination temperature investigated, $Ag/Al_2O_3$ supported catalyst showed the lowest surface area. Because at higher calcination temperature sintering occurred. The silver metal agglomerated into the bigger particles so it could block the pore of support. At higher silver loading, lower surface area was obtained. Because more silver particles attached on the surface of support, they could fill or block in pores of alumina support.

The sol-gel alumina supported catalysts had the narrow pore size distribution. The average pore radius of sol-gel prepared silver alumina supported catalyst was about 7.2±0.2°A.

**Table 4.1** Surface area and mean pore size of silver supported catalysts

| Catalyst* | Calcination temperature (°C) | Surface area (m²/g) | Pore volume (cm³/g) | Pore radius (°A) |
|---|---|---|---|---|
| $Al_2O_3$ | 500 | 490.2 | 0.1685 | 6.873 |
| 1 % $Ag/Al_2O_3$ | 500 | 436.4 | 0.1560 | 7.148 |
| 3 % $Ag/Al_2O_3$ | 500 | 424.5 | 0.1084 | 7.314 |
| 5 % $Ag/Al_2O_3$ | 500 | 398.6 | 0.1192 | 7.412 |
| 9 % $Ag/Al_2O_3$ | 500 | 387.3 | 0.1263 | 7.004 |
| 10 % $Ag/Al_2O_3$ | 500 | 373.6 | 0.1336 | 7.152 |
| $Al_2O_3$ | 550 | 391.1 | 0.1416 | 7.242 |
| 1 % $Ag/Al_2O_3$ | 550 | 402.7 | 0.1442 | 7.159 |
| 3 % $Ag/Al_2O_3$ | 550 | 395.0 | 0.1299 | 7.129 |
| 5 % $Ag/Al_2O_3$ | 550 | 382.0 | 0.1252 | 7.442 |
| 9 % $Ag/Al_2O_3$ | 550 | 358.5 | 0.1089 | 7.416 |
| 10 % $Ag/Al_2O_3$ | 550 | 330.5 | 0.1236 | 7.478 |
| 5 % $Ag/Al_2O_3$ | 570 | 359.6 | 0.1285 | 7.492 |
| 9 % $Ag/Al_2O_3$ | 570 | 357.5 | 0.1109 | 7.326 |
| $Al_2O_3$ | 600 | 358.8 | 0.1292 | 7.203 |
| 1 % $Ag/Al_2O_3$ | 600 | 363.3 | 0.1322 | 7.276 |
| 3 % $Ag/Al_2O_3$ | 600 | 342.5 | 0.1253 | 7.244 |
| 5 % $Ag/Al_2O_3$ | 600 | 372.8 | 0.1299 | 7.529 |
| 9 % $Ag/Al_2O_3$ | 600 | 332.3 | 0.1183 | 7.233 |
| 10 % $Ag/Al_2O_3$ | 600 | 322.4 | 0.1163 | 7.216 |

* prepared by sol-gel method

Table 4.2 shows the BET surface area of gold catalysts prepared by sol-gel and deposition-precipitation (DP) methods. The gold

supported $Al_2O_3$ catalysts that were prepared by sol-gel method have much higher surface areas than those gold supported on $TiO_2$ catalysts prepared by DP method. For DP method, the surface area depended on the initial surface area of support, which was about 17 $m^2/g$ for $TiO_2$. Because this preparation method produced a deposition of gold particle only outside the support pores (Perego and Villa, 1997). The surface area of gold catalysts prepared by deposition-precipitation was slightly effected by calcination temperature. With an increase in calcination temperature, the surface area decreased.

**Table 4.2** Surface area of gold supported catalysts

| Catalyst | Calcination temperature ($^oC$) | Surface area ($m^2/g$) |
|---|---|---|
| 2.5 % Ag + 2.5 % Au on $Al_2O_3$ SG | 600 | 296.7 |
| 1 % Au/$Al_2O_3$ SG | 400 | 514.6 |
| 1 % Au/$TiO_2$ DP | 400 | 16.4 |
| 1 % Au/$TiO_2$ DP | 500 | 15.7 |
| 1.5 % Au/$TiO_2$ DP | 500 | 14.2 |
| $TiO_2$ support | - | 17.2 |

Notes:　SG - Sol-gel preparation method

　　　　DP - Deposition-precipitation method

### 4.1.2 X-ray Diffraction Analysis

X-ray diffraction analysis was carried out for all silver catalysts. The XRD pattern in Figure 4.1 shows that all silver catalysts mainly consisted of $Al_2O_3$ which were amorphous. It can be seen that for higher silver loading catalysts, the XRD patterns were identical to the pure $Al_2O_3$ catalyst. All peaks represented the $Al_2O_3$ compound. There was no evidence of metallic
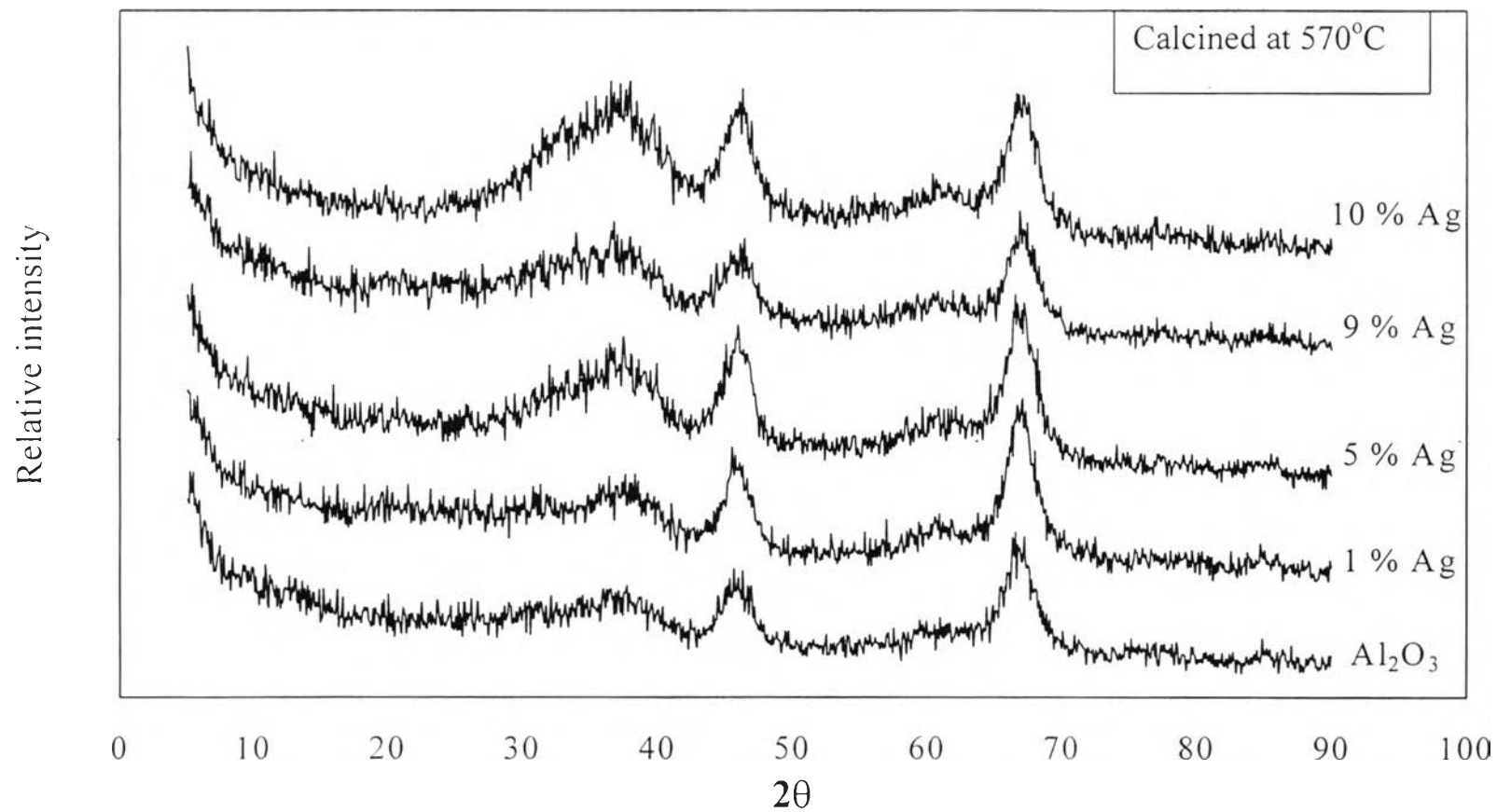
**Figure 4.1** XRD patterns of silver supported on $Al_2O_3$ at different loadings of Ag.

silver in the sol-gel catalysts. This was due to the fact that silver had very good dispersion on alumina active surface and was stabilized by alumina support.

Figure 4.2 shows the XRD spectra for 1, 5, and 10 % $Ag/Al_2O_3$ sol-gel catalysts at different calcination temperatures. The XRD spectra showed similar results as seen in Figure 4.1. At different calcination temperatures there was no effect on XRD patterns. The calcination temperatures in the range of 500-600°C could not change the crystal structure of the support. It produced the same alumina support crystal phase, which was gamma alumina.

## 4.2 Catalyst Activity Testing

The catalyst activity testing was divided into two parts. Part one was the study on activity of the silver supported on alumina catalysts prepared by sol-gel method while the other part was the activity testing on the gold supported on $TiO_2$ catalysts prepared by DP method. All experiments were accomplished at different reaction conditions.

### 4.2.1 Activity of Silver Supported Catalysts

The catalytic activity of $Ag/Al_2O_3$ prepared by sol-gel catalysts was investigated at different % loadings of silver, calcination temperatures, feed stream compositions and space velocities. Conditions for all experimental runs are shown in Table 4.3.
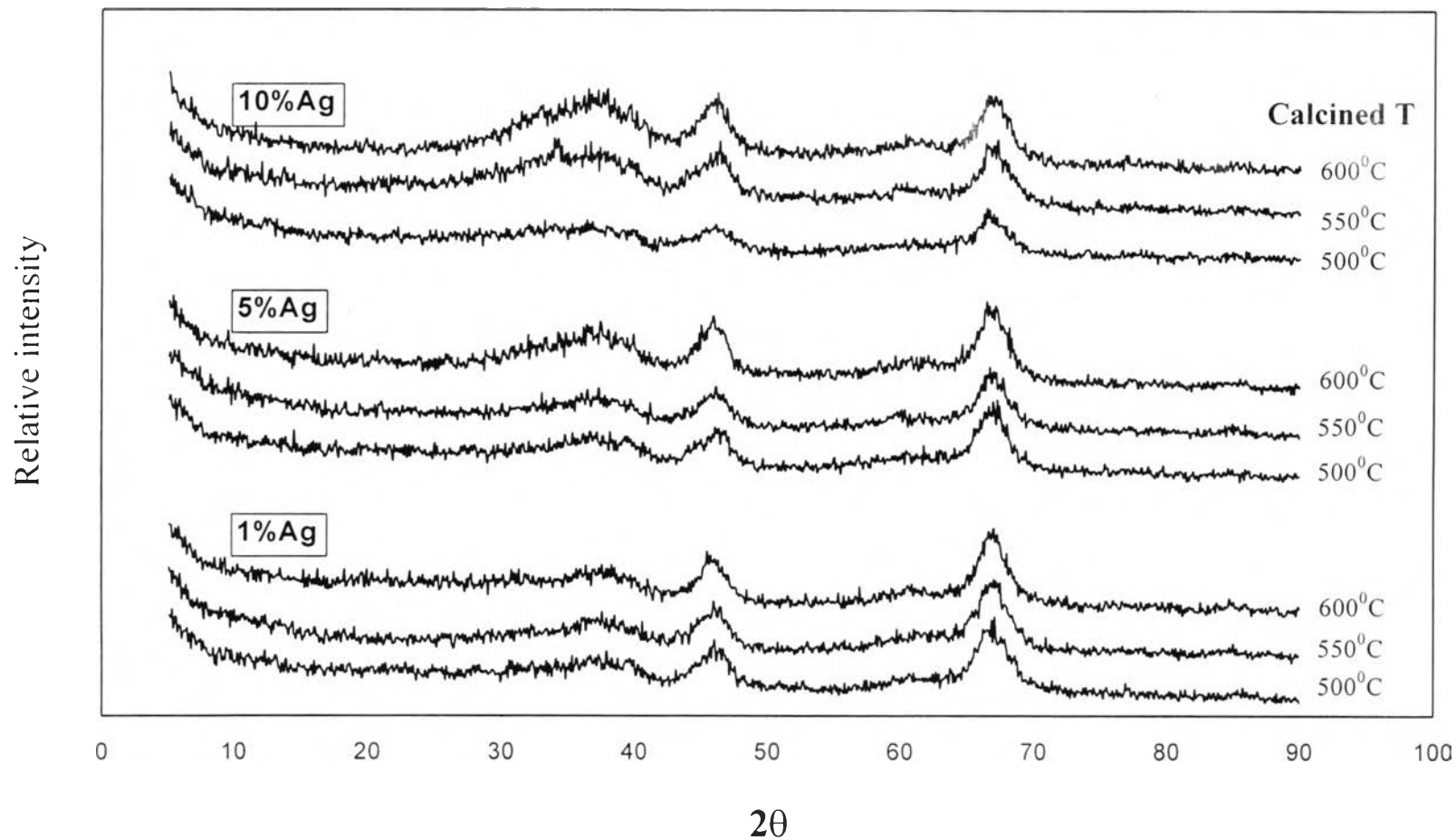
**Figure 4.2** XRD patterns at different loadings and calcination temperatures of $Ag/Al_2O_3$ catalysts.

**Table 4.3** Experimental runs over silver supported catalysts

| Catalyst* | Calcination temp ($^{\circ}$C) | $C_3H_6:O_2:H_2$ ( mol %) | Total flow rate (ml/min) | Reaction temp ($^{\circ}$C) |
|---|---|---|---|---|
| 1 % Ag/Al$_2$O$_3$ SG | 500 | 10 : 10 : 10 | 50 | 50-225 |
| 1 % Ag/Al$_2$O$_3$ SG | 600 | 10 : 10 : 10 | 50 | 50-200 |
| 5 % Ag/Al$_2$O$_3$ SG | 550 | 10 : 10 : 0 | 100 | 100-225 |
| 5 % Ag/Al$_2$O$_3$ SG | 570 | 5 : 5 : 0 | 100 | 100-225 |
| 5 % Ag/Al$_2$O$_3$ SG | 570 | 5 : 5 : 5 | 100 | 100-225 |
| 5 % Ag/Al$_2$O$_3$ SG | 570 | 10 : 10 : 0 | 100 | 100-225 |
| 5 % Ag/Al$_2$O$_3$ SG | 570 | 10 : 10 : 5 | 100 | 100-225 |
| 10 % Ag/Al$_2$O$_3$SG | 500 | 10 : 10 : 5 | 100 | 100-200 |
| 10 % Ag/Al$_2$O$_3$SG | 570 | 3.3 :10 :3.3 | 100 | 100-225 |
| 10 % Ag/Al$_2$O$_3$SG | 570 | 10 : 10 : 0 | 100 | 100-225 |
| 10 % Ag/Al$_2$O$_3$SG | 570 | 10 : 10 : 5 | 100 | 200 |
| 10 % Ag/Al$_2$O$_3$SG | 570 | 10 : 10 : 5 | 80 | 200 |
| 10 % Ag/Al$_2$O$_3$SG | 570 | 10 :10 :5 | 50 | 80-250 |

* prepared by sol-gel method

The catalytic activity of Ag/Al$_2$O$_3$ catalysts was selective to PO only at some operating conditions. Some of the results are as shown in Table 4.4.
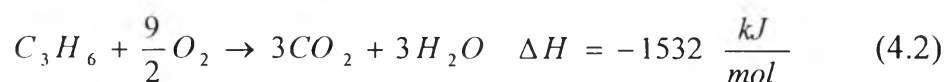
**Table 4.4** Catalytic activity of $Ag/Al_2O_3$ catalysts

| Catalyst | | Reaction temperature ($^{o}C$) | | | | |
|---|---|---|---|---|---|---|
| | | 80 | 100 | 150 | 200 | 225 |
| 1 % $Ag/Al_2O_3$* Calcined T. 600$^{o}$C | PO production rate (mmol/hr/g cat.) | 0.043 | 0.029 | 0.031 | 0.033 | - |
| | PO selectivity (%) | 14.6 | 39.6 | 4.4 | 0.6 | - |
| 5 % $Ag/Al_2O_3$** Calcined T. 550$^{o}$C | PO production rate (mmol/hr/g cat.) | - | 0.066 | 0.188 | 0 | 0 |
| | PO selectivity (%) | - | 51.0 | 10.0 | 0 | 0 |
| 10 % $Ag/Al_2O_3$*** Calcined T. 570$^{o}$C | PO production rate (mmol/hr/g cat.) | 0.430 | 0.118 | 0.089 | 0.063 | 0 |
| | PO selectivity (%) | 33.3 | 15.84 | 25.34 | 0.11 | 0 |

\* feed 10 : 10 : 10 of $C_3H_6$ : $O_2$ : $H_2$, total flow 50 ml/min

\*\* feed 10 : 10 : 0 of $C_3H_6$ : $O_2$ : $H_2$, total flow 50 ml/min

\*\*\* feed 10 : 10 : 5 of $C_3H_6$ : $O_2$ : $H_2$, total flow 50 ml/min

Silver catalysts showed low selectivity to PO and produced $CO_2$ and $H_2O$ as major products. Only at some reaction temperatures that PO was formed. At reaction temperatures below 150$^{o}$C, $Ag/Al_2O_3$ catalyst produced PO in the higher rate and higher selectivity. But at higher reaction temperature $CO_2$ and $H_2O$ were produced as major products because $Ag/Al_2O_3$ catalyst prepared by sol-gel method had very high surface area and active site, the total oxidation was easily occurred. There are two major competitive reactions which are the partial oxidation (or epoxidation of propylene) and the total oxidation of propylene.

$$C_3H_6 + \frac{1}{2}O_2 \rightarrow C_3H_6O \qquad \Delta H = -206 \ \frac{kJ}{mol} \qquad (4.1)$$

$$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O \quad \Delta H = -1532 \ \frac{kJ}{mol} \qquad (4.2)$$

From the thermodynamic data, the total oxidation was easier to occur as it is more exothermic.

When using supported silver catalyst, the low selectivity of propylene partial oxidation results from an increasing in the combustion rate coupled with a decreasing in epoxidation rate. Propylene combustion was believed to initiate by methyl hydrogen abstraction, ultimately leading to $CO_2$ and $H_2O$. Coadsorbed water and PO do not react over silver catalyst. The interactions between propylene oxide and oxygen appear to form hydroxyl groups that lead to low selectivity of partial oxidation of propylene (Ranney, 1998).

### 4.2.1.1 Effect of Calcination Temperature

The calcination is useful for the removal of extraneous materials, which contaminated in the catalyst during the forming operations. During the calcination, a sintering of the precursor or the formed oxide and a reaction of formed oxide with the support can occur.

Figure 4.3 shows the effect of calcination temperature on 1 % $Ag/Al_2O_3$ supported sol-gel catalyst at 10 % propylene, 10 % oxygen, and 10 % hydrogen feeding composition with 50 ml/min reactant flow rate. At 500 and 600°C calcination temperature, the PO production rate was nearly the same. The calcination temperatures in the range of 500-600 °C had no effect on the activity of propylene epoxidation.
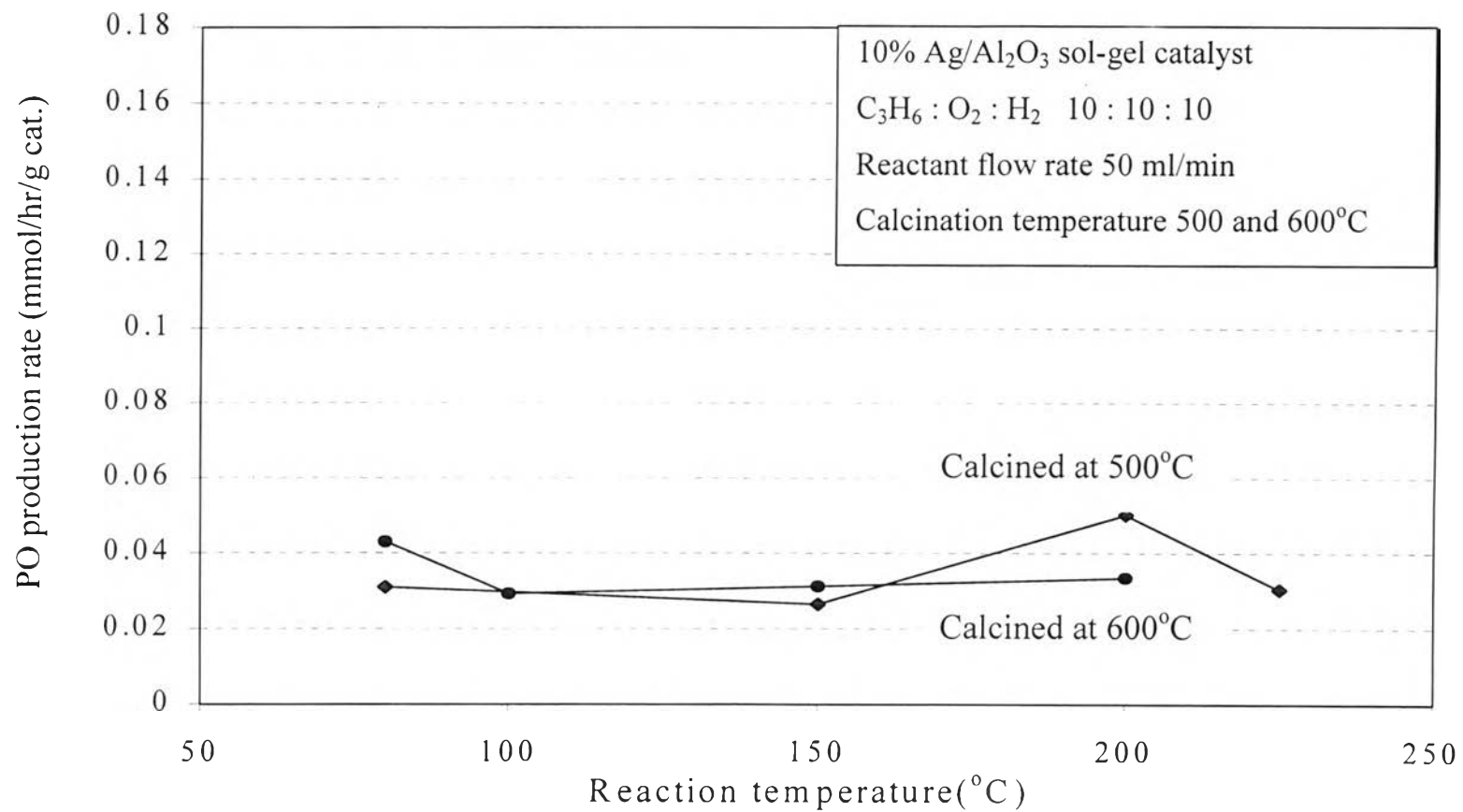
**Figure 4.3** Effect of calcination temperature.

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### 4.2.2 Activity of Gold Supported Catalysts

The catalytic activities of gold supported on $Al_2O_3$ prepared by sol-gel and $TiO_2$ prepared by deposition-precipitation catalysts were investigated at different operating conditions as shown in Table 4.5.

**Table 4.5** Experimental runs over gold supported catalysts

| Catalyst | Calcined temp ($^oC$) | $C_3H_6:O_2:H_2$ (mol %) | Total flow (ml/min) | Reaction temp ($^oC$) |
|---|---|---|---|---|
| 1 % Au/TiO$_2$ DP | 400 | 10 : 10 : 10 | 50 | 50-100 |
| 1 % Au/TiO$_2$ DP | 400 | 10 : 10 : 10 | 100 | 50-200 |
| 1 % Au/TiO$_2$ DP | 400 | 10 : 10 : 0 | 100 | 80 |
| 1 % Au/TiO$_2$ DP | 400 | 10 : 10 : 5 | 100 | 80 |
| 1 % Au/TiO$_2$ DP | 400 | 10 : 10 : 20 | 100 | 80-175 |
| 1 % Au/Al$_2$O$_3$ SG | 400 | 10 : 10 : 10 | 50 | 50-175 |
| 1.5 % Au/TiO$_2$ DP | 500 | 10 : 10 : 10 | 50 | 50-200 |
| 5 % Au/Al$_2$O$_3$ SG | 300 | 10 : 10 : 5 | 50 | 100-250 |

Notes:   DP - deposition-precipitation method

SG - sol-gel preparation method

#### 4.2.2.1  Effect of Catalyst Type

Table 4.6 shows comparison between the catalytic activity of 1 % Au over $Al_2O_3$ prepared by sol-gel method and $TiO_2$ prepared by deposition-precipitation method catalysts at different reaction temperatures. The 1 % Au/TiO$_2$ catalysts showed higher PO production rate for all reaction temperatures investigated. Because DP method usually forms hemispherical gold particle in shape attached to flat planes providing longest distance around perimeter interface (Haruta, 1997a) which is an active surface that was selective to partial oxidation of propylene. At 50 and 80°C the PO production

rate of 1 % Au/TiO₂ catalyst was about three times higher than Au/Al₂O₃ supported catalyst. The 100 % PO selectivity was obtained for both supported catalysts at 50°C. But the selectivity over Au/TiO₂ catalyst decreased to 68 % at 80°C and continously decreased at higher reaction temperature. This is due to there was enough energy supplied for total oxidation at higher temperature. Gold supported on TiO₂ prepared by DP method catalyst produced higher PO production rate but lower selectivity at high reaction temperature.

**Table 4.6** Comparison between 1 % Au/Al₂O₃ and 1 % Au/TiO₂ catalysts

| Catalyst | | Reaction temperature (°C) | | |
|---|---|---|---|---|
| | | 50 | 80 | 100 |
| 1 % Au/Al₂O₃ Calcined at 400°C | PO production rate (mmol/hr/g cat.) | 0.017 | 0.026 | 0.055 |
| | PO selectivity (%) | 100 | 100 | 64.77 |
| 1 % Au/TiO₂ Calcined at 400°C | PO production rate (mmol/hr/g cat.) | 0.047 | 0.074 | 0.063 |
| | PO selectivity (%) | 100 | 67.7 | 50.5 |

*4.2.2.2 Effect of Gas Flow Rate*

Table 4.7 shows the effect of gas flow rate at 50 and 100 ml/min on PO production rate. The reactions were carried out at 80°C over 1 % Au/TiO₂ prepared by DP method catalyst, calcined at 400°C. It can be seen that at higher gas flow rate, the production rate of propylene oxide and PO yield increased. The higher space velocity is the shorter contact time so it can inhibit the total oxidation of propylene. The 100 ml/min total flow rate produced higher activity for selective oxidation over this 1 % Au/TiO₂ catalyst at 10 % C₃H₆, 10 % O₂ and 10 % H₂ feed composition at 80°C, which 100 % selectivity was obtained.

**Table 4.7** The effect of total flow rate on 1 % $Au/TiO_2$

| Total flow rate (ml/min) | 50 | 100 |
|---|---|---|
| Calcination temperature (°C) | 400 | 400 |
| Feed composition $C_3H_6 : O_2 : H_2$ | 10 : 10 : 10 | 10 : 10 : 10 |
| Reaction temperature (°C) | 80 | 80 |
| PO yield (%) | 0.0020 | 0.0024 |
| PO production rate (mmol /hr /g cat.) | 0.074 | 0.200 |
| PO selectivity (%) | 100 | 100 |

*4.2.2.3 Effect of % Hydrogen in the Reactant Gas*

The effect of % hydrogen in the reactant gas, varied between 0 to 20 % $H_2$, on the PO production rate is shown in Figure 4.4. The reaction was carried out over 1 % $Au/TiO_2$ catalyst prepared by DP method with 100 ml/min gas flow rate. At hydrogen feed composition in the range of 0 to 10 %, the PO production rates were nearly the same. But it sharply decreased thereafter. Because of the higher amount of hydrogen used, the oxygen would be more preferential to react with hydrogen. The water formation occurred, resulting in a decrease in PO production rate. The presence of $H_2$ in the reactant mixture could enhance the partial oxidation of propylene. Hayashi *et al.* (1996) found that with the presence of hydrogen in feed composition over $Au/TiO_2$ based catalysts, dioxygen can be assumed to be transformed through the reduction with hydrogen to an active species, which then had the ability to selectively oxidize hydrocarbon to oxygenate. Hydrogen was consumed more than the stoichiometric amount required to produce oxygenate.

Ranney (1998) had found that a decrease in the PO desorption activation energy is one of the reasons why water vapor can enhance
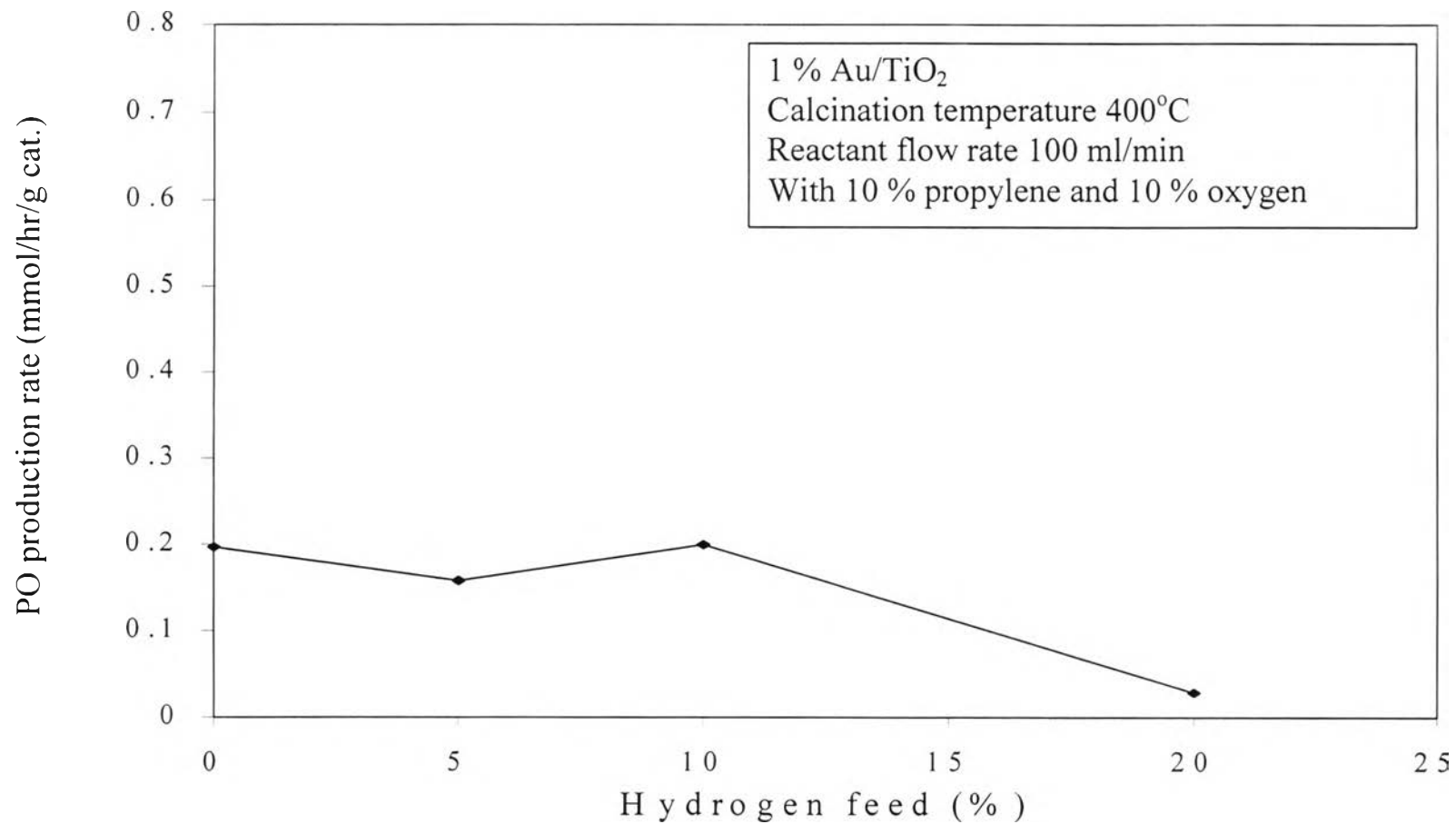
**Figure 4.4** Effect of % $H_2$ in the reactant gas.

the selectivity of propylene partial oxidation by reducing the concentration of PO on the catalyst surface during reaction.

### 4.2.2.4 Comparison with Other workers

The $Au/TiO_2$ supported catalysts prepared by DP method showed the best activity of PO production. The highest PO production rate was obtained at 80°C with 10 % propylene, 10 % oxygen, and 10 % hydrogen feed compositions. These results are comparable to Hayashi et al. (1998) work as shown in Table 4.8.

**Table 4.8** Comparison with other workers

| 1% Au/TiO₂ | This work | Hayashi's work |
|---|---|---|
| $TiO_2$ support surface area ($m^2/g$) | 20 | 50 |
| Feed composition $C_3H_6 : O_2 : H_2$ | 10 : 10 : 10 | 10 : 10 : 10 |
| Reaction temperature (°C) | 80 | 80 |
| Space velocity ($hr^{-1}$) | $0.92 * 10^4$ | $1.75 * 10^4$ |
| Propylene conversion (%) | 0.87 | 1.1 |
| PO production rate (mmol /hr /g cat.) | 0.205 | 0.200 |
| PO selectivity (%) | 100 | > 99 |

Hayashi et al. (1998) had studied over $Au/TiO_2$ catalyst. They found that when using 1% $Au/TiO_2$ catalyst with the operating condition as seen in Table 4.8, over 99% selectivity was obtained. It can be seen that in this work the lower propylene conversion was obtained with the higher PO production rate compared to their work. The higher PO production rate was obtained due to the difference in the $TiO_2$ support surface area and the space velocity.