

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

The specific surface areas of the sol-gel silver supported on alumina ($\text{Ag}/\text{Al}_2\text{O}_3$) catalysts and impregnated silver supported on α -alumina ($\text{Ag}/\alpha\text{-Al}_2\text{O}_3$) catalysts were determined by five-point BET method using surface area analyzer.

The effect of silver loading on surface area, pore volume, and pore radius of both catalysts are shown in Table 4.1. As shown in the table, the surface areas of all $\text{Ag}/\text{Al}_2\text{O}_3$ sol-gel catalysts, are almost the same and no significant changes found from pure alumina. Also the surface areas of all $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts are close to each other and also to surface area of pure α -alumina. It seems to be that the silver constitutes low fraction of the surface area in these types of catalysts. All catalysts have a very small pore size between 3^0A and 7^0A .

Phase composition of all fresh catalysts was determined by XRD analysis. The XRD patterns for Al_2O_3 , 3, 5 and 10 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ sol-gel catalysts, which calcined in air at 600^0C for 5 hours, are shown in Figure 4.1. All patterns appeared to be amorphous in structures. Moreover, these patterns described that no crystals of both silver and silver oxide are detected and patterns of different silver loading catalysts were the same as the pattern of Al_2O_3 . This can indicate that either no crystallite of silver and silver oxide form is present in the catalyst or the crystallites are too small to be detected by this method. These small crystals are known to exhibit no catalytic activity possibly due to the over-oxidation of small Ag particles to inactive Ag_2O , which can decrease the epoxidation rate.

Table 4.1 Catalyst Characterization

Catalyst	Method	T (⁰ C)	Surface Area ^① (m ² /g)	Pore Volume ^② (cm ³ /g)	Pore Radius ^③ (⁰ A)
Al ₂ O ₃	Sol-Gel	600 ^⑤	358.8	0.12920	7.203
3%Ag/Al ₂ O ₃	Sol-Gel	600 ^⑤	342.5	0.12530	7.244
5%Ag/Al ₂ O ₃	Sol-Gel	600 ^⑤	372.8	0.12990	7.529
10%Ag/Al ₂ O ₃	Sol-Gel	600 ^⑤	322.4	0.11630	7.216
α-Al ₂ O ₃	IWI ^④	500 ^⑥	0.5438	0.00010	3.686
13%Ag/α-Al ₂ O ₃	IWI	500 ^⑥	0.8844	0.00016	5.511
15%Ag/α-Al ₂ O ₃	IWI	500 ^⑥	0.5629	0.00015	5.288
17%Ag/α-Al ₂ O ₃	IWI	500 ^⑥	0.4568	0.00012	5.441
20%Ag/α-Al ₂ O ₃	IWI	500 ^⑥	0.7394	0.00015	4.012

① : From 5 point BET

② : Total pore volume for pores with radius less than 8⁰A at P/P₀=0.10841

③ : Average pore radius

④ : Incipient wetness impregnation

⑤ : Calcine in air

⑥ : Calcine in 10% O₂

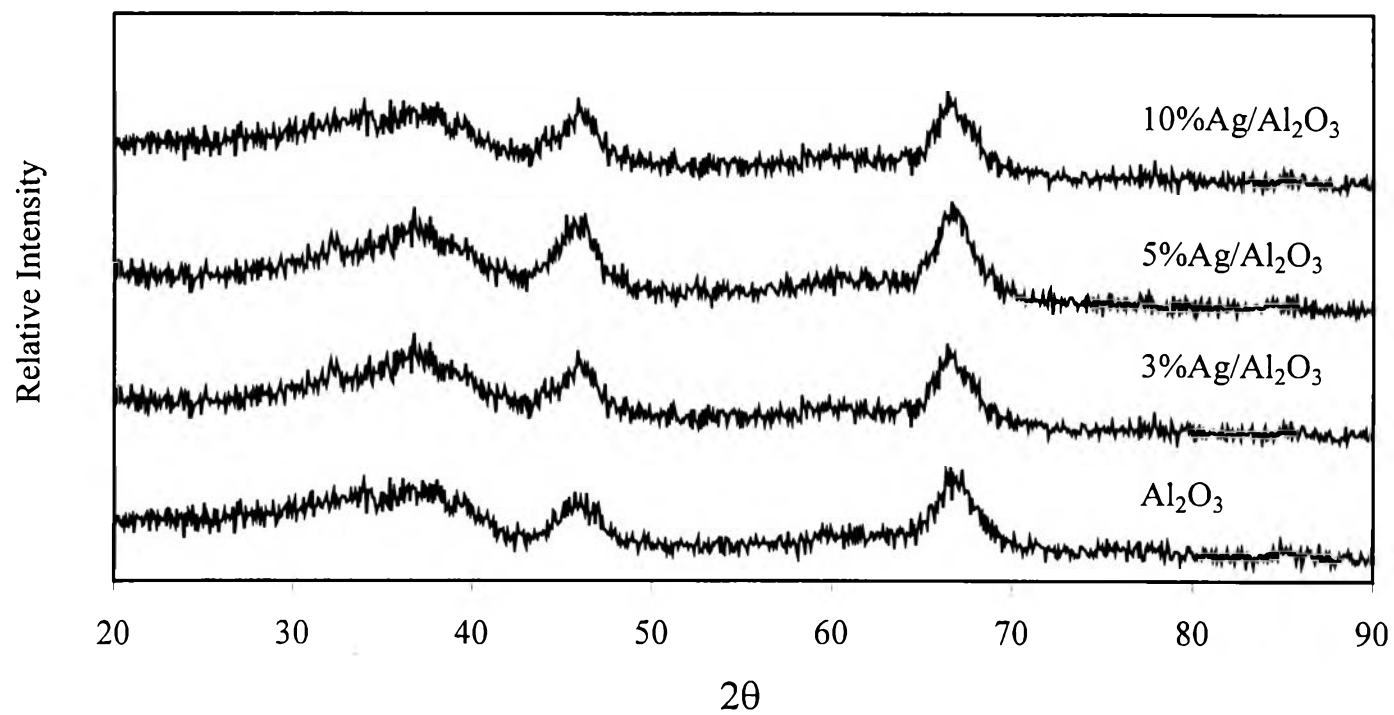


Figure 4.1 X-ray diffraction patterns for (HSA) Ag/Al₂O₃ sol-gel catalysts at different silver loadings.

The XRD patterns of α -Al₂O₃, 13, 15, 17, 20 wt% Ag/ α -Al₂O₃ catalysts, which calcined in 10% O₂ (40 ml/min) at 500⁰C for 2 hours, are shown in Figure 4.2. The peaks due to the silver and silver oxide were sharply increased when the silver loading was increased. In addition, from the calculation of crystallite size, the crystallite size of silver became larger with increasing silver loading. The crystallite size of silver in the range 268-366 ⁰A was found. This is possibly due to an increase in silver concentration combined with silver agglomeration and silver attenuation. The large silver crystal is more active for the ethylene epoxidation than the small one (Goncharova *et al.*, 1995).

4.2 Catalyst Activity Measurement

Catalytic activity measurement for selective oxidation of ethylene with oxygen over both (HSA) Ag/Al₂O₃ sol-gel catalysts and (LSA) Ag/ α -Al₂O₃ catalysts were carried out at atmospheric pressure in the fixed-bed flow reactor.

4.2.1 Catalytic Activity Test for (HSA) Ag/Al₂O₃ Sol-Gel Catalyst

4.2.1.1 *Effect of Silver Loading*

The Ag/Al₂O₃ sol-gel catalysts with different silver loadings of 3, 5, and 10 wt% were used to determine the effect of silver loading on the selective oxidation of ethylene. The experimental data showed that these (HSA) Ag/Al₂O₃ sol-gel catalysts are non-selective catalysts and only have a higher selectivity to combustion products. Thus clearly indicating that EO oxidizes readily over these (HSA) catalysts. The absence of EO as a product was mainly due to the secondary reaction of EO oxidation, and the primary oxidation of ethylene directly to carbon dioxide and water.

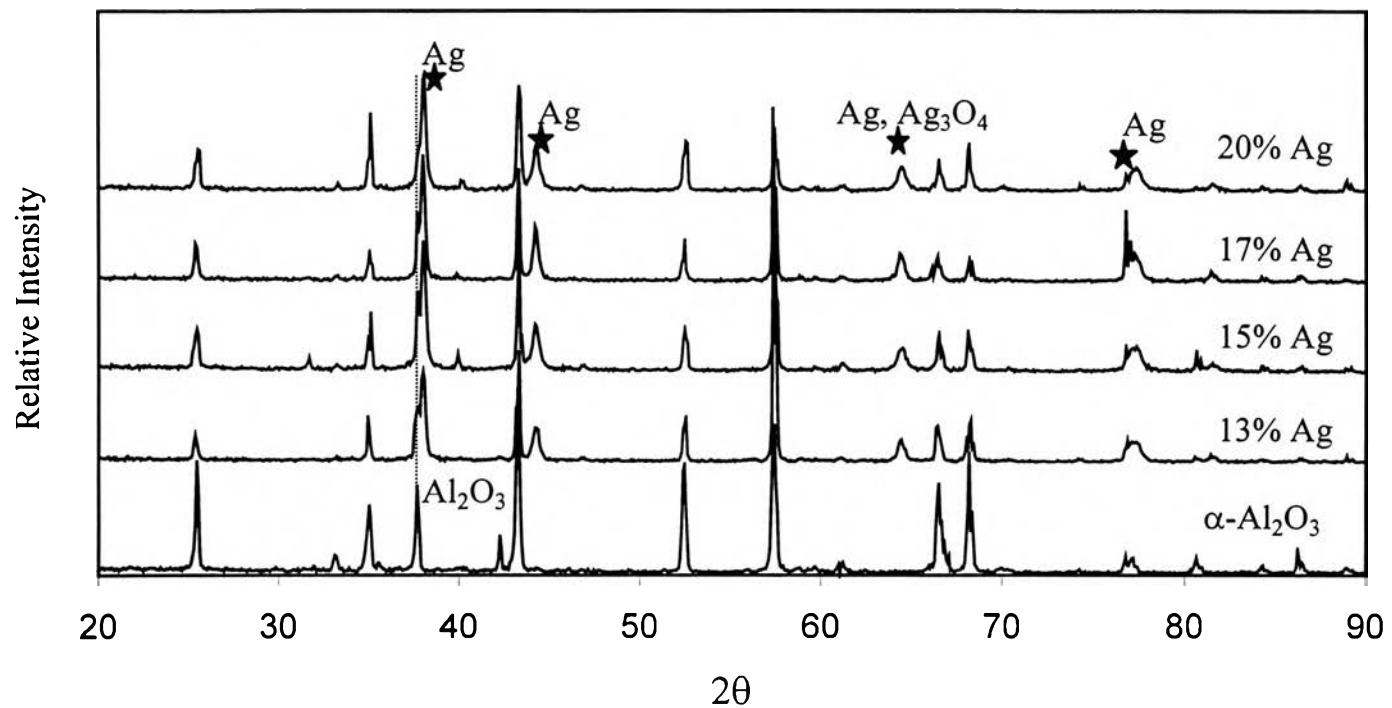


Figure. 4.2 X-ray diffraction patterns for (LSA) Ag/α-Al₂O₃ catalysts at different silver loadings.

In addition, the secondary reaction including isomerization of EO to acetaldehyde proposed as the principal reason for poor selectivity (Mao and Vannice, 1995). Hence, the dependence of catalytic activity, in terms of carbon dioxide formation, on the silver loading at various reaction temperatures, is shown in Figure 4.3.

As seen from Figure 4.3, the reaction started to occur at a temperature of 200⁰C and the higher silver loading was more active and gave the higher carbon dioxide formation.

4.2.1.2 Effect of Hydrogen Gas

Hydrogen was used as a gas phase promoter and tested the promoting effect on the catalytic activity of (HSA) Ag/Al₂O₃ sol-gel catalyst. This result is shown in Figure 4.4. As shown in the figure, when hydrogen was used as promoter, that reaction started to occur at lower temperature and more carbon dioxide produced than without hydrogen. However, there was no ethylene oxide occurred. This may be due to the hydrogen enhances the combustion reaction rate.

4.2.1.3 Effect of Calcination and Oxidation-Reduction Method

Since the partial oxidation is favored on the metallic silver, the (HSA) Ag/Al₂O₃ sol-gel catalysts were calcined in pure oxygen atmosphere and then reduced with hydrogen to get metallic silver. From the experimental results, despite the metallic silver form, the final products were carbon dioxide and water. The effect of oxidation-reduction treatment can be expressed in terms of carbon dioxide formation and is shown in Figure 4.5.

As shown in the figure, the reduced catalyst produced more carbon dioxide while the oxidized catalyst gave low amount of carbon dioxide for both presence and absence of hydrogen. This could be due to the formation of metallic silver when a catalyst was reduced with hydrogen. Not only the hydrogen reduced the catalyst to metallic silver but also when it was

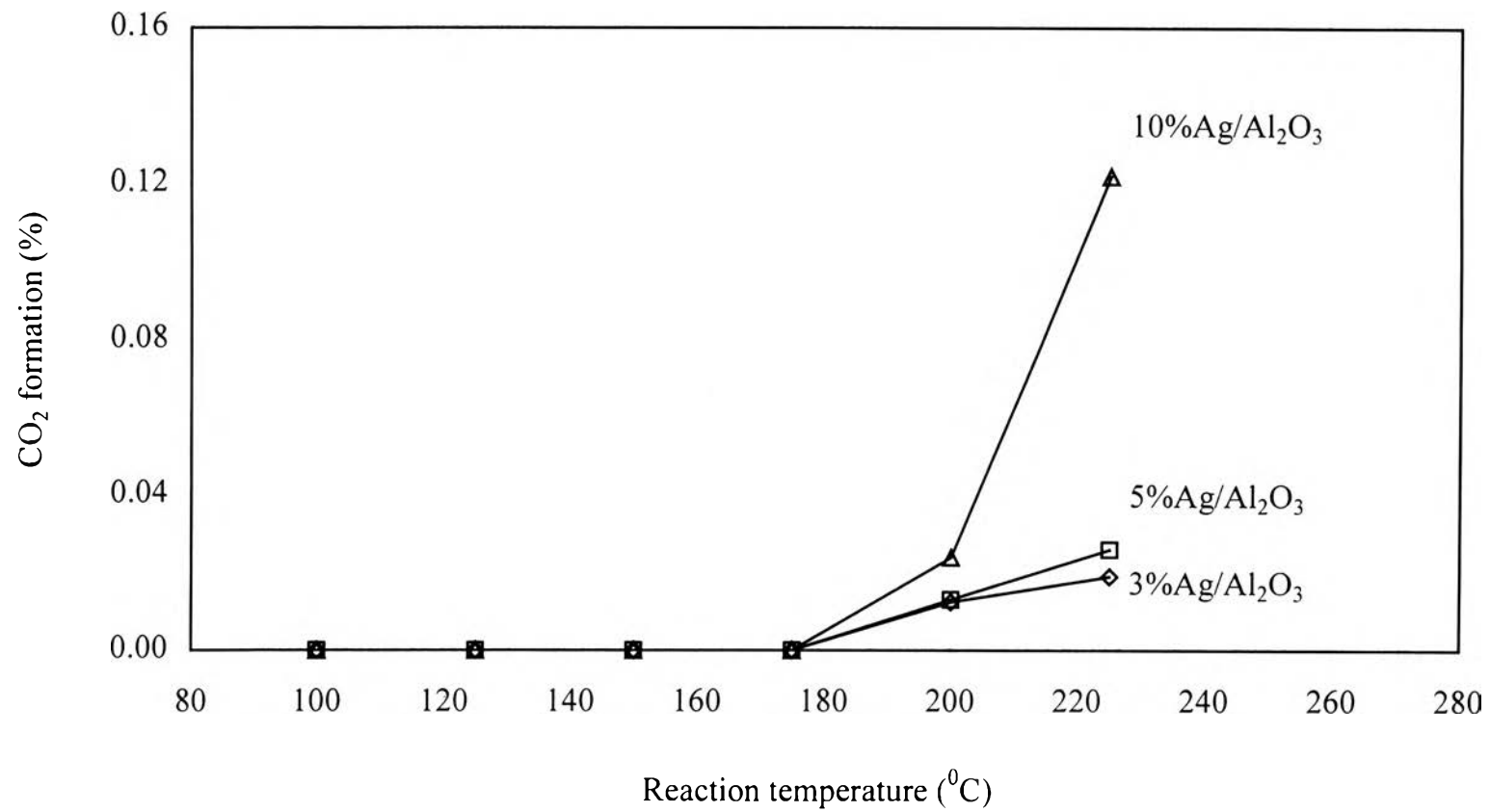


Figure 4.3 Effect of silver loading on activity of (HSA) Ag/Al₂O₃ sol-gel catalysts at different reaction temperatures.

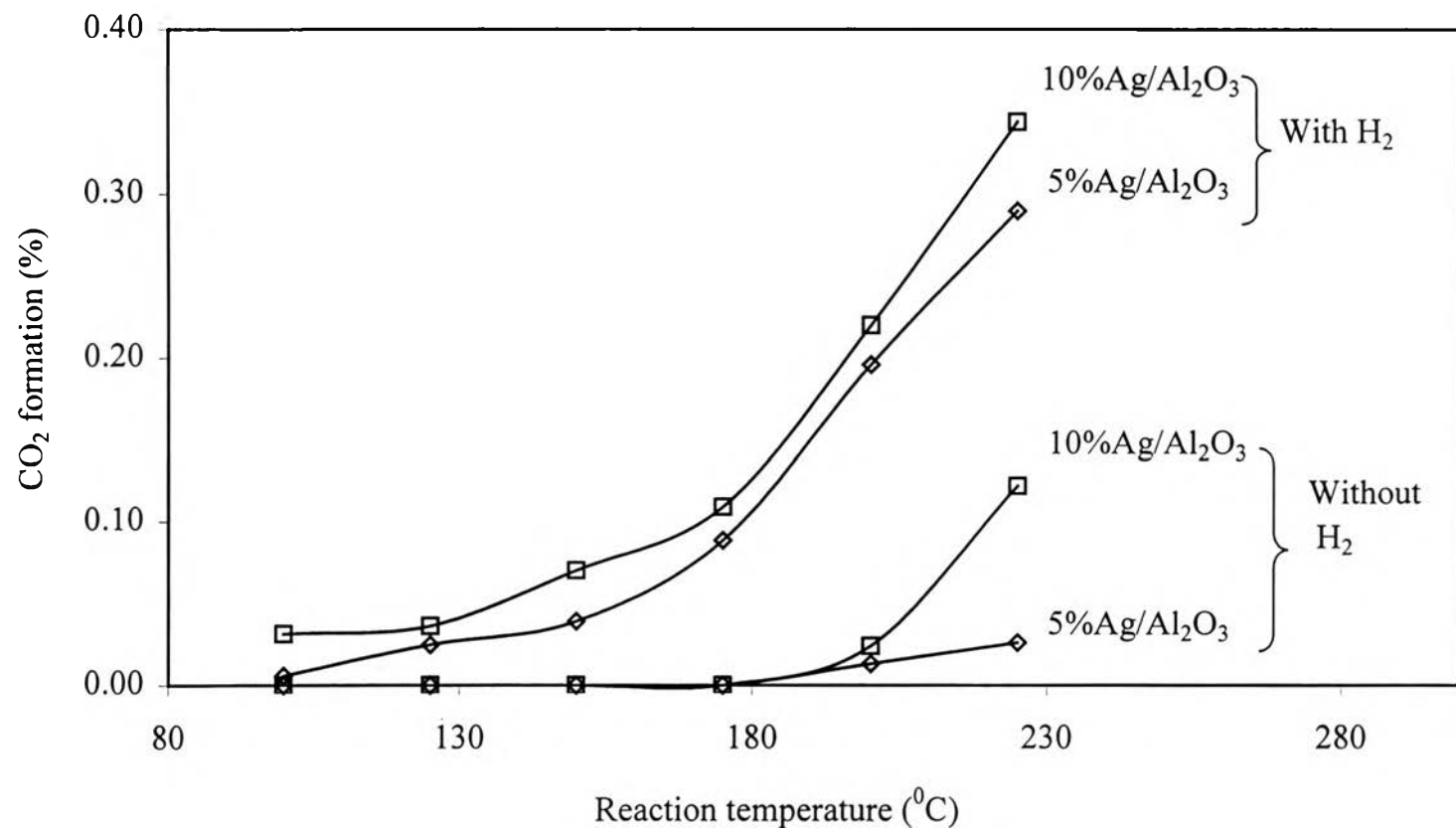


Figure 4.4 Effect of hydrogen on activity of (HSA) Ag/Al₂O₃ sol-gel catalysts at different reaction temperatures.

used as a gas phase promoter, it could enhance the water formation, which in turn could oxidize the hydrocarbon faster.

4.2.2 Catalytic Activity Test for (LSA) Ag/ α -Al₂O₃ Catalyst

4.2.2.1 *Effect of Silver Loading*

To investigate the effect of silver loading on the activity of (LSA) Ag/ α -Al₂O₃ catalyst for selective oxidation of ethylene, experiments were carried out using (LSA) Ag/ α -Al₂O₃ catalysts with the different silver loadings of 13, 15, 17, and 20 wt%.

All the (LSA) Ag/ α -Al₂O₃ catalysts had selectivities to ethylene oxide (EO). The effect of silver loading on the selectivity to EO and percent yield of EO at different reaction temperatures are shown in Figures 4.6 and 4.7 respectively.

As shown in Figure 4.6, the selectivities to EO for all catalysts decreased with increasing the reaction temperature. The 15 wt% (LSA) Ag/ α -Al₂O₃ catalyst gave a maximum selectivity to EO of 72% with 1.8% yield of EO at the reaction temperature of 210⁰C. The change in selectivity with varying silver loading was possibly due to an increase in silver concentration combined with increase in catalytic activity. However, when too high silver loading was used, the catalyst became too active and produced more carbon dioxide and decrease in EO production. This effect can be seen at the 17 and 20 wt% Ag/ α -Al₂O₃ catalyst.

Figure 4.7 indicates that yield of EO for all (LSA) Ag/ α -Al₂O₃ catalysts increased with increasing temperature. The 15 wt% Ag/ α -Al₂O₃ catalyst gave higher yield of EO than other silver loading catalysts. This is due to the more carbon dioxide formation at 17 and 20 wt% silver loadings and 13 wt% silver catalyst has lower activity to produce EO than higher silver loading.

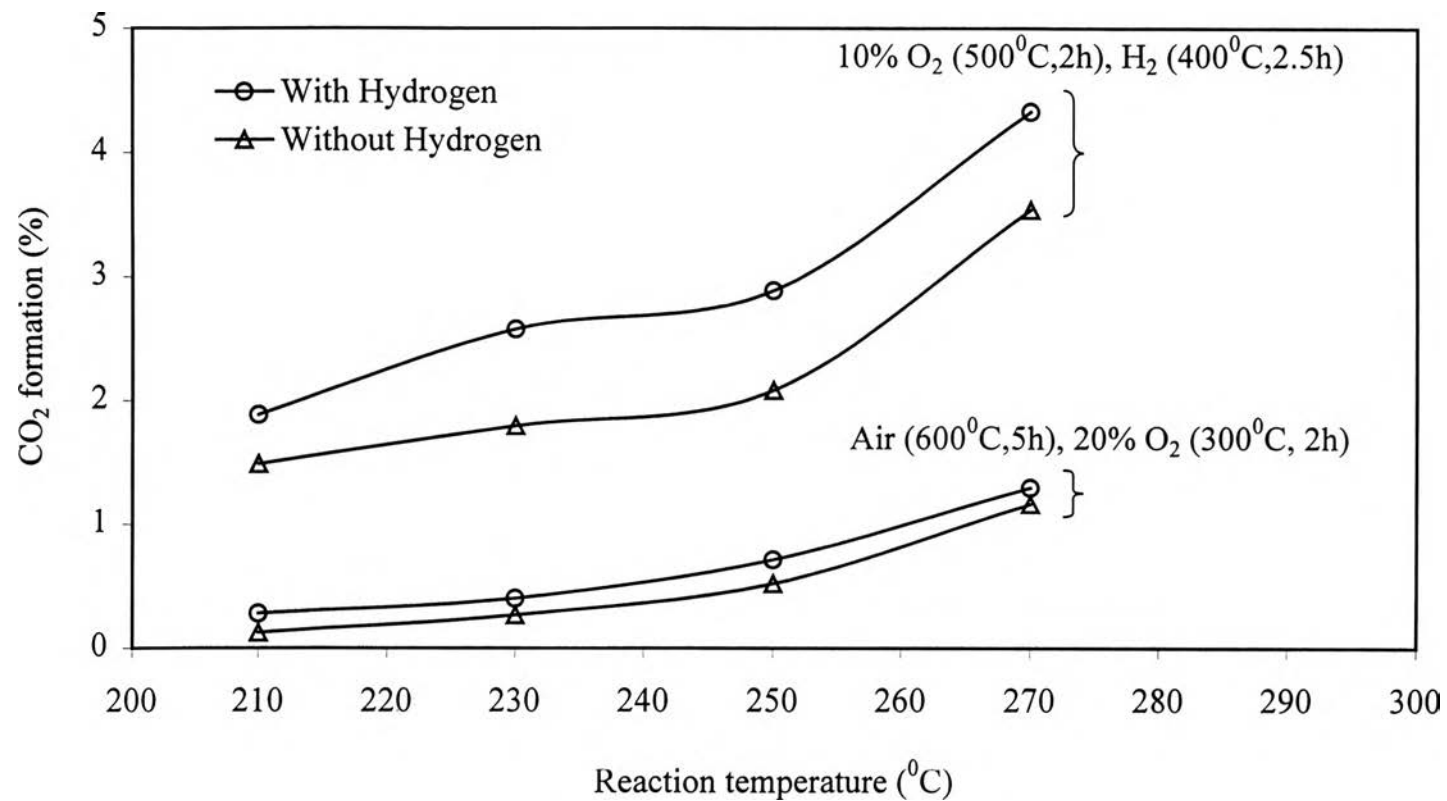


Figure 4.5 Effect of calcination and oxidation-reduction method on activity of (HSA) 10% Ag/Al₂O₃ sol-gel catalyst at different reaction temperatures.

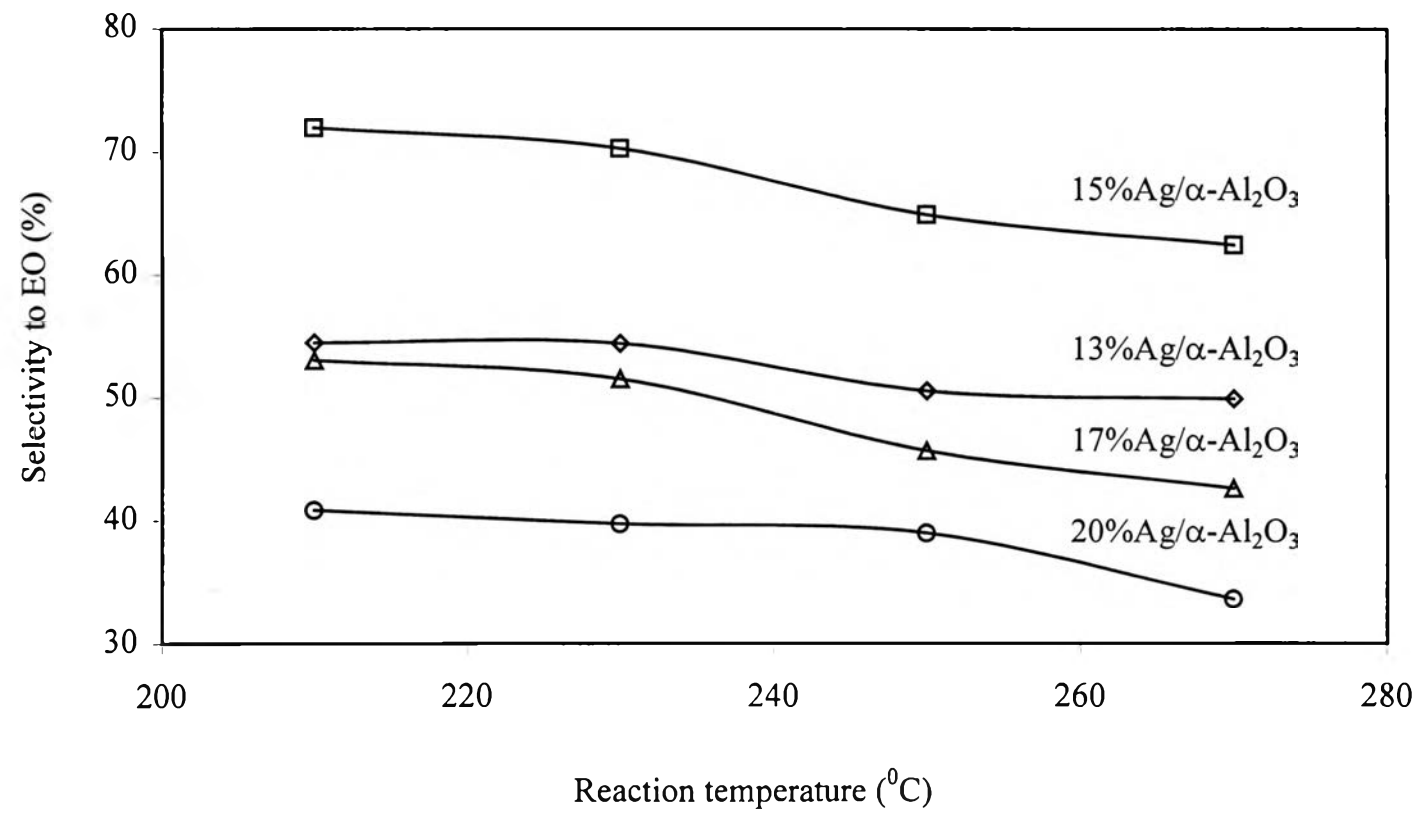


Figure 4.6 Effect of silver loading on selectivity to EO at different reaction temperatures.

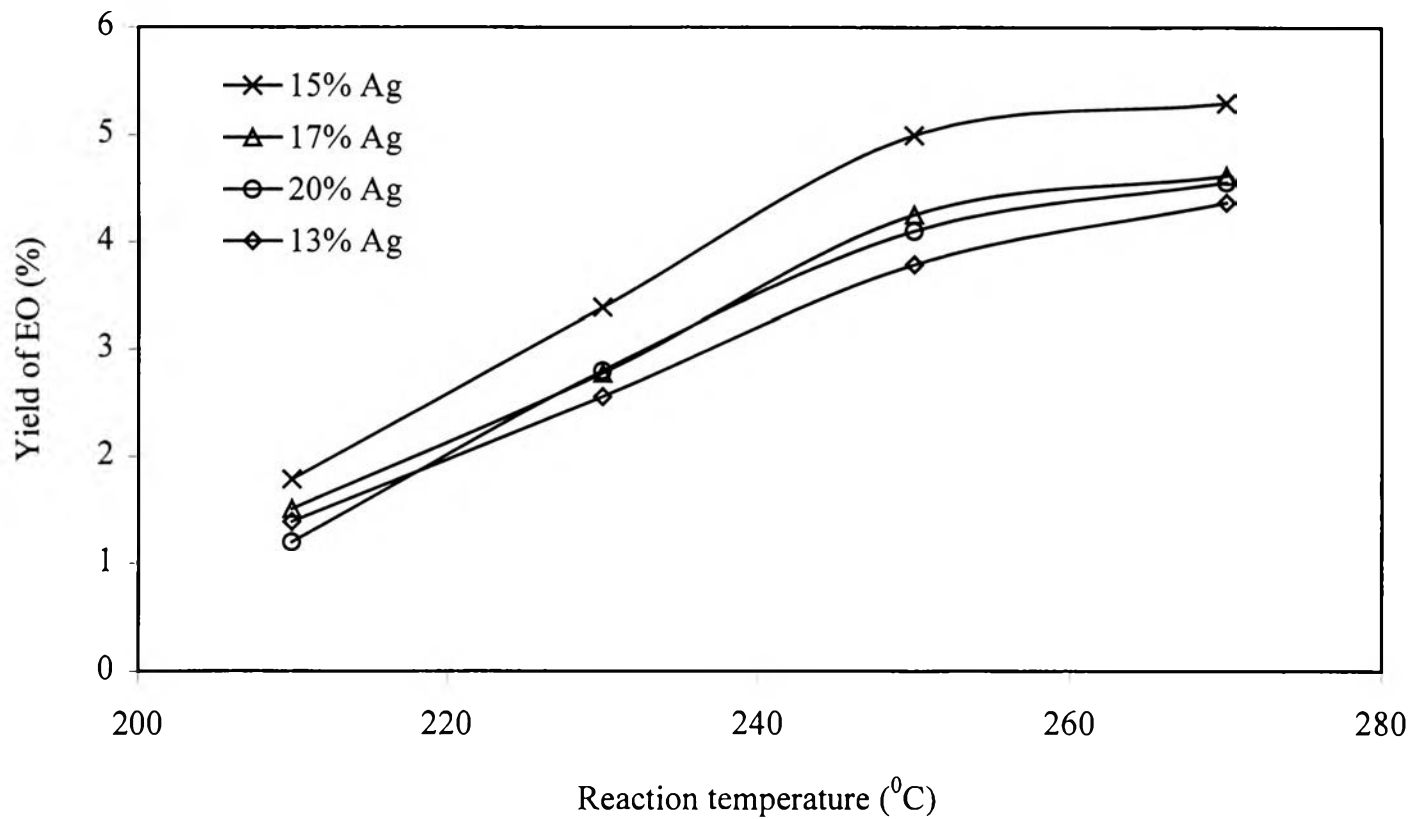


Figure 4.7 Effect of silver loading on yield of EO at different reaction temperatures.

4.2.2.2 Effect of Reactant Molar Ratio

The study of the effect of reactant molar ratio was carried out by using the 15 wt% (LSA) Ag/ α -Al₂O₃ catalyst with various reactant concentrations. The activities in terms of selectivity to EO and yield of EO are shown in Figures 4.8 and 4.9, respectively.

As seen from Figure 4.8, all selectivities decreased with increasing in reaction temperature. This is due to an increase in the formation of carbon dioxide with increasing temperature. The 0.5 molar ratio (6% C₂H₄, 12% O₂) gave the maximum selectivity to EO of 72% at the temperature of 210⁰C.

Consequently, Figure 4.9 displays the yield of EO vs reaction temperature curves for various reactant molar ratios. In the case of reactant molar ratio 0.5, although the yield of EO sharply increased with increasing the temperature until 250⁰C, it slightly increased at the temperature 270⁰C. This is possibly due to the EO combustion at higher temperature. For reactant molar ratio 0.67, 1.0, and 3.75, yields of EO reached a plateau at temperature 270⁰C. This may be due to oxygen being the limiting reactant. On the other hand, the significant decrease of reactant concentrations along the catalytic bed caused the decline of the yield of EO. This result agreed to that reported in the literature (Pena *et al.*, 1998) which suggests that a higher oxygen concentration promote the selectivity of the reaction toward EO. But the risk of explosion also grows with the oxygen concentration, so the maximum allowable oxygen concentration in the reaction gas mixture must be considered.

4.2.2.3 Effect of Calcination and Oxidation-Reduction Method

To investigate the dependence of the activity of (LSA) Ag/ α -Al₂O₃ catalyst on calcination and oxidation-reduction method, 15 wt% (LSA) Ag/ α -Al₂O₃ catalyst was calcined by two different pretreatments. The first pretreatment included calcination in air at 600⁰C for 5 hours followed by

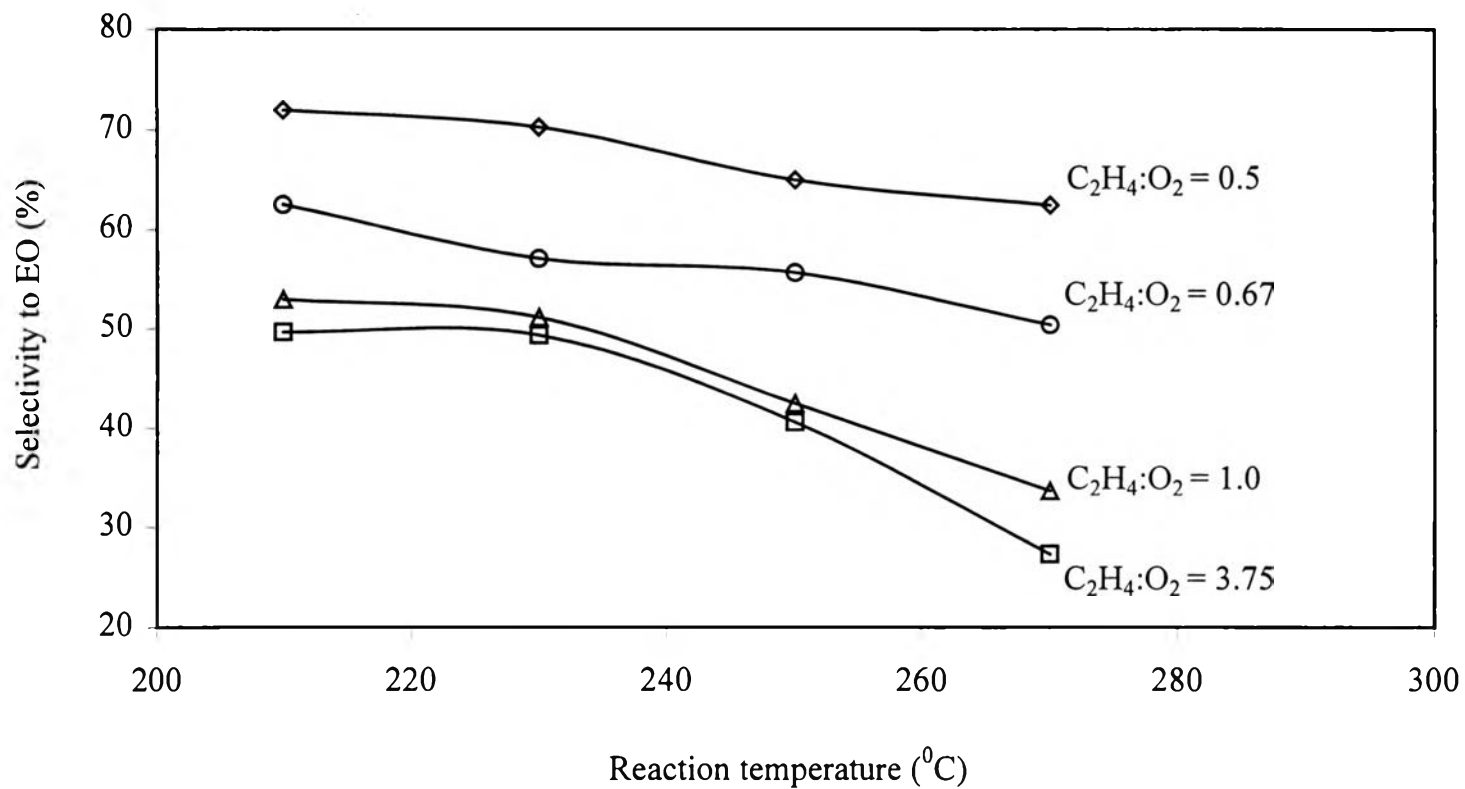


Figure 4.8 Effect of reactant molar ratio on selectivity to EO at different reaction temperatures.

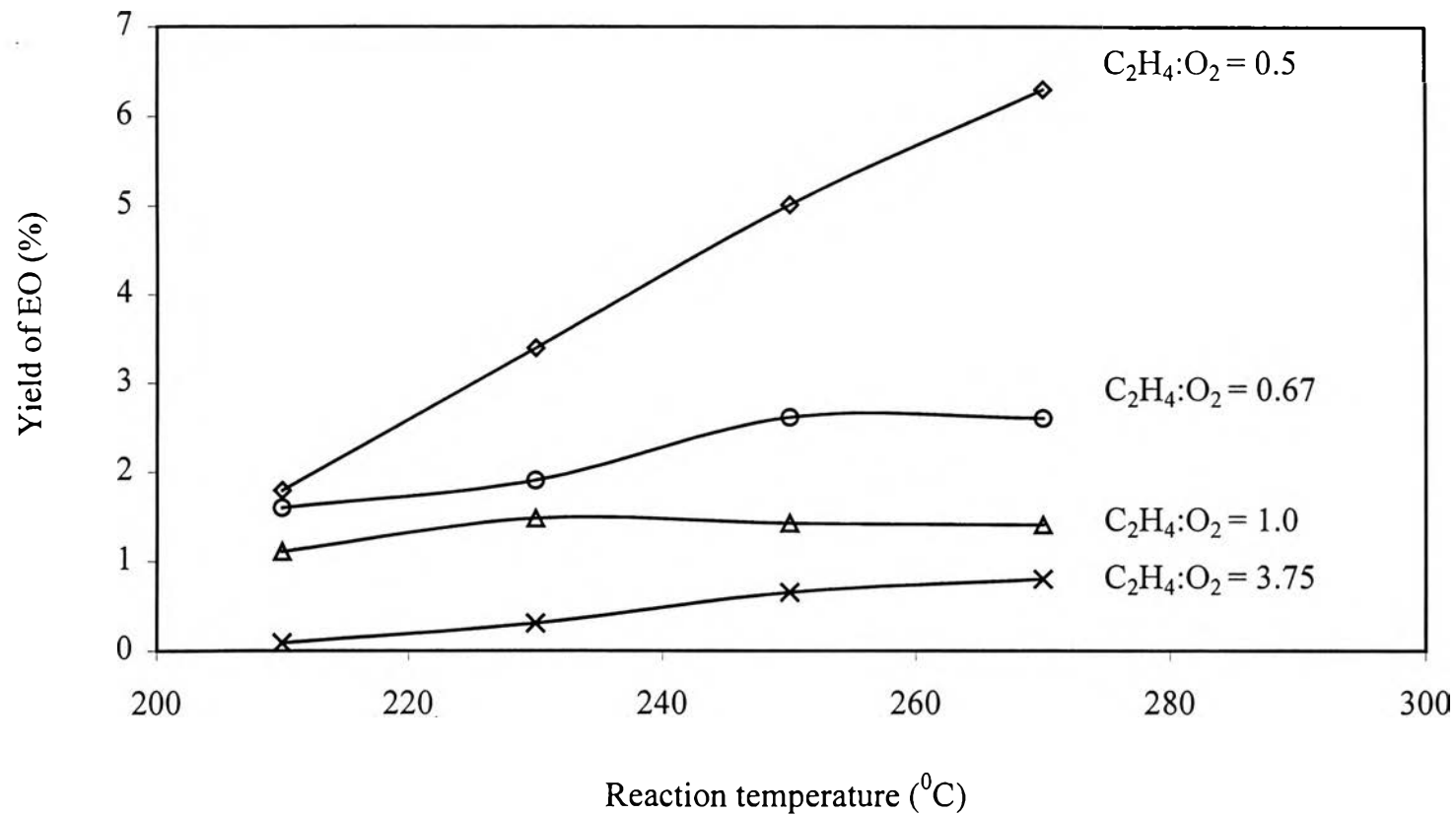


Figure 4.9 Effect of reactant molar ratio on yield of EO at different reaction temperatures.

oxidation in 20% O₂ at 300⁰C for 2 hours, while the second pretreatment consisted of calcination in 10% O₂ (40 ml/min) at 500⁰C for 2 hours followed by reduction in H₂ (20 ml/min) at 400⁰C for 2.5 hours. After that the activity of these catalyst were tested for selective oxidation of ethylene. The selectivities to EO at different reaction temperatures are shown in Figure 4.10. The reduced (LSA) Ag/ α -Al₂O₃ catalyst, which pretreated by second pretreatment method, gave the higher selectivities at entire reaction temperature range than the oxidized catalyst, which pretreated with the first pretreatment method.

Figure 4.11 shows the yield of EO at different reaction temperatures. As shown in the figure, the reduced catalyst gave higher yields of EO than the oxidized catalyst for all temperatures. Since the partial oxidation is favored on the metallic silver, the reduced catalyst has a higher activity than the oxidized catalyst.

4.3 Comparative Studies

The results of a study using both high surface area (HSA) α -alumina and low surface area (LSA) α -alumina supports for the ethylene epoxidation reaction has been reported recently by Mao and Vannice (1995).

In their experiment, two different high surface areas (HSA) α -Al₂O₃ were used as supports, denoted as α -Al₂O₃ (Alcoa, 78 m²/g) and α -Al₂O₃ (Alcoa, 104 m²/g). A low surface area (LSA) α -Al₂O₃ (Norton SA-5202, 0.92 m²/g) was also used.

In the present work, the silver supported on Al₂O₃ high surface area (HSA) (322 m²/g) catalyst, which prepared by sol-gel method, was used. The low surface area (LSA) α -Al₂O₃ (Aldrich, 0.54 m²/g) support was also used for comparison.

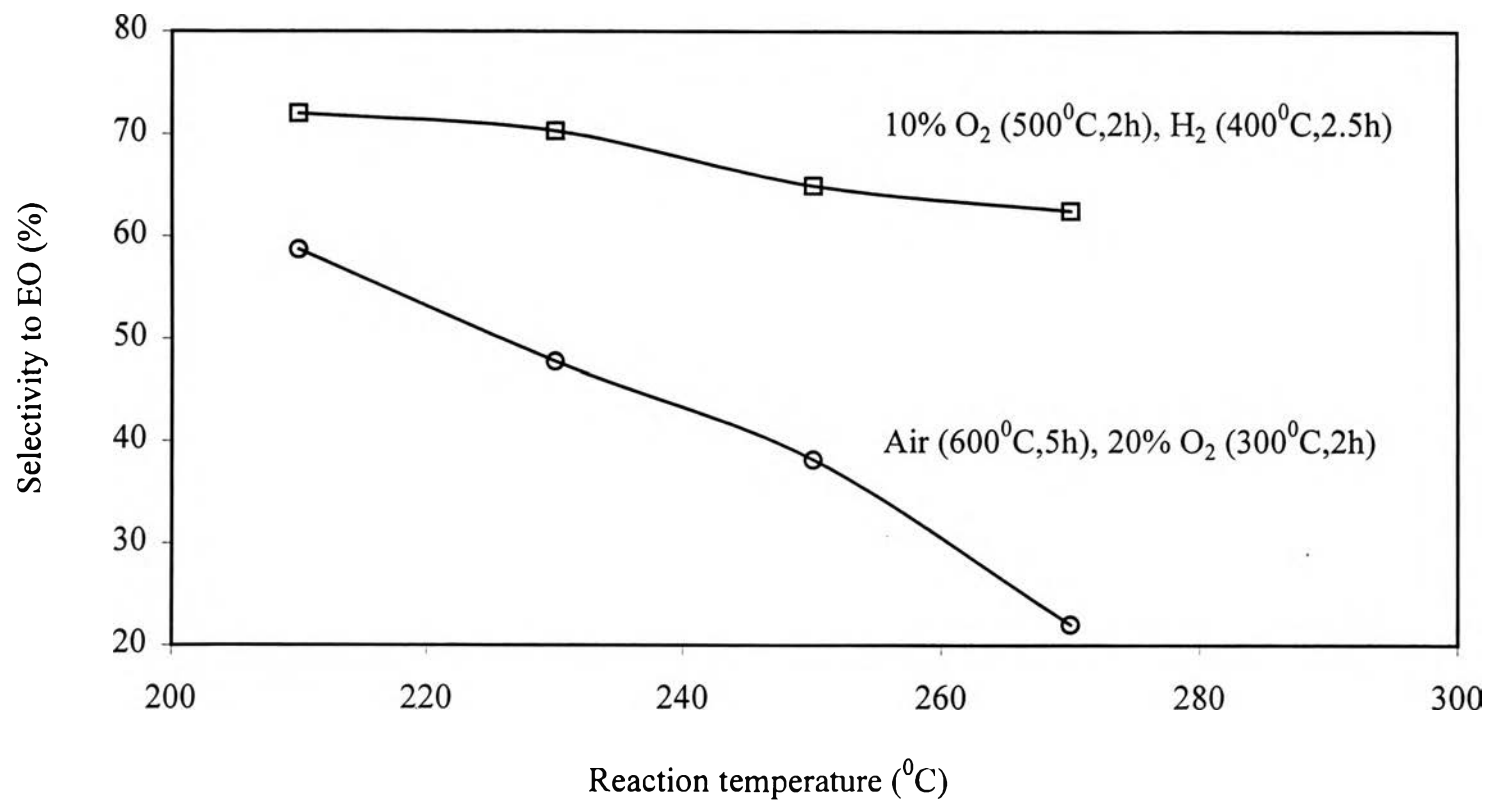


Figure 4.10 Effect of calcination and oxidation-reduction method on selectivity to EO at different reaction temperatures.

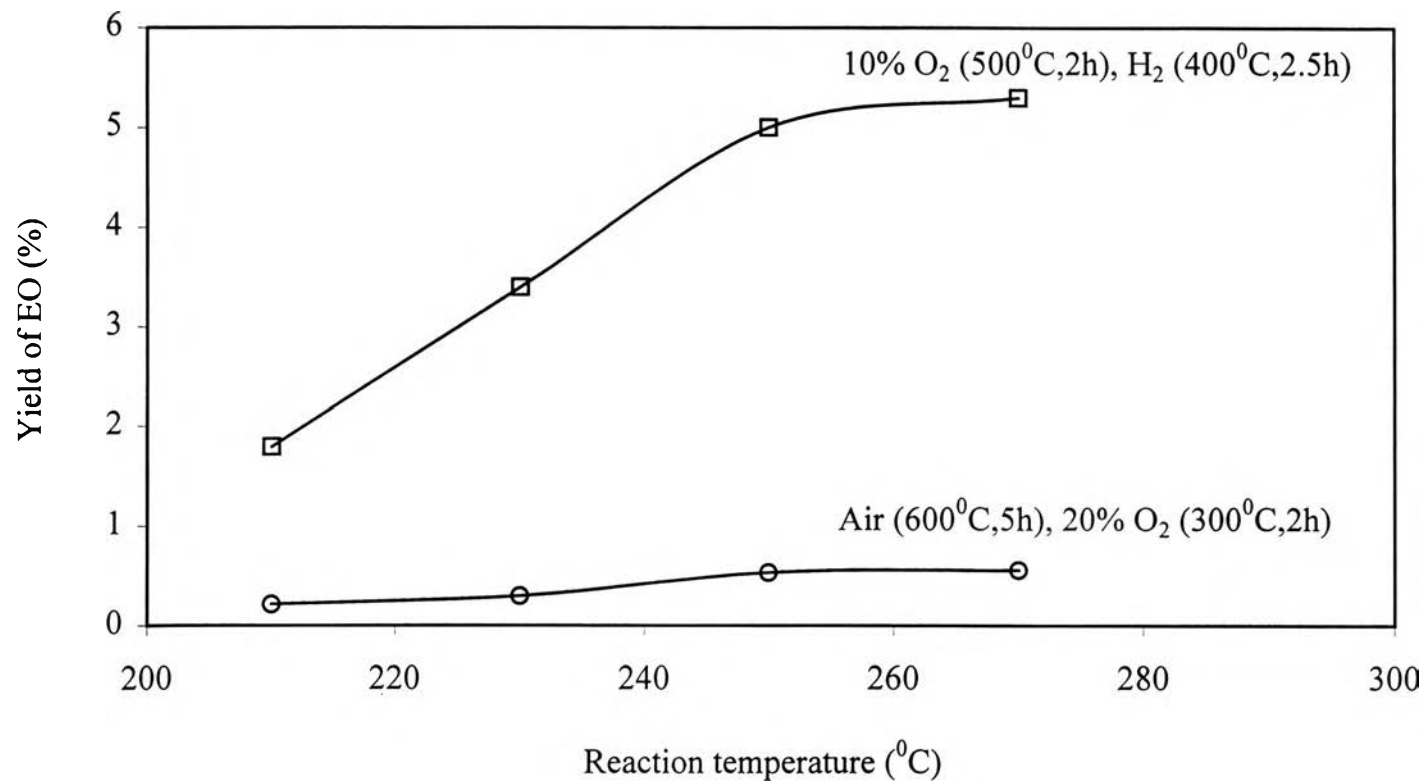


Figure 4.11 Effect of Calcination and oxidation-reduction method on yield of EO at different reaction temperatures.

4.3.1 Comparison for High Surface Area (HSA) Ag/Al₂O₃ Catalyst

Experimental conditions	Present work	Mao & Vannice's work
Catalyst	10 wt% Ag/Al ₂ O ₃	12.7 wt% Ag/ α -Al ₂ O ₃
Catalyst weight	0.44 g	0.3 g
Calcination of catalyst	10% O ₂ (500 ⁰ C, 2 hrs)	10% O ₂ (500 ⁰ C, 2 hrs)
Pretreatment of catalyst	H ₂ (400 ⁰ C, 2.5 hrs)	H ₂ (400 ⁰ C, 2.5 hrs)
Reactant (C ₂ H ₄ , O ₂)	6%, 12%	30%, 8%
Flow rate	50 ml/min	30 ml/min
Space velocity	4,000 h ⁻¹	2,000 h ⁻¹
Temperature	210 to 270 ⁰ C	210 to 270 ⁰ C
Selectivity	0 %	0 %

4.3.2 Comparison for Low Surface Area (LSA) Ag/ α -Al₂O₃ Catalyst

Experimental conditions	Present work	Mao & Vannice's work
Catalyst	15 wt% Ag/ α -Al ₂ O ₃	16.5 wt% Ag/ α -Al ₂ O ₃
Catalyst weight	1.07 g	0.3 g
Calcination of catalyst	10% O ₂ (500 ⁰ C, 2 hrs)	10% O ₂ (500 ⁰ C, 2 hrs)
Pretreatment of catalyst	H ₂ (400 ⁰ C, 2.5 hrs)	H ₂ (400 ⁰ C, 2.5 hrs)
Reactant (C ₂ H ₄ , O ₂)	30%, 8%	30%, 8%
Flow rate	30 ml/min	30 ml/min
Space velocity	2,386 h ⁻¹	2,000 h ⁻¹
Temperature	230 ⁰ C	230 ⁰ C
Selectivity	49 %	60 %