

## CHAPTER IV

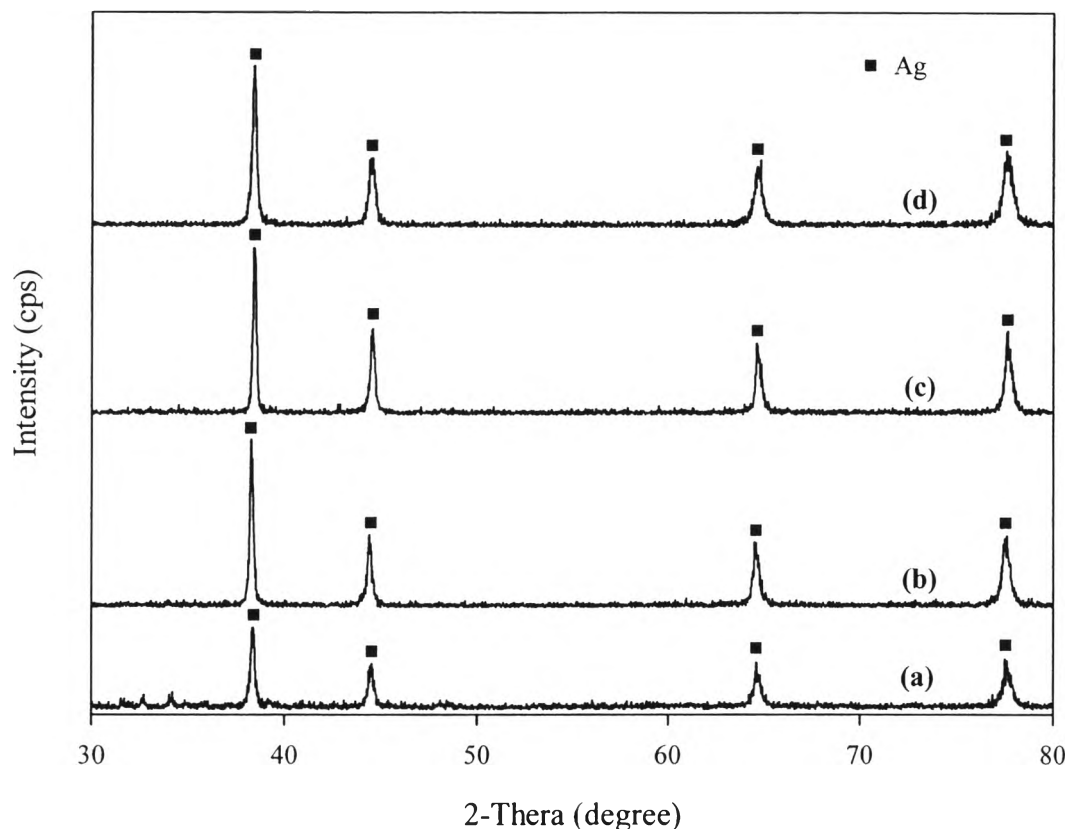
### RESULTS AND DISCUSSION

According to the previous work (Suwannabart *et al.*, 2008), the mixed feed reactants (ethylene and oxygen) to produce ethylene oxide in the dielectric barrier discharge (DBD) system gave low selectivity and yield. Hence, in this research, the dielectric barrier discharge system is selected to further study the effects of ethylene feed position, Ag/SiO<sub>2</sub> catalyst existence as well as other operating parameters, for enhancing the performance of ethylene oxide (desired product) production.

#### 4.1 Catalyst Characterization Results

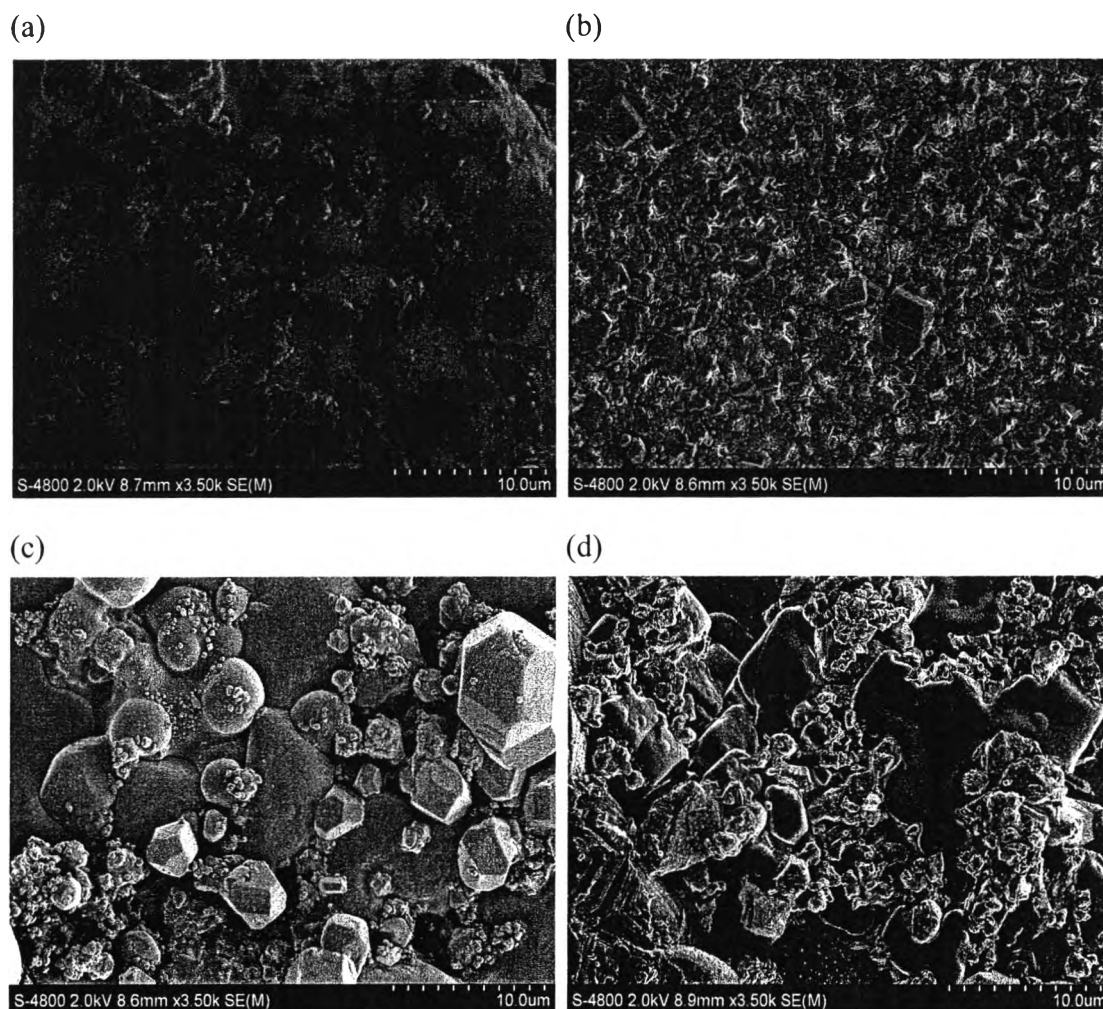
The specific surface areas of SiO<sub>2</sub> supported Ag catalyst with different Ag loadings were examined. It was found that the specific surface area was almost constant in range from 0.85 m<sup>2</sup>/g to 5.27 m<sup>2</sup>/g with increasing Ag loading up to 20%. This implies that the presence of Ag loading does not significantly affect the surface areas, or the surface area of SiO<sub>2</sub> support is too low to be significantly affected by Ag loading (Suttikul *et al.*, 2011)

Figure 4.1 shows the XRD patterns of SiO<sub>2</sub> supported Ag catalyst at different Ag loadings. The Ag phase was found at different peaks of approximately 38, 44, 64, and 77 degree and its intensity increased significantly with increasing Ag loading from 5% to 20%. The calculated mean Ag crystallite sizes on the SiO<sub>2</sub> support was also found in the range of 16.72 nm to 21.96 nm.



**Figure 4.1** XRD patterns of SiO<sub>2</sub> supported Ag catalyst: (a) 5 wt.% Ag/SiO<sub>2</sub>, (b) 10 wt.% Ag/SiO<sub>2</sub>, (c) 15 wt.% Ag/SiO<sub>2</sub>, and (d) 20 wt.% Ag/SiO<sub>2</sub>

The SEM images of the SiO<sub>2</sub> supported Ag catalysts with different Ag loading is shown in Figure 4.2. The distribution of Ag over the SiO<sub>2</sub> supported was rapidly increase with increasing Ag loading from 5% to 20%. As shown in Figure 4.2(a) (5 wt.% Ag/SiO<sub>2</sub>), the surface was incompletely covered with Ag particles, when compared to Figure 4.2(b) (10 wt.% Ag/SiO<sub>2</sub>), the Ag particles was more completely covered the surface. With further increasing Ag loading (especially 15 wt.% Ag/SiO<sub>2</sub> and 20 wt.% Ag/SiO<sub>2</sub>) some Ag particles was grown out from the SiO<sub>2</sub> support. Therefore Ag loading of 10% was considered to be an optimum.



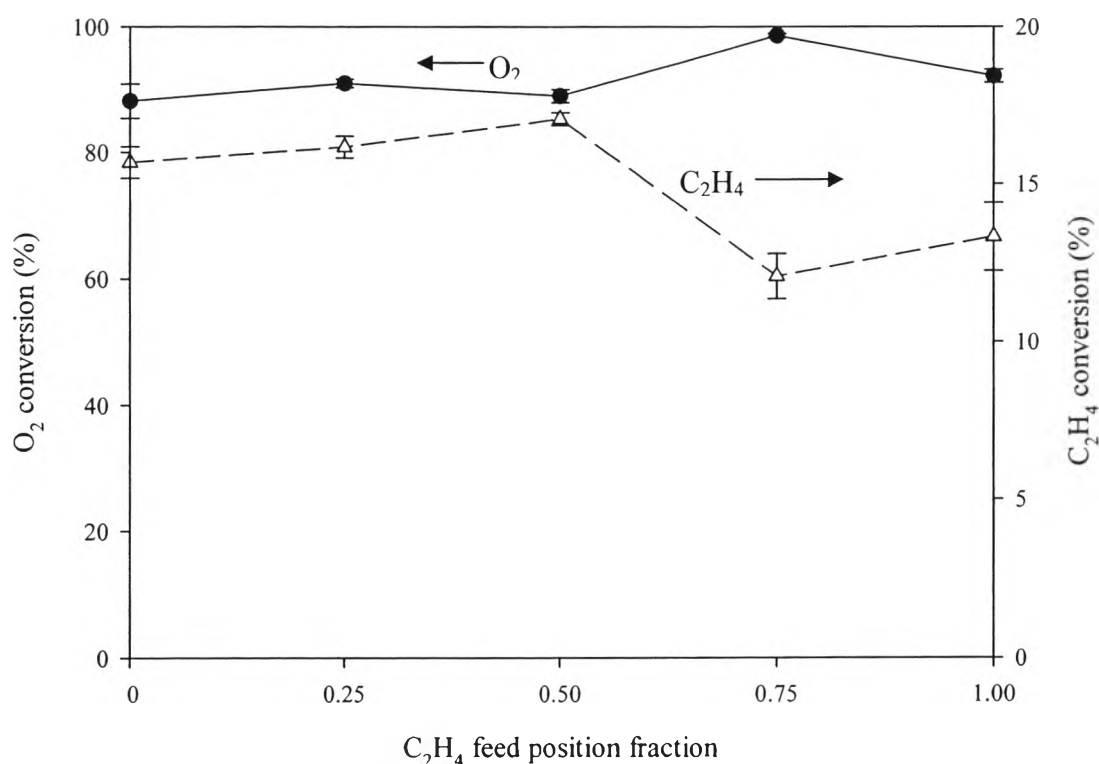
**Figure 4.2** SEM images of SiO<sub>2</sub> supported Ag catalysts: (a) 5 wt.% Ag/SiO<sub>2</sub>, (b) 10 wt.% Ag/SiO<sub>2</sub>, (c) 15 wt.% Ag/SiO<sub>2</sub> and (d) 20 wt.% Ag/SiO<sub>2</sub>

## 4.2 Reaction Activity Performance

### 4.2.1 Effect of Ethylene Feed Position

The effect of ethylene (C<sub>2</sub>H<sub>4</sub>) feed position was initially studied in order to obtain the most suitable position for ethylene epoxidation reaction in the low-temperature DBD system. In this study, the ethylene feed position was varied in the fractional range from 0 to 1, while the feed molar ratio of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> of 0.25:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and a total feed flow rate of 50 cm<sup>3</sup>/min were used as base conditions to operate the DBD system.

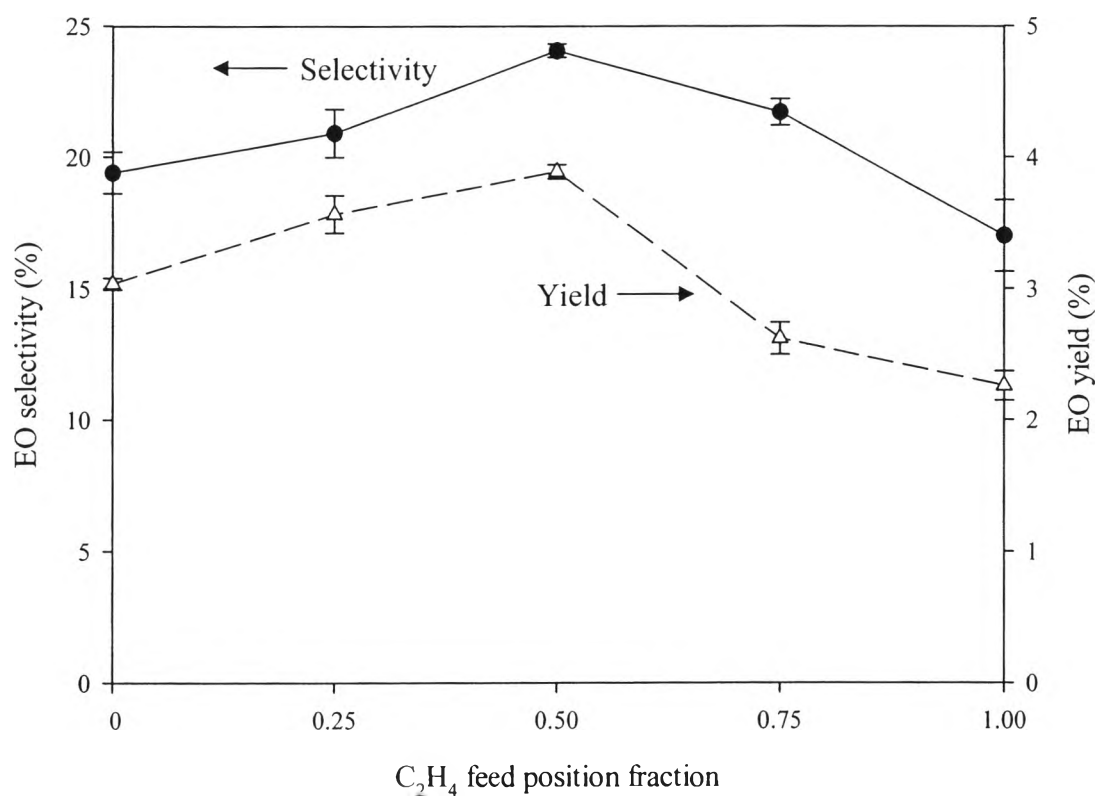
The effect of ethylene feed position on the ethylene and oxygen conversion is shown in Figure 4.3. The conversion of oxygen is almost constant with increasing ethylene feed position fraction. However, the conversion of ethylene tended to increase with increasing ethylene feed position fraction ranging from 0 to 0.5. At a higher ethylene feed position fraction, the ethylene conversion tended to decrease, and it reached a minimum at the ethylene feed position fraction of 0.75.



**Figure 4.3** C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> conversions as a function of ethylene feed position fraction at an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.25:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of 50 cm<sup>3</sup>/min.

The EO selectivity and EO yield are shown in Figure 4.4. The increase in the ethylene feed position fraction slightly affected the EO selectivity, EO yield and reactant conversions, especially in the ethylene feed position fraction range between 0 to 0.5. The EO selectivity and EO yield are highest at the ethylene feed position fraction of 0.5 and decreased with further increasing ethylene feed

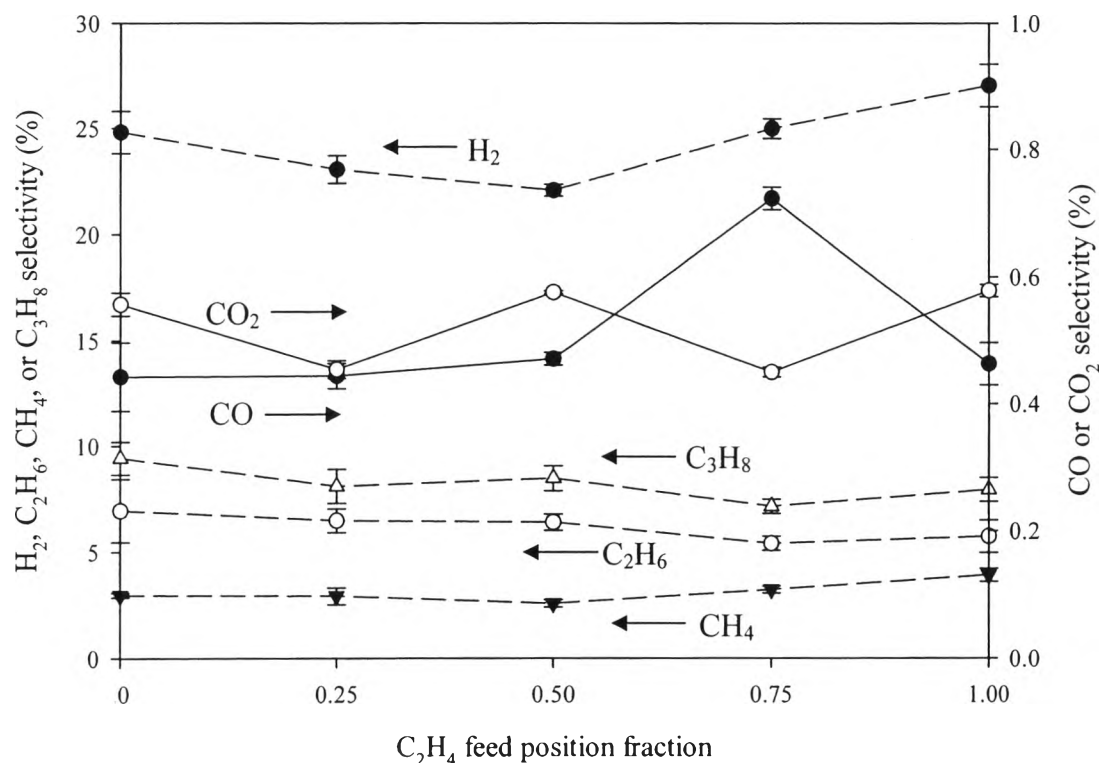
position fraction. Furthermore, at the highest ethylene feed position fraction of 1, the selectivity for EO is lowest. This can be explained in that a lower ethylene feed position fraction leads to more opportunity of ethylene molecule to be cracked before colliding with  $O_2$  active species, whereas at a higher ethylene feed position fraction the ethylene has a short residence time for epoxidation reaction.



**Figure 4.4** EO selectivity and yield as a function of ethylene feed position fraction at an  $O_2/C_2H_4$  feed molar ratio of 0.25:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50\text{ cm}^3/\text{min}$ .

The selectivities of  $CO$ ,  $CO_2$ ,  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , and  $C_3H_8$  are shown in Figure 4.5. The selectivities for  $CO$ ,  $CO_2$ ,  $C_2H_6$ ,  $C_3H_8$  and  $CH_4$  tended to decrease, but in contrast, the selectivity for  $H_2$  remain almost unchanged with increasing ethylene feed position. The selectivity for  $CO$  and  $CO_2$  tended to increase in the study range of ethylene feed position fraction from 0.5 to 1. The  $CO$  selectivity increase when

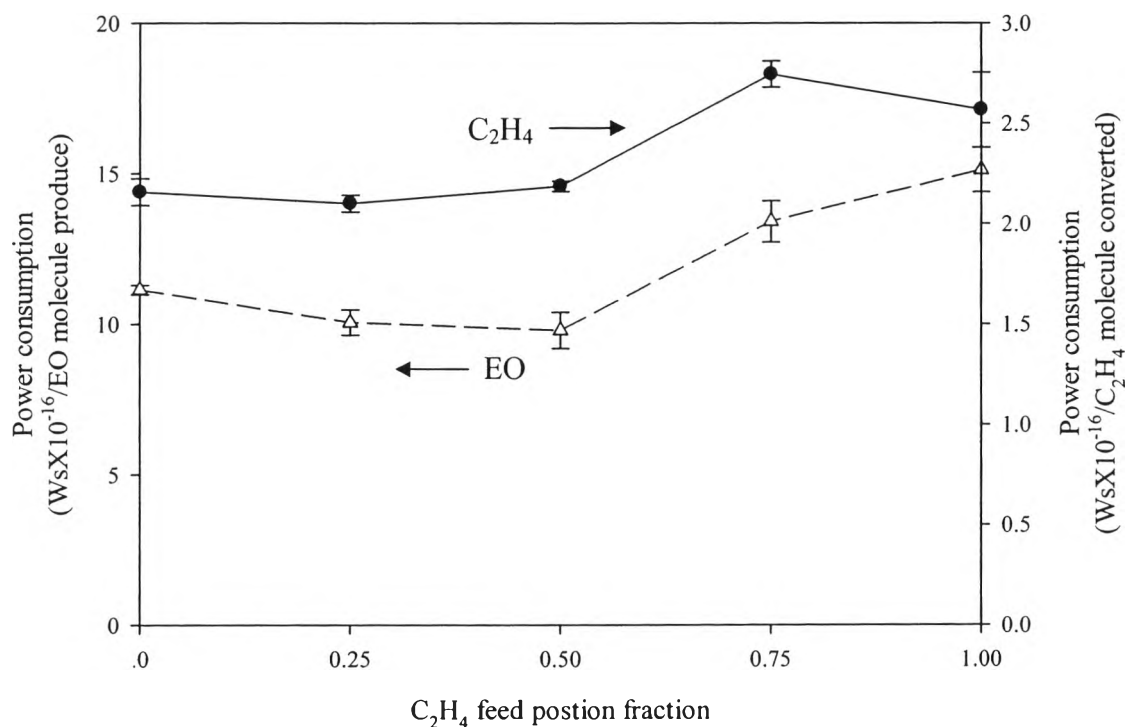
the ethylene feed position fraction increase, and it reached a maximum at the ethylene feed position fraction of 0.75.



**Figure 4.5** Other product selectivities as a function of ethylene feed position fraction at an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.25:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of 50 cm<sup>3</sup>/min.

Figure 4.6 shows the power consumptions to convert an ethylene molecule and to produce an EO molecule at different ethylene feed position fractions. The power consumption per molecule of converted ethylene reached a minimum when the ethylene feed position fraction increased up to 0.5 and rapidly increased with further increasing feed position fraction up from 0.5 to 1. However, It is significant increasing in the power consumption per molecule of produced EO with further increasing ethylene feed position fraction, especially at the feed position fraction higher than 0.5. Hence, an ethylene feed position fraction of 0.5 is therefore

selected for further investigation because it provided the highest selectivity and yield for EO and the lowest power consumption per molecule of EO produced.



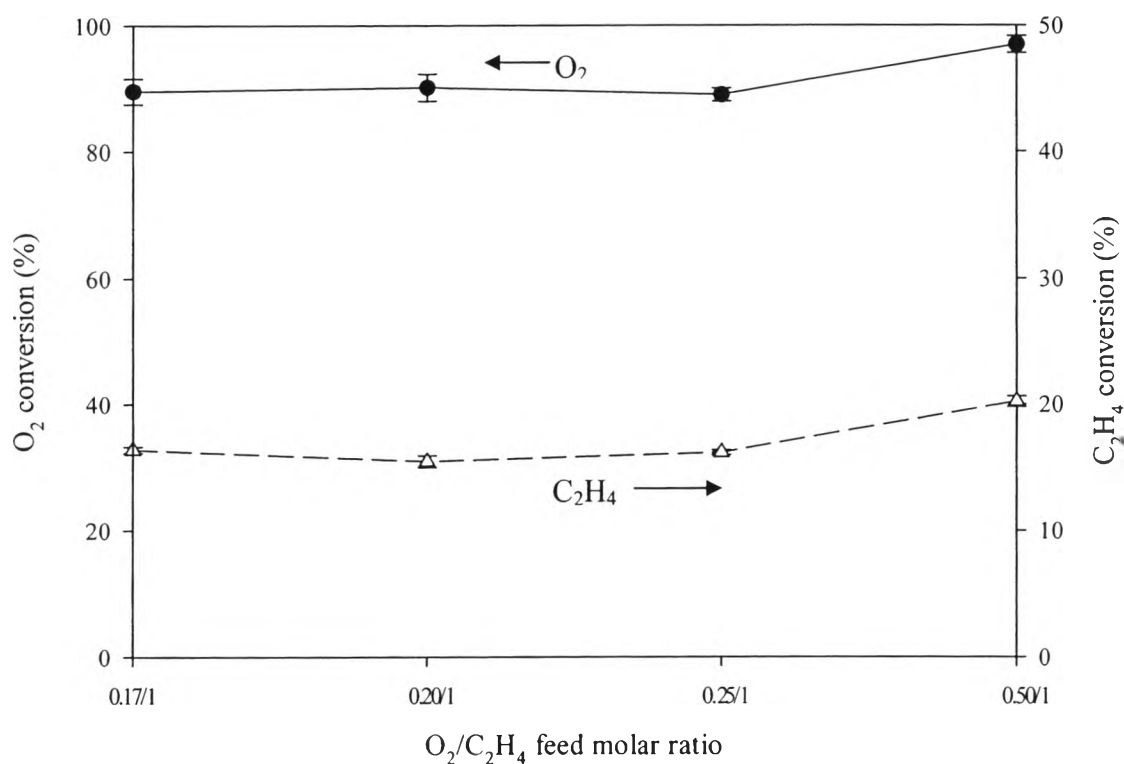
**Figure 4.6** Power consumptions as a function of ethylene feed position fraction at an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.25:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of 50 cm<sup>3</sup>/min.

#### 4.2.2 Effect of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> Feed Molar Ratio

To determine the influence of the feed gas composition, the O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio is next varied in the range of 0:1 to 0.5:1 (O<sub>2</sub>-lean conditions), while the other operating parameters are fixed at a C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5 (optimum condition), an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of 50 cm<sup>3</sup>/min.

As shown in Figure 4.7, an increase in O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio slightly affects the C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> conversions, and the highest conversions of both reactants are obtained at the highest O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.5:1. The explanation is that an increase in the molar ratio of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> results in having more

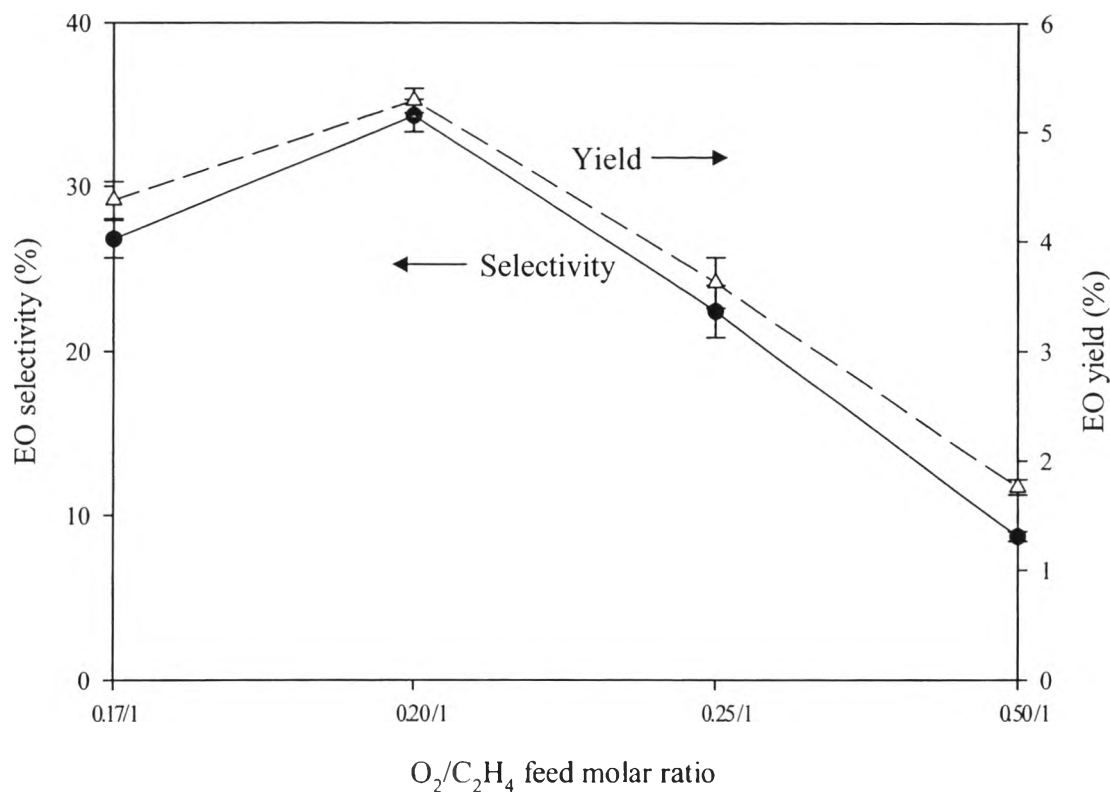
$O_2$  available to react with ethylene molecules, leading to higher ethylene conversion and  $O_2$  conversion.



**Figure 4.7**  $C_2H_4$  and  $O_2$  conversions as a function of  $O_2/C_2H_4$  feed molar ratio at a ethylene feed position fraction of 0.5, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50 \text{ cm}^3/\text{min}$ .

The effect of the  $O_2/C_2H_4$  feed molar ratio on EO selectivity and EO yield are shown in Figure 4.8. Both of them increased with increasing  $O_2/C_2H_4$  feed molar ratio from 0.17:1 to 0.2:1 and rapidly decreased with further increasing  $O_2/C_2H_4$  feed molar ratio greater than 0.2:1, suggesting that EO can be formed dominantly under the deficient  $O_2$  condition. The highest EO selectivity and EO yield is found at an  $O_2/C_2H_4$  feed molar ratio of 0.2:1

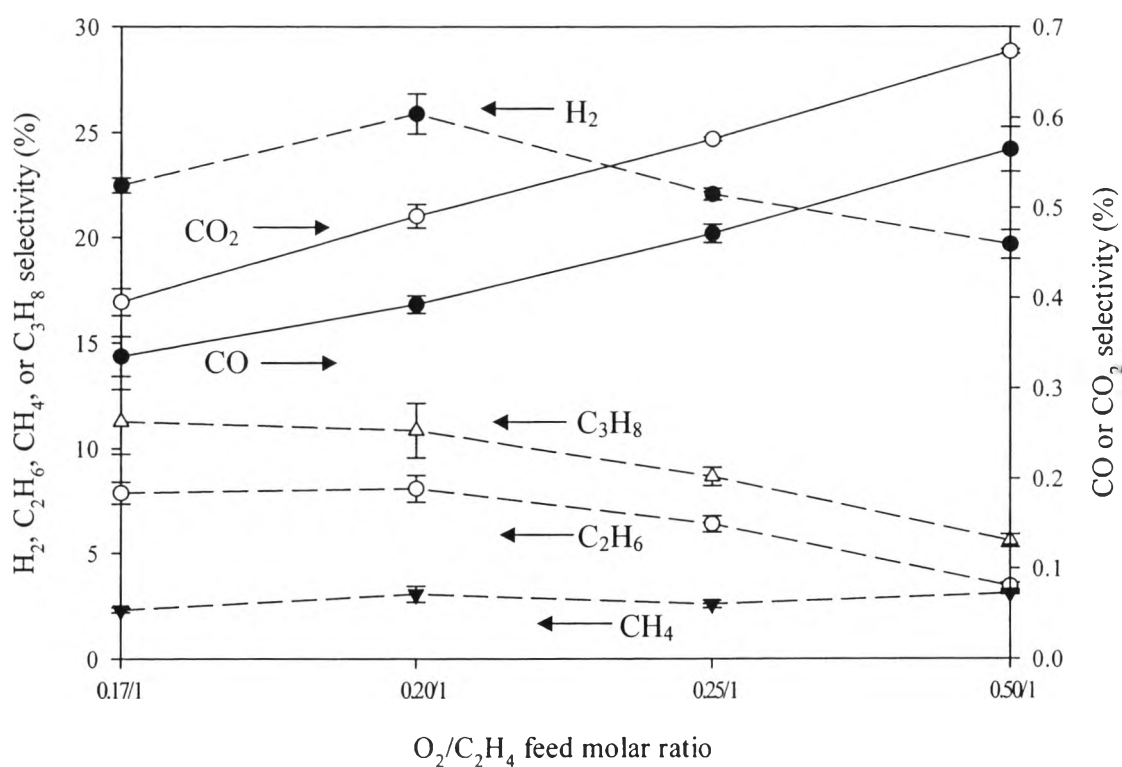




**Figure 4.8** EO selectivity and yield as a function of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio at a ethylene feed position fraction of 0.5, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of 50 cm<sup>3</sup>/min.

The effect of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> fed molar ratio on the selectivities for other products is shown in Figure 4.9. The H<sub>2</sub>, CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>2</sub>H<sub>6</sub> tended to decrease, but in contrast, the selectivities for CO and CO<sub>2</sub> increased with increasing O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio, as aforementioned. Interestingly, The CO and CO<sub>2</sub> selectivities increased when the O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio increased, and they reached a maximum at the O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.5:1. Under the studied conditions, the main products were CO and CO<sub>2</sub> with significant amounts of EO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>2</sub>H<sub>6</sub> product. The largest hydrocarbon, i.e. C<sub>3</sub>H<sub>8</sub>, was found in a very small fraction. The results can be explained by the fact that, both complete and partial oxidation reactions are controlled by the ratio of oxygen in the system. The decreases in the selectivities for these hydrocarbons and H<sub>2</sub> and the increase in the selectivities for CO and CO<sub>2</sub> with increasing oxygen fraction in feed clearly reveal that the oxidative dehydrogenation and coupling reactions unfavorably occur under O<sub>2</sub>-rich conditions,

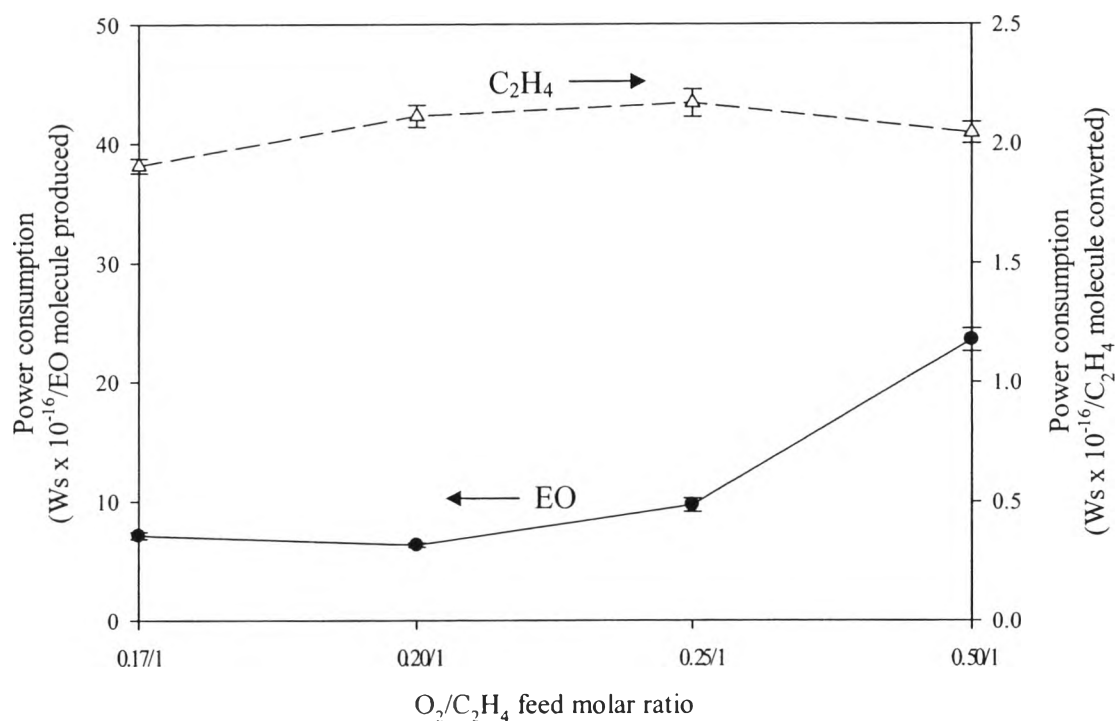
as expected. Furthermore, at a very high  $O_2/C_2H_4$  feed molar ratio of 0.5:1, the selectivity for EO dropped to zero level since this high  $O_2/C_2H_4$  feed molar ratio induced the complete combustion to occur more favorably than the partial oxidation, as well as the epoxidation, indicating that the epoxidation reaction to produce EO is more likely to occur under  $O_2$ -lean conditions.



**Figure 4.9** Other product selectivities as a function of  $O_2/C_2H_4$  feed molar ratio at a ethylene feed position fraction of 0.5, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50 \text{ cm}^3/\text{min}$ .

The power consumptions required to convert  $C_2H_4$  molecule and to produce EO molecule at different  $O_2/C_2H_4$  feed molar ratios are shown in Figure 4.10. The power consumption per molecule of produced EO reached a minimum at an  $O_2/C_2H_4$  molar ratio of 0.2:1, which corresponded well with the obtained highest EO selectivity. However, The power consumption per molecule of converted  $C_2H_4$  remained almost unchanged in the  $O_2/C_2H_4$  feed molar ratio range of 0.2:1-0.25:1,

but then slightly decreased with increasing  $O_2/C_2H_4$  feed molar ratio to 0.5:1, at which the lowest EO selectivity is observed.

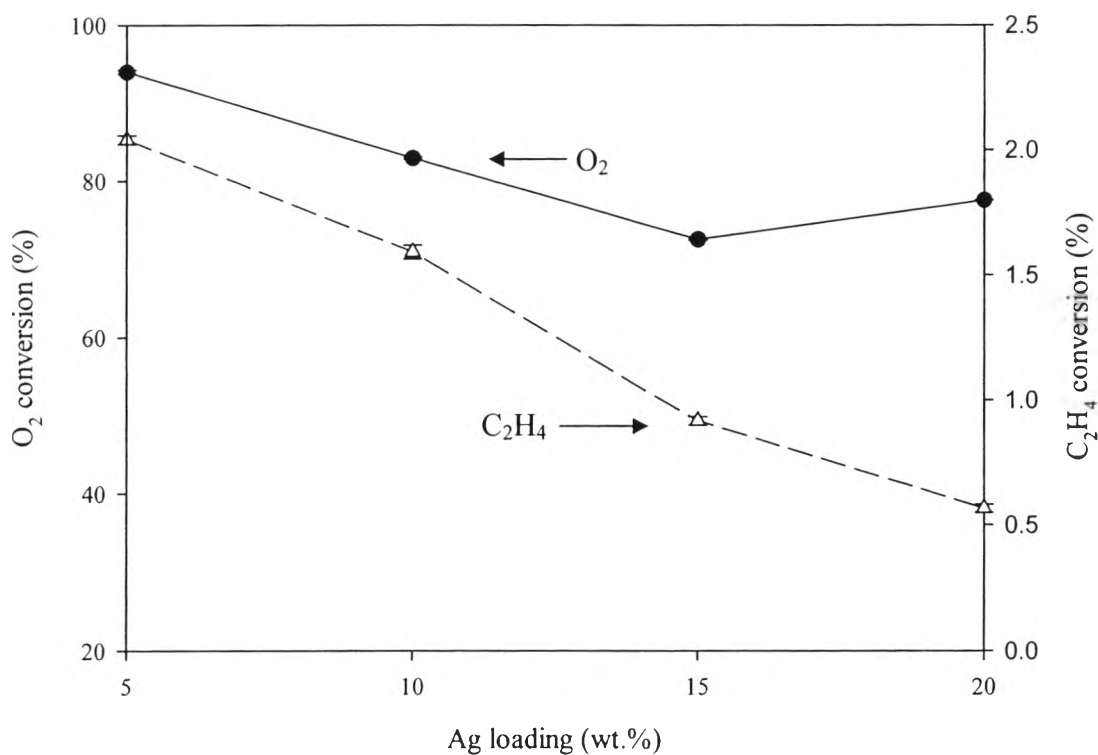


**Figure 4.10** Power consumptions as a function of  $O_2/C_2H_4$  feed molar ratio at a ethylene feed position fraction of 0.5, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50 \text{ cm}^3/\text{min}$ .

#### 4.2.3 Effect of Ag Loading on $SiO_2$ Support

To determine the influence of Ag/ $SiO_2$  catalyst existence, the loading of Ag on  $SiO_2$  support was next varied in the range of 5% to 20%, while the other operating parameters were fixed at an optimum conditions followed by  $C_2H_4$  feed position fraction of 0.5, an oxygen to ethylene feed molar ratio of 0.2:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50 \text{ cm}^3/\text{min}$ .

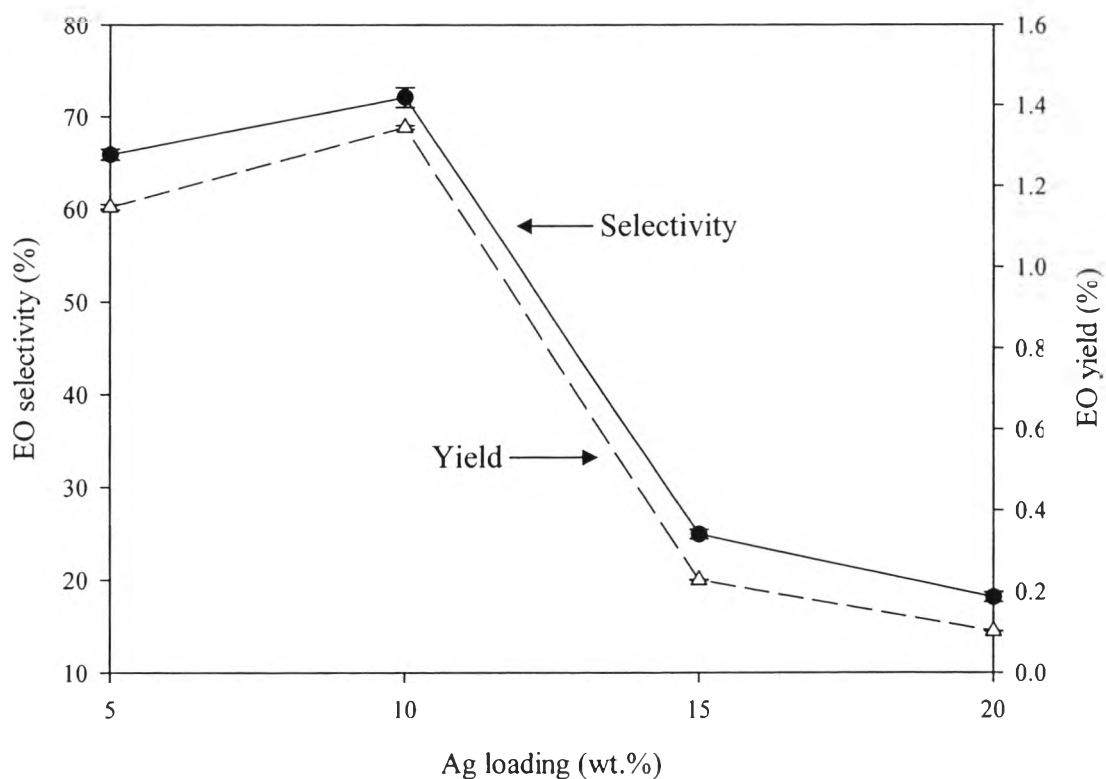
The effect of Ag loading on SiO<sub>2</sub> for the ethylene and oxygen conversion are shown in Figure 4.11. The conversion both of ethylene and oxygen rapidly decrease with increasing Ag loading. In contrast, the conversion of oxygen slightly increased with increasing Ag loading rang from 15% to 20% and react a minimum at 15% of Ag loading. The results can be explained in that, when increasing Ag loading up to 20% the distribution of Ag over SiO<sub>2</sub> supported catalyst was decreased as indicated by crystallite size result and SEM result (Figure 4.2).



**Figure 4.11** C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> conversions as a function of Ag loading on SiO<sub>2</sub> support at an ethylene feed position fraction of 0.5, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.20:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of 50 cm<sup>3</sup>/min.

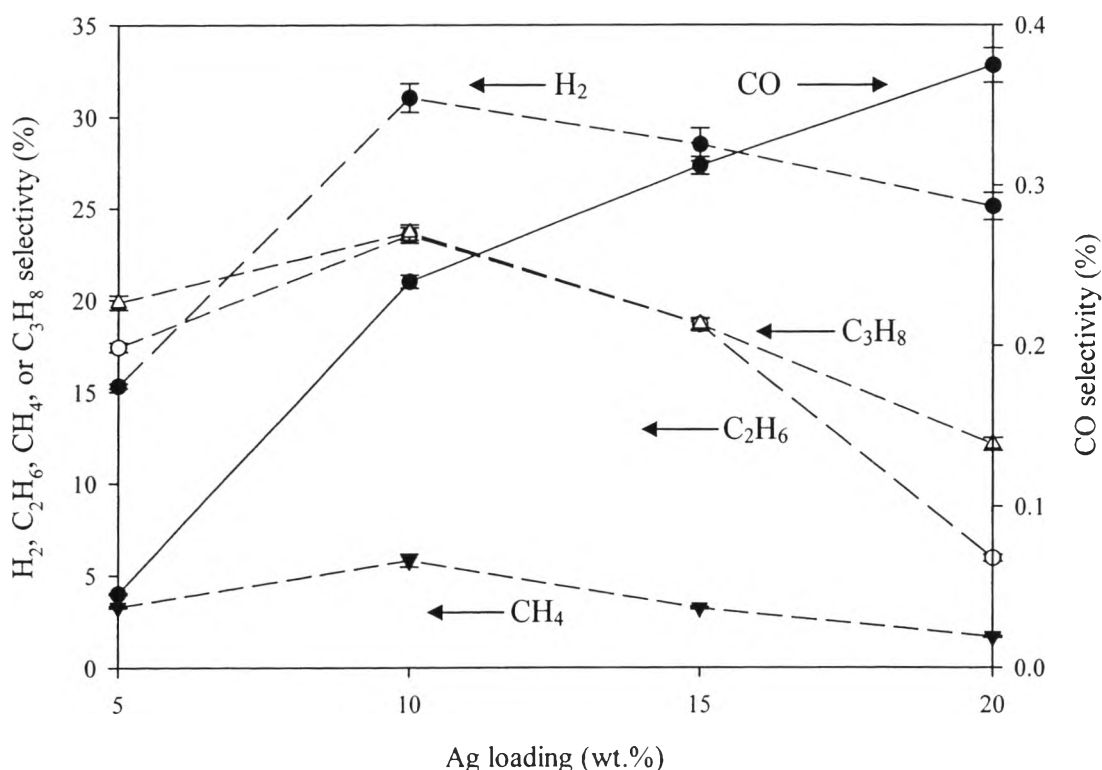
The EO selectivity and EO yield are shown in Figure 4.12. The increase of Ag loading mainly affected the EO selectivity and EO yield, especially in the Ag loading range between 5% to 10%. The EO selectivity and EO yield were

highest at the Ag loading of 10% and then decreased with further increasing Ag loading. However, the EO yield was not significantly changed with increase Ag loading because, the  $C_2H_4$  conversion decreased when increasing Ag loading up to 20% as shown in Figure 4.11. For these caused was corresponded to effect of EO yield. Furthermore, at a highest Ag loading of 20%, both of selectivity and yield for EO were lowest. These results imply that the amount of the catalyst as used in the DBD system has a significant influence on the ethylene epoxidation activity. Moreover, the combined of catalyst in DBD system with 10 wt.% of Ag loading on  $SiO_2$  provided much higher EO selectivity as compared to the sole DBD system (Figure 10). This finding indicated that the present of catalyst in the DBD system can enhance the ethylene epoxidation performance in term of EO selectivity.



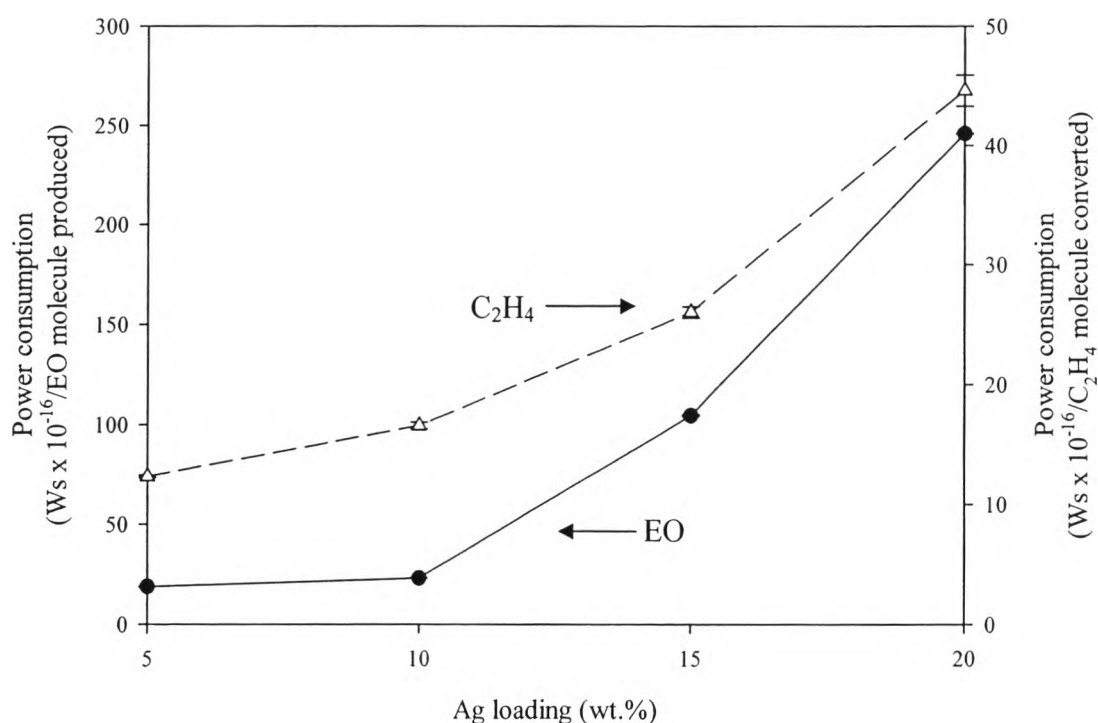
**Figure 4.12.** EO selectivity and yield as a function of Ag loading on  $SiO_2$  support at an ethylene feed position fraction of 0.5, an  $O_2/C_2H_4$  feed molar ratio of 0.20:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50\text{ cm}^3/\text{min}$ .

The effect of Ag loading on the selectivities for other products are shown in Figure 4.13. The  $H_2$ ,  $CH_4$ ,  $C_3H_8$ , and  $C_2H_6$  tended to increase with increasing Ag loading range from 5% to 10%, rapidly decreased with further increase Ag loading, and finally reached a minimum at Ag loading of 20%. In contrast, the selectivities for CO sharply increased with increasing Ag loading. The results can be explained by the fact that, the existence of Ag active sites on the  $SiO_2$  supported not only catalyze the ethylene epoxidation, but also affect to further reactions during the plasma process, especially CO. However when compared the combined catalyst in DBD system with the sole DBD system, it can be seen that the selectivity for CO under the combined catalyst in DBD system was lower than the sole DBD system and that also prevented to produce  $CO_2$ .



**Figure 4.13.** Other product selectivities as a function of Ag loading on  $SiO_2$  support at an ethylene feed position fraction of 0.5, an  $O_2/C_2H_4$  feed molar ratio of 0.20:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50\text{ cm}^3/\text{min}$ .

Figure 4.14 shows the power consumptions to convert an ethylene molecule and to produce an EO molecule at a different Ag loading. The power consumption per molecule of converted ethylene slightly increased when the Ag loading increased and reached a maximum at the Ag loading of 20%. Whereas the power consumption per molecule of produced EO almost unchanged with increasing Ag loading range from 5% to 10%. The power consumption per molecule of produced EO sharply increased and reach a maximum at the Ag loading of 20%. Therefore, at an Ag loading of 10% was considered to be selected for the optimum value because it provided the highest EO selectivity and EO yield with relatively low power consumption per molecule of EO produced.



**Figure 4.14.** Power consumptions as a function of Ag loading on SiO<sub>2</sub> support at an ethylene feed position fraction of 0.5, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.20:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of 50 cm<sup>3</sup>/min.