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APPENDICES

Appendix A To Verify The Presence of Ethylene Oxide Using Mass Spectrometry

A.1 Subsequence Reaction

An amount of 300 mg of 13.18% Ag/Al₂O₃ catalyst was placed in the middle of a quartz tube reactor equipped with furnace. The catalyst was pretreated with 30 ml/min of 20% O₂/He for an hour at 200°C and then was purged with He for 10 min in order to get rid of the oxygen in the bulk gas phase as well as the physisorbed oxygen resulting in only oxygen adsorbed chemically on the catalyst surface. After that, temperature was raised up to 220°C and introduced 2% ethylene balance with helium to react with the oxygen on the silver surface. The effluent gas was analyzed by a quadrupole mass spectrometer of Thermo star model from Blazers Instrument Company. Next, the ethylene flow was stopped and helium was introduced alternatively. Finally, the ethylene was reintroduced.

A.2 Results

Figure A.1 shows the ethylene reaction over the Ag catalyst with full oxygen coverage. Spectra of Ethylene oxide and CO₂ are exhibited at 29 and 44 a.m.u., respectively. It can be explained for each state as followed:

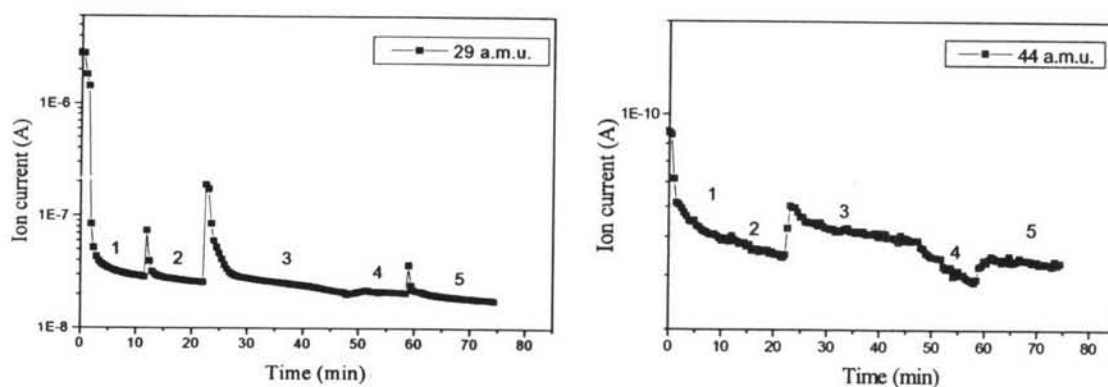


Figure A.1 Ethylene oxide (29 a.m.u.) and CO₂ (44 a.m.u.) spectra after introducing ethylene over 13.19% Ag/Al₂O₃ with full oxygen coverage.

- State 1 Catalyst was pretreated with oxygen in helium for an hour.
 State 2 Purge with helium for 10 min.
 State 3 Introduce with 2% C₂H₄/He on Ag catalyst with full oxygen coverage.
 State 4 Purge with helium again for 10 min.
 State 5 Reintroduce with 2% C₂H₄/He.

From Figure A.1, it can be noticed that when ethylene was introduced over oxygen coverage, there was the change of signal (state 3) for both spectra at 29 a.m.u. and 44 a.m.u. There was no change of signal at 29 a.m.u. when purged with helium again as shown in state 4. It meant that the reaction did not occur on this state. After that both signals were significantly changed again when reintroduced ethylene (state 5). As be seen on figure, the spectrum at 29 a.m.u. was declined along the time; it meant that the production of ethylene oxide was gone down due to less oxygen coverage on the Ag catalyst. The spectrum at 44 a.m.u. showed more dominant than spectrum 29 a.m.u., especially when reaction occurred as shown in state 3 and 5. However, this spectrum appeared to decline along the time as well.

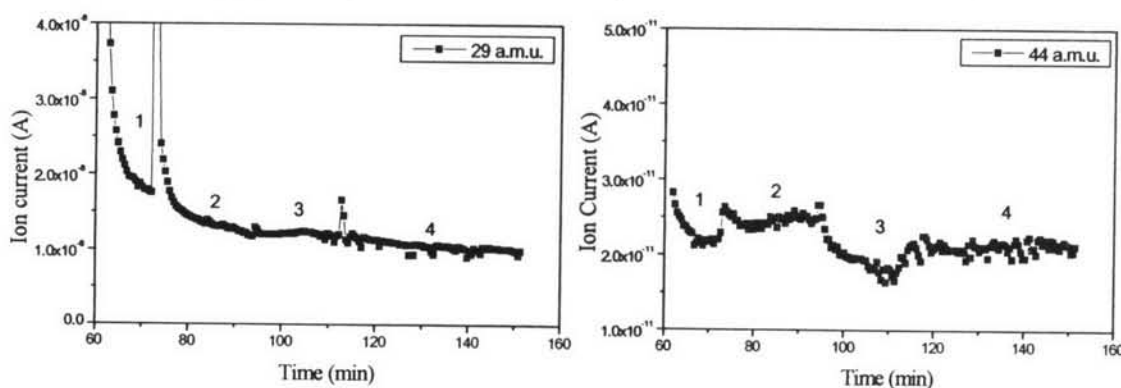


Figure A.2 Ethylene oxide (29 a.m.u.) and CO₂ (44 a.m.u.) spectra after introduced ethylene on 0.96% Au/TiO₂ with impregnation with full oxygen coverage.

- State 1 Purge with helium after pretreatment with O₂/He for an hour.
 State 2 Introduce with 2% C₂H₄/He on Au/TiO₂ catalyst with full oxygen coverage.
 State 3 Purge with helium again for 10 min.

State 4 Reintroduce with 2% C₂H₄/He.

From Figure A.2, 0.96% Au/TiO₂ with impregnation was used as a catalyst. The results showed that both spectra at 29 a.m.u. and 44 a.m.u. had a significant change. It was noticed that there was change of signal (state 2) when ethylene was flowed in the system. After purged with helium into the system, there was no change of signal as shown in state 3 and changed again when reintroduced ethylene. The results showed that both spectra were declined along the time when ethylene was introduced due to the less amount of oxygen coverage after reaction.

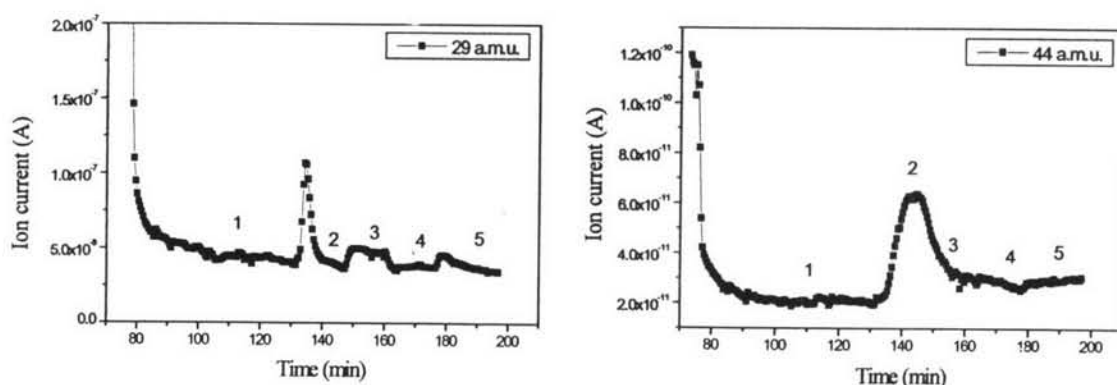


Figure A.3 Ethylene oxide (29 a.m.u.) and CO₂ (44 a.m.u.) spectra after introduced ethylene on 1.03% Au/CeO₂ single step sol gel with full oxygen coverage.

State 1 Purge with helium after pretreatment with O₂/He for an hour.

State 2 Introduce with 2% C₂H₄/He on Au/CeO₂ catalyst with full oxygen coverage and operate at 220°C.

State 3 Change operation temperature from 220°C to 140°C.

State 4 Purge with helium again for 10 min.

State 5 Reintroduce with 2% C₂H₄/He and operate at 140°C.

From Figure A.3, it was shown that the deep oxidation was dominant than partial oxidation (state 2) when ethylene was introduced and operated at 220°C. After reduced temperature to 140°C, the spectrum at 44 a.m.u. was declined as shown in state 3. The change of signal at 29 a.m.u. was stable when helium was purged again for 10 min. When reintroduced C₂H₄/He in the system, the signal was changed (state

5). The results showed that both spectra were declined along the time when ethylene was introduced due to the less amount of oxygen coverage after reaction.

Appendix B Characterization Results of Ag/TiO₂ and Ag/Commercial CeO₂

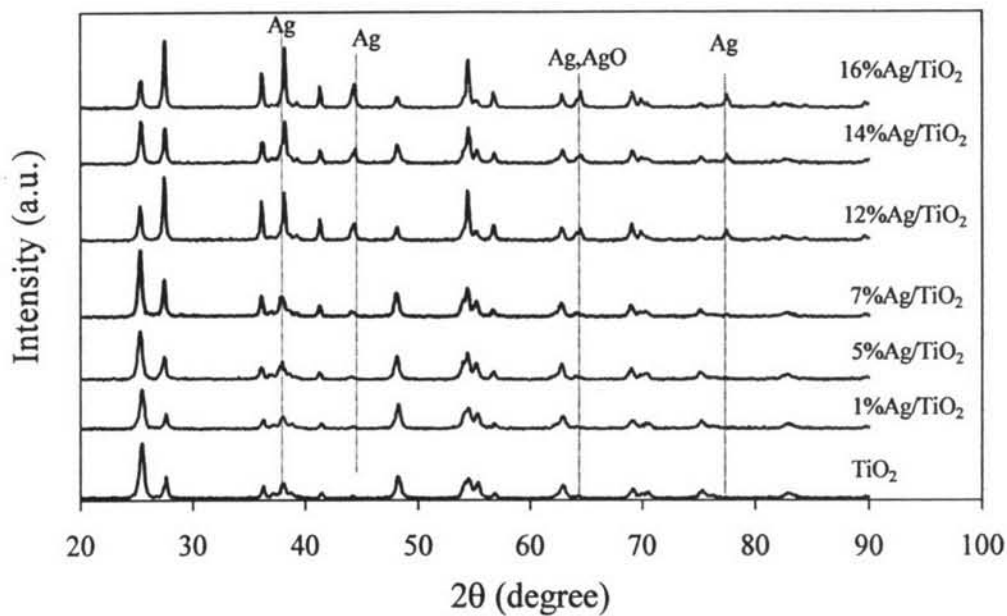


Figure A.4 XRD pattern of the Ag/TiO₂ catalysts at various silver loadings.

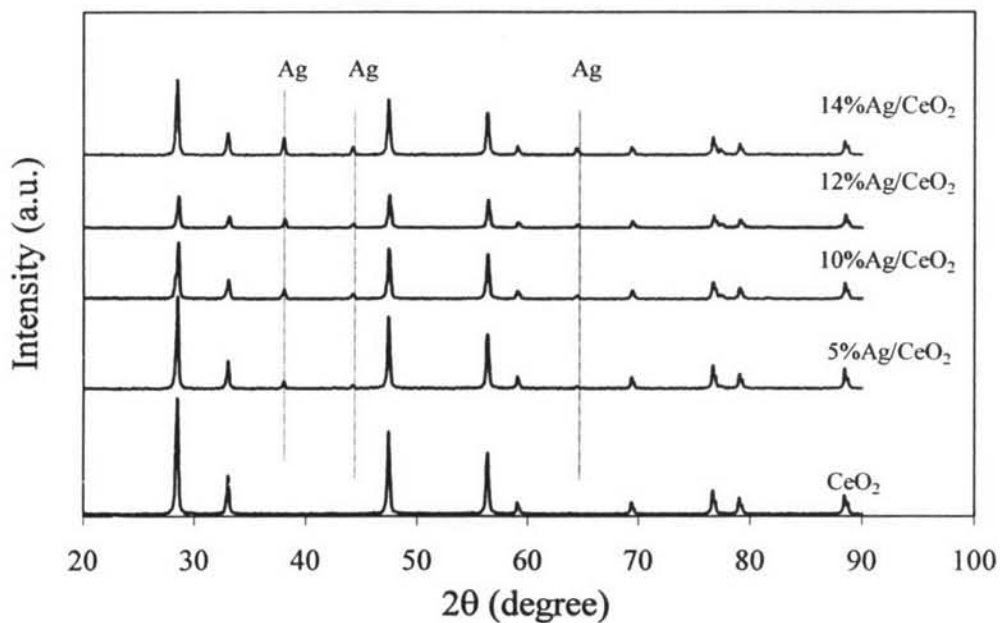


Figure A.5 XRD pattern of the Ag/commercial CeO₂ catalysts at various silver loadings.

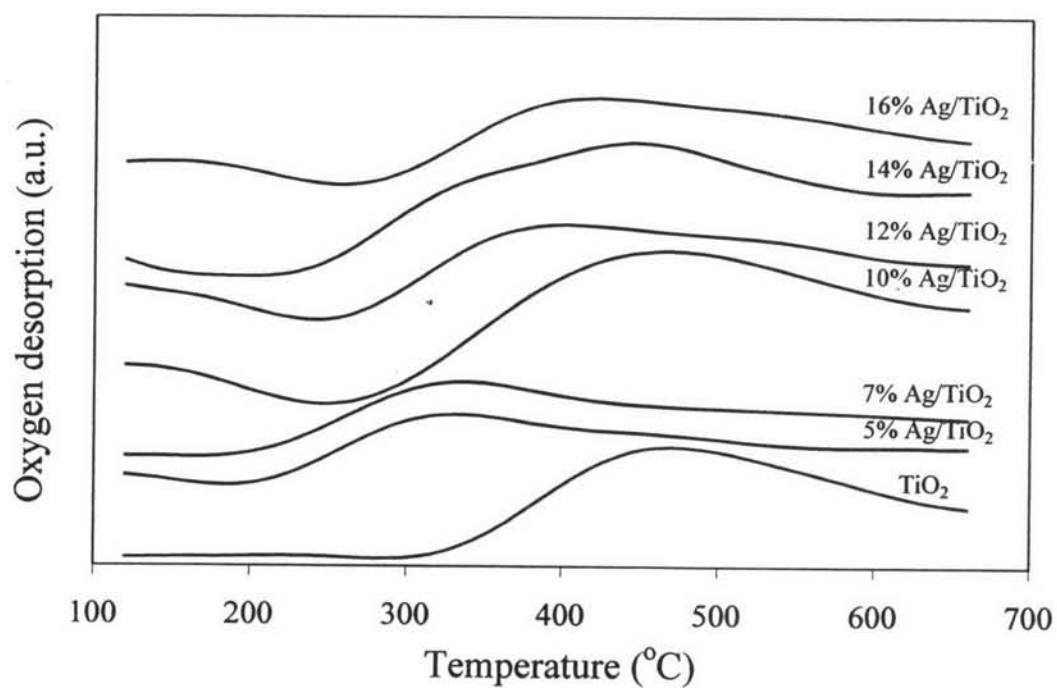


Figure A.6 TPD profiles of O_2 of the Ag/TiO_2 at various silver loadings.

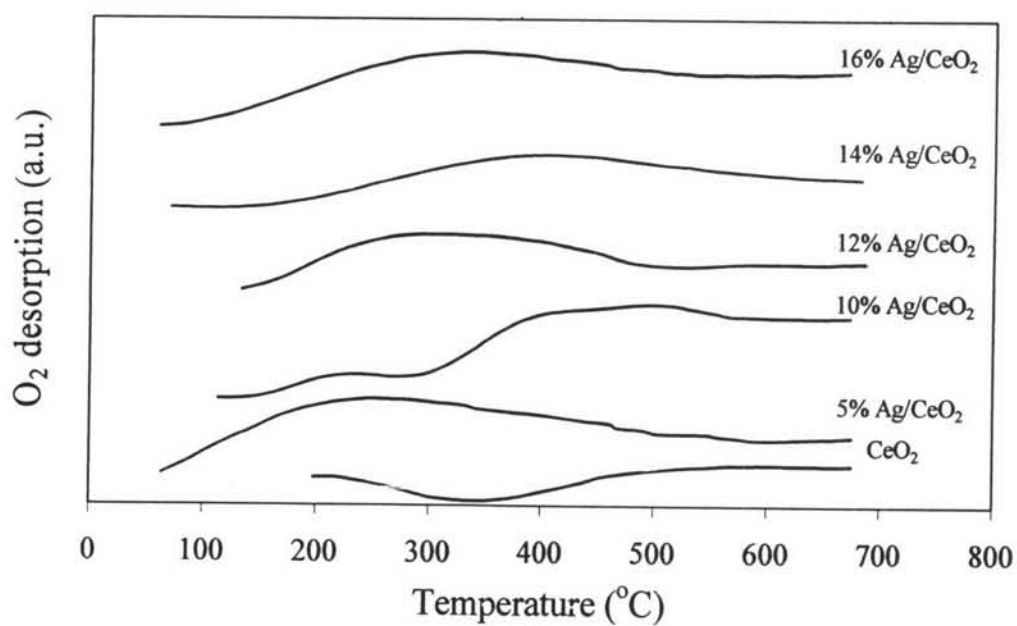


Figure A.7 TPD profiles of O_2 of the Ag/CeO_2 at various silver loadings.

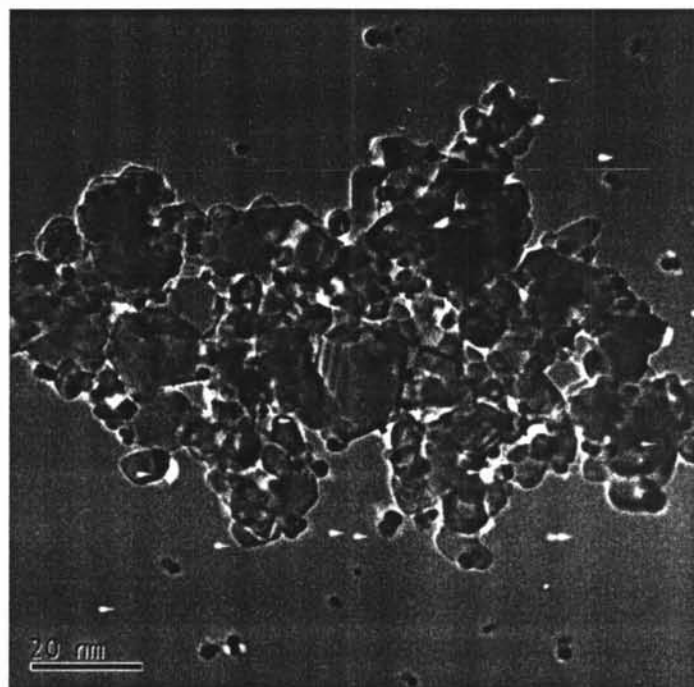


Figure A.8 TEM micrograph of 10% Ag/TiO₂.

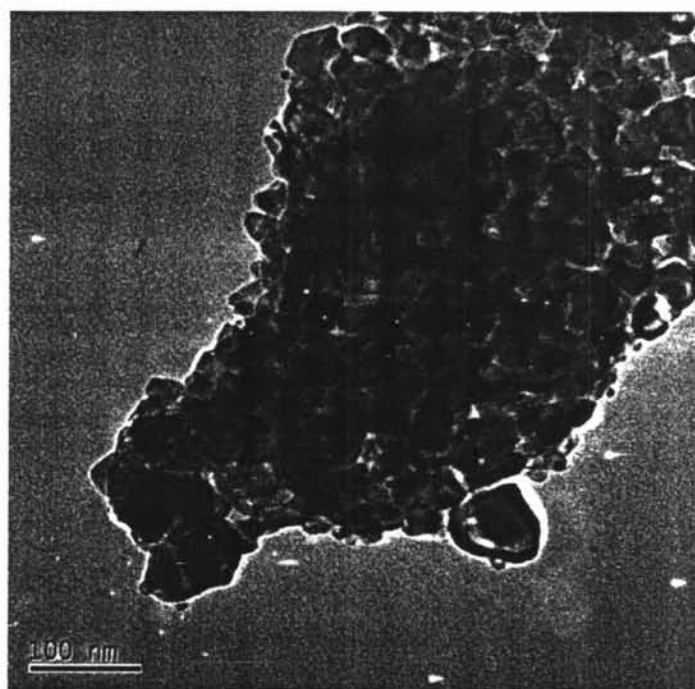
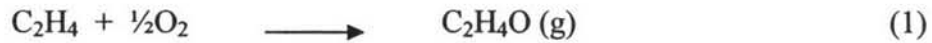


Figure A.9 TEM micrograph of 10% Ag/commercial CeO₂.

Appendix C Calculation of Ethylene Oxide Using C-Balance and O₂-Balance



Raw data

	O ₂	C ₂ H ₄	CO ₂
Input (ppm)	64746	61757.5	-
(mole/min)	0.064746	0.0617575	-
Output (ppm)	62650	61080	171
(mole/min)	0.062650	0.061080	0.000171

C- Balance

$$\text{C input} = \text{C output}$$

$$\text{C in C}_2\text{H}_4 \text{ in} = \text{C in C}_2\text{H}_4 \text{ out} + \text{C in CO}_2 + \text{C in C}_2\text{H}_4\text{O}$$

$$\text{C in C}_2\text{H}_4 \text{ (mole/min)} = 2 \times 0.0006775 = 0.001355$$

$$\text{C in CO}_2 \text{ (mole/min)} = 0.000171$$

$$\text{C}_2\text{H}_4 \text{ consume for CO}_2 \text{ (mole/min)} = 0.000171/2 = 0.0000855$$

$$\text{Thus, C}_2\text{H}_4 \text{ consumed for C}_2\text{H}_4\text{O (mole/min)} = (0.001355 - 0.000171)/2 = 0.000592$$

$$\text{C}_2\text{H}_4 \text{ conversion (\%)} = (0.0006775/0.0617575) \times 100 = 1.10$$

$$\text{C}_2\text{H}_4\text{O selectivity (\%)} = (0.000592/0.0006775) \times 100 = 87.38$$

O₂- Balance

$$\text{O}_2 \text{ input} = \text{O}_2 \text{ output}$$

$$\text{O}_2 \text{ in} = \text{O}_2 \text{ out} + \text{O}_2 \text{ in CO}_2 + \text{O}_2 \text{ in H}_2\text{O} + \text{O}_2 \text{ in C}_2\text{H}_4\text{O}$$

$$\text{O}_2 \text{ consumed (mole/min)} = 0.064746 - 0.062650 = 0.002096$$

$$\text{O}_2 \text{ in CO}_2 \text{ (mole/min)} = 0.000171$$

$$\text{O}_2 \text{ in H}_2\text{O (mole/min)} = 0.000171/2 = 0.0000855$$

$$\text{Thus, O}_2 \text{ consumed for C}_2\text{H}_4\text{O (mole/min)} = (0.002096 - 0.000171 - 0.0000855) \times 2 \\ = 0.003679$$

$$\text{O}_2 \text{ conversion (\%)} = (0.002096/0.064746) \times 100 = 3.24$$

$$\text{C}_2\text{H}_4\text{O selectivity (\%)} = (0.003679/(2 \times 0.002096)) \times 100 = 87.7$$

Therefore, the deviation value from O₂-balance compared to C-balance

$$= (87.70-87.38)*100/87.38$$

$$= 0.3662$$

Appendix D Paper Publications

Activity of Ethylene Epoxidation over High Surface Area Alumina Support Au–Ag Catalysts

Siriphong ROJLUECHAI¹, Sumaeth CHAVADEJ¹,
Johannes W. SCHWANK² and Vissanu MEEYOO³

¹The Petroleum and Petrochemical College,
Chulalongkorn University, Bangkok 10330, Thailand

²Department of Chemical Engineering, The University of Michigan,
Ann Arbor, MI 48109, U.S.A.

³Department of Chemical Engineering, Mahanakorn University,
Bangkok 10530, Thailand

Keywords: Silver Catalyst, Au–Ag Bimetallic, Ethylene Oxide, Ethylene Epoxidation

In this study, the effect of gold-added silver catalyst supported on high surface area alumina on the ethylene epoxidation activity was investigated. An addition of Au with a small amount was found to create Au–Ag bimetallic which favors the ethylene epoxidation reaction. Gold as a diluting agent on silver surface resulting in destroying multiple Ag sites which favor atomic oxygen adsorption. As a result, adding gold simply creates new adsorption sites for molecular oxygen which is responsible for the ethylene epoxidation reaction. However, at high gold loadings of Ag/Al₂O₃ catalyst, the formation of Au–Ag alloys was found resulting in decreasing the ethylene epoxidation activity since the Au–Ag alloy favors a complete oxidation reaction. For the ethylene epoxidation reaction, the optimum Ag to Au ratio was 13.18 wt% to 0.63 wt% in the optimum temperature range of 510–520 K.

Introduction

Typically, silver on low surface area inert supports has been used for the ethylene epoxidation for decades but it yields both low selectivity and activity. By introducing electronegative moderators to the Ag catalyst, the selectivity of ethylene oxide is improved remarkably. The moderators used to improve the selectivity of silver are Cl, Br, I, S, Se, Te, P and Bi. Chlorine is the most commonly used moderator added in the form of organic chlorides such as 1,2-ethylene dichloride with a low concentration of a few parts per million. The role of the moderator is thought to change not only the relative concentrations of atomic and molecular oxygen but also to increase the probability of molecular oxygen to react with ethylene to form ethylene oxide. Moreover, the role of the promoters is also to stabilize silver against sintering (Matar *et al.*, 1989).

Rhenium and cesium are the other alternative promoters for the epoxidation reaction. The effect of rhenium is to weaken the silver-oxygen bond and to reduce the electron density of the adsorbed oxygen, which could be the reason for the enhancement of the selectivity of ethylene oxide (Jun *et al.*, 1992). However, it has been found that for high surface area α -alumina, an addition of cesium contributes to the neu-

tralization of surface acidity which promotes complete combustion (Mao and Vannice, 1995). Cesium adding likely stabilizes the defects on the Ag surface, where electrophilic oxygen is probably localized. On the other hand, it can decrease the concentration of nucleophilic oxygen (surface Ag₂O), which is responsible for the deep oxidation of C₂H₄ (Goncharova *et al.*, 1995).

With regard to the role of gold, Kondarides and Verykios (1996) studied the effect of alloying silver with gold on the oxygen adsorption properties of Ag over a set of 15 wt% Ag–Au/ α -Al₂O₃ catalysts of variable alloy composition and reported that alloying Ag with Au influenced the bond strength of oxygen and the silver surface, which results in modifying the relative population of the adsorbed species. They confirmed the presence of three adsorbed species of oxygen at elevated temperatures, namely molecular, atomic and subsurface. In the oxidation of ethylene, Geenen *et al.* (1982) reported that the selectivity to ethylene oxide decreased sharply with increasing gold content of Au–Ag alloy on α -alumina support. On the catalysts with gold rich alloys, no ethylene oxide was formed, the only products being carbon dioxide and water. The reason is that the reaction of ethylene with molecular oxygen (O₂) results only in ethylene oxide if the adsorbed complex is sterically hindered by adjacent adsorbed species, such as O²⁻ or Cl⁻, such that abstraction of hydrogen from the ethylene molecule in the way depicted above cannot occur. In the case of

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the Au–Ag alloy, the O_2^- species are separated from one another and hence the adsorbed ethylene complex will react with atomic oxygen to form carbon dioxide and water.

In this paper, we investigated the role of gold on the catalytic activity of silver catalysts over ethylene epoxidation. High surface area alumina was used as a support aiming to clearly investigate the interaction between Au and Ag.

1. Experimental

1.1 Catalyst preparation

In this work, a silver catalyst was prepared by the incipient wetness method using aluminum oxide (fumed alumina, Degussa C, 85–115 m^2/g , Degussa AG) with a silver nitrate solution to achieve a nominal silver loading of 14 wt% (actual Ag loading = 13.18 wt%) since this loading was found to provide both of high yield and selectivity of ethylene oxide (Roatluechai *et al.*, 2001). Next, the Ag catalyst prepared was impregnated with different amounts of chloroauric acid ($HAuCl_4$, Sigma-Aldrich Co.) solutions to obtain different concentrations of nominal gold loadings of 0.3, 0.5, 0.7 and 1.0 wt%. Then, the catalyst samples were dried overnight in an oven at 383 K followed by calcination in air at 773 K for 5 h.

1.2 Catalyst characterization

Specific surface areas of all catalyst samples prepared were determined by N_2 adsorption at 77 K (BET method) using a surface area analyzer (Autosorb 1, Quantachrome Instruments). Prior to the measurement, the samples were outgassed at 523 K for 3 h. The metal contents (Au and Ag) in the catalyst samples were analyzed by an atomic adsorption spectrophotometer (Spectr AA-300, Varian Inc.).

The crystalline structures of the catalyst samples were examined by X-ray diffraction (XRD) on a RINT 2000 diffractometer (Rigaku Corp.) equipped with a Ni filtered $Cu K\alpha$ radiation source ($\lambda = 0.1542$ nm) of 40 kV and 30 mA. The catalyst samples were scanned in the range of 2θ from 20° to 90° in the continuous mode with a rate of 5°min^{-1} . Mean crystallite sizes were calculated by the Scherrer equation from X-ray line broadening, using the full line width at half maximum of intensity.

The existence of all metal particles present on the surface of each catalyst sample prepared was verified by using a transmission electron microscope (TEM) (2010, JEOL Ltd.) operating at 200 kV equipped with energy dispersive spectroscopy (EDS). Particle sizes were determined by the statistical data of TEM image.

Temperature programmed desorption (TPD) experiments were carried out by placing 100 mg of each catalyst into a U-tube quartz reactor. To make the catalyst's surface free from any adsorbing organic compounds, the catalyst was first pretreated in a continu-

ous flow of O_2 (8% O_2/N_2) at 473 K for 1 h. Then, it was flushed with N_2 for 0.5 h in order to remove the gas phase of O_2 . After that, the reactor temperature was ramped from 473 K to 873 K with a linear heating rate of 40 K min^{-1} in a continuous flow of N_2 (30 ml min^{-1}). The desorbing oxygen was detected by a thermal conductivity detector.

1.3 Ethylene oxidation reaction experiment

The ethylene oxidation reaction was conducted in a differential flow reactor, which was operated at 3.6 mPa and different reaction temperatures. Typically, 30 mg of each catalyst was placed inside a Pyrex tube and secured with Pyrex glass wool plugs. The tubular reactor having 10 mm diameter was placed in a furnace equipped with a temperature controller. The catalyst was initially pretreated with oxygen at 473 K for 2 h in order to diminish all impurities and residual moisture from the catalyst. The feed gas was a mixture of 15% oxygen in helium, 30% ethylene in helium and pure helium (HP grade) obtained from Thai Industrial Gases Plc. (TIG). The flow rates of these three gas streams were regulated by mass flow controllers to obtain a feed gas composition of 6% oxygen and 6% ethylene with helium balance. The feed gas was passed through the reactor at a constant space velocity of $6,000 \text{ h}^{-1}$ and the reaction temperature was varied from 493 to 543 K. After the studied system reached steady state, the compositions of the feed gas and the exit gas were analyzed by using an on-line gas chromatograph (5890 Series II, Hewlett-Packard Development Company, L.P.) equipped with a HayeSeb D 100/120-packed column (Valco Instruments Co. Inc.), capable of separating carbon dioxide, ethylene and oxygen. The ethylene oxide product was calculated from the carbon material balance with 0.25% carbon atom error (Yeung *et al.*, 1998; Lafarga *et al.*, 2000). Moreover, the calculated values of ethylene oxide produced were confirmed by performing O_2 mass balance with 0.3% oxygen atom error.

2. Results and Discussion

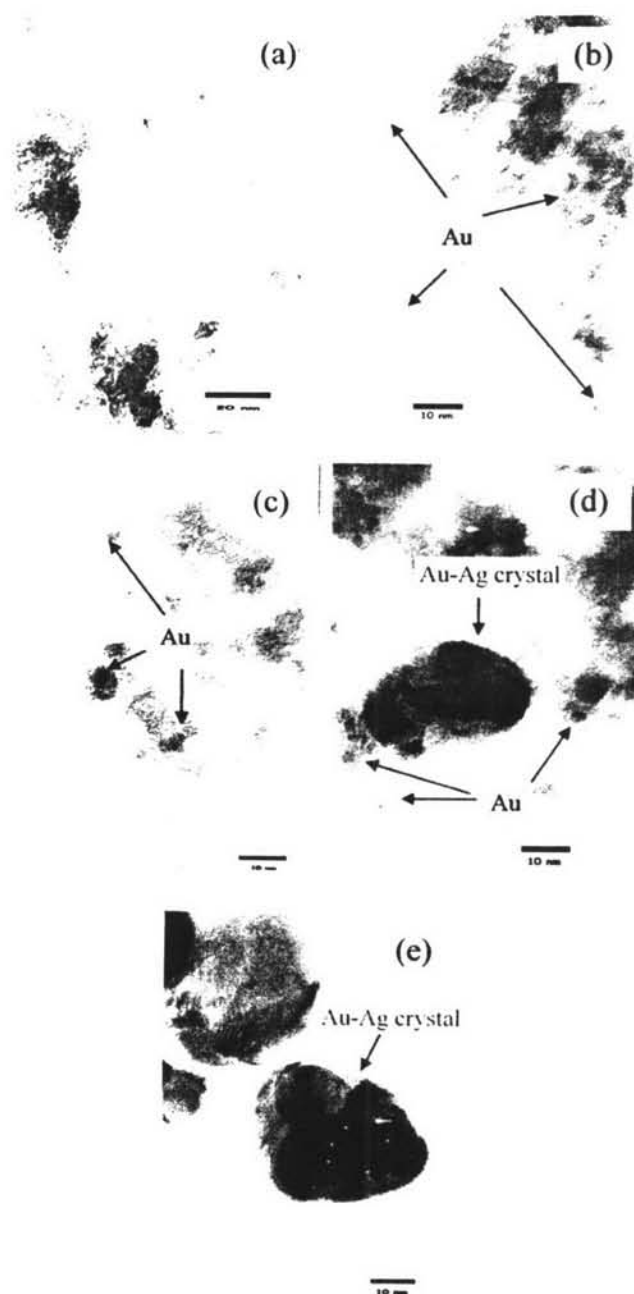
2.1 BET, XRD and TEM results

The BET surface areas of the catalysts prepared are shown in Table 1. It was found that the surface areas of the catalysts are similar to that of the blank support and in the range of 90–100 m^2/g . This result implies that both Ag and Au are evenly dispersed on the surface of alumina support. The use of high surface area alumina in this study aims to clearly investigate the interaction between Ag and Au.

In this study, TEM equipped with EDS was employed to identify the elemental composition of individual particle on the surface of the studied catalysts. The results from the TEM with EDS analysis show that Ag particles are highly dispersed on the alumina support with the average particle size of about 40 nm as

Table 1 Physical properties of Ag and Au–Ag catalysts prepared in this study

Catalyst	BET surface area [m ² /g]	Mean crystallite size [nm]	Total oxygen desorption × 10 ⁻⁷ [mol/g-catalyst]
Degussa-Al ₂ O ₃	98	—	—
13.18% Ag/Al ₂ O ₃	90	19.2	2200
0.27% Au–13.18% Ag/Al ₂ O ₃	90	18.6	2017
0.54% Au–13.18% Ag/Al ₂ O ₃	89	18.3	1943
0.63% Au–13.18% Ag/Al ₂ O ₃	101	18.6	1870
0.93% Au–13.18% Ag/Al ₂ O ₃	99	18.0	1393

**Fig. 1** TEM micrographs of 13.18 wt% Ag/Al₂O₃ catalysts at various gold loadings: (a) 0 wt% Au; (b) 0.27 wt% Au; (c) 0.54 wt% Au; (d) 0.63 wt% Au; (e) 0.93 wt% Au

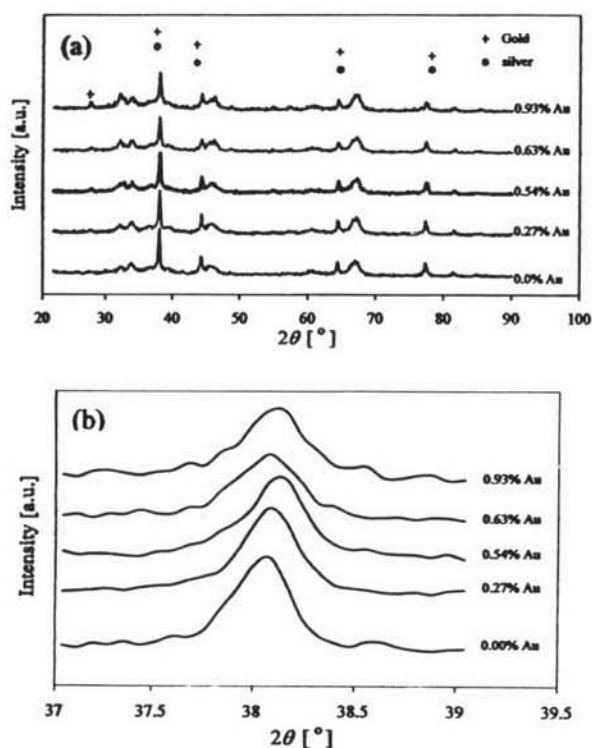


Fig. 2 XRD patterns of the Ag/Al₂O₃ catalysts at various gold loadings for the whole range (a) and at around $2\theta = 38^\circ$ (b)

shown in Figure 1(a). By using the TEM with EDS technique, the addition of a small amount of Au on the Ag/Al₂O₃ catalyst was found to result in formation of small particles of Au of around 2–3 nm on the Ag particles indicating the formation of Au–Ag bimetallic (Figures 1(b) and (c)). At Au loadings greater than 0.54 wt%, apart from individual tiny Au particles scattering throughout the alumina surface, there were a number of large particles about 40 nm in diameter. By using the EDS scanning on some of the large particles, both Au and Ag were detected with almost the same intensities throughout the whole particle (Figures 1(d) and (e)). This leads to a possibility that the formation of Au–Ag bimetallic at a low Au loading while a high Au loading may cause alloy formation between Au and Ag. Kondarides and Verykios (1996) reported an evidence of alloy formation at an Au:Ag ratio 1:10 which is very close to the ratio of 1:9 in our present study.

The XRD patterns of the studied catalysts showed a typical fcc phase of Ag giving visible tailing at about $33, 38, 44$ and 64° (2θ) which represent the indices of (111), (200), (220) and (311). The presence of Au does not alter the typical XRD pattern of the Ag catalyst in the studied range of Au loading (Figure 2(a)). Figure 2(b) illustrates the comparison of the peak maxima at around $2\theta = 38^\circ$ of Ag catalyst at different Au loadings. The temperature of the peak maxima was found to in-

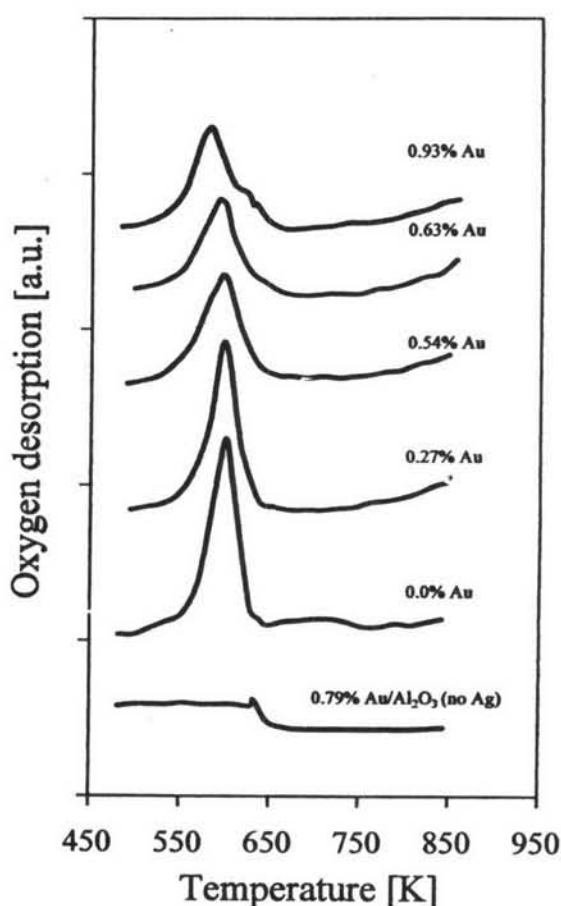


Fig. 3 TPD profiles of O₂ of 13.18 wt% Ag/Al₂O₃ at various gold loadings and 0.79 wt% Au/Al₂O₃

crease with increasing Au loading in the range of 0–0.54 wt%. Interestingly, for an Au loading greater than 0.54 wt%, the peak maxima temperature decreased with increasing Au loading. The XRD results showing the structural differences of Ag with Au loading can be used to support the TEM-EDS results as indicating the formation of Au–Ag bimetallic at low Au loadings and Au–Ag alloys at high Au loadings.

As shown in Table 1, the mean measured crystallite sizes of the Au–Ag catalysts are in the range of 18–18.6 nm while the crystallite size of Ag catalyst is 19.2 nm. The results indicate that gold addition does not significantly affect the crystallite size of Au–Ag catalysts. It is interesting to point out that the mean crystallite sizes obtained from XRD were much smaller than the particle sizes from TEM. This is because the particle size basically consisted of several crystallites.

2.2 Temperature programmed desorption (TPD) results

Temperature programmed desorption was carried out to investigate the interaction between oxygen and the catalyst surface with respect to temperature. Figure 3 shows the TPD of oxygen on Au–Ag catalysts at

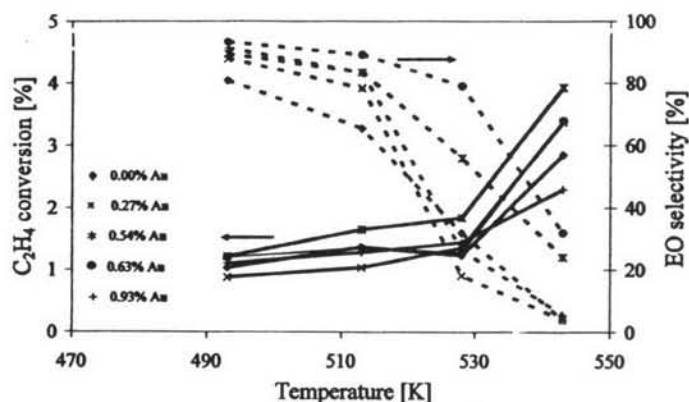


Fig. 4 Ethylene conversion and ethylene oxide selectivity for 13.18 wt% Ag/Al₂O₃ at various gold loadings at the space velocity of 6,000 h⁻¹, $P = 3.6$ mPa and 6% O₂ and 6% C₂H₄ with He balance

different Au loadings as compared to both pure Ag and Au catalysts. The TPD results of oxygen reveal that an addition of a small amount of Au on Ag catalyst does not alter the peak maxima temperature of oxygen as shown in Figure 3. However, a significant shift to a lower temperature of the peak maxima temperature was found at the highest Au loading of 0.93 wt%. As shown in Table 1, the calculated amount of oxygen adsorbed on the catalysts decreases with increasing Au content. Interestingly, the oxygen adsorption on Ag catalyst decreased when the Au loading increased. This indicates that the interaction between silver and oxygen is weakened remarkably in the presence of gold. The presence of Au atoms has been found to affect the electronic properties of Ag (Tories and Verikios, 1987; Kondarides and Verykios, 1996). In general, the dissociative adsorption of oxygen on Ag requires a charge transfer from Ag to oxygen. Hence, it is not unexpected that the electron deficiency induced on Ag atoms by the presence of neighboring Au atoms would result in weakening the Ag–O bond. The result confirms that under the presence of small amounts of Au on Ag catalyst, the interaction between gold and silver affects significantly the oxygen adsorption. Kondarides and Verykios (1996) also reported that the added Au simply weakened the bond strength between silver and oxygen.

2.3 Catalyst activity for epoxidation of ethylene

The study of the catalytic epoxidation of ethylene was carried out over Ag/Al₂O₃ and Au doped Ag/Al₂O₃ catalysts at the temperature range of 473–573 K. As shown in Figure 4, the catalytic activity of the Ag/Al₂O₃ catalyst is governed by both the reaction temperature and Au loading. For any given Au loading on the Ag/Al₂O₃ catalyst, the ethylene conversion was low in the temperature range from 493 to 528 K but increased drastically with increasing reaction temperature when the reaction temperature was above 528 K. On the contrary for the temperature below 513 K, the ethylene

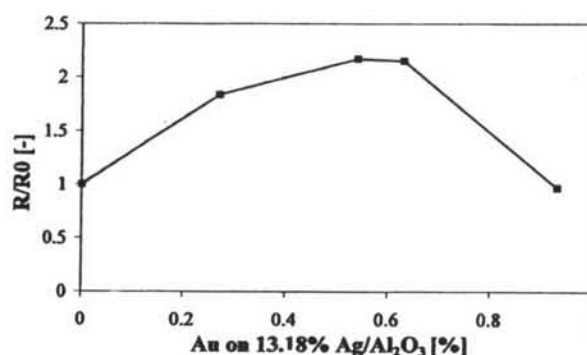


Fig. 5 Normalized turnover number of ethylene epoxidation on 13.18 wt% Ag/Al₂O₃ at various gold loadings and the reaction temperature of 513 K (turnover number obtained on 13.18 wt% Ag/Al₂O₃ with various gold loadings (R) over that obtained on 13.18 wt% Ag/Al₂O₃ with no Au loading (R_0))

oxide selectivity decreased slightly with increasing reaction temperature. Interestingly, for the temperatures above 513 K the selectivity of ethylene oxide decreased substantially when the reaction temperature increased. This is due to the fact that total oxidation of ethylene is favorable at high temperatures, owing to more accessible dissociated oxygen. In the present work, the ethylene oxide selectivity of Ag/Al₂O₃ at 513 K was around 65% which is in good agreement with the literature value of 60% (Lee *et al.*, 1989; Seyedmonir *et al.*, 1990). Figure 5 illustrates the effect of Au loading of Ag/Al₂O₃ catalyst on the ethylene epoxidation reaction by plotting Au loading versus the normalized turnover number (the turnover number ratio of the Au–Ag catalyst to the Ag catalyst). The normalized turnover number of ethylene oxide slightly increased with increasing Au loading and reached the maximum value at the Au loading between 0.54 and 0.64 wt%. It decreased with increasing Au

loading above 0.63 wt%. The results indicate that an addition of gold with an appropriate amount on the Ag catalyst can promote the ethylene epoxidation reaction by weakening the Ag–O bond. Regarding to the ethylene oxide selectivity as shown in Figure 4, the optimum Au loading is about 0.63 wt% on 13.18 wt% Ag/Al₂O₃. Above this point a decrease in oxygen adsorption capacity results in a decreasing activity due to the formation of Au–Ag alloy at high gold loadings. Under the studied conditions with Au–Ag catalysts on the high surface area alumina support, the optimum range of reaction temperature is around 510–520 K for the ethylene epoxidation reaction.

Conclusions

In conclusion, there is still a debate concerning the existence of atomic oxygen and molecular oxygen adsorption over the silver catalyst and which the oxygen species is the determining step for ethylene epoxidation. However, in this research it was found that gold acts as a diluting agent on the silver surface and creates new single silver sites which favor molecular oxygen versus atomic oxygen adsorption leading to enhancement of the epoxidation reaction. It was believed to be the Ag atom sites that molecular oxygen may adsorb with its axis perpendicular to the surface. Adding a small amount of gold on the silver catalyst is to form a bimetallic species which has a lower electron density at the surface resulting in increasing its capacity for chemisorption of the electron acceptor species. However, an addition of Au at very high loadings was found to form Au–Ag alloy resulting in the reduction of the ethylene epoxidation activity.

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Catalytic activity of ethylene oxidation over Au, Ag and Au–Ag catalysts: Support effect

Siriphong Rojluechai^a, Sumaeth Chavadej^{a,*}, Johannes W. Schwarzk^b, Vissanu Meeyoo^c

^a *The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*

^b *Department of Chemical Engineering, The University of Michigan, Ann Arbor, MI 48109, USA*

^c *Department of Chemical Engineering, Mahanakorn University, Bangkok 10530, Thailand*

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10 Abstract

11 Au, Ag and Au–Ag catalysts on different supports of alumina, titania and ceria were studied for their catalytic activity of ethylene
12 oxidation reactions. An addition of an appropriate amount of Au on Ag/Al₂O₃ catalyst was found to enhance the catalytic activity
13 of the ethylene epoxidation reaction because Au acts as a diluting agent on the Ag surface creating new single silver sites which favor
14 molecular oxygen adsorption. The Ag catalysts on both titania and ceria supports exhibited very poor catalytic activity toward the epox-
15 idation reaction of ethylene, so pure Au catalysts on these two supports were investigated. The Au/TiO₂ catalysts provided the highest
16 selectivity of ethylene oxide with relatively low ethylene conversion whereas, the Au/CeO₂ catalysts was shown to favor the total oxida-
17 tion reaction over the epoxidation reaction at very low temperatures. In comparisons among the studied catalysts, the bimetallic Au–Ag/
18 Al₂O₃ catalyst is the best candidate for the ethylene epoxidation. The catalytic activity of the gold catalysts was found to depend on the
19 support material and catalyst preparation method which govern the Au particle size and the interaction between the Au particles and the
20 support.

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22 *Keywords:* Ethylene oxidation; Al₂O₃; TiO₂; CeO₂; Ag; Au; Au–Ag

24 1. Introduction

25 Ethylene oxide is an important starting chemical in sev-
26 eral petrochemical processes. The most widely used process
27 for ethylene oxide manufacture is the direct catalytic oxida-
28 tion of ethylene with air or oxygen over supported silver
29 catalysts [1]. A unique support material for silver catalysts
30 is commercial α -alumina because it provides highly selec-
31 tive ethylene epoxidation. This is due to its inertness for
32 the isomerization of ethylene oxide to acetaldehyde [2].
33 Low surface area α -alumina supports (surface area
34 <1 m²/g) with high silver loadings are typically used for
35 the commercial production of ethylene oxide. In these com-
36 mercial silver catalysts, silver is poorly dispersed over an
37 alumina support [3]. As a result, these catalysts possess rel-

atively low yields of ethylene oxide. This is the reason why
many researchers try to find other alternative supports to
provide a better silver dispersion which, in turn, will
improve the activity of the ethylene epoxidation. However,
some supports may give the undesirable step of the second-
ary oxidation reaction of ethylene oxide to carbon dioxide.
Seyedmonir et al. [4] conducted a systematic study of the
catalytic activity of Ag on different supports of η -Al₂O₃,
TiO₂, α -Al₂O₃, and SiO₂. They reported that both ethylene
oxide selectivities over Ag/ η -Al₂O₃ and Ag/TiO₂ were very
low, about 10%, as compared to a high value of about 60%
over the Ag/ α -Al₂O₃ catalysts in the presence of 0.5 ppm
EDC (ethylene dichloroethane). In contrast, in the absence
of EDC and CO₂ at 523 K, the ethylene oxide selectivities
of 17% and 55% were obtained over 4.4 and 7.6 nm Ag
crystallites on SiO₂, respectively, compared to 23% over
1 μ m Ag crystallites on α -Al₂O₃. Mao and Vannice [5]
investigated the use of a high surface area (HSA) α -alumina

* Corresponding author. Tel.: +66 22120905.

E-mail address: sumaeth.c@chula.ac.th (S. Chavadej).

(about 100 m²/g) as support for silver catalysts. They reported that the (HSA) α -alumina was a poor support for the ethylene epoxidation reaction due to the formation of small nanoparticles of Ag. The reaction rate was found to increase with increasing the surface area of catalyst, but the ethylene oxide selectivity decreased.

TiO₂ and CeO₂ have some special properties which are believed to enhance the catalytic activity of ethylene oxidation reactions. Both TiO₂ and CeO₂ have gained a great deal of attention because they are nonstoichiometric oxide materials which possess the ability for oxygen migration from reduced support particles onto the surfaces of the metallic particles of catalysts, which, in turn, promotes oxidative reactions [6]. It has been reported that group VIII noble metals supported on TiO₂ exhibit a strong metal-support interaction (SMSI) effect. Not only did Seyedmonir et al. [4] study the ethylene oxide reaction over Ag/TiO₂, but Yong et al. [2] reported that silver supported on TiO₂ showed zero ethylene oxide selectivity. It was also concluded that the zero selectivity of the silver catalyst supported on TiO₂ for the ethylene epoxidation is due to the isomerization of ethylene oxide to acetaldehyde on the support followed by the complete oxidation reaction. Shastri et al. [7] studied the catalytic behavior of gold supported on TiO₂. They pointed out that the high gold dispersion on TiO₂ was stabilized up to 973 K and the agglomeration of gold into large particles was found to coincide with the phase transformation into rutile at 1073 K. The stability of the gold dispersion was explained to be not due to the SMSI effect. A temperature of 973 K appeared sufficient to accomplish the complete phase transformation of anatase to rutile in blank TiO₂. Mallick and Scurrill [8] reported that introducing ZnO onto TiO₂ caused a surface modification of titania and is associated with a negative effect on the catalytic activity. Compared with Au/TiO₂, Au/TiO₂-ZnO was found to behave as a moderately good catalyst up to a certain temperature, but appeared to suffer from mere severe deactivation with an increase in the time on stream at higher temperatures.

Ceria is one of the most important catalysts among commercial catalytic processes in terms of economic relevance and tonnage, such as three-way catalytic converters (TWC) and fluid catalytic cracking units (FCC). Ceria is known as having a good thermal stability resulting in the maintaining of its high surface area at high temperatures. In addition, the use of ceria as a support can also minimize the sintering effect of loaded catalyst particles. Interestingly, ceria also behaves as an oxygen reservoir so that it has been widely employed for CO oxidation and water-gas shift reactions [9,10]. Bera and Hegde [11] reported that the Au dispersed on a CeO₂ surface was found to be metallic in structure (Au⁰) as well as ionic in form (Au³⁺) and both Au⁰ and Au³⁺ species act as catalytic sites. All the oxidation reactions of NO, CO and hydrocarbon over 1% Au/CeO₂ with heat treatment (1073 K for 100 h) were found to occur at significantly lower temperatures, as compared to those with 1% Au/TiO₂ and 1% Au/Al₂O₃.

In this study, the effect of support material on ethylene oxidation reactions over Au and Au–Ag catalysts was determined. TiO₂ and CeO₂, as reducible oxide supports, were investigated for their effects, in comparison with a high surface area alumina support.

2. Experimental

2.1. Catalyst preparation

In this work, silver catalysts were prepared by the incipient wetness method using aluminum oxide (fumed alumina, Degussa C, 85–115 m²/g, Degussa AG) and silver nitrate precursor solutions to achieve various nominal silver loadings. From our previous results [12], the optimum Ag loading of 13.18 wt.% was found to provide the maximum selectivity of ethylene oxide and a relatively high ethylene conversion. Hence, this Ag loading was used to prepare Ag–Au catalysts at different Au loadings using the impregnation method and chloroauric acid precursor [18].

Apart from alumina, titania and ceria were used to prepare catalysts in order to determine the effect of support material on ethylene oxidation reactions. First, silver loaded on either titania or ceria was prepared at different silver loadings using a silver nitrate precursor. All of these silver catalysts on both supports were found to have no activity toward the ethylene epoxidation. Hence, bimetallic Au–Ag catalysts on these two supports were not studied, but only pure gold catalysts on these reducible oxide supports were investigated instead. Au catalysts on the two supports of TiO₂ (Degussa P25, Degussa AG) and CeO₂ (sol gel urea hydrolysis) were prepared with aqueous gold precursor (HAuCl₄, Sigma–Aldrich Co.) solutions to obtain different gold loadings by using the impregnation method. Then, the catalyst precursors were dried at 383 K overnight followed by calcination in air at 773 K for 5 h. The other Au/TiO₂ catalysts were prepared by the deposition–precipitation and single-step sol gel methods, which are described elsewhere [13–15].

The CeO₂ support was synthesized by the hydrolysis of a cerous nitrate solution with a urea solution. For preparing the first solution, 6.5135 g of Ce(NO₃)₃·6H₂O (purity 99%, Sigma–Aldrich Co.) was dissolved in 150 ml of distilled water. Next, the second solution was prepared by dissolving 1.2012 g of urea, (NH₂)₂CO (purity 99%, Sigma–Aldrich Co.) in 50 ml of distilled water. Then, these two solutions were mixed in a 250 ml Pyrex bottle with a screw cap. The resultant mixture was placed in an oven at 373 K for 50 h to achieve the hydrolysis step. The mixture solution was then allowed to cool to room temperature and was centrifuged to separate the precipitate. The separated precipitate was washed with hot distilled water (353 K) 4 to 5 times and finally was washed with ethanol. The resulting precipitate was dried overnight at 383 K and calcined at 773 K for 4 h to obtain CeO₂. There were two methods used to prepare the Au/CeO₂ catalysts. For the single-step

167 sol gel with urea hydrolysis method, 0.0447 g of HAuCl₄
 168 was added to the mixture of the two prepared solutions
 169 of cerous nitrate and urea. For the second preparation
 170 method of Au/CeO₂, the CeO₂ synthesized by the sol gel
 171 method was impregnated with different Au loadings. The
 172 same procedure was used for the preparation of Au/TiO₂.

173 2.2. Catalyst characterization

174 Measurement of the specific surface areas of all catalyst
 175 samples prepared was determined by N₂ adsorption at
 176 77 K (BET method) using a surface area analyzer (Auto-
 177 sorb 1, Quantachrome Instruments). Prior to the analysis,
 178 the catalyst samples were outgassed at 523 K for 3 h. The
 179 metal contents in all of the catalyst samples were analyzed
 180 by an atomic adsorption spectrophotometer (Spectr AA-
 181 300, Varian Inc.).

182 The crystalline structures of all catalyst samples were
 183 examined by X-ray diffraction (XRD) on a RINT 2000
 184 diffractometer (Rigaku Corp.) equipped with a Ni filtered
 185 CuK α radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and
 186 30 mA. Then, the catalyst samples were scanned in the
 187 range of 2θ from 20° to 90° in the continuous mode with
 188 a rate of 5° min⁻¹. Mean crystallite sizes of the studied cat-
 189 alysts were calculated by the Scherrer equation from X-ray
 190 line broadening using the full line width at half maximum
 191 of intensity of X-ray peaks.

192 The morphological surfaces of the catalyst samples were
 193 investigated under a transmission electron microscope
 194 (TEM) (2010, JEOL Ltd.) operated at 200 kV. The exist-
 195 ence of Au and Ag particles on these three supports was
 196 verified by using the TEM equipped with an energy disper-
 197 sive spectroscopy (EDS). The particle sizes of Au and Ag
 198 were determined by the statistical data of TEM images.

199 2.3. Ethylene oxidation reaction experiments

200 Ethylene oxidation reaction experiments over all studied
 201 catalysts were conducted in a differential flow reactor,
 202 which was operated at a constant pressure of 3.6 MPa
 203 and different reaction temperatures. The tubular reactor
 204 having 10 mm internal diameter was placed in a furnace
 205 equipped with a temperature controller. Typically, 30 mg
 206 of a catalyst sample was placed inside the Pyrex tube reac-
 207 tor and secured with Pyrex glass wool plugs. The packed
 208 catalyst was initially pretreated with oxygen at 473 K for
 209 2 h in order to diminish all impurities and to remove resid-
 210 ual moisture from the catalyst. The feed gas was a mixture
 211 of 15% oxygen in helium, 30% ethylene in helium and pure
 212 helium. All of the gases were high purity grade and
 213 obtained from Thai Industrial Gases Plc. (TIG). The flow
 214 rates of these three gas streams were regulated by mass flow
 215 controllers. From preliminary results, the optimum condi-
 216 tions of 6% of both oxygen and ethylene were found to
 217 yield the maximum selectivity of ethylene oxide over
 218 13.18 wt.% Ag/Al₂O₃ [12]. Therefore, this composition of
 219 feed gas mixture was selected as the base conditions for fur-

220 ther experiments in order to compare the effect of support
 221 material on the ethylene epoxidation reaction as well as the
 222 total oxidation. The feed gas was passed through the reac-
 223 tor at a constant space velocity of 6000 h⁻¹ and the reac-
 224 tion temperature was varied from 493 to 543 K for all
 225 catalysts, except that the Au/CeO₂ catalysts were per-
 226 formed in the temperature range of 413–473 K. At temper-
 227 atures lower than these studied ranges, the ethylene
 228 conversion was extremely low and all reaction products
 229 were lower than the detectable concentrations. Inlet and
 230 exit gases were analyzed by using an on-line gas chromato-
 231 graph (5890 Series II, Hewlett–Packard Development
 232 Company, L.P.) equipped with a HaYeseb D 100/120-
 233 packed column (Valco Instruments Co. Inc.), capable of
 234 separating carbon dioxide, carbon monoxide, ethylene
 235 and oxygen. Under the studied conditions for all prepared
 236 catalysts, the concentrations of carbon monoxide were
 237 below the detectable limit, indicating that the formation
 238 of CO can be neglected. The ethylene oxide selectivity
 239 was calculated from the carbon material balance with
 240 0.25% carbon atom error [16,17]. Moreover, the calculated
 241 values of ethylene oxide produced were confirmed by per-
 242 forming O₂ mass balance with 0.3% oxygen atom error.

243 3. Results and discussion

244 3.1. Characteristics of catalysts

245 The measured values of the BET surface areas of all
 246 the studied catalysts prepared with different support
 247 materials at the optimum catalyst loadings are shown
 248 comparatively in Table 1. For either commercial alumina
 249 or titania, an addition of either silver or gold did not
 250 affect its surface area significantly. Interestingly, the
 251 BET surface area of the alumina support was not altered
 252 significantly even through a large amount of silver was
 253 loaded up to 13.18 wt.%, implying that the silver particles
 254 are well dispersed without the sintering effect. The good
 255 dispersion of the silver and gold particles on Al₂O₃ is
 256 clearly verified by the existence of nanosized particles in
 257 all studied catalysts measured by both XRD and TEM
 258 as shown in Table 1. For the high surface-area-alumina
 259 support, the mean crystallite sizes of Ag obtained by
 260 XRD were found to be lower than those obtained by
 261 TEM. The differences are probably because the XRD
 262 broadening line in a direction perpendicular to reflecting
 263 planes is used to estimate the mean effective thickness
 264 of each crystallite, while the mean particle diameter is cal-
 265 culated from the TEM monographs. The particle size
 266 measured by TEM basically consists of several crystal-
 267 lites. As expected, no Au peak was detectable by XRD
 268 because the crystallite sizes of the Au particles present
 269 on all of the studied supports were too small. Therefore,
 270 the mean Au crystallite sizes were only obtained by using
 271 TEM equipped with EDS. From Table 1, the mean crys-
 272 tallite size of the Au particles on the TiO₂ with the
 273 impregnation method gives the largest, as compared to

Table 1
Structural characteristics of prepared catalysts on different support materials at optimum catalyst loadings

Support	Ag content (wt.%)	Au content (wt.%)	BET surface area (m ² /g)	Metal crystallite size (nm)	
				XRD	TEM
Al ₂ O ₃ ^a (Imp)	13.18	0	90	19 (Ag)	30 (Ag)
Al ₂ O ₃ ^a (Imp)	13.18	0.54	89	18 (Au-Ag)	30 (Ag) 4 (Au)
TiO ₂ ^b (Imp)	0	0.96	60	–	3.2 (Au)
TiO ₂ (DP)	0	1.28	58	–	2.5 (Au)
TiO ₂ (sol gel)	0	0.96	60	–	1.2 (Au)
CeO ₂ (sol gel–Imp)	0	0.69	105	–	6.2 (Au)
CeO ₂ (single step sol gel)	0	1.03	102	–	5.6 (Au)

Note: Imp—Impregnation method.

DP—Deposition-precipitation method.

(Ag) means Ag particle.

(Au) means Au particle.

(Au–Ag) means Au–Ag crystallite.

^a BET surface area of Al₂O₃-Degussa is 98 m²/g.

^b BET surface area of TiO₂-Degussa P25 is 61 m²/g.

274 those on the TiO₂ prepared by the deposition-precipitation and single-step sol gel methods. In a comparison
275 between the two preparation techniques of Ag/CeO₂ cat-
276 alysts, the sol gel/impregnation method provided a higher
277 mean crystallite size of Au particles than the single-step
278 sol gel technique did. This is because the single-step sol
279 gel technique gives a better dispersion than the impregna-
280 tion method. Interestingly, all Au catalysts on three stud-
281 ied supports provided Au particles in the nanorange.
282

283 The TEM/EDS technique was used to localize both Ag
284 and Au particles on the studied supports. Based on both
285 XRD and TEM results, the Ag particles prepared on the
286 commercial alumina were in the nanorange (see Table 1
287 and Fig. 1a), indicating that silver is highly dispersed on
288 the alumina support. The addition of Au on the

289 13.18 wt.% Ag/Al₂O₃ catalyst resulted in the formation of
290 small particles of Au on the Ag particles with the Au par-
291 ticle size of about 4 nm (see Fig. 1b). As mentioned in our
292 previous observation, at a low Au loading not higher than
293 0.54 wt.%, the formation of an Au–Ag bimetallic occurred,
294 while a high Au loading greater than 0.54% caused the
295 alloy formation [18]. Fig. 2a–c reveal the presence of the
296 gold particles as dark spots with highly uniform dispersion
297 in nanosizes on three TiO₂ supports. In contrast, the inho-
298 mogeneous dispersion of gold particles on the CeO₂ sup-
299 port prepared by the impregnation method is noticed in
300 the random region of dark spots, as shown in Fig. 3a.
301 Interestingly, Fig. 3b shows that the single-step sol gel tech-
302 nique provides good dispersion of Au on CeO₂, indicating
303 a strong interaction between CeO₂ and Au. From the

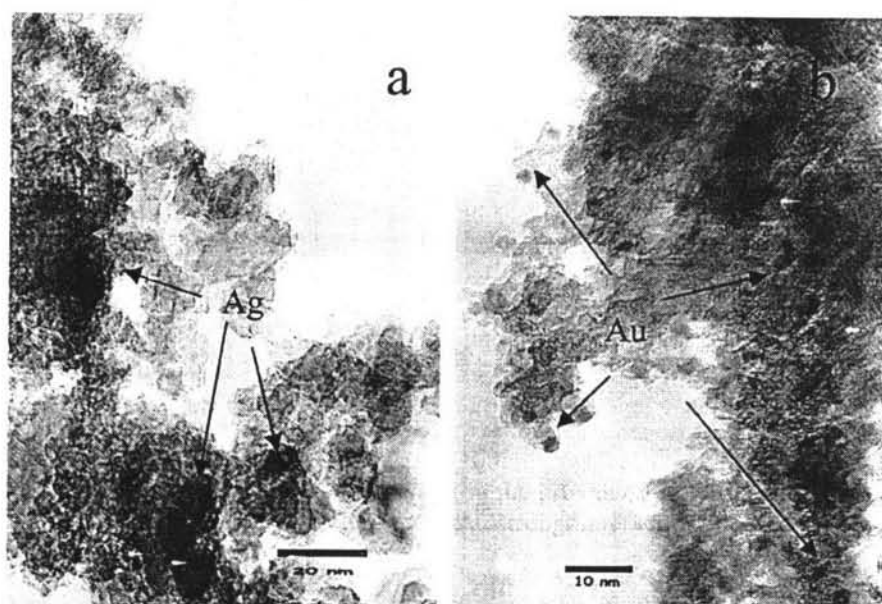


Fig. 1. TEM micrographs of: (a) 13.18% Ag/Al₂O₃; (b) 0.63% Au–13.18% Ag/Al₂O₃.

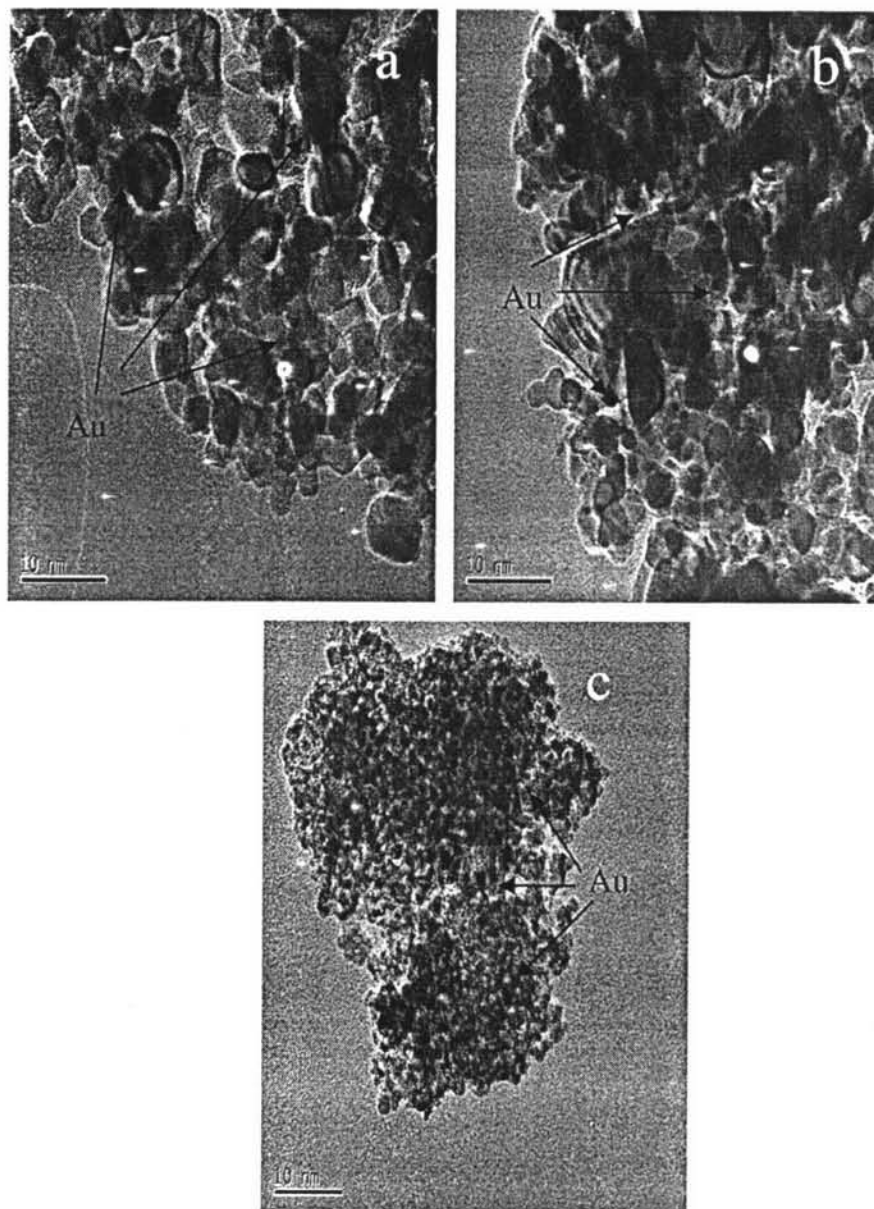


Fig. 2. TEM micrographs of: (a) 0.96% Au/TiO₂ (impregnation); (b) 1.28% Au/TiO₂ (deposition–precipitation); (c) 0.96% Au/TiO₂ (sol gel).

304 results, good dispersion of Au particles with nanosizes can
 305 be obtained from all studied supports of high surface area
 306 alumina, titania and ceria. In comparing the three sup-
 307 ports, ceria provided the largest particle size of Au. From
 308 the results, it can be concluded that Au particle size
 309 depends on preparation method and the nature of the
 310 support.

311 3.2. Catalyst activities of ethylene oxidation reactions

312 3.2.1. Ethylene conversion

313 The effect of reaction temperature on the ethylene con-
 314 version over various prepared catalysts having the opti-
 315 mum loadings of Ag and Au on different supports is

316 shown in Table 2. The optimum catalyst loading on each
 317 support is reported elsewhere [12,18]. Both Ag/Al₂O₃ and
 318 Au–Ag/Al₂O₃ catalysts were operated at the temperature
 319 range of 493–573 K since the ethylene conversion was too
 320 low to be detected at a temperature lower than 493 K. It
 321 was noticed that the ethylene conversion was low in the
 322 temperature range from 493 to 528 K but significantly
 323 increased with increasing reaction temperatures above
 324 528 K. However, for any given temperature, the Au–Ag/
 325 Al₂O₃ catalyst provided nearly the same ethylene conver-
 326 sion as the Ag/Al₂O₃ catalyst.

327 For the Au/TiO₂ catalysts, the ethylene conversion
 328 gradually increased with increasing temperature in the
 329 range of 493–543 K. For all Au/TiO₂ catalysts, the ethylene

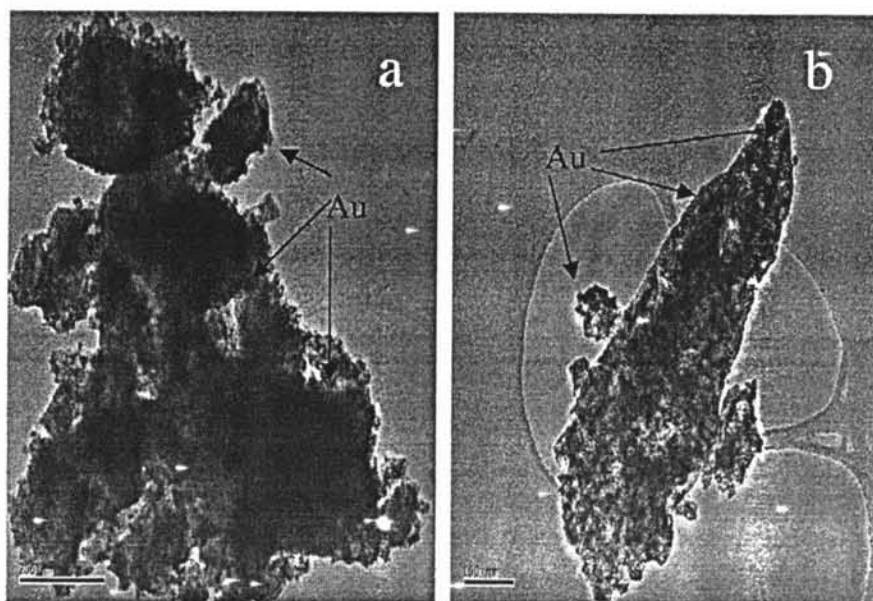


Fig. 3. TEM micrographs of: (a) 0.69% Au/CeO₂ (sol gel—impregnation); (b) 1.03% Au/CeO₂ (single step sol gel).

Table 2

Activity of each prepared catalyst at a space velocity of 6000 h⁻¹, *P* = 3.6 MPa and 6% O₂ and 6% C₂H₄ balanced with He

Support	Ag content (wt.%)	Au content (wt.%)	Temp. (K)	C ₂ H ₄ conv. (%)	EO sel. (%)	O ₂ sel. (%)
Al ₂ O ₃	13.18	–	493	0.9	84	16
			513	1.6	83	17
			528	1.8	62	38
			543	3.1	38	62
Al ₂ O ₃	13.18	0.63	493	1.2	93	7
			513	1.6	89	11
			528	1.8	79	21
			543	3.9	32	68
TiO ₂ (Imp)	–	0.96	493	1.0	99	1
			513	1.1	96	4
			528	1.3	88	12
			543	1.3	76	24
TiO ₂ (DP)	–	1.28	493	0.9	88	12
			513	0.9	82	14
			528	1.1	77	23
			543	1.2	56	44
TiO ₂ (sol gel)	–	0.96	493	0.6	86	14
			513	0.8	78	22
			528	0.9	66	34
			543	1.1	42	58
CeO ₂ (sol gel—Imp)	–	0.69	413	0.7	55	45
			433	1.2	0	100
			453	2.1	0	100
			473	4.3	0	100
CeO ₂ (single step sol gel)	–	1.03	413	0.5	77	23
			433	0.9	51	49
			453	1.1	18	82
			473	2.6	0	100

330 conversion did not appear at temperatures below 493 K.
 331 For any given reaction temperature, 0.96% Au on TiO₂
 332 with the impregnation method was found to give a higher
 333 ethylene conversion than those with the other two prepara-

tion methods, deposition–precipitation and single-step sol
 gel. 334

335
 Interestingly, the ethylene conversion over the Au/CeO₂
 catalysts was found in the temperature range of 413–433 K, 336
 337

338 which is much lower than those over the Au–Ag/Al₂O₃ and
339 Au/TiO₂ catalysts. The ethylene conversion over each Au/
340 CeO₂ catalyst substantially increased with increasing reac-
341 tion temperature, and 0.69 wt.% Au/CeO₂ with the sol gel/
342 impregnation method had a higher ethylene conversion
343 than the Au/CeO₂ with the single-step sol gel method.

344 In comparison, among these three supports, the Au/
345 TiO₂ catalysts provided a slightly lower ethylene conver-
346 sion than the catalysts on Al₂O₃ and CeO₂. In addition,
347 for any given ethylene conversion, CeO₂ gave a much lower
348 temperature since CeO₂ has an oxygen storage property or
349 is reducible to supply the atomic oxygen species to react
350 with ethylene.

351 3.2.2. Ethylene oxide selectivity and CO₂ selectivity

352 Table 2 shows the comparison of the catalytic activity of
353 the epoxidation and total oxidation of ethylene over all
354 studied catalysts. The ethylene oxide selectivity of either
355 the Ag/Al₂O₃ or Au–Ag/Al₂O₃ catalysts drastically
356 decreased with increasing reaction temperature but the
357 CO₂ selectivity intensely increased. This is due to the fact
358 that the total oxidation of ethylene is favorable at high
359 temperatures, owing to more accessible dissociated oxygen.
360 An addition of an appropriate amount (0.63 wt.%) of Au
361 on 13.18 wt.% Ag catalyst which exists in a bimetallic
362 structure was found to promote the ethylene epoxidation
363 reaction by weakening the Ag–O bond in the reaction tem-
364 perature range of 493–528 K [18,19]. When the Au loading
365 was higher than 0.63 wt.%, the activity of the ethylene
366 epoxidation decreased corresponding to the formation of
367 Au–Ag alloy which results in decreasing the adsorption
368 capacity of molecular oxygen [18].

369 It was found that there was zero selectivity of ethylene
370 oxide over Ag catalysts on both TiO₂ and CeO₂. Therefore,
371 gold on both supports was studied in this research. Table 2
372 shows that 0.96 wt.% Au on commercial TiO₂ prepared by
373 the impregnation method gives the highest ethylene oxide
374 selectivity among the three catalysts. The other two cata-
375 lysts were prepared by the deposition–precipitation and
376 single-step sol gel methods. In contrast, 0.96 wt.% Au on
377 sol gel TiO₂ prepared by the single-step sol gel method pro-
378 vided the highest CO₂ selectivity. From the results, it is
379 clearly seen that there is a good correlation between the
380 particle size of gold, which is determined by TEM (Table
381 1) and the ethylene epoxidation reaction. The ethylene
382 oxide selectivity increased when the gold particle size
383 became larger. It has been reported that oxygen species
384 are formed at the perimeter interface between the gold par-
385 ticles and the TiO₂ support when the particle size is greater
386 than 2 nm [20]. The oxygen species located at the perimeter
387 interface is mostly molecular oxygen [21,22] which is
388 believed to react directly with ethylene in the gas phase
389 to produce ethylene oxide. Among the three preparation
390 methods of Au catalysts on titania, the impregnation
391 method was found to give the largest gold particle size
392 (3.2 nm) compared to the other two methods (2.5 and
393 1.2 nm). Our present work has confirmed that ethylene

oxide selectivity depends on the particle size of gold and
the interaction between gold and the support. Again, the
impregnation method also provides both the highest ethyl-
ene conversion and ethylene oxide selectivity as compared
to the other two preparation techniques. It is explained that
the impregnation method provides more active reaction
sites of the Au particles to generate more active oxygen spe-
cies than the other two preparation methods.

For the Au/CeO₂ catalysts, CO₂ selectivity increased
substantially with increasing reaction temperature whereas
the ethylene oxide selectivity decreased (see Table 2). In
comparing the two preparation methods, the Au on
CeO₂ prepared by the sol gel/impregnation method was
shown to favor the total oxidation reaction over the epoxi-
dation reaction as compared to that prepared by the sin-
gle-step sol gel method. This is because the impregnation
method provides more active Au reaction sites than the
other preparation technique, single-step sol gel. Table 1
shows that the Au particle sizes of both catalyst prepara-
tion methods are less than 10 nm which are believed to
favor the total oxidation reaction according to literature
[20]. It is also believed that the high oxygen mobility of
reducible CeO₂ is responsible for the enhancement of
the total oxidation reaction at much lower temperatures
as compared to the other supports, alumina and titania.
The same phenomenon was also reported by Wootsch
et al. [23] whereby Pt/CeO₂ catalysts were more active
at lower temperatures for both CO and H₂ oxidation
reactions than Pt/Al₂O₃. Pozdnyakova et al. [24] studied
selective CO oxidation in hydrogen-rich environments
over Pt/CeO₂ catalysts. Complete CO oxidation was
observed at over 1% Pt/CeO₂ at the very low temperature
of 370 K. Another possible mechanism is the further oxi-
dation of ethylene oxide by the bulk atomic oxygen of the
CeO₂ support.

4. Conclusions

Among the three support materials—Al₂O₃, TiO₂ and
CeO₂, the ethylene epoxidation was found to occur over
the Ag catalysts on Al₂O₃ while Ag catalysts on both
TiO₂ and CeO₂ gave only the total oxidation reaction.
For the Au catalysts on Al₂O₃, no activity was found
toward the ethylene epoxidation reaction. The addition
of an appropriate quantity of Au on 13.18% Ag/Al₂O₃ cat-
alyst was found to enhance both the ethylene conversion
and the selectivity of ethylene oxide. Under the optimum
gold loading of 0.63 wt.%, the existence of the bimetallic
Au and Ag structure creates new single silver sites which
favor molecular oxygen adsorption leading to the enhance-
ment of the ethylene oxide selectivity. Interestingly, the Au
catalysts on TiO₂ also was shown to be a good candidate
for the ethylene epoxidation reaction, provided that Au
particle size is greater than 2 nm. CeO₂ is a poor support
for Au catalysts because of its reducible characteristic,
which promotes total oxidation instead of epoxidation.
The results also show that the catalytic activity of Au

449 catalysts depends on not only the size of the Au particle
450 and support material, but also the catalyst preparation
451 method which was revealed experimentally on both TiO₂
452 and CeO₂ supports.

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505

CURRICULUM VITAE

Name: Mr. Siriphong Rojluechai

Date of Birth: August 9, 1970

Nationality: Thai

University Education:

1990-1994 Bachelor Degree of Science in Chemical Engineering,
Faculty of Science, Chulalongkorn University, Bangkok,
Thailand

Working Experience:

1994-1997 Technical Service and Chemist, TPI Polyol Co., Ltd.

Awards/Honors:

Royal Golden Jubilee Scholarship from the Thailand Research Fund for
Ph.D. Program.

Publications:

1. Rojluechai S., Chavadej S., Schwank J. W. and Meeyoo V. (2006) Activity of Ethylene Epoxidation over High Surface Area Alumina Support Au-Ag Catalysts. Journal of Chemical Engineering of Japan, 39 (3), 321-326.
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