

## DEVELOPMENT OF CATALYSTS FOR ETHANE EPOXIDATION REACTION

*Kingsuda Mahunee<sup>a</sup>, Krittiya Pornmai<sup>a</sup>, Sitthiphong Pengpanich<sup>c</sup>, Sumaeth Chavadej<sup>\*a,b</sup>*

<sup>a</sup> The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

<sup>b</sup> Center of Excellence on Petrochemical and Materials Technology, Bangkok, Thailand

<sup>c</sup> PTT Global Chemical Public Company Limited

Keywords: Ethylene oxide, Partial oxidation, Ethane epoxidation, Second metal.

### ABSTRACT

Ethylene oxide (EO) is an important intermediate in the manufacture of several petrochemical products such as ethylene glycol, surfactants, thickener, ethanolamine glycol, polyglycol ether, lubricants, plasticizers, and solvents. EO is commercially produced through the partial oxidation of ethylene with air or oxygen over Ag catalysts loaded on a low-surface-area  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. Ethylene is mainly produced by the steam cracking of hydrocarbons, which is considered as a high energy consumption process. It is of a great interest to develop a new EO production process from ethane. This study aimed to improve the selectivity and yield of ethylene oxide from ethane epoxidation reaction. Ag catalysts on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and SrTiO<sub>3</sub> supports were preliminary tested to find out the Ag optimum loads on both support for EO production. An optimum feed molar ratio of ethane to oxygen and reaction temperature for the ethane epoxidation reaction were then studied. Among the various catalysts, the 10 wt.%Ni-17.5 wt.%Ag/SrTiO<sub>3</sub> exhibited good performance to produce EO, with a EO yield of 0.13% and EO selectivity of 0.009% under the studied conditions of a C<sub>2</sub>H<sub>6</sub> to O<sub>2</sub> molar ratio of 4:1, a space velocity of 6000 h<sup>-1</sup> and a reaction temperature of 723 K.

\*[sumaeth.c@chula.ac.th](mailto:sumaeth.c@chula.ac.th)

### INTRODUCTION

Ethylene oxide (EO) is an important intermediate in the manufacture of several petrochemical products such as ethylene glycol, surfactants, anti-freezes, adhesives, explosives, lubricants, plasticizers, and solvents. EO is commercially produced through the partial oxidation of ethylene with either air or oxygen over Ag based catalysts loaded on a low surface area  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support (Chongterdtoonskul *et al.*, 2014). Ethylene feed is mainly produced by the thermal pyrolysis of ethane or naphtha and the oxidative dehydrogenation of ethane (ODHE) at 873 K (Wu *et al.*, 2010), a process operating under severe conditions, resulting in high-energy consumption.

In addition, EO can theoretically be produced from ethane directly by combined step of dehydrogenation and ethylene epoxidation using bi-functional catalysts. The design of catalysts for ethane epoxidation reaction has two main problems, which are the differences of the reaction temperature and the oxygen species for the dehydrogenation and epoxidation steps. Fundamentally, a high reaction temperature promotes further oxidation of the desire product (EO) to CO<sub>2</sub> (Gao *et al.*, 2013).

In this study aimed to improve the selectivity and yield of ethylene oxide from ethane epoxidation reaction. The effects of various catalysts prepared by using a sequential impregnation method were investigated to determine the best reaction conditions for the ethylene epoxidation reaction. The prepared catalysts were characterized by several techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), O<sub>2</sub> and ethane-temperature programmed desorption (O<sub>2</sub>-TPD, C<sub>2</sub>H<sub>6</sub>-TPD), temperature programmed oxidation (TPO), X-ray photoelectron microscopy (XPS), a BET surface area analysis.

## EXPERIMENTAL

### A. Catalyst preparation

In this study, a number of catalysts of Ag loaded on two supports of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and SrTiO<sub>3</sub> and various second metals loaded on the best Ag/SrTiO<sub>3</sub> were prepared by a sequential impregnation method. The mesoporous-assembled SrTiO<sub>3</sub> support was synthesized by a sol-gel process. Firstly, tetraisopropyl orthotitanate (TIPT) and acetylacetone (ACA) were mixed at a molar ratio of 1:1. The mixed TIPT/ACA solution was jolted to obtain a homogeneous mixture. At the same time, the Sr(NO<sub>3</sub>)<sub>2</sub> was dissolved in distilled water. Next, ethanol was mixed with an alkaline earth nitrate solution. After that, laurylamine hydrochloride (LA) and HCl were added to the alkaline earth nitrate solution. The mixed solution was poured in to the TIPT/ACA solution. Next, the mixture was stirred homogeneously at room temperature. After that, the mixture solution was dried at 353 K for 4 days to achieve complete gelation. Finally, the gel was calcined at 923 K to produce the SrTiO<sub>3</sub> support.

The Ag-based catalysts on the two supports of SrTiO<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were prepared by incipient wetness impregnation with an aqueous silver nitrate solution to achieve different Ag loadings of 5, 10, 15 and 17.5 wt%. After the impregnation step, the catalysts were dried at 383 K for 12 h, and finally followed by calcination at 773 K for 5 h.

The bimetallic catalysts were prepared by the impregnation method on the best Ag-based catalysts by using different precursors (Cu, Nb, Ni, Au, Sn) to obtain various second metal loadings of 1, 5, 10 and 10 wt%. After that, the catalysts were dried at 383 K for 12 h and then calcined at 673 K for 2 h to produce bimetallic catalysts.

### B. Catalyst Characterization

The actual metal loadings on all synthesized catalysts were analyzed by an atomic absorption spectrophotometer (AAS, Varian, Spectro AA-300). The N<sub>2</sub> adsorption-desorption isotherms were obtained by a Brunauer-Emmett-Teller (BET) surface area analyzer (Quantachrome, SAA-1MP) to determine the specific surface areas of all studied catalysts. An X-ray diffractometer (XRD, Rigaku, RINT 2200 HV) was used to identify the crystallinity of the synthesized catalysts. The diffractometer was equipped with a Ni filter and a Cu K $\alpha$  radiation source ( $\lambda = 1.542 \text{ \AA}$ ), operated at 40 kV and 30 mA. Each catalyst sample was scanned for 2 $\theta$  up to 90° in a continuous scanning mode with a rate of 5° min<sup>-1</sup>. The catalyst surface morphologies were investigated by a field emission scanning electron microscope (FE-SEM, JEOL 5200-2AE).

The oxygen and ethane uptakes of the investigated catalysts were examined using a temperature-programmed desorption (TPD) analyzer (Quantachrome, Chembet 3000). Initially, oxygen (4.99 % O<sub>2</sub> in He) or pure ethane (99.99 % C<sub>2</sub>H<sub>6</sub>) was allowed to adsorb onto the catalyst surface at 473 K for 2 h for the TPD experiments. Then, the catalyst samples were cooled down to room temperature in a high-purity of He stream. After that, the catalyst samples were heated from room temperature up to 1173 K with a heating rate of 10 K/min, and the desorbed gas was swept by a high-purity He at a flow rate of 20 cm<sup>3</sup>/min. A thermal conductivity detector (TCD) was used to determine the desorption profiles which were used to calculate both oxygen and ethane uptakes.

The oxidation states of the loaded metals were analyzed by an X-ray photoelectron spectroscopy (XPS, Shimadzu, Kratos). A monochromatic Al K $\alpha$  source was used as the X-ray source. The relative surface charging of the samples was removed by referencing all the energies to the C1s level as an internal standard at 284.8 eV. The coke formation on the spent catalysts was quantified by using a thermogravimetric and differential thermal analyzer (TG-DTA, PerkinElmer, Pyris Diamond).

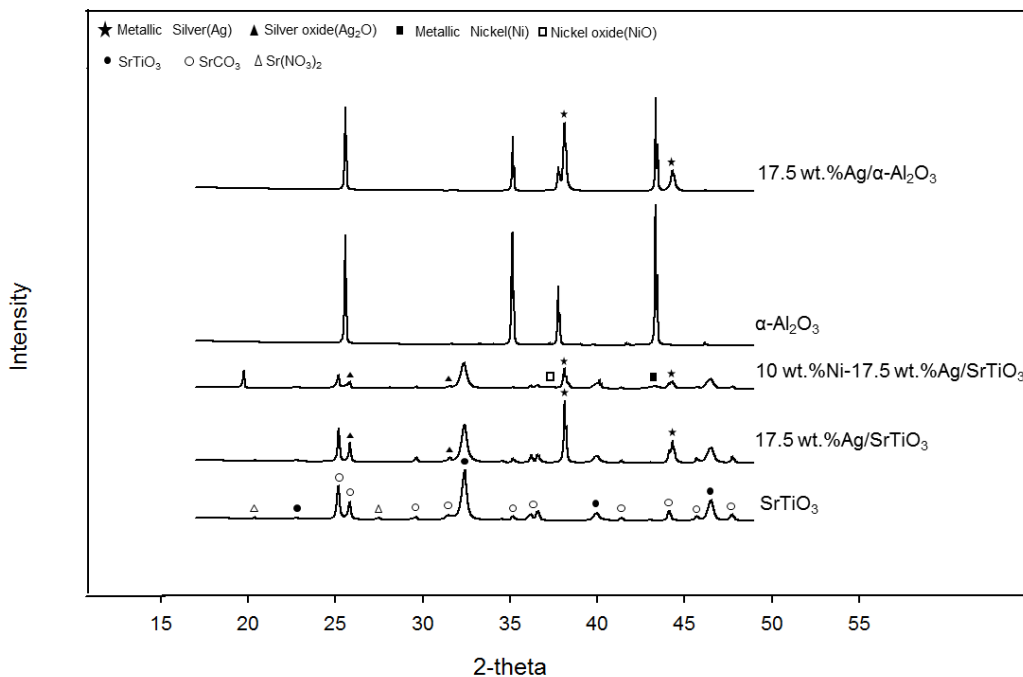
### C. Catalytic activity testing

The ethane epoxidation reaction experiments over all prepared catalysts were carried out in a packed-bed 8 mm ID tubular reactor, which was operated at atmospheric (14.7 psi) and packed 0.30 g catalyst powder in a quartz tube reactor. The catalyst was pretreated with oxygen at 473 K for 2 h. The composition of the feed mixture was controlled to have different molar ratios of ethane to oxygen balance with helium and a constant space velocity of 6,000 h<sup>-1</sup>. The reaction temperature was varied from 473-723 K. The compositions of feed and product gases were analyzed using an on-line gas chromatography equipped with a HP-MOLESIEVE column (capable of separating carbon monoxide, carbon dioxide, and oxygen) and a Rt-U PLOT capillary column (capable of separating ethylene oxide, ethane, ethylene and propane).

## RESULTS AND DISCUSSION

### A. XRD results

The XRD patterns of the Ag catalysts on the two supports at 17.5 wt.% Ag loading shown in Figure 1. The XRD patterns demonstrated the peaks of SrTiO<sub>3</sub> at 2-theta about 22.8°, 32.5°, 40°, and 46.6° correspond to (0,0,2), (1,1,2), (2,0,2), and (0,0,4), respectively (Klaytae *et al.*, 2013). For the peaks of metallic silver at 2-theta around 38° and 44° according to (1,1,1) and (2,0,0) planes, indicating the Ag loading on Al<sub>2</sub>O<sub>3</sub> and SrTiO<sub>3</sub> supports. The Ag/SrTiO<sub>3</sub> catalyst had two extremely small Ag<sub>2</sub>O peaks at 2-theta around 26° and 32° correspond to (1,1,0) and (1,1,1) planes. Moreover, the XRD results showed that the Ag/SrTiO<sub>3</sub> catalyst possessed the largest Ag crystallite size while the Ag/Al<sub>2</sub>O<sub>3</sub> had the smallest Ag crystallite size. The 10 wt.% Ni-17.5 wt.% Ag/SrTiO<sub>3</sub> catalyst indicated peak metallic nickel at 2-theta of 44.37 corresponding to (1,1,1) plane and the nickel oxide peak at 2-theta of 37.44 corresponding to (1,1,1) plane.



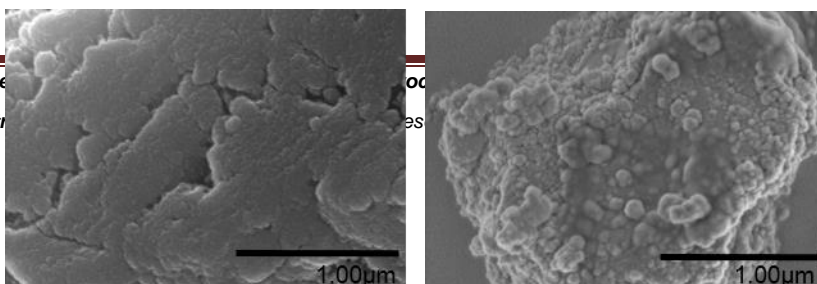
**Figure 1** XRD patterns of the  $\text{Al}_2\text{O}_3$  and  $\text{SrTiO}_3$  supports with the Ag loading and the second metal loading.

### B. Specific surface area results

The specific surface areas of some synthesized catalysts were selected to report (based on the catalytic activity results in terms of EO production). The results showed that the 17.5 wt.%Ag/ $\alpha\text{-Al}_2\text{O}_3$  support catalyst possessed the lowest specific surface area ( $0.037 \text{ m}^2/\text{g}$ ), followed by the  $\alpha\text{-Al}_2\text{O}_3$  support catalyst, 10 wt.%Ni-17.5 wt.%Ag/ $\text{SrTiO}_3$  catalyst ( $7.647 \text{ m}^2/\text{g}$ ), the 17.5 wt.%Ag/ $\text{SrTiO}_3$  catalyst ( $8.916 \text{ m}^2/\text{g}$ ), while the  $\text{SrTiO}_3$  support had the highest specific surface area ( $11.42 \text{ m}^2/\text{g}$ ).

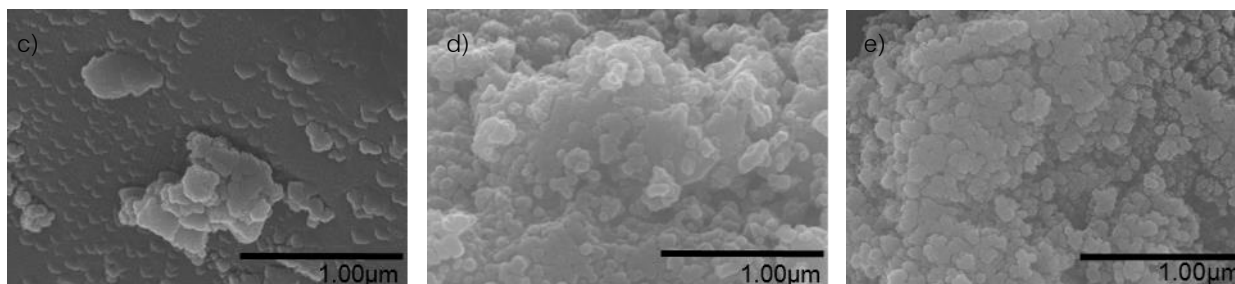
### C. Surface morphology

Figure 2 displays the SEM images of the 10 wt.%Ni-17.5 wt.%Ag/ $\text{SrTiO}_3$  catalysts with pure  $\alpha\text{-Al}_2\text{O}_3$  support and  $\text{SrTiO}_3$  catalyst compared with the 17.5 wt.%Ag/ $\alpha\text{-Al}_2\text{O}_3$  and the 17.5 wt.%Ag/ $\text{SrTiO}_3$  catalyst.



a)

b)



**Figure 2** SEM images a)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> b) SrTiO<sub>3</sub> c) 17.5 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> d) 17.5 wt.% Ag/SrTiO<sub>3</sub> e) 10 wt.% Ni-17.5 wt.% Ag/SrTiO<sub>3</sub>

#### D. Ethane epoxidation activity results

**Table 1** The catalytic activity results of various synthesized catalysts in this study

Catalysts	Temperature (K)	Feed ratio C <sub>2</sub> H <sub>6</sub> :O <sub>2</sub>	C <sub>2</sub> H <sub>6</sub> conversion	Selectivity		EO yield
				EO	CO <sub>2</sub>	
1) 17.5 wt.% Ag/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	523	4:1	8.17	0	0	0
	548	1:1	0.09	0	89.88	0
		2:1	8.43	0	0	0
		4:1	11.88	0	83.13	0
	573	2:1	14.45	0	0	0
		4:1	12.74	0	0	0
2) 17.5 wt.% Ag/SrTiO <sub>3</sub>	523	4:1	3.81	0	0	0
	533	4:1	3.22	0	56.13	0
	548	1:1	33.85	0	69.55	0
		2:1	3.68	0	0	0
		4:1	2.74	0.0142	89.84	0.06
	558	4:1	14.28	0	89.95	0
	573	2:1	3.91	0	78.74	0
4:1		11.76	0.0292	93.53	0.07	
3) 10 wt.% Ni-17.5 wt.% Ag/SrTiO <sub>3</sub>	473	4:1	5.94	0	0	0
	523	4:1	1.11	0	0	0
	548	4:1	4.41	0	0.74	0
	573	4:1	0.92	0	0	0
	623	4:1	7.94	0	21.73	0
	673	4:1	13.56	0	14.97	0
	723	4:1	14.98	0.0089	10.66	0.13

Table 1 shows the ethane epoxidation activity results of some selected catalysts at different reaction temperatures and feed molar ratios. The results showed that at a feed molar ratio of  $C_2H_6:O_2$  of 4:1, EO was produced when using both 17.5 wt.% Ag/SrTiO<sub>3</sub> and 10 wt.% Ni-17.5 wt.% Ag/SrTiO<sub>3</sub>. For the 17.5 wt.% Ag/Al<sub>2</sub>O<sub>3</sub>, the conversion of ethane increased as the reaction temperature increased from 523 to 573 K while EO was not generated. In contrast, for 17.5 wt.% Ag/SrTiO<sub>3</sub>, the ethane conversion decreased with increasing reaction temperature from 523 to 548 K and then increased with further increasing reaction temperature to 558 K and finally decreased when the reaction temperature increased from 558 to 573 K. In comparisons among the studied catalysts, the 10 wt.% Ni-17.5 wt.% Ag/SrTiO<sub>3</sub> catalyst was selected as a best catalyst, which provided the highest EO yield of 0.13% and the EO selectivity of 0.009% at the reaction temperature of 723 K.

## CONCLUSIONS

In this study, the direct process to produce EO from ethane was investigated over different reaction temperatures, and feed molar ratios of  $C_2H_6:O_2$  over various catalysts. The most promising catalyst for EO production was found to be 10 wt.% Ni-17.5 wt.% Ag/SrTiO<sub>3</sub> operated at a reaction temperature of 723 K, a feed molar ratio of  $C_2H_6:O_2$  of 4:1, which provided the highest EO yield of 0.13% with the EO selectivity of 0.009%.

## ACKNOWLEDGEMENTS

The authors would like to thank The Thailand Research Fund (the TRF Senior Research Scholar grant (RTA578008)) for partially financial support. The Petroleum and Petrochemical College and Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Thailand, are also acknowledged. In addition, the authors would like to thank PTT Global Chemical Public Company Limited, Thailand, for providing a scholarship in this research.

## REFERENCES

- Chongterdtoonskul, A., Schwank, J., and Chavadej, S.** (2012). Effects of oxide supports on ethylene epoxidation activity over Ag-based catalysts. Chemical, Journal of Molecular Catalysis A, 358, 58-66.
- Chongterdtoonskul, A., Schwank, J., and Chavadej, S.** (2013). Comparative study on the influence of second metals on Ag-loaded mesoporous SrTiO<sub>3</sub> catalysts for ethylene oxide evolution. Chemical, Journal of Molecular Catalysis A, 372, 175-182.
- Chongterdtoonskul, A., Suttikul, T., Santikunaporn, M., Schwank, J., and Chavadej, S.** (2014). Effect of diluent gas on ethylene epoxidation activity over various Ag-based catalysts on selective oxide supports. Chemical, Journal of Molecular Catalysis A, 386, 5-13.
- Gao, J., Zhou, D., Wu, Y., and Wu, T.** (2013). Direct conversion of ethane to ethylene oxide over NiAgYO catalyst. Catalysis Communications, 30, 51-55.



**Klaytae, T., Panthong, P., and Thountom, S.** (2013). Preparation of nanocrystalline strontium titanate( $\text{SrTiO}_3$ ) powder by sol-gel combustion method. Scientific Research and Essays, Academic Journals, 8(1), 32-38.

**Wu, Y., Yan, A., He, Y., Wu, B., and Wu, T.** (2010). Ni-Ag-O as catalyst for a novel one-step reaction to convert ethane to ethylene oxide. Catalysis Today, 158, 258-262.