Effect of Rhenium on Ag/ SrTiO3 Catalyst in Ethylene Epoxidation Reaction: Synthesize, Characterization and Evaluation

Shiva Darake[1,2], Reza Golhosseini[1*], Alireza Mohammadrezaei[2], Morteza Asghar[1]

[1] Department of Chemical Engineering, Faculty of Engineering, University of Kashan, Kashan, Iran
[2] Research and Development Group, Exir Novin Farayand Asia Company, Tehran 1389714361, Iran

Abstract: In this study, silver catalysts on $SrTiO_3$ support contain cesium, and rhenium promoters are synthesized using the impregnation method for ethylene epoxidation reaction. SEM results show a small decrease in metal dispersion by adding cesium (<70 ppm) and rhenium (< 300 ppm) to the Ag (10 wt. %) /$SrTiO_3$ catalyst. Rhenium leads to the weakening of the peaks intensity in the crystalline structure of the catalysts. In addition, the predominance of Ag (111) surface facets compared to the Ag (110) and Ag (100) surface facets are obvious in the XRD results. The ability of the catalysts in oxygen adsorption and desorption is studied through O_2-TPD results. Ethylene conversion increases by adding rhenium to the Ag-Cs/$SrTiO_3$ catalyst in the temperature range of 210 to 220 °C. Ethylene oxide selectivity increases slightly from 80% to 84% in the Ag-Cs-Re/$SrTiO_3$ while this value in the Ag-Cs/$SrTiO_3$ catalyst decreases from 65% to 34%, in the mentioned temperature range. Severe sensitivity of the rhenium-conation catalyst to the inlet concentration of carbon dioxide (6 mol %) is observed through a 50% drop in the produced ethylene oxide compared to the product which doesn't have any carbon dioxide in the feed.

keywords: Ethylene epoxidation, Ethylene oxide, Rhenium, Silver, Strontium Titanate

1. Introduction

Ethylene oxide (EO) is a valuable compound in different industries such as the production of petrochemical compounds, sterilization of medical instruments, antifreeze, etc. [1]. In the ethylene to ethylene oxide catalytic process, silver metal is used as an active phase commercially due to its high oxygen adsorption capability [2], while alumina acts as the support of this catalyst. Between different types of alumina, α-alumina with its low surface area and high crush strength is the common support for the ethylene oxide catalyst. Meanwhile, researchers have studied other low surface materials for this reaction. Silicalite zeolites such as MCM-41 and HMS were investigated as the silver supports for ethylene epoxidation by Fotopoulos and Triantafyllidis [3]. Chongterdtoonskul et al. have shown that $SrTiO_3$ not only has higher oxygen uptake but it also higher ethylene uptake in comparison to alumina support [4]. Additionally, they investigated the effect of gold, copper, barium, palladium, and tin on strontium titanate support at the temperature of 548 K and pressure of 24.7 psi [5] which is not in the industrial operation condition range. Their results were restricted to the catalyst's characterization analysis such as XRD, TEM, TPD, etc. While the effect of operation condition on the catalyst performance was not seen [6]. Adhami et al. [7] investigated calcination time and surfactant-alkoxide ratio in the sol-gel method in synthesizing Ag/$SrTiO_3$ catalyst (without any promoters).

Cs, Cu, Cd, Pt, Re, and Mo are the promoters that were used in the ethylene oxide production catalysts [8-10]. According to the high economic value of ethylene oxide, selectivity is an important parameter in this reaction. Over the years, new methods and various promoters have been applied to ethylene oxide catalysts for improving the selectivity and conversion within the process [11-12]. Using Re and Mo promoters in the Cs promoted Ag/α-Al_2O_3 catalyst have led to the EO selectivity increase from 79% to 83% [13]. Optimum Cs loading in the catalyst containing 12 wt.% Ag, was reported between 300-450 ppm, while this value for Mo and Re was less than 200 ppm. Different reasons were explained for the positive effects of promoters in the

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[*] **Corresponding Author.**
Authors' Email Address: [1] **Sh. Darake** (shivadarake@yahoo.com), [2] **R. Golhosseini** (rgolhosseini@kashanu.ac.ir),
[3] **A. Mohammadrezaei** (rezaei.a@exirnovnco.com), [4] **M. Asghari** (asghari@kashanu.ac.ir)

ethylene oxide catalysts, for example, neutralizing acid sites on the catalyst support [14], uniform dispersion of silver [15-16], the geometric effect on silver crystals [17], electronic field-effect [18], etc. However, none of the reasons are so clear-cut for scientists in this area. Induce a dipole field on the catalyst surface due to the cesium presence was introduced as a factor for improving selectivity in Ag-Cs catalyst by Hus and Hellman [19]. Density Function Theory (DFT) studies show that Cu-Re dual promoted silver catalyst releases higher selectivity in ethylene epoxidation on alumina support compared to the Cs-Re dual metal catalyst [20]. Ramirez, et al. [21] investigated the Ag-Cu/alumina catalyst using a tubular copper oxide matrix. Their results showed that the presence of copper metal leads to improve selectivity at the lower temperatures. A sequence of adding promoters (Re and Cs) to the $Ag/\alpha-Al_2O_3$ was studied by Ren et al. [22]. Facilitation oxygen adsorption on the catalyst surface and improve ethylene oxide selectivity were mentioned as a result of the rhenium effect on the $Ag-Cs/Al_2O_3$ catalyst. Effect of rhenium on Ag-Cu/alumina and Ag-Cs/alumina catalysts were investigated at a low value of ethylene conversion (1.8%) by Dellamorte, et al. [23]. Despite the high reaction temperature (more than 513 K) and the absence of chlorine moderator in the reactor feed, they could not reach the desirable ethylene conversion. A theoretical study revealed that the formation of CsReOx species in the presence of Cs and Re promoters in the silver catalyst leads to the oxygen atom adsorption more electrophilic strengthens the bonding of initial compounds, intermediates, and products which improve the EO selectivity [24].

According to the recent patents [25-26] about the production of high-efficiency ethylene oxide catalysts containing rhenium, the significance of this promoter is distinguished. So, the new generation of commercial ethylene oxide catalysts usually has rhenium in their composition. In the literature, no investigation around the effect of carbon dioxide feed impurity on the performance of a Re-contain catalyst is observed. Moreover, no before the study was done around the effect of rhenium on $Ag/SrTiO_3$ catalyst performance. In this study, three catalysts with the same silver weight percent are synthesized by an impregnation method. Catalyst characterization analysis is done for each of the prepared catalysts. In order to control this highly exothermic reaction, a reactor equipped with a molten salt bath is used at a pressure of 17.5 barg. In order to perform catalysts evaluation, the effect of temperature, carbon dioxide, and chlorine moderator on the selectivity and the conversion are investigated.

2. Material and Methods

2.1. Catalyst Preparation

In this research, silver oxalate salt is used as the silver source for synthesizing catalysts [27]. Ethylene diamine (Sigma-Aldrich) is used as a solvent and reducing agent for silver oxalate salt. The solution is prepared with the goal of catalysts inclusive 10 wt.% Ag. Incipient wet impregnation using the solution with a volume equal to 1.1 times of calculated pore volume of strontium titanate powder (Sigma-Aldrich, 99% and BET: 6.81 m^2/gr), is done. The promoters such as cesium (Cs_2CO_3) are impregnated on the support, sequentially. The impregnation process is done under vacuum at 60 °C. After complete impregnation, calcination is done under airflow at a temperature of 260 °C for 10 min.

2.2. Catalyst Characterization

The nominal weight loading of silver and rhenium are confirmed by the Vista MPX Simultaneous ICP-OES device, while cesium is measured using the Varian Atomic Absorption Spectrometer. Table 1 shows the composition of the synthesized catalysts. Scanning electron microscopy (SEM) is used for the survey of the catalyst powder morphology through the Phenom Pro Desktop SEM device. The effect of promoters on the crystalline structure of strontium titanate support and various surface facets of Ag in the catalysts are determined by X-ray Diffraction (XRD) using PANalytical X'Pert PRO X-Ray Diffractometer (Cu-Kα radiation). Reactivity of the oxygen species with silver oxide on the catalyst surface is investigated by the O_2-TPD procedure using BELCAT II, JAPAN, Inc. 0.05 gr of the catalyst is purified by 50 ml/min He gas up to 300 °C. The cooldown process from 300 to 50 °C is done. The oxygen adsorption process with 5% O_2/He is achieved up to 300 °C. Finally, oxygen desorption under He flow of 30 ml/min with the temperature rate of 5 °C/min is recorded up to 600 °C.

Table 1. Composition of synthesize catalysts

Catalyst	Code	Ag (wt. %)	Re (ppm)	Cs (ppm)
$Ag/SrTiO_3$	ST2	10.9	0	0
$Ag-Cs/SrTiO_3$	ST1	10.00	0	64.7
$Ag-Cs-Re/SrTiO_3$	ST3	9.2	230	78.6

2.3. Catalyst Evaluation

A schematic diagram of the experimental setup used in this study is shown in Fig. 1. A fixed bed reactor equipped with the molten salt bath is charged by the synthesized catalysts. Heating and cooling of the reactor are achieved using this molten salt with the melting point of 180 °C. This salt is a mixture of three different compounds. The reactor feed includes six gases, which are mixed in a tracer-heating chamber with water vapor. Ethane, water vapor, and carbon dioxide are impurities of recycling feed in the industrial plant. In order to supply a chlorine moderator, a N_2+ethylene dichloride (EDC) cylinder is prepared with a specific concentration of chlorine. Flow rates of each gas are adjusted with mass flow controllers (MFC) of the Brooks Instrument SLA5850 series. The pressure of the reactor is set at 17.5 barg using GO backpressure device (0-40 bar). Two thermocouples for indicating and controlling the temperature in the catalytic bed and molten salt bath are installed. The outlet product is analyzed by two gas chromatography (3800 Varian GC) columns after passing the water vapor condenser equipment (volume:1.5 liters, cooled by chilled water of 4 °C). Besides, outlet humidity is measured for the determination of produced water in the process using Drager Tube Water Vapor 5/a-P (6728531).

Three important parameters in the ethylene epoxidation reaction are formulated according to the equation 1-3, as bellow:

$$\text{EO Selectivty}\% = 100 * \frac{\text{produced ethylene oxide}}{\text{total consumed ethylene}} \quad (1)$$

$$\text{C2H4 Conversion}\% = 100 * \frac{\text{total consumed ethylene}}{\text{total inlet value of ethylene}} \quad (2)$$

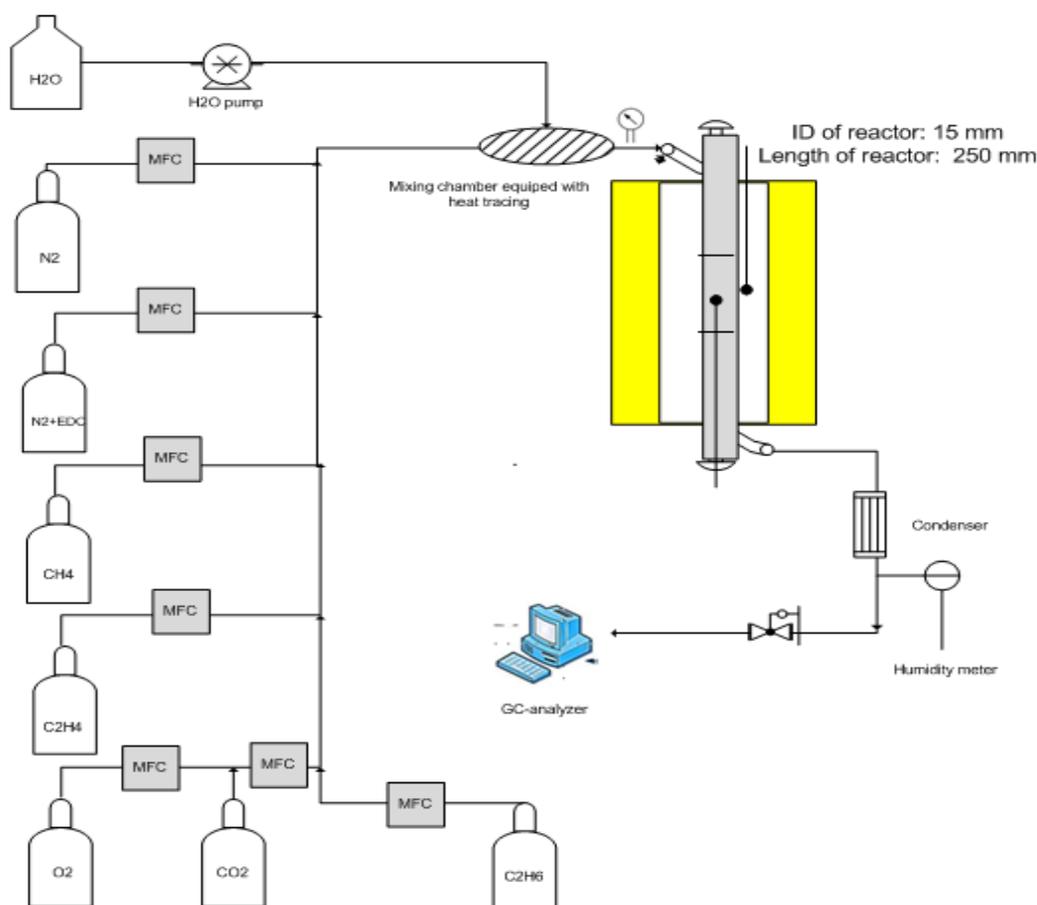$$\text{Yield}\% = 100 * \text{Selectivty} * \text{conversion} \quad (3)$$

Figure 1. Schematic diagram of fixed bed catalytic reactor setup

3. Results and Discussion

3.1. XRD Characterization

The XRD patterns of the prepared catalysts are shown in Fig. 2. The crystalline structure of silver particles is observed through sharp peaks in the obtained patterns. Results show that the presence of Re leads to decrease peak intensity in Ag-Cs-Re/SrTiO$_3$. According to the Scherrer equation, peaks with smaller intensities show the smaller crystalline size in a crystalline structure. The presence of metallic Ag with different surface facets of (111), (100) and (110) at 2θ of 38.1^0, 44.4^0, 64.8^0 is obtained. Other peaks are related to SrTiO$_3$ support which is weakened through adding Re and Cs promoters. As the Ag (111) peak shows more intensity relative to types of (100) and (110), it can be concluded that Ag (111) has the most concentration in the catalyst. This result verified literature that Ag(111) is the most stable form of silver for ethylene epoxidation production catalysts [28, 29].

3.2. SEM Characterization

Fig. 3 shows the SEM micrographs of the prepared catalysts. The SrTiO$_3$ support is shown with light gray and silver metal particles, which appear as a bright white color in the figures. The particle agglomeration is visible in the Ag-Cs-Re/ SrTiO$_3$. According to the same catalyst support with the same surface area, adding promoter to the Ag/SrTiO$_3$ catalyst led to a decrease in vacant surfaces. Probably, promoters such as rhenium or cesium deposit on the vicinity of the silver particles and lead to the formation of agglomerated particles with a larger size, as it is shown in SEM results. Hence, metal particle dispersion is more sensible in Ag/SrTiO$_3$ relative to the other catalysts. These results confirm the increasing particle size by adding promoters in silver catalyst obtained by Ren et al. [28]. Since that silver dispersion decreases by adding promoters to the catalyst, the amounts of the promoters must be optimized.

The large pore size of strontium titanate in the range of about 4 micrometers, which leads to a small surface area in this perovskite-structure compound, is obvious in the SEM results. This pore size is the same as the alpha-alumina support pore size used in synthesizing the ethylene oxide catalyst by Rosendahl, et al. [30].
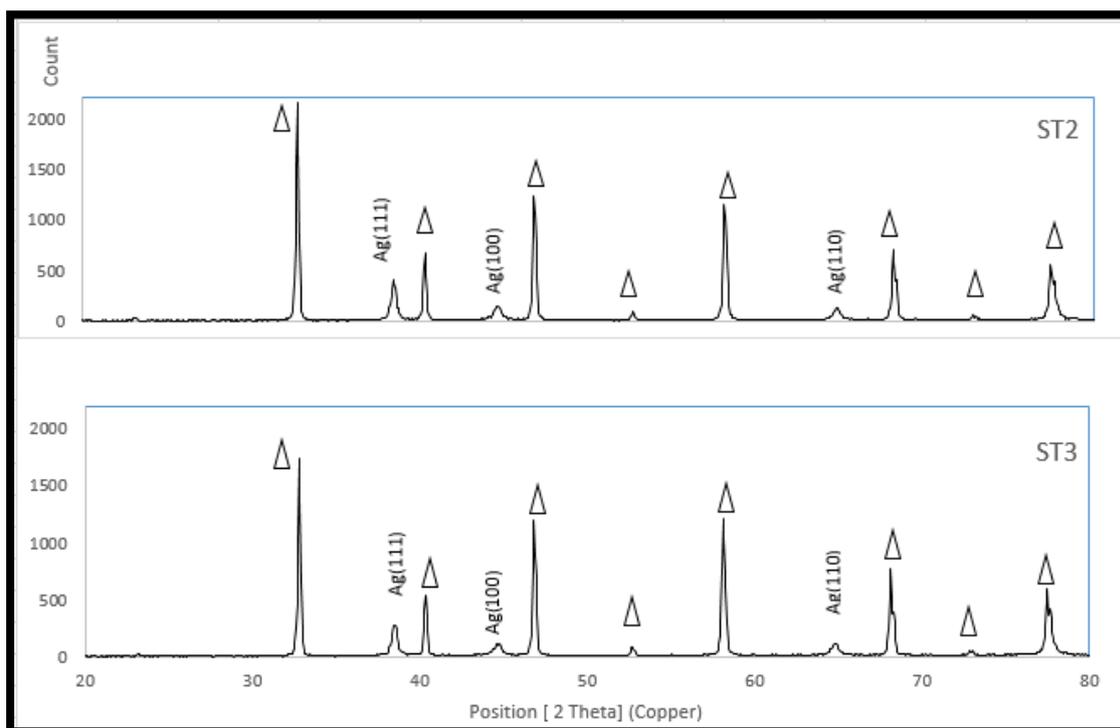

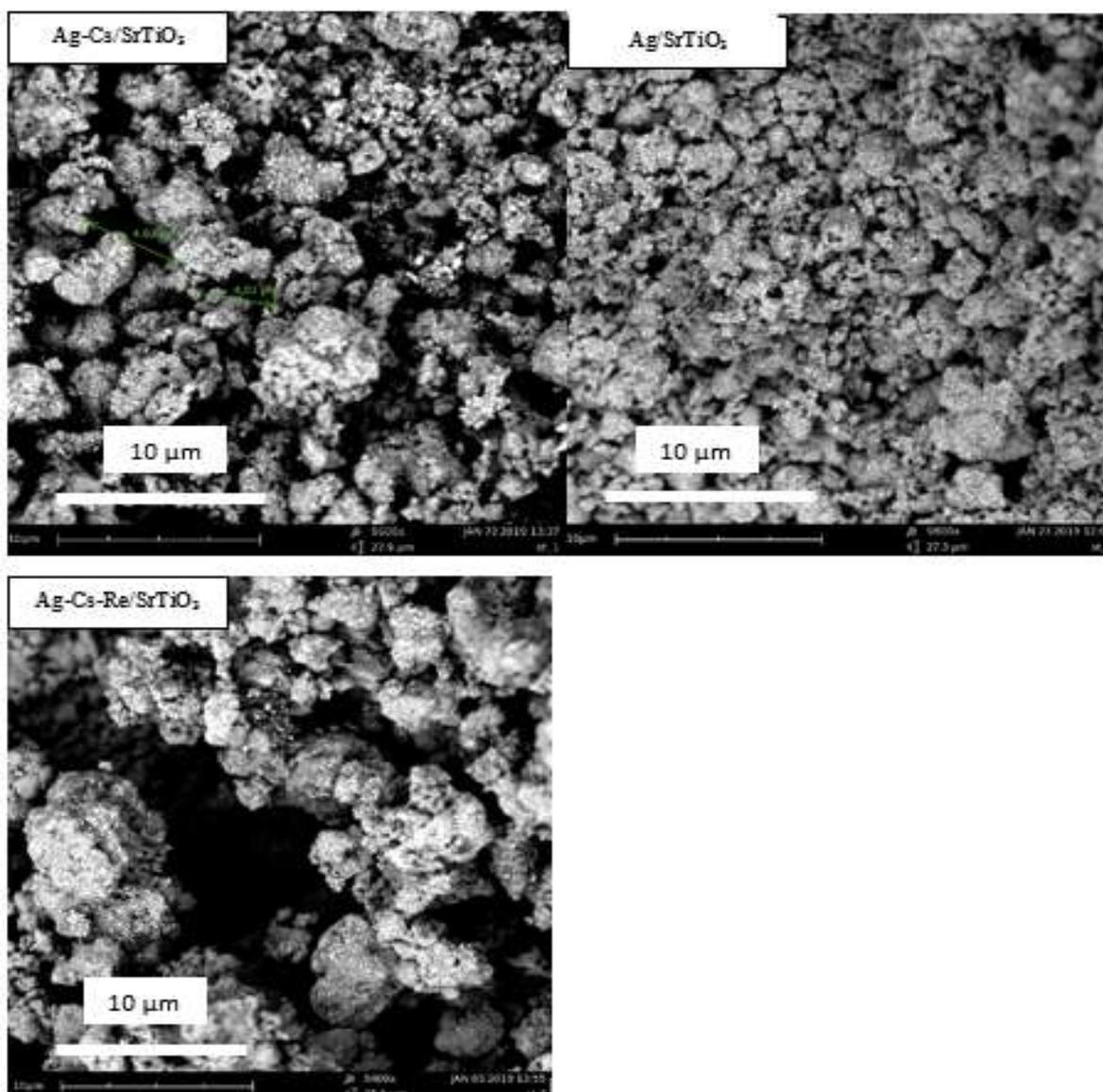**Figure 2.** X-ray Diffraction characterization of Ag/SrTiO3 and Ag-Cs-Re/SrTiO3

Figure 3. SEM micrographs of synthesized catalysts on the SrTiO₃ support

3.3. O₂-TPD Characterization

Adsorption and desorption of oxygen is a key parameter in the ethylene epoxidation and total oxidation of ethylene. The oxygen adsorption capacity of Ag-Cs/SrTiO₃ and Ag/SrTiO3 catalysts are studied through oxygen temperature-programmed desorption (O₂ –TPD). As it can be seen (Fig. 4), two peaks are observed in the desorption pattern in ST1 and ST2. The desorption temperature of 204 °C and 414 °C is observed in Ag/SrTiO₃, while 266 °C and 439 °C are the desorption temperatures of the ST1 catalyst. The second sharp peaks in both of the catalysts are the result of SrTiO₃ decomposition, which Chongterdtoonskul, et al. [6] has shown, too. This decomposition happens at a lower temperature with lower intensity in Ag/SrTiO₃. The presence of cesium in the catalyst structure leads to an increase in SrTiO₃ resistance against temperature decomposition. The oxygen desorption temperature which is responsible for ethylene epoxidation happens in higher temperatures with less concentration in ST1 relative to ST2. This higher desorption temperature (ST1) shows that cesium leads to make stronger binding between oxygen atoms and catalyst surface. Two reasons can be caused to the less concentration in ST1 compared to the ST2: 1. less adsorption of oxygen on the catalyst surface, 2. No desorption of the total oxygen which is adsorbed on the catalyst surface up to the temperature of 266 °C.

3.4 Effect of Temperature on Ethylene Oxide Selectivity and Ethylene Conversion

According to the highly exothermic reactive nature of ethylene epoxidation, the determination of a suitable reaction temperature has an important influence on the catalyst performance. Fig. 5 shows the effect of temperature on ethylene conversion in the synthesized catalysts. As can be seen, the presence of rhenium in the catalyst structure leads to increase conversion more than twice over. Hence, the positive effect of Re on the conversion is obvious. Increasing the temperature from 210 °C to 220 °C leads to improve conversion from 2% to 4% in Ag-Cs/SrTiO₃, while for the Re-contain catalyst,

this value increases from 5 to more than 10%. According to Fig. 2, no intensive difference in crystalline structure through adding promoters can be seen. Besides, SEM results show no egregious difference in Re-contain catalyst morphology (Fig. 3). Hence, it has been determined that the effect of promoters on the ethylene epoxidation most likely has an electronic origin as Diao, et al. have concluded for ethylene epoxidation over the Ag/Al_2O_3 catalyst [31]. The electric field which is formed due to the rhenium ions on the catalyst surface can change the transition state of total oxidation and partial oxidation products. Density function theory (DFT) calculation can clear these metal ions' effects and activation barriers for the reactions.
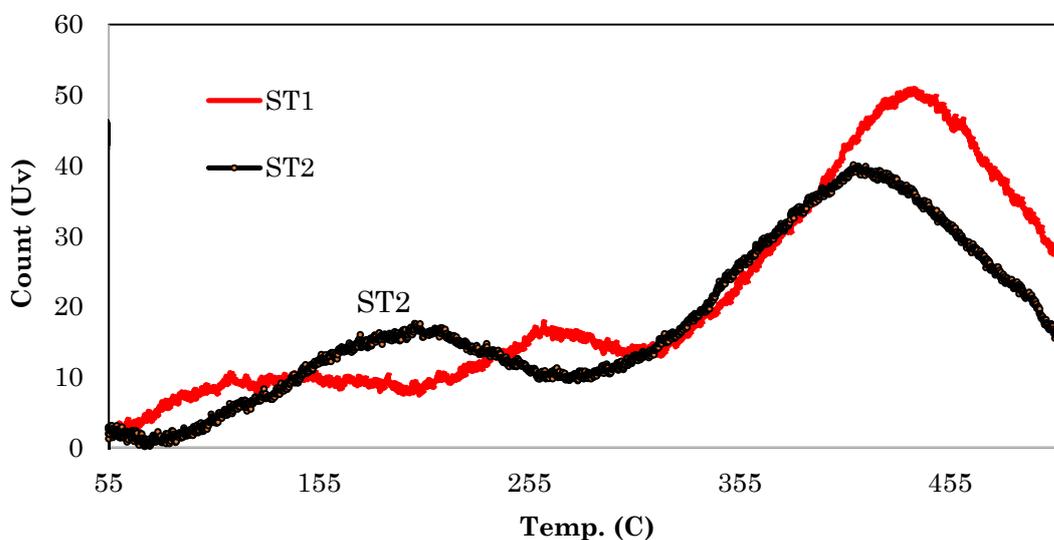

Figure 4. O_2-TPD Results of Ag-Cs/SrTiO₃ (ST1) and Ag/ SrTiO₃ (ST2)
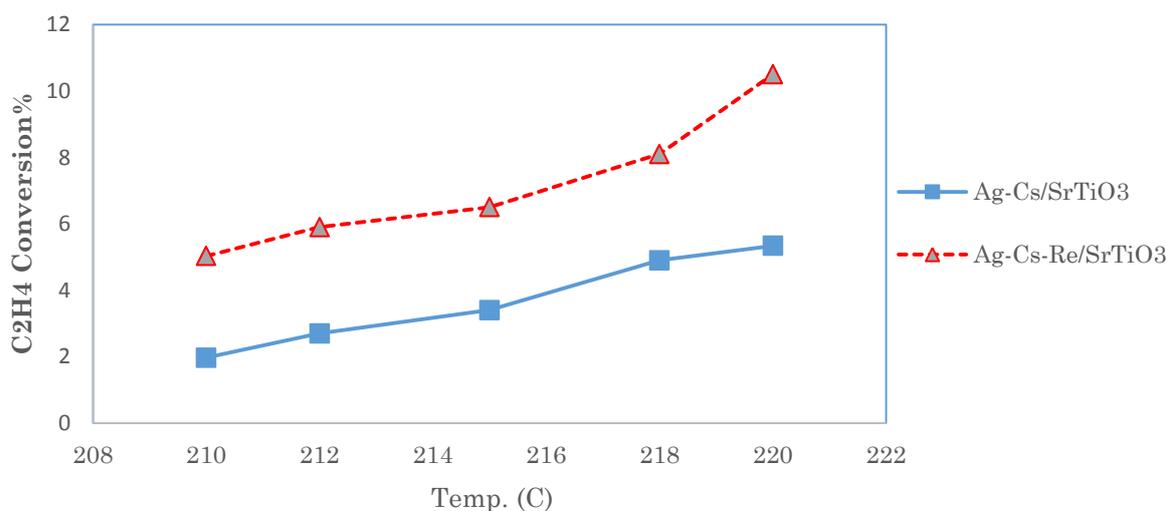

Figure 5. Effect of Temperature on ethylene conversion, Chlorine: 1.3 ppm, CO₂ at inlet: 0

The dependence of the ethylene oxide selectivity to the reaction temperature is shown in Fig. 6. Ethylene oxide selectivity and ethylene conversion have a trade-off behavior. As can be seen, by increasing the temperature, selectivity drops in both catalysts. In the temperature range of 210-220 °C, selectivity in the Re-contain catalyst with little drops reaches to 80%, while for Ag-Cs/SrTiO$_3$, selectivity drops sharply from 65.1% to less than 47%. An obvious preference of Ag-Cs-Re/SrTiO$_3$ over Ag-Cs/SrTiO$_3$ in the ethylene oxide selectivity is distinguished, such as in Fig. 5.

The total and partial oxidation of ethylene increases with the reaction temperature. Meanwhile, the ability of partial oxidation active sites is weakened relative to the complete oxidation ones at higher temperatures. Hence, the ratio of total oxidation to partial oxidation increases, which leads to a decrease in the selectivity. Using Re as a catalyst promoter leads to better control of reaction towards ethylene epoxidation at the higher temperature.

3.5 Effect of Chlorine Moderator on the Yield of Ethylene Oxide

The concentration of chlorine strongly depends on the catalyst composition such as cesium and impurities of the reactor feed including hydrocarbon compound especially ethane. Carbon dioxide concentration also influences the optimum value of the chlorine moderator.

The chlorine moderator effect on the yield of ethylene oxide is shown in Fig. 7. Chlorine concentration between 1-1.5 ppm is determined as an optimum value to maximize the yield of ethylene oxide at both catalysts. This compound certainly decreases the conversion of ethylene. In the optimum chlorine value, the rate of decrease in total oxidation reaction is more than in the partial oxidation one. Hence, the co-feeding of this compound at optimum value leads to improve the selectivity of the ethylene oxide. Previous studies on silver/alumina epoxidation have also shown an optimum value of chlorine moderator [32]. The preference of a Re-contain catalyst compared with Ag-Cs/SrTiO$_3$ is obvious such as in previous figures (Fig. 5 and Fig. 6). Using more than 1.3 ppm chlorine leads to not only a conversion drop but also ethylene oxide selectivity decrease. According to Fig. 7, increasing chlorine from 1.3 to 2.2 ppm causes a decrease in ethylene oxide yield from 1.3% to 0.42% in Ag-Cs/SrTiO$_3$ and a decrease from 1.97% to 1.15% in Ag-Cs-Re/SrTiO$_3$. In addition, using excess chlorine compounds on the catalyst surface is considered one of the silver catalyst deactivation agents by some researchers [33-34]. Hence, the optimum value of the chlorine moderator is a crucial parameter in the ethylene epoxidation reaction.
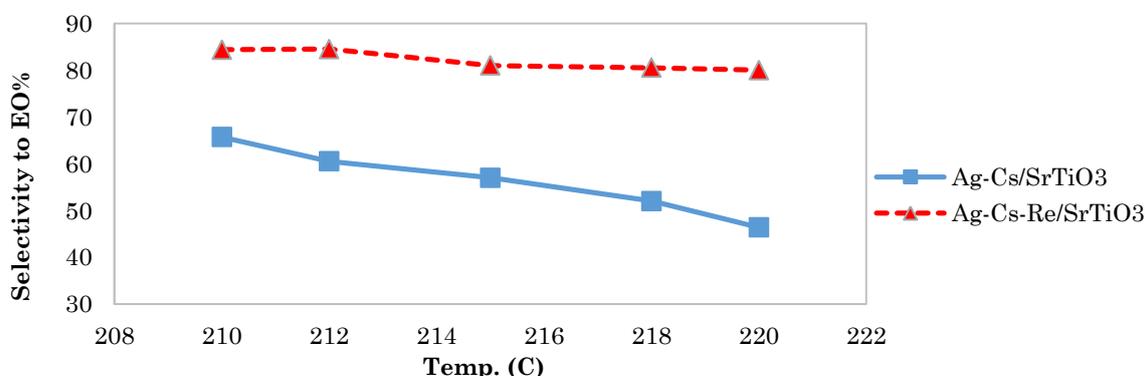

Figure 6. Effect of temperature on ethylene oxide selectivity, Chlorine: 1.3 ppm, CO$_2$ at inlet: 0
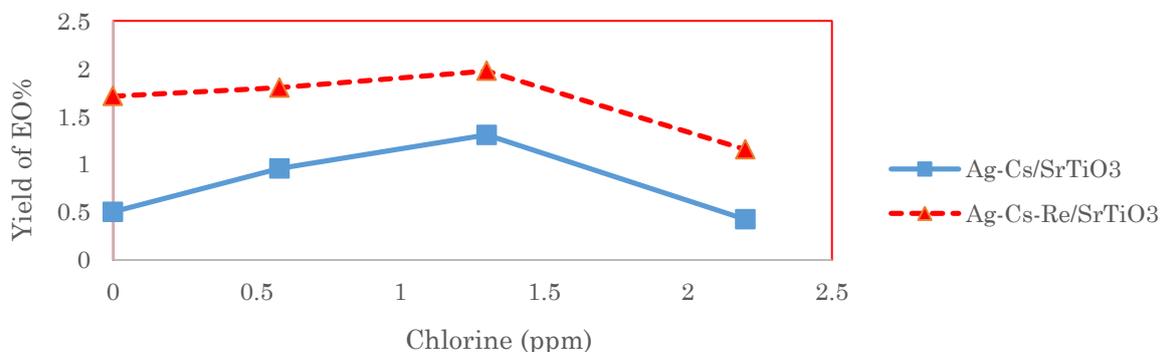

Figure 7. Effect of chlorine moderator on yield of ethylene oxide, CO$_2$ at inlet: 4 mol%, Temp.: 215 ^{0}C

3.6. Effect of CO₂ on Ethylene Oxide Production

The carbon dioxide effect on produced ethylene oxide is shown in Fig. 8. As can be seen, by increasing carbon dioxide concentration in the reactor feed, ethylene oxide concentration decreases by about 50% in all the catalysts. Carbon dioxide is a by-product of this reaction which shows negative effects on ethylene conversion and ethylene oxide selectivity. The Re-contain catalyst shows more sensibility to carbon dioxide concentration compared to other catalysts. The effect of carbon dioxide on desirable active sites in the Re-contain catalyst is more destructive. By increasing the carbon dioxide concentration, the discrepancy between the produced ethylene oxides in the Ag-Cs-Re catalyst with other catalysts is reduced. Hence, to utilize the positive effect of Re in the silver catalyst, carbon dioxide in the reactor feed should be minimized. Besides, Re is a precious metal, which should be used in optimal value in ethylene epoxidation catalyst synthesizing and used under the optimum operating condition of the process.

According to Fig. 8, the presence of cesium in the catalyst causes ethylene oxide concentration to increases from 0.25 to 0.41 mol% at the reactor outlet. While, in the Re-contain catalyst, this value reaches 1.01 mol% at zero carbon dioxide concentration in the reactor feed. Furthermore, the Re-conation catalyst shows a better performance relative to two others at the carbon dioxide concentration of 6 mol%. Because of that, the ethylene oxide concentration at the reactor outlet for Ag/SrTiO₃, Ag-Cs/SrTiO₃ and Ag-Cs-Re/SrTiO₃ are 0.08, 0.27 and 0.428 mol%, respectively.

4. Conclusion

By adding rhenium and cesium promoters to the Ag/SrTiO₃, no strictly particle morphological changes are observed. In addition, no considerable changes in the crystalline structure of catalysts are distinct. Ethylene conversion increases about twofold when 230 ppm rhenium was added to the catalyst. Increasing temperature from 210 °C to 220 °C leads to a slight decrease in selectivity in Ag-Cs-Re/SrTiO₃ compared to the strict selectivity drop in the no Re-contain catalyst. The optimum value of chlorine, which is around 1.3 ppm, leads to an ethylene oxide yield of 1.9% and 1.3% in Ag-Cs-Re and Ag-Cs catalysts, respectively. In order to obtain the desired results by adding precious metal of rhenium to the catalyst, carbon dioxide in the inlet reactor feed should be minimized.
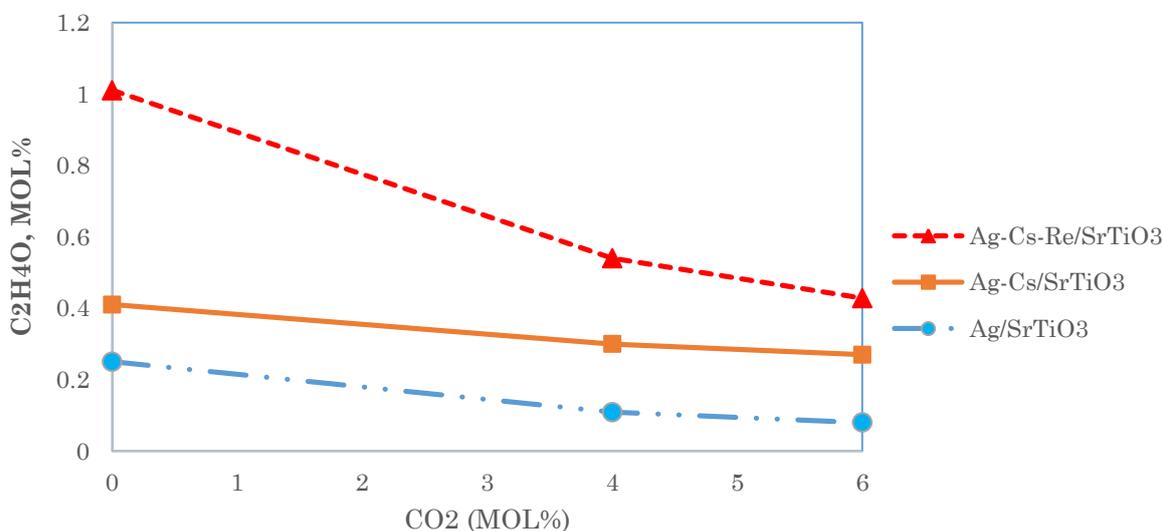

Figure 8. Effect of carbon dioxide concentration on produced ethylene oxide at temp.: 215 °C, chlorine: 1.3 ppm

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