

CHAPTER VII
EFFECT OF DILUENT GAS ON ETHYLENE EPOXIDATION ACTIVITY
OVER VARIOUS Ag-BASED CATALYSTS ON SELECTIVE OXIDE
SUPPORTS

(Submitted to Catalysis Communications)

7.1 Abstract

The influence of different diluent gases (He, Ar, N₂, CH₄, and CH₄ balanced with He) on the epoxidation of ethylene was comparatively studied over a commercial 14.86 wt.% Ag/ α -Al₂O₃, a bimetallic 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ and 0.32 wt.% Sn-promoted 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalysts. The best diluent gas was found to be CH₄ balanced with He over all studied catalysts for the ethylene epoxidation. CH₄ enhanced C₂H₄ conversion while He provided both high EO selectivity and yield. Thus, the diluent gas 35 % CH₄ balanced with 53 % He could give the highest synergistic effect towards ethylene epoxidation reaction, corresponding to the lowest coke formation.

Keywords: Diluent gases; CH₄ balanced He; SrTiO₃; Cu-Ag; Ethylene epoxidation

7.2 Introduction

Ethylene oxide (EO) is an important intermediate in manufacturing of several petrochemical products, such as ethylene glycol, surfactants, anti-freezers, adhesives, explosives, lubricants, plasticizers, and solvents [1-3]. EO is commercially produced through the partial oxidation of ethylene using either air or oxygen over Ag catalysts loaded on a low surface area α -Al₂O₃ support, based on the original concept by Lefort in 1931 [4-5]. A generalized reaction stoichiometry of the process is as follows:



Apart from the ethylene oxide formation, the by-products including CO, CO₂, and H₂O are simultaneously formed [6]. The selectivity towards ethylene oxide production has been improved by the use of different catalyst preparation techniques [7-15], different silver precursors [16-21], and different promoters [22-24].

Cesium as an alkali metal promoter has been received a great interest over the recent decades. The presence of Cs was found to result in the complete coverage of Ag on the support and it mainly lied in the subsurface region with a small amount at the catalyst surface, suggesting that Cs acts as a binder between the Ag and α -Al₂O₃ support through stabilizing or creating the bond between two phases [25]. Grant and Lambert [26] found that Cs neutralizes acid sites on the oxide support which are responsible for isomerization of the epoxide to acetaldehyde, followed by combustion. It also increases the crystalline lattice defects (electrophilic oxygen located area) and decreases the amount of nucleophilic oxygen which leads to the total oxidation of ethylene. After that, Campbell [27] investigated the electronic effect of added Cs on Ag catalysts. The influence of Cs on Ag(111) was observed and a surface cesium oxide species (CsO₃) existed in islands which was decomposed to form gaseous Cs and O₂ at 610 K. Linic and Barteau [28] pointed out that ethylene oxide was produced through the formation of an oxametallacycle intermediate (favor the transition state). Thus, the addition of Cs promoter which modifies the electric field or dipole-dipole interactions (electronic effect) resulted in the higher transition state, leading to more ethylene oxide. Epling et al. [29] showed that there was a chemical interaction (electronic effect) between the Al, Cs, and Ag which might be

responsible for changes in the electronic properties of the Ag catalysts. Moreover, Yinsheng et al. [30] compared the Ba and Cs promoting effects on a silver surface, affecting the ethylene epoxidation reaction. Ba was found to increase the activity in terms of conversion but slightly lower EO selectivity. On the contrary, Cs enhanced the EO selectivity with a lower activity in terms of ethylene conversion.

Some chlorine-containing compounds i.e. 1,2-dichloroethane (DCE), HCl, ethyl chloride, etc. is used as the feed additive to promote the EO selectivity over Ag catalysts in an industrial practice [22,27,31]. Meanwhile, the added chlorinate promoter on the surface of Ag catalysts produces more AgCl in which can poison the catalysts. To overcome the poisoning problem by 1,2-dichloroethane (DCE), paraffins are added to the feed. Compared with methane and ethylene, ethane is the most effective dechlorinating agent. Lafarga and Varma [32] investigated the effect of 1,2-dichloroethane (DCE) addition in the ethylene epoxidation reaction. The EO selectivity increased to greater than 80 % but the ethylene conversion decreased with increasing DCE concentration in the feed (0-3.3 ppm). The deactivation of the catalyst for the highest level of DCE was observed after a few hours of the reaction. Thus, ethane with a relatively low concentration (ca. 1 %) was added in the feed to moderate the deactivation (control the amount of chlorine adsorbed on the catalyst surface) to maximize the benefit from the DCE addition. The optimum DCE level was found to be 1-2 ppm to yield the maximum EO yield with highly stable activity. Recently, Dellamorte et al. [33] studied the promotional effect of Re on Ag and Cu-Ag bimetallic catalysts for the epoxidation of ethylene. Rhenium addition enhanced the selectivity at very small loadings with a large decrease in the catalytic activity. The optimum rhenium loading was 25 ppm on the Ag catalyst and between 50 and 100 ppm on the bimetallic Cu-Ag catalyst to obtain the maximum EO selectivity. The Re-promoted Ag catalysts were found to contain more uniform distribution of the reaction sites for oxygen adsorption than the unpromoted ones, resulting in the enhancement of the EO selectivity. Moreover, the Re promoter might improve the EO selectivity through the stabilization of defect regions or through weakening the Ag-O bond.

The ethylene epoxidation processes comprise of ethylene, oxygen, and diluent gas (balanced gas in the feed beyond the reactant gases, C₂H₄ and O₂, so

called “third gas”) in the reactant feed. Most researchers used helium [16,34-35] or nitrogen [3,36-37] as the diluent gas with various oxygen to ethylene ratios. However, the effect of diluent gas on the ethylene epoxidation activity has not been reported in the scientific literature.

From our previous work [38-40], the most promising catalyst was the 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst. followed by 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst. In this part of the study, these two catalysts were employed in the ethylene epoxidation experiments, as compared to the 14.86 wt.% Ag/ α -Al₂O₃ catalyst (commercial catalyst) in various diluent gases i.e. He, Ar, N₂, CH₄, and CH₄ balanced with He. The optimum O₂ to C₂H₄ ratio, as well as the most effective diluent gas, was investigated to obtain the best reaction conditions for the ethylene epoxidation reaction.

7.3 Experimental

7.3.1 Materials

α -Al₂O₃ (0.109 m²/g) was purchased from Fluka. Silver nitrate (AgNO₃) was purchased from S.R. Lab. Tetraisopropyl orthotitanate (TIPT, Ti(OCH(CH₃)₂)₄), strontium nitrate (Sr(NO₃)₂), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), and laurylamine (LA, CH₃(CH₂)₁₁NH₂) were supplied by Merck. Acetylacetone (ACA, CH₃COCH₂COCH₃) was obtained from S.D. Fine-Chemical. Tin chloride (SnCl₂) was purchased from Aldrich. Hydrochloric acid (HCl) and ethanol (C₂H₅OH) were supplied by Labscan. All chemicals used were an analytical grade and used as received without further purification.

7.3.2 Catalyst preparation procedures

The mesoporous-assembled SrTiO₃ nanocrystal support was synthesized via a sol-gel process with the aid of a structure-directing surfactant [38-40]. Briefly, ACA was first added to TIPT at an equimolar ratio. In a separate beaker, the LA surfactant was dissolved with 0.5 ml of the HCl and then was added to a Sr(NO₃)₂ solution containing a specified amount of Sr(NO₃)₂ and ethanol to obtain the Sr(NO₃)₂/LA/HCl solution. Afterwards, this mixed solution was poured into the

TIPT/ACA solution and kept continuously stirring. The resultant mixture was incubated at 353 K for 4 d to obtain a complete gel formation and was further dried at 353 K for 4 d. Finally, the dried gel was calcined at 923 K, which was found to be the optimum support calcination temperature in our previous work [39], to produce the mesoporous-assembled nanocrystal SrTiO₃ support.

The Ag catalysts used in this work were prepared by the incipient wetness impregnation using the α -Al₂O₃ and SrTiO₃ supports with a silver nitrate solution to obtain the nominal Ag loadings of 15 wt.% (actual Ag loading = 14.86 wt.%) and 17.5 wt.% (actual Ag loading = 17.16 wt.%), respectively which were found to provide the best catalytic performance towards the ethylene oxide formation [38-40]. After that, the Ag impregnated on the α -Al₂O₃ or SrTiO₃ support was dried at 383 K overnight and calcined at 773 K for 5 h to produce Ag/ α -Al₂O₃ and Ag/SrTiO₃ catalysts. Next, the Ag/SrTiO₃ catalyst was further impregnated with the Cu(NO₃)₂·3H₂O precursor to obtain a nominal Cu loading of 1.5 wt.%. Following that, the catalyst sample was dried at 383 K overnight and then calcined in air at 773 K for 5 h to obtain the bimetallic Cu-Ag catalyst.

After that, the bimetallic Cu-Ag catalyst was promoted by tin using tin chloride precursor with the optimum nominal tin loading of 0.4 wt.% [40]. The mixture was first dried at 383 K overnight and finally calcined at 673 K for 2 h to produce the 0.32 wt.% Sn-promoted 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst [41].

7.3.3 Activity testing experiments

The catalytic performance towards the ethylene epoxidation reaction on the 14.86 wt.% Ag/ α -Al₂O₃, 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃, or 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst was performed in a packed-bed 8-mm ID tubular reactor under 24.7 psia and a reaction temperature of 548 K [40] with various diluent gas systems. Initially, 30 mg of any studied catalyst powder packed in the reactor was pretreated with oxygen at 473 K for 2 h. The feed gas was a mixture of 40 % ethylene in He, pure oxygen (HP grade), and a diluent gas (He, Ar, N₂, CH₄ or CH₄ balanced with He). The feed gas compositions of 6 % ethylene and 3-7.5 % oxygen with different diluent gas balance (He, Ar, N₂, CH₄ or

CH₄ balanced with He) were achieved by using mass flow controllers. The space velocity of the feed gas through the reactor was maintained at 6000 h⁻¹ for all experimental runs. The compositions of the feed and effluent gases were analyzed by using an on-line gas chromatograph (Perkin Elmer, ARNEL) equipped with a 60/80 CARBOXEN 1 packed column (capable of separating carbon monoxide, carbon dioxide, ethylene, and oxygen) and a Rt-U PLOT capillary column (capable of separating EO, ethane, and propane). The formation of acetaldehyde was not detected under the studied conditions because of further oxidation to carbon dioxide and water so it appeared only in trace amounts [42]. The catalytic activity of each investigated catalyst was compared at 6 h of operation. The experimental data with less than 5 % error were averaged to assess the catalytic performance. Moreover, the studied catalysts with different diluent gases under their own optimum conditions were operated at 72 h of time on stream to investigate their long-term stability and performance. Finally, the best catalyst (0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃) was operated up to 7 d (168 h) to observe the long-term stability and performance towards ethylene epoxidation reaction.

7.3.4 Catalyst characterization techniques

The N₂ adsorption-desorption isotherms of the prepared catalysts were obtained by using a surface area analyzer (Quantachrome, SAA-IMP). The Brunauer-Emmett-Teller (BET) approach was applied to determine the specific surface areas using the adsorption data. The actual metal loadings of the investigated catalysts were analyzed by an atomic absorption spectrophotometer (AAS, Varian, Spectr AA-300).

The oxygen and ethylene uptakes of the synthesized catalysts were calculated from the desorption peaks which were obtained by using a temperature-programmed desorption (TPD) analyzer (Quantachrome, Chembet 3000). Oxygen (4.99 % O₂ in He) or pure ethylene (99.99 % C₂H₄) was initially adsorbed onto the catalyst surface at 473 K for 2 h for the TPD experiments. After that, the catalyst samples were cooled down to room temperature in a high-purity of He stream. Then, the catalyst samples were heated from room temperature to 1173 K with a heating rate of 10 K/min, and the desorbed gas was swept by the high-purity He at a flow

rate of 20 cm³/min. A thermal conductivity detector (TCD) was used to measure the concentration profile of oxygen or ethylene in the effluent gas.

The surface morphologies of the studied catalysts before and after the reaction experiments with their own optimum diluent gas systems were observed by a field emission scanning electron microscope (FE-SEM, JEOL 5200-2AE). Prior to analysis, the samples were coated with Pt to improve their conductivity. Furthermore, the particle sizes of loaded metals on the catalyst samples were examined by transmission electron microscopes (TEM, JEOL 3011 at 300 kV and JEOL 2010 at 200 kV). The specimens for TEM analysis were prepared by ultrasonically dispersing the catalyst powders in ethanol and then placing drops of the suspension onto a grid coated with a carbon film. The existence of Ag, Cu, and Sn particles on either the α -Al₂O₃ or SrTiO₃ support was verified by using an energy dispersive X-ray spectroscope (EDS) attached to the TEM. The metal particle sizes were determined from statistical data of the TEM images.

The amounts of coke deposited on the spent catalysts were quantified by a thermogravimetric-differential thermal analyzer (TG-DTA, PerkinElmer, Pyris Diamond).

7.4 Results and Discussion

7.4.1 Catalyst characterization results

7.4.1.1 *Specific surface area results*

The characterization results of all investigated catalysts (14.86 wt.% Ag/ α -Al₂O₃, 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ and 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalysts), including specific surface areas, metal particle sizes, O₂ uptakes and C₂H₄ uptakes are summarized in Table 7.1. All studied catalysts had very low specific surface areas and the 14.86 wt.% Ag/ α -Al₂O₃ catalyst possessed the lowest specific surface area. The tin promoter slightly decreased the specific surface area of the bimetallic Cu-Ag catalyst.

Table 7.1 Characteristics of 14.86 wt.% Ag/ α -Al₂O₃, 1.41 wt.% Cu-Ag/SrTiO₃ and 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-Ag/SrTiO₃ catalysts at their own optimum metal loadings (corresponding to the highest ethylene epoxidation activity)

Characteristics	14.86 wt.% Ag/ α -Al ₂ O ₃	1.41 wt.% Cu-Ag/SrTiO ₃ [*]	0.32 wt.% Sn-1.39 wt.% Cu-Ag/SrTiO ₃ [*]
Specific surface area (m ² /g)	0.03	1.1	0.8
Ag particle size ^a (nm)	43.6 ± 0.4	58 ± 0.5	58 ± 0.5
2 nd metal particle size ^a (nm)	-	4.7 ± 0.4 (Cu)	2.8 ± 0.3 (Sn ^{**}), 5.5 ± 0.4 (Cu)
O ₂ uptake ^b (μ mol g ⁻¹)	6	6935	7429
C ₂ H ₄ uptake ^c (μ mol g ⁻¹)	0	5767	6065
CH ₄ uptake ^d (μ mol g ⁻¹)	259	486	403

^a From TEM analysis

^{*} 17.16 wt.% Ag loading (actual)

^{**} Sn-promoted on Cu-Ag bimetallic catalyst

^b based on the temperature range of 400-700 K

^c based on the temperature range of 400-700 K

^d based on the temperature range of 325-600 K

7.4.1.2 TPD results

Table 7.1 also summarizes the adsorption capabilities of oxygen, ethylene, and methane on the catalyst surfaces, in terms of O₂, C₂H₄, and CH₄ uptakes. The main oxygen and ethylene desorption peaks in the temperature range of 400-700 K, together with the main methane desorption peak at 325-600 K were used to calculate the uptake results [40]. The highest amounts of both O₂ and C₂H₄ uptakes were found on the 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst, followed by the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst. However, the 14.86 wt.% Ag/ α -Al₂O₃ catalyst adsorbed only a very small amount of oxygen with the absence of ethylene adsorption. Among the investigated catalysts, the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst had the highest methane uptake while the lowest amount of the methane uptake was found on the 14.86 wt.% Ag/ α -Al₂O₃ catalyst. The results indicate that the strong interaction between Ag-Cu and the SrTiO₃ support greatly enhances both ethylene and oxygen uptakes as compared with the weak interaction between Ag and the α -Al₂O₃ support. The addition of a small amount of Sn promoter can increase both ethylene and oxygen uptakes significantly.

7.4.1.3 Surface morphology

The TEM/EDS technique was applied to verify the existence of metal nanoparticles of the studied catalysts. The average catalyst particle sizes are summarized in Table 7.1. Both promoted and unpromoted bimetallic 1.41 wt.% Cu-17.16 wt.% Ag catalysts had larger Ag particle sizes (58 nm) than the 14.86 wt.% Ag/ α -Al₂O₃ catalyst (44 nm). Moreover, the Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst possessed the slightly higher Cu particle size (5.5 nm) than the unpromoted one (4.7 nm). After the reaction, the average Ag particle sizes slightly increased from 58 nm for the fresh catalyst to 60 nm for the spent catalyst, while the average Cu particle sizes slightly increased from 5.5 to 5.8 nm and the average Sn particle sizes slightly increased from 2.8 to 2.9 nm for the 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst at the optimum conditions with 6 % O₂, 6 % C₂H₄ and 35 % CH₄ balanced with 53 % He diluent gas system. Moreover, for the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst, the average Ag particle sizes slightly increased from 58 nm for the fresh catalyst to 61 nm for the spent catalyst, while the

average Cu particle sizes increased from 4.7 to 5.8 nm after the reaction testing experiment conducted at the optimum conditions (6 % O₂, 6 % C₂H₄ with 30 % CH₄ balanced with 58 % He diluent gas system, a pressure of 24.7 psia, and reaction temperature of 548 K). On the other hand, for the 14.86 wt.% Ag/ α -Al₂O₃ catalyst, the average Ag particle sizes increased from 44 nm for the fresh catalyst to 49 nm for the spent catalyst after the reaction testing experiment conducted at the optimum conditions with 25 % CH₄ balanced with 63 % He diluent gas system. The small increases in the metal particle sizes of all studied catalysts after the reaction testing experiments point out that the sintering or agglomeration of the investigated catalysts during the studied reaction conditions is not a great deal because of the low temperature (548 K) used for the reaction experiments.

The surface morphologies of the best catalyst (0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst) under various diluent gas systems after the reaction, as compared to the fresh catalyst, are illustrated in Figure 7.1. The insignificant changes in surface topologies can be clearly observed after the reaction for all diluent gas systems except the system with 35 % CH₄ balanced with 53 % He, showing a larger size with rounder shape of the Ag particles. Furthermore, Figure 7.2 compares the surface morphologies of the studied catalysts under their own optimum conditions with CH₄ balanced with He as diluent gases before and after the reaction. The most significant changes on the catalyst surface morphology after the reaction in terms of surface agglomeration was seen for the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst, becoming smoother with a less amount of attached particles (Figure 7.2c and 7.2d).

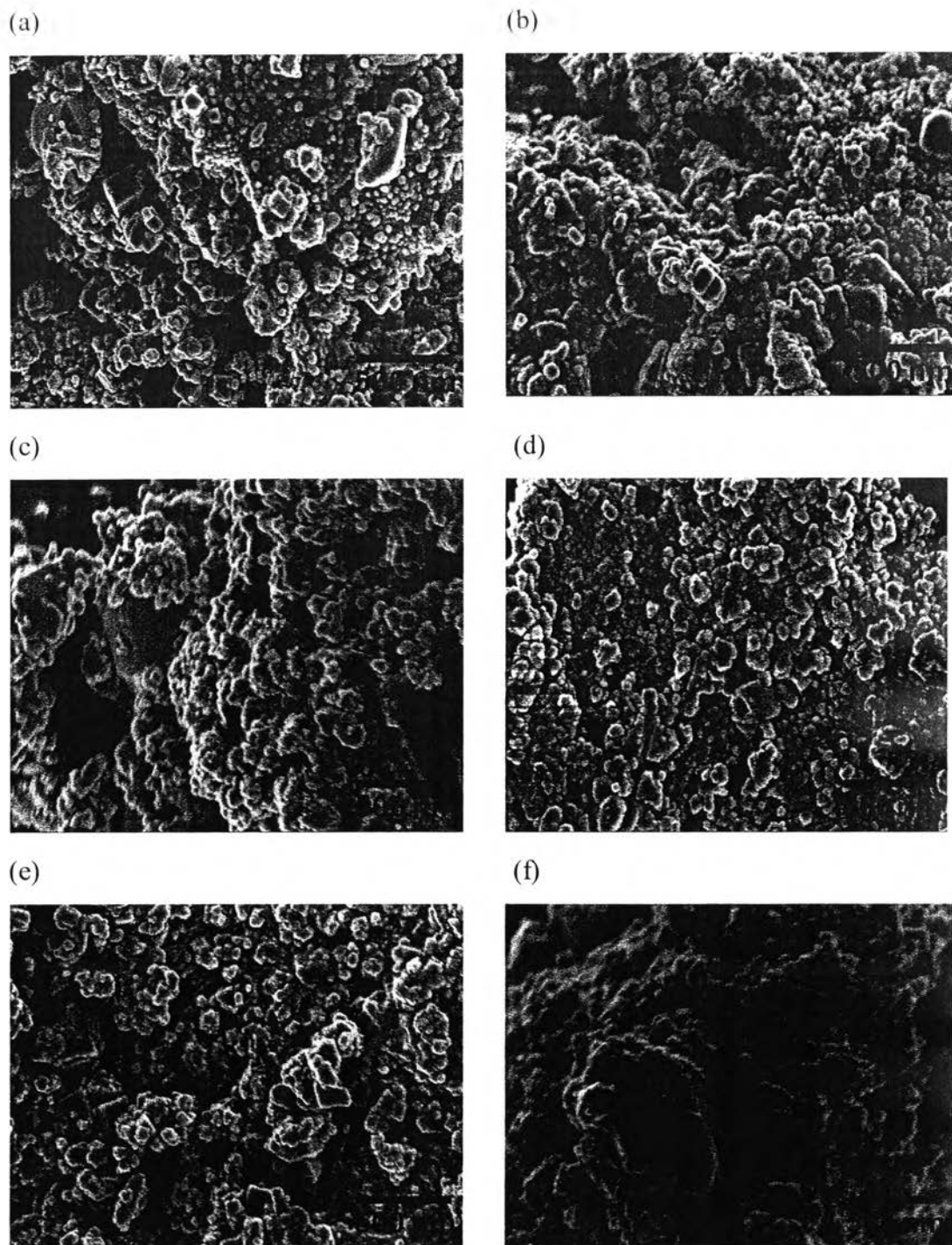


Figure 7.1 SEM images of 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalysts after the reaction at various diluent gas systems (a) fresh catalyst, (b) He, (c) Ar, (d) N₂, (e) CH₄, and (f) 35 % CH₄ balanced with 53 % He (50,000x).

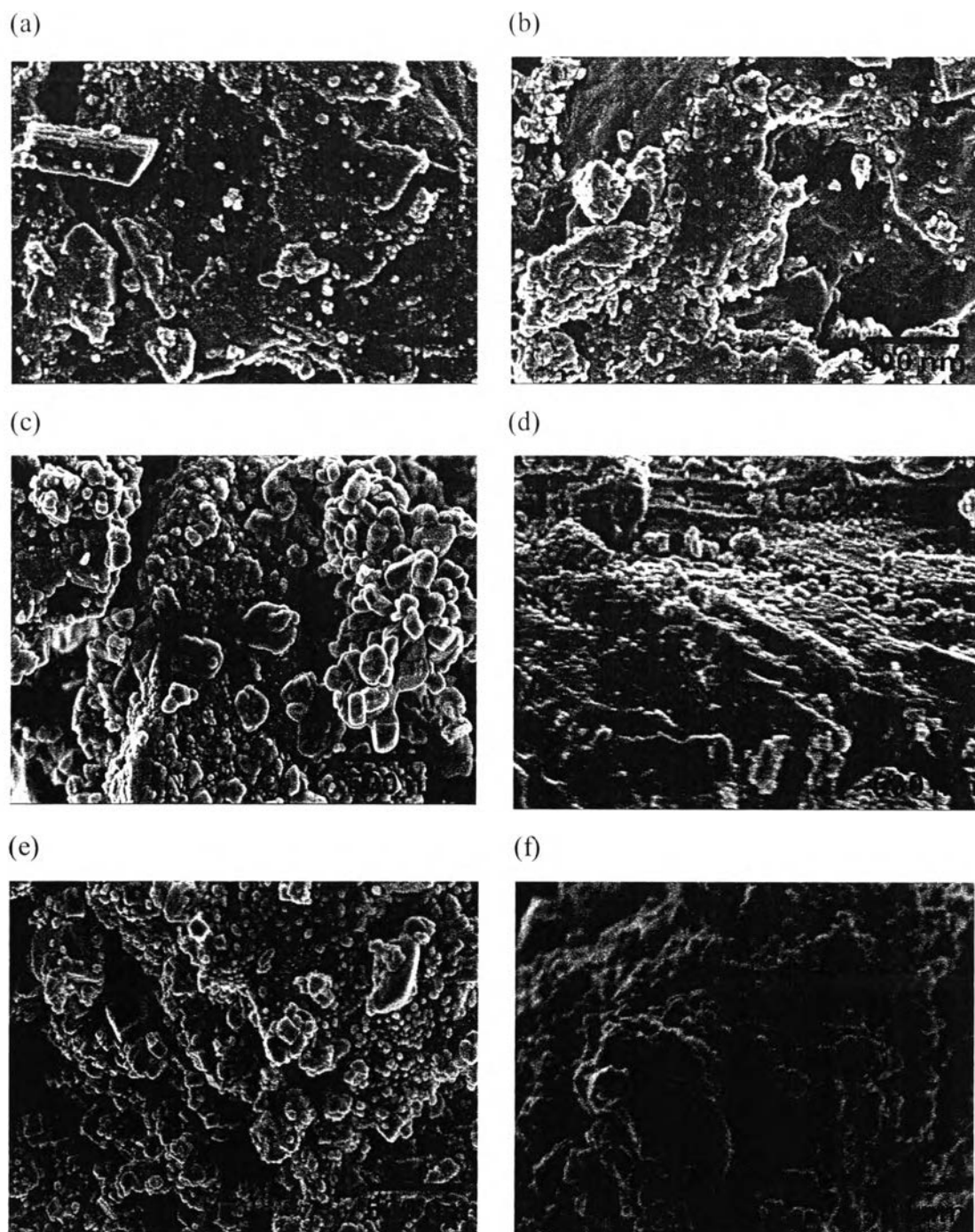


Figure 7.2 SEM images of 14.86 wt.% Ag/ α -Al₂O₃ catalysts before the reaction (a) and after the reaction in 25 % CH₄ balanced with 63 % He (the diluent gas system) (b); 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalysts before the reaction (c) and after the reaction in 30 % CH₄ balanced with 58 % He (d); 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalysts before the reaction (e) and after the reaction in 35 % CH₄ balanced with 53 % He (f) (50,000x) (the reaction conditions: 6 % O₂, 6 % C₂H₄, a space velocity of 6000 h⁻¹, a pressure of 24.7 psia, and a reaction temperature of 548 K).

7.4.1.4 Coke formation results

Table 7.2 summarizes the amounts of coke formation on different spent catalysts after the ethylene epoxidation reaction at 6 and 72 h with various diluent gas systems. The highest coke formation was found on the 14.86 wt.% Ag/ α -Al₂O₃ catalyst (6.4 % at 6 h and 17.6 % at 72 h) with CH₄ as the diluent gas. On the contrary, the 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst possessed the lowest coke formation of 1.7 % at 6 h (He as the diluent gas) and 2.7 % at 72 h (35 % CH₄ balanced with 53 % He as the diluent gas), followed by the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst (2.4 % at 6 h and 4.0 % at 72 h) with He as the diluent gas. From the results, the tin addition leads to the decrease in the coke formation. For any given catalyst, the diluent gas containing CH₄ balanced with He generally provided the lowest coke formation.

7.4.2 Ethylene epoxidation activity results

The effects of various oxide supports (α -Al₂O₃, Al₂O₃ C, Al₂O_{3,Acid}, SiO₂ 90, TiO₂, SrTiO₃, MgTiO₃, CaTiO₃, and BaTiO₃) and several loaded metals (Ag, Au, Au-Ag, Cu-Ag, Ba-Ag, Pd-Ag, and Sn-Ag) on the best support (SrTiO₃) for the ethylene epoxidation reaction were investigated in our previous work [38-40]. The 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst provided the highest catalytic performance in terms of EO yield and EO selectivity, enhancing the EO selectivity to 95.1 %, the highest EO yield of 5.2 %, and the best long-term stability at 72 h of time on stream. Furthermore, the secondly best catalyst was found to be the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst. As a result of that, these two catalysts were comparatively studied with the 14.86 wt.% Ag/ α -Al₂O₃ catalyst (commercial catalyst) in this present work. The effect of various diluent gases (Ar, N₂, CH₄, and CH₄ balanced with He) compared to He diluent gas which used in the previous work was further investigated to improve the ethylene epoxidation system.

Table 7.2 Coke formation on spent catalysts after 6 h and 72 h on stream of the ethylene epoxidation reaction (a space velocity of 6000 h^{-1} , a pressure of 24.7 psia, and a reaction temperature of 548 K)

Catalysts	Diluent gas	Coke formation at 6 h (wt.%)	Coke formation at 72 h (wt.%)
14.86 wt.% Ag/α-Al₂O₃	88 % He	4.3	11.7
	88 % Ar	5.1	12.2
	89.5 % N ₂	5.8	13.8
	88 % CH ₄	6.4	17.6
	25 % CH ₄ +63 % He	4.9	12.3
1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃	88 % He	2.4	4.0
	88 % Ar	3.0	4.9
	89.5 % N ₂	2.9	5.4
	88 % CH ₄	4.8	7.7
	30 % CH ₄ +58 % He	2.6	4.5
0.32 wt.% Sn-1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃	88 % He	1.7	2.9
	88 % Ar	2.5	3.8
	89.5 % N ₂	2.7	4.6
	88 % CH ₄	3.9	7.1
	35 % CH ₄ +53 % He	2.2	2.7

Note: The optimum concentrations of 6 % O₂ and 6 % C₂H₄ were found for all systems, except for the N₂ diluent gas system which its optimum concentrations of O₂ and C₂H₄ were 4.5 % and 6 %, respectively.

Figure 7.3 shows the ethylene epoxidation activity of the studied catalysts as a function of O₂-to-C₂H₄ ratio in various diluent gases (He, Ar, N₂, and CH₄) at 6 h on stream. The optimum O₂-to-C₂H₄ molar ratio of 1:1 (6 % O₂ and 6 % C₂H₄) was found to provide the highest EO selectivity and/or yield for all diluent gases, except N₂ with the optimum ratio of 0.75:1 (4.5 % O₂ and 6 % C₂H₄). The He diluent system had the highest EO selectivity in all investigated catalysts and the maximum EO yield in some cases. However, the CH₄ diluent system provided the highest EO yield for the 14.86 wt.% Ag/ α -Al₂O₃ and the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalysts at 6 h of operation. Hence, the CH₄ gas was mixed with He gas to investigate the synergistic effect of these two diluent gases at different percentages of CH₄ to obtain the optimum % CH₄ balanced with He for the three studied catalysts. The ethylene epoxidation activity of the studied catalysts at 6 and 72 h on stream under different diluent gases is summarized in Table 7.3. The addition of CH₄ gas with a proper fraction balanced with He was found to improve the ethylene conversion (the data not shown here) with high EO selectivity and yield at 6 h on stream for all studied catalysts. The ethylene conversion increased from 3.6 % for He diluent gas to 3.8 % for 25 % CH₄ balanced with He (14.86 wt.% Ag/ α -Al₂O₃ catalyst), 5.8 % for He diluent gas to 6.0 % for the 30 % CH₄ balanced with He (1.41 wt.% Cu-Ag/SrTiO₃ catalyst), and 5.5 % for He diluent gas to 5.6 % for the 35 % CH₄ balanced with He (0.32 wt.% Sn-promoted on Cu-Ag/SrTiO₃ catalyst). For any given catalyst, the EO selectivity dropped substantially after 72 h of operation. Among all the investigated diluent gases, the most effective diluent gas was the CH₄ balanced with He, providing the maximum EO selectivity and the superior long-term stability at 72 h of time on stream. Moreover, the 0.32 wt.% Sn-promoted on Cu-Ag/SrTiO₃ and the 1.41 wt.% Cu-Ag/SrTiO₃ catalysts showed a much better catalytic performance than the 14.86 wt.% Ag/ α -Al₂O₃ catalyst. It should be noted that for any given catalyst, the CH₄ conversion was higher in the CH₄ diluent system than that of the CH₄ balanced with He system. Moreover, the conversion of CH₄ was considerably very low for all cases.

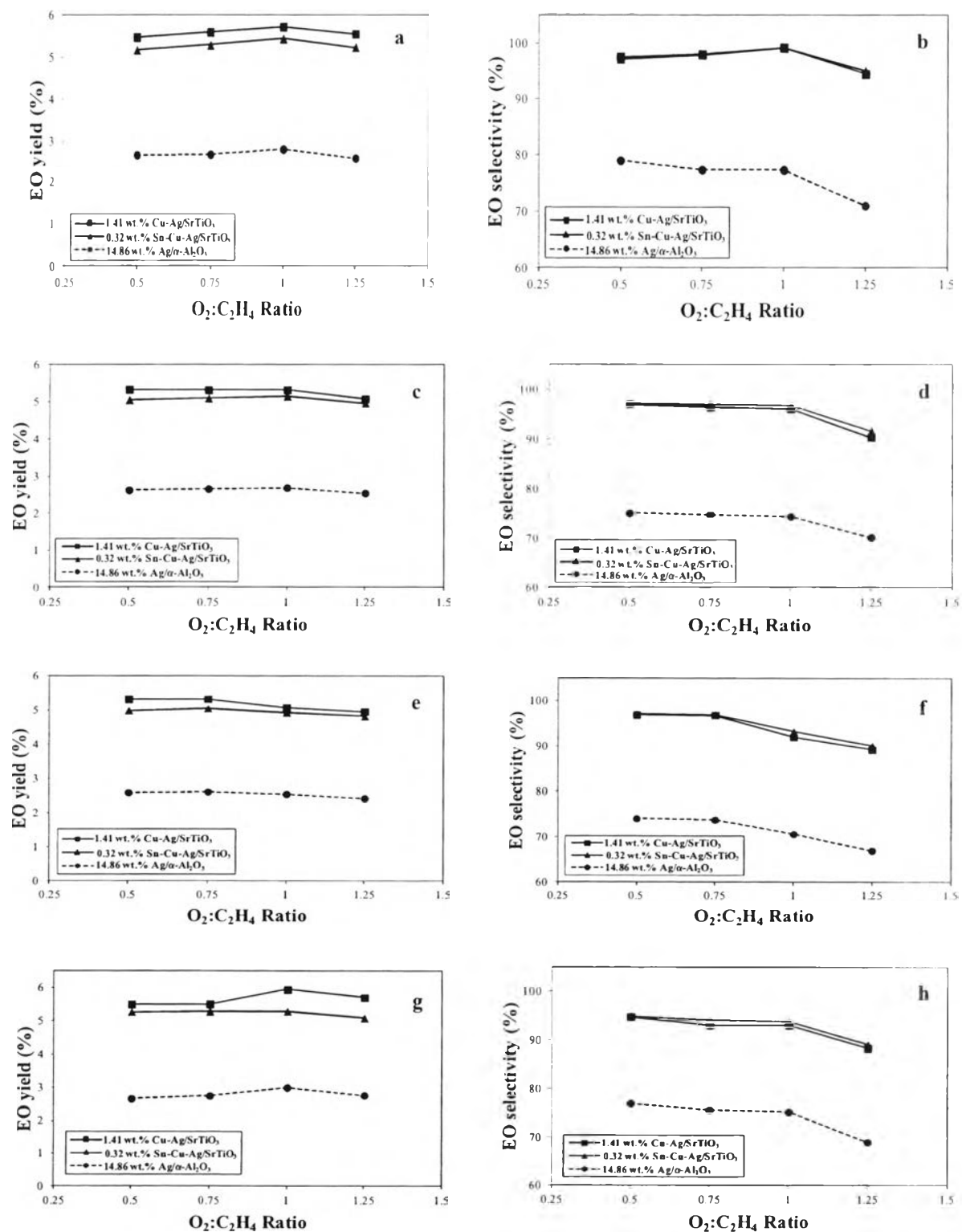


Figure 7.3 EO yield and EO selectivity as a function of O₂ to C₂H₄ ratio of the studied catalysts at 6 h on stream in various diluent gas systems: (a) and (b) in He, (c) and (d) in Ar, (e) and (f) in N₂, (g) and (h) in CH₄ (a fixed C₂H₄ concentration of 6 %, a space velocity of 6000 h⁻¹, a pressure of 24.7 psia, and a reaction temperature of 548 K).

Table 7.3 Ethylene epoxidation activity of studied catalysts at 6 h and 72 h on stream (a space velocity of 6000 h⁻¹, a pressure of 24.7 psia, reaction temperature of 548 K)

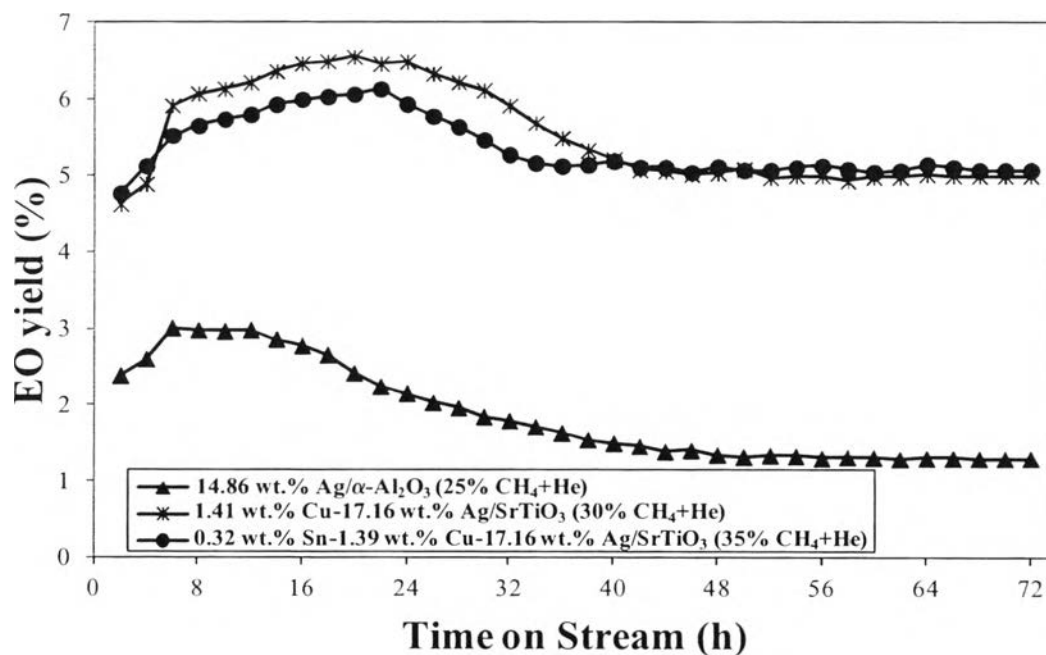
Catalysts	Diluent gas	6 h of time on stream		72 h of time on stream		
		EO selectivity (%)	EO yield (%)	EO selectivity (%)	EO yield (%)	CH ₄ conversion (%)
14.86 wt.% Ag/α-Al₂O₃	88 % He	77.39	2.8	43.37	1.3	-
	88 % Ar	74.43	2.7	41.02	1.2	-
	89.5 % N ₂	73.86	2.6	37.18	1.1	-
	88 % CH ₄	75.32	3.0	28.35	0.9	3.0
	25 % CH ₄ +63 % He	79.96	3.0	40.01	1.3	2.4
1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃	88 % He	99.27	5.7	90	4.5	-
	88 % Ar	96.05	5.3	86.62	4.2	-
	89.5 % N ₂	96.89	5.3	83.5	4.0	-
	88 % CH ₄	93.09	6.0	76.9	4.1	2.2
	30 % CH ₄ +58 % He	99.29	5.9	91.3	5.0	1.7
0.32 wt.% Sn-1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃	88 % He	99.2	5.4	95.08	5.2	-
	88 % Ar	96.84	5.2	91.75	4.8	-
	89.5 % N ₂	97.04	5.1	89.42	4.5	-
	88 % CH ₄	93.89	5.3	79.81	4.0	2.6
	35 % CH ₄ +53 % He	99.45	5.5	96.72	5.1	2.2

Note: The optimum concentrations of 6 % O₂ and 6 % C₂H₄ were found for all systems, except for the N₂ diluent gas system which its optimum concentrations of O₂ and C₂H₄ were 4.5 % and 6 %, respectively.

These results can be used to correlate with the higher coke formation in the CH₄ diluent system as compared with that in the CH₄ balanced with He system for any given catalyst (Table 7.2). CH₄ may help to increase the ethylene conversion, improve the activity of the catalysts, as well as suppress the CO₂ formation [43] while He simultaneously maintains the high selectivity of ethylene oxide, resulting in the synergistic effects for the EO formation. When CH₄ was completely replaced by ethylene in the feed, the product was found to contain mainly CO₂ (the data not shown here). This result points out that the CH₄ addition can enhance the catalytic activity towards ethylene epoxidation reaction only when a proper amount of CH₄ is applied in the He diluent gas.

The best diluent gas (CH₄ balanced with He) was next applied in the long-term stability experiments of the studied catalysts and the results are shown in Figure 7.4. The catalytic activity of all catalysts declined with time and reached the steady state at around 50 h of time on stream. The 0.32 wt.% Sn-promoted on Cu-Ag/SrTiO₃ was found to be the most effective catalyst which its EO selectivity slightly dropped from 99.5 % at 6 h to 97 % at 72 h and EO yield decreased from 5.5 to 5.1 %. The secondly best catalyst was the 1.41 wt.% Cu-Ag/SrTiO₃ which the EO selectivity decreased to 91 % and EO yield to 5 % after 72 h of operation. On the other hand, the 14.86 wt.% Ag/ α -Al₂O₃ catalyst exhibited the worst long-term stability, providing the EO selectivity of only 40 % and EO yield of 1.3 % after 72 h of time on stream. The reason for the decline in the catalytic activity of all studied catalysts is mainly due to the coke formation on the spent catalysts (see Table 7.2).

(a)



(b)

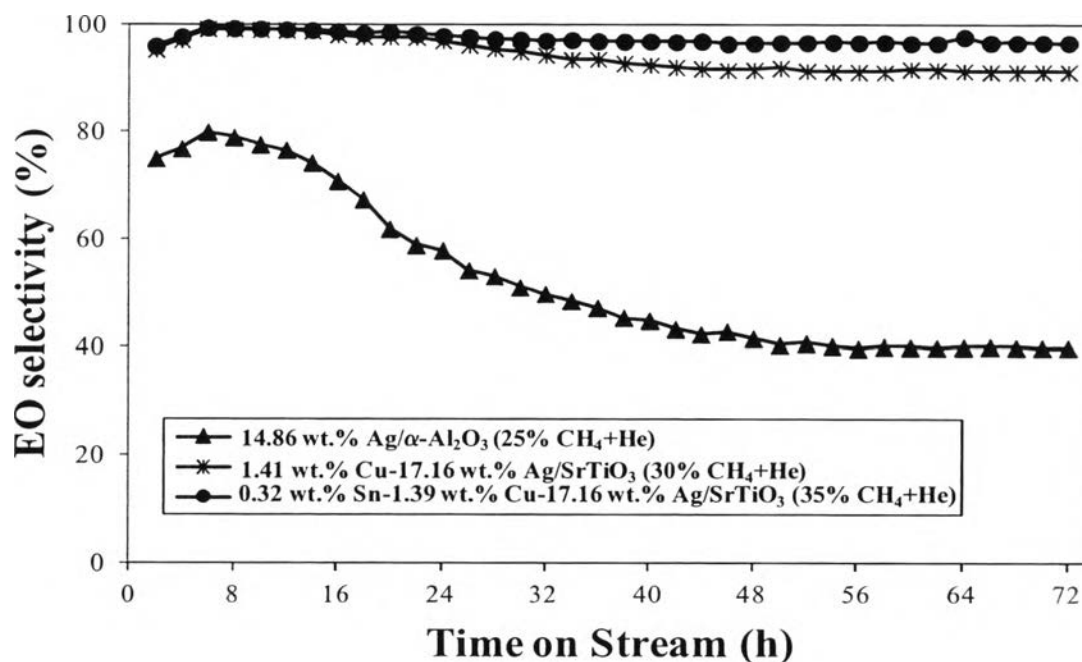


Figure 7.4 EO yield (a) and EO selectivity (b) as a function of time on stream for the studied catalysts at their optimum % CH₄ balanced with He as the diluent gas systems (6% O₂ and 6% C₂H₄, a space velocity of 6000 h⁻¹, a pressure of 24.7 psia, a reaction temperature of 548 K).

After that, the ethylene epoxidation experiment for the best catalyst (0.32 wt.% Sn-promoted on Cu-Ag/SrTiO₃) was conducted for 7 days (168 h) to confirm the superior long-term stability of this catalyst (Figure 5). The EO selectivity remained almost stable after 72 h of experiment and it slightly dropped from 97 % at 72 h to 96 % at 168 h. The EO yield also depicted the same trend, decreasing from 5.1 % at 72 h to 4.9 % at 168 h. The best catalytic activity of this catalyst can be related to the significantly high oxygen and ethylene adsorption capabilities and the tin promoter that prolonged the stability towards the ethylene epoxidation reaction [40].

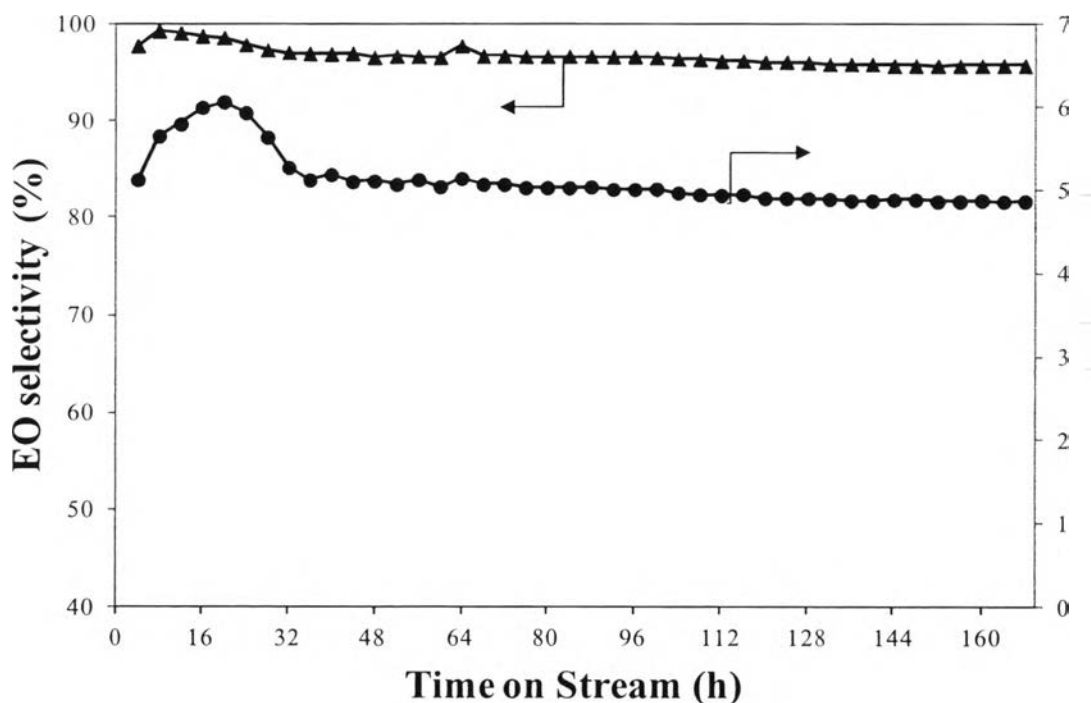


Figure 7.5 EO selectivity and EO yield as a function of 7 days of time on stream for 0.32 wt.% Sn-1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst (6% O₂ and 6% C₂H₄ balanced with 35% CH₄+He, a space velocity of 6000 h⁻¹, a pressure of 24.7 psia, a temperature of 548 K).

7.5 Conclusions

In this study, the effect of diluent gas on ethylene epoxidation was investigated over the best catalyst (0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO₃) in comparison to the 1.41 wt.% Cu-17.16 wt.% Ag/SrTiO₃ catalyst and the 14.86 wt.% Ag/ α -Al₂O₃ catalyst (commercial catalyst). The type of diluent gas was found to greatly affect the ethylene epoxidation in the following order: He > N₂ ~ Ar > CH₄ which corresponded to the coke formation very well. Interestingly, the addition of CH₄ in the He diluent gas with a proper fraction was found to enhance the ethylene epoxidation performance for all studied catalysts, especially for the long-term activities.

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7.7 References

- [1] S.S. Hassani, M.R. Ghasemi, M. Rashidzadeh, Z. Sobat, *Cryst. Res. Technol.* 44 (2009) 948-952.
- [2] Y.Ch. Kim, N.C. Park, J.S. Shin, S.R. Lee, Y.J. Lee, D.J. Moon, *Catal. Today* 87 (2003) 153.
- [3] J.T. Jankowiak, M.A. Barteau, *J. Catal.* 236 (2005) 366.
- [4] T.E. Lefort, French Patent 729 (1931) 952.
- [5] G. Ertl, H. Knozinger, J. Weitkamp, *Handbook of Heterogeneous Catalysis*, VCH, Weinheim, 1997.
- [6] R.E. Kenson, M. Lapkin, *J. Phys. Chem.* 74 (1970) 1493-1502.
- [7] T. Tsumura, K. Sogabe, M. Toyoda, *Mater. Sci. Eng., B* 157 (2009) 113-115.
- [8] L. Chen, S. Zhang, L. Wang, D. Xue, S. Yin, *J. Cryst. Growth* 311 (2009) 746-748.
- [9] J.C. Dellamorte, J. Lauterbach, M.A. Barteau, *Top. Catal.* 53 (2010) 13-18.
- [10] S. Pak, A. Rokicki, S. Kawabata, US Patent 0016617 A1 (2010).
- [11] A.I. Korchagin, N.K. Kuksanov, A.V. Lavrukhin, S.N. Fadeev, R.A. Salimov, S.P. Bardakhanov, V.B. Goncharov, A.P. Suknev, E.A. Paukshtis, T.V. Larina, V.I. Zaikovskii, S.V. Bodanov, B.S. Balzhinimaev, *Vacuum* 77 (2005) 485-491.
- [12] V.G. Nenajdenko, A.Y. Vasilkov, A.A. Goldberg, V.M. Muzalevskiy, A.V. Naumkin, V.L. Podshibikhin, A.V. Shastin, E.S. Balenkova, *Mendeleev Commun.* 20 (2010) 200-202.
- [13] J. Rebelli, A.A. Rodriguez, S. Ma, C.T. Williams, J.R. Monnier, *Catal. Today* 160 (2011) 170-178.
- [14] X. Liu, A. Wang, X. Yang, T. Zhang, C.Y. Mou, D.S. Su, J. Li, *Chem. Mater.* 21 (2009) 410-418.
- [15] V. Abdelsayed, K.M. Saoud, M.S. Shall, *J. Nanopart. Res.* 8 (2006) 519-531.
- [16] C.F. Mao, M.A. Vannice, *Appl. Catal., A* 122 (1995) 61-76.
- [17] G.B. Hoflund, D.M. Minahan, *Nucl. Instrum. Methods Phys. Res., Sect. B* 118 (1996) 517-521.
- [18] A.P. Fotopoulos, K.S. Triantafyllidis, *Catal. Today* 127 (2007) 148-156.
- [19] Y. Shiraishi, N. Toshima, *J. Mol. Catal. A: Chem.* 141 (1999) 187-192.

- [20] S.R. Lee, Y.J. Lee, S.G. Hong, Y.C. Kim, N.C. Park, D.J. Moon, *Appl. Chem.* 7 (2003) 229-232.
- [21] M. Epifani, C. Giannini, L. Tapfer, L. Vasanelli, *J. Am. Ceram. Soc.* 83 (2000) 2385-2393.
- [22] K.L. Yeung, A. Gavriilidis, A. Varma, M.M. Bhasin, *J. Catal.* 174 (1998) 1-12.
- [23] Ch. Karavasilis, S. Bebelis, C.G. Vayenas, *J. Catal.* 160 (1996) 205-213.
- [24] E.A. Podgornov, I.P. Prosvirin, V.I. Bukhtiyarov, *J. Mol. Catal. A: Chem.* 158 (2000) 337-343.
- [25] D.M. Minahan, G.B. Hoflund, *J. Catal.* 158 (1996) 109.
- [26] R.B. Grant, R.M. Lambert, *J. Catal.* 92 (1985) 364.
- [27] C.T. Campbell, *J. Catal.* 99 (1986) 28.
- [28] S. Linic, M.A. Barteau, *J. Am. Chem. Soc.* 126 (2004) 8087.
- [29] W.S. Epling, G.B. Hoflund, D.M. Minahan, *J. Catal.* 171 (1997) 490-497.
- [30] P. Yinsheng, Z. Shi, T. Liang, D. Jingfa, *Catal. Lett.* 12 (1992) 307-318.
- [31] C.T. Campbell, B.E. Koel, *J. Catal.* 92 (1985) 272.
- [32] D. Lafarga, A. Varma, *Chem. Eng. Sci.* 55 (2000) 749-758.
- [33] J.C. Dellamorte, J. Lauterbach, M.A. Barteau, *Catal. Today* 120 (2007) 182-185.
- [34] C.N. Marta, A. Carvalho, F.B. Passos, M. Schmal, *J. Catal.* 248 (2007) 124-129.
- [35] A. Ayame, Y. Uchida, H. Ono, M. Miyamoto, T. Sato, H. Hayasaka, *Appl. Catal., A* 244 (2003) 59-70.
- [36] J.C. Dellamorte, J. Lauterbach, M.A. Barteau, *Appl. Catal., A* 391 (2011) 281-288.
- [37] V.M. Mastikhin, S.N. Goncharova, V.M. Tapilin, V.V. Terskikh, B.S. Balzhinimaev, *J. Mol. Catal. A: Chem.* 96 (1995) 175-179.
- [38] A. Chongterdtoonskul, J.W. Schwank, S. Chavadej, *J. Mol. Catal. A: Chem.* 358 (2012) 58-66.
- [39] A. Chongterdtoonskul, J.W. Schwank, S. Chavadej, *Catal. Lett.* 142 (2012) 991-1002.
- [40] A. Chongterdtoonskul, J.W. Schwank, S. Chavadej, Submitted to *Journal of Molecular Catalysis A: Chemical*.

- [41] S.M. Lima, A.M. Silva, G. Jacobs, B.H. Davis, L.V. Mattos, F.B. Noronha, *Appl. Catal.*, B 96 (2010) 387-398.
- [42] S. Rojluechai, Ph.D. Dissertation, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand, 2006.
- [43] Y. Liu, S. Shen. *Appl. Catal.*, A 121 (1995) 57-68.