



## Effect of diluent gas on ethylene epoxidation activity over various Ag-based catalysts on selective oxide supports



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### ARTICLE INFO

#### Article history:

Received 6 December 2013

Received in revised form 1 February 2014

Accepted 4 February 2014

Available online 15 February 2014

#### Keywords:

Diluent gases

CH<sub>4</sub> balanced He

SrTiO<sub>3</sub>

Cu–Ag

Ethylene epoxidation

### ABSTRACT

The influence of different diluent gases (He, Ar, N<sub>2</sub>, CH<sub>4</sub>, and CH<sub>4</sub> balanced with He) on the epoxidation of ethylene was comparatively studied over three different catalysts, including a commercial 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub>, a bimetallic 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub>, and a 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst. The best diluent gas for ethylene epoxidation was CH<sub>4</sub> balanced with He over all catalysts. CH<sub>4</sub> enhanced C<sub>2</sub>H<sub>4</sub> conversion while He provided both high EO selectivity and yield. Thus, the 35% CH<sub>4</sub> balanced with 53% He diluent gas provided the highest synergistic effect toward the ethylene epoxidation reaction, while also leading to the lowest level of coke formation.

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## 1. Introduction

Ethylene oxide (EO) is an important intermediate in the manufacture of several petrochemical products—ethylene glycol, surfactants, anti-freezes, 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-Al<sub>2</sub>O<sub>3</sub> support, based on the original work by Lefort in 1931 [4,5]. A generalized reaction stoichiometry of the process is:



Apart from EO formation, by-products including CO, CO<sub>2</sub>, and H<sub>2</sub>O are simultaneously produced [6]. EO selectivity has been improved by the use of different catalyst preparation techniques [7–15], silver precursors [16–21], and promoters [22–24].

Cesium (Cs), as an alkali metal promoter, has been researched extensively. The presence of Cs has been found to facilitate coverage of Ag on a support. Cs is mainly located in the subsurface region with only a small amount at the catalyst surface [25]. This suggests that Cs acts as a binder between the Ag and α-Al<sub>2</sub>O<sub>3</sub> support by creating and stabilizing interactions between the two phases. Grant and Lambert [26] established that Cs neutralizes acid sites on the oxide support that are responsible for isomerization of the epoxide to acetaldehyde, followed by combustion. Cs also increases the concentration of crystalline lattice defects located in the electrophilic oxygen area and decreases the amount of nucleophilic oxygen that is involved in the total oxidation of ethylene.

Campbell [27] investigated the electronic effect of adding Cs on Ag catalysts. The influence of Cs on Ag(111) was observed and surface cesium oxide species (CsO<sub>3</sub>), which existed in islands, decomposed to form gaseous Cs and O<sub>2</sub> at 610 K. Linic and Barateau [28] stated that EO was produced through the formation of an oxametallacycle intermediate (favoring the transition state). Thus, the addition of a Cs promoter, which modified the electric field or dipole–dipole interactions (electronic effect), resulted in a higher transition state, causing more EO production. Epling et al. [29] showed that there was a chemical interaction (electronic effect) between Al, Cs, and Ag, which led to change in the electronic

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

In industrial practice, chlorine-containing compounds, i.e. 1,2-dichloroethane (DCE), HCl, ethyl chloride, etc., are used as feed additives to increase EO selectivity over Ag catalysts [22,27,31]. Conversely, the added chlorinated promoters on the surface of Ag catalysts produce AgCl, which can poison the catalysts. To overcome the poisoning problem by 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 DCE addition in the ethylene epoxidation reaction. EO selectivity increased to greater than 80% but 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 reaction. Thus, ethane, at a relatively low concentration (ca. 1%), was added to the feed to moderate the deactivation (controlling the amount of chlorine adsorbed on the catalyst surface) to maximize the benefit of the DCE addition. The optimum DCE level was 1–2 ppm, which gave 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. The rhenium addition enhanced the selectivity at small loadings with a large decrease in the catalytic activity. The optimum rhenium loading for maximum EO selectivity was 25 ppm on the Ag catalyst and between 50 and 100 ppm on the bimetallic Cu–Ag catalyst. The Re-promoted Ag catalysts had more uniform distribution on the reaction sites for oxygen adsorption than the unpromoted ones, resulting in the enhancement of EO selectivity. Moreover, the Re promoter might improve the EO selectivity through the stabilization of defect regions or through weakening of the Ag–O bond.

Typical ethylene epoxidation processes are comprised of ethylene, oxygen, and diluent gas (balanced gas in the feed beyond the reactant gases, C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub>, so-called “third gas”) in the reactant feed. Many researchers have used helium [16,34,35] or nitrogen [3,36,37] as the diluent gas with various oxygen to ethylene ratios. However, no systematic study of the effect of diluent gas on ethylene epoxidation activity has been reported in 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/SrTiO<sub>3</sub> catalyst, followed by the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst. In this part (Part IV of the study), the two catalysts were employed in ethylene epoxidation experiments, and compared to the 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalyst (commercial catalyst) with various diluent gases – He, Ar, N<sub>2</sub>, CH<sub>4</sub>, and CH<sub>4</sub> balanced with He. The optimum O<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> molar ratio and the most effective diluent gas were investigated to identify the best reaction conditions for the ethylene epoxidation reaction.

## 2. Experimental

### 2.1. Materials

Silver nitrate (AgNO<sub>3</sub>) was purchased from S.R. Lab and α-Al<sub>2</sub>O<sub>3</sub> (0.109 m<sup>2</sup>/g) was purchased from Fluka. Tetraisopropyl orthotitanate (TIPT; Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>), strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>), copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), and laurylamine (LA, CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>NH<sub>2</sub>) were supplied by Merck. Acetylacetone (ACA; CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>) was obtained from S.D. Fine-Chemical. Tin chloride (SnCl<sub>2</sub>) was purchased from Aldrich. Hydrochloric acid (HCl)

and ethanol (C<sub>2</sub>H<sub>5</sub>OH) were supplied by Labscan. All chemicals used were of analytical grade and used as received without further purification.

### 2.2. Catalyst preparation

A mesoporous-assembled SrTiO<sub>3</sub> 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 HCl and then added to a Sr(NO<sub>3</sub>)<sub>2</sub> solution containing a specific amount of Sr(NO<sub>3</sub>)<sub>2</sub> and ethanol to obtain the Sr(NO<sub>3</sub>)<sub>2</sub>/LA/HCl solution. Next, this solution was poured into the TIPT/ACA solution and continuously stirred. The resultant mixture was incubated at 353 K for 4 d to obtain complete gel formation and was further dried at 353 K for 4 d. Finally, the dried gel was calcined at 923 K, which was the optimum support calcination temperature identified in our previous work [39], to produce the mesoporous-assembled nanocrystalline SrTiO<sub>3</sub> support.

The Ag catalysts used in this work were prepared by incipient wetness impregnation using the α-Al<sub>2</sub>O<sub>3</sub> and SrTiO<sub>3</sub> supports with a silver nitrate solution to obtain nominal Ag loadings of 15 wt.% (actual Ag loading = 14.86 wt.%) and 17.5 wt.% (actual Ag loading = 17.16 wt.%), respectively, which provided the best catalytic performance for EO formation [38–40]. Then, the AgNO<sub>3</sub> precursor impregnated on the α-Al<sub>2</sub>O<sub>3</sub> or SrTiO<sub>3</sub> support was dried at 383 K overnight and calcined at 773 K for 5 h to produce Ag/α-Al<sub>2</sub>O<sub>3</sub> and Ag/SrTiO<sub>3</sub> catalysts. Next, the Ag/SrTiO<sub>3</sub> catalyst was further impregnated with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O precursor to obtain a nominal Cu loading of 1.5 wt.%. 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.

The bimetallic Cu–Ag catalyst was promoted by tin using tin chloride precursor with an 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 on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst [41].

### 2.3. Activity testing experiments

The catalytic performance of the ethylene epoxidation reaction on the 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub>, 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub>, or 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst was tested in a packed-bed 8-mm ID tubular reactor under 24.7 psia at 548 K [40] with various diluent gas systems. Initially, 30 mg of catalyst powder was packed in the reactor and 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, N<sub>2</sub>, CH<sub>4</sub> or CH<sub>4</sub> balanced with He). The 6% ethylene and 3–7.5% oxygen feed gases, with different diluent gas balances (He, Ar, N<sub>2</sub>, CH<sub>4</sub> or CH<sub>4</sub> balanced with He), were regulated by using mass flow controllers. The space velocity of the feed gas through the reactor was maintained at 6000 h<sup>-1</sup> for all experimental runs. The composition of the feed and effluent gases was analyzed by using an on-line gas chromatograph (Perkin Elmer, ARNEL) equipped with a 60/80 CAR-BOXEN 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. Trace amounts of acetaldehyde were formed, but were below the detection limit of the analytical system [42]. The catalytic activity of each 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 catalysts, with different optimum diluent gases, were operated for 72 h on stream to investigate long-term

stability and performance. Finally, the best catalyst (0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub>) was operated up to 7 d (168 h) to observe the long-term stability and performance of the ethylene epoxidation reaction.

#### 2.4. Catalyst characterization

The N<sub>2</sub> adsorption–desorption isotherms of the catalysts were obtained by using a surface area analyzer (Quantachrome, SAA-1MP). 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, SpectraAA-300).

The oxygen and ethylene uptake of the synthesized catalysts was calculated from the desorption peaks that were obtained by using a temperature-programmed desorption (TPD) analyzer (Quantachrome, Chembet 3000). Oxygen (4.99% O<sub>2</sub> in He) or pure ethylene (99.99% C<sub>2</sub>H<sub>4</sub>) was initially adsorbed onto the catalyst surface at 473 K for 2 h for the TPD experiments. The catalyst samples were then cooled to room temperature in a high-purity He stream. Next, 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 cm<sup>3</sup>/min. A thermal conductivity detector (TCD) was used to measure the concentration profile of the oxygen or ethylene in the effluent gas.

The surface morphology of the studied catalysts before and after the reaction experiments, under optimum diluent gas system, was characterized using a field emission scanning electron microscope (FE-SEM; JEOL 5200-2AE). Prior to analysis, the samples were coated with Pt to improve conductivity. Furthermore, the particle size of loaded metals on the catalyst samples was 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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or SrTiO<sub>3</sub> support was verified by using an energy dispersive X-ray spectroscope (EDS) attached to the TEM. The metal particle size was determined from measurements of multiple particles, followed by statistical analysis of the TEM images.

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

### 3. Results and discussion

#### 3.1. Catalyst characterization results

The XRD and XPS results of the 14.86 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> commercial catalyst were reported in Part I of the series [38]. The XRD pattern revealed a highly crystalline structure of the SrTiO<sub>3</sub> support with dominant peaks of metallic Ag and a minor peak of AgO. For the XPS results of the 14.86 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst, the atomic ratio of Ag-to-Ag<sub>2</sub>O of 92.02%/7.98% before the reaction was changed to 82.07%/17.93% after the reaction. The XRD and XPS results of the other two catalysts (1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> and 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub>) were also reported in Part III of this series [40]. The XRD patterns also clearly showed the highly crystalline structure of the SrTiO<sub>3</sub> support with dominant peaks of metallic Ag and a minor peak of AgO. The Cu second metal was also detected by XRD in metallic form while the Sn promoter was not detected due to an insignificant amount of Sn. The XPS results for the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst showed that the metallic

Ag-to-Ag<sub>2</sub>O molar ratio changed from 11.5:1 before the reaction to 5.4:1 after the reaction while the metallic Cu-to-CuO molar ratio decreased from 14.9:1 before the reaction to 2.8:1 after the reaction. For the 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst, the metallic Ag-to-Ag<sub>2</sub>O molar ratio decreased from 14.4:1 before the reaction to 11.2:1 after the reaction, whereas the metallic Cu-to-CuO molar ratio was changed from 15.7:1 before the reaction to 10.6:1 after the reaction. It can be concluded that an addition of the Cu second metal and/or Sn promoter can provide higher metallic forms of both Ag and Cu, which, in turn, enhance the ethylene epoxidation reaction in terms of high selectivity and long-term stability [40].

#### 3.1.1. Specific surface area results

The characterization results of all catalysts (14.86 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> and 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalysts), including specific surface area, metal particle size, O<sub>2</sub> uptake and C<sub>2</sub>H<sub>4</sub> uptake are summarized in Table 1. All catalysts had extremely low specific surface area, with the 14.86 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst possessing the lowest specific surface area. The tin promoter slightly decreased the specific surface area of the bimetallic Cu–Ag catalyst.

#### 3.1.2. TPD results

Table 1 also summarizes the adsorption capabilities of oxygen, ethylene, and methane on the catalyst surfaces, in terms of O<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> uptake. The main oxygen and ethylene desorption peaks in the 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 the O<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> uptake were found on the 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst, followed by the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst. However, the 14.86 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst only adsorbed an insignificant amount of oxygen, while there was no measurable ethylene adsorption. Among the investigated catalysts, the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst had the highest methane uptake while the lowest amount of the methane uptake was found on the 14.86 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The results indicate that the strong interaction between Ag–Cu and the SrTiO<sub>3</sub> support greatly enhanced both ethylene and oxygen uptake as compared to the weak interaction between Ag and the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. The addition of a small amount of Sn promoter significantly increased both the ethylene and oxygen uptake.

#### 3.1.3. Surface morphology

The TEM/EDS technique was applied to verify the existence of metal nanoparticles in the catalysts. The average catalyst particle sizes are summarized in Table 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/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst (44 nm). Moreover, the Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst possessed a slightly larger Cu particle size (5.5 nm) than the unpromoted catalyst (4.7 nm). For the 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst operated at optimum conditions with 6% O<sub>2</sub>, 6% C<sub>2</sub>H<sub>4</sub> and 35% CH<sub>4</sub> balanced with 53% He diluent gas, the average Ag particle size increased from 58 nm for the fresh catalyst to 60 nm for the post-reaction catalyst, while the average Cu particle size increased from 5.5 to 5.8 nm, and the average Sn particle size increased from 2.8 to 2.9 nm, respectively. Moreover, for the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst, the average Ag particle size increased from 58 nm for the fresh catalyst to 61 nm for the post-reaction catalyst, while the average Cu particle size increased from 4.7 to 5.8 nm after operating under optimum conditions (6% O<sub>2</sub>, 6% C<sub>2</sub>H<sub>4</sub> with 30% CH<sub>4</sub>

**Table 1**

Characteristics of 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub>, 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub>, and 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalysts at their own optimum metal loadings (corresponding to the highest ethylene epoxidation activity).

Characteristic	14.86 wt.% Ag/α-Al <sub>2</sub> O <sub>3</sub>	1.41 wt.% Cu–17.16 wt.% Ag/SrTiO <sub>3</sub> <sup>*</sup>	0.32 wt.% Sn–1.39 wt.% Cu–17.16 wt.% Ag/SrTiO <sub>3</sub> <sup>*</sup>
Specific surface area (m <sup>2</sup> /g)	0.03	1.1	0.8
Ag particle size <sup>a</sup> (nm)	43.6 ± 0.4	58 ± 0.5	58 ± 0.5
2nd metal particle size <sup>a</sup> (nm)	–	4.7 ± 0.4 (Cu)	2.8 ± 0.3 (Sn <sup>**</sup> ), 5.5 ± 0.4 (Cu)
O <sub>2</sub> uptake <sup>b</sup> (μmol g <sup>-1</sup> )	6	6935	7429
C <sub>2</sub> H <sub>4</sub> uptake <sup>c</sup> (μmol g <sup>-1</sup> )	0	5767	6065
CH <sub>4</sub> uptake <sup>d</sup> (μmol g <sup>-1</sup> )	259	486	403

<sup>a</sup> From TEM analysis.

<sup>b</sup> Based on 400–700 K.

<sup>c</sup> Based on 400–700 K.

<sup>d</sup> Based on 325–600 K.

\* 17.16 wt.% Ag loading (actual).

\*\* Sn-promoted on Cu–Ag bimetallic catalyst.

balanced with 58% He diluent gas, 24.7 psia, and 548 K). On the other hand, for the 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalyst, the average Ag particle size increased from 44 nm for the fresh catalyst to 49 nm for the post-reaction catalyst after operating at optimum conditions with 25% CH<sub>4</sub> balanced with 63% He diluent gas. The small increases in the metal particle size of all catalysts after reaction reveal that sintering or particle agglomeration was not of major concern.

The surface morphology of the best catalyst (0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst) under various diluent gas systems after the reaction, as compared to the fresh catalyst, are illustrated in Fig. 1. There were no significant changes in surface topologies after the reaction for all diluent gas systems except for the system with 35% CH<sub>4</sub> balanced with 53% He, where a larger Ag particle size with a rounder shape was observed. Fig. 2 compares the surface morphologies of the catalysts that had been operated under optimum conditions with CH<sub>4</sub> balanced with He as diluent gases before and after the reaction. The only catalyst that showed any significant change in surface morphology was the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst, where surface agglomeration was observed after the reaction, resulting in a smoother appearance with fewer attached particles (Fig. 2c and d).

### 3.1.4. Coke formation

Table 2 summarizes the amount of coke formation on the different post-reaction catalysts after carrying out the ethylene epoxidation reaction for 6 and 72 h, respectively, with various diluent gas systems. The highest amount of coke formation was found on the 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalyst (6.4% at 6 h and 17.6% at 72 h) with CH<sub>4</sub> as the diluent gas. The 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst possessed the lowest amount of coke formation of 1.7% at 6 h (with He as the diluent gas) and 2.7% at 72 h (with 35% CH<sub>4</sub> balanced with 53% He as the diluent gas), followed by the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst (2.4% at 6 h and 4.0% at 72 h) with He as the diluent gas. The results show that the addition of tin leads to a decrease in coke formation. For any given catalyst, operation with diluent gas containing CH<sub>4</sub> balanced with He generally provided the lowest coke formation.

### 3.2. Ethylene epoxidation activity

The effects of various oxide supports (α-Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> C, Al<sub>2</sub>O<sub>3</sub>Acid, SiO<sub>2</sub> 90, TiO<sub>2</sub>, SrTiO<sub>3</sub>, MgTiO<sub>3</sub>, CaTiO<sub>3</sub>, and BaTiO<sub>3</sub>) and several loaded metals (Ag, Au, Au–Ag, Cu–Ag, Ba–Ag, Pd–Ag, and Sn–Ag) on the best support (SrTiO<sub>3</sub>) 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/SrTiO<sub>3</sub> catalyst provided the highest catalytic performance in terms of EO

yield, at 5.2%, and enhanced EO selectivity to 95.1%, and the best long-term stability at 72 h on stream. Furthermore, the second best catalyst was the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst. Therefore, in this present work the two catalysts were studied as a comparison to the commercial 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalyst. The effect of various diluent gases (Ar, N<sub>2</sub>, CH<sub>4</sub>, and CH<sub>4</sub> balanced with He) on ethylene epoxidation was compared to the effect of the He diluent gas that was used in the previous work [38–40].

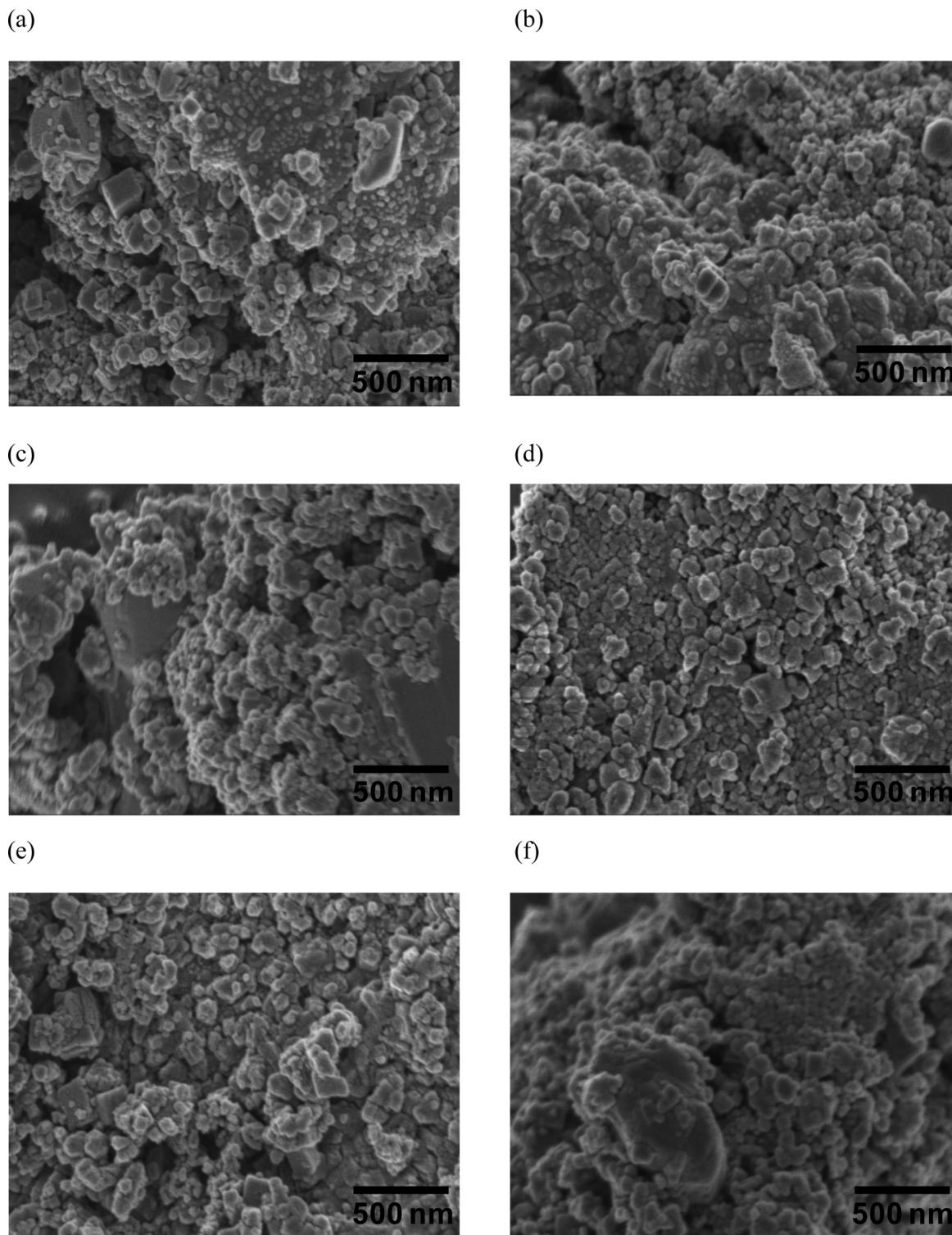
Fig. 3 shows the ethylene epoxidation activity of the catalysts as a function of O<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> molar ratio at various diluent gases (He, Ar, N<sub>2</sub>, and CH<sub>4</sub>) at 6 h on stream. The optimum O<sub>2</sub>-to-C<sub>2</sub>H<sub>4</sub> molar ratio of 1:1 (6% O<sub>2</sub> and 6% C<sub>2</sub>H<sub>4</sub>) provided the highest EO selectivity and/or yield for all diluent gases, except for N<sub>2</sub> with an optimum ratio of 0.75:1 (4.5% O<sub>2</sub> and 6% C<sub>2</sub>H<sub>4</sub>). The He diluent system had the highest EO selectivity in all investigated catalysts and the maximum EO yield in some cases. However, the CH<sub>4</sub> diluent system provided the highest EO yield for the 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> and the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalysts at 6 h of operation. Hence, the CH<sub>4</sub> gas was mixed with He gas to investigate the synergistic effect of the two diluent gases at different percentages of CH<sub>4</sub> to obtain the optimum CH<sub>4</sub> balance with He for the three catalysts. The ethylene epoxidation activity of the catalysts at 6 and 72 h on stream under different diluent gases is summarized in Table 3. The addition of CH<sub>4</sub> gas with a proper fraction balanced

**Table 2**

Coke formation on spent catalysts after 6 and 72 h on stream of the ethylene epoxidation reaction (a space velocity of 6000 h<sup>-1</sup>, a pressure of 24.7 psia, and a reaction temperature of 548 K).

Catalyst	Diluent gas	Coke formation at 6 h (wt.%)	Coke formation at 72 h (wt.%)
14.86 wt.% Ag/α-Al <sub>2</sub> O <sub>3</sub>	88% He	4.3	11.7
	88% Ar	5.1	12.2
	89.5% N <sub>2</sub>	5.8	13.8
	88% CH <sub>4</sub>	6.4	17.6
	25% CH <sub>4</sub> + 63% He	4.9	12.3
1.41 wt.% Cu–17.16 wt.% Ag/SrTiO <sub>3</sub>	88% He	2.4	4.0
	88% Ar	3.0	4.9
	89.5% N <sub>2</sub>	2.9	5.4
	88% CH <sub>4</sub>	4.8	7.7
	30% CH <sub>4</sub> + 58% He	2.6	4.5
0.32 wt.% Sn–1.39 wt.% Cu–17.16 wt.% Ag/SrTiO <sub>3</sub>	88% He	1.7	2.9
	88% Ar	2.5	3.8
	89.5% N <sub>2</sub>	2.7	4.6
	88% CH <sub>4</sub>	3.9	7.1
	35% CH <sub>4</sub> + 53% He	2.2	2.7

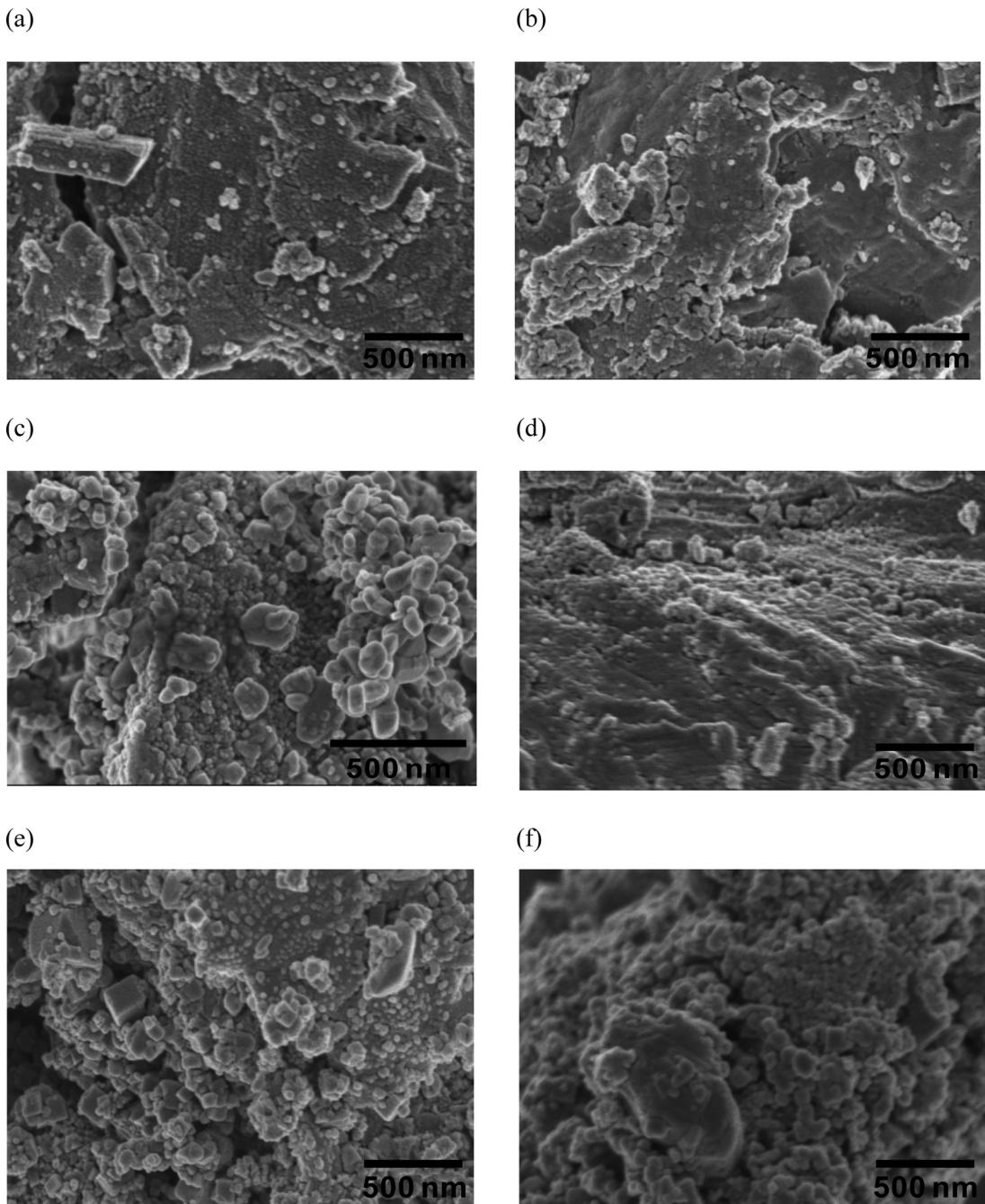
Note: The optimum concentrations of 6% O<sub>2</sub> and 6% C<sub>2</sub>H<sub>4</sub> were found for all systems, except for the N<sub>2</sub> diluent gas system which its optimum concentrations of O<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> were 4.5% and 6%, respectively.



**Fig. 1.** SEM images of 0.32 wt.% Sn-promoted on 1.39 wt.% Cu-17.16 wt.% Ag/SrTiO<sub>3</sub> catalysts after the reaction at various diluent gas systems (a) fresh catalyst, (b) He, (c) Ar, (d) N<sub>2</sub>, (e) CH<sub>4</sub>, and (f) 35% CH<sub>4</sub> balanced with 53% He (50,000×).

with He improved ethylene conversion (the data not shown here) with high EO selectivity and yield at 6 h on stream for all catalysts. The ethylene conversion increased from 3.6% for He diluent gas to 3.8% for 25% CH<sub>4</sub> balanced with He (14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalyst), 5.8% for He diluent gas to 6.0% for the 30% CH<sub>4</sub> balanced with He (1.41 wt.% Cu-Ag/SrTiO<sub>3</sub> catalyst), and 5.5% for He diluent gas to 5.6% for the 35% CH<sub>4</sub> balanced with He (0.32 wt.% Sn-promoted on Cu-Ag/SrTiO<sub>3</sub> catalyst). For any given catalyst, EO selectivity

dropped substantially after 72 h of operation. Among all the investigated diluent gases, the most effective diluent gas was the CH<sub>4</sub> balanced with He, providing maximum EO selectivity and superior long-term stability at 72 h. Moreover, the 0.32 wt.% Sn-promoted on Cu-Ag/SrTiO<sub>3</sub> and the 1.41 wt.% Cu-Ag/SrTiO<sub>3</sub> catalysts showed much better catalytic performance than the 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalyst. It should be noted that for any given catalyst, the CH<sub>4</sub> conversion was higher in the CH<sub>4</sub> diluent system than that of the

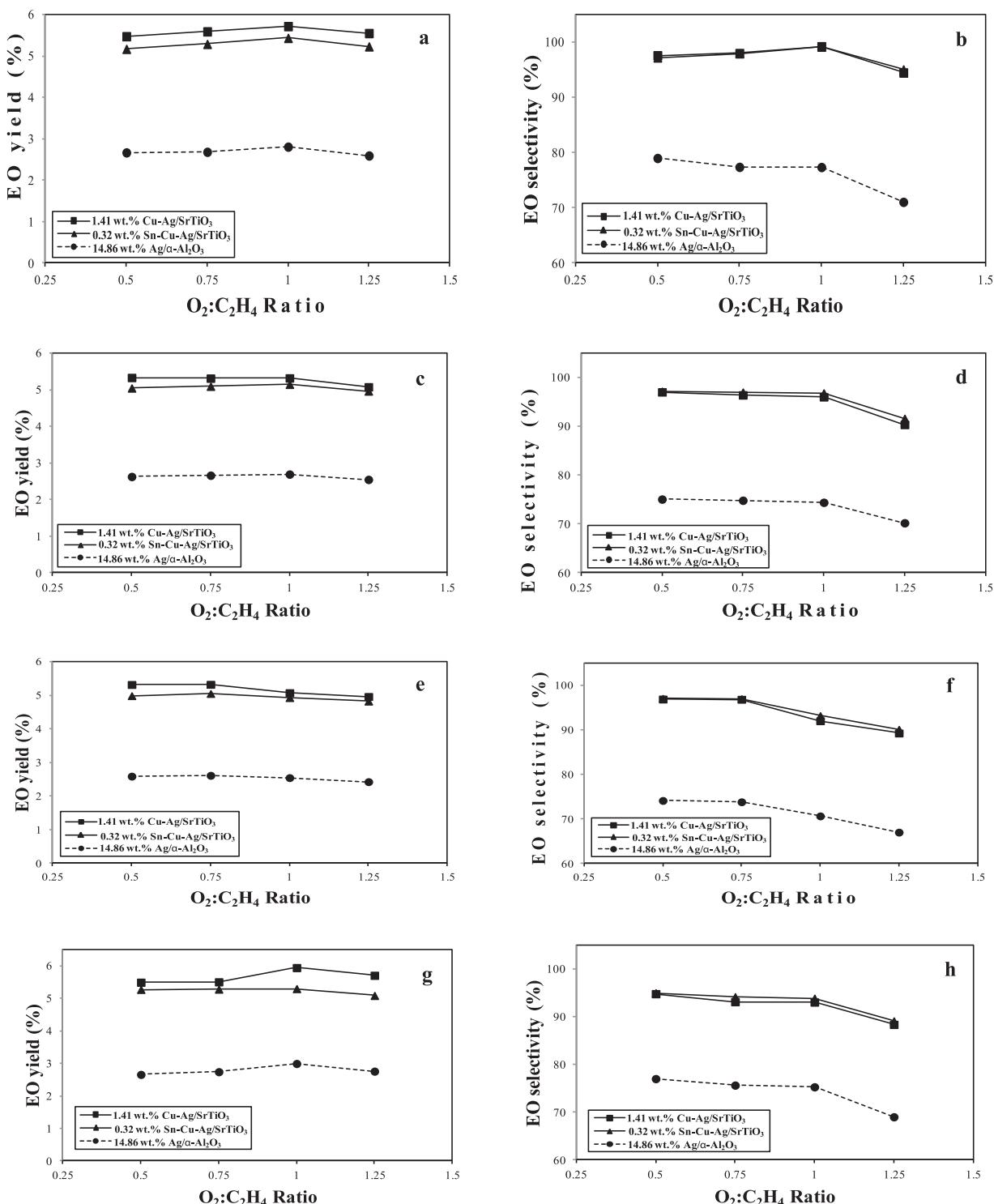


**Fig. 2.** SEM images of 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalysts (a) before the reaction and (b) after the reaction in 25% CH<sub>4</sub> balanced with 63% He (the diluent gas system); (c) 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalysts before the reaction and (d) after the reaction in 30% CH<sub>4</sub> balanced with 58% He; (e) 0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalysts before the reaction and (f) after the reaction in 35% CH<sub>4</sub> balanced with 53% He (50,000×) (reaction conditions: 6% O<sub>2</sub>, 6% C<sub>2</sub>H<sub>4</sub>, a space velocity of 6000 h<sup>-1</sup>, 24.7 psia, and 548 K).

CH<sub>4</sub> balanced with He system. Moreover, the conversion of CH<sub>4</sub> was always low for all cases. The results can be used to correlate the higher amount of coke formation in the CH<sub>4</sub> diluent system as compared to the CH<sub>4</sub> balanced with He system (Table 2). CH<sub>4</sub> may help to increase the ethylene conversion, improve the activity of the catalysts as well as suppress CO<sub>2</sub> formation [43] while He simultaneously maintains high EO selectivity, resulting in synergistic effects for EO formation. When CH<sub>4</sub> was completely replaced by ethylene in the feed, the product was found to contain mainly CO<sub>2</sub> (the data not shown here). This result illustrates that the CH<sub>4</sub> addition can enhance the catalytic activity of the ethylene

epoxidation reaction only when a proper amount of CH<sub>4</sub> is added to the He diluent gas.

The best diluent gas (CH<sub>4</sub> balanced with He) was next applied in the long-term stability experiments of the catalysts, with the results shown in Fig. 4. The catalytic activity of all catalysts declined with time and reached a steady state at ~50 h on stream. The 0.32 wt.% Sn-promoted on Cu–Ag/SrTiO<sub>3</sub> was found to be the most effective catalyst, in 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 second best catalyst was the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst where the EO selectivity decreased to 91% and EO yield to



**Fig. 3.** EO yield and EO selectivity as a function of O<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> molar 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 N<sub>2</sub>, (g) and (h) in CH<sub>4</sub> (a fixed C<sub>2</sub>H<sub>4</sub> concentration of 6%, a space velocity of 6000 h<sup>-1</sup>, a pressure of 24.7 psia, and a reaction temperature of 548 K).

5% after 72 h of operation. On the other hand, the 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the worst long-term stability, providing an EO selectivity of only 40% and EO yield of 1.3% after 72 h on stream. The reason for the decline in catalytic activity of all catalysts was mainly due to coke formation (see Table 2).

An ethylene epoxidation experiment to determine the best catalyst (0.32 wt.% Sn-promoted on 1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub>) was conducted for 7 days (168 h) to confirm the superior

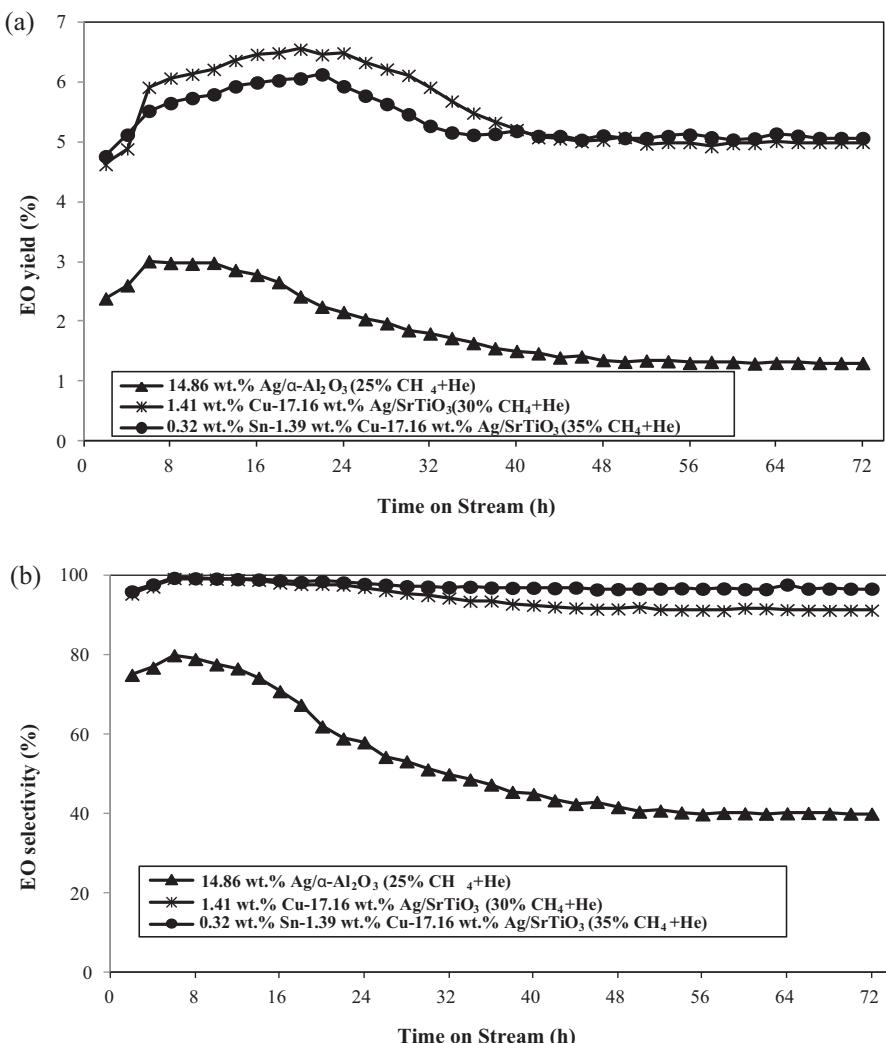
long-term stability of this catalyst (Fig. 5). The EO selectivity remained almost stable after 72 h on stream and slightly dropped from 97% at 72 h to 96% at 168 h. The EO yield also depicted the same trend, decreasing from 5.1% at 72 h to 4.9% at 168 h. The good catalytic activity of this catalyst can be related to the relatively high oxygen and ethylene adsorption capabilities and the tin promoter, which prolongs stability of the ethylene epoxidation reaction [40].

**Table 3**

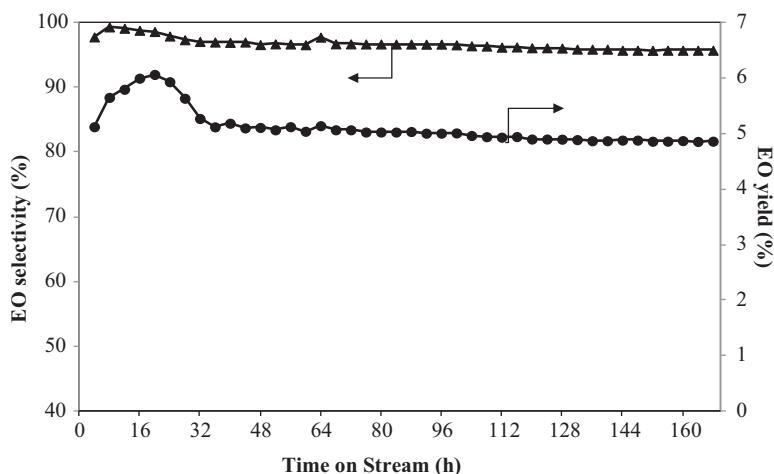
Ethylene epoxidation activity of studied catalysts at 6 and 72 h on stream (a space velocity of  $6000\text{ h}^{-1}$ , a pressure of 24.7 psia, reaction temperature of 548 K).

Catalysts	Diluent gas	6 h of time on stream		72 h of time on stream		
		EO selectivity (%)	EO yield (%)	EO selectivity (%)	EO yield (%)	CH <sub>4</sub> conversion (%)
14.86 wt.% Ag/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	88% He	77.4	2.8	43.4	1.3	–
	88% Ar	74.4	2.7	41.0	1.2	–
	89.5% N <sub>2</sub>	73.9	2.6	37.2	1.1	–
	88% CH <sub>4</sub>	75.3	3.0	28.4	0.9	3.0
	25% CH <sub>4</sub> + 63% He	80.0	3.0	40.0	1.3	2.4
1.41 wt.% Cu-17.16 wt.% Ag/SrTiO <sub>3</sub>	88% He	99.3	5.7	90.0	4.5	–
	88% Ar	96.1	5.3	86.6	4.2	–
	89.5% N <sub>2</sub>	96.9	5.3	83.5	4.0	–
	88% CH <sub>4</sub>	93.1	6.0	76.9	4.1	2.2
	30% CH <sub>4</sub> + 58% He	99.3	5.9	91.3	5.0	1.7
0.32 wt.% Sn-1.39 wt.% Cu-17.16 wt.% Ag/SrTiO <sub>3</sub>	88% He	99.2	5.4	95.1	5.2	–
	88% Ar	96.8	5.2	91.8	4.8	–
	89.5% N <sub>2</sub>	97.0	5.1	89.4	4.5	–
	88% CH <sub>4</sub>	93.9	5.3	79.8	4.0	2.6
	35% CH <sub>4</sub> + 53% He	99.5	5.5	96.7	5.1	2.2

Note: The optimum concentrations of 6% O<sub>2</sub> and 6% C<sub>2</sub>H<sub>4</sub> were found for all systems, except for the N<sub>2</sub> diluent gas system with optimum concentrations of O<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> at 4.5% and 6%, respectively.



**Fig. 4.** (a) EO yield and (b) EO selectivity as a function of time on stream for the studied catalysts at their optimum % CH<sub>4</sub> balanced with He as the diluent gas systems (6% O<sub>2</sub> and 6% C<sub>2</sub>H<sub>4</sub>, a space velocity of  $6000\text{ h}^{-1}$ , a pressure of 24.7 psia, a reaction temperature of 548 K).



**Fig. 5.** EO selectivity and EO yield as a function of time on stream for 0.32 wt.% Sn–1.39 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst (6% O<sub>2</sub> and 6% C<sub>2</sub>H<sub>4</sub> balanced with 35% CH<sub>4</sub> + He, a space velocity of 6000 h<sup>-1</sup>, a pressure of 24.7 psia, a temperature of 548 K).

#### 4. 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/SrTiO<sub>3</sub>) in comparison to the 1.41 wt.% Cu–17.16 wt.% Ag/SrTiO<sub>3</sub> catalyst and a 14.86 wt.% Ag/α-Al<sub>2</sub>O<sub>3</sub> commercial catalyst. The type of diluent gas affected ethylene epoxidation in the following order: He > N<sub>2</sub> ~ Ar > CH<sub>4</sub>, which corresponded to coke formation. Interestingly, the addition of CH<sub>4</sub> in the He diluent gas, at a proper fraction, enhanced the ethylene epoxidation performance for all studied catalysts, especially for long-term activity.

#### Acknowledgments

This work was supported by the Royal Golden Jubilee Ph.D. Program (RGJ-Industry) awarded by The Thailand Research Fund with the in-kind support from PTT Global Chemical Public Co., Ltd.; the Sustainable Petroleum and Petrochemicals Research Unit, Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University (Thailand); the postdoctoral research fellowship under the Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University (Thailand); and the Transportation Energy Center, Department of Chemical Engineering, University of Michigan (USA).

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