



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

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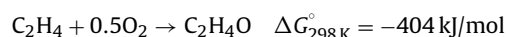
### ABSTRACT

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 Barteau [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/ $\alpha$ -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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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/ $\alpha$ -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/ $\alpha$ -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 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. 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

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