CHAPTER I
INTRODUCTION

1.1 State of Problems

The epoxidation of ethylene to ethylene oxide (EO) over Ag catalysts is an important industrial process since EO is one of the highest volume petrochemicals, accounting for approximately 40-50 % of the total value of organic chemicals with 86 % of the global capacity utilization (Jankowiak and Barteau, 2005). It is mainly used to produce ethylene glycol (EG), surface-active agents, lubricants, anti-freezer, plasticizers, adhesives, explosives, and solvents (Hassani *et al.*, 2009).

Ethylene oxide, first produced by the reaction of ethylene chlorohydrin and potassium hydroxide in 1859 by Lefort, has been produced commercially via gas-phase ethylene epoxidation since ca. 1931 (Ozero *et al.*, 1984; Dever *et al.*, 1994). The most widely used process for ethylene oxide manufacture is the direct catalytic oxidation of ethylene with air or oxygen over supported silver catalysts (Ertl *et al.*, 1997). Ag-based catalysts on a low surface area α-Al_2O_3 support (surface area < 1 m^2/g) with high silver loadings are widely used because they provide highly selective ethylene epoxidation, as well as their inertness for the isomerization of ethylene oxide to acetaldehyde (Yong *et al.*, 1991). However, these catalysts possess relatively low yields of ethylene oxide as a result of poorly dispersed silver over this commercial alumina support (Matar *et al.*, 1989). Most industrial processes use this catalyst for the ethylene epoxidation reaction, obtaining EO yield of 2-3 % and EO selectivity of 77 %. Therefore, there is a motivation to develop new catalyst compositions with alternative supports to offer higher catalytic performance of ethylene epoxidation.

One of the most interesting developments for catalysis is the modification of the surface structure and electronic properties of nano-particles in which directly affects the activity and selectivity of nano-systems in heterogeneous catalysis (Korchagin *et al.*, 2005). Moreover, alkali metals (i.e. Cs and Na), as well as organohalides which used as feed additives (i.e. Cl) (Minahan and Hoflund, 1996; Yeung *et al.*, 1998), have been added as promoters to improve the catalyst performance and the selectivity of the reaction process.

Furthermore, a number of researchers have extensively investigated new preparation methods, i.e. deposition-precipitation, atomic layer deposition, etc., to improve the performance of catalysts for individual reactions (Eldridge *et al.*, 2009; Wolf and Schuth, 2002). The sol-gel process has recently emerged as an effective technique for the synthesis of noble metal-dielectric nanocomposites with enhanced nonlinear optical properties. The advantages of the sol-gel process are high homogeneity of the starting solutions in the molecular scale, low processing temperatures, and the possibility of incorporating many different metal dopants into different matrixes, leading to a variety of synthesized materials for various applications (Epifani *et al.*, 2000). As a result of that, this promising catalyst preparation method has been used to develop new mesoporous supports with uniform porous structures to improve the activity towards specific reactions (Sreethawong *et al.*, 2005; Puangpetch *et al.*, 2010).

Several attempts have been made in order to improve the catalytic properties of catalysts by adding several second metals i.e. Au, Cu, etc. onto Ag metal, known as "bimetallic catalysts". In many cases, these catalysts enhance the specific physical and chemical properties due to the synergistic effects, leading to more attention on the application for ethylene oxide production (Dellamorte *et al.*, 2011; Torres *et al.*, 2006). Further development of new catalysts under proper reaction conditions i.e. oxygen-to-ethylene ratio, diluent gas composition, etc. is still needed to investigate for the catalytic activity improvement in terms of EO selectivity, EO yield, as well as prolonging the stability of the catalysts for the ethylene epoxidation reaction. In this study, a new bimetallic catalyst with Sn promoter on $SrTiO_3$ operated under CH_4 balanced with He was used, for the first time, to develop the best process for ethylene oxide production.

1.2 Objectives

The main objectives of this study were to find better supports than the traditional support (low-surface-area α-Al_2O_3), to identify the effect of second metal addition, to assess the effect of diluent gas, and to assess the operational parameters, affecting the process performance for the epoxidation of ethylene. The overall objectives of this work were as follows:

1. To explore the effects of oxide supports, including mesoporous-assembled perovskite titanate supports, for Ag catalysts on EO selectivity and yield, as compared to a commertial catalyst (Ag catalyst on low-surface-area Al_2O_3),
2. To modify the optimum Ag catalysts with various second metals to improve the catalytic performance and to find the most effective catalyst for the epoxidation of ethylene,
3. To study the effects of operational parameters on the efficiency of ethylene oxide formation, and
4. To find the best diluent gas for ethylene epoxidation reaction.

1.3 Scope of Work

In this study, a packed-bed tubular reactor with the application of Ag catalysts and bimetallic catalysts was used to produce ethylene oxide via a gas phase ethylene epoxidation reaction. The Ag catalyst supported on α-Al_2O_3 was used as a benchmark catalyst for catalytic activity in comparisons with other catalysts on various oxide supports. The catalytic activity was measured in terms of EO selectivity, EO yield, and ethylene conversion. The catalytic performance was correlated with the physical properties of the prepared catalysts, including specific surface area, crystallinity, Ag particle size, surface morphology, oxidation state, oxygen and ethylene adsorption characteristics, and coke formation. The catalytic activity towards the epoxidation of ethylene was investigated by varying operational parameters: support type, metal loading, reaction temperature, O_2 to C_2H_4 feed ratio, and diluent gas.

The TiO_2, $MgTiO_3$, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ supports were used to determine the influence of mesoporous-assembled titanate supports on the ethylene epoxidation. The effect of the second metal addition (Au, Cu, Ba, Pd, and Sn) on Ag metal was studied to investigate the improvement of the catalytic properties. The most appropriate catalyst which enhanced EO selectivity, EO yield, and long-term stability for epoxidation of ethylene was investigated. Moreover, the addition of Sn promoter was also investigated its effect on the epoxidation reaction. Finally, the optimum diluent gas for the ethylene epoxidation was also determined.