

CHAPTER I

INTRODUCTION

1.1 Statement of Problem

The selective oxidation of ethylene depends on the choice of the catalytic system and the reaction conditions. Silver-based catalysts are commonly employed for the production of ethylene oxide since they give both adequate activity and selectivity. The unique epoxidation activity of silver has been attributed to its ability to adsorb oxygen not only on its surface but also to incorporate oxygen into the subsurface of silver. This subsurface oxygen in silver, which has low bond strength, is believed to be a key factor in imparting the high selectivity for epoxidation of ethylene. It has also been known that a significant subsurface oxygen concentration in silver with low bond strength (13 kJ/mole) can only be achieved when the silver surface has an oxygen coverage of more than 50 %. At lower oxygen surface coverage, the oxygen bond strength increases to 63 kJ/mole and the catalyst loses its high epoxidation selectivity.

Unfortunately, at typical operational conditions of the industrial ethylene epoxidation process (~550 K), oxygen surface coverage of silver becomes small. This low oxygen surface coverage limits the selectivity of epoxide formation. One strategy to increase the oxygen surface coverage is to lower the operational temperature but then the catalytic activity becomes too low for a practical process. In practice, a small amount of halogenated hydrocarbons such as vinyl chloride or 1, 2 dichloroethane is added to the gas stream as a moderator to inhibit CO₂ formation, thereby increasing the selectivity at a slight sacrifice of conversion.

1.2 Purpose of Research

Silver catalysts are known as highly selective catalysts for ethylene epoxidation. Small amounts of promoters and modifiers can improve the activity of ethylene and the selectivity towards ethylene oxide. The promoters and modifiers, such as alkali earth metal, and chloride, appears to exert a synergistic effect (Karavasilis *et al.*, 1996). The presence of a small amount of metal promoter acts to stabilize silver against sintering (Matar *et al.*, 1989). The role of modifiers can be explained in terms of electronic interactions between the silver crystallite and the support. It has been known that the presence of atomic oxygen favors complete oxidation while molecular oxygen enhances ethylene oxide formation. Chlorine containing modifiers are believed to not only change the relative concentrations of atomic and molecular oxygen, but also to increase the probability of molecular oxygen to give ethylene oxide (Matar *et al.*, 1989). In addition, on pure metallic Au, molecular oxygen does not adsorb. Atomic oxygen, on the other hand, will adsorb. On supported Au, especially when Au is present in a state of high dispersion, oxygen will adsorb at temperature of about 200°C, and very high activity for oxygen transfer has been adsorbed even at room temperature, for example in the oxidation of CO of CO₂. Given these unusual oxygen transfer properties of gold, it appears interesting to explore how adding small amount of gold to silver would change its activity and selectivity for epoxidation of ethylene.

1.3 Objectives

In this research, the objectives were as follows:

1. to conduct a fundamental study of the effect of gold addition to silver on the activity and selectivity of the ethylene oxidation reaction;
2. to investigate the effect of different support materials (high surface area, non porous alumina, titania and ceria) on the selectivity of Ag in ethylene oxidation;
3. to study the activity of gold on titania and ceria