

## **CHAPTER I**

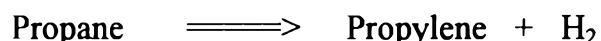
### **INTRODUCTION**

In the past, lower olefins were obtained as by-products of refinery and petrochemical industries. However, olefins prices in international markets have increased due to a substantially increasing demand for olefins. The rapid growth of demand for lower olefins is also generating alternative routes not based on by-products of petrochemical or refinery processes. This provides the opportunity for catalytic dehydrogenation processes as a commercial application. Moreover, the raw materials, lower alkanes, of these processes are relatively cheap and plentiful. Because lower alkanes, which are available globally, can be separated at the source from natural gas and crude oil, and their production cost is rather low and little more than the cost of separation. These make the dehydrogenation process economically attractive.

Nowadays, the market for propylene is rapidly rising because of the high value of its derivatives such as polypropylene, which has the highest growth rate among all polymers. Other important uses of propylene include the production of acrylonitrile, oxo-alcohols and propylene oxide. This has resulted in the development of propane dehydrogenation processes in countries with limited access to traditional source of propylene as a by-product (Resasco et al., 1994).

The propane dehydrogenation reaction is thermodynamically limited by its equilibrium. And it is an endothermic reaction which means that the added heat is needed to overcome the heat absorbed by the reaction. However, the unwanted reactions such as hydrogenolysis and cracking can be promoted under the severe condition (Le Page, 1987). From a thermodynamic

point of view, the dehydrogenation reaction is favored at high temperatures and low pressures. The low pressures are much more significant because this reaction proceeds with an increase in a number of moles,



In addition, the activity of the catalyst can be maintained if the feed contains one of the products, either hydrogen or propylene. But this leads to a decrease in equilibrium conversion limit. For each particular catalyst, a H<sub>2</sub>/hydrocarbon ratio must be determined for which it indicates a compromise between activity maintenance and equilibrium conversion. The thermodynamics indicates that propane dehydrogenation must be carried out under conditions that are severely deactivating for many catalysts. The conditions of high temperatures, low pressures and low H<sub>2</sub>/hydrocarbon ratios that are necessary to obtain attractive conversions impose a technological challenge for catalyst development.

Usually, the catalyst consists of the active agent and a support. The high surface area of the support helps to increase the available sites of active agent for contacting with the reactants. Alumina is the most widely used support because it is inexpensive, structurally stable and because it can be prepared with a wide variety of pore sizes and pore size distributions. The most important aluminas for use as carriers are the transition aluminas (Satterfield, 1991).  $\gamma\text{-Al}_2\text{O}_3$  is of the greatest interest since it has a high surface area and is relatively stable over the temperature range of interest for most catalytic reactions.

Platinum has been the principal active agent in most dehydrogenation catalysts due to its high activity for C-H bonds rupture coupled with its poor ability to cleavage C-C bonds. However, the selectivity and stability of Pt catalysts can be apparently improved by the addition of a

second metal which is called a promoter. The bimetallic Pt-Sn supported on  $\text{Al}_2\text{O}_3$  has been much studied because of the effect of tin as a promoter. Tin can modify the catalytic behavior through ensemble and/or ligand effects (Cortright and Dumesic, 1994). The ensemble and ligand effects can be explained by the reduction of groups of surface Pt sites in the presence of Sn via these effects. It is known that the unwanted cracking reactions require larger groups of platinum sites than the dehydrogenation reactions. Therefore, the promotion by tin can increase the selectivity and effective lifetime of catalysts.

In addition, the intrinsic acidity of the catalyst can promote the side reactions such as cracking. This implies that if the acidity of catalyst can be neutralized or lowered, higher activity and selectivity can be obtained. Alkali metals are one of the basic substances which are commonly used to neutralize or reduce the acidity of catalyst.

Although much work has concentrated on the effect of promoters on activity and selectivity of catalysts. Little work has focused on the influence of lithium as a promoter. Thus, if the functions or roles of lithium are understood, the development of high performance catalysts can be carried out.

The objectives of this work are to study the effect of lithium on the bimetallic Pt-Sn/ $\text{Al}_2\text{O}_3$  catalyst by comparing with the Li-unpromoted catalyst and to determine the most suitable amount of the added lithium on the catalyst.