



CHAPTER I INTRODUCTION

Direct dehydrogenation of alkanes can be found in literatures since 1930s. Commercially, however, alkanes are mainly produced by fluid catalytic cracking or as a by-product from pyrolysis/cracking furnaces. Beside economic reasons two main fundamental problems are responsible for the lack of the commercial applications of the direct dehydrogenation. First, the dehydrogenation reaction is endothermic.



For dehydrogenation of propane (C_3H_8), ΔH_{773}^0 is about 130 kJ/mole, and the equilibrium conversion (X_{eq}) is around 18% at 773 K and around 50% at 873 K under atmospheric pressure. According to Le Chatelier's principle, the reaction is best done at low pressure due to the increased-volume nature. The second reason for the lack of commercial applications of the reaction is that the activity of the commercial catalysts for this reaction are not very high and that deactivation due to coke formation is rather fast (less than 1 hour at 873 K). Platinum/alumina (Pt/Al_2O_3) and (Cr_2O_3/Al_2O_3) are the two types of commonly-used catalysts.

In recent years a completely different approach has been considered. The concept of membrane reactor has shown high potential for applications in the fields of biological and chemical reaction engineering during the past several decades. One of the major applications of membrane reactor is for overcoming an equilibrium conversion by combining reaction and separation in a single unit operation. The dehydrogenation of propane to propene is one of the reactions of interest in this type of applications. One of the reaction product (H_2) is removed from the reaction mixture using a gas-separative membrane. By selectively removing the hydrogen, the reaction mixture does not reach the equilibrium composition and the production of propene should increase.

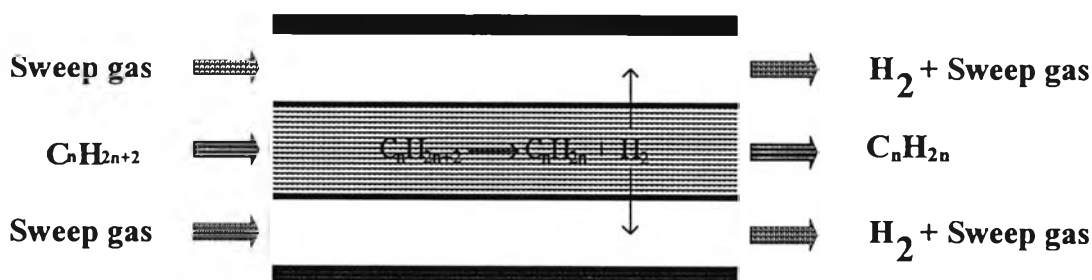


Figure 1.1 Membrane reactor concept for dehydrogenation reaction.

Although the principle of the catalytic membrane reactor is easily understood, in practice the concept is much more complex. Figure 1.1 describes the main features of a multifunctional reactor incorporating porous or dense membrane system for application in catalytic dehydrogenation. It shows reacting gas species being fed into the inner tube containing catalytic material which initiates the chemical reaction. As the reaction proceeds, product concentration increases and because the membrane is selectively permeable to the product(s), they are transported across the membrane into the shell side. By sweeping these products with an appropriate stream, it is possible to increase the transfer rate across the membrane and therefore considerably affect the conversion in an equilibrium-limited reaction.

A number of researchers have studied this reaction using various types of membrane materials and catalysts. Ziaka *et al.* (1993) studied the reaction in sol-gel alumina membrane. They found that yields to propene are higher than the corresponding equilibrium yields at the same temperature and pressure condition. Sheintuch and Dessau (1996) used a Pd/Ru (or Pd/Ag) membrane reactor packed with a supported Pt catalyst. They found that the yield is limited by the deactivation of the catalyst due to low partial pressure of hydrogen in the reaction side. Weyten *et al.* (1997) investigated the system using a H_2 -selective silica membrane with a chromia/alumina catalyst. They found that propene yield is at least twice as high as the value obtained at thermodynamic equilibrium in a conventional reactor. Yildirim *et al.* (1997) evaluated the relative performance of three composite membranes; namely Pd/Ag, silica and Pd-dispersed porous membranes. They found that the dense

Pd-Ag composite system possessed higher performance levels in the temperature range studied. However, metal-dispersed porous systems have advantages due to their significantly higher contact surface-to-volume ratio. High hydrogen permselectivity is confirmed as a key factor in determining reactor performance in terms of conversion enhancement.

From the concept of membrane reactor, the following three aspects of the reactor and their relationship to each other have to be taken into account.

1. The membrane performance: H_2 permeation rate and H_2 selectivity with respect to the feed, sweep gas, and reaction products, long term stability and performance of the membrane under operating conditions are important for the performance of membrane reactor.

2. The catalyst performance: intrinsic activity and selectivity of the catalyst are, of course, important, but it is often forgotten that the activity and selectivity under operating conditions (when H_2 is removed from the reaction zone) can be different from these intrinsic values.

3. Operating condition: the process parameters have significant effects on the membrane and catalyst performance, and thus determine the conversion, yield and selectivity of the propane/propene reaction. The relationship between the reaction rate, flow rate, and permeation rate are very important in optimizing the process condition.

Although a number of researches have been carried out in this area, there is little effort to select catalysts, which are suitable for the system. In addition, data on reaction rate constants of the propane dehydrogenation have not been studied extensively in the literature, even though the data are very useful especially in the modeling of the dehydrogenation of propane in a membrane reactor. The objective of this research is to study the performance of membrane reactor with the following details; 1) the kinetic of Pt-Sn-K/ γ -Al₂O₃ catalyst which shows good resistance to deactivation by coking and high propane selectivity; 2) the permeation of H₂ through a Pd membrane and; 3) membrane reactor performance both from experiments and mathematical simulation.