

CHAPTER I

INTRODUCTION

A number of strategic, commercial, and economic factors of growing importance make the dehydrogenation of lower alkanes particularly interesting. These factors include raw material supply and price considerations, shifts in the geographic sources of olefinic feedstocks and of derivative production capacity, changes in olefin and derivative market demands, and the technical, economic, and strategic limitations of existing technology.

Olefins and aromatics are largely used as raw materials in industrial processes. A strong market pressure compels increasing optimization of the present processes. Cost reduction can be obtained either by setting up new engineering concepts or by using cheaper raw materials (particularly alkanes) combined in some cases with the use of more sophisticated catalysts. In fact, in the past years, there has been a clear tendency to use light alkanes for the direct production of oxygenates via partial oxidation or for the production of olefins via dehydrogenation or oxidative dehydrogenation (ODH) due to the large availability and low price of natural gas.

Platinum has been a key ingredient in most dehydrogenation catalysis due to its high activity for C-H bond rupture coupled with its poor ability to cleave C-C bonds. The selectivity and stability of Pt catalysts can be notably improved by the addition of a second metal which in this case plays the role of a promoter. Several studies have proved that the addition of Sn to Pt/Al₂O₃ yields higher selectivity and catalyst stability. It accelerates the dissociative adsorption of the alkane, which is thought to be rate limiting, reduces the rate of coking, increases the coke tolerance, and facilitates the gasification of coke.

Alumina supported platinum catalysts are widely used in several hydrocarbon processes. The effect of alkali doping upon a catalyst can frequently be attributed to a neutralization of acidic centers. Moreover, it can also increase the dehydrogenation selectivity and improve resistance of the catalyst to deactivation.

The three most important aspects of the application of any heterogeneous catalyst are activity, selectivity, and life. Of these, catalyst life has received the least attention, despite the fact that deactivation can often dictate the viability of a given process.

The most important cause of catalyst deactivation in all of the alkane dehydrogenation processes is carbon deposition. The high temperatures and low hydrogen concentrations necessary to achieve relatively high equilibrium conversions, which in turn represent high concentrations of olefins, create an ideal environment for the rapid formation of coke. The presence of promoters and the hydrogen/hydrocarbon feed ratio have important effects on the process of carbon deposition.

This project focuses on the effect of tin on the decoking performance for butane dehydrogenation over Pt-Sn-Li/Al₂O₃ catalysts. Spent catalysts with different tin-platinum weight ratios were studied. The research was divided into two parts. The first part was the long term study that investigated the regeneration performance during multiple reaction-regeneration cycles. The amount of coke on the metal and on the support after the first reaction cycle was characterized by the temperature programmed oxidation (TPO) method and was compared with that found after the eighth reaction cycle. The second part was the short term study, the partially regenerated catalyst, at various burning times, was characterized by means of Elemental analysis (CHNS/O), Fourier transform infrared spectroscopy (FTIR), and Simultaneous thermal analysis (STA) in order to investigate how coke deposits on the catalyst were changed during regeneration.