

CHAPTER I

INTRODUCTION

Dehydrogenation technology, which has been available for a number of years, is proven commercially for the production of diolefins from lower alkanes and for the production of long-chain mono-olefins from the corresponding paraffins. Dehydrogenation units may not be economically and commercially justified in all cases. Over the next ten years, the number of dedicated plants feeding propane and butanes is expected to increase significantly in many part of the world. These plants use propane and butane feeds, recovered as natural gas liquids (NGL) or liquefied petroleum gas (LPG), to produce olefins and olefinic derivatives.

One of the largest fuel uses for LPG, especially butanes, is as a direct additive to the gasoline pool. This usage is based on three factors. First is the increased availability of low cost LPG. Second is the implementation of refinery processes that produce LPG. Processes that produce LPG, especially butanes, include catalytic cracking and reforming. Butanes are also recovered from fuel gases. Third is the growing demand for octane resulting from the need to reduce lead content. In an effort to reduce the formation of atmospheric ozone, the U.S. Environmental Protection Agency (EPA) has reduced the allowed volatility of gasoline. This action has severely limited the quantity of butane that can be added to gasoline pool (Clark, 1988) and has changed refiners from net consumers to net producers of butanes. Indeed a large surplus of butane is now available.

Wide interest was given some decades ago to this catalytic system when dehydrogenation of n-butane was the main source for the synthesis of butenes

and butadiene. Renewed interest has developed in recent years due to the increased need for isobutene for MTBE synthesis, and also because of the possibility to compete with high capital-investment steam-cracking for synthesis of pure light olefins for specific applications, such as the synthesis of high-purity propylene and butenes for the polymer industry (F. Cavani et al., 1995).

Usually, the catalytic agent is to be on a support and it becomes necessary to select an optimum support material according to the criteria of stability, inertness, cost and whether or not their use is governed by patent rights. For this research platinum supported on alumina is known as a good dehydrogenation catalyst (Cortright and Domesic, 1994). Since the dehydrogenation is an endothermic reaction, high temperature is required to achieve high conversion. However the rate of side reaction, isomerization, hydrogenolysis, and coking reactions become significant at this high temperature (Le Page et al., 1987).

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 activity for cleavage of C-C bonds. However, the selectivity and stability of platinum catalysts can be apparently improved by the addition of a second metal which is called a promoter. Addition of tin to a platinum on alumina catalyst is known to promote the desired reaction and inhibit coking reactions which are unavoidable side reactions in catalytic processing of hydrocarbons and cause severe deactivation (Kirzensztejn et al., 1991). Some authors have revealed that tin modifies the catalytic behavior of supported platinum catalysts through ensemble and/or ligand effect but many researchers have provided evidence that tin in the supported catalyst is mainly present as Sn^{2+} . According to the surface model, the platinum clusters locate on the tin aluminate surface (Burch, 1981; Burch and Garla, 1981; and Lieske and Volter, 1984).

Alkali doping in heterogeneous catalysts is employed in order to neutralize the intrinsic acidity of the support or improve the catalyst (Afonso et al., 1994). The action of the alkali can manifest itself in various different ways. Alkali can increase the selectivity, activity and prolong the effective lifetime of the catalyst (Mross, 1983). Moreover, alkali promotes the redispersion of platinum in the presence of oxygen which causes platinum to separate from the platinum crystallite and disperse on the carrier during regeneration (Lieske et al., 1983).

Although a large amount of work has gone into development and performance evaluations of these catalysts, very little comparison in activity and study in coking performance on the n-butane dehydrogenation over platinum-tin catalysts which are neutralized by alkali treatment are available. To contribute further understanding, we should conduct an investigation of the effect of platinum catalyst modified by tin.