



CHAPTER I

INTRODUCTION

Environmentally friendly transportation is a major driving force for the reduction of aromatic contents in fuel in many countries around the world (Cooper and Donnis, 1996). The aromatic compounds strongly affect human health and also cause the low efficiency of diesel engine operation. Due to the continuous decrease in aromatic contents in the fuel regulations and the incessant increase in aromatic concentrations in crude oil, the reduction of aromatics becomes an even more challenging issue for industrial processes (Ertl *et al.*, 1997). Typically, aromatic contents in fuel are effectively reduced via the hydrogenation reaction using a two-stage process. Besides the reduction of aromatics, cetane number in the diesel fuel is subsequently increased. However, the improvement of cetane number due to the saturation of aromatics alone might not be enough to achieve the fuel specifications in the near future. Even worse in the case of gasoline fuel, the reduction of aromatic concentrations drastically decreases the octane number.

Recently, ring opening was initially introduced as one of the promising reactions to boost cetane number in diesel fuel. It was observed that the ring opening of naphthenes yielded alkane products with different degrees of branching depending on the positions of the C-C bond rupture (Santana *et al.*, 2006). For example, the primary products obtained from the cleavage of the C-C bond of 1,3-dimethylcyclohexane (1,3-DMCH) at secondary-tertiary (C2-C3, substituted) positions were products with less degree of branching (2-methylheptane and 4-methylheptane) than that from the breakage of the C-C bond at the secondary-secondary (C2-C2, unsubstituted) positions (2,4-dimethylhexane). Therefore, successive improvement in cetane number can be accomplished using selective ring opening catalysts toward the cleavage of the C-C bond at substituted positions. Interestingly, the same concept could also be considered as a potential reaction for octane number improvement in the case that the catalyst is selective to open the ring to alkane products with a high degree of branching (Hongbin *et al.*, 2005).

The different reactivities in subsequent ring-contraction and ring-opening reactions (C_{10} products) between the two products from the hydrogenation of tetralin,

cis-decalin and trans-decalin were elucidated in a previous work (Santikunaporn *et al.*, 2004). It was observed that trans-decalin only converted at high temperatures with low selectivity to C₁₀ products while cis-decalin resulted in substantial selectivity to indanes and alkyl-cyclohexanes (C₁₀ products) over HY catalysts. Therefore, the increase in cis-decalin production from the hydrogenation of tetralin increases the possibility of obtaining ring opening products in subsequent process. However, studies of the role of the metal catalysts in the hydrogenation of tetralin toward each product are still limited.

In this contribution, tetralin and 1,3-DMCH molecules were selected as model molecules which represent the compounds present in the fuel. In the first part (Chapter IV) the hydrogenation of tetralin was carried out on conventional catalysts (Pt/Al₂O₃, Pd/Al₂O₃, and Ni/Al₂O₃) at 3540 kPa and 548 K. The operating conditions were selected to ensure that the gas phase reaction occurs and to avoid the dehydrogenation reaction. The role of the metal catalysts in the tetralin hydrogenation reaction was clarified. The kinetics study of tetralin hydrogenation and cis- to trans-decalin isomerization using a Langmuir-Hinshelwood model was implemented to obtain the kinetic parameters. The interesting relationships between trans/cis-decalin ratios as a function of tetralin conversion on the prepared catalyst were observed, according to the trend observed on Pt/Al₂O₃ and Pd/Al₂O₃ catalysts which has been reported in the previous work (Jongpatiwut *et al.*, 2004). As a result, which catalyst would be an appropriate catalyst for using in a deep hydrogenation process to accompany a subsequent ring opening step can be determined. Then ring opening of naphthenic molecule is further investigated in order to obtain alkane products with higher octane or cetane number compared to naphthenic ring. The contribution initially studied on the cleavage of C-C bond of a simple naphthenic molecule, 1,3-dimethylcyclohexane (1,3-DMCH). The ring opening of 1,3-DMCH was evaluated on Ir catalysts and modified Ir catalysts with the addition of K and Ni are investigated in Chapters V and VI, respectively. The addition of K may alter the catalytic activity and selectivity of Ir/SiO₂ due to both geometric and electronic effects. The promoted and unpromoted Ir catalysts were characterized using several techniques; for example, chemisorption of CO, temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), etc. The other selected promoter is

nickel. The formation of Ir-Ni alloy or the transformation of alumina support to nickel aluminate due to the strong interaction between nickel and alumina may be observed. It was expected that the catalytic behavior of Ir catalysts would be modified. In this work, an attempt to adjust the selectivity of catalyst towards the high octane number products and to maintain the vapor pressure in the desirable range to gasoline was investigated at the same time.

The aftermath of the hydrogenation of tetralin and of the ring opening of 1,3-DMCH are summarized in Chapter VII. Some recommendations for improving the fuel properties via the ring opening process are provided.