

## CHAPTER I

### INTRODUCTION

Hydrogenation is the most ubiquitous reaction in organic chemistry as well as in the commercial organic chemical industry. Both heterogeneous and homogeneous catalysts are used, but heterogeneous catalysts dominate commercial practices, especially for large-scale production, because it does not require separation process between product and catalyst. Also the catalyst can be easily separated for regeneration. The reactions are exothermic and reversible so temperature control is necessary. However, a standard catalyst can usually be selected that has a high activity, permitting operation at mild temperatures that favor high yields of the hydrogenated product.

Hydrogenation is the chemical addition of hydrogen when refining. The hydrogen is added to unsaturated hydrocarbon molecules to result in very stable saturated hydrocarbons, and also hydrogen removes impurities such as containing compounds. Also, the hydrogenation is the process for treating in diesel fuel.

The further lowering maximum limit in diesel is considered. As a result new fuel standards announced in July 2004 will see sulfur in diesel reduced from 500 milligrams per kilogram to 50 milligrams per kilogram on 1 January 2006 and capped at 10 milligrams per kilogram in 1 January 2009. The increase in more stringent environmental legislation for diesel emissions in exhaust gases demands new diesel fuel specifications, including lower level of sulfur, aromatic content, and higher cetane number. High aromatic content in diesel fuel has been recognized for both lower fuel quality and the formation of undesired emissions in exhaust gases. In order to reduce the harmful emission from exhaust gases, the amount of particulate matter (PM) emissions in diesel can be reduced by decreasing the sulfur content and decreasing the aromatic content of the fuel which raises the cetane number (Navarro *et al.*, 2000). In addition, the quality of diesel fuel, generally shown as cetane number (CN), decreases with increasing aromatic compounds (Rojas *et al.*, 2003). Because of the health hazards associated with these emissions, environmental regulations governing the composition of diesel fuel are being tightened in both Europe and the United States, leading to limitations on aromatics.

As a result of these stringent environmental regulations, processes for aromatic reduction in middle distillates have received considerable attention in recent years. Clean fuels are the result of changes in the chemical composition of gasoline and diesel. The removal of lead from gasoline in the 1970s, the addition of oxygenates in the 1990s, and the current removal of sulfur each impacted the chemical composition of fuels. Understanding the interaction between fuel composition and process chemistry enables not only the optimal application of current refining processes but also the development of new approaches to producing clean fuels.

The hydrogenation of naphthalene has been widely used as a model reaction for evaluating hydrogenation properties. However, the hydrogenation of monoaromatics is more difficult than that of polyaromatics, so we have chosen tetralin as the model molecule to test the catalytic performance of catalysts for the deep hydrogenation of aromatics.

Hydrogenation of tetralin is rarely reported, although it represents the simplest form of partly hydrogenated polyaromatics. The hydrogenation of tetralin is typically incorporated as a sequential reaction step in naphthalene hydrogenation, as shown in Figure 1.1 (Huang and Kang, 1995).



**Figure 1.1** The sequential hydrogenation reaction of naphthalene.

Hydrogenation is an important process for reducing the aromatic content in liquid fuels or solvents, because they usually still contain a relatively high percentage of aromatics after a desulfurization and denitrogenation treatment, which not only generate undesired emissions of particles in exhaust gases but also decrease the cetane number. The restrictions for exhaust emissions can be met by deep hydrotreating, which typically consists of a two-stage process with a conventional

hydrotreating catalyst (CoMo, NiMo, NiW) at the first stage and a more active hydrogenation catalyst (Ni, Pt, Pd) at the second stage as reviewed by Cooper and Donnis. Moreover, the effect of catalyst preparation on aromatic hydrogenation process is critical and still limited. Therefore, this present work is an attempt to elucidate the optimal parameters in catalyst preparation of platinum and palladium for tetralin hydrogenation, such as calcination temperature (250, 300, and 350°C) and the order of impregnation between metal and F-promoter on a  $\gamma$ -alumina support. A series of mono- and bi-metallic catalysts (with and without F) was prepared by incipient wetness impregnation method and calcined at different temperatures (250, 300 and 350°C). The reaction was carried out at 275°C with a total pressure of 300 psig and a H<sub>2</sub>/aromatics molar ratio of 25. The relationship of catalyst properties to catalytic activity was also investigated.