

CHAPTER I

INTRODUCTION

Hydrogenation is a class of reductive chemical reactions in which the net result is an addition of hydrogen (H_2). Hydrogenation is commonly used for removing impurities, such as sulfur and nitrogen, by targeting the unsaturated bonds between the carbon atoms. Most hydrogenation involves the direct addition of diatomic hydrogen over a catalyst under pressurized conditions.

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 the commercial practice, especially for large-scale production, because we can separate out the catalyst and regenerate it. The reactions are exothermic and reversible, so temperature control is necessary. However, a standard catalyst can usually be selected that has high activity, permitting operation at mild temperatures which favor high yields of the hydrogenated product.

Recently, environmental regulations in many countries, including Thailand, have been setting more and more strict standards for diesel emissions in exhaust gases. For example, Thailand recently limited sulfur content in diesel to 350 ppm, and will reduce the diesel standard further in 2010 to reach levels below 50 ppm, so the new diesel fuel specifications, including a lower level of sulfur, aromatic content, and higher cetane number are demanded. 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 and 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).

As a result of the stringent environmental regulations, lowering the aromatic content in diesel fuel by aromatic hydrogenation is becoming one of the most important technologies in the petroleum refining industry.

Tetralin was chosen as model molecule for studying the hydrogenation properties of these catalysts. It is well known that mono-aromatics are more difficult to convert and should be then more representative of the aromatic compounds present in diesel fuel. 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 Sequential hydrogenation reaction of naphthalene.

Platinum – palladium (Pt-Pd) catalysts are noble metal catalysts which are widely used in the hydrogenation reaction. An advantage of these catalysts is that they are active at significantly lower temperature, minimizing the severe thermodynamic limitations found at higher temperature for any exothermic hydrogenation reaction. The drawbacks of these catalysts are their extremely low tolerance to sulfur. Recent investigations have shown some sulfur tolerance when acidic supports, such as β - and γ -zeolites, were employed (Yasuda *et al.*, 1997). It has been proposed that the electron-withdrawing ability of acidic supports can modify the metal particles, making them electron-deficient and, consequently, disfavoring the formation of metal-S bonds. At the same time, the addition of a second metal (e.g. Pt-Pd or Pt-Ge) was found to enhance the sulfur tolerance, and this promotion has also been ascribed to changes in electronic properties (Kovach *et al.*, 1974). Sulfur-tolerant bimetallic Pt-Pd catalysts have been the subject of investigation in a number of recent publications (Yasuda *et al.*, 1999). The combination of the bimetallic Pt-Pd and acidic supports has resulted in promising catalysts. However, excessive acidity supports may cause undesired cracking products and coke. Coke formation significantly lowers reactivity, particularly, in zeolite supports on which pore plugging may become a serious obstacle. In this

contribution, we have incorporated the acidic function by addition of controlled amounts of fluorine. It has long been known that the incorporation of fluorine to oxide supports enhances their activity for acid-catalyzed reactions such as cracking, isomerization, alkylation, and disproportionation. Since F is very electronegative, as it replaces O or OH groups, it increases the acidity of both protonic (Brønsted) and non-protonic (Lewis) sites on the surface. Recent studies have reported the use of F to promote aromatic hydrogenation activity in the presence of sulfur and the selected model of sulfur compound is dibenzothiophene (DBT) because not only is its desulfurization chemistry known, but it is also one of the main S-containing compounds in diesel.

In this work, the sulfur tolerance of γ -alumina supported mono- and bi-metallic Pt-Pd catalysts in the deep hydrogenation of tetralin in the presence of DBT and the optimal parameters in the catalyst preparation of platinum and palladium for tetralin hydrogenation, such as calcination temperature (400, and 500°C) and the order of impregnation between metal and F-promoter on a γ -alumina support were studied. A series of mono- and bi-metallic catalysts (*with* and *without* F) was prepared by incipient wetness impregnation and calcined at 500°C. All of the catalysts were characterized by temperature programmed reduction (TPR), Hydrogen Chemisorption, X-ray photoelectron spectroscopy (XPS), atomic adsorption spectroscopy (AAS) and transmission electron microscopy (TEM). The reaction was carried out at 300°C with a total pressure of 500 psig and a H_2 /aromatics molar ratio of 11. The catalytic activities are presented in terms of tetralin conversion as a function of time. The relationship of catalyst properties to catalytic activity was also investigated.