CHAPTER I

INTRODUCTION

Petroleum contains not only hydrocarbon but also impurities, such as compounds of sulfur, nitrogen, oxygen and metal. Amount of these impurities varies, depending on sources of crude. Sulfur compounds are present in a much more amount than other impurities. Sulfur compounds are usually found in the forms of mercaptan, sulfide, disulfide and thiophene. Removal of sulfur compounds are important for the following reasons 1) to improve quality of petroleum feedstock prior to further processing, 2) to protect the performance of catalysts used in down stream operations, and 3) to improve the quality of the down-stream products.

Catalytic hydrodesulfurization (HDS) is a modern process to remove sulfur compounds from feedstocks. This process was carried out by which sulfur containing compounds react with hydrogen gas over suitable catalyst, resulting in products having lower sulfur content and hydrogen sulfide. Commercial catalyst used for HDS process is $CoMo/Al_2O_3$ in sulfided form.

In the catalytic process, catalysts usually lose their activities while in operation. The time required for the activity to fall to an undesirable level varies with the severity of the process conditions and type of reaction. Three kinds of catalyst deactivation may occur

a) sintering which is changes in the catalyst structure; b) poisoning which is an irreversible chemisorption of some impurities in the feed stream; and c) coking which is the desorption of carbonaceous residue from reactant, product or some intermediates. These phenomena may occur singly or in combination, but the overall results is the removal of active sites from the catalyst surface.

At HDS condition, other impurities such as compounds of nitrogen, oxygen and metal can interfere with the catalyst in HDS process. In petroleum the interesting weight ratio of N/S, varies from 1/2 to 1/5 in some crudes. Many investigators (Desikan and Amberg, 1964; Lo, 1981, etc.) showed that basic nitrogen compounds can poison hydrotreating catalysts by strong chemisorption on the catalyst surface. The presence of these species even at low concentrations may limit the observed catalytic activity and necessitate the use of higher pressure and temperatures to obtain the desired conversions. HDS and hydrodenitrogenation (HDN) reaction occur simultaneously at severe condition. At mild condition, only HDS reaction occur. From these points, the purpose of this thesis is to study the influence of nitrogen compounds on reaction at mild condition.

Nitrogen compounds found in petroleum, include heterocyclic and non heterocyclic compounds. Heterocyclic nitrogen compounds are presented in a great amount, and are in co-operated in five- or six- membered ring, most of which are unsaturated. The heterocyclic nitrogen compounds are often grouped into strong bases (quinoline, pyridine) and weak basic (indole, pyrrole, carbazole).

In this study, the roles of nitrogen compounds, on catalytic reaction of thiophene as sulfur model compound in liquid carrier as toluene mixed with n-hexane, were investigated. The catalyst used is $CoMo/Al_2O_3$ in sulfided form. The amount of each nitrogen adding to undoctored feedstock was kept constant in equimolar (equivalent to 0.5 wt % of nitrogen). Heterocyclic nitrogen compounds were chosen to compare the effects of type and structure on HDS of thiohene as followed;

1) The influence of basicity was compared between: pyridine and pyrrole.

2) The influence of number of aromatic ring was compared between : pyridine and quinoline.

3) The influence of saturated ring was compared between: quinoline and 1,2,3,4-Tetrahydroquinoline.

4) The influence of stearic hindrance was compared between: pyridine and 2,6-lutidine.