CHAPTER I

INTRODUCTION

Today, the use of petroleum substances has substantially increased. Due to the shortage of crude oil supply, there have been the increase in demand for upgrading heavy petroleum fractions such as residual oils and coal-derived liquids. These heavy fractions usually contain high concentrations of impurities such as asphaltenes, heteroatoms like sulfur, nitrogen and oxygen compounds, and metallic impurities. These impurities are mainly responsible for the catalyst deaction during the catalytic hydroprocessing. Removal of the impurities is necessary for improving petroleum feedstocks perior to further processing. Therefore, a major purpose in upgrading of these feedstocks are to convert asphaltene into lighter oils with low heteroatom content and removal the impurities by using catalytic hydrotreatment [1-4].

In a modern refinery, hydrotreating is considered to be one of the most important processes. Feedstocks, either petroleum or coal-derived liquids, usually contain impurities such as nitrogen, oxygen, sulfur, and metal compounds. These compounds were removed for one of the following reasons: (1) to improve the quality of the downstream product, (2) to protect and improve the performance of catalysts used in downstream operations, (3) to reduce the sulfur content of the fuel to meet environmental restrictions, and (4) to improve the stability of the product. Hydrotreating is the process by which nitrogen, oxygen, sulfur, and metals are removed from the feedstocks via catalytic reactions with hydrogen.

The catalysts commonly used for this process are Mo and W on alumina support. Ni and Co are also used as promoters to improve catalyst activities. During normal operation, the catalyst gradually loses its activities due to (1) coke formation, (2) nitrogen poisoning , and (3) permanent deposition of metal compounds. Coke formation on the catalyst surface results in the plugging of the catalyst pores by carbonaceous material. This obstruction of the pores increses the mass transfer resistance and reduces the rate of transfer of the reactants to the active sites of the catalyst. Nitrogen compounds in the feedstocks can adsorb on the acidic sites of the catalyst surface and destroy the sites. Trace metal impurities can permanently deposit on the active sites of the catalyst surface and cause a loss of catalyst activity whereas coke deposition can be burned off the catalyst surface by controlled combustion. Studies show that the deposition of carbonaceous material is the major factor in deactivation of the catalysts, while the deposition of metal impurities is considered to have a long term deactivation effect.

There are differenct types of metal impurities in petroleum and coal-derived liquid feedstocks. Nickel and vanadium are commonly found in petroleum feedstocks while titanium and iron are found in coal-derived liquids. The form of titanium in coal-derived liquids is not positively identified, but an organometallic compound like titanocene was proposed by Filby et al. [5].

In this study, the roles of organometallic compounds on catalytic hydrodesulfurization of thiophene are investigated. The catalyst used is Ni-Mo/alumina catalyst. Thiophene and toluene are selected to represent pure compounds and titanocene dichloride, ferrocene, vanadyl acetylacetonate are selected to represent organometallic compounds containing titanium, iron and vanadium metals, respectively.