

## CHAPTER I

### INTRODUCTION



Petroleum consists predominantly of various hydrocarbon and also contains other elements such as sulfur, nitrogen, oxygen, and metal, called impurities. The elements in petroleum are combined to form a complex mixture of organic compounds that range in molecular weight from 16 (methane) to several thousands. Some metal may be found in organic or inorganic form.

The impurities in petroleum vary greatly between crudes. Sulfur is found in all crudes in concentrations ranging from 0.5 - 8.0 %. Its concentration tends to increase with boiling point. Nitrogen is found predominantly in the higher boiling fraction and in the residue. Its concentration is found to be in the range from 0.2 - 1.6 %. Metals found in petroleum are such as nickel (Ni), vanadium (V), iron (Fe), titanium (Ti), or mercury (Hg). The metals in petroleum range in concentration from about 1000 ppm to less than 1 ppb.

In petroleum, nitrogen is present largely in the form of heterocyclic compounds having five or six-membered rings, mostly unsaturated. The heterocyclic and other nitrogen compounds are often grouped into strong bases such as quinolines, pyridines, and acridines and weak bases or nonbasic compounds such as indoles, pyrroles, and carbazoles. These nitrogen compounds must be reduced not only to assure an environmentally

acceptable  $\text{NO}_x$  emission upon combustion but also to prevent nitrogen-containing compounds from poisoning the acidic function of catalyst used in the downstream processes (1,2).

The removal of undesirable nitrogen compounds from petroleum and synthetic crudes derived from coal and oil shale is best achieved by catalytic hydrodenitrogenation (HDN). Hydrodenitrogenation of heterocyclic nitrogen compounds proceeds in general via saturation of heterocyclic ring, followed by ring fracture at a C-N bond. Nitrogen is removed from the resulting amine or aniline as ammonia.

The catalysts commonly used for hydrodenitrogenation reaction are the sulfides of metals group VIA (Mo, W) promoted by the sulfides of the metals group VIII (Ni, Co). The various pairs of sulfides do not have the same activity for various chemical conversion and depending on the purpose. For hydrodenitrogenation reaction, the NiMo pair is preferred (1). During reaction, one of the most serious problems occurring in catalytic hydroprocessing is the loss of the catalytic activity.

The loss of the catalytic activity may result from catalyst deactivation. The deactivation of catalyst may be divided into 3 groups as follows:

1. Poisoning is catalyst deactivation due to the adsorption of some of the impurities in the feed stream, such as nitrogen, sulfur, oxygen, and metal, or the adsorption of a product of the reaction onto the active site of the catalyst. The poisoning may be either temporary or permanent. The latter is an irreversible process

because the poison is adsorbed too strongly. It is a major problem, so the catalyst has to be discharged ultimately. The poisoning deactivation by metal impurities, such as Ni, V, Hg, Fe, or Ti etc., can permanently deposit on the active sites of the catalyst and cause a loss of catalytic activity.

2. Fouling is a process of catalyst deactivation that may be either physical or chemical process in nature. It can occur by the physical blockage of the carbonaceous material, coke, or the deposition of metal sulfide from organometallic compounds which react with the sulfur-containing molecules and deposit within the pores of the catalyst during operation.

3. Sintering or thermal deactivation is an irreversible physical process leading to loss of area of the catalyst when the catalyst is operated above the normal temperature range. This process can occur not only by reduction of the support area but by a loss of dispersion of the metal crystallites when the active metal ingredient is supported on a high-area oxide support.

The reasons of catalyst deactivation show that metal compounds can be affected by the catalyst activity. Therefore, the study of the effects of metal compound on reaction and catalyst is necessary. The aim of this work is to study the effects of organometallic compound on catalytic hydrodenitrogenation. Quinoline has received considerable study as a model nitrogen compound. It is commonly used as model compounds and many derivatives of its are detected in shale oil. Since it has complex reaction mechanisms, a knowledge of the effects

of organometallic compounds on the HDN reaction networks of quinoline on representative catalyst assumes some importance to guide studies of the HDN of representative feedstock. Organometallic compounds used are titanocene dichloride, ferrocene, and diphenylmercury which contain titanium, iron, and mercury, respectively. These metal were found in petroleum (2, 9).