

CHAPTER I

INTRODUCTION

Hydrodesulfurization process is widely used in refineries and petrochemical industries. This process is used to remove sulfur compounds from crude oil or chemical feedstock. Amount of sulfur compounds vary with type of crudes. It is less than 0.2 per cent by weight in some Pennsylvanian, Algerian and Russian crudes to over 6 per cent by weight in some Mexican and Middle East crudes (Staff of the Royal Dutch / Shell Group of companies, 1993). It has been shown that the sulfur content increases with the increment of the boiling point of the feedstock. At low boiling point, sulfur is present in a form of aliphatic compounds. As the boiling point increases, the sulfur compounds tend to be more cyclic, and in the heaviest fraction the sulfur is almost exclusively present in complex ring structure.



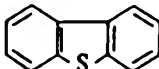
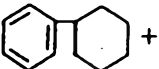
The main reasons for the removal of sulfur compounds are:

1. To reach the emission limit on air-pollution-control of fuel oil and gasoline;
2. To prevent the poisoning of catalysts such as hydrocracking catalysts and reforming catalysts;
3. To prevent the corrosion during refining and improve the odor of the products (Satterfield, 1991).

Besides hydrodesulfurization, the sulfur removal processes are solvent extraction and adsorption on molecular sieves. However, these two processes are mostly employed for natural gas and light hydrocarbons. The processes, which require low sulfur level in feedstock such as catalytic reforming or have a heavy fraction as a feedstock, still need the catalytic hydrodesulfurization process.

The hydrodesulfurization reactions are all exothermic. The various sulfur compounds have very different reactivities, with mercaptan sulfur much easier to eliminate than resonant sulfur molecules like thiophene or dibenzothiophene (Page, 1987). Table 1.1 shows the reaction and heat of reaction of different sulfur compounds.

Table 1.1 Hydrogenolysis of some simple molecules representative of the families of sulfur compounds present in petroleum fractions

Type	Reaction	ΔH (kcal . mol ⁻¹)
Mercaptans	$R-SH + H_2 \rightarrow RH + H_2S$	-17
Sulfides	$R-S-R' + 2H_2 \rightarrow R-H + R'-H + H_2S$	-28
Thiophane	 + 2H ₂ → C ₄ H ₁₀ + H ₂ S	-29
Thiophene	 + 4H ₂ → C ₄ H ₁₀ + H ₂ S	-67
Dibenzothiophene.....	 + 5H ₂ →  + H ₂ S	

Thiophenic compounds are the most refractory of sulfur compounds in heavy gasoline. Consequently, thiophene is frequently chosen as representative of the sulfur compounds in light feedstock.

The HDS catalysts are manufactured with the metal in an oxide state. Group VIB metals (chromium, molybdenum and tungsten) are normally used for desulfurization and promoted with metals from an iron group (iron, cobalt, nickel). The catalysts are active when they are in the sulfided state, which is obtained by sulfiding the catalysts either prior to use or with the feed during actual use (McKetta, 1990). Sulfiding agents are easily decomposed sulfur compounds such as carbon disulfide, dimethylsulfide (DMS), dimethyldisulfide (DMDS) or even hydrogen sulfide. While sulfiding with feed, having low sulfur compounds, may take many days of operation to fully activate the catalyst (Twigg, 1989).

The most widely used hydrodesulfurization catalysts in industry are molybdenum catalysts on high surface area alumina support with cobalt promoters. Nickel-molybdenum catalysts are chosen instead of cobalt-molybdenum when a higher activity for polyaromatics saturation or nitrogen removal is required.

The hydrodesulfurization is operated at temperature of 300 to 380 degrees Celsius and pressure of 40 to 60 bars. Rate of hydrodesulfurization is the first order with respect to the sulfur compounds. The order of reaction with respect to a partial pressure of hydrogen lies between zero-order and first order, depending on the nature of sulfur compounds present.

Deactivation of catalysts depends mainly on crude oil. The large complex molecular structure of asphaltenes may cause the catalyst replacement every 6 to 12 months. The catalysts deactivate mainly from pore plugging by metal sulfides and coke. Narrow pores plug earlier, but have a large catalytic surface area for the reaction. The optimization of pore diameter and activity of

the catalysts is important. Improvement of catalyst resistance to poisoning is especially important because of the economics of changing low-valued residues to high-valued lighter hydrocarbon products.