CHAPTER I
INTRODUCTION

Due to a concern about the environmental problems, the reduction of sulfur content in transportation fuels must be carried out because of SO_x, which is produced from the combustion of transportation fuels containing organic sulfur compounds. These compounds not only cause acid rain, but also poison catalysts in catalytic converters designed for lowering CO and NO_x. Generally, gasoline comprises sulfur compounds like mercaptans, sulfides, disulfides, thiophene, and its alkylated derivatives and benzothiophene (BT) while the major sulfur compounds found in the diesel are alkylated BT, DBT and alkylated derivatives (Bhandari *et al*, 2006). In recent years, the regulation of sulfur level has been revised by the US Environmental Protection Agency (USEPA) that the sulfur concentrations in gasoline and diesel must be reduced from 300 and 500 ppmw to 30 and 15 ppmw by 2006, respectively (Ma *et al.*, 2002). European legislation also limits the sulfur level to less than 50 ppmw for both fuels by 2005. It is expected that similar regulation will be implemented in other countries as well. To reach this target, the effective processes must be applied to control the sulfur content to the acceptable level.

There are several techniques used to remove sulfur compounds from fuels. The most widely used one, conventional hydrodesulfurization (HDS) process operated at elevated temperatures (300-340 ^{o}C) and pressures (20-100 atm H_2) by using Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 as catalysts is highly efficient in removing thiol, sulfides and disulfides but it is not effective for thiophene and thiophene derivatives (Hernandez-Moldonado *et al.*, 2004d). After HDS, 4-methyldibenzothiophene and 4, 6-dimethyl dibenzothiophene, known as refractory sulfur compounds, still remain in the fuels. These compounds, which have low reactivity, are difficult to eliminate by HDS because of the steric hinderance of alkyl groups that obstruct the sulfur atom to the active sites (Kim *et al.*, 2006). In order to reach the standard of sulfur concentration in fuels by using current hydrotreating processes, these processes have to use three times of reactor volume size. It is affected to capital and operating cost because increase in the volume of high-temperature and high-pressure reactor is extremely expensive. The significant octane losses due to saturation of olefins and a large amount of H_2 consumption are also the problems in deep desulfurization process (Ma *et al*., 2002). From these problems, a new process has to be developed so as to produce low-sulfur fuels at ambient temperature and pressure without using H_2.

Adsorption process is a promising approach for desulfurization as it can be operated at ambient conditions and without using H_2. However, adsorbents are another challenge that should be considered to produce the adsorbents that have highly selective to sulfur compounds with a high sulfur capacity. In the past few years, many attempts have been made to develop zeolite-based adsorbents that adsorb sulfur compounds via π-complexation bonding which is stronger than van der Waals interaction, but it can be easily broken by using only increasing temperature or decreasing pressure (Hernandez-Moldonado *et al*., 2004d). Some metal ions can form π-complexation with sulfur compounds such as Cu^+, Ag^+, Ni^{2+}, etc. Thus, modification of zeolitic adsorbents by ion-exchanging between metal ions and supported material is being proposed to prepare new adsorbents for adsorptive removal of refractory sulfur compounds.

This research work focuses on modifying NaY zeolite using Cu^{2+} and Ni^{2+} ions and studying the efficiency in removing refractory sulfur compounds such as benzothiophene, 3-methylthiophene and dibenzothiophene in gasoline and diesel representing fuels, respectively. The metal adsorption isotherms will be generated to examine the metal loading on zeolites and be used to determine the amount of sulfur compound that can adsorb on the ion-exchanged zeolites.