CHAPTER I

INTRODUCTION

There has been increasing the stringent environmental regulations on the sulfur content in transportation fuels. The attention towards these compounds is due to the emission of sulfur oxide (SO_x) that constitutes a significant source of atmospheric pollution. Moreover, even trace levels of sulfur impurities can poison the catalysts used in the refining applications. Consequently, the sulfur content in transportation fuels is reduced by national and international directives all over the world. The U.S. Environmental Protection Agency (U.S. EPA) and the European Parliament promulgated clean-fuel regulations that are lowering the sulfur content of gasoline and diesel fuels that must be reduced to lower than 30 ppmw in gasoline and lower than 15 ppmw in diesel (Hsu and Robinson, 2006). In addition, according to the recently announced Euro V norms, the fuel sulfur content have to be reduced to as low as 10 ppmw (Srivastav and Srivastava, 2009). However, even with the so-called ultra-low sulfur clean fuels, the sulfur contents are still too high for fuel cell applications (Song, 2002) that required the use of a fuel with sulfur content lower than 1 ppmw in order to avoid poisoning and deactivation of the reformer catalyst. To use gasoline or diesel fuels, which are the ideal feeds for fuel cells because of their high energy density, ready availability, and safety and ease for storage, the sulfur concentration should be preferably below 0.1–0.2 ppmw (Hernández *et al.*, 2005a).

Nowadays, conventional hydrodesulfurization (HDS) process has been widely used to remove sulfur compounds from liquid fuels. To meet the new federal government mandates, reactors with volumes 5–15 times larger than those currently used are needed. This makes HDS an inappropriate solution and, thus, the use of adsorption to selectively remove the sulfur compounds at ambient conditions is an excellent option (Hernández and Yang, 2003; Kim *et al.*, 2006; Zhang *et al.*, 2008).

In the adsorptive desulfurization technique, the active adsorbent is placed on a porous, non-reactive substrate that allows high surface area for the adsorption of sulfur compounds. Adsorption occurs when the sulfur molecules attach to the adsorbent and remain there separate from the fuel. There have been great recent interests in developing sorbents for selective desulfurization at ambient temperature and pressure. One of them, chemical complexation adsorbents, such as that for π-complexation, have been utilized in industrial adsorption applications. The π-complexation bonds are stronger than those formed by van der Waals interactions, but they are also weak enough to be broken by traditional engineering means such as increasing temperature and/or decreasing pressure. Hernández and coworkers (2005) used a $CuCl/\gamma\text{-}Al_2O_3$ sorbent prepared by incipient wetness impregnation methods for desulfurization of a commercial diesel fuel (297.2 ppmw S). They found that these cuprous π-complexation sorbents selectively adsorb thiophenic compounds over aromatics and olefins. $CuCl/\gamma\text{-}Al_2O_3$ is a promising sorbent for selective removal of all sulfur compounds from a commercial jet fuel and a BP diesel. Moreover, in 2009, Srivastav and Srivastava studied the usage of commercial grade activated alumina (aluminum oxide) as adsorbent for the removal of sulfur from model oil (dibenzothiophene (DBT) dissolved in n-hexane). They concluded that the alumina could be used as adsorbent for the desulfurization of liquid fuels.

This research aims to study the complexation adsorbents for the desulfurization of simulated hydrocarbon feeds by π-complexation adsorption. As Cu^+ and Ni^{2+} are known for their π-complexation ability, the adsorbents (activated alumina) were impregnated with Cu^+ and Ni^{2+} by using incipient wetness impregnation method and then were characterized their properties by means of BET surface area analysis, as well as particle, structural density and pore volume analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), temperature-programmed desorption (TPD) by thermogravimetric analysis coupled with mass spectrometer (TGA-MS), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and mainly focus on their adsorptive removal of sulfur compounds ability by using inverse gas chromatography (IGC) experiments.