CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Materials

Both NaX, and NaY zeolite adsorbents were provided by Institut Français du Pètrole (IFP, France).

Three thiophenic sulfur compounds used in this study, 3-methylthiophene (C_5H_6S, 99%), benzothiophene (C_8H_6S, 97%), dibenzothiophene ($C_{12}H_8S$, 99%), and decane ($C_{10}H_{22}$, 99%), were purchased from ACROS ORGANICS (New Jersey, USA) which was used to represent diesel.

Isooctane (C_8H_{18}, 99.5%) supplied by FAMITALIA CARLO ERBA (Milan, Italy) was used to represent gasoline whereas *o*-xylene (C_8H_{10}, >98%) was used to represent aromatic compound supplied by Fluka (Switzerland).

3.1.2 Equipment

- Gas Chromatography (HP 5890 Series2) with FID detector and HP-5 column (30 m*0.32mm*0.25mm film thickness)
- 10 μL and 50 μL Micro syringe
- Crimp-cap glass vial with a volume of 20 mL

3.2 Experiment

3.2.1 Preparation of the Adsobents and Simulated Transportation Fuels

3.2.1.1 Adsorbents

NaX and NaY zeolites were weighed and then calcined at 800 degree centigrade with the rate of 10°C/min for 3 hours, where water in the zeolites were completely eliminated. The adsorbents were weighed again to register for their dry weight basis. To adjust the water content of the adsorbents, first the adsorbents were dried at 400 degree centigrade (Moise *et al.*, 2001) with the rate of 10°C/min for 3 hours. Then, the adsorbents were allowed to adsorb moisture from air in the

sealed cabinet in order to vary their water content. The adsorbent weight was then calculated to determine the desired water content (1.5%, 3.0% and 4.5%).

3.2.1.2 Simulated Transportation Fuels

In this study, decane and isooctane were used as simulated transportation fuels to represent diesel and gasoline, respectively. The model sulfur compounds used were benzothiophene (BT) and 3-metylthiophene (3MT) for simulated gasoline and dibenzothiophene (DBT) for simulated diesel. For the single-solute system, the samples were prepared by mixing benzothiophene or 3-methylthiophene with isooctane and dibenzothiophene with decane. The initial sulfur concentration was in the range of 500-3500 ppmw. In the mixed-solute systems, the equal weight ratio of benzothiophene and 3-methylthiophene was mixed with isooctane for simulated gasoline. The initial total sulfur concentration was in the range of 500-4000 ppmw. In order to determine the effect of aromatic content in simulated fuels, *o*-xylene was used at varied concentrations (0%, 4%, 8%, 12% and 16% by weight).

3.2.2 Adsorption of Sulfur Compounds

3.2.2.1 Equilibrium Adsorption

Batch liquid adsorption experiments were carried out in crimp-cap glass vial with a volume of 20 ml. 0.15 g of adsorbent was mixed with 13 g of simulated fuels. Vials were equilibrated on a shaker at room temperature for 5 hours in each system of simulated fuels (Chansa, 2004). Once the system reached equilibrium, samples were withdrawn by using syringe with the volume of 10 µl and then analyzed by gas chromatography (HP 5890 Series2) with FID detector and HP-5 column. Concentration of sulfur compound in the liquid phase was determined before and after adsorption. A simple mass balance was performed to determine amount of sulfur adsorbed on the adsorbent. Then the adsorption isotherms were constructed to evaluate the adsorption capacity and selectivity of the adsorbent. The conditions used for the analysis in this research were summarized in the Table 3.1.

Table 3.1 GC conditions for the analysis

Setting	Condition
Injection temperature	250°C
Oven temperature	50°C/5min, 10°C/min to 250°C, hold for 1 min
Detector temperature	280°C
Carrier gas	Helium 99.99%purity
Injection volume	1 µl

3.2.2.2 Adsorption Isotherms of Sulfur Compounds

Adsorption isotherms of sulfur compounds were constructed by plotting the adsorbed amounts of sulfur compound on the adsorbent versus equilibrium concentration of sulfur compound in the vial. At the beginning, the isotherms were constructed for the sulfur adsorption at 25 degree centigrade. Fuel to adsorbent weight ratio used in this study was fixed at 85 according to the previous study (Chansa, 2004).

After the adsorption isotherms were constructed as described above, the adsorption data were fitted with an appropriate model. The model adsorption isotherm used in this study was Langmiur isotherm which was described as follows (Satterfield, 1991):

Single component

$$Q_A = \frac{Q_{Amax}K_AC_A}{1+K_AC_A}$$

Multi component (Binary system)

$$Q_A = \frac{Q_{Amax}\,K_AC_A}{1+K_AC_A+K_BC_B}$$

$$Q_B = \frac{Q_{Bmax}\,K_BC_B}{1+K_AC_A+K_BC_B}$$

Q_A = adsorption capacity of sulfur compound type A (mmol/g)

Q_B = adsorption capacity of sulfur compound type B (mmol/g)

Q_{Amax} = maximum adsorption capacity of sulfur compound type A (mmol/g)

Q_{Bmax} = maximum adsorption capacity of sulfur compound type B (mmol/g)

K_A = adsorption equilibrium constant of sulfur compound type A $(\mu mol/g)^{-1}$

K_B = adsorption equilibrium constant of sulfur compound type B $(\mu mol/g)^{-1}$

C_A = equilibrium concentration of sulfur compound type A (μmol/g)

C_B = equilibrium concentration of sulfur compound type B (μmol/g)

3.2.3 Desorption of Sulfur Compounds

Batch liquid desorption experiments were set up to study the desorption of sorbed sulfur on NaX and NaY adsorbents. The experiment was started by mixing the simulated fuels and the adsorbents in a vial. The equilibrium time was determined to be 5 hours for each system. When the system reached cquilibrium, samples were withdrawn by using syringe and then analyzed for sulfur concentration by gas chromatography so that the adsorbed amount could be determined. In another identical experimental set up, the adsorption was carried out in exactly the same manner and under the same conditions to study the desorption. After equilibrium, the system was heated up to desired temperature. The temperature used was in the range of 45-75 degree centigrade. When the system reached equilibrium at desired temperature, samples were withdrawn by using syringe and then analyzed by gas chromatography. The concentration of sulfur compounds on NaX and NaY adsorbents and amount of sulfur desorbed were calculated.