

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

NaY zeolite used to exchange cation with metal ions was provided from Institut Français du Pétrole (IFP, France).

$\text{Cu}(\text{NO}_3)_2$  (99-102%) and  $\text{Ni}(\text{NO}_3)_2$  (99%) used to exchange cation in NaY zeolite were purchased from Riedel-deHaen and CARLO ERBA, respectively.

3-methylthiophene ( $\text{C}_6\text{H}_6\text{S}$ , 99%), benzothiophene ( $\text{C}_8\text{H}_6\text{S}$ , 97%) and dibenzothiophene ( $\text{C}_{12}\text{H}_8\text{S}$ , 99%), which represented sulfur compounds in gasoline and diesel models, were purchased from ACROS ORGANICS (New Jersey, USA). Their relevant properties are shown in Table 3.1.

Isooctane ( $\text{C}_8\text{H}_{18}$ , 99.5%) and decane ( $\text{C}_{10}\text{H}_{22}$ , 99%) represented gasoline and diesel were supplied by FAMITALIA CARLO ERBA (Milan, Italy) and ACROS ORGANICS (New Jersey, USA), respectively.

**Table 3.1** Physical properties of sulfur compounds and simulated transportation fuels

Material	Molecular weight	Boiling point (°C)	Density (g cm <sup>-3</sup> )
Isooctane	114.23	99	0.692
Decane	142.15	171-174	0.735
3-Methylthiophene	98.612	114 at 738 mm Hg	-
Benzothiophene	134.195	221	-
Dibenzothiophene	184.255	332-333	-

## 3.2 Methodology

### 3.2.1 Sorbent Preparation

The ion-exchanged zeolites were prepared using the liquid-phase ion-exchange technique (LPIE) at room temperature. Firstly, NaY zeolite was dehydrated at 450°C for 2 hours to remove water adsorbed on zeolite. Secondly, the Cu<sup>2+</sup> and Ni<sup>2+</sup> nitrate solutions : NaY zeolite ratio (S/A) were varied from 50, 100, 200 cm<sup>3</sup>/g-NaY and exchanged at ambient temperature for 48 hours (Xue *et al*, 2005). Next, the ion-exchanged zeolites were filtered by filter paper no.5 and washed with deionized water 1000 cm<sup>3</sup> to remove any salt or excess solution. After that, the sorbents were dried at 110°C overnight and then calcined at 450°C for 2 hours.

### 3.2.2 Characterization of Adsorbents

#### 3.2.2.1 *Atomic Absorption Spectrometer (AAS)*

The amounts of metal loading (Cu<sup>2+</sup>, Ni<sup>2+</sup>) on zeolite were obtained by using Atomic Absorption Spectrometer (Varian, SpectrAA 300 model). Hydrogenfluoric (HF) is used to digest the ion-exchanged zeolites.

#### 3.2.2.2 *Surface Area Analysis (SAA)*

Surface area and pore volume were determined by BET surface area analyzer (Themo Finnigan, Sorptomatic model) and analyzed by nitrogen gas adsorption and desorption. Before analyzed, volatile compounds adsorbed on zeolite or ion-exchanged zeolite must be eliminated by heating the samples at 300°C for at least 3 hours.

#### 3.2.2.3 *X-ray Diffraction Spectroscopy (XRD)*

X-ray diffraction (XRD) analysis was conducted by using a Rigaku, Rint 2200 HV model so as to observe the structure of ion-exchanged zeolite after calcined at 450°C. The instrument was set up by using 2θ 10-70°, scan speed 5°/min, step size 0.04°/s, and slit number is equal to 1, 1, 0.3.

### 3.2.3 Preparation of the Simulated Transportation Fuels

Decane and isooctane were used as simulated transportation fuels to represent diesel and gasoline, respectively. Sulfur compounds used were 3-

methylthiophene (3-MT) and benzothiophene (BT) for isooctane and dibenzothiophene (DBT) for decane. The samples were prepared by mixing 3-methylthiophene or benzothiophene with isooctane and dibenzothiophene with decane.

#### 3.2.4 Adsorption Experiment

Batch liquid adsorption experiments were carried out in a vial 15 cm<sup>3</sup> in which ion-exchanged zeolites and simulated gasoline and diesel were mixed. The ratio of fuel : adsorbent was fixed at 85 (Chansa, 2004) with constant stirring. The equilibrium time was first determined for each system of simulated gasoline and diesel. Once the system reached equilibrium, samples were withdrawn by using syringe and then analyzed by gas chromatography (HP 5890 Series2) with FID detector and HP-5 column (30 m\*0.32mm\*0.25mm film thickness). The conditions of gas chromatography used in this experiment are summarized in Table 3.2.

**Table 3.2** 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

#### 3.2.5 Sulfur Compounds Analysis

Sulfur compounds were analyzed by using gas chromatography (HP 5890 Series2) with FID detector and HP-5 column (30 m\*0.32mm\*0.25mm film thickness). 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.

### 3.2.6 Adsorption Isotherm of Sulfur Compounds

Adsorption isotherms of sulfur compounds were constructed by plotting the adsorbed amounts of sulfur compound on the adsorbent versus metal loading on zeolites in batch reactor. At the beginning, the isotherms were constructed for the sulfur adsorption at 25°C. Fuel to adsorbent weight ratio is initially fixed at 85.

### 3.2.7 Model of Adsorption Isotherm on Sorbents

After the adsorption, isotherms were constructed by varying the concentration of sulfur compounds and that isotherms were fitted with an appropriate model. The model adsorption isotherm used in this study is Langmuir isotherm which can be described as followed:

$$q = \frac{q_{\infty} k C_e}{1 + k C_e}$$

- where,  $q$  = the amount of adsorbed (mole g<sup>-1</sup> adsorbent)  
 $q_{\infty}$  = the maximum amount of adsorbed (mole g<sup>-1</sup> adsorbent)  
 $C_e$  = equilibrium concentration (mole m<sup>-3</sup>)  
 $k$  = the adsorption equilibrium constant (m<sup>3</sup> mole<sup>-1</sup>)