



CHAPTER III EXPERIMENTAL

3.1 Materials

- 3.1.1 Mesoporous (m-Al₂O₃) and macroporous (M-Al₂O₃) activated alumina used as adsorbent were provided by IFP Energies nouvelles. Their physical and chemical properties are shown in Table 3.1
- 3.1.2 Copper (II) chloride (CuCl₂, 97%) and nickel (II) chloride (NiCl₂, 98%) used as a metal precursor impregnated on both activated alumina were purchased from Sigma-Aldrich and Alfa Aesar, respectively.
- 3.1.3 Citric acid, anhydrous (C₆H₈O₇, 99.5+%) used as a dispersing agent was purchased from Alfa Aesar.
- 3.1.4 Toluene (C₇H₈, 99.8%) represented as composition in simulated hydrocarbon feed and used as polar probe molecule in IGC characterization was purchased from Carlo Erba Reactifs - SDS.
- 3.1.5 Dibenzothiophene (C₁₂H₈S, 98%) represented as sulfur compound in simulated hydrocarbon feed was purchased from Alfa Aesar.
- 3.1.6 Thiophene (C₄H₄S, 99%) used as a polar probe molecule in IGC characterization was purchased from Alfa Aesar.
- 3.1.7 Hexane (C₆H₁₄, 99%) used as a probe molecule in IGC characterization was purchased from Carlo Erba Reactifs – SDS.
- 3.1.8 Heptane (C₇H₁₆, 99%) used as a probe molecule in IGC characterization was purchased from Carlo Erba Reactifs – SDS.
- 3.1.9 Octane (C₈H₁₈, 99+%) used as a probe molecule in IGC characterization was purchased from Acros Organics.
- 3.1.10 Nonane (C₉H₂₀, 99%) used as a probe molecule in IGC characterization was purchased from Acros Organics.
- 3.1.11 Decane (C₁₀H₂₂, 99+%) used as a probe molecule in IGC characterization was purchased from Acros Organics.

Their relevant properties are shown in Table 3.2.

Table 3.1 Properties of activated alumina adsorbents

Adsorbent	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Density (g/cm^3)	Boiling Point ($^{\circ}\text{C}$)	Melting Point ($^{\circ}\text{C}$)
m- Al_2O_3	278	0.761	0.914	2,977	2,050
M- Al_2O_3	194	0.674	1.008		

Table 3.2 Physical and chemical properties of chemicals used

Chemicals	Chemical Formula	Structure	Molecular Weight (g/mol)	Boiling Point ($^{\circ}\text{C}$)	Melting Point ($^{\circ}\text{C}$)	Density (g/cm^3)
Copper (II) chloride	CuCl_2	$\text{Cl}-\text{Cu}-\text{Cl}$	134.45	993	498	3.386
Nickel (II) chloride	NiCl_2	$\text{Cl}-\text{Ni}-\text{Cl}$	129.62	-	1,100	3.550
Citric acid	$\text{C}_6\text{H}_8\text{O}_7$		192.124	none ^a	152– 159	1.665
Toluene	C_7H_8		92.14	110– 111	-93	0.865
DBT	$\text{C}_{12}\text{H}_8\text{S}$		184.26	332– 333	97–100	1.252
Thiophene	$\text{C}_4\text{H}_4\text{S}$		84.14	84	-38	1.051
Hexane	C_6H_{14}		86.18	68	-95	0.6603
Heptane	C_7H_{16}		100.21	98.4	-90.61	0.684
Octane	C_8H_{18}		114.23	125.52	-57	0.708
Nonane	C_9H_{20}		128.2	151	-53	0.718
Decane	$\text{C}_{10}\text{H}_{22}$		142.15	174.1	-27.9	0.735

^a Decomposition at the temperature above 175 $^{\circ}\text{C}$.

3.2 Equipments

- 3.2.1 Micromeritics ASAP 2420.
- 3.2.2 Hg porosimeter, AutoPore IV 9500 series.
- 3.2.3 Scanning electron microscopy (SEM), Hitachi S4800 model at PPC and ZEISS SUPRA™40 Model at IFP Energies nouvelles, both coupled with EDX.
- 3.2.4 X-ray diffraction spectroscope (XRD), Rigaku, Rint 2200 HV model.
- 3.2.5 X-ray photoelectron spectroscopy (XPS), KRATOS Axis Ultra ESCA Spectrometer with Al monochromator X-ray source.
- 3.2.6 Temperature-programmed reduction (TPR) (TPD/R/O 1100 Thermo Finnigan with Thermo Quest Program of CE instruments)
- 3.2.7 Thermogravimetric analyzer (TGA) (Perkin Elmer, TGA 7 model)
- 3.2.8 Gas chromatograph, Hewlett Packard 5890 Series II with FID detector.
- 3.2.9 Gas chromatograph, Agilent Technologies 6890N model coupled with both FID and TCD detector and with Galaxie Chromatography Software.
- 3.2.10 Fixed-bed column for reduction in plant T179, IFP Energies nouvelles (1/2" OD, 3/8" ID, 12.5 cm of length)
- 3.2.11 Fixed-bed column for IGC characterization in plant T172, IFP Energies nouvelles (1 cm ID, 10 cm of length)
- 3.2.12 Calcination equipment
- 3.2.13 Oven (Kendro Laboratory Products, D-63450 model)
- 3.2.14 Flowmeter (Agilent Technologies ADM1000)
- 3.2.15 Stub
- 3.2.16 Platinum pan
- 3.2.17 Magnetic stirrer
- 3.2.18 5.0 µL Micro syringe
- 3.2.19 Vial 1.5 cm³
- 3.2.20 Glassware

3.3 Methodology

3.3.1 Adsorbents Preparation

3.3.1.1 *Preparation of Cu⁺ Impregnated on Activated Alumina by Using CuCl₂ in Deionized Water*

Impregnated activated alumina adsorbent was prepared by incipient wetness impregnation method. Firstly, the activated alumina was activated at 350 °C under N₂ flowrate of 50 cm³/h/g with the rate of 5 °C/min for 2 hours in order to remove volatile and its water adsorbed. To impregnate Cu⁺ on the adsorbent, unfortunately CuCl cannot be used because it is insoluble in water. Thus CuCl₂ was used instead because it is very soluble in water. Afterwards, it is necessary to reduce Cu²⁺ to Cu⁺ by means of TPR experiment. A known amount of CuCl₂, calculated from the theoretical monolayer coverage (Gui *et al.*, 1984), was magnetically stirred in a predetermined volume of deionized water sufficient to fill the pores. It involves contacting the support with a solution drop by drop where the activated alumina imbibes the metal-containing solution into its pore structure. The impregnation time was set to reach equilibrium approximately a day. After that the sample was dried and the water was removed under N₂ flowrate of 50 cm³/h/g with the rate of 5 °C/min for 2 hours at 250 °C. The two different adsorbents (the mesoporous and macroporous activated alumina) were prepared with different metal loadings of 10, 20 and 30 % of the theoretical monolayer coverage with CuCl₂, respectively. Finally, the Cu²⁺ cation impregnated on the adsorbent was reduced by using reduction gas (H₂) with the proper amount of heat (reduction temperature was determined by TPR characterization) in order to make a reduction from Cu²⁺ to Cu⁺. Such Cu⁺ modified alumina has a π -complexation activity, needed to study further for sulfur compounds removal.

3.3.1.2 *Preparation of Ni²⁺ Impregnated on Activated Alumina by Using NiCl₂ in Deionized Water*

Impregnated activated alumina adsorbent was prepared by incipient wetness impregnation method. Firstly, the activated alumina was activated at 350 °C under N₂ flowrate of 50 cm³/min/g with the rate of 5 °C/min for 2 hours in order to remove volatile and its water adsorbed. To impregnate Ni²⁺ on the

adsorbent, NiCl₂ was used. A known amount of NiCl₂ was magnetically stirred in deionized water (NiCl₂ monolayer was calculated). A volume of the solution equal to the total pore volume of the adsorbent was brought into contact with the activated alumina drop by drop where the activated alumina imbibes the metal-containing solution into its pore structure. The impregnation time was set until it reach equilibrium which is approximately a day. Finally, the sample was dried where the water was removed under N₂ flowrate of 50 cm³/min/g with the rate of 5 °C/min for 2 hours at 250 °C. The two different adsorbents (the mesoporous and macroporous activated alumina) were prepared with different metal loadings of 10, 20 and 30 % of the theoretical monolayer coverage with NiCl₂, respectively.

3.3.1.3 Preparation of Cu²⁺ with Dispersing Agent (Citric Acid, CA) Impregnated on Activated Alumina by Using CuCl₂ and CA in Deionized Water

The CuCl₂ dispersion over the surface of alumina adsorbent may be inappropriate to be used as an adsorbent for ultra deep desulfurization. For example, a molecule of dibenzothiophene (DBT), which is a big sulfur molecule remaining in the fuel, is really hard to be removed in the desulfurization process. Its steric hindrance is one of the limitations. To modify the adsorbent for a better sulfur adsorption activity, the dispersion of the CuCl₂ has to be improved. In this study, citric acid (CA) was used as a dispersing agent.

Impregnated activated alumina (both mesoporous and macroporous alumina) modified with dispersing agent was prepared mainly by the incipient wetness impregnation method. The step of preparation was quite the same as aforementioned method but with a different metal-containing solution. These adsorbents were prepared by using copper chloride (CuCl₂) mixed together with dispersing agent (CA). They were prepared with different metal loadings of 10 and 30 % CuCl₂, respectively, and with different Cu/CA molar ratios of 2.5, 5 and 10, respectively, in order to study the metal dispersion. The impregnation time was set for 24 hours (Golden *et al.*, 1992; Golden *et al.*, 2003).

3.3.2 Reduction

The CuCl_2 impregnated on alumina was reduced to Cu^+ by using reduction gas (H_2). This procedure is necessary because stable Cu^+ salt is water-insoluble, and CuCl_2 must be used instead. The reduction condition was obtained from TPR characterization. One gram of CuCl_2 impregnated on alumina placed in a fixed-bed column was reduced to Cu^+ under H_2 atmosphere at a flow rate of $75 \text{ cm}^3/\text{min}/\text{g}$, heated up to 300°C at a heating rate of $5^\circ\text{C}/\text{min}$ then hold for 2 hours. Then the temperature was reduced to ambient temperature.

3.3.3 Characterization of the Adsorbents

3.3.3.1 *BET Surface Area of the Adsorbents*

The BET surface area was measured by Nitrogen adsorption/desorption method at 77 K using Micromeritics ASAP 2420. To eliminate adsorbed volatile compounds from the pores, before being analyzed, adsorbents were dried and evacuated at 300°C for at least 3 hours.

3.3.3.2 *Particle Density, Structural Density and Pore volume of the Adsorbents*

The particle density, structural density and pore volume of the adsorbents were measured by Mercury porosimeter, AutoPore IV 9500 series.

3.3.3.3 *Temperature-Program Reduction (TPR)*

The temperature of reduction Cu^{2+} to Cu^+ was obtained by using temperature-programmed reduction (TPR) (TPD/R/O 1100 Thermo Finnigan with Thermo Quest Program of CE instruments). The amount of adsorbent used is approximately 0.1 g and it was held in place by glass wool plugs. The gas mixture used was 4.95% H_2 in N_2 at flow rate of $20 \text{ cm}^3/\text{min}$, the heating rate was $10^\circ\text{C}/\text{min}$. The analysis temperature was 900°C , hold at this temperature for 2 hours, and after that cooled down to room temperature.

3.3.3.4 *Scanning Electron Microscopy (SEM) Coupled with Energy Dispersive X-Ray Spectroscopy (EDX)*

The porosity within the adsorbents and the metal dispersion over the adsorbents were studied by using SEM (Hitachi S4800 model) coupled with energy dispersive X-ray spectroscopy (EDX). It was performed on the cut impregnated samples. The samples were fractured at the cross section to study the

internal surface. The cut samples were coated with Pt before examination. Simultaneous detection of Cu or Ni was performed by energy-dispersive X-ray spectroscopy (EDX). The analysis was done at both PPC and IFP Energies nouvelles. At PPC, it was done at a resolution of 30 k, a working distance (WD) of 3.8 mm at 1.5 kV under high vacuum and ambient temperature and at IFP Energies nouvelles, it was done at a resolution of 60 k, a working distance (WD) of 8.3 mm at 15.0 kV under high vacuum and ambient temperature. These samples were observed by backscattered electrons (chemical contrast) mode.

3.3.3.5 *X-Ray Diffraction (XRD)*

X-ray diffraction (XRD) (Rigaku, Rint 2200 HV model) analysis was conducted to verify the structure of the adsorbents after modification by impregnation and heat treatment (calcined at 350 °C) by comparing with the original structure of the activated alumina.

3.3.3.6 *X-Ray Photoelectron Spectroscopy (XPS)*

X-ray photoelectron spectroscopy (XPS) (KRATOS Axis Ultra ESCA Spectrometer with Al monochromator X-ray source) was used to characterize the elemental surface composition of the metal compounds. The samples were analyzed at the surface of about 5–10 nm depth below the surface. In the case of references, samples were protected from air for humidity and O₂ control. For the technical parameters used in this characterization, the excitation energy was 1486.6 eV, the excitation power was 15 kV and 10 mA, the energy pitches were 40 eV, and the surface area for analysis was 700 by 300 μm. The position of the calibration spectrum was made on the carbon contamination at 284.6 eV. The results (wt%) were estimated on the average of two tests with a maximum relative error of +/- 20%.

3.3.3.7 *Temperature-Programmed Desorption (TPD) Experiments by using Thermogravimetric Analysis Coupled with Mass Spectrometer (TGA-MS)*

These techniques were used to study the adsorption or desorption of some sulfur compounds on the solid adsorbents, and to compare the results obtained from non-impregnated samples with impregnated ones.

The samples were first heated to remove adsorbed water, and then put into contact with a solution of a sulfur compound to allow the adsorption on

the solids. In this work, dibenzothiophene (DBT) in toluene with different concentrations (1, 3 and 5 wt% DBT in toluene) were used as simulated hydrocarbon feeds. After a given time, long enough to reach equilibrium which is approximately five days, the samples were placed in the thermogravimetry apparatus (TGA-MS), and then heated under helium flowrate of 3 nL/h (50 cm³/min) from ambient temperature to elevated temperature of 800 °C at the heating rate of 10 °C/min. The desorption profiles and the mass losses were obtained. The metal dispersion informations can be determined by comparing the desorption profiles on non-impregnated adsorbents with those on impregnated adsorbents and by comparing the different desorption profiles derived from different simulated hydrocarbon feeds on the same adsorbent. Similar additional experiments have been done with pure toluene and pure thiophene instead of Toluene/DBT solutions.

3.3.3.8 Inverse Gas Chromatography (IGC)

Chromatographic measurements were carried out with a Agilent Technologies 6890N gas chromatograph with a thermal conductivity detector (TCD). The adsorbent was placed into a 10 cm length of stainless steel column, with passivated inner walls and an inside diameter of 1 cm. In order to obtain an homogeneous packing, the adsorbents were crushed, and then sieved to give the diameter approximately of 500 µm. Especially for copper impregnated sorbents, the reduction step was applied by flowing a hydrogen flowrate of 75 cm³/min/g for 2 h, at 300 °C. Then it was introduced in small quantities, accompanied by mechanical vibration. In order to avoid the effect of packed-bed length, the adsorbent loading used in this work was obviously filled in the column in the amount of approximately 5 grams. The column was then stabilized on the GC system at 300 °C for 2 hours and at working temperature of 200 °C for 14 hours under a helium flowrate of 2 nL/h. This flowrate turned out to be the best compromise for diffusion and nonequilibrium effects in various test experiments (Díaz *et al.*, 2004a; Thielmann and Baumgarten, 2000). In order to avoid detector contamination, the outlet of the column was not connected to the detector during this period.

The injector and detector temperatures were set at 200 and 250 °C, respectively. Measurements were carried out in the temperature range of 200–250 °C. Helium was used as carrier gas, and flowrates were measured using a

calibrated Agilent Technologies ADM1000 gas flowmeter. Injections were carried out with a syringe via the manual injector port of the chromatographic device. In order to meet the requirement of adsorption at infinite dilution, symmetry of the peaks and retention times reproducible, amounts injected were in the range from 0.5 to 5.0 μL . The chromatograms were collected with a Galaxie Chromatography Data System (version 1.9.301.220), and the retention times were determined at the peak maxima (Perruchot *et al.*, 2006). For each measurement, at least two repeated injections were taken, obtaining reproducible results. From the evaluated retention time (t_R , min) and flow rate (F , cm^3/min) of the carrier gas, the retention volume (V_R , cm^3) was calculated. The specific retention volume, V_g (cm^3/g) is given as (Díaz *et al.*, 2004a):

$$V_g = Fj \frac{(t_R - t_M)}{m} \left(\frac{p_0 - p_w}{p_0} \right) \left(\frac{T}{T_{\text{meter}}} \right), \quad (1)$$

where t_R is the retention time (min), t_M the retention time of non-adsorbing marker (hold up time), p_0 the outlet column pressure, p_i the inlet pressure, (Pa), T the column temperature, T_{amb} , the ambient temperature (K), and j the James–Martin compressibility factor defined as:

$$j = \frac{3}{2} \left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \right]. \quad (2)$$

In this study, thermodynamic parameters for adsorption of hydrocarbons (*n*-alkanes, C_6 – C_{10}), aromatic compound (toluene), and sulfur compound (thiophene) on pure aluminas and modified aluminas were determined in the infinite dilution region, in the so-called Henry's law region (Díaz *et al.*, 2004b). The molecular probes are injected at infinite dilution in order to rule-out lateral probe–probe interactions and favor probe–stationary phase (gas–solid) interactions only. These solutes have been chosen in order to characterize the surface thermodynamic properties of the packed material and analyze the influence of molecular structure in adsorption.

Thermodynamic data describing the adsorption process were derived from the temperature dependence of the specific retention volume. At low

surface coverage, the heat of adsorption is obtained by plotting $\ln V_g$ against $1/T$, according to the following equation:

$$\Delta H_{\text{ads}} = -R \frac{\partial(\ln V_g)}{\partial(1/T)}. \quad (3)$$

At infinite dilution, the standard free energy to transfer 1 mol of adsorbate from the gas phase to the surface at standard state, defined as the variation in the standard free energy of adsorption, ΔG_{ads} (J/mol), can be expressed as:

$$\Delta G_{\text{ads}} = -RT \ln \left[\frac{p_0 V_g}{\pi_0 A} \right] \quad (4)$$

or its equivalent form

$$\Delta G_{\text{ads}} = -RT \ln V_g + C, \quad (5)$$

where A is the specific surface area, and π_0 is the spreading pressure of the adsorbed gas in the De Boer standard state, which was taken as $338 \mu\text{N/m}$ (Díaz *et al.*, 2004a). The parameter, C , is a constant related to the standard states. The standard free energy of adsorption takes into account the standard free energy of adsorption of polar solutes on solid surfaces, namely, the dispersive contribution, $\Delta G_{\text{ads}}^{\text{d}}$, and the specific contribution, $\Delta G_{\text{ads}}^{\text{s}}$ (Montes-Morán *et al.*, 2002),

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\text{d}} + \Delta G_{\text{ads}}^{\text{s}}. \quad (6)$$

One of the most commonly measured parameters for the description of the energetic situation on the surface of a solid is the surface energy. The surface energy is defined as the energy required to form (or increase the surface by) a unit surface under reversible conditions and is the analogue to the surface tension of a liquid. This means in practical terms that the higher the surface energy the more reactive the surface. This can affect for example catalytic activity or the strength of particle–particle interaction (Thielmann, 2004).

As in the case of the free energy of adsorption, the surface free energy of the adsorbent, γ_s (J/m²), may be split into dispersion, γ_s^{d} , and specific,

γ_s^s , contributions, corresponding to the dispersion and specific interactions, respectively (Bailey and Persaud, 1998):

$$\gamma_s = \gamma_s^d + \gamma_s^s. \quad (7)$$

For solid materials, London dispersive interactions are usually described by the dispersive component of the free surface energy (γ_s^d). A standard method by IGC to determine γ_s^d of the stationary phase relies on the use of a series of linear alkane molecular probes. Dorris and Gray proposed that the dispersive free energy component (γ_s^d) of the stationary phase be related to the free energy of adsorption of a methylene group by:

$$\gamma_s^d = \frac{1}{4} \frac{\Delta G_{\text{CH}_2}^2}{\gamma_{\text{CH}_2} N^2 a_{\text{CH}_2}^2}, \quad (8)$$

where N is the Avogadro number, a_{CH_2} is the area occupied by a $-\text{CH}_2$ group (0.06 nm^2), and γ_{CH_2} (mJ/m^2) is the surface free energy of a solid material constituted by methylene groups only, which is a function of temperature:

$$\gamma_{\text{CH}_2} = 35.6 + 0.058(20 - T), \quad (9)$$

where T is the column temperature in $^\circ\text{C}$.

The term, ΔG_{CH_2} , corresponds to the free energy of adsorption of a methylene group and is defined as the energy difference for the adsorption of two successive alkanes (Herry *et al.*, 2001), and is calculated from:

$$\Delta G_{\text{CH}_2} = -RT \ln \frac{V_{g(n)}}{V_{g(n+1)}}, \quad (10)$$

where $V_{g(n)}$ and $V_{g(n+1)}$ are the specific retention volumes of two consecutive n -alkanes having n and $(n + 1)$ carbon atoms, respectively. ΔG_{CH_2} is independent of the reference state of the adsorbed molecule (Milonjić, 1999). The plot of ΔG_{ads} values versus the number of carbon atoms, χ_T , results in a linear correlation. The slope of the straight line corresponds to the free energy of adsorption of a methylene group (ΔG_{CH_2}).

The specific component (γ_s^s) of the surface free energy is closely related with the parameter of specific interaction of polar solutes (I^{sp}). The specific interactions are the interactions other than London or dispersive interactions. This parameter involves the surface properties in terms of polar, ionic electrical, magnetic, metallic, and acid–base interactions and may be determined from the difference of free energy of adsorption, $\Delta(\Delta G)$, between a polar solute and the real or hypothetical *n*-alkanes:

$$\gamma_s^s = I^{sp} = \frac{|\Delta(\Delta G)|}{Na_p}, \quad (11)$$

where a_p is the polar solute surface area. In this work, a_p , is calculated from the liquid density, ρ , and the molar weight of the solute, M , assuming spherical molecular shape in a hexagonal close-packed configuration:

$$a_p = 1.09 \times 10^{14} \left(\frac{M}{\rho N} \right)^{2/3} \quad (12)$$

where 10^{14} is the conversion factor in order to convert from cm^2 to nm^2 .

To compare the thermodynamic parameters, for example, γ_s^s or I^{sp} , of the polar probe molecules (toluene and thiophene) with non-polar probe molecules (*n*-alkanes, C_6 – C_{10}) which is a reference, it is necessary to compare them on the same basis namely the same carbon atoms number, χ_T .

The equivalent carbon atoms number or topological index (χ_T) were obtained by performing the topological index via Wiener index method. The χ_T of toluene and thiophene are 6.26 (Brendlé and Papirer, 1997b) and 3.84, respectively. The calculation procedures are described in Appendix B.

3.3.4 Preparation of the Simulated Hydrocarbon Feeds

To make a solution for pre-adsorption analysis, DBT was chosen to be used as a sulfur compound and toluene was used as a hydrocarbon feed (solvent).

The solution was prepared in various concentrations which are 1, 3 and 5 wt% DBT in toluene.

3.3.5 Adsorption of DBT in Toluene on Activated Alumina

The chosen adsorbents (non-impregnated and impregnated alumina) were placed in a small bottle where adsorption takes place. The amount of adsorbent used was 0.5 g. Then a precise DBT in toluene solution was added into the bottle. Typical ratio is 0.5 g of adsorbent per 5 g of simulated hydrocarbon feeds. To allow the adsorption reaches its equilibrium, normally it takes more than a day so let the adsorption occur for 5 days. While let the adsorption go, shake it from time to time. At equilibrium, the adsorbents that adsorbed sulfur compounds were studied by using TGA-MS in order to determine how sulfur compounds can be adsorbed (at which temperature that they can desorb); to study the effect of aromatics on the adsorption and to figure out that the studied adsorbent is whether well-dispersed or not.

Furthermore, monolayer adsorption is significant to study. It is necessary to determine the monolayer adsorption because the TGA-MS results will lead misunderstanding if there is a multilayer adsorption on the analyzed adsorbent, thus, the sufficient concentration of simulated hydrocarbon feeds was studied by varying the concentration of simulated hydrocarbon feeds at 0, 1, 3 and 5 wt% DBT in toluene. The adsorbents that were used to adsorb those sulfur compounds in different simulated hydrocarbon feeds were further studied by TGA-MS.