



ORIGINAL ARTICLE

Silica, alumina and aluminosilicates as solid stationary phases in gas chromatography



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Abstract Silica, alumina and Aluminosilicates of different Si/Al ratios were prepared by conventional precipitation or co-precipitation methods and then subjected to thermal treatment at 800 °C. The parent and thermally treated materials were characterized by means of FTIR, SEM and thermal analysis (DTA and TGA) in order to elucidate the main structural properties. Surface textural characteristics were investigated by means of nitrogen adsorption–desorption isotherms at –196 °C. Pore size distribution curves indicated the presence of mesopores (10–150 Å) exhibiting maxima at 35 Å. The maxima were shifted toward higher values by increasing the alumina content. Thermodynamic parameters, ΔH , ΔG and ΔS , were determined by means of inverse gas chromatography using *n*-hexane as a probe. The untreated and thermally treated materials were tested as solid stationary phases in gas chromatography. The separation efficiency of various non polar and polar compounds was explained in terms of surface texture and thermodynamic parameters.

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1. Introduction

Numerous scientific publications mention the use of silica or alumina as stationary phase in gas chromatography (Halpaap, 1973; Kiselev, 1970; Mikhail et al., 1979). Silica and alumina offer surface properties covering wide range of acidity, surface

reactivity and pore structure (Mikhail et al., 1979; El-fadly et al., 1997; Faramawy et al., 1997). Silica gel is an amorphous form of SiO₂ with a very porous structure and the surface of the hydrated silica is covered with hydroxyl groups which are attached to silicon atoms, and these surface hydroxyls may be classified into free and bound hydroxyl groups (Iller, 1979; Synderm and Ward, 1966). The activity of alumina is affected by two main factors, namely the chemical nature of the surface, which involves the number of hydroxyl groups and acid sites on the surface, as well as the texture of the solid, and the availability of various reactants to reach an active site which depends on the pore sizes and their distribution (Mikhail et al., 1979). These packing materials are characterized by the high selectivity, thermal stability and resistance to different external factors (Cagniant, 1992; Pool and Pool, 1992; Rykowska

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and Wasiak, 2000). The thermodynamic parameters of these packings form a good base to study interactions between solid stationary phases and the adsorbate molecules (El-Naggar and Turkey, 2001; El-Naggar, 2006; Voelkel, 2009).

The presented work is devoted to different silica–alumina ratios and both their thermal treatment and their polymer coated. Such solid samples may be used as packings in gas chromatography. These modifications offer the additional advantages of improving separation and increasing peak capacity. The effect of different ratios of silica–alumina and the correlations between the types of modification and the surface characteristics (e.g., surface area, pore volume and pore radii) and gas chromatographic separation are studied in order to select the adequate stationary phase to elute the components of the mixture.

2. Experimental

2.1. Preparation of solid phases

The reagents used for the preparation are: Aluminium sulfate $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (Adwic), Sodium silicate (water glass; Winlab), Hydrochloric acid (Adwic) and Ammonium hydroxide (Adwic).

2.1.1. Preparation of alumina

Aluminium hydroxide was precipitated from 500 ml of 0.4 M aluminium sulfate using ammonium hydroxide (pH 12) as a precipitant. The hydroxide gel was then left to age overnight then freed from sulfate ions by decantation and washing several times with deionized water till the filtrate was sulfate free. Filtration was carried out using centered glass G-4. The filtrate was then dried at 110 °C to a constant weight. The produced pieces were crushed and sieved using sieves between (0.4–0.16 mm); the resulting sample mesh size was 35–80 mesh. The obtained solid was calcined at 250 °C.

2.1.2. Preparation of silica

Mesoporous silica was obtained from a solution of water glass containing ~27 wt% sodium silicate using concentrated HCl as precipitating agent. Silicic acid was precipitated at pH ~4. The precipitate was aged for 24 h, filtered and dried at 110 °C overnight. The solid obtained was washed with deionized water several times till the filtrate was chloride ion free. Then, silica gel was dried, crushed and sieved as mentioned above. The obtained silica gel was calcined at 250 °C.

2.1.3. Preparation of different silica–alumina ratios

The silica gel–alumina ratios were precipitated by the addition of aluminium sulfate solution (0.4 M) to sodium silicate solution (27 wt% $\text{Na}_2\text{O} \cdot \text{SiO}_2$). Then, a complete precipitation was achieved using concentrated HCl as a precipitant. The precipitate was aged, filtered, washed and dried according to the procedure mentioned in the case of silica preparation. Also, the obtained solids were crushed, sieved and calcined in a similar manner. In this context, five solids of silica–alumina ratios were prepared using the same technique but with different weights of the raw materials aluminium sulfate and sodium silicate as given in Table 1.

The hydro silica–alumina gel was precipitated by the same addition of sodium silicate to aluminium sulfate in the case of silica–alumina containing relative high alumina concentrations. Then, a complete precipitation was achieved using concentrated ammonium hydroxide solution (pH 12) as a precipitant. The precipitate was aged, filtered, washed and dried according to the procedure mentioned in the case of alumina preparation. Also, the obtained solids were crushed, sieved and calcined in a similar manner.

The precipitation of silica–alumina ratios, following the procedures mentioned above, could be different than those cited in the literature (de Boer, 1971; Yao et al., 2002). The obtained solids could exhibit some characteristics and textural properties which could be different than those of conventional silica, alumina or silica–alumina. This may reflect on their behaviors as solid stationary phases in gas chromatographic applications.

2.2. Methods of modification

2.2.1. Thermal Treatment

The above mentioned prepared samples were calcined in a muffle furnace at 800 °C for 18 h.

2.2.2. Coating with polyethylene glycol

The parent silica–alumina samples, when used as solid support, were coated with polyethylene glycol (Carbowax 20 M) as liquid stationary phase (El-Naggar and Turkey, 2001; Aue et al., 1973). The parent samples were coated with layer thickness 25% (w/w) by a conventional technique of rotary evaporation. The polymer was dissolved in a suitable solvent (chloroform) and deposited on each parent sample by slow evaporation of the solvent with gentle stirring and heating in a rotary evaporation until complete evaporation of the chloroform. The coated samples were dried at 120 °C for 24 h. The

Table 1 Codes of abbreviation of the studied solids and the results of Gravimetric analysis.

% Silica expected	Parent solids	Thermally treated solids	Gravimetric analysis	
			% of Silica	% of Alumina
100% Alumina	Al	Al-T	—	100
10% Silica	AlSi(8)	AlSi(8)-T	8.0	92.0
30% Silica	AlSi(26)	AlSi(26)-T	26.0	74.0
50% Silica	AlSi(39)	AlSi(39)-T	39.0	61.0
70% Silica	AlSi(57)	AlSi(57)-T	57.0	43.0
90% Silica	AlSi(77)	AlSi(77)-T	77.0	23.0
100% Silica	Si	Si-T	100	—

coated samples were packed with the aid of a mechanical vibrator into stainless steel columns. The packed column was activated at moderate temperature (120–170 °C) in a stream of nitrogen according to the maximum recommended temperature of the used polymer.

2.3. Characterization of solid materials

2.3.1. Gravimetric analysis

Silica content in the samples was determined gravimetrically via dissolution of SiO₂ in HF (Vogel, 1961).

2.3.2. Thermal analysis

Thermal analysis including thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the studied samples, were carried out using Scimadzu apparatus with detector type Scimadzu TGA-50H (for TGA) and Schimadzu DTA-50H (for DTA). The instrument settings were as follows:

Cell	Platinum
Atmosphere	Nitrogen
Rate Flow	20.00 [ml/min]
Temperature	From ambient to 1200.0 °C
Heating Rate	10 °C/min

2.3.3. Scanning electron microscope (SEM)

SEM micrographs were carried out using equipment of JEOL (Japan) model JSM-5500. The samples were examined after gold plating was carried out. The magnification range was from 650 to 20,000.

2.3.4. Fourier transform infrared spectroscopy (FTIR)

The infrared spectra were obtained using FTIR-Perkin Elmer (USA)-Spectrum-I, Supplied with Selector Diffuse Reflectance (Specac) and Environmental Chamber (Specac). The samples were examined under vacuum at 150 °C for parent and thermally treated samples. The sample percent with KBr was kept constant (5% wt/wt).

2.3.5. Surface textural characteristics

Surface textural characteristics including surface area (S_{BET}), pore volume, pore radius and pore size distribution, were measured using nitrogen adsorption technique at low temperature. The instrument used was Quantachrome-Nova 2000. The gas used was nitrogen, and bath temperature was 77.35°K.

The adsorbent was first thoroughly out gassed at 200 °C for 3 h to 10⁻⁵ Torr. Specific surface area was measured through the application of the BET (Brunauer, Emmett, and Teller) equation (Brunauer et al., 1938) in its normal range of applicability. The porosity was detected by applying the BJH (Barret, Joyner, and Halenda) method (Barrett et al., 1951).

2.4. Gas chromatography

All parent, modified and coated samples were tested in gas chromatography to evaluate their efficiency when used as a solid stationary phases. The gas chromatograph used was Agilent 6890⁺ (England) equipped with a flame ionization detector (FID). Temperature of both the detector and injector

was maintained at 350 °C. Nitrogen was used as the mobile phase at optimum flow rate of 35 ml min⁻¹.

The column used was a stainless steel tube of 2 m in length and 1/8 inch of internal diameter. The columns are first washed with dilute hydrochloric acid, then with deionized water and finally with acetone. The columns were then purged with dry air until complete dryness. The packing with the investigated samples inside the column was achieved under vacuum. The packed columns were activated at 300 °C for parent and thermally treated samples and at 200 °C for coated packed column under flow of nitrogen (30 ml min⁻¹). The solutes used for chromatographic characterization were selected to cover the wide range of polarity such as natural gas, *n*-paraffin, aromatic hydrocarbons, *n*-alcohols and ketones as well as petroleum fraction (C₆–C₂₀). The polarity indices were assessed with respect to the reference non-polar column SE-30 (20% SE-30 on chromosorb W.A.W., 60–80 mesh).

2.5. Thermodynamic parameters (El-Naggar, 2006)

The thermodynamic parameters were measured from the retention chromatographic data obtained from the gas chromatography mentioned above as follows:-

n-hexane was injected at five different temperatures on the studied parent and modified stationary phases. The enthalpies ΔH were calculated from the relation between the logarithm of retention time and reciprocal of temperature. Accordingly, ΔH can be determined from the slope of this relation:

$$t_m = \text{LAB}/F \exp(-\Delta H/RT)$$

where t_m = retention time, R = linear velocity of zone, A = intestinal area of column, B = constant, F = gas velocity, and ΔH = The enthalpy.

The excess partial molar free energy of solution can be expressed as:-

$$\Delta G = RT \log V_g$$

where T is the column temperature and V_g is the retention volume.

The entropy of solution can be calculated by knowing ΔH and ΔG from the relation:

$$\Delta S = (\Delta H - \Delta G)/T$$

In this study, ΔH and ΔS are calculated at temperature 110 °C.

$$\Delta S = (\Delta H - \Delta G)/T$$

3. Results and Discussion

3.1. Gravimetric analysis

The prepared solids silica–alumina ratios were analyzed gravimetrically in order to elucidate their basic composition. The codes of abbreviations of the studied solids and the results of the analysis are given in Table 1. It is obvious that silica content is always lower than what is expected in the parent reaction mixture utilized in the preparation of the investigated solids, namely, aluminum sulfate and sodium silicate solutions. The decrease of silica content in the thermally pretreated samples as compared with the composition of the parent reaction mixture seemed to be dependent on the original silica precursor, ageing, and Al₂O₃ content in the reaction mixture.

The composition of the reaction mixture seemed to be critical toward the stability of hydrous gel which may be reflected on the silica content in the prepared silica–alumina samples.

3.2. Scanning electron microscopy

The objective of the analysis using SEM is to study the morphology of the silica–alumina samples. Fig. 1 shows the scanning electron micrograph, taken with a magnification order ranging from 650 to 20,000. The micrograph of alumina

shows an amorphous phase containing different types of pores. These pores could cover a wide range of sizes. With respect to the silica sample, the micrograph indicates amorphous gel of non-porous material beside a slight porosity. For silica–alumina samples, it has been noticed that the porosity increases by increasing the alumina content.

One may expect that the prepared samples give different surface textural properties which could reflect on their performance as solid stationary phases in gas chromatographic separation.

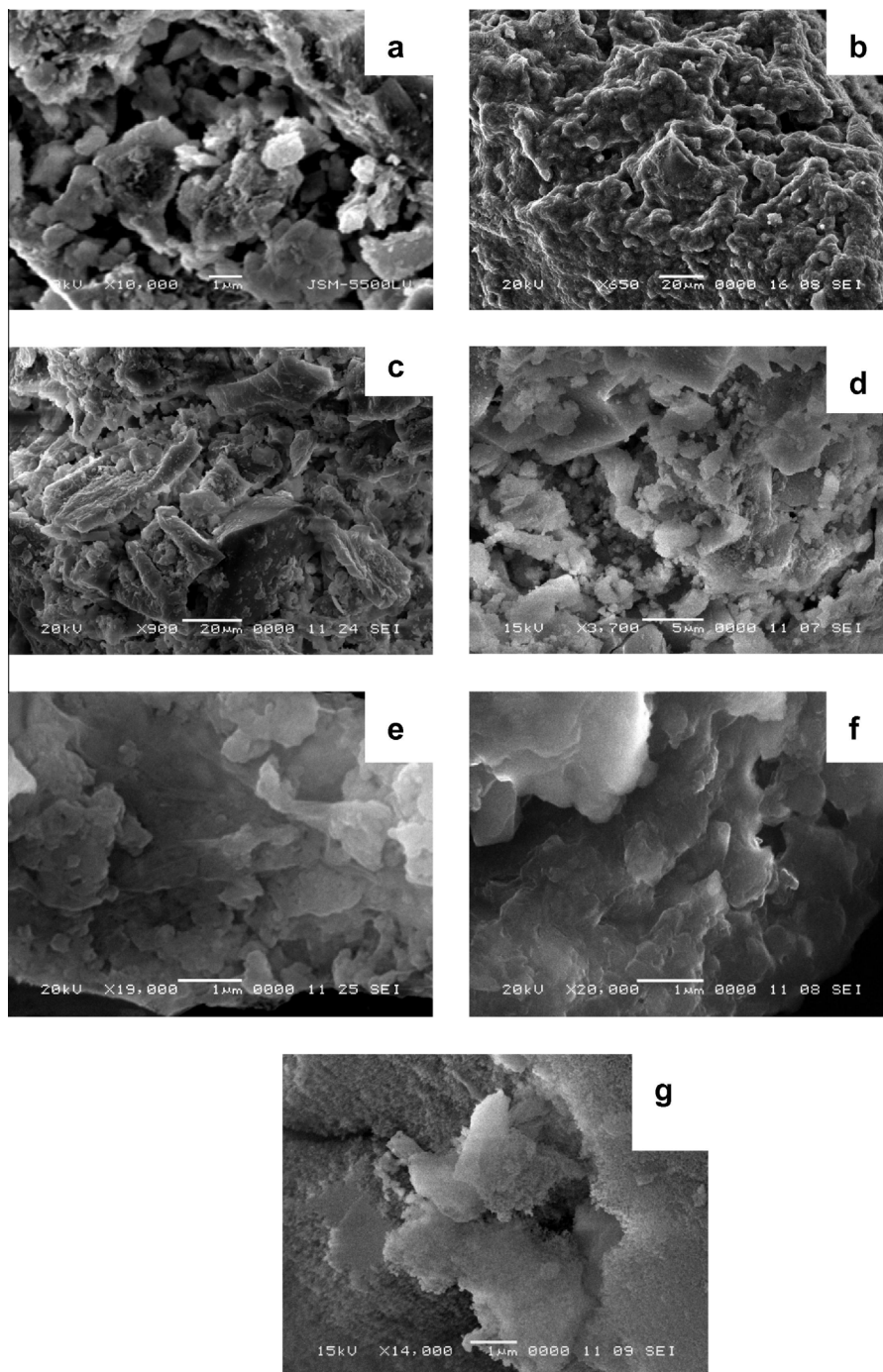


Figure 1 Scanning electron microscope micrographs for the parent samples namely: (a) Al; (b) AlSi(8); (c) AlSi(26); (d) AlSi(39); (e) AlSi(57); (f) AlSi(77); and (g) Si.

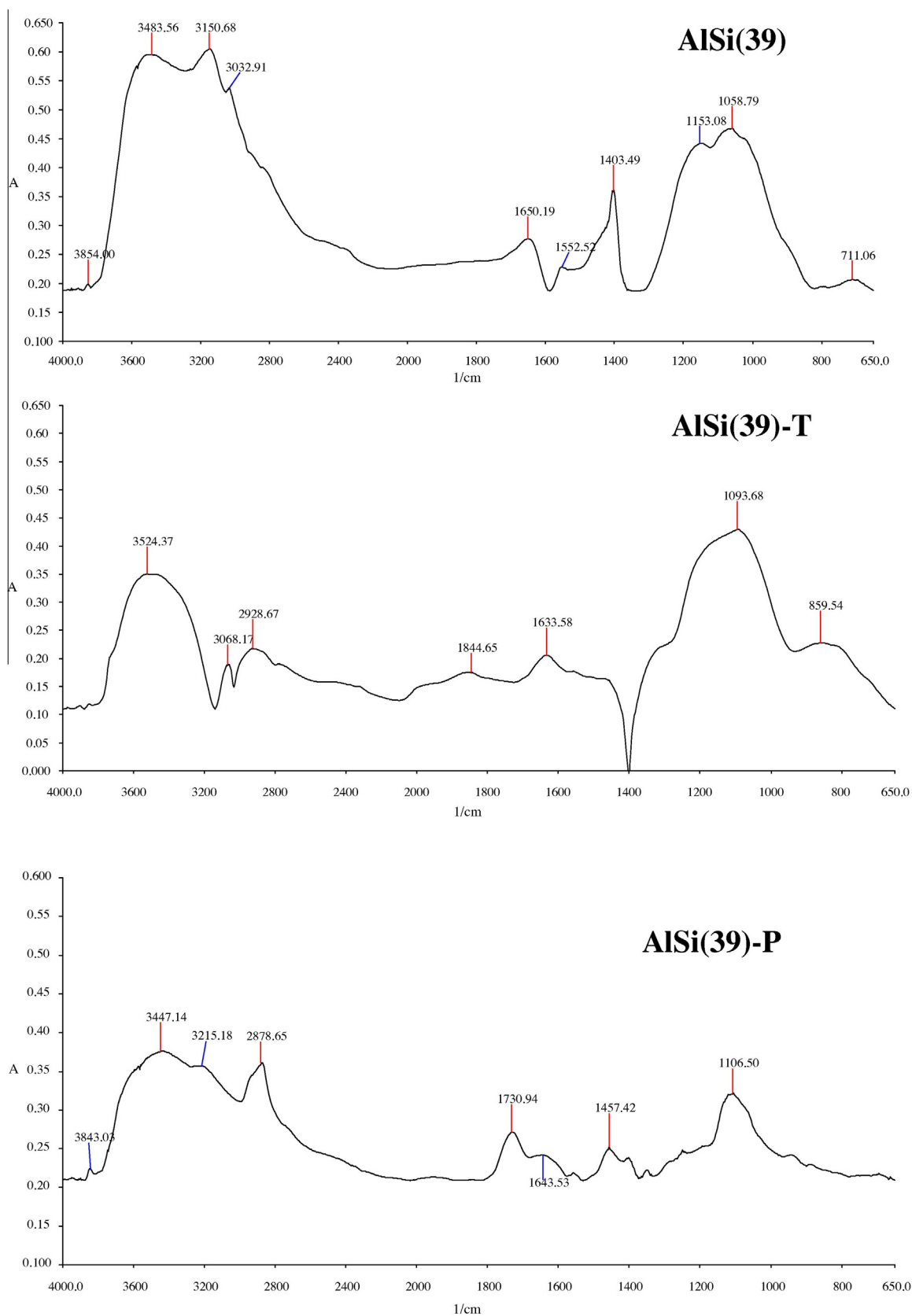


Figure 2 The spectra of parent [AlSi(39)], thermally treated [AlSi(39)-T], and polymer coated [AlSi(39)-P] samples.

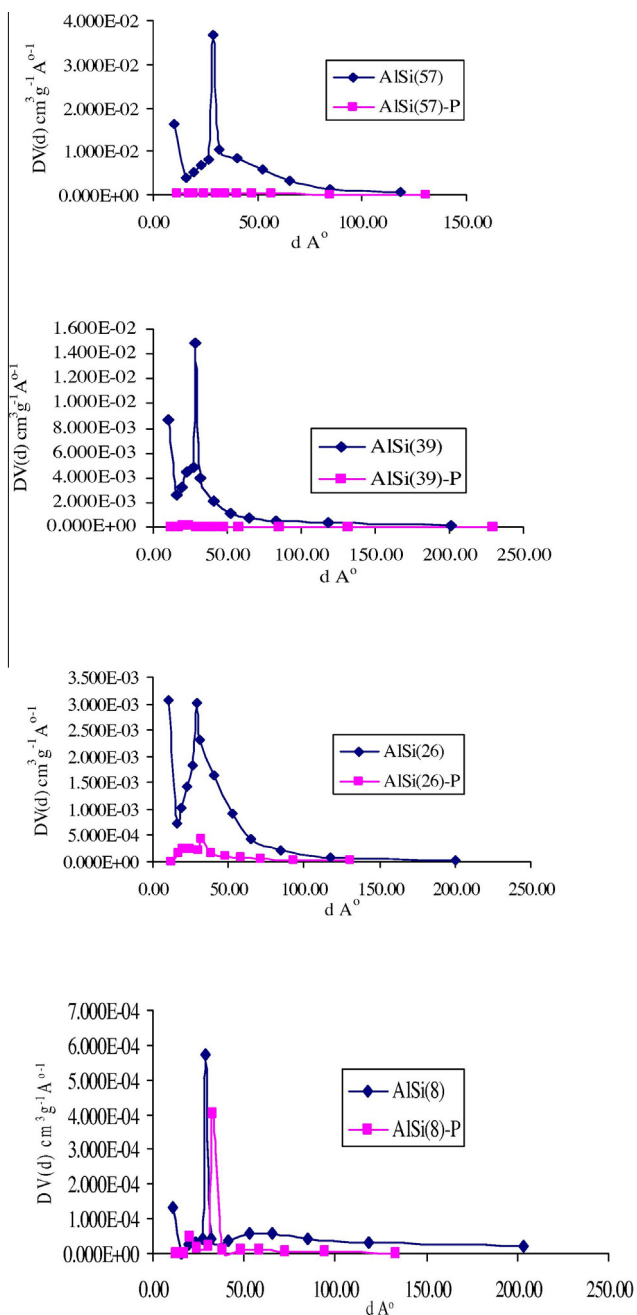


Figure 3 PSD for selected silica–alumina samples.

Table 2 Surface characteristics of parent samples.

Sample ID	V_p ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	\bar{r} (\AA)	BET-C
Al	0.033	19.814	33.310	61.306
AlSi(8)	0.011	3.736	58.893	144.457
AlSi(26)	0.089	76.283	23.334	81.857
AlSi(39)	0.194	182.125	21.304	80.000
AlSi(57)	0.476	401.009	23.740	109.000
AlSi(77)	0.155	118.455	26.170	92.250
Si	0.064	12.302	104.050	145.490

Table 3 surface characteristic of thermally treated samples.

Sample ID	V_p ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	\bar{r} (\AA)	BET-C
Al-T	0.184	88.841	41.422	164.000
AlSi(8)-T	0.204	85.706	47.605	255.000
AlSi(26)-T	0.167	109.275	30.565	100.000
AlSi(39)-T	0.160	117.185	27.307	62.167
AlSi(57)-T	0.194	163.097	23.790	67.000
AlSi(77)-T	0.100	39.379	50.789	158.149
Si-T	0.005	5.125	19.510	4.211

Table 4 surface characteristic of polymer coated samples.

Sample ID	V_p ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	\bar{r} (\AA)	BET-C
Al-P	0.004	2.846	28.109	5.644
AlSi(8)-P	0.001	0.681	29.379	3.332
AlSi(26)-P	0.010	8.458	23.647	4.016
AlSi(39)-P	0.032	2.261	283.088	5.896
AlSi(57)-P	0.034	12.743	53.100	26.589
AlSi(77)-P	0.311	55.895	111.280	87.545
Si-P	0.006	4.434	27.067	4.082

Table 5 Percent of polymer covering on the solid surfaces.

Sample ID	$V_{p2_{\text{parent}}}$	$V_{p1_{\text{coated}}}$	$\alpha\%$
Al	0.0326	0.004	87.730
SiAl(8)	0.0111	0.001	90.909
SiAl(26)	0.0890	0.010	88.764
SiAl(39)	0.1942	0.032	83.934
SiAl(57)	0.4758	0.034	92.854
SiAl(77)	0.1549	0.311	High percent
Si	0.0636	0.006	90.566

3.3. Fourier transform infrared (FTIR) spectroscopy Okkerse, 1970; Peri, 1965; Saravanan and Subramanian, 2005

The prepared, thermally treated and coated samples were subjected to FTIR spectroscopy. An example of spectra is shown in Fig. 2. Generally, the spectrum consists of two regions (hydroxyl group and structural regions). It was stated in the literature that the strength and abundance of the acidic surface OH groups play an important role on the adsorption properties of polar and non-polar solutes. Accordingly, we are reporting the changes that occurred in this region as a result of thermal treating and decreasing the silica content Fig. 3.

The spectrum of the coated silica–alumina sample exhibits additional peaks mainly at 1745 cm^{-1} assigned for polyethylene glycol.

3.4. Thermal analysis (DTA and TGA)

The parent samples were subjected to differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) to investigate changes that might occur during thermal treatment. The temperature range adopted for this purpose was from ambient up to $1200 \text{ }^\circ\text{C}$.

Table 6 Thermodynamic parameters of silica–alumina samples using *n*-hexane.

Stationary Phase	$-\Delta H$ (Kcal mol ⁻¹)	$-\Delta G$ (Kcal mol ⁻¹)	ΔS (cal mol ⁻¹ deg ⁻¹)
Al	6.947	5.988	-1.869
AlSi(8)	5.027	5.553	1.111
AlSi(26)	6.285	6.519	0.495
AlSi(39)	8.451	8.428	-3.944
AlSi(57)	8.445	7.279	-2.465
AlSi(77)	4.920	5.544	1.321
Si	0.684	2.164	3.128

Table 7 Thermodynamic parameters of thermally treated samples using *n*-hexane as a prob.

Stationary Phase	$-\Delta H$ (Kcal mol ⁻¹)	$-\Delta G$ (Kcal mol ⁻¹)	ΔS (cal mol ⁻¹ deg ⁻¹)
Al-T	8.108	7.518	-1.186
AlSi(8)-T	8.118	6.837	-2.571
AlSi(26)-T	8.003	6.485	-3.209
AlSi(39)-T	7.114	6.114	-2.115
AlSi(57)-T	8.725	7.085	-3.465
AlSi(77)-T	2.774	5.471	5.702
Si-T	0.788	4.097	7.822

Table 8 Thermodynamic parameters of polymer coated solid supports using *n*-hexane as a prob.

Stationary Phase	$-\Delta H$ (Kcal mol ⁻¹)	$-\Delta G$ (Kcal mol ⁻¹)	ΔS (cal mol ⁻¹ deg ⁻¹)
Al P	1.385	4.024	7.075
AlSi(8)-P	1.306	3.211	5.249
AlSi(26)-P	1.387	4.037	7.104
AlSi(39)-P	1.068	1.935	2.323
AlSi(57)-P	8.779	5.394	-9.075
AlSi(77)-P	4.987	5.133	0.391
Si-P	1.865	3.514	4.419

Generally, the all studied treated and untreated solid samples are stable at the working chromatographic temperature 300 °C except the coated ones at only 225 °C which is the maximum recommended temperature of the poly ethylene glycols. The DTA thermograms reveal endothermic peaks at 345 °C and 380 °C, which are due to dehydration of hydroxide. And any exothermic peaks are due to the solid phase change.

3.5. Surface textural properties

The adsorption–desorption isotherms of nitrogen at -196 °C obtained on the treated and untreated silica–alumina samples, were of type IV isotherm according to Brunauer *et al.* classification (Brunauer *et al.*, 1940). The observed hysteresis of the isotherm for all samples indicates the mesoporosity character. It was observed that, in some cases the internal area in the hysteresis is opened, this may be due to swelling of the adsorbent in the course of adsorption (Sing, 2001). The adsorption data are summarized in Tables 2–4, the Results including sur-

face area (*S*), pore volume (*V_p*), pore radius (\bar{r}) and BET-C constant estimated from the saturation values of adsorption isotherms.

From the results, the surface areas and pore volume of alumina and silica are much lower than those of the silica–alumina solids. Moreover, the sample containing 57 wt% SiO₂ exhibits the maximum values of surface area and pore volume. The major phase of this solid is porous silica–alumina. In contrast, the other silica–alumina samples contain a considerable portion of either free alumina or free silica. In conclusion, the combination of alumina and silica forming silica–alumina, upon precipitation and heat treatment, improves the surface textural properties as a porous solid support.

For thermally treated samples, alumina and alumina-rich samples showed an increase of surface area and pore volume. This is due to the dehydration of aluminium hydroxide and dehydrated alumina during calcinations. This leads to the formation of a well known porous alumina solid. For silica and silica-rich sample, the surface area and pore volume decrease after thermal treatment. This may due to deformation of polymeric structure of silica via removing of hydroxyl groups. It was stated in the literature that the removal of hydroxyl group from the surface of silica leads to a decrease in the adsorption, and the surface acquires more hydrophobic properties (Cooper, 1989).

Parent silica exhibits highest pore radius and BET-C constant than parent alumina and parent silica–alumina solids. In contrast, the thermally treated silica and polymer coated silica samples exhibit lowest value of both pore radius and BET-C constant than the other thermally treated and polymer coated solid samples may be due to treatment techniques.

In a rough approximation, the percentage of pore volume occupied by polymer, $\alpha\%$, could be derived from the pore volumes of coated samples and the corresponding solid support (*V_{p1}* and *V_{p2}*, respectively) according to the following equation:

$$\alpha\% = (V_{p2} - V_{p1}) \times \frac{100}{V_{p2}}$$

The values of $\alpha\%$ are also given in Table 5. It can be noticed that most of the volume of pores are occupied by the polymer. This could be explained based on the mechanism of the coating process and the allowed surface of the monolayer coverage. In this context, one can point out that the most of solid support, exceptionally AlSi(57) gave small values of surface area. Accordingly, the amount of polymer consumed for surface coverage is relatively lower than that used for the pore filling. The load percentage used for the polymer coating was kept constant, viz., 25 wt%, for the studied solid support. In some cases having very low surface areas, it can be expected that multilayer or aggregates polymeric structure may be formed in their surface texture.

For pore Size analysis (Barrett *et al.*, 1951), the distribution curves of some selected solids and their modifications are given in Fig. 5. For the parent solids, the curves indicate the presence of mesopores having pore diameters in the range of 10–150 Å exhibiting maxima at ~30 Å. This indicates that most of the surface is located in the mesopores region. Upon calcinations, the maxima are shifted to higher value ~35 Å. Moreover, this shift increases by increasing the alumina content. For the coated samples, the distribution curves indicate that most of the pores are occupied by the polymer.

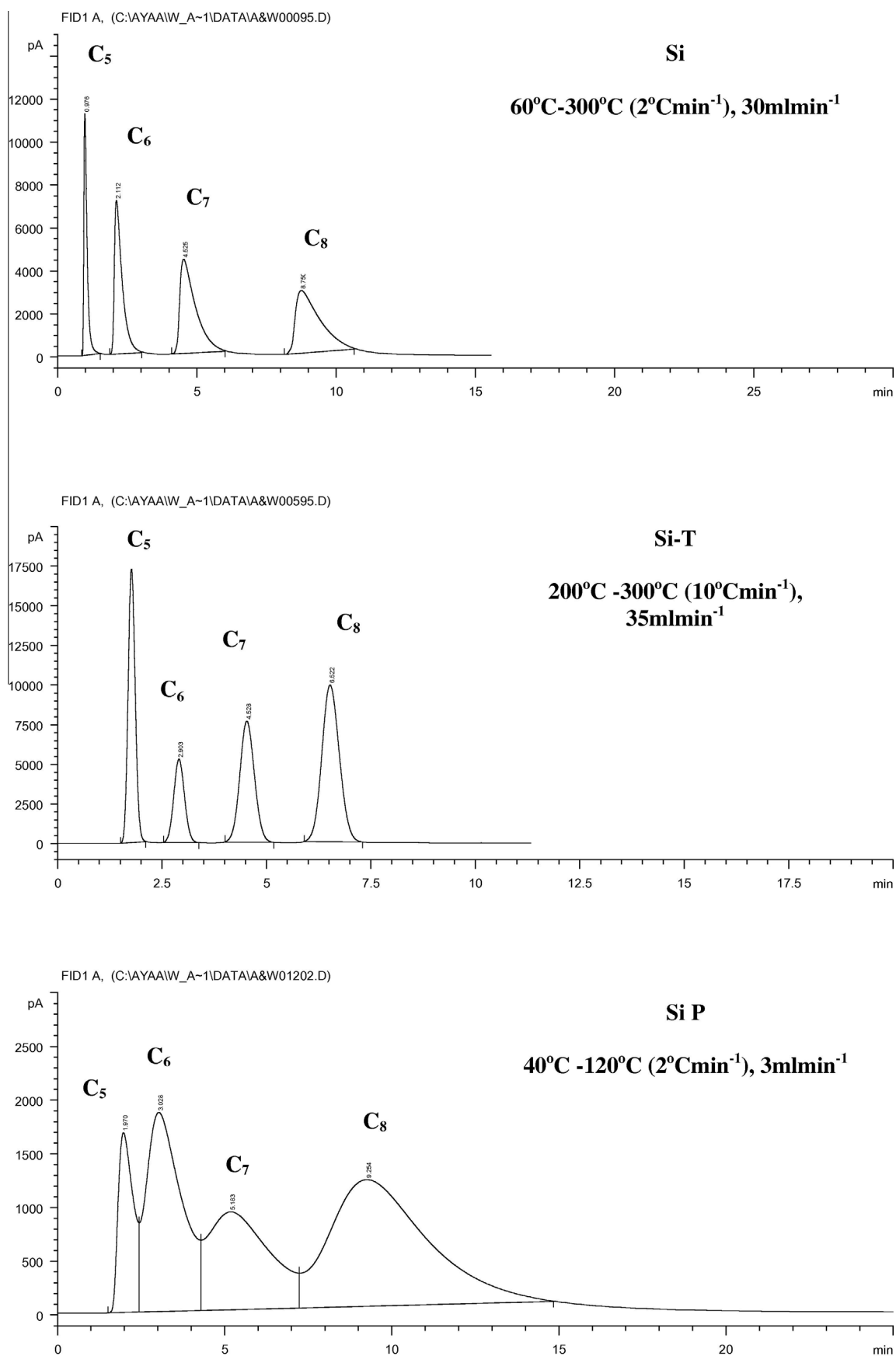


Figure 4 Gas chromatographic separation of paraffins using the parent and modified silica samples at the optimum conditions.

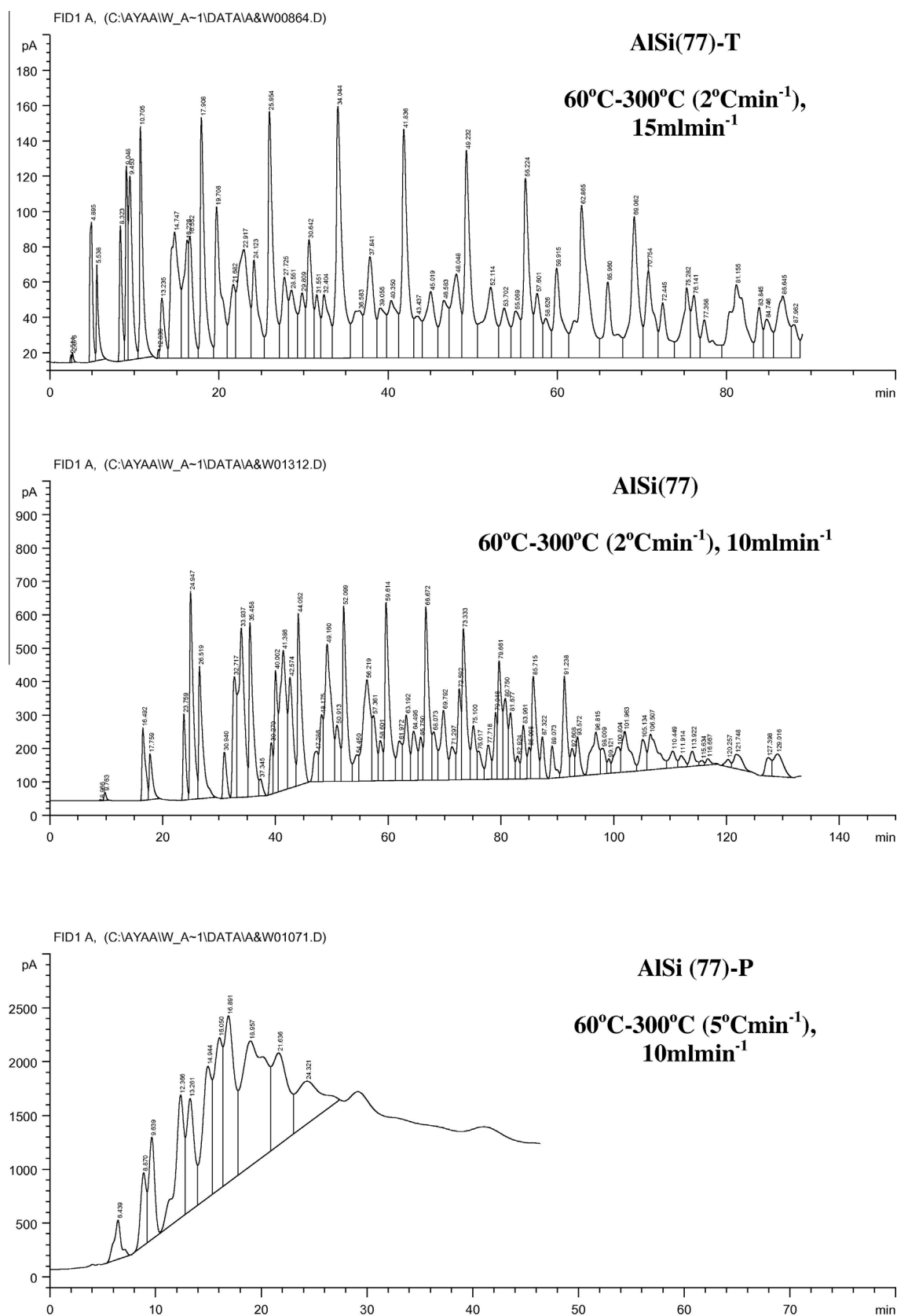


Figure 5 Gas chromatographic separation of mixture of petroleum saturated compound (C₆+) using the parent and modified AISi (77) samples at the optimum conditions.

3.6. Chromatographic characterizations

3.6.1. Thermodynamic parameters

Data, presented in Tables 6–8, indicate that the thermodynamic parameters (ΔH and ΔG) for **Al** and **Al-T** solids have higher negative values than those of **Si** and **Si-T** solids. This may be due to the higher surface area of both **Al** and **Al-T**, which may reflect on greater interaction between the adsorbate (*n*-hexane) and the surface of both the solids (Barrett et al., 1951).

Silica solids, either untreated or thermally treated (**Si** or **Si-T**), exhibited good separation of *n*-paraffins. For the alumina solids (**Al** and **Al-T**), the untreated solid shows a bad gas chromatographic separation. In contrast, the thermally treated alumina as solid stationary phase separated *n*-paraffins. With respect to the coated solids (**Al-P** and **Si-P**) showed the bad separation of *n*-paraffins. This is due to deposition of polymer macromolecules as multi-layer and aggregates on the surface of alumina and silica.

It was found that ΔS has negative values for **Al** and positive values for **Si**, which indicate that the adsorption produces a more ordered system on **Al** solid surface. In conclusion, **Si** stationary phase is preferred than **Al** stationary phase in the separation of paraffinic mixture.

For silica–alumina samples, it was observed that the **AlSi(57)**, **AlSi(57)-T**, and **AlSi(57)-P** solid samples gave higher values of (ΔH and ΔS) than those of the other silica–alumina samples indicating the high reactivity of the surface of these solid stationary phases. This is in agreement with the data obtained from the N_2 -adsorption measurements which indicate that **AlSi(57)** has the highest surface area and pore volume.

Thermal treatment of the studied silica, alumina and silica–alumina samples was preferred as a modification technique compared with the parent and the coated samples. This leads to short time of gas chromatographic separation of paraffinic hydrocarbons as shown in Figs. 4 and 5. It was observed that the silica–alumina solids, except **AlSi(8)**, showed a better separation than alumina and silica. Separation was improved when these samples are thermally treated. In this context, one should refer to the pore structural characteristics of the silica–alumina solids. It was mentioned that silica–alumina have much better porosity than silica and alumina. Moreover, the pore size distribution curves indicated that the pore diameter has been shifted to a larger range upon thermal treatment.

From the result obtained, it may be expected that **AlSi(77)** and **Si** solids **AlSi(77)-T** and **Si-T** solids are selectively able to separate a mixture of aromatic compounds and ketones or a mixture of aromatic compounds and fused nitrogen compounds. However, high efficiency of separation could be obtained by using the stationary phase **AlSi(77)-T**.

4. Conclusions

- (1) I-SEM micrographs showed an amorphous phase of alumina containing different types of pores and amorphous gel of non-porous material of silica. For silica–alumina samples, it was noticed that the porosity increased by increasing the alumina content.

- (2) The all studied treated and untreated solid samples are stable at the working chromatographic temperature 300 °C except the coated ones at only 225 °C which is the maximum recommended temperature of the poly ethylene glycols.
- (3) Surface area and pore volume of alumina and silica were much lower than those of the silica–alumina solids reaching the maximum for **AlSi(57)**. The combination of alumina and silica forming silica–alumina, upon precipitation and heat treatment, improves the surface textural properties as a porous solid support.
- (4) 4-Results of $\alpha\%$ and surface area indicated that the amount of polymer consumed for surface coverage is relatively lower than that used for the pore filling. It can be concluded that multilayer or aggregates polymeric structure may be formed in the surface texture of the coated samples.
- (5) 5-Pore size distribution analysis of the parent solids showed the presence of mesopores having pore diameters in the range of 10–150 Å exhibiting maxima at ~ 30 Å. Upon calcinations, the maxima were shifted to higher value ~ 35 Å. Moreover, this shift increased by increasing the alumina content. For the coated samples, the distribution curves indicate that the most of pores are occupied by polymer. This could be confirmed from the other assessed surface textural parameters.
- (6) 6-Thermodynamic parameters indicated that thermal treatment of the studied silica, alumina and silica–alumina samples was preferred as a modification technique compared with the parent and the coated samples tackling lower duration of gas chromatographic separation of paraffinic hydrocarbons. This is due to the enhancement of mesoporosity by thermal treatment adopted at 800 °C.

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