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Calcination and alkali metal modification of alumina as solid stationary phase in GC

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Abstract

Alumina has unique textural properties and functionalized surface. The single or multi-treatments of alumina with calcination and alkali metal treatment (NaCl) are of prime one importance not only for determining the structure, textural and surface chemistry of the phase but also to understand how modification is related to the changes in these properties and also to the change in its performance as solid stationary phase. Thermodynamic parameters (ΔH, ΔG and ΔS) were determined using n-hexane as a probe in order to show the adsorbate-adsorbent interaction. It was observed that the non-polar solutes could be separated independent of the reactivity and porosity of the alumina surfaces. Alkali metal modification of the calciened alumina is a selective stationary phase for eluting natural gas sample exhibiting good separation.

Key Words:- Alkali metal; Calcinations; Solid stationary phases; Thermodynamic parameters.

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Introduction

The main driver for gas chromatography (GC) is the column and the stationary phase. Thus, using packing that is characterized by high selectivity and effectiveness is a base requirement for GC separation of complex mixtures. Modifications of stationary phases continue with advances in deactivating and coating techniques (1-4). This permits for many applications to be optimized and realized, which had been earlier thought to be impossible by GC. Solid adsorbents such as molecular sieves, porous polymer beads, graphitized carbon black, alumina, and silica gel are widely used as stationary phases for packed column. This shows highly selective separation especially for gases, volatile polar and non polar compounds, sulfur gases and hydrocarbon impurities air pollutants e.g. CO, CO_2 in air, …..etc.

Alumina (Al_2O_3) is known as a good adsorbent for gas-solid chromatographic separation (5) (9) and of large specific surface area solid support (6) (25), a model for the liquid phase distribution is covered with two different types of liquid films, a monolayer and a bulk liquid layer, depending on liquid loading.

In the present study alumina was selected to investigate the influence of several surface modification on the separation performance and stability of such stationary phases. These materials have relative high stability potential and can be synthesized from inexpensive starting materials (7). Moreover, it can be easily modified by different techniques such as calcinations and alkali metal treatment. These modifications can improve the separation, reduce peak asymmety and lower retention times.

Experimental

1. Preparation of alumina (7)

Alumina (aluminum hydroxide gel) was precipitated from a solution of 25% wt/v $Al_2(SO_4)_3.18H_2O$ from Winlab, Cat. No.102183. Precipitation was made using ammonia solution of pH=12, and the precipitation pH was adjusted at 8.6. After complete precipitation the gel was stirred for 30min, aged at 90°C for 24hr, washed with deionized water until free from sulphate and dried at 120°C till constant weight. The dried alumina sample was then crushed and sieved to 60-80 mesh. The concentration of OH^- is decided by the pH value of the precipitation reagent, which is adjusted by ammonia water.

2. Modification methods

a) Calcination (8)

alumina samples were calcined in a muffle furnace at 500°C for 16hr and at 1000°C for 5h to stabilize the number and type of active sites.

b) Treating with alkali metal:

The modification of the surface properties of alumina with alkali metal chloride (NaCl) is described for parent and calcined samples dependence on a 10% salt loading. This was performed by evaporating 30 ml of a solution containing 15g of the alumina samples and 1.67g of NaCl on a water-bath with occasional stirring. This salt-coated alumina was dried for 3h at 120°C and then post heated at 750°C for 2h (9).

Table (1): Notation of the prepared alumina samples

Notation	Treatments
Al	Parent alumina (60-80 mesh)
Al_{C500}	Alumina calcined at 500°C
Al_C	Alumina calcined at 1000°C
$Al_{Na10\%}$	Alumina coating with NaCl and then calcined at 700°C
$Al_{CNa10\%}$	Calcined alumina coating with NaCl and then calcined at 700°C

3. Methods of characterization

3.1. Thermal analysis (10)

Thermal analysis (TGA & DTA) was carried out in the temperature range ambient - 1000°C at a heating rate of 10°C /min and under a flow of Ar using Rigaku Thermo Plus 2 TG-DTA TG8120 to trace the structural changes brought about by the thermal treatment

3.2. Fourier transforms infrared spectroscopy (FTIR) (11)

Infrared Spectroscopic Analysis (FTIR) was carried out to characterize the main constituents of the prepared samples using FTIR-Perkin Elmer-Spectrum-I, Supplied with Selector Diffuse Reflectance (Specac) and Environmental Chamber (Speecac). The samples were examined under vacuum at 150°C. The sample percent with KBr powder was kept constant (5% wt/wt). Workbench Spectra were recorded from 5000 to 600cm^{-1}. For each sample, 32 scans were accumulated at a spectral resolution of 4cm^{-1}.

Results and Discussions

Figure 1 (a-d) illustrates the differential thermal analysis (DTA) and thermal gravimetric profiles (TGA) of parent and modified alumina samples; Al, Al_{C500}, Al_{Na} and Al_{CNa}. The TGA & DTA analysis of Al sample is shown in Fig. (1-a) The curves can be divided into several regions. Between ambient temperature and 210^{o}C, both TG and DTA, indicate the release of free bound water (12). Between 230 and 480oC, TGA and DTA show pronounced change; these changes have been reported to be related to the release of crystallization water (13). The endotherm centered on 400oC is well developed and covers a wide range of temperature region. An exothermic peak around 500oC is also shown in Fig. (1-a) which may indicate a phase change corresponding to the transition from pseudo-boehmite into γ-Al2O3, which occurs through partial dehydroxylation (14). TGA curve for Al_{C500} (Fig. 1-b), show only desorption of physical adsorbed water. It is not surprising to the author to find no thermal change upon heating alumina precalcined at 1000^{o}C. This particular sample is of extremely low surface and pore volume as well as water sorption center-free surface.

Table (2): Weight loss% of parent and modified alumina samples

Temp. ^{o}C	**Weight loss %**						
	Al	**Al_{C500}**	**Al_{C}**	**Al_{HT}**	**Al_{CHT}**	**Al_{Na}**	**Al_{CNa}**
100	7.195	4.377	-	1.994	0.45	1.3	2.05
200	11.657	9.454	-	2.862	0.6	2.8	2.8
300	14.786	11.366	-	3.448	0.97	3.3	3.1
400	20.634	12.47	-	6.17	2	4.5	3.2
500	25.387	13.287	-	16.955	12.22	4.6	3.8
600	26.328	13.872	-	17.896	14.763	4.6	3.8
700	26.875	14.392	-	18.384	15.348	4.6	3.8
800	27.422	14.828	-	18.677	15.571	4.6	3.8

Figure (1) shows weight loss curves for parent and modified alumina samples. From this figure and the data presented in Table (2). Parent alumina exhibits the lowest stability. Modification by any of the methods applied is associated with a pronounced increase in the thermal stability. Parent alumina is characterized by high surface area, high porosity and OH groups-rich surface. Modifications decreased the weight loss, this decrease depending on the modification process.

Weight %

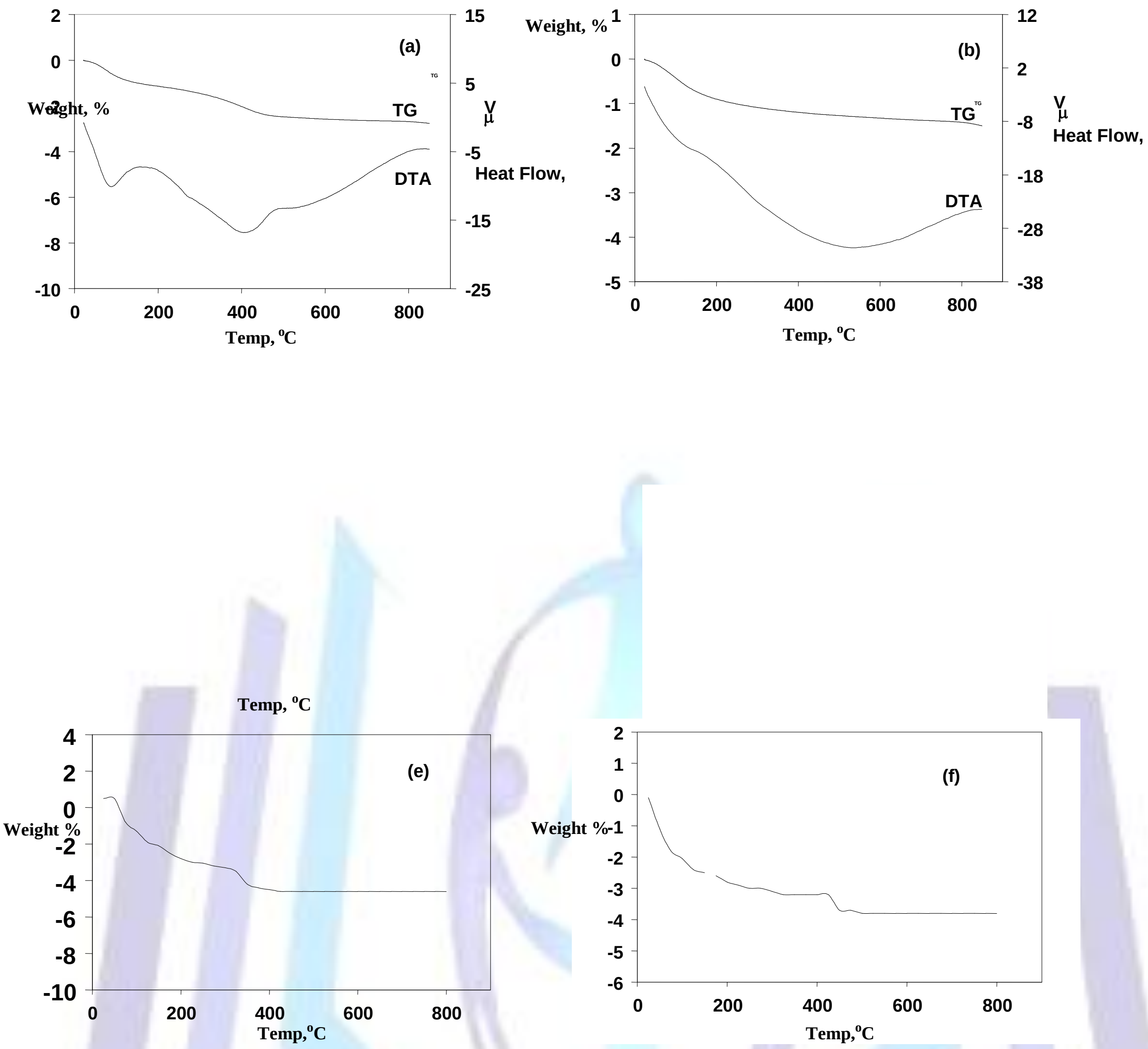


Fig. (1): DTA and TGA profiles for
a) Al b) Al_{C500^oC}

c) $Al_{Na\ 10\%}$ d) $Al_{CNa10\%}$

Figure (2), shows the FTIR spectrograms of Al_{Na} and Al_{CNa} respectively. Table (3) lists the bands, band location and band assignment when these spectrograms are compared with that of Al, one can suggest that, the most pronounced effect of treating alumina with NaCl is the decrease of the intensity and area of the -OH band located at 3566cm^{-1}, i.e. the band characteristic of the surface OH and the formation of sodium aluminate (15).

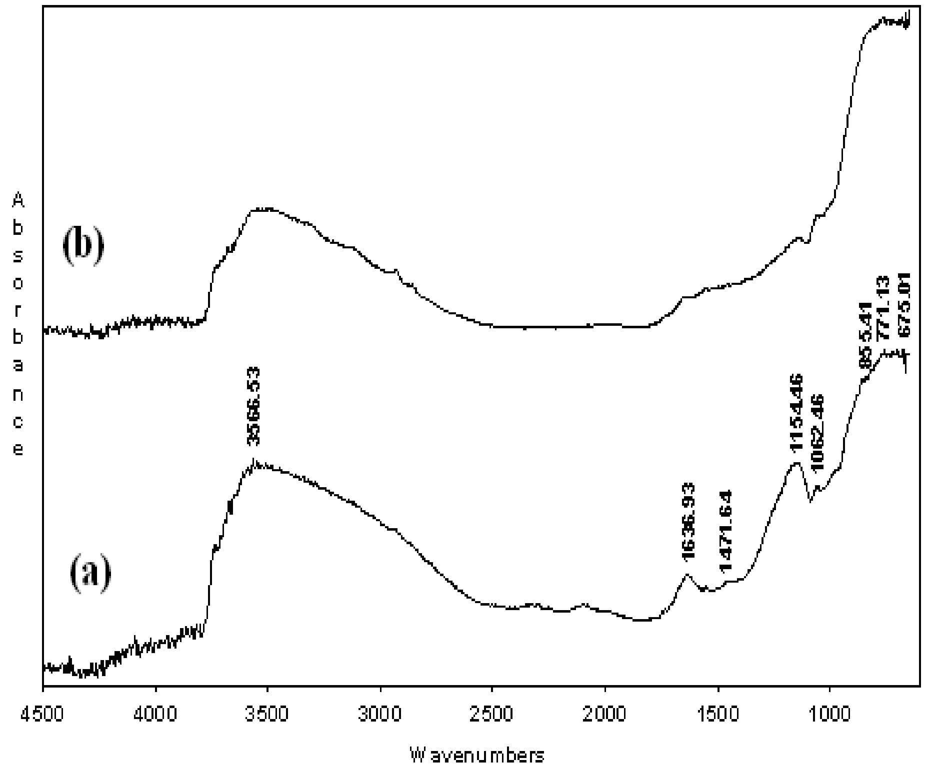


Figure (2): DRIFT spectra of a- Al_{Na}& b- Al_{CNa}.

With respect to alumina and modified alumina stationary phases (Table 4). It is clear that, alumina stationary phase has highest thermodynamic parameter values indicating that the strong interaction of this adsorbent with adsorbate. It remains now

Table (3): DRIFT bands that characterizing alkali metal treated alumina samples

Bands cm^{-1}	**Assignment**	**Absorbance**	
		Al_{Na}	**Al_{CNa}**
3566	The hydroxyl groups adsorbed on the surface (for free Al2O3)	0.38	0.31
1636	Bending of the H–O–H bonds	0.26	0.18
1053	Cluster of Al3+ and O2- ions on the surface of alumina	0.36	0.31
856	Al–O stretching	0.47	0.59
727		0.5	0.6
653		0.5	0.6

to point out that all modification methods applied to alumina decreased the thermodynamic parameters due to pronounced removal of surface active sites.

The efficiency of gas chromatographic separation for the studied samples can be evaluated in terms of resolution, separation factor and uniformity criterion. Results of these three parameters for the studied solid stationary phases using the selective solutes are summarized in Table (5) and portrayed in Figure (3). The gas chromatographic separations which exhibit resolution less than unity was neglected. It has been found that all modifications have different separation efficiencies.

Table (4): Thermodynamic parameters of parent and modified alumina stationary phases

Columns	Solutes	□ □ G KJmol^{-1}	□ □ H KJmol^{-1}	□ □ S Jmol^{-1}degree^{-1}
Al	n-Heptane	30.36	56.77	70.81
	Methylcyclohexane	27.07	47.28	54.18
	Toluene	40.27	71.79	84.50
Al_{C}	n-Heptane	21.05	41.26	54.18
	Methylcyclohexane	19.98	38.85	50.6
	Toluene	27.35	50.42	61.85
Al_{C500}	n-Heptane	28.08	50.18	59.26
	Methylcyclohexane	26.74	46.64	53.36
	Toluene	35.99	62.13	70.09
$Al_{CNa10\%}$	n-Heptane	18.18	35.12	45.41
	Methylcyclohexane	17.04	31.88	39.80
	Toluene	23.86	44.04	54.09
$Al_{Na10\%}$	n-Heptane	21.68	30.77	24.37
	Methylcyclohexane	20.68	28.15	20.02
	Toluene	28.46	42.08	36.50

Table (5): Separation efficiency parameters of selected stationary phases using paraffins as probes

Columns	C_6, C_7		C_7, C_8		C_8, C_9		C_9, C_{10}		Uniformity criterion
	ά	R	ά	R	ά	R	Ά	R	
Al	1.349	3.33	1.237	2.885	1.183	2.247	1.261	2.125	0.161
$Al_{Na10\%}$	1.42	3.71	1.3	3.35	1.22	3.18	1.17	2.98	0.403
Al_{C500}	1.33	3.44	1.23	3.14	1.17	2.867	1.17	2.45	0.243
Al_{C}	1.562	5.04	1.353	4.21	1.242	3.454	1.81	2.925	0.404
$Al_{CNa10\%}$	1.69	3.81	1.47	4.07	1.33	4.03	1.24	3.42	0.439

Efficiency of separation

a) Separation of n-Alkanes

The separation of n-Alkanes mixture (C_6- C_{10}) is capable of testing nonspecific interaction between solute and studied stationary phases, as given in Table (5), and shown in Fig. (3) depicts chromatograms illustrating the separation of n-Alkanes mixture on the selected columns. For parent and modified alumina stationary phases, the separation of n-alkane could not be eluted in a reasonable time on parent alumina. Using these stationary phases, there is no satisfactory separation of high molecular weight hydrocarbons (> C_{10}). This proved by the decrease in column efficiency ($\Delta = 0.161$) and reflected on peak broadening as the function of chain length. As can be seen in Fig. (50), the separation of paraffins was highly improved on $Al_{CNa10\%}$, Al_{C} and $Al_{Na10\%}$ stationary phases. In addition, the separation was performed at low temperature and through short time compared with the parent sample.

It was postulated that, the elution was directly correlated to adsorption sites on the alumina surface. Accordingly, the modification with calcinations, alkali metal and polymer treatment decrease the surface area and change the pore structure as given from BET study, consequently the surface shows much more gentle adsorption properties than the original surface of alumina due to the remove of most active sites.It was concluded that, the parent silica (Si) without any treatment and coating the calcined alumina with sodium (**Al$_{CNa10\%}$**) can elute the paraffinic mixture exhibiting good resolution.

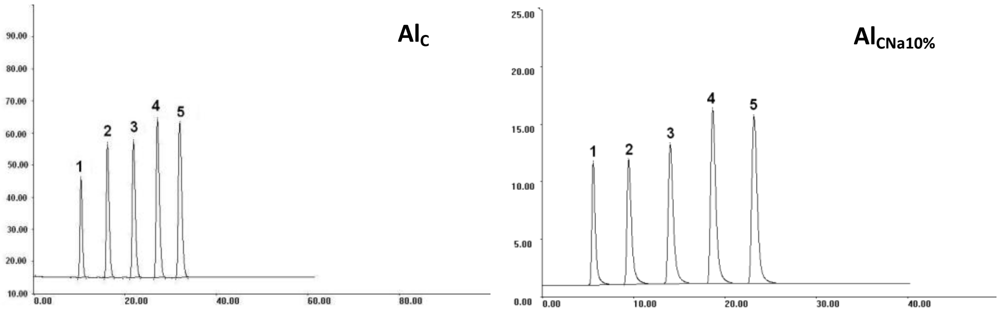


Figure (3): GC separation of paraffinic hydrocarbons on modified alumina at optimum condition (100°C; 5°C/min to 220°C Where 1- C_6, 2- C_7, 3-C_8, 4- C_9 and 5- C_{10}.

b) Separation of aromatic hydrocarbons

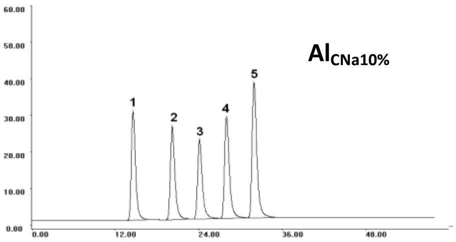
Table (6) and Figure (4) illustrate the chromatographic separation of aromatic hydrocarbons mixture on parent and modified alumina samples. Large active sites with high surface area of alumina as solid stationary phase make its surface unsuitable for separating aromatics, this bad separation was evidenced with its lower uniformity criterion value ($\Delta = 0.131$). However, the deactivation of alumina surface by calcinations, hydrothermal treatment, alkali metal modification and polymer treatment decreases the retention indices of benzene as shown in Table (19). Consequently, the separation of aromatic hydrocarbons were improved on the calcined alumina Al$_C$ ($\Delta = 0.3$). Moreover, their separation on the Al$_{CCo10\%}$ or Al$_{CNa10\%}$ was achieved at lower temperature giving good separation. This separation accompanied by short duration time, symmetrical and sharp peaks; this was evidenced with the high uniformity criterion values.

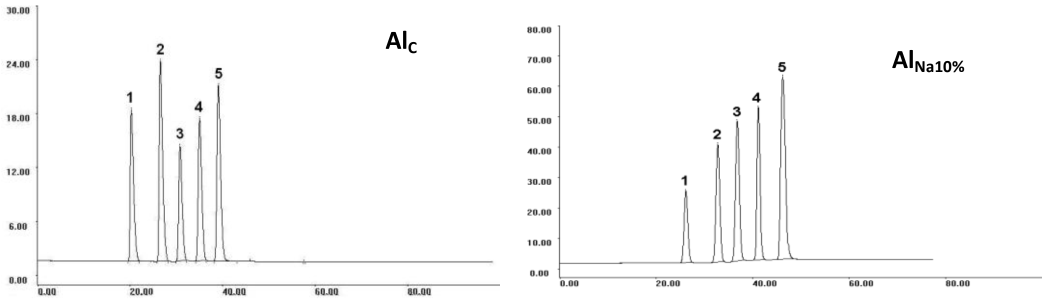
Table (6): Separation efficiency parameters of selected stationary phases using aromatics as probes

Column	Benzene, Toluene		Toluene, Ethylbenzene		Ethyl benzene, Propylbenzene		Propylbenzene, Butylbenzene		Uniformity Criterion
	ά	R	ά	R	ά	R	ά	R	
Al	1.216	1.82	1.137	1.186	1.275	1.656	1.447	1.721	0.131
Al$_{Na10\%}$	1.25	4.42	1.12	2.48	1.112	2.2	1.12	2.36	0.300
Al$_{C500}$	1.21	2.68	1.12	1.57	1.19	1.79	1.29	1.94	0.236
Al$_C$	1.31	3.142	1.16	2.237	1.138	2.361	1.116	2.132	0.300
Al$_{CNa+}$	1.39	4.84	1.195	2.95	1.16	2.74	1.14	2.63	0.370

The high performance of sodium treatment of calcined alumina (Al$_{CNa10\%}$) was focused, suggesting that the more adsorptive calcined alumina surface is covered with a less adsorptive surface layer which increase the surface homogeneity and lead to decrease in retention time with significant improvement in peak shape for aromatic solutes, this confirmed with Fukazawa et al **(15)**, they conclude that a sodium aluminate layer which is less adsorptive is formed by reaction of alumina with NaCl. Also, good separation was achieved on directly coating the pare alumina surface with sodium chloride (Al$_{Na10\%}$) having high separation factor, high resolution and high uniformity criterion ($\Delta = 0.3$) this suggested that the less adsorptive surface layer is distributed in the same form on the alumina surface regardless of the preheated temperature. Thus, the post heating treatment of the salt coated alumina results in the formation of a uniform and less adsorptive surface layer on the alumina.

Figure (4): Gas chromatographic separation of aromatic hydrocarbons on modified alumina, at optimum condition (80°C for 2min; 20°C/min to 220°C; final time 10min, 30ml/min).





Alcohols (propanol, butanol, hexanol, octanol, decanol and dodecanol) are the most polar organic compounds which interact with electron-donor groups of the surface with a hydrogen bond evolving, reflecting on their bad resolution and their highly tailing peaks.

c) Saturated and unsaturated hydrocarbons

The mixture of saturated and unsaturated hydrocarbons is one of the most important products in petrochemical industry, and their separation was difficult via gas chromatography. The mixture of paraffins and olefins namely n-Hexane, 1-hexene, n-heptane and 1-heptene take our attention to try to separate them through our modified alumina stationary phases (Fig. 5).

The saturated hydrocarbons are eluted before olefins of equivalent carbon number because the electron rich unsaturated bonds of the olefin are more firmly bound to the electropositive sites of the alumina lattice. Interestingly, the separation of alkanes and alkenes mixture on $Al_{CNa10\%}$ using TCD detector was found to be better than FID one. According to Hoffmann and Evans (17), the separation efficiency of hydrocarbons on activated alumina is strongly influenced by the type of carrier gas employed, therefore the use of H_2 as a carrier gas may be the reason of enhancing the selectivity of stationary phase ($Al_{CNa10\%}$) under investigation besides the linearity and response of the thermal conductivity detector.

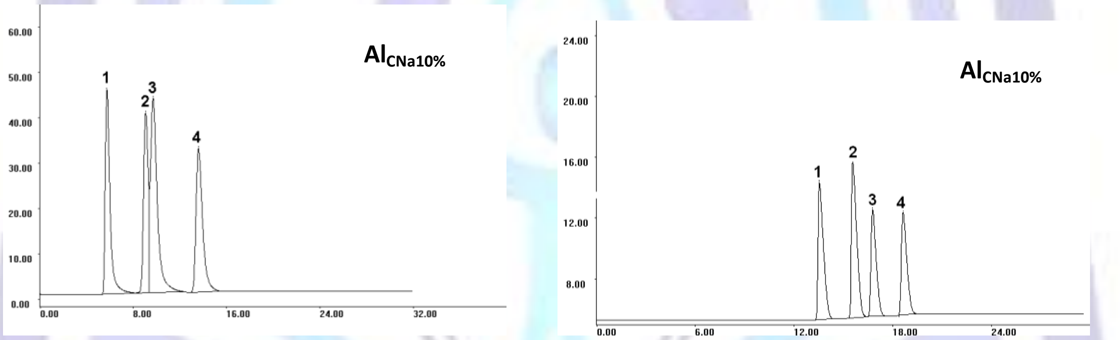


Figure (5): GC Separation of paraffins and olefins mixture on alumina and modified alumina stationary phases. 1- n-hexane 2- 1- hexane 3- n-heptane 4- 1- heptene

d) Separation of gases

The analyses of low molecular weight hydrocarbon gases such as, natural gas and volatile hydrocarbons in polluted air by GC are very difficult and required very selective stationary phases. Therefore, the comparison of the elution of gas sample in alumina columns were carried out using both FID and TCD detectors. The separation of natural gases (methane, ethane, propane, iso-butane, n-butane, iso-pentane and n-pentane) on selected silica and alumina stationary phases using FID detector was shown in Fig. (6). alumina and modified alumina have been found as good stationary phases for separation of natural gases giving base line separation.

The unique retentive properties of alumina and its modified stationary phases for the separation of gases take our attention to try to separate different mixtures of natural gases (air, methane, ethane, propane, iso-butane, n-butane, iso-pentane and n-pentane). Using TCD detector (Fig. 7), the separation of this probes give another examples of the superior selectivity of modified alumina especially $Al_{CNa10\%}$.

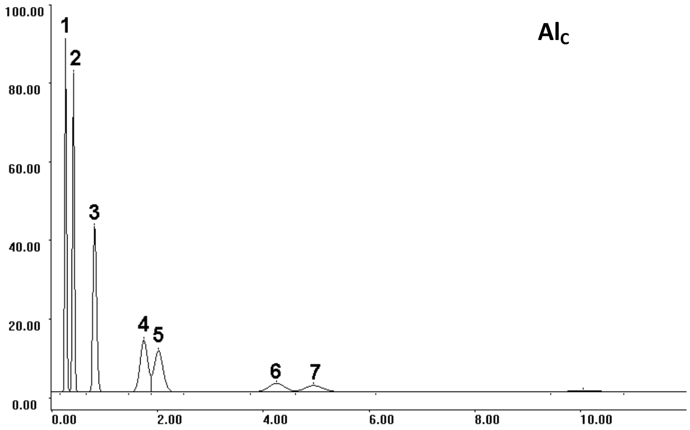


Figure (6): Gas chromatographic separation of natural gases on studied stationary phases using FID detector.

It is clear that, the variation in modified techniques at the surface of alumina make it possible to obtain adsorbent with different surface type and, consequently, with different elution order.

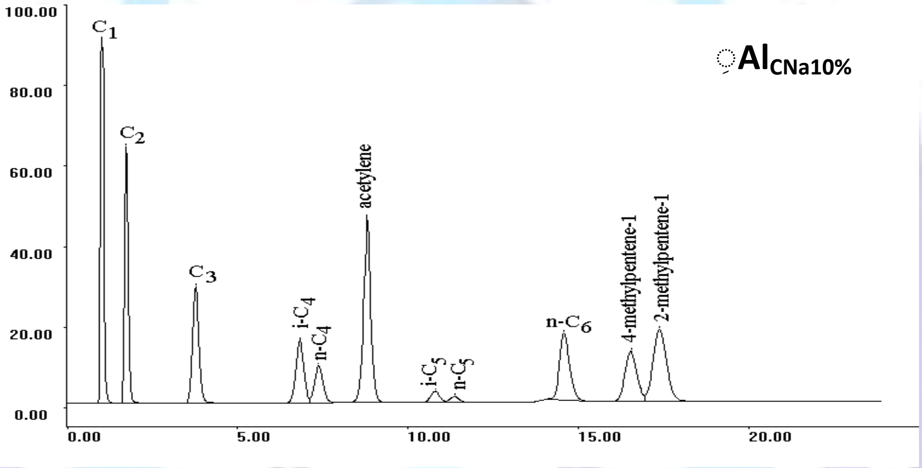


Figure (7): Gas chromatographic separation of natural gas sample on studied stationary phases using TCD detector.

Conclusions

- In the present study alumina was selected based on the fact that this sorbents is characterized by unique textural properties and functionalized surface. The Calcination, and alkali metal treatment of alumina sorbents performed in this investigation single or multi-treatments.
- TGA and DTA profiles of alumina (Al) indicate the existence of several thermal processes: release of free water from ambient up to 210^{o}C, release of water of crystallization between 230 and 480^{o}C. The exothermic effect at 500^{o}C correspond phase change to pseudo-boehmite-γ-Al_2O_3 transition which occurs through partial dehydroxylation. On the other hand, most modified alumina proved to be more thermally stable compared to the parent one.
- DRIFT spectroscopy represents the strength and abundance of surface acidic OH which determine the adsorption properties of polar and nonpolar sorbents. Generally, all treated samples exhibit decrease of OH groups compared with those of parent one and the drastic decrease were observed upon calcination at 1000^{o}C.
- Thermodynamic parameters assisted to study interaction between the adsorbents and probes of different polarities and elucidate the separation mechanism. Also, alkali metal modification of parent and calcined alumina (Al$_{CNa10\%}$, and Al$_{Na10\%}$) are able to selectively interact with a particular component based on its size and relative polarity.
- Modification of alumina with NaCl exhibited high separation efficiency of mixtures from paraffins. Alkali metal modification of precalciened alumina is a selective stationary phase for eluting natural gas sample exhibiting good separation.

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