

Research Article

Alkali Metal Modification of Silica Gel-Based Stationary Phase in Gas Chromatography

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Received 6 May 2013; Revised 7 August 2013; Accepted 7 August 2013

Academic Editor: Wen-Hua Sun

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Modification of the precipitated silica gel was done by treatment with alkali metal (NaCl) before and after calcination. The silica surfaces before and after modification were confirmed by infrared spectroscopy in order to observe the strength and abundance of the acidic surface OH group bands which play an important role in the adsorption properties of polar and nonpolar solutes. The surface-modified silica gels were tested as GC solid stationary phases in terms of the separation efficiency for various groups of non-polar and polar solutes. Also, 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 on the reactivity and porosity of the silica surfaces. The efficiency of the surface-modified silica gels to separate the aromatic hydrocarbons seemed to be strongly influenced by the density of the surface hydroxyls.

1. Introduction

The technique of bonding with transition metal complexes involves bonding the transition metals to support surface with the help of suitable ligand (mostly silanes) having their hydrocarbon chain terminated with appropriate functional group in order to form π -complexes [1]. Using such complexes in GC is characterized by high selectivity to separate compounds of similar chemical structure and boiling temperatures (like separation of different types of isomers and isotopes), thermal stability, and high resistance to external factors [2]. Moreover, the feasibility of wide control of complexing parameters makes the packings interesting not only from the analytical but also from the physical and chemical points of view.

The nature of stationary phases [3–11] in gas chromatography is the main GC part for covering many applications [12–14] with high efficiency of separation in addition to the used detector type [15] and the optimum conditions [16]. The separation mechanism of transition metal complexes depends on the formation of metastable complexes either of organic type or with cations of transition metals. The cations of metals showing electron deficiency have at least

one empty valence orbital which can be involved in the coordinative interactions [17]. Wasiak et al. [18–22] produced selective complexing sorbent which solves many analytical problems such as (i) the use of Ni and Co complexes bonded to the silica surface via β -diketonate groups to elute alkane-alkene pairs [18] or via thiol groups for separation of cyclic hydrocarbons, cyclic ethers, and chloro derivatives of aliphatic hydrocarbons [19] and (ii) bonded Cu, Ni, and Cr to the silica surface via ketoamino groups to elute halogenated hydrocarbons, geometric isomers, olefin, ethers, thioethers, cyclic hydrocarbons, aromatic, and ketones [20–22]. Slizhov and Gavrilenko [23] examined the GC properties of Silochrom with a surface layer of nickel-dimethylglyoximate and acetylacetone complexes. Complexation with metal chelates was studied at the phase interface in gas chromatography [24]. And enantioselective complexation gas chromatography has been reviewed [25].

2. Experimental

2.1. Preparation of Silica. Sodium Meta Silicate (Na_2SiO_3) used was from Avocado, Cat. no. 10688 (England) with SiO_2

TABLE I: The parent, calcined, and modified silica samples.

Notation	Treatments
Si	Parent silica gel (60–80 mesh)
Si _{C500}	Silica gel calcined at 500°C
Si _C	Silica gel calcined at 1000°C
Si _{Na}	Parent silica gel exchanged by NaCl using soaking method
Si _{Na10%}	Silica gel calcined at 500°C and then exchanged with 10% NaCl using evaporation method
Si _{CNa}	Silica gel calcined at 500°C and then exchanged with NaCl using soaking method

content 45.8–47.3%. Silica substrate was prepared according to according to Kopečni et al. [26]. Thus, hydrochloric acid and a solution of 17% wt/v sodium meta silicate was added simultaneously during continuous thorough stirring to acidified water until a pH = 2.0 was maintained at which a clear silicic acid solution could be obtained. Ammonia solution as a precipitating agent was then quickly added until pH = 7.7. The gel formed was aged for 24 h at 90°C, crushed, and dried at 120°C for 24 h, and further at 150°C for 48 h to insure complete drying. The dried sample was washed by dilute HCl (pH = 2) in order to neutralize the excess of ammonia and then with deionized water until becomes free from chloride (negative AgNO₃ test) and dried again at 120°C till constant weight. The dried silica sample was then crushed and sieved to 60–80 mesh.

2.2. Modification Methods

2.2.1. Calcination [4, 5, 9]. Silica sample was calcined in a muffle furnace at 500°C for 16 hr and at 1000°C for 5 h to stabilize the number and type of active sites.

2.2.2. Treating with Alkali Metal

Soaking Method. The silica sample was soaked in 1 molL⁻¹ NaCl solution. NaOH was added to maintain pH = 10 [27]. The mixture was allowed to equilibrate for 5 hr. The sample was then filtered, washed by deionized water, and dried at 120°C overnight. The same procedure was followed for silica sample calcined at 500°C.

Evaporation Method. In this method the calcined silica sample at 500°C was put in 10% NaCl solution, followed by evaporating the NaCl solution, then washed by deionized water, and dried at 120°C overnight.

The prepared calcined and alkali metal modified silica samples were given in Table I.

2.3. Gas Chromatography. All parent and modified samples were subject to an inverse gas chromatography to evaluate their efficiency when used as a solid stationary phases or solid support. The gas chromatograph used is Unicam 610 equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). Nitrogen (oxygen free) and

hydrogen were used as the mobile phase for FID and TCD, respectively. The optimum flow rate was determined depending on the column efficiency. The optimum was found to be 30 mL min⁻¹.

The column used was stainless steel tube of 2 m in length and 1/8 inch of internal diameter. The column is first washed with dilute hydrochloric acid, then with deionized water, and finally with acetone. The column then purged with dry air until complete dryness. The packing of the studied sample inside the column was achieved as follows; a silanised glass wool plug was inserted into one side of the column which was then connected to a vacuum pump. The packing material was introduced from the other end of the column using a funnel and packed down by action of the pressure differential with simultaneous vibration of column to ensure uniform distribution of the column material. The packed column was activated at 300°C for solid stationary phase and 180°C for the polymer coated and bonded samples under flow of nitrogen (15 mL min⁻¹) for 24 h. The solutes used for chromatographic characterization were selected to cover the wide range of polarity such as n-paraffin, olefins, aromatics, polyaromatics, esters, ketones, ether, and alcohols as well as wax, natural gases, and condensate samples. The polarity indices were assessed with respect to the reference nonpolar column SE-30 (20% SE-30 on chromosorb W. A. W., 60–80 mesh).

3. Result and Discussion

3.1. Diffuse Reflectance Infrared Fourier Transforms Spectroscopy (DRIFT). DRIFT spectroscopy is often used for the investigation and characterization of modification reactions proceeding on the silica surfaces. The observations of the strength and abundance of the acidic surface OH group bands play an important role on the adsorption properties of polar and nonpolar solutes. So that the structure of the modified surface was revealed by DRIFT spectra which permits better understanding of the reactions and the properties of the modified samples. Accordingly, we are reporting the changes occurred in hydroxyl group changes as well as the structure changes as a result of alkali metal treating coating of both parent silica and calcined silica.

The infrared spectrum of silica gel has been the subject of intense investigation [28]; the strong adsorption bands at 1200, 1100, and 800 cm⁻¹ have been assigned to silicon oxygen fundamental vibrations, while those in the 3006–4000 cm⁻¹ region have been attributed to surface hydroxyls and molecular water.

Figures 1 and 2 show representative DRIFT spectra of parent and modified silica samples. Parent silica sample (Figure 1(a)) shows a broad band in the OH stretching vibration region (3500–2500 cm⁻¹) centered at about 3426 cm⁻¹ attributed to the fundamental stretching and combinations of stretching and in-plane bending vibrations of surface hydroxyl groups and/or bridged and vicinal (strongly hydrogen-bonded) Si-OH [8]. Weak band at 3648 cm⁻¹ may be assigned to bridged and internal (weakly hydrogen-bonded) Si-OH [29]. Also, weak shoulder can be distinguished at about 3723 cm⁻¹, which is often ascribed to the

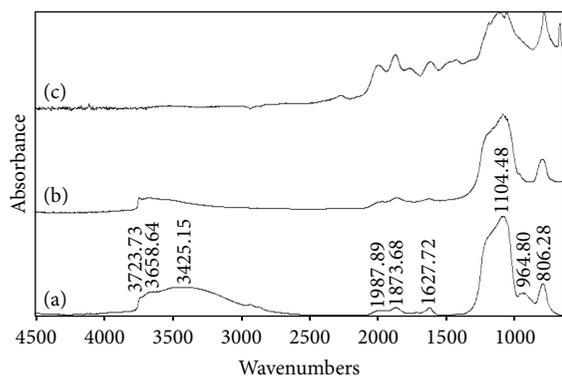


FIGURE 1: DRIFT spectra of (a) Si, (b) Si_{C500}, and (c) Si_C.

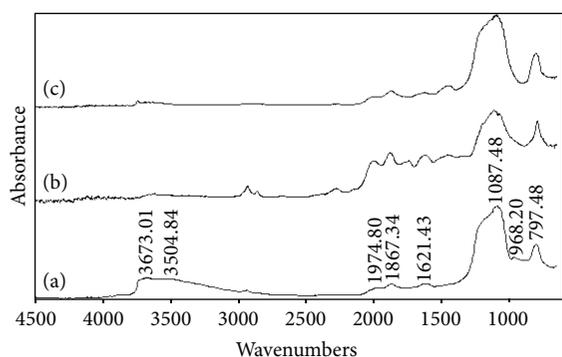


FIGURE 2: DRIFT spectra of (a) Si_{Na}, (b) Si_{CNa}, and (c) Si_{Na10%}.

presence of terminal or geminal silanol groups. Band at 1630 cm^{-1} indicates the presence of physically adsorbed water [30].

For the skeleton characteristic bands, bands at about 1997 and 1873 cm^{-1} were assigned to the combination vibration band of SiO₂ [31]; the band at 960 cm^{-1} is due to the presence of Si-OH [32]. Strong band in the range 1000 – 1250 cm^{-1} assigned to the asymmetric bending of the Si-O-Si bonds and that at approximately 800 cm^{-1} is attributed to symmetric stretching vibration of Si-O-Si [33].

Exchange of the silica sample with NaCl (Figure 2) decreases the intensity of the band at 3500 – 3000 cm^{-1} and the bands at 3723 cm^{-1} are not observed which eliminates the possibility of single hydroxyls being present [34].

3.2. Chromatographic Characterizations. The characteristics of alkali metal modification of the parent and calcined silica samples have been evaluated in terms of polarity and thermodynamic properties. These parameters are used to assess the outer surface contributions and the degree of surface deactivation brought about by the modification techniques.

3.2.1. Polarity Assessment of Stationary Phases. The parent and modified silica samples were identified and arranged in their polarities according to the Rohrschneider scheme [35]. This method depends on the determination of retention indices (I) for five solutes, namely, benzene, ethanol, methyl

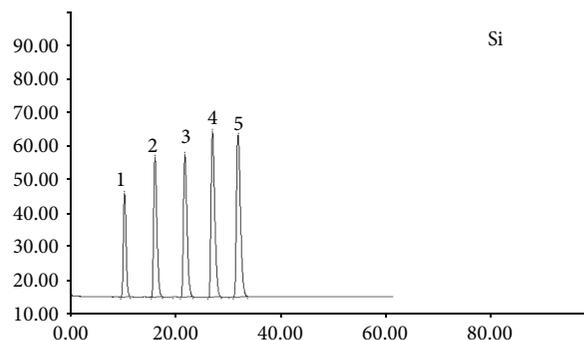


FIGURE 3: Gas chromatographic separation of paraffinic hydrocarbons on parent silica stationary phase, at optimum conditions (60°C for 2 min; $15^\circ\text{C}/\text{min}$ to 220°C ; final time 10 min, 30 mL/min).

ethyl ketone, nitromethane, and pyridine, on SE-30 as non polar stationary phase and then on the modified stationary phases to be characterized. The retention index differences (ΔI) can be calculated and then the so called Rohrschneider constants x , y , z , n , and s of the selected probes, respectively, are listed in Table 2. As expected, the overall polarity of the alkali metal modified silica samples was lower than that of the parent silica the modification of silica surface with alkali metal decreases the retention index of polar compounds. In this instance the elution order of the Rohrschneider probes is different for the parent silica and alkali metal modified silica samples. On some adsorbents Si, Si_{Na}, Si_{Na10%}, Si_{C500}, and Si_C, the order is benzene, nitromethane, ethanol, methyl ethyl ketone, and pyridine, and the calculated ΔI values indicate high polarity.

3.2.2. Thermodynamics. It is evident from the data that negative ΔH values increase in the sequence methylcyclohexane < n-heptane < toluene on all studied stationary phases; the more negative the ΔH , the greater the interaction between the adsorbate and adsorbent. A similar study was also done by Oguz et al. [36]; they evaluated the thermodynamic parameters (ΔH , ΔS , and ΔG) of some probes, each representing a class of organic compounds (n-hexane, cyclohexane, and benzene) on 4A and 13X Zeolites; it was found that thermodynamic parameters increase in the sequence cyclohexane < n-hexane < Benzene. Also, Bilgic and Askin [37] obtained the same result for activated alumina stationary phase. Although, n-heptane and methylcyclohexane interact nonspecifically, but n-heptane interacts more intensively than methylcyclohexane, this result indicates a better contact of an open chain structure molecules with the surface of stationary phases. The stronger adsorption of toluene on silica surface than n-heptane and methylcyclohexane most probably was attributed to the contribution of the specific interaction between the SiO₂ surface and the π -electrons of the toluene ring. According to the Kiselev and Yashin [38], silica has free hydroxyl groups on the surface, and OH groups linked to silicon act as a weak acid, with hydrogen partly protonized. So, silica can interact specifically with the molecules containing π -electrons. In addition to the three π -bonds of benzene ring, toluene has electron-donor character

TABLE 2: Rohrschneider index of parent and alkali metal modified silica stationary phases.

Column		Benzene (X)	Ethanol (Y)	Methyl ethyl ketone (Z)	Nitro methane (U)	Pyridine (S)	Average
Si	<i>I</i>	808	1043	1302	956	1568	542
	ΔI	144	602	720	418	830	
Si _{Na}	<i>I</i>	749	1047	1401	882	1514	526
	ΔI	84	606	819	345	776	
Si _{Na10%}	<i>I</i>	791	1029	1101	820	1314	418
	ΔI	127	588	520	282	576	
Si _C	<i>I</i>	802	1020	1138	930	1234	432
	ΔI	138	578	556	392	497	
	ΔI	349	537	414	714	582	
Si _{CNa}	<i>I</i>	792	844	1108	775	1662	443
	ΔI	128	402	526	237	925	

TABLE 3: Thermodynamic parameters of parent and modified silica stationary phases.

Columns	Solutes	$-\Delta G \text{ KJmol}^{-1}$	$-\Delta H \text{ KJmol}^{-1}$	$-\Delta S \text{ Jmol}^{-1} \text{ degree}^{-1}$
Si	n-Heptane	12.38	37.66	67.79
	Methylcyclohexane	12.19	35.12	61.47
	Toluene	18.35	45.79	73.54
Si _{Na}	n-Heptane	8.89	36.58	74.25
	Methylcyclohexane	9.45	32.76	62.49
	Toluene	12.77	41.19	76.22
Si _{Na10%}	n-Heptane	12.2	24.84	33.9
	Methylcyclohexane	12.07	23.86	31.62
	Toluene	15.30	28.27	34.78
Si _{C500}	n-Heptane	9.38	34.89	68.38
	Methylcyclohexane	9.10	31.27	59.44
	Toluene	14.01	40.84	71.93
Si _C	n-Heptane	4.55	26.68	59.33
	Methylcyclohexane	4.37	25.21	55.88
	Toluene	9.39	29.81	54.73
Si _{CNa}	n-Heptane	8.48	21.37	34.56
	Methylcyclohexane	8.64	19.86	30.10
	Toluene	10.75	23.63	34.53

of the methyl group, which enhanced the interaction of toluene with silica surface. The influence of modification methods on the adsorption properties of parent and modified silica is given in Table 3. The parent silica sample has the highest $-\Delta H$ value indicating a strong interaction with the adsorbate.

The high decrease in surface area and strong removal of the active hydroxyl groups due to calcination lead to small ΔH value. Chemical modification of silica sample with PEG and DMDCS also deactivates the silica surface decreasing, thus the thermodynamic parameters.

In alkali metal modification the methodology of preparation causes a great effect on thermodynamic parameters. $-\Delta H$ value of Si_{Na} was found to be higher than that for Si_{Na10%}. This may be attributed to the drastic decrease of OH group of Si_{Na10%}, as a result of its calcination at 700°C. Furthermore, the lower negativity of the entropy of Si_{Na10%}

may reflect the inertness of surface associated with lower degree of freedom.

Separation Efficiency. The calcined silica sample (Si_C) has bad separation of paraffin; this may be related to the decrease of surface area and formation of crystallite silica (cristobalite) as mentioned before. On the other hand, Si_{Na10%} sample gives better separation of paraffin than Si_{Na}; this is due to the effect of postheat treatment of Si_{Na10%} after impregnation with alkali metal. But with slightly lower efficiency of separation ($\Delta = 0.46$) as compared with the parent silica. The separation of n-Alkanes mixture (C6–C10) is capable of testing nonspecific interaction between solute and studied stationary phases, Table 4 and Figure 3 depict that parent silica gives suitable surface for eluting paraffins as the previous works (264, 265). On the other hand, Si_{Na10%} sample can separate n-paraffin but with slightly lower efficiency of separation ($\Delta = 0.46$) as compared with the parent silica.

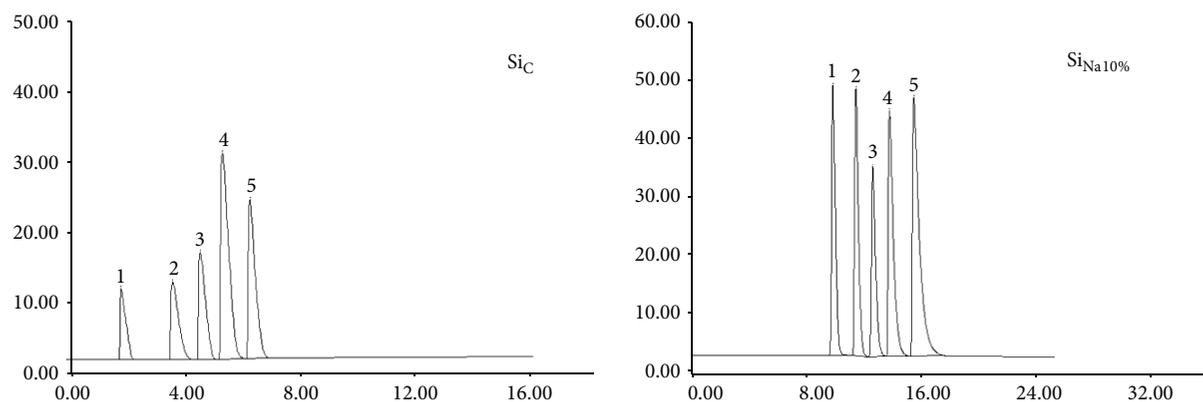


FIGURE 4: Gas chromatographic separation of aromatic hydrocarbons on modified silica gel, at optimum condition (80°C for 2 min; 20°C/min to 220°C; final time 10 min, 30 mL/min).

TABLE 4: 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 Δ
	α	R	α	R	α	R	α	R	
Si	1.237	3.132	1.177	2.9	1.135	2.6	1.110	2.4	0.51
Si _{Na10%}	1.25	3	1.2	2.52	1.15	2.38	1.12	2.67	0.46

TABLE 5: Separation efficiency parameters of selected stationary phases using aromatics as probes.

Column	Benzene, toluene		Toluene, ethyl benzene		Ethyl benzene, propylbenzene		Propylbenzene, butylbenzene		Uniformity criterion
	α	R	α	R	α	R	α	R	
Si	1.183	2.732	1.113	2	1.101	2	1.123	2.28	0.33
Si _{Na10%}	1.16	3.2	1.1	2.33	1.09	1.87	1.12	1.94	0.465

TABLE 6: Separation efficiency parameters of selected stationary phases using polyaromatics as probes.

Column	Naphthalene, fluorine		Fluorene, acenaphthene		Acenaphthene, anthracene		Anthracene, pyrene		Uniformity criterion
	α	R	α	R	α	R	α	R	
Si	1.24	2.06	1.09	1.03	1.103	1.2	1.14	1.79	0.246
Si _{Na}	1.364	2.467	1.121	1.16	1.144	1.54	1.124	1.467	0.27

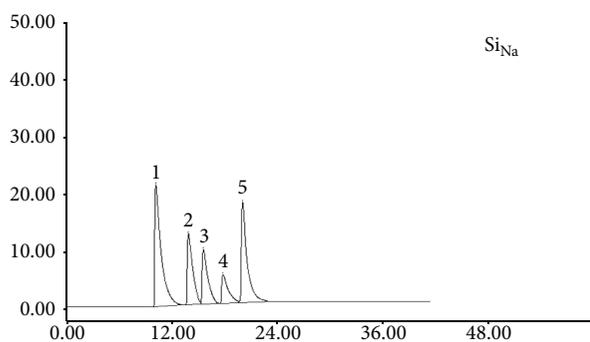


FIGURE 5: Gas chromatographic separation of PAHs on alkali metal modified silica as solid stationary phase, at optimum condition (temperature is 120°C; 10°C/min to 220°C for Si_{CB010%} and to 300°C for others; final time 20 min).

The aromatic hydrocarbons (Benzene, toluene, ethyl benzene, propylbenzene, and butylbenzene) are important

industrial chemicals. They generally coexist in the catalytic reforming process in aromatic production. Furthermore they were used as probes to investigate π -complex formations. Table 5 and Figure 4 depict the performance of the studied column on the separation of aromatic mixture. Si_{Na10%} is the best studied stationary phase for separating aromatic hydrocarbons obtaining good separation with high resolution. This could be directly linked with decreasing the surface hydroxyl groups which interact specifically with molecules containing π -electrons. This decrease of surface hydroxyl groups could be evidenced by the low polarity values and low negative values of both heat enthalpy (ΔH) and entropy (ΔS) for benzene. The calcined silica sample Si_C can elute the aromatics giving acceptable chromatogram depending on lower sample capacity.

The elution of polyaromatic hydrocarbons (PAHs) was tested on the alkali metal modified silica as solid stationary phase and its separation was given in Table 6 and shown in Figure 5. It was found that Si_{Na} successfully separated the

PAHs showing good separation at suitable duration time of analysis. These good results may be due to the handling methodology of silica preparation and modifications which produce homogenous silica surface with deactivation degree enough for eluting the di- and polyaromatic hydrocarbons.

4. Conclusion

- (i) Alkali metal modification of silica before and after calcinations was shown to be very useful, leading to materials with suitable surface properties for advanced applications, especially the chromatographic separation of petroleum like separation of various kinds of organic solute such as paraffins, monoaromatics, and polyaromatics.
- (ii) From another point of view, inverse gas chromatography was used for investigating surface structure and interaction between solid surface and probe solute. In addition, thermodynamic parameters give a clear picture about the mechanism of separation.

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