Preparation and Silylation of Silica Gels and Their Usage as Solid Stationary Phases in Gas Chromatography

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Abstract: Silica gels were prepared by means of DeBore method. The prepared silica gel was crushed and sieved using an automatic mechanical sieve; the portion from 60-80 mesh was selected and acid washed by 6 mole hydrochloric acid. The acid washed silica gel was calcined at 1000 °C temperature and modified by silylation method through refluxing in a soxhelet by 30 vol. % of dimethyldichlorosilane (DMDCS) in toluene. The characteristics of untreated and modified silica gels as solid stationary phases via GC have been evaluated in terms of polarity, selectivity, and separation efficiencies. The silylation technique of the calcined silica gel has a pronounced effect on the surface deactivation due to the formation of the silanol group with the remainder hydroxyl groups. This column is selective one for the elution of polar compounds including alcohols giving sharp and symmetric peaks.

Keywords: Gas chromatography, polarity, selectivity, calcination, and silylation

1. Introduction

Gas-solid chromatography (GSC) is not just an analytical tool; it is a powerful and accurate method for measuring many retention properties and investigating the properties of solvents and the behavior of solutes in stationary phases. The retention time and the peak elution profiles of standard
solute affected by interactions between the solutes and stationary phase are used to estimate those interactions \(^{(1,2)}\). Surface character is most often characterized with the use of parameters describing surface ability to undergo dispersive and interaction properties. Dispersive compound of surface free energy and specific interaction parameters describing surface ability to act as electron acceptor or electron donor are used to quantify the properties of the liquid and solid surface \(^{(3-8)}\).

Silica gels have long attracted attention since they are widely used and find many applications in several fields of investigation related to chromatography, catalysis, extraction, filtration, etc. since it offers surface properties covering a wide range of acidity surface reactivity and pore structure \(^{(9-11)}\). The surface of silica gel can be modified easily by physical or chemical treatments leading in each case to different adsorptive properties. These treatments may include calcinations \(^{(2)}\), hydrothermal treatment \(^{(12)}\), silylation and incorporation of inorganic salts or organic compounds \(^{(15,16)}\).

The present work is devoted to synthesis and modification of silica gel with organic and inorganic compounds on its surface and capable of electro donor-acceptor interactions. Also, this study concentrates on study the interaction of various silica surface modifiers with selective organic probes in order to evaluate the different silica surfaces as solid stationary phases in gas chromatography in relation to the elution of polar and non-polar organic petroleum compounds with special emphasis on the role of surface reactivity and pore structure. Using GC, such packing was characterized by the inverse gas chromatography through the polarity, selectivity, thermodynamic parameters and resistance to different external factors \(^{(17-20)}\).

2. Materials and Methods

2.1. Preparation of Silica Gel

Wide porous silica gel as a parent material was prepared by a conventional precipitation method according to DeBore method \(^{(21)}\). The prepared silica gel was crushed and sieved using an automatic mechanical sieve. The portion from 60-80 mesh was selected, washed by 6 mol. of HCl and stored for different physical and chemical treatments.

2.2. Different Silica Gel Treatments

The acid–washed silica gel (60-80 mesh) was subjected to various treatments, namely thermal treatment and silylation treatment with the aim of producing different surface-modified silica gels.

Thermal treatments were carried out by calcinations in air for 5h at 1000 °C. For silylation treatment, silica gel was refluxed in a soxhelet by 30 vol. % of dimethyldichlorosilane (DMDCS) in toluene according to the procedure described in Ref. \(^{(13)}\). In addition, silica gels were obtained by combination of two modifications in order to improve their properties as solid gas chromatographic
stationary phases. The studied silica samples obtained by using different treatments are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Notation</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si</td>
<td>Acid washed silica gel (60-80 mesh)</td>
</tr>
<tr>
<td>2</td>
<td>SiC500</td>
<td>Silica gel calcined at 500°C</td>
</tr>
<tr>
<td>3</td>
<td>SiC</td>
<td>Silica gel calcined at 1000°C</td>
</tr>
<tr>
<td>4</td>
<td>SiS</td>
<td>Silylated silica gel using DMDCS</td>
</tr>
<tr>
<td>5</td>
<td>SiC-S</td>
<td>Calcined Silica gel followed by silylation using DMDCS</td>
</tr>
</tbody>
</table>

2.3. Gas Chromatography

The untreated silica and surface-modified silica gels were subjected to an inverse gas chromatography with the aim of investigating their performance as solid stationary phases. The solid material was packed in a stainless steel column (1/8 inch and 7 feet) by charging under vacuum. The packed column was activated at 200 °C for 24 h in a stream of pure nitrogen gas at a flow rate of 15 ml min⁻¹.

The gas chromatograph used was an AT Unicam-610 equipped with FID. Nitrogen gas was used as a carrier at a flow rate of 25 ml min⁻¹. The analysis was carried out at different temperatures depending on the column efficiency resulting in the optimum separation of the studied solutes. Different solutes, namely mixtures of n-Paraffins, aromatic and polyaromatic hydrocarbons, Ketones, acetates, ethers and n-alcohols were used as probes for the chromatographic characterization.

3. Results and Discussion

3.1. Rohrschneider Scheme

Characterization of silica modified stationary phases according to Rohrschneider’s method is based on the determination of retention indices for five solutes namely benzene, ethanol, methyl ethyl ketone, nitro methane and pyridine on SE-30 (non-polar stationary phase) and then on the solid stationary phases to be characterized. The retention index differences (ΔI) at 100 °C can be calculated and then the so called Rohrschneider constants x, y, z, u and s are obtained in Table 2. The elution order of the Rohrschneider probes is the same for all the studied silica-modified samples except the silylation technique for both untreated and thermally treated silica gels. This proves the higher
deactivation degree brought about by the effect of silylation technique than parent and calcined treatment.

Table 2: Rohrschneider index for the prepared stationary phase

<table>
<thead>
<tr>
<th>Column</th>
<th>Benzene (X)</th>
<th>Ethanol (Y)</th>
<th>methyl ethyl ketone (Z)</th>
<th>Nitro methane (U)</th>
<th>pyridine (S)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>808.908</td>
<td>1043.952</td>
<td>1302.65</td>
<td>956.394</td>
<td>1568.054</td>
<td>542.8</td>
</tr>
<tr>
<td>Si</td>
<td>144</td>
<td>602</td>
<td>720</td>
<td>418</td>
<td>830</td>
<td></td>
</tr>
<tr>
<td>Si_{C500}</td>
<td>714.345</td>
<td>1025.922</td>
<td>1262.966</td>
<td>865.089</td>
<td>1501.363</td>
<td>480.8</td>
</tr>
<tr>
<td>Si_{C1000}</td>
<td>49</td>
<td>584</td>
<td>681</td>
<td>327</td>
<td>763</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>802.736</td>
<td>1020.403</td>
<td>1138.229</td>
<td>930.066</td>
<td>1234.639</td>
<td>432.2</td>
</tr>
<tr>
<td>Si</td>
<td>138</td>
<td>578</td>
<td>556</td>
<td>392</td>
<td>497</td>
<td></td>
</tr>
<tr>
<td>Si_{S}</td>
<td>677.015</td>
<td>762.447</td>
<td>722.081</td>
<td>808.497</td>
<td>994.625</td>
<td>200</td>
</tr>
<tr>
<td>Si</td>
<td>12</td>
<td>321</td>
<td>140</td>
<td>270</td>
<td>257</td>
<td></td>
</tr>
<tr>
<td>Si_{CS}</td>
<td>665.83</td>
<td>512.31</td>
<td>585.895</td>
<td>572.337</td>
<td>750.708</td>
<td>24.4</td>
</tr>
<tr>
<td>Si_{CS}</td>
<td>70</td>
<td>4</td>
<td>34</td>
<td>13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The polarity of the chromatographic columns depends not only on the solid stationary phases under study but also on the solutes to be analyzed. Thus each solute of the five solutes selected for this scheme of characterization may refer to a certain type of interaction between stationary phases and solutes.

Most retention indices of the calcined and silylated silica surface given in Table 2 were below that of the untreated silica sample. The average retention indices of the silylation of both parent and calcined silica samples show the low values. This indicates the higher deactivation degree of Siₚ and Siₜ compared with the parent silica. The orderly classification of stationary phases with numerical data is very valuable for comparison of columns for particular type of analysis. Also, this characterization concerning the correlation between the deactivation degree and polarities of these silica samples towards each type of solutes.

3.2. Separation Efficiencies

The efficiency of gas chromatographic separation for the studied silica samples can be evaluated in terms of resolution and separation factor. Some solute pairs were chosen as test samples for evaluation of the selectivity of the untreated and modified silica gels as solid stationary phases in gas chromatography. These solutes represent their corresponding families, the results of separation expressed as separation factor and resolution are listed in table 3.
Table 3: Separation Factor and resolution of some solute pairs on the untreated and modified silica samples

<table>
<thead>
<tr>
<th>Column</th>
<th>Paraffin</th>
<th>Aromatic</th>
<th>Alcohol</th>
<th>Acetate</th>
<th>Ether</th>
<th>polyaromatic</th>
<th>ketones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;6&lt;/sub&gt;, C&lt;sub&gt;7&lt;/sub&gt;</td>
<td>Benzene, toluene</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;-OH, C&lt;sub&gt;8&lt;/sub&gt;-OH</td>
<td>Hexyl, Octyl acetate</td>
<td>ethyl-t-butyl, di-n-butyl ether</td>
<td>Naphthalene, fluorene</td>
<td>Diethyl, di-t-isobutyl ketone</td>
</tr>
<tr>
<td></td>
<td>α</td>
<td>R</td>
<td>α</td>
<td>R</td>
<td>α</td>
<td>R</td>
<td>α</td>
</tr>
<tr>
<td>Si</td>
<td>1.237</td>
<td>3.132</td>
<td>1.183</td>
<td>2.732</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Si&lt;sub&gt;c500&lt;/sub&gt;</td>
<td>1.58</td>
<td>3.918</td>
<td>1.41</td>
<td>2.11</td>
<td>NA</td>
<td>NA</td>
<td>1.39</td>
</tr>
<tr>
<td>Si&lt;sub&gt;c&lt;/sub&gt;</td>
<td>1.429</td>
<td>1.286</td>
<td>2.07</td>
<td>2.05</td>
<td>NA</td>
<td>NA</td>
<td>1.38</td>
</tr>
<tr>
<td>Si&lt;sub&gt;c&lt;/sub&gt;</td>
<td>1.416</td>
<td>4.462</td>
<td>1.34</td>
<td>2.668</td>
<td>1.593</td>
<td>2.15</td>
<td>1.5</td>
</tr>
<tr>
<td>Si&lt;sub&gt;cs&lt;/sub&gt;</td>
<td>1.567</td>
<td>1.7</td>
<td>1.47</td>
<td>1.28</td>
<td>1.78</td>
<td>4.79</td>
<td>2.19</td>
</tr>
</tbody>
</table>

For separation of alcohols, the silylation technique for both parent and calcined silica samples success in this type of analysis is that they gave good elution accompanied with sharp and symmetric peaks.

Generally, Si<sub>cs</sub> column exhibits the highest resolution and separation factor than other columns. It has been found that Si<sub>cs</sub> column is the only one succeeds in elution of polar props like acetate, ether, polyaromatics, ketones and alcohols. This may be due to the maximum deactivation degree brought about by the silylation technique for the thermally treated silica column.

3.4. Selectivity and Applications

The selectivity of the studied silica samples can be verified by using the uniformity criterion ($\Delta$) for model systems comprising normal paraffines, aromatic and polyaromatic hydrocarbons, ethers, ketones, acetate and alcohols.

$$\Delta = n_k \frac{t \cdot k_{\text{eff}}}{\tau}$$

where $n_k$ is the number of peaks on the chromatogram, $t$ is the base width of the narrowest peak; $k_{\text{eff}}$ is the separation factor for the worst separated pair of components and $\tau$ is the duration of analysis. From Table 4 and the illustration in Figs. 1, 2 and 3, it has been found that all modifications differ in their separation efficiency according to the separated solutes. The saturated hydrocarbons can be separated as shown in Fig. 1 with high efficiency by the order: Si<sub>s</sub>, Si<sub>c500</sub> and Si columns ($\Delta = 0.522$, 0.403 and 0.45 respectively).
Paraffines

Aromatics

Separation of paraffinic hydrocarbons on selected Silica
Separation of aromatic hydrocarbons on Silica

Separation of aromatic hydrocarbons on modified Silica

Fig. 1: Separation of paraffinic and aromatic hydrocarbons on selected Silica.
Paraffines: (1-C₆, 2-C₇, 3-C₈, 4-C₉ and 5-C₁₀)
Aromatics: (1-Benzene, 2-Toluene, 3-Ethylbenzene, 4-Propylbenzene and Butylbenzene)

The silylated silica (\( \Delta = 0.467 \)) is the most efficient column for separation of aromatic hydrocarbons followed by the thermally treated silica at 500 °C (\( \Delta = 0.357 \)) as shown in fig. 1. With respect to the separation of polyaromatic hydrocarbons as shown in fig. 2, the Si₃c₅ column (\( \Delta = 0.347 \)) is the best one for these purpose followed by parent silica (\( \Delta = 0.27 \)).
Fig. 2: Separation of alcohols and polyaromatic hydrocarbons on selected silica – modified stationary phases.
Alcohols: (1: C₃-OH, 2: C₄, 3: C₆, 4: C₈, 5: C₁₀ and 6: C₁₂)
Polyaromatics: (1: Naphthalene, 2: Fluorine, 3: Acenaphthene, 4: Anthracene and 5: Pyrene)

For separation of alcohols, the only Siₙ column (Δ = 0.21) successes in these type of separation giving symmetric and sharp peaks without tailing and broadening. It is concluded that from separating n-alcohols, it is preferred to calcined the silica surface before silylation technique in order to obtain inactive silica surface suitable for eluting polar compounds without hydrogen bonds formation which is responsible for peak tailing.
Fig. 3: Separation of ketones and acetates on the silica-modified stationary phases.
Ketones: (1: Acetone, 2: Methyl Ethyl Ketone, 3: Diethyl Ketone and 4: Di-t-Isobutyl Ketone)
Acetate: (1: Ethyl acetate, 2: Butyl acetate, 3: Hexyl acetate and 4: Octyl acetate)

Table 4. Uniformity criterion for studied columns

<table>
<thead>
<tr>
<th>Column</th>
<th>paraffin</th>
<th>aromatic</th>
<th>polyaromatic</th>
<th>ether</th>
<th>ketones</th>
<th>acetate</th>
<th>alcholes</th>
<th>Nitro cpd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.45</td>
<td>0.3</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiC500</td>
<td>0.403</td>
<td>0.357</td>
<td>0.25</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiC</td>
<td>0.161</td>
<td>0.3</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiS</td>
<td>0.522</td>
<td>0.467</td>
<td>0.26</td>
<td>-</td>
<td>-</td>
<td>0.28</td>
<td>0.14</td>
<td>0.2</td>
</tr>
<tr>
<td>SiCS</td>
<td>0.243</td>
<td>0.3</td>
<td>0.347</td>
<td>0.11</td>
<td>0.15</td>
<td>0.167</td>
<td>0.21</td>
<td>0.19</td>
</tr>
</tbody>
</table>
4. Conclusions

From this study, we have the following conclusions:

- The elution consequence of the Rohrchneder props on the studied solid stationary phase are the same for all the modification techniques except the silylation technique of both untreated and calcined silica, this reflected its higher deactivated degree on the silica surface.
- The untreated silica gives suitable surface enough for eluting Paraffinc hydrocarbons as previous works. The both silylated silica and that calcined at 500 °C exhibit higher resolution values 4.462, 3.918 for normal paraffins respectively. All these characteristic data confirmed with good separation of paraffines giving symmetric and sharp peaks.
- The aromatic hydrocarbons give nearly the same behavior of paraffines. The resolution of aromatic hydrocarbons on Sic, and Sis columns show the high values. The silylated silica columns give good separation for aromatic hydrocarbons due to the higher deactivation degree resulting from the formation of ether bond (C-O-Si) on silica surface.
- The silylation of thermally treated silica (SiCS) decreases the surface hydroxyl groups as given from its low polarity value reflecting the decrease in the reactivity of silica surface. Also, its high resolution and separation factor reflect their high separation efficiency of polar organic compounds like alcohols, ketones, acetates and ethers giving sharp and symmetric peaks. Also Sis column succeeded in separation of polar organic compounds but lower degree than SiCS column.

References