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A Gas Chromatographic Analysis of Light Hydrocarbons on a Column Packed with Modified Silica Gel

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Abstract: A one-meter long column packed with silica gel is used to separate light hydrocarbons. The silica gel has been modified with several kinds of gas chromatography stationary phases. Among these, PEG 2000 shows fairly good effect when using 80-100 meshes silica gel for the separation of mixture of methane, ethane, ethylene, acetylene, propane, propylene and n-, i-butane. The different behavior of silica gel between batch to batch is also found. When silica gel is coated with a small amount of Al_2O_3 prepared with sol-gel method, better resolution has been observed on a 2-meter column compared with the non-modified silica gel.

Keywords: Gas chromatography, light hydrocarbon, packed column, silica gel, modifier.

Introduction

Analysis of light hydrocarbons achieved by gas-solid chromatography is important in petrochemical industry, environmental protection and some other areas. A variety of columns have been used, including conventional packed column[1], Al_2O_3 and graphitized carbon black PLOT column[2, 3] and silica gel SCOT column[4]. Al_2O_3 PLOT column is excellent for the analysis of light hydrocarbons. Conventional packed column also has its own advantages, such as easy column preparation, resistance to contamination, short retention time. The column packings include silica gel, alumina, graphitized carbon black, porous polymer beads and zeolites *etc*[5]. Silica gel has a large specific surface area which is beneficial to the separation of the light hydrocarbons. However, the property of the silica gel is often different from batch to batch which makes the modification difficult. Details about the modification of the silica gel have seldom been reported. In this article, we present the results of separating light hydrocarbens on the packed columns of silica gel modified with different organic stationary phases and Al_2O_3. Al_2O_3 as a modifier for silica gel used in this case has never been reported before.

Experimental

Chemicals and instrument

Squalene was purchased from A.E.C, France. Dinonyl phthalate (DNP) was produced by the British Drug House Ltd. Dioctyl sebacate was from the Carlo Erba, Italy. Hexamethylene dinitrile was purchased from GMBH & Co., Germany. Polyethylene glycol (PEG) was bought from Guangzhou Chemicals and Glass Instrument Store. Light hydrocarbons sample and super fine boehmite powder (S B powder) AlO (OH) were a gift from State Key Laboratory of Catalysis of Dalian Institute of Chemical Physics, CAS. Macro porous silica gel was obtained from Qingdao Ocean Chemical Factory. Acetone, chloroform and nitric acid were all of analytical grade.

All the analysis was performed on a model 8820 gas chromatograph (Shanghai Analytical Instrument Factory, Shanghai) equipped with a FID. The sample mixture comprises methane, ethane, ethylene, acetylene, propane, propylene, n-, iso-butane, 1-butene, isobutene and 1,3-butadiene. *Cis, trans*-2-butene mixture was injected separately.

Modification method for silica gel

Modifying silica gel (60-80 mesh and 80-100 mesh, respectively) with organic stationary phases was performed with conventional method. The silica gel was packed into a 1 m×3 mm stainless steel column.

Al_2O_3 was used to modify the silica gel according to the sol-gel method[6]. The SB powder was added to 85℃ deionised water. Half an hour later, a certain amount of nitric acid, making the ratio of $[H^+]/[Al^+]$ in the solution to be 0.09, was poured into the solution and the solution was aged for 4-5 h. The $Al(OH)_3$ sol obtained was mixed with silica gel and then the blend was filtered under partial vacuum. The wet silica gel was put into an empty drier and let the water evaporate slowly till dryness. Then heated the silica gel in an electric oven at 550℃ for 4-5 h. In this process, $Al(OH)_3$ on the silica gel surface was transformed into Al_2O_3. At last it was packed into a 2 m×2 mm stainless steel column.

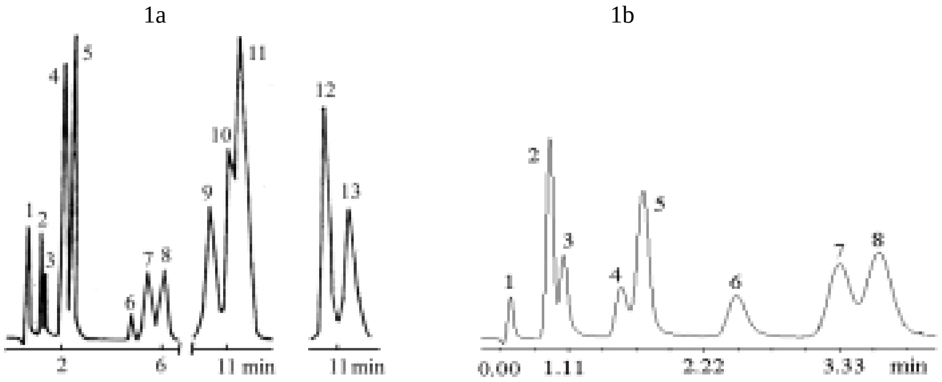
Results and discussion

When silica gel, 60-80 mesh and 80-100 mesh, was modified with different organic stationary phases, chromatographic results differed. For example, if the modifiers are non-polar and medium-polar, such as squalene, dinonyl phthalate and dioctyl sebacate, acetylene and propane cannot be separated. If the polarity of the modifier became stronger, such as hexamethylene dinitrile, ethane and ethylene eluted simultaneously. As the silica gel was modified with a series of PEG of different average molecular weight, namely 400, 600, 1000, 6000,10000, retention varied with their molecular weight, or the polarity of the stationary phase, decreasing with increasing molecular weight. When PEG 400 acts as modifier, acetylene and propane come into one peak. In the case of PEG 6000, not only acetylene and propane but also ethane and ethylene cannot be separated. Separation of the other five compounds in the sample, C4 unsaturated hydrocarbons, was dissatisfactory.

In the study, we found that when silica gel of 80-100 mesh was modified with 8.3% (w/w) PEG 2000, eight components in the mixture, *i.e.*, methane, ethane, ethylene, acetylene, propane, propylene, iso-butane and n-butane, elute successively. The above experiments were carried out with one batch of silica gel. When another batch of silica gel modified with the same method was used, only seven peaks eluted; acetylene and propane could not be separated. As the PEG 2000 content was changed to about 4% (w/w), eight peaks appeared again. **Figure 1a** is the chromatogram of 80-100 mesh silica gel modified with 4.2 % (w/w) PEG 2000 while **Figure 1b** that of 3.7% (w/w) PEG 2000.

When the silica gel was modified with Al_2O_3, a small amount of Al_2O_3 spread on the surface of silica gel and better resolution was obtained compared with non-modified

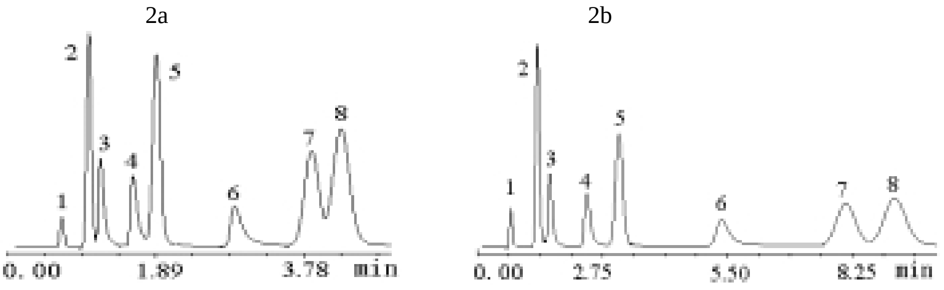
Figure 1 Separation of mixture of light hydrocarbons on packed column of silica gel modified with PEG 2000


1a

1b

Column: 1 m×3 mm 80-100 mesh silica gel coated with (a) 4.2% (w/w) (b) 3.7% (w/w) PEG 2000
Oven temperature: 65℃
1. methane, 2. ethane, 3. ethylene, 4. acetylene, 5. propane, 6. propylene, 7,8. i,n-butane, 9,10. isobutene and 1-butene, 12,13. *cis*,*trans*-2-butene, 11. 1,3-butdiene.

Figure 2 Separation of mixture of light hydrocarbons on packed column of silica gel modified with Al_2O_3


2a

2b

Column: 2 m×2 mm (a) 60-80 mesh silica gel (b) 80-100 mesh silica gel
Oven temperature: 76℃
1. methane, 2. ethane, 3. ethylene, 4. acetylene, 5. propane, 6. propylene, 7,8. i,n-butane.

silica gel (chromatogram not shown). In the research, we found that high Al (OH) $_3$ sol concentration (*e.g.* more than 1 mol/L) and too small size of silica gel particle (*e.g.* less than 120 mesh) were proved to be unfavorable to the separation. This phenomenon might be due to the decreasing of the efficiency after coating Al_2O_3 on the surface of silica gel. So we used relatively low concentration of Al (OH) $_3$ sol, being less than 0.5 mol/L, and 60-100 mesh silica gel in the experiments. **Figure 2a** and **Figure 2b** were the chromatograms when using 0.36 mol/ L Al (OH) $_3$ sol to mix with 80-100 mesh and 60-80 mesh silica gel prior to heating, respectively.

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