Separation of Aromatic and Alcoholic Mixtures using Novel MWCNT-Silica Gel Nanocomposite as an Adsorbent in Gas Chromatography

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Abstract

The separations of alcohols with hydrophilic and hydrophobic parts, and the separation of aromatic mixtures, are extremely important processes in gas and petroleum industries. Choosing an adsorbent for performing this separation is the most important part of the process. Silica gel is used as an adsorbent is various techniques such as pressure swing adsorption (PSA) and gas and liquid chromatography. Due to the polarity of silica gel, it is used for the separation of polar molecules. Carbon materials such as activated carbon and recently carbon nanotube (CNTs) are widely used for the separation of nonpolar materials. In the course of this study, a new composite was fabricated using sol-gel methods. Multiwall carbon nanotubes (non-polar carbon-based adsorbents with high surface areas) were mixed with a silica gel base (a strong polar adsorbent). The composite was then used in the separation of mixtures of both aromatic hydrocarbons and alcohols.

Keywords: MWCNTs-SiO2, Nanocomposite, Sol-Gel process, Gas Chromatography, Aromatic Hydrocarbons, Primary Alcohols
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1. Introduction

Molecular sieves, porous polymers (e.g. Porapak), activated carbons and silica are different sorbents that have long been used in gas chromatography and other gas separation techniques. Almost all of these sorbents have an upper temperature limit about 250-350 °C. Different methods for the fabrication and modification of packed columns and capillary columns are employed according to column type (1).

The characteristics and capabilities of silica gel make this material one of the most important bases for the separation of polar mixtures. It is considered as a good sorbent for packed column GC. The Sol-gel method is effective for the fabrication of silica gel and the formation of silica composite (2), (3). One petrochemical application of silica gel is the adsorption of H_2S, N_2O_4 and some other gases (4).

Silica gel has good properties for the separation of certain materials. However, this sorbent does not provide enough surface area for performing separations. Also, The surface specification of silica gel is

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fixed, and in some instances it needs to be able to separate a mixture of gases with different physical conditions. Carbon nanotube (CNTs) is one of the most interesting materials for gas-solid chromatography (GSC) and has been used as a sorbent in both capillary and packed columns (5). MWCNTs is a good candidate for adsorption applications due to its different capabilities. These include polarity or non-polarity (based on its functional groups), good inner hollow cavity, outside surface and the interstitial spaces between its nano bundles (6). Based on the superior characteristics of MWCNTs (1), (7) and the good compatibility of C and SiO2 (8), MWCNT-SiO2 composite can be applicable to the separation of some analytes (9), (10).

In this investigation, the Sol-gel technique is used for the fabrication of MWCNT-SiO2 sorbent. The separation of alcohol mixture and hydrocarbon mixture is performed using this sorbent. A strong advantage of this technique is the covalent bond between C-SiO2 in MWCNT-SiO2 composite, ensuring the stability of the sorbent during the separation process and allowing for this separation to be easily reproduced.

2. Experiment

2.1. Chemicals

For the preparation of silica gel particles using the Sol-gel method, the following compounds are required: glass water (sodium silicate) with NaO:Si ratio of 7.5% and Si-concentration of 14% mol/lit , deionized water, and sulfuric acid (96%). All chemicals are from Merck. The MWCNTs (-COOH derivative) are produced by the Research Institute of Petroleum Industry (RIPI) using the CVD process.

2.2. Apparatus

The equipped Shimadzu 14B Gas Chromatograph (GC) with thermal conductivity detector (TCD) was used in all experiments. Samples storage was achieved via a trap embedded between the carrier gas and the sample injector.

2.3. Synthesis of MWCNT-SiO2 nanocomposite (Sol-Gel process).

Water glass (Na2SiO3) is the base compound for the formation of silica gel. First, a mixture of 5% MWCNT (W.V), 7.5 % water glass (Na2SiO3) was obtained. Next, this solution was dispersed using an ultrasonic bath to make it homogenous. After preparing the homogeneous dark solution, the mixture was added slowly to an appropriate volume of sulfuric acid solution until the pH level reached 2.5-3.5.

$$Na2\ SiO3 + H+ \rightarrow [SiO2.xH2O] + 2Na\ X$$
Silica Gel
$$Na2\ SiO3 + H++ MWCNTs \rightarrow [SiO2.xH2O, MWCNTs] + 2NaX$$
CNTs-Silica Gel

The Sol process was performed in acidic pH (2.5-3.5). In this pH range, proper networks among molecules are created. MWCNTs became stuck in these networks, and proper gel was created ((11), (12)). The next step was the gelation process. The solvent was removed from the sol. In this sol, water is the main solvent and hence must be removed. To achieve this, a spraying nozzle with d = 0.222 mm was installed on a proper reservoir. The solution was then sprayed at high pressure into the hot glycerol oil. This step was carried out using the oil drop method. The goal of this process was the production of spherical granules with a mesh size of 60-80 mesh. Sprayed sol of MWCNT-SiO2 created proper spherical granules. Due to the solubility of water in glycerol, hot oil was able to remove the water from the granules, completing the gelation process, after which the temperature of the glycerol was reduced and the glycerol decanted. The granules were then washed in order to remove the oil from the MWCNT- SiO2 composite and the remaining solvent also is removed by blowing warm air. The next step was the calcination of the mixture in a 200°C oven. Finally, there was the meshing process (60-80), after which the sorbent was ready for packing in a suitable GC packed column.

Figure 1 shows an AFM (Atomic force microscopy) image of the new adsorbent. The AFM images were obtained through the use of a CSM instrument. In order to analyze the samples, their dissolution speed was increased by sonication in dimethylformamide (0.1 mg/mL) for at least 1 h, after which 5 μL was scattered onto a mica sheet. Scans were then carried out using a scan rate of 1.0 Hz.

The most important factor in gelation time is pH levels, which must be adjusted in order to obtain the best mesh of the highest quality. If not, there is the risk of aggregation occurring, and the desired mesh cannot be produced after the oil drop method has been applied (11). The lowest gel formation occurred at pH=2, and fastest gelation time was at pH=6 (12). Due to importance of the solution being homogenously mixed, pH=2.5-3.5 was the value decided upon.

2.4. Preparation of gas chromatography for analysis

Before separations could begin, the adsorbent had to be prepared by passing the carrier gas in proper column conditions. The TCD detector also needed to be checked. The instrument was conditioned at 200 °C with a He carrier gas flow of 35 ml/min for 3 hours. All important factors are listed in Table 1. Also, a proper gas loop for the injection of gas sample was installed on the GC.

Table 1 Parameters of Gas Chromatography for analysis

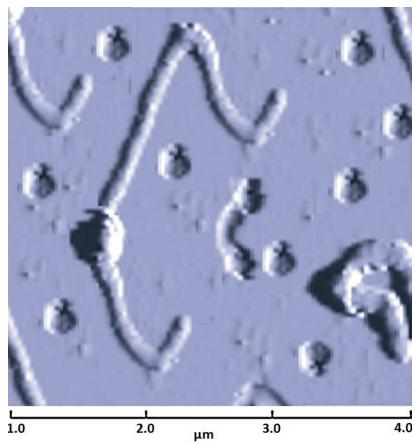| Columns	Carrier gas	TCD detector	injection
Stainless steel columns 1.5 m long and 3mm thick. Column is packed with CNT-SiO2, mesh 60-80 (0.16-0.125 mm)	He Flow rate:35 ml/min	Temperature: 180 °C Current: 150 mA	Sample loop Volume:1ml, 2ml

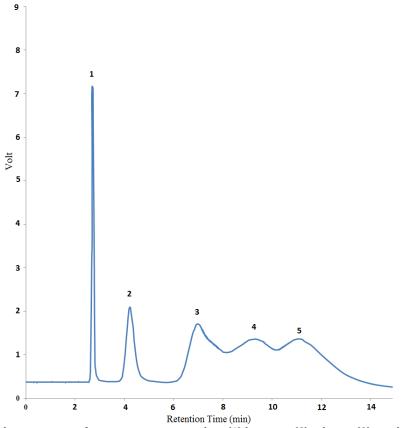**Figure 1**: The AFM images of MWCNT-Silica gel gas chromatography adsorbent.

Figure 2: The gas chromatogram of aromatic mixture involves (1) benzene, (2) toluene, (3) p-xylene, (4) m-xylene, and (5) o-xylene using unmodified silica in the gel stationary phases (detector temperature =180 ˚C, column temperature = 150°C). Other gas chromatography parameters are mentioned in Table 1.

3. Results and Discussion

3.1 Separation of Aromatic Hydrocarbons

In first stage, GC instrument and two packed columns with specific parameters (see Table 1) were prepared. A specially designed shaker was used for packing the columns. After conditioning the columns, the separation of the aromatic mixture, including benzene, toluene, p-xylene, m-xylene and o-xylene, was performed using unmodified silica gel (Figure 2) and modified silica gel-MWCNT columns (Figure 3). As shown in Figure 2, unmodified silica gel was not able to separate p-xylene, m-xylene and o-xylene completely. Their peaks became broad and asymmetric. This was due to differences in molecular mass, shape, and the partial polarity of molecules on the surface of the adsorbent. Based on these factors, the consequence of elution was determined. Also, the same molecular formula and different configurations of p-xylene, m-xylene and o-xylene cause broad and unseparate peaks to form on the silica gel column. Their retention time is summarized in Table 2.

Table 2. Retention times of benzene, toluene, p-xylene, m-xylene, and o-xylene by unmodified silica gel.

	benzene	toluene	p-xylene	m-xylene	o-xylene
Ret. Time (min)	2':51"	4':12"	7':08"	9':18"	11':08"

Under the same column conditions, the silica gel-MWCNT column showed sharp and separate peaks. Five symmetrical peaks were created with previous consequence (Figure 4). Due to the higher adsorption of this composite, the sorption and desorption processes for these volatile aromatic compounds required a

different set of conditions. Functional MWCNTs are open-ended tubes and they have two different areas: the inside and outside of the tube. The Internal area has CNT properties and can adsorb aromatic compounds based on their free π orbitals and C-C unoccupied orbital interactions. The external area has –COOH functional groups in addition to C-C unoccupied orbitals, and all these properties improve its affinity for adsorption. These molecular characteristics reduce free energy of adsorption and facilitate sorption process. As shown in Figure 3 and Table 3, the elution consequence is determined by molecular mass and partial polarity based on molecular shapes. Hydrophobic compounds had the best peaks, and the separation of hydrophobic aromatic compounds was performed in a lower retention time.

Table 3. Retention times of benzene, toluene, p-xylene, m-xylene, and o-xylene by modified MWCNT-silica gel.

	benzene	**toluene**	**p-xylene**	**m-xylene**	**o-xylene**
Ret. Time(min)	4':26"	6':36"	11':12	14':07"	15':22"

3.2 Separation of Alcohols
In this part of experiment, the ability of columns to separate a mixture of alcohols was measured. Unmodified and modified silica gels were used for the separation of methanol, ethanol, 2-propanol, n-propanol, iso-butanol, and n-butanol. As shown in Figure 4, all peaks had tails and separation was not completely achieved using unmodified silica gel at 200 °C. As such, it was not sufficient for the separation of this mixture. Based on the tailing and asymmetric peaks in Figure 4, it can be concluded that the process of adsorption and desorption on the surface of the adsorbent was irreversible. The hydrophilic surface of silica gel did not have the necessary gradient for the adsorption process, and the gradient in this column was hence insufficient. Retention times for this mixture are summarized in Table 4.
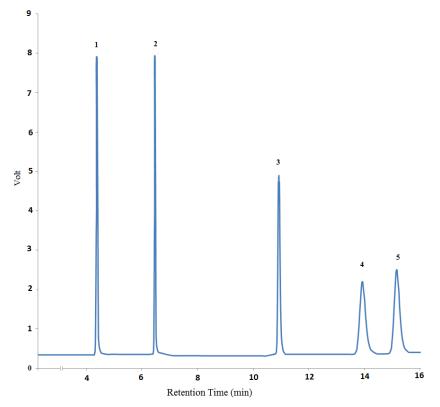

Figure 3: The gas chromatogram of aromatic mixture involves (1) benzene, (2) toluene, (3) p-xylene, (4) m-xylene and (5) o-xylene using modified silica gel-MWCNT for the stationary phases (detector temperature =180 °C, column temperature = 150°C). Other gas chromatography parameters are mentioned in Table 1.
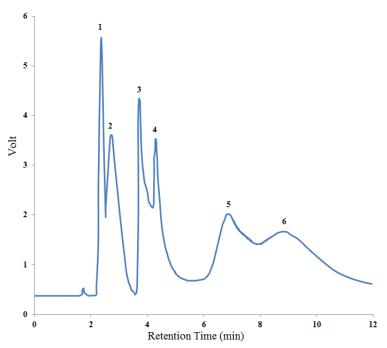
Figure 4: The gas chromatogram of mixed alcohols involves (1) methanol, (2) ethanol, (3) 2-propanol , (4) n-propanol, (5) iso-butanol and (6) n-butanol, using unmodified silica gel for the stationary phases (detector temperature =180 ˚C, column temperature = 200°C). Other gas chromatography parameters are mentioned in Table 1.

Table 4. Retention time of methanol, ethanol, 2-propanol, n-propanol, iso-butanol and n-butanol by unmodified silica gel.

	methanol	ethanol	2-propanol	n-propanol	iso-butanol	n-butanol
Ret.time(min)	2':26"	2':46"	3':55"	4':31"	7':04"	8':57"

As indicated in Figure 5, silica gel-MWCNT adsorbent showed a strong ability to separate the mixture. Due to its simultaneous hydrophobic (MWCNT) and hydrophilic (silica gel and –COOH functional groups of MWCNT) properties, separation was improved. Adsorption and desorption of molecules occurred under a gradient based –OH. Hydrocarbon tails of alcohols were present, as well as space occupation of molecules. As show in Figure 4, peaks of methanol and ethanol and also peaks of 2-propanol and n-propanol are overlapped, and iso-butanol and n-butanol had long tails and their intensity was low. But in Figure 5, all peaks are separated and there was no tail or asymmetry to the peaks, and separation was performed in a longer retention time. The retention times for this mixture are summarized in Table 5.

Table 5. Retention times of methanol, ethanol, 2-propanol, n-propanol, iso-butanol, and n-butanol by modified MWCNT-silica gel.

	methanol	ethanol	2-propanol	n-propanol	iso-butanol	n-butanol
Ret. Time(min)	3':46"	4':36"	6':35"	7':28"	9':56"	10':57"

4. Conclusion

As demonstrated by these experiments, silica gel-MWCNT adsorbent shows high ability in the separation of mixtures whose molecules consist of hydrophobic and hydrophilic parts. The modification of silica gel by MWCNT and its impressive characters not only provides this an opportunity to use the hydrophilic characteristics of silica gel in the separation process, but also extends to the separation of hydrophobic parts by MWCNT. Some important properties of this new adsorbent are: (1) increased surface area for performing separation, (2) simultaneous separation of molecules with hydrophobic and hydrophilic parts, (3) reduced plate number, and (4) increased retention times and the presence of symmetrical peaks.
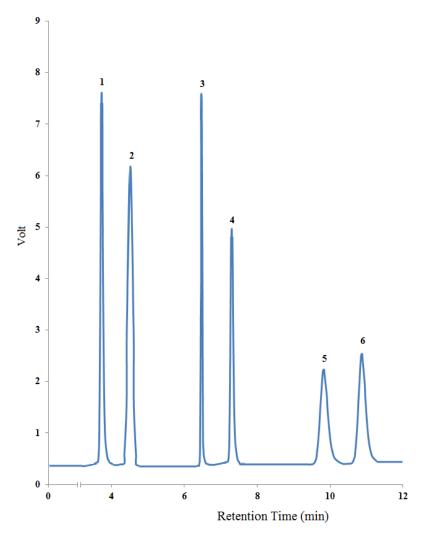
Figure 5: The gas chromatogram for the alcohols mixture involves (1) methanol, (2) ethanol, (3) 2-propanol , (4) n-propanol, (5) iso-butanol and (6) n-butanol using modified MWCNT-silica gel for the stationary phases (detector temperature =180 ˚C, column temperature = 200°C). Other gas chromatography parameters are mentioned in Table 1.

5. Acknowledgment

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