APARATURA
BADAWCZA I DYDAKTYCZNA

Application of M41S type mesoporous adsorbents in gas chromatography

TEIMURAZ ANDRONIKASHVILI, LUBA EPRIKASHVILI, MARINA ZAUTASHVILI, TEIMURAZ KORDZAKHIA, NINO PIRTSKHALAVA, MAIA DZAGANIA

IV. JAVAKHISHVILI TBILISI STATE UNIVERSITY; P. G. MELIKISHVILI INSTITUTE OF PHYSICAL AND ORGANIC CHEMISTRY (IPOC), GEORGIA

ABSTRACT

Zeolites are fine-porous sorbents widely used in the practice of gas chromatography for the separation of gas systems and mixtures of volatile organic compounds. However, capabilities of zeolites are limited because of small-sized "entrance apertures" (~0,9 nm) that limitate of their application in the analysis of the organic compounds with significant molecular volumes and active functional groups. Synthesis of the mesoporous materials with considerable sizes of the "entrance apertures" and retaining their molecular-sieve properties as well open up new possibility of their application in gas-adsorption chromatography for the separation of the mixtures consisting of the large molecules characterized with greater kinetic diameters (poly-nuclear aromatic compounds). Currently, the mesoporous materials of the M41S family have a greater application.

The adsorption-separation properties of new materials and their cationmodified forms were studied in different variants of the surface-layer sorbents - mesoporous materials have been coated on the solid support Celite-545.

Investigation of the chromatographic behavior of the M41S mesoporous adsorbent has shown that the benzene derivatives can be successfully separated on both initial and modified forms of the above adsorbent. This adsorbent and its modified forms may be applied as adsorbents in gas-chromatography for the analysis of difficult-to-separate mixtures of some polycyclic compounds.

Zastosowanie mezoporowatych adsorbentów typu M41S w chromatografii gazowej

Słowa kluczowe: adsorpcyjna chromatografia gazowa, mezoporowaty adsorbent M41S, węglowodory policykliczne

STRESZCZENIE

Zeolity są wąskoporowatymi adsorbentami szeroko stosowanymi w praktyce chromatografii gazowej do rozdzielania mieszanin gazów i lotnych związków organicznych. Jednakże przydatność zeolitów do tego celu jest ograniczona ze względu na małe rozmiary „otworów wejściowych". To ogranicza ich zastosowanie w analizie związków organicznych o dużej objętości cząsteczek z aktywnymi grupami funkcyjnymi. Synteza mezoporowatych materiałów ze znacznymi rozmiarami „otworów wejściowych" z zachowanymi właściwościami sit cząsteczkowych daje nowe możliwości ich zastosowania w adsorpcyjnej chromatografii gazowej do rozdzielania mieszanin zawierających duże cząsteczki charakteryzujące się większymi średnicami kinetycznymi (wielopierścieniowe węglowodory aromatyczne). Obecnie duże znaczenie mają mezoporowate materiały należące do grupy M41S.

Adsorpcyjno-rozdzielcze właściwości nowych materiałów i ich kationowych modyfikacji badano w różnych wariantach sorbentów warstwowo-powierzchniowych – mezoporowate materiały osadzano na nośniku Celit-545.

Badanie chromatograficznych właściwości mezoporowatego adsorbentu M41S wykazało, że na wyjściowym materiale i jego formie modyfikowanej mogą być z powodzeniem rozdzielane pochodne benzenu. Wykazano możliwość zastosowania tych materiałów jako adsorbentów w chromatografii gazowej do analizy trudnych do rozdzielania mieszanin pewnych związków policyklicznych.

1. INTRODUCTION

Zeolites, that is molecular sieves are used in gas chromatography mainly for the separation of the mixtures component molecules of which are able to penetrate into the pores of these adsorbents [1]. This property limits their application in the analysis of large organic compounds containing active functional groups. Nevertheless, synthesis of the mesoporous materials with considerable sizes of "entrance apertures" for retaining their molecular-sieve properties open up new possibilities of their application in gas-adsorption chromatography.

Currently, M41S mesoporous materials (offered by the company "Mobile R & D Corporation" in 1992) are widely used in chemistry [2]. These mesoporous materials are silica, containing insignificant amount of cation-exchange Na^+ and are characterized by "aperturesof equal size" (at about 8,0 nm). The work [3] shows that substitution of one type of cations by others significantly alters their chromatographic properties. M41S type mesophorous molecular sieve is one of the representative of mesophorous silica dioxide MCM 41. Depending on the conditions of the synthesis, diameter of its porous varies from 2,0 to 10,0 nm. This material is characterized by regular structure and its specific surface reaches 100 m^2/g [4].

The presented study aims to show the feasibility of application of the mesoporous materials in gas-adsorption chromatography and proves the effect of the complexing metals (cadmium and thallium) on the separation of various model mixtures [5, 6].

2. EXPERIMENTAL

M41S type mesoporous adsorbent (MA) was synthesized at the Laboratory of Physical Chemistry of Institute of Physical and Organic Chemistry [7]. The diameters of the "apertures" of the obtained mesoporous material is about 4 nm and have molecular sieve property.

Cation modification of the samples was peformed by their treatment with 0.1 N aqueous solutions of cadmium (II) nitrate and thallium (I) sulfate in order to completely substitute Na^+ by Ca^{+2} and Tl^+ cations [8]. Both the initial sample and the cation modified forms were washed by distilled water, dried at room temperature and activated by

heating at 250 °C for 3 hrs in the nitrogen flow. The investigated powdered adsorbents were coated on the solid support Celite-545 of 50/60 mesh of granulation [9, 10]. Chromatographic properties of the initial and the modified adsorbents were investigated in the version of surface-layer sorbents: mesoporous sorbents were coated on Celite-545. The sorbent was activated in chromatographic column at 300 °C for an hour in the flow of nitrogen. The chromatographic analyses were carried out at different column temperatures (200÷250 °C). Polycyclic hydrocarbons were used as model mixtures [11].

The all columns used were of the same length and diameter (1 m x 4 mm).

The number of theoretical plates was determined according to the well known formula using the half-height width of peaks of chromatographed compounds.

Increment of column selectivity (K_{sel}) is calculated in the following way:

$$K_{sel} = 2 \frac{t_{R2} - t_{R1}}{t_{R2} + t_{R1}} \qquad (1)$$

Where t_{R1} and t_{R2} are the retention times of the chromatographed components.

The separation coefficients (K_{sep}) of a binary mixtures were calculated as:

$$K_{sep} = \frac{\Delta l}{\mu_{0,5(1)} + \mu_{0,5(2)}} \qquad (2)$$

where Δl is the distance between the maxima of two chromatographic peaks and $\mu_{0,5(1)}$ and $\mu_{0,5(2)}$ are the peaks widths at their half-height.

The value of uniformity criterion (Δ) is calculated using the following relationship:

$$\Delta = (n_p \times w_{b(n)} \times R) / t \qquad (3)$$

where n_p is the number of peaks on a chromatogram, $w_{b(n)}$ is the width at the base of the narrowest peak, t is the total analysis time and R is the resolution of the worst separated peak pair calculated from the retention times (t_R) and the width at the half height (w_h) of the two peaks ($t_{R2} > t_{R1}$):

$$R = \frac{t_{R2} - t_{R1}}{w_{h1} + w_{h2}} \qquad (4)$$

3. RESULTS AND DISCUSSION

Analysis of the obtained data evidenced that the order of elution of $C_{24}H_{30}$ isomers can not be associated with their melting points: *o*-isomer

(with higher melting temperature) is eluted earlier than corresponding *m*- and *p*-isomers. This is apparently conditioned by their structure: *p*-isomer is more strongly adsorbed by the surface of the mesoporous adsorbent than the corresponding *o*- and *m*- isomers. The isomers of $C_{27}H_{34}$ are eluted similarly. The relative retention times (t'_R), calculated against benzene, for the separate components on the investigated mesoporous adsorbents at the optimal chromatographic column temperature (250 °C) are presented in Table 1.

It should be noted that the retention times of the components of the investigated model mixture on the modified forms of sorbents increase compared with those on the initial form (MA), depending on the type of cations, in the following order: MA $_{initial\ form}$ <Cd^{+2}-MA<Tl$^+$-MA.

The observed difference in the retention times evidences the possibility of their separation in chromatographic column.

The values of the number of theoretical plates (calculated for 1 m column) for each peak of the isomers of $C_{24}H_{30}$ and the increase in the number of theoretical plates on modified sorbents compared with that on the initial form are entered in Table 2. According to the data, efficiencies of the columns packed with the investigated adsorbents increased in the following order:
MA $_{initial\ form}$ <Cd^{+2}-MA<Tl$^+$-MA.
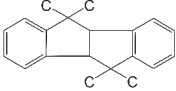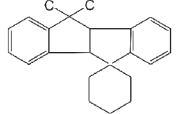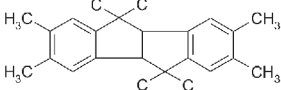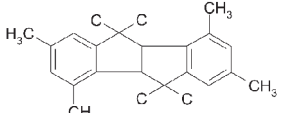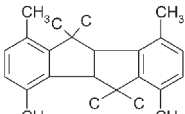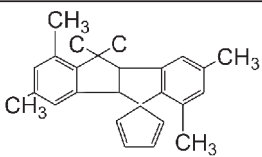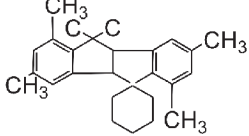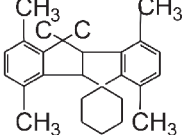
Degree of increase of chromatographic column efficiency (with the modified adsorbents) compared with that of initial form is far greater than the degree of broadening of the corresponding peak on the chromatogram. Modification of M41S type mesoporous adsorbent by cadmium salts enables us to increase the chromatographic column efficiency in the average by 11.74 %, by the use of thallium salts – 29.76 % compared with the initial sample (MA); difference between the column efficiencies on Tl$^+$ and Ca^{+2} forms equals to 16.53 %.

The Table 3 presents the values of relative changes of the selectivity (K_{sel}) and separation (K_{sep}) coefficients of the binary mixtures [12], expressed in percents relative to the data obtained with the initial form.

As it is seen from the above data, modification of the initial mesoporous material (MA) contributes to significant increase of selectivity of the adsorbents in the order Cd^{+2}-MA<Tl$^+$-MA, which is expressed correspondingly in the change of selectivity and separation coefficients (K_{sel} and K_{sep}).

Table 1 Relative retention times (t'$_R$) of polycyclic hydrocarbons of the investigated samples

Tabela 1 Względne czasy retencji (t'$_R$) węglowodorów policyklicznych

Sorbate	Formulae	Melting point °C	Initial form of MA coated on Celite-545	Cadmium form of MA coated on Celite-545	Thallium form of MA coated on Celite-545
			t'$_R$	t'$_R$	t'$_R$
1	2	3	4	5	6
C_6H_6		T$_{boil.}$ 80.1	1.00	1.00	1.00
$C_{20}H_{22}$		83-84	3.19	3.23	3.72
$C_{23}H_{26}$		168-169	4.63	4.72	5.56
o-$C_{24}H_{30}$		147-148	6.82	8.12	9.42
m-$C_{24}H_{30}$		116-117	8.78	9.82	10.14
p-$C_{24}H_{30}$		136-137	10.12	10.73	12.57
$C_{26}H_{32}$		118-119	14.91	17.78	22.57
m-$C_{27}H_{34}$		137-140	27.27	33.00	39.86
p-$C_{27}H_{34}$		179-180	32.64	39.56	48.72

Table 2 Number of theoretical plates (N) and their increment (in %) for the isomers of $C_{24}H_{30}$ on the investigated adsorbents (calculated against 1 m of the chromatographic column)

Tabela 2 Liczba półek (N) i ich inkrement (w %) dla izomerów $C_{24}H_{30}$ na badanych adsorbentach (obliczone dla 1 m długości kolumny)

Sorbate	Adsorbent					
	MA $_{initial\ form}$		Cd^{+2}-MA		Tl$^+$-MA	
	N	increment, %	N	increment, %	N	increment, %
C_6H_6	754	-	935	24.00	1014	34.48
o-$C_{24}H_{30}$	850	-	996	17.17	1147	34.94
m-$C_{24}H_{30}$	987	-	1027	4.05	1296	31.30
p-$C_{24}H_{30}$	1114	-	1133	1.70	1318	18.31

Table 3 Increment of column selectivity (K_{sel}) and separation coefficients (K_{sep}) of the binary mixtures on the investigated adsorbents compared with the initial form (MA)

Tabela 3 Inkrement selektywności kolumny (K_{sel}) i współczynnika rozdzielenia (K_{sep}) dwuskładnikwych mieszanin na badanych adsorbentach w porównaniu z ich formą pierwotną (MA)

| Binary mixture	Increment, %			
	Cd^{+2}-MA		Tl^{+}-MA	
	K_{sel}·	$K_{sep.}$	K_{sel}·	$K_{sep.}$
C_6H_6 - $C_{20}H_{22}$	8.96	12.50	9.52	25.00
$C_{20}H_{22}$ - $C_{23}H_{26}$	35.89	14.28	42.50	35.72
$C_{23}H_{26}$ - o-$C_{24}H_{30}$	15.72	11.12	38.57	22.23
o-$C_{24}H_{30}$ - m-$C_{24}H_{30}$	14.28	8.34	35.00	33.34
m-$C_{24}H_{30}$ - p-$C_{24}H_{30}$	57.14	15.38	65.00	46.15
p-$C_{24}H_{30}$ - $C_{26}H_{32}$	71.87	28.57	73.64	35.72
$C_{26}H_{32}$ - m-$C_{27}H_{34}$	9.45	5.56	10.57	11.12
m-$C_{27}H_{34}$ - p-$C_{27}H_{34}$	11.12	8.34	12.50	16.67

The value of uniformity criterion (Δ) (characteristic of the peak distributions on a chromatogram) is the analogue of selectivity coefficient in case of separation of a multi-component mixture. The above regularity was observed for the values of uniformity criterion [13] of the nine-component mixture of polycyclic hydrocarbons on the investigated sorbents (Tab. 4).

Here again we observe the increase in criterion of uniform separation that proves the improvement of the peak resolution of the model mixture (Fig. 1) [14].

Table 4 Increment of the uniformity criterion (Δ) on the modified forms of mesoporous adsorbent compared with those of the initial form

Tabela 4 Inkrement kryterium jednorodności (Δ) na modyfikowanych mezoporowatych adsorbentach w porównaniu z ich formą wyjściową

Model mixture	Increment, %	
	Cd^{+2}-MA	Tl^{+}-MA
C_6H_6 - $C_{20}H_{22}$ - $C_{23}H_{26}$ - o-$C_{24}H_{30}$ - m-$C_{24}H_{30}$ - p-$C_{24}H_{30}$ - $C_{26}H_{32}$ - m-$C_{27}H_{34}$ - p-$C_{27}H_{34}$	12.50	23.07
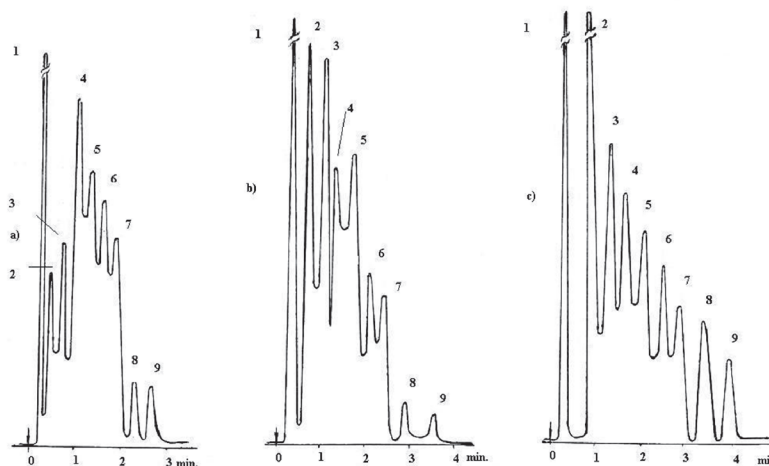
Figure 1 Chromatogram of nine-component mixture of polycyclic hydrocarbons: a) on the initial adsorbent (MA); and on its modified forms: b) Cd^{+2}-MA, c) Tl^{+}-MA. Column dimensions: 1 m x 4 mm. Nitrogen carrier gas flow rate: 20 ml min^{-1}. Column temperature 250 °C. Thermal conductivity detector.
1. C_6H_6; 2. $C_{20}H_{22}$; 3. $C_{23}H_{26}$; 4. o-$C_{24}H_{30}$; 5. m-$C_{24}H_{30}$; 6. p-$C_{24}H_{30}$; 7. $C_{26}H_{32}$; 8. m-$C_{27}H_{34}$; 9. p- $C_{27}H_{34}$

Rysunek 1 Chromatogram dziewięcioskładnikowej mieszaniny węglowodorów policyklicznych: a) na adsorbencie wyjściowym (MA) i na jego formach modyfikowanych: b) Cd^{+2}-MA, c) Tl^{+}-MA. Wymiary kolumny 1 m x 4 mm. Przepływ gazu nośnego (azotu): 20 ml min^{-1}. Temperatura kolumny 250 °C. Detektor cieplno-przewodnościowy.
1. C_6H_6; 2. $C_{20}H_{22}$; 3. $C_{23}H_{26}$; 4. o-$C_{24}H_{30}$; 5. m-$C_{24}H_{30}$; 6. p-$C_{24}H_{30}$; 7. $C_{26}H_{32}$; 8. m-$C_{27}H_{34}$; 9. p- $C_{27}H_{34}$

Analysis of the given data enables us to conclude that the most selective adsorbent (modified by Tl^+) gives good separation of the hydrocarbons at 250 °C on the surface-layer sorbents not observed in gas-adsorption chromatography on the common (volumetric) sorbents [15].

4. CONCLUSIONS

Calculations of the separation and the selectivity coefficients of the definite binary mixtures, and the uniformity criterion of the nine-component mixture showed that their values increase depending on the type of the modifying cations in the order: $MA_{\text{initial form}} < Cd^{+2}\text{-}MA < Tl^+\text{-}MA$.

Thus, investigation of gas-chromatographic behavior of mesoporous adsorbent M41S showed that benzene derivatives might be successfully separated on the initial form of this adsorbent as well as on its modified forms. Study of the synthesized material M41S and its modified forms proved the possibility of their application as the adsorbents in gas-adsorption chromatography for the analysis of difficult to separable mixtures of some polycyclic compounds.

REFERENCES

[1]   Andronikashvili T., Tsitsishvili G. Chromatographic separation of low-boiling inorganic and hydrocarbon gas mixtures on zeolites. J. Chromatogr., 1984, 292, 3-8.

[2]   Kresge C.T., Leonowicz M.E., Roth W.J., Vartuli J.C., Beck J.S. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. Nature, 1992, 359, 710-712.

[3]   Andronikashvili T., Tsitsishvili G., Sabelashvili Sh., Chromatographic properties of type X zeolites containing alkali metal cations. J. Chromatogr., 1971, 58, 47-54.

[4]   Wu C.- G. , Bein T. Science, 1994, v. 266, 1013- 1014.

[5]   Zautashvili M., Andronikashvili T., Eprikashvili L. On the possibility of using the mesoporous adsorbents for the chromatographic separation of pikoline isomers. Georgian Engineering News, 2000, 2, 128-130.

[6]   Andronikashvili T., Eprikashvili L., Zautashvili M., Dzagania M. The estimation fitness of using mesoporous adsorbent for type M41S for separation isomers some organic combinations. Proceedings of the Georgian Academy of Sciences, chemical series, 2002, 28, 101-108. (in Russian)

[7]   Tsitsishvili G., Tsitsishvili V., Dolaberidze N., Alelishvili M., Chipashvili D., Tsintskaladze G., Sturua G. Syntesis and structure of M41S type mesoporous molecular sieves. Proceedings of the Georgian Academy of Sciences, chemical series, 1999, 25, 1-2, 117-120. (in Russian)

[8]   Tsitsishvili G.V., Andronikashvili T.G. In: «Synthetic Zeolites», M., Ed. Acad.Sci USSR, 1962, p. 117-128. (in Russian)

[9]   Bombaugh K. Improved efficiency in gas chromatography by molecular sieve flor. Nature, 1963, 197, 1102-1103.

[10]   Andronikashvili T., Eprikashvili L., Eprikashvili Z. Influence of the nature of solid support and the dispersity of the active agent on the performance of chromatographic columns packed with surface-layer sorbents. Chromatographia, 1997, 46, 156-160.

[11]   Lagidze R.V. Synthesis and reactions of substituted dibenzopentalanes and aralkylhalogenides. Tbilisi, "Metsniereba", 1984, 289 p. (in Russian)

[12]   Supina W. The packed column in gas chromatography. Transl. from English by Berezkin V.G., Mir, 1977, 254 p. (in Russian)

[13]   Petsev N., Kotsev N. Reference book in gas chromatography. Mir, 1971, 260 p. (in Russian)

[14]   Vigdergauz M.S. Calculations in gas chromatography. Khimia, 1978, 246 p. (in Russian)

[15]   Zautashvili M.G., Eprikashvili L.G., Tsintsadze G.V., Kutsiava N.A. Towards the increase of resolution capacity of M41S type mesoporous adsorbents by their cation modification. Zhurnal Khromatographichnogo Tovaristva (Ukraine), 2002, II, No 4, 15-21.