COMBINING MOLECULAR SIEVE AND COMPLEXING PROPERTIES OF THE COLUMN PACKING IN GAS CHROMATOGRAPHY

L. Eprikashvili, N. Pirtskhalava, T. Andronikashvili, T. Kordzakhia, M. Zautashvili, M. Dzagania

Melikishvili Institute of Physical and Organic Chemistry of Georgia
5 Jikia Street, Tbilisi 0186, Georgia, physorgchem@pochta.ru

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Influence of modifying pentasyl group synthetic zeolites (Silicalite-1 and Silicalite-2) with metal cations capable to specific interactions on the separation ability of the chromatographic column has been studied.

INTRODUCTION

Zeolites belong to the selective sorbents which strongly adsorb some compounds (normal chained hydrocarbons) but do not adsorb others (aromatic, cyclic) depending on the configuration of the adsorbate molecule. The selectivity of zeolites is due to their molecular sieve properties [1]. The use of zeolites in gas chromatography ensures the separation of a complex mixture of oil origin [2].

Mixtures of meta-, ortho- and para-isomers of different hydrocarbons are difficult to separate. For their separation, such sorbents as Benton-34 and liquid crystal phases are known to be used [3, 4]. The selectivity of adsorbents is probably due to their structural properties. Zeolite Silikalite also exhibits increased selectivity to para-isomers. Because of its molecular sieve properties, it can retain linear molecules of para-isomers and does not adsorb ortho- and meta-isomers [5–8].

In this paper, we present the results of studying a selective adsorbent that combines molecular sieve properties with complexation properties, namely, a zeolite (Silicalite) modified with metal cations capable of forming complexes with benzene hydrocarbons.

EXPERIMENTAL

Two samples of Silicalite: Silicalite-1 (analog of ZSM-5) and Silicalite-2 (analog of ZSM-11) from the pentasyl group have been investigated [9]. These zeolites are characterized by an ideal unit cell of the following composition: Na₈(Al₉Si₉₀O₂₉₂)·16H₂O n~3 [10].

The adsorbents studied are high-silica zeolites. In contrast to conventional zeolites, they exhibit hydrophobic properties.

The structures of both zeolites are almost identical: ten-membered rings form two systems of intersecting channels lying in perpendicular planes. The main difference between them is as follows: in Silicalite-1, the two channel systems bearing oxygen rings of the size 0.51–0.56 nm are of both round-shape and ellipsoid configuration whereas all rings in Silikalite-2 possess ellipsoid configurations of the size 0.54x0.56 nm [10]. Barrer in [10] believed that even such a small difference in zeolite structures could strongly affect their adsorption properties.

In our experiments, powders of Silikalite-1 and Silikalite-2 (the Silikalite sample was synthesized at the Center for porous Materials of Manchester and kindly provided by Dr. R.J. Paisted) were modified with cadmium, thallium, and silver cations by ion exchange [11]. These cations can form unstable complexes with some benzene compounds. In the course of modification, the initial sodium forms of Silikalites were treated three times with a 0.1 M solution of corresponding metal nitrates. After each treatment, the powder was washed with distilled water to remove excess sodium cations and then dried at 150°C for four to six hours. In the chromatography column, zeolite was used in the surface-layer version [12] that is a powder of dispersity of 25–60 µm applied onto a solid support, celite-545, grains 60–80 mesh using the procedure proposed by Bombauch [13]. The zeolite and solid support (1:2) were mixed in a rotating porcelain cylinder. In the resulting adsorbent, the fraction of zeolite was ~27–29% relative to the mass of the solid support.

The experiments were conducted on LKhM-8MD Model 3 chromatograph using a column of 0.5 m in length and 3 mm in inside diameter. The adsorbent packed in the column was thermally activated by heating the column to 250°C in a
flow of a carrier gas (nitrogen) for 4–6 h. Column temperature in the experiments was maintained at 230°C under isothermal conditions. The flow rate of the carrier gas (nitrogen) was of 50 mL/min. A flame ionization detector was used.

Model test mixtures consisted of the following isomers: (1) meta-, ortho-, and para-xylenes; (2) meta-, ortho-, and para-chlorotoluenes; (3) meta-, ortho-, and para-dichlorobenzenes; (4) para-xylene, para-chlorotoluene, and para-dichlorobenzene. We determined parameters characterizing the process of chromatographic separation [14].

RESULTS AND DISCUSSION

Table 1 presents relative retention times of all the studied compounds and corresponding asymmetry coefficients of chromatographic peaks on both the initial (sodium) forms of Silikalites and cation-exchanger forms. As can be seen in Table 1, selectivity to para-isomers for all the studied compounds was much higher than to ortho- and meta-isomers of the same triad. The retention times of these isomers were almost equal. In going to cation-exchanger forms, the retention times of ortho-, meta-, and para-isomers increased in the order Na< Cd< Tl< Ag, depending on the nature of the cation incorporated into the Silikaliite. The increase was more pronounced for para-isomers and less pronounced for ortho- and meta-isomers. This effect was enhanced as the molecular mass of compounds was increased. The asymmetry coefficients for ortho- and meta-isomers insignificantly changed depending on the isomery and the type of the cation-modified form; a noticeable increase was observed for para-isomers.

According to the tabular data, relative retention times of the components on Silicalite-2 are higher as compared to those on Silicalite-1 on average by 170% and they are higher on both on the initial (sodium) and cation (Cd⁺, Tl⁺, and Ag⁺) modified forms; as for the asymmetry coefficients, they are higher, i.e. $K_{as} \rightarrow 1$.

By comparing retention times, we calculated the increase in selectivity of the retention of para-isomers compared to ortho-isomers cation-exchanger forms of Silikalites (Table 2). The data in Table 2 indicate that, for all isomers, selectivity increases in the order Cd< Tl< Ag depending on the cation nature in comparison with initial (sodium) forms.

As was shown in our earlier paper [15], the introduction of Cd and Ag cations into type X zeolites significantly increased the retention volumes for unsaturated hydrocarbons in comparison to those for saturated ones. This effect was more pronounced for silver than for cadmium-containing zeolite and be explained by the formation of two complexes differing in stability. Thus, the interaction of AgX with ethylene proceeds as overlapping of two orbitals, the occupied π orbital of ethylene with the vacant 5sp orbital of the silver ion and the occupied 4d orbital of silver with the vacant π orbital of ethylene. In the case of CdX, interaction proceeds as overlapping of only π and 5sp orbitals.

It is likely that, for the studied isomeric benzene derivatives, π bonds the benzene rings of isomers also interact with corresponding orbitals of Cd, Tl, and Ag cations to form complexes differing in stability (it increases in the above order) which results in an increase in the retention volumes of all isomers.

A significant increase in the selectivity of the adsorbent to para-isomers is due to the molecular sieve properties of the zeolite which more strongly adsorbs these isomers because of their configuration. As a result, the rate of molecular diffusion, which is also determined by the nature of the radical at the benzene ring, decreases.

The data in Table 2 also indicate that the selectivities of thallium- and silver-containing Silikalites to para-isomers are very high and almost equal. This can be explained by the fact that the physical and chemical properties of Tl⁺ and Ag⁺ cations are similar [12].

Thus, we can conclude that the selectivity of cation-modified Silikalites to para-isomers is determined by two factors: (1) the effect of molecular sieves and (2) the ability of analytes to form complexes with cadmium, thallium, and silver cations whereas only the complexation effect is responsible for the adsorbent selectivity to ortho- and para-isomers.

As follows from aforesaid, cation-modified Silikalites, in particular, those containing thallium and silver ions can be attributed to adsorbents selective to para-isomers.

The values of the criterion of uniformity of separation $\Delta$ [14] of a model ternary mixture of para-isomers on the studied adsorbents are presented in Table 3.

It can be seen that the sharpness of the separation of the model mixture increases in the above order depending on the cation nature. Both increase in the retention times of the individual components and more symmetrical peaks (Table 1) on Silicalite-2 compared to those on Silicalite-1 define higher values of the criterion of uniformity on Silicalite-2 (Table 3).
Table 1. Relative retention times ($t_R$) of some benzene derivatives and asymmetry coefficients of chromatographic peaks ($K_{as}$) of corresponding compounds [14] (column temperature 230°C)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial (sodium) form of Silikalite-1 applied onto Celite-545</td>
</tr>
<tr>
<td></td>
<td>$t_R$</td>
</tr>
<tr>
<td>benzene</td>
<td>1.00</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.37</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.43</td>
</tr>
<tr>
<td>p-xylene</td>
<td>0.89</td>
</tr>
<tr>
<td>o-chlorotoluene</td>
<td>0.43</td>
</tr>
<tr>
<td>m-chlorotoluene</td>
<td>0.49</td>
</tr>
<tr>
<td>p-chlorotoluene</td>
<td>1.31</td>
</tr>
<tr>
<td>o-dichlorobenzene</td>
<td>0.54</td>
</tr>
<tr>
<td>m-dichlorobenzene</td>
<td>0.49</td>
</tr>
<tr>
<td>p-dichlorobenzene</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Table 2. Increase in selectivity of the sorbent (%) p-isomers on the o-isomers of the corresponding triads in all the modified samples of the sorbent

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Silikalite-1 + Cd$^{2+}$ - Celite-545</th>
<th>Silikalite-2 + Cd$^{2+}$ - Celite-545</th>
<th>Silikalite-1 + Tl$^+$ - Celite-545</th>
<th>Silikalite-2 + Tl$^+$ - Celite-545</th>
<th>Silikalite-1 + Ag$^+$ - Celite-545</th>
<th>Silikalite-2 + Ag$^+$ - Celite-545</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-xylene/o-xylene</td>
<td>5.5</td>
<td>35</td>
<td>34.9</td>
<td>59</td>
<td>38.4</td>
<td>72</td>
</tr>
<tr>
<td>p-chlorotoluene/o-chlorotoluene</td>
<td>29.3</td>
<td>39</td>
<td>37.4</td>
<td>194</td>
<td>38.8</td>
<td>236</td>
</tr>
<tr>
<td>p-dichlorobenzene/o-dichlorobenzene</td>
<td>40.6</td>
<td>56</td>
<td>49.3</td>
<td>311</td>
<td>52.7</td>
<td>323</td>
</tr>
</tbody>
</table>

Table 3. Criterion ($\Delta$) of uniformity of the separation of a ternary model mixture of para-isomers on selective sorbents (column temperature 230°C)

<table>
<thead>
<tr>
<th>Model mixture</th>
<th>Initial (sodium) form of Silikalite-1 applied onto Celite-545</th>
<th>Initial (sodium) form of Silikalite-2 applied onto Celite-545</th>
<th>Cadmium form of Silikalite-1 applied onto Celite-545</th>
<th>Cadmium form of Silikalite-2 applied onto Celite-545</th>
<th>Thallium form of Silikalite-1 applied onto Celite-545</th>
<th>Thallium form of Silikalite-2 applied onto Celite-545</th>
<th>Silver form of Silikalite-1 applied onto Celite-545</th>
<th>Silver form of Silikalite-2 applied onto Celite-545</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-xylene–p-chlorotoluene–p-dichlorobenzene</td>
<td>0.24</td>
<td>0.27</td>
<td>0.37</td>
<td>0.40</td>
<td>0.44</td>
<td>0.47</td>
<td>0.56</td>
<td>0.58</td>
</tr>
</tbody>
</table>
CONCLUSION
After modification of corresponding stationary phases, the developed adsorbent can be successfully used in gas chromatography for the separation and analysis of mixtures of ortho-, meta-, and para-isomers of aromatic organic compounds.

REFERENCES

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Combining Molecular Sieve and Complexing Properties of the Column Packing

Посидання молекулярно-ситових і комплексоутворюючих властивостей насадок в газовій хроматографії

Л. Епіркашвілі, Н. Пірихалава, Т. Андронікашвілі, Т. Кордахія, М. Зауташвілі, М. Дзаганія

Інститут фізичної та органічної хімії ім. П. Меліксішвілі
вулиця Джкія 5, Білісі 0186, Грузія, physorgchem@pochta.ru

Вивчено вплив модифікації синтетичних цеолітів сімейства пентасілів (Сілікаліту-1 і Сілікаліту-2) катіонами металів, здатних до специфічних взаємодій, на роздільну здатність хроматографічної колонки.

Сочетание молекулярно-ситовых и комплексообразующих свойств насадок в газовой хроматографии

Л.Эприкашвили, Н.Пирихалава, Т.Андроникашвили, Т.Кордахия, М.Зауташвили, М.Дзаганія

Институт физической и органической химии им. П. Меликишвили
ул. Джикия 5, Тбилиси 0186, Грузия, physorgchem@pochta.ru

Изучено влияние модификации синтетических цеолитов семейства пентасилов (Силікаліту-1 и Силікаліту-2) катионами металлов, способными к специфическим взаимодействиям, на разделительную способность хроматографической колонки.