

GRANULAR RICE HUSK BASED SORBENTS FOR SORPTION OF VAPORS OF ORGANIC AND INORGANIC MATTERS

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ABSTRACT

This article is dedicated to the development of a method for the manufacture of granulated carbon sorbents made of powdered rice husk (RH) and lignosulphonate (LS) aimed at absorption of organic and inorganic vapors. The microstructure analysis of the samples reveals that the activation promotes the formation of a higher amount of small pores and the development of a spongy texture of the sorbents leading to carbon content increase when compared to that of the initial sample. The final samples have apparent mesoporosity confirmed by the form of the isotherms referring to the low-temperature adsorption of nitrogen and the results of pore size distribution using the DFT method.

Keywords: sorption materials, nanostructure, toxic gases, rice husk, adsorption.

INTRODUCTION

Nowadays, the cleaning of aspiration and ventilation emissions from harmful substances is one of the main air protection measures for most of the industrial enterprises. The specific feature of most of the industrial emissions refers to the content of a large number of harmful gaseous components in addition to solid and liquid particles (dusts, gases, mists)[1, 2]. The cleaning of the gas flows from such contaminants requires corresponding knowledge of the theory to develop gas purification methods. The adsorption method becomes more and more valuable among other known methods of industrial emissions cleaning as it allows almost complete removal of the contaminations of the gas flows [3 - 5]. The solid materials of an extended surface made in form of granules (balls, pills, cylinders, etc.) or fine-grained materials are generally used as adsorbents [6 - 9].

Depending on their chemical composition there are carbon and mineral adsorbents. Active coals and

activated carbon fibers belong to the first group, while silicagels, aluminogels refer to the second one. The adsorptive properties and the capacity of these adsorbents to regenerate are determined, in general, by the chemical nature and the porosity of their surface. The highly developed surface is peculiar for highly porous substances, substances with a spongy structure or fine-grained ones. The leading role among all adsorbents used in practice belongs to different active coals (wood coal, bone coal, etc.) [10 - 14].

Many countries (Russia, USA, China, etc.) study intensively the problem of air cleaning. The scientists from the Institute on Combustion Problems perform studies [15 - 17] connected with the manufacture of modified carbon adsorbents for medical applications, waste waters cleaning from heavy metals ions, biomolecules division, etc. But the elaboration of carbon sorbents for toxic gases sorption has not been studied so far. This omission is treated in the present communication.

EXPERIMENTAL

Initial raw materials were chosen for the preparation of the granulated carbon sorbents. Rice husk were ground using the planetary mill “Activator 4M” with 300 pcs of 5 mm metal balls. The grinding time was 3 min. A mixture containing the powdered rice husk and lignosulphonate (LS) in proportions of 2:1, 3:1 and 4:1 with water addition (40 ml per 100 g) was prepared. Then granules were made using a screw granulator. They were dried under a room temperature within 6 h - 12 h. The carbonization was conducted under isothermal conditions and strict control using a rotating reactor under an inert gas-argon blanket, which was constantly fed at a flow rate of 50 cm³/min. The temperature provided referred to 750°C and 800°C. The sorption properties were improved through activation with chemical agents.

The impact of the bonding agent amount on the yield and the properties of the obtained sorbents were investigated. The proportion of the bonding agent and the powdered rice husk in the samples were varied in accordance with data provided in Table 1.

According to the data obtained by the specific surface analyzer “Sorbometer-M”, the specific surface of the samples obtained after activation was within 146 m²/g - 883 m²/g.

The values of the yield and the specific surface of the samples were compared aiming to find the perfect proportion of the sorbent and the bonding agent in the composition of the final product. The data in Table 1 shows, that it refers to 3:1 at a carbonization temperature of 800°C.

The structural and the physico-chemical properties of the granulated materials obtained were studied using electronic microscopy, low temperature adsorption of nitrogen, and adsorption of carbon dioxide. The density functional method, DFT, was used to determine the products pore size, while the BET method was applied to determine the adsorbents specific surface. The morphology and the geometry of the surface of the carbon sorbent samples were investigated using the electron microscope JSM-6510 LA. The contrast electronic micro images of the samples surface were made under voltage 15 kV - 20 kV and a current of 10 mA - 30 mA.

The device used in this study allowed analyzing the component composition of the granulated sorbent prior to and after activation. The analysis was made using the up-to-date energy-dispersion spectrometer JED-2300 EDS manufactured by “JEOL”, Japan. It is a supplementary device for the scanning electronic microscope JSM-6510 LA made by the same manufacturer.

RESULTS AND DISCUSSION

Fig. 1. Electron micrographs and geometry of the binder material – lignosulfonate and the granules obtained on the ground of RH and LS prior to and following carbonization.

The obtained micro images show that the bonding material has a solid surface and a small amount of rounded mainly large sized pores. Fig. 1 shows that the initial material (rice husk) is securely fixed in the

Table 1. Characteristics of the granular samples obtained.

| Ratio RH/LS | t, °C | Carbonization time, min | m ₀ , g | m ₁ , g | m ₂ , g | S ² _{sur} , m ² /g | Specific pore volume, cm ³ /g | Sorption activity by methylene blue mg/g |
|--------------|-------|-------------------------|--------------------|--------------------|--------------------|---|--|--|
| 67:33 2:1 | 800 | 90 | 58.12 | 11.48/10 | 4.35 | 684 | 0.272 | 368 |
| 67:33 2:1 | 750 | 90 | 40.39 | 12.31/11,6 | 7.03 | 146 | 0.065 | 363 |
| 80:20 4:1 | 800 | 90 | 25.81 | 8.25 | 4.33 | 336 | 0.147 | 365 |
| 75:25 3:1 | 800 | 90 | 45.56 | 12.11 | 6.78 | 883 | 0.337 | 373 |
| 75:25 3:1 | 800 | 110 | 51.55 | 12.73 | 5.14 | 803 | 0.344 | 373 |

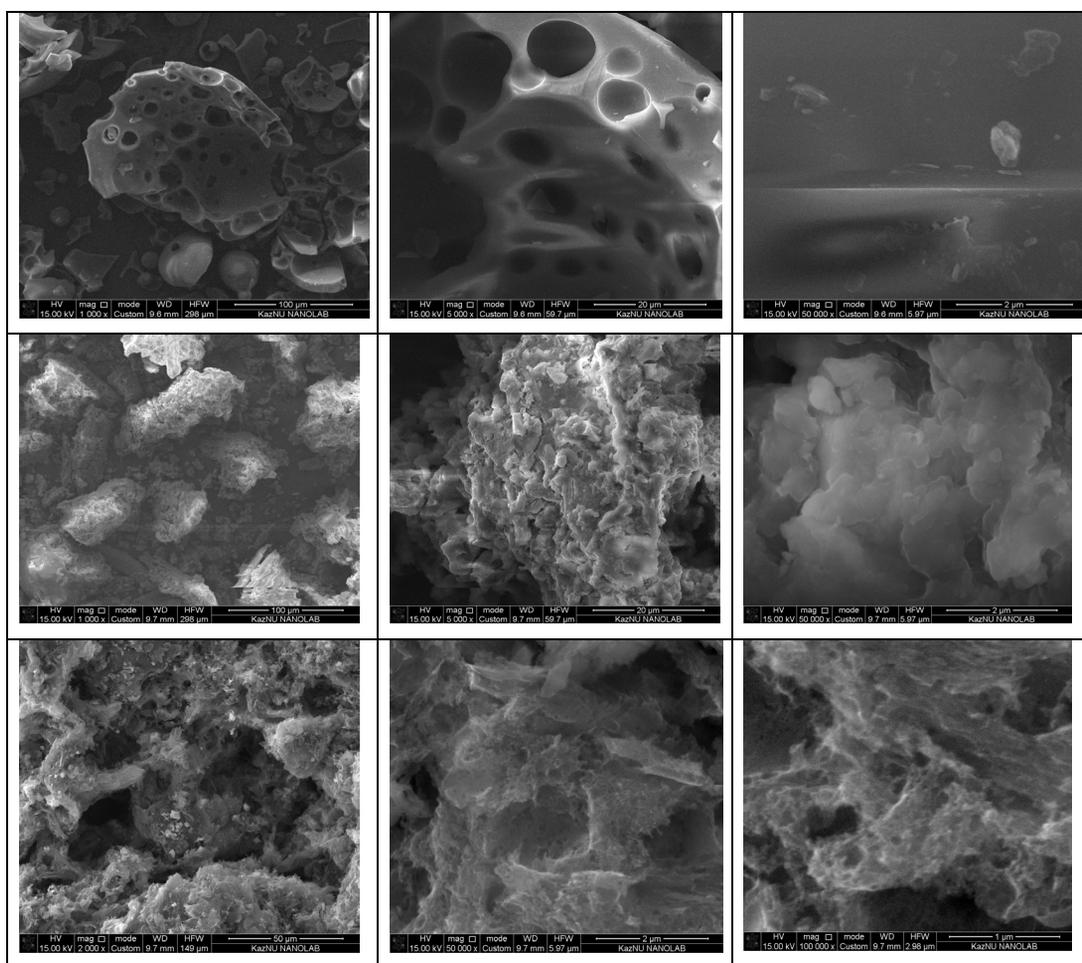


Fig. 1. Electron micrographs and geometry of the binder material – lignosulfonate and the granules obtained on the ground of RH and LS prior to and following carbonization.

matrix of the bonding agent– the lignosulphonate. The activation of the granules contributes to the formation of a greater amount of small pores and the development of a spongy texture of the sorbents.

The results referring to the element composition of the samples studied are provided in the Table 2.

As evident from the Table 2, the activation leads to

significant reduction of the oxygen amount. However, there is simultaneous decrease to zero of the content of sodium and sulfur, as they both escape during carbonization. This has a positive impact on the quality of the carbonized material. The analysis shows also that the carbon content increases in the activated samples in comparison with that of the initial samples of the

Table 2. Element composition of the samples studied.

| binder - lignosulfonate | | | granules from RH and LS prior to carbonization | | | granules after activation | | |
|-------------------------|-------|-------|--|-------|-------|---------------------------|-------|-------|
| Element | wt % | at % | Element | wt % | at % | Element | wt % | at % |
| C | 55.19 | 63.57 | C | 56.00 | 65.16 | C | 86.96 | 90.23 |
| O | 38.28 | 33.10 | O | 33.35 | 29.14 | O | 11.87 | 9.25 |
| Na | 1.47 | 0.89 | Na | 6.13 | 3.73 | Si | 1.17 | 0.52 |
| Si | 4.20 | 2.07 | S | 4.53 | 1.97 | | | |
| S | 0.87 | 0.37 | | | | | | |

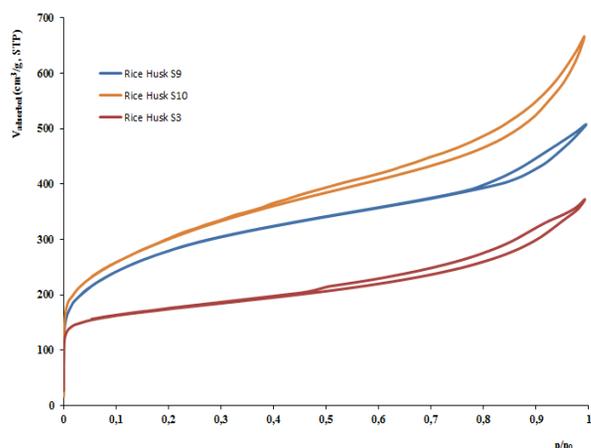


Fig. 2. Isotherms of low-temperature nitrogen adsorption on the samples studied.

granulated sorbents.

The adsorption of nitrogen and carbon dioxide is the most important method of porous structure analysis as it allows determining the specific surface, the pore volume and the pore-size distribution in the structure of such materials. Despite of the wide range of methods used for the analysis of the structural characteristics of the samples (BJH, DFT, BET), the problem of the accurate and reliable evaluation of the properties of the porous structures is still unsolved. It concerns in particular the methods used for pore size distribution determination. Our choice is based on the special features of the surfaces and the structural heterogeneity of the synthesized samples.

The data on the low-temperature adsorption of nitrogen proves mainly a microporous texture of samples S9, S3, S10. The conclusion is primarily based on the form of the nitrogen adsorption isotherm (Fig. 2).

These materials are featured by fast absorption in the area of low relative pressure (lower than 0.01). This limit exists due to the fact that the adsorbents pore sizes are so small that only a single layer of molecules can form on the walls of the pores. The adsorption potential in the micropores is increased due to aggregation of the closely spaced walls of the pores. Thus, such pores are filled under low values of the relative pressure (p/p_0). In this case the heat of adsorption is higher than the heat of condensation of the gas adsorbate. The pores smaller than 0.7 nm are filled without formation of a monolayer on the surface. In this case, the adsorption mechanism is related to volume filling of the micropores. In case of pores of a size from 0.7 nm to 2 nm, a monolayer is

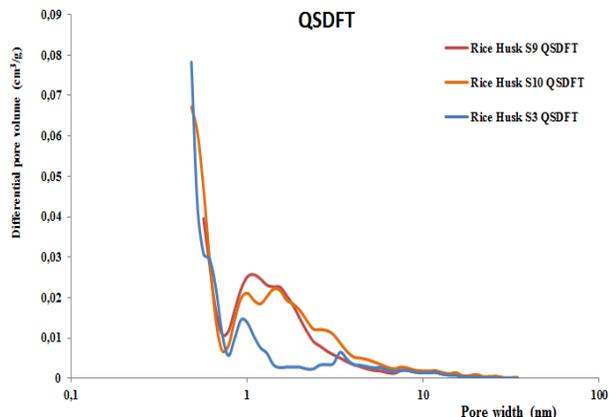


Fig. 3. Pore size distribution for samples S9, S10, S3.

initially forms. Then spontaneous volume filling of the pores commences.

The BET method is used to determine the specific surface of the adsorbents of a pore size of 0.7 nm, i.e. the areas of the adsorption isotherms referring to monomolecular and polymolecular adsorption prior to the start of the capillary condensation ($p/p_0 = 0.05 - 0.35$ is used for N_2 at 77 K) are followed. The Dubinin-Radushkevich model based on the theory of micropore volume filling is used to evaluate the microporosity area at $p/p_0 < 0,01$.

The pore size is usually determined by the density functional theory method DFT which refers to condensed and liquid states (Fig. 3).

Samples S12, S13 and S14 have apparent mesoporosity confirmed both by the form of the corresponding isotherms and the calculation results referring to the pore size distribution (Fig. 4). The isotherms of the samples are characterized by a hysteresis loop in the area of relative pressures of $p/p_0 > 0.5$. The hysteresis is attributed to the nonconvertible capillary condensation of the adsorbate in the mesopores with walls wetted by the adsorbed phase. Capillary condensation appears under the corresponding degree of coverage of the adsorbent, when the additional energy is compensated to a significant extent and the intermolecular forces of adsorbate-adsorbate interaction become determining. The adsorption heat at this stage is equal to the heat of the adsorbate condensation.

In order to provide more detailed characterization of the materials microporous structure, carbon dioxide adsorption is also followed in this study. It is known that this molecule is polar and capable to penetrate the

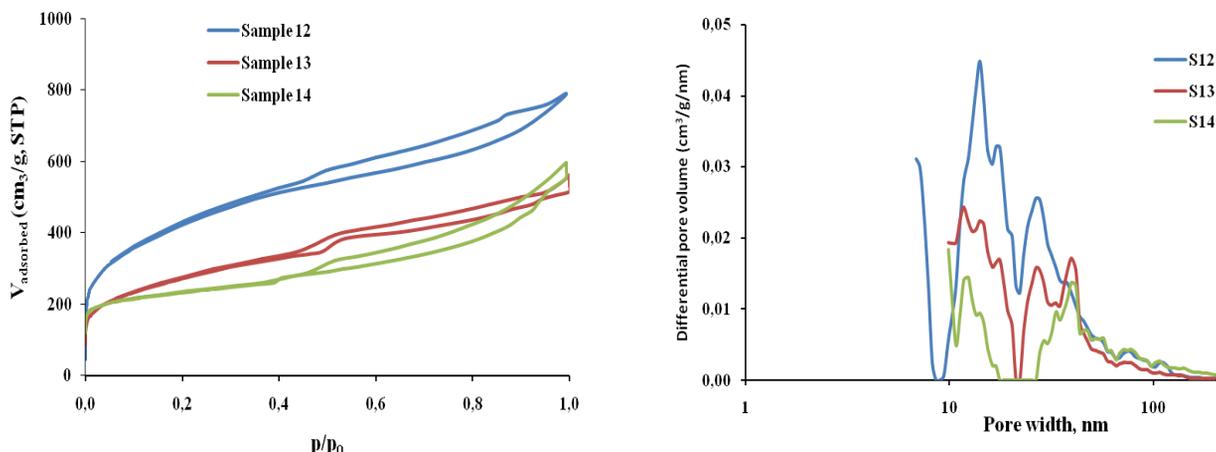


Fig. 4. Low-temperature nitrogen adsorption isotherms and pore size distribution for samples S12, S13, S14.

smallest micropores, which are inaccessible for other adsorbates (in terms of N_2). The results referring to carbon dioxide adsorption are provided in Table 3.

It is found that the largest specific surfaces refer to samples S9 and S10. However, almost half of the specific surface has a microporous structure ($401\text{ m}^2/\text{g}$ and $502\text{ m}^2/\text{g}$). The residual surface is most likely formed due to the high level of dispersion of the materials, as the pore size distribution does not show availability of any other pores except that of micro pores. Sample S3 has the smallest surface ($643\text{ m}^2/\text{g}$) among the three surfaces considered, but almost the entire surface belongs to micro pores ($511\text{ m}^2/\text{g}$). So, sample S3 has no high values of an outer specific surface, i.e. it consists of large particles. This fact and the relatively high value of the specific

surface of the micro pores provide to conclude that the adsorbent considered can be used for analyzing organic and inorganic vapors breakthrough through a filter.

Cyclohexane adsorption is studied. It is chosen because it is used as model substance in adsorbent quality determination following the European standard EN 14387:2004¹. This substance is tested for the first time using the materials synthesized (12, 13 and 14), (Fig. 5).

It is clearly seen that samples 13 and 14 show very short breakthrough time. Only sample 12 (with a maximum specific surface) shows a higher activity. After considering the kinetics, we can conclude that the breakthrough process becomes faster in samples with the highest amount of narrow micro pores (BPL and 14). This is verified by the presence of a sharp bend-

Table 3. Structural-adsorption characteristics of the samples synthesized (according to N_2 and CO_2 adsorption).

| Samples | S BET | V total (cm^3/g) | DR model | | | |
|---------|-------|---------------------------------------|----------------|-----------|----------------------------------|-----------------------------------|
| | | | Eo (KJ/mol) | L (nm) | Wo (cm^3/g) | S dr (m^2/g) |
| S9 | 1025 | 0.776 | 18 | 1.7 | 0.348 | 401 |
| S10 | 1095 | 1.022 | 19 | 1.4 | 0.363 | 502 |
| S3 | 643 | 0.569 | 22 | 1.0 | 0.252 | 511 |
| S12 | 1516 | 1.220 | 14 | 1.82 | 0.49 | 1376 |
| S13 | 886 | 0.87 | 16 | 1.63 | 0.322 | 904 |
| S14 | 765 | 0.922 | 21 | 1.23 | 0.316 | 884 |

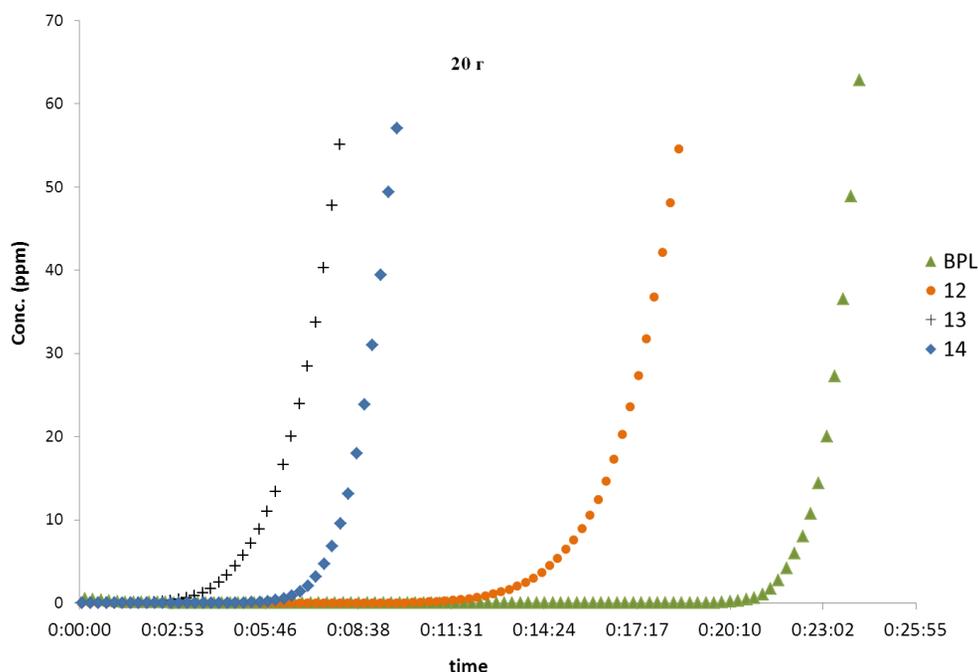


Fig. 5. Experimental curves of cyclohexane breakthrough time using different samples of an amount of 20 g.

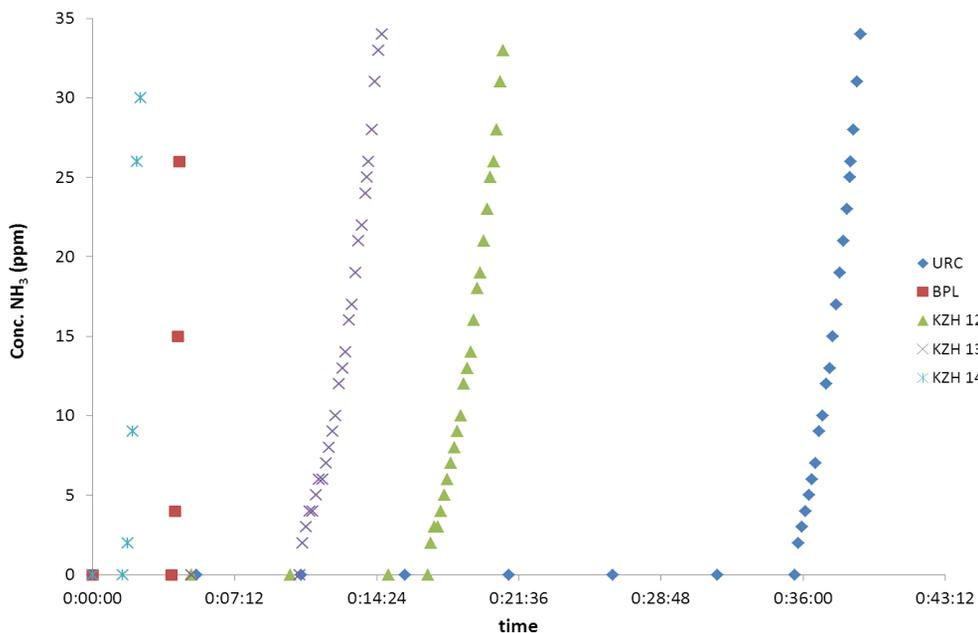


Fig. 6. Experimental breakthrough curves (NH₃).

ing in the nitrogen isotherm, and the high volumes of adsorbed CO₂.

The results obtained provide to conclude that only sample 12 has the optimal features to be used as an adsorbent of organic vapors.

The synthesized carbon sorbents 12, 13 and 14 are used to study the breakthrough time of inorganic vapors.

The commercially available sorbents BPL and URC are applied as a reference. The experimental curves referring to the breakthrough time are shown in Fig. 6.

As evident from Fig. 6, samples 14 and BPL provide a very short breakthrough time. On the other hand, among the three synthesized materials the most efficient retention of NH₃ is obtained in case of using sample

12. This is due to the combination of high porosity and acidic surface (as a result of the chemical activation with H_3PO_4). The breakthrough requires more time in presence of samples 12 and 13. Thus, the findings obtained show that the activated sample 12 is the most efficient universal sorbent intended to retain a wide range of vapors.

CONCLUSIONS

The study reported shows that the perfect proportion of rice husk and a bonding agent of sorbents of organic and inorganic vapors amounts to 3:1, while the carbonization temperature is equal to 800°C. The microstructure analysis of the samples reveals that the activation applied promotes the formation of a higher amount of small pores and the development of a spongy texture of the sorbents leading thus to carbon content increase. The activated samples have apparent mesoporosity confirmed by the corresponding isotherms of low-temperature adsorption of nitrogen and the pore size-distribution values obtained by the DFT method. It is shown that sample 12 is able to retain cyclohexane and ammonia vapors more than 15 min and 17 min, correspondingly. Sample 12 is the most suitable for retaining of a wide range of vapors among those synthesized.

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