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Silica-Resorcinol-Formaldehyde Aerogels Nanostructure Modelling

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The work is devoted to the study and modelling of the internal nanostructure of silica-resorcinol-formaldehyde aerogels. These aerogels are highly porous (up to 98 %) functional materials with a high specific surface area, low thermal conductivity, and good sound insulation. This material is of interest for use in thermal insulation, gas sorption, and also as a soundproof material. In addition, silica-resorcinol-formaldehyde aerogels are a material for further pyrolysis to obtain silica-carbon aerogels. Several aerogel samples experimental data were analysed. The experimental data includes amount of solvent, silica to resorcinol-formaldehyde ratio, pore size distribution, density, and specific surface area. The size and volume of different pores and specific surface area vary depending on the gelation conditions of the samples. This fact indicates the gelation conditions have a significant effect on the final aerogel structure. However, the input parameters of the model are the pore size distribution and sample density. Analysis and comparison of two methods for the generation of porous structures of silica-resorcinol-formaldehyde aerogels including Diffusion-Limited Cluster Aggregation (DLCA) and Reaction-Limited Cluster Aggregation (RLCA) are carried out and the advantages of these two methods are shown in this paper.

1. Introduction

Aerogels are a new generation of highly porous nanostructured materials with low density (0.003-0.15 kg/m^3) and large specific surface area (500-1,000 m^2/g) (De Marco et al., 2017). The silica-resorcinol-formaldehyde aerogels considered in this work are used as sorbent and heat-insulating material (Gordienko et al., 2017). Silica-carbon aerogels can be obtained with pyrolysis process from these aerogels. The internal structure of the silica-resorcinol-formaldehyde aerogels depends on their production conditions, such asratio of reagents, type and amount of catalyst, and amount of solvent. Variations of these parameters allow to obtain aerogels with different structures and characteristics.

Modeling of the structure formation process allows obtaining model structures similar to real ones. This work is devoted to modelling the structure of the silica-resorcinol-formaldehyde aerogels. Computational model of aerogels structure enables to calculate various properties such as thermal conductivity and mechanical strength, without using expensive experiments. This process would reduce time and costs needed for the experiments.

To obtain adequate modelling structure of the silica-resorcinol-formaldehyde aerogels, the following tasks need to be solved:

1) Study the experimental data on the production of silica-resorcinol-formaldehyde aerogels.
2) Select the development method and model.
3) Model adequacy validation.

The result of the work is cellular automaton model of silica-resorcinol-formaldehyde aerogel structure generation.

2. Experimental data

The aerogels production process consists of 2 stages: gel formation by sol-gel process and supercritical fluid drying process. The silica-resorcinol-formaldehyde aerogels in this work are obtained by forming separate sols. The sols with organic and inorganic constituents are separately prepared and mixed. Ethanol is solvent in both

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sols. Consequently, in a combined solution, the simultaneous formation of structures occurs both from organic and inorganic components. The solvent (ethanol) is then replaced with isopropanol. The gels are dried in supercritical carbon dioxide to remove isopropanol. The structure of obtained aerogels is presented in Figure 1.

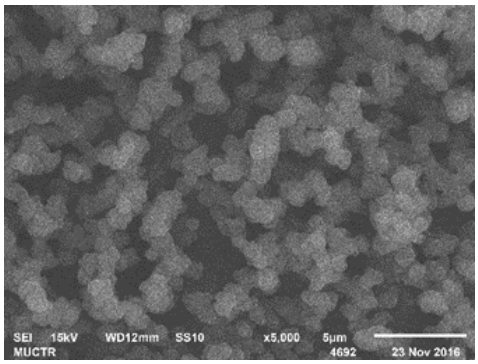


Figure 1: SEM of the Silica-Resorcinol-Formaldehyde aerogels

The key parameters that characterise the internal structure of the aerogel are the specific surface area and pore size distribution. According to the pore classification of the International Union of Pure and Applied Chemistry (IUPAC), each pore size interval (diameter) has characteristic adsorption properties. There are 3 types of pores: micropores (pores with diameter <2 nm), mesopores (pores with diameter 2 - 50 nm), and macropores (pores with diameter exceeding 50 nm).
This classification shows that the aerogel has a mesoporous structure, which contains pores with diameter 2 - 50 nm. Figure 1 shows that the aerogel structure consists of spherical clusters that include elementary structure-forming particles - globules. The size and distribution of mesopores are determined by the size of the clusters (Fung et al., 2010). The size of globules and their number directly affect the structure of the aerogels.

3. Porous structure modeling

The aerogel structure is mesoporous. A method that allows to model porous structures at mesoscale should be used in this study. During gel formation, individual particles of substance should be combined to form clusters. Different methods which simulate particle aggregation can be classified in 2 categories: particle-cluster aggregation (PCA) methods and cluster-cluster aggregation (CCA) methods.
In PCA methods, the clusterisation center, which consists of a single particle, is placed in generation space and fixed. Other particles are generated in random points and start their motion. Particles aggregate with clusterisation center forming a cluster.
In CCA methods, a number of particles are placed in random points. All particles simultaneously move and collide with each other. When two particles collide, they aggregate into a cluster. Each cluster also moves colliding and aggregating with other clusters and particles.
Both in PCA and CCA methods particles can implement two types of motion: diffuse and ballistic. According to these types, there are diffusion-limited aggregation (DLA) and ballistic particle-cluster aggregation (BPCA) for PCA and diffusion-limited cluster aggregation and ballistic cluster-cluster aggregation for CCA. In diffuse motion, particle periodically changes the direction of its motion. In ballistic motion, particle moves in one random direction until it collides with another particle/cluster (Markutsya et al., 2010).
In this work, the diffusion-limited cluster aggregation (DLCA) and its modification, reaction-limited cluster aggregation (RLCA), applied because these methods are preferred to model nanoporous aerogel structure (Naddeo et al., 2016). In RLCA, particles and clusters don't aggregate every collision, but with certain probability. Probability of aggregation depends on the size of colliding clusters.
Cellular automaton models have been developed to implement these methods. The choice of cellular automation models is due to the ability to adapt models for aerogels of different nature with relatively low requirements for computational resources (Gelb et al., 2011). The developed models should have the following assumptions:
1) The modeling space consists of cells of the same size.
2) Each cell can have one of three states including “inorganic substance”, “organic substance”, and “pore”.
3) At the beginning of the process, there are only spherical clusters, which then aggregate into a single structure.

4) Each spherical cluster is a collection of neighboring cells with a state of organic substance or inorganic substance, which have a spherical shape or a circular shape for three-dimensional and two-dimensional cases, respectively. The diameter of the clusters is chosen empirically.
5) Spherical clusters move chaotically, imitating Brownian motion. In this case, they do not experience the influence of any external forces.
6) Globules and clusters aggregate with certain probability depending on the size of the cluster (for RLCA). If possibility of aggregation is 100 % for each collision, RLCA model transforms to DLCA model.
The flowchart of DLCA and RLCA models is presented on figure 2:

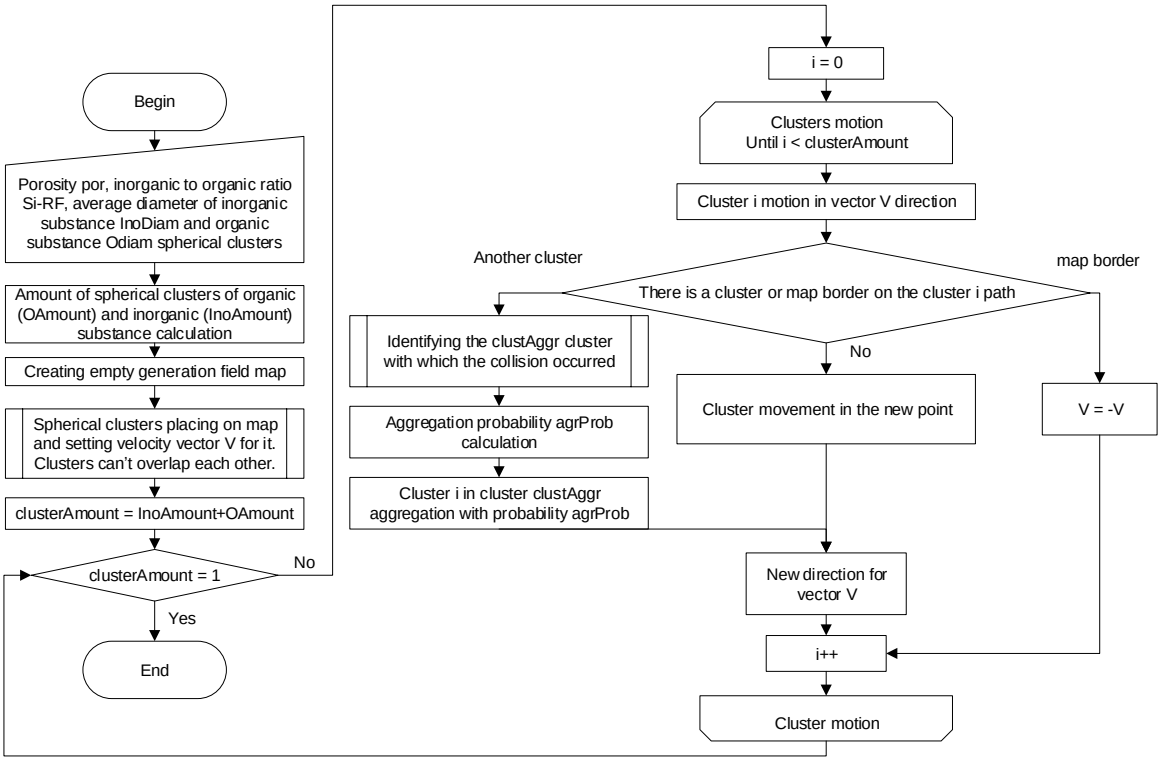
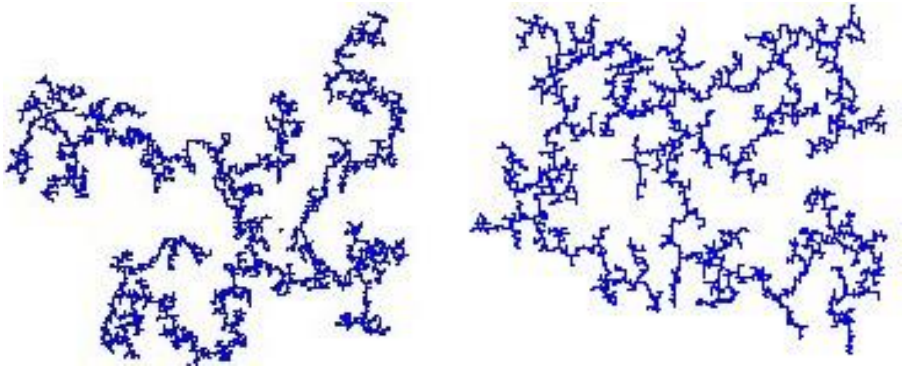


Figure 2: Flowchart of DLCA and RLCA methods

The input parameters of the models are porosity of the structure, inorganic to organic substance ratio, and spherical clusters diameter for organic and inorganic substance. The structure is modeled on the field divided on equal size square cells, forming a grid. Each cell can have only one of three states in each moment ("inorganic substance", "organic substance", "pore"). Spherical clusters are placed on the generation field. They can't overlap each other. Also velocity vector is set for each cluster. Then clusters begin to move and aggregate with each other into larger clusters and, eventually, into a single structure. It should be noted that in the case of RLCA, at the moment of collision of clusters, the probability of their aggregation is calculated as a function of size the cluster in which aggregation takes place. In the case of DLCA, the clusters aggregate with a 100 % probability. The algorithm is ended when all clusters form a single structure (i.e., until there is one cluster remaining in the field containing all the others). The output parameter of the model is a two-dimensional or three-dimensional structure.
Figure 3 presents the structures obtained with DLCA and RLCA (2D structure).



(a) (b)

Figure 3: 2D Silica-Resorcinol-Formaldehyde aerogel structure: (a) DLCA model; (b) RLCA model

Figure 3 shows the results for the 2D structure. The model enables to obtain a three-dimensional structure of the sample. These sample structures show the difference between DLCA and RLCA structures. They have 200x200 nm size, single cells as initials clusters, and only silica as a substance. In this model aggregation probability depends on the size of the cluster – large clusters aggregate less often then little ones. The structure was obtained using the RLCA method (right), which has a more branched structure. Such variation of probability leads to an increase in the number of branched nodes.

4. Modeling results comparing

The developed model was used to carry out a numerical experiment on real samples of silica-resorcinol-formaldehyde aerogels. As a criterion for the adequacy of the structures obtained, the pore size distribution was chosen. The experimental data of the test samples are presented in Table 1.

Table 1: Experimental data of the test samples

Sample	1	2
Resorcinol mass, g	0,31	0,55
Formaldehyde mass, g	0,9	1,62
AEAPTMS mass, g	0,62	1,11
TEOS mass, g	0,76	1,36
Ethanol mass, g	8,04	6,72

In these samples, the ratio of solvent (ethanol) to other reagents was changed. All other relationships remained unchanged. Aminoethylaminopropyl Trimethoxysilane (AEAPTMS) and Tetraethoxysilane (TEOS) are used to produce an inorganic (silicic) component.

The pore size distribution for the experimental samples was obtained with nitrogen porosimetry. To determine the distribution of mesopores by size, the Barrett-Joyner-Halenda method (BJH) is used. The sample is placed in adsorbate (nitrogen) at a given relative pressure. At this pressure, some of the pores are filled. As the relative pressure rises, larger pores are filled. Using these data, it is possible to plot the curve of the volume of nitrogen that filled the sample from the relative pressure. In the future, the resulting curve can be converted into a dependence of the volume of nitrogen that filled the sample, on the diameter of the pores. Such a curve is called a cumulative (integral) curve for pore size distribution. It expresses the dependence of the total pore volume on their diameter. In order to avoid the influence of random errors, a differential curve of pore size distribution is used. The differential curve represents the change in the pore volume per unit of the pore diameter from pore diameter. The model structures of samples 1 and 2 are obtained with DLCA and RLCA models, which are shown in Figure 4. The experimental and model differentials curves for these samples are given in Figure 5.

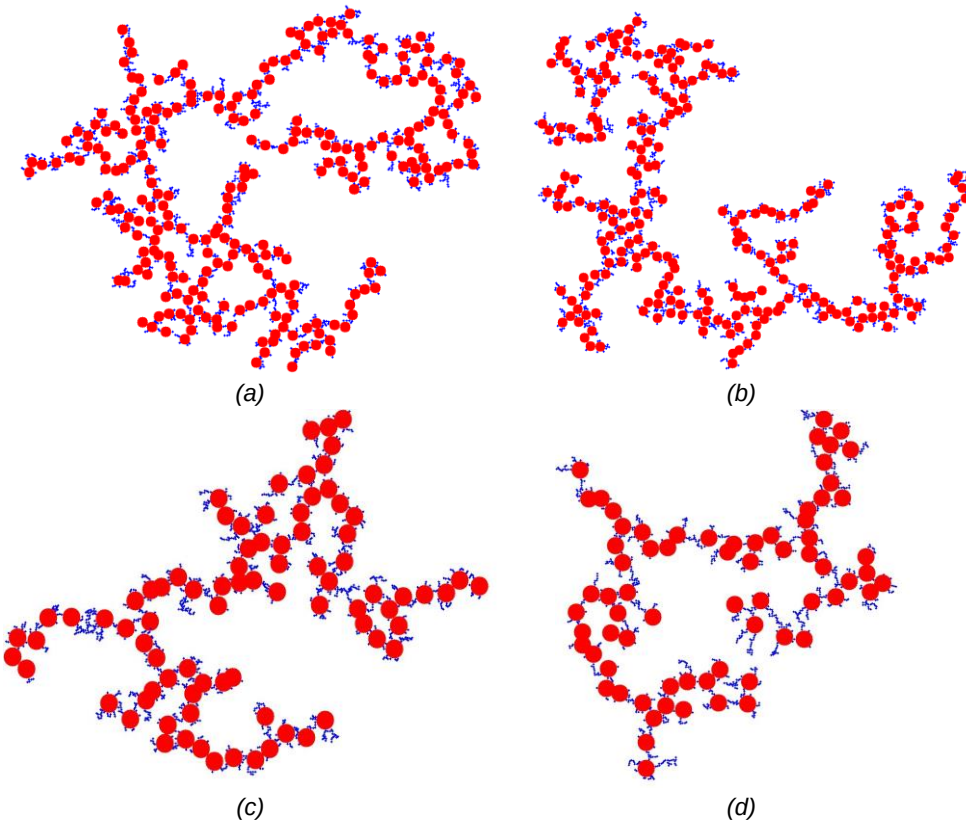


Figure 4: Model structures: (a) sample 1 – DLCA; (b) sample 1 – RLCA; (c) sample 2 – DLCA; (d) sample 2 – RLCA

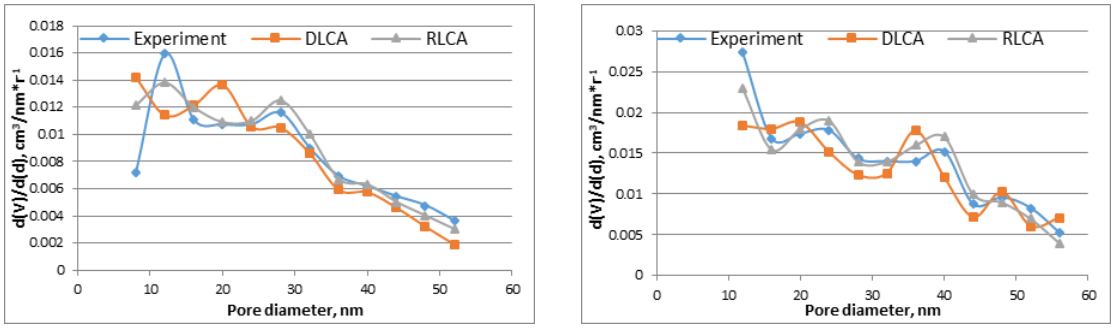


Figure 5: Experimental and model differential curves of samples 1 (a) and 2 (b)

For each pair of curves, the difference coefficient was calculated. The coefficient of difference (f_1) shows the error percentage between the two curves over all points of the diameter and is calculated by the following formula:

$$f_1 = \frac{\sum_{j=1}^{n} |dV(d)/d(d)_{\text{эксп},j} - dV(d)/d(d)_{\text{мод},j}|}{\sum_{j=1}^{n} dV(d)/d(d)_{\text{эксп},j}} \times 100\%, \quad (1)$$

where n — number of diameter points; $dV(d)/d(d)_{\text{эксп,j}}$ и $dV(d)/d(d)_{\text{мод,j}}$ – values of dV(d)/d(d) - the change in the pore volume per unit of the pore diameter in diameter j. The smaller value of the coefficient of difference, the more identical the curves.

Table 2 shows the values of the coefficient of difference for the calculated and experimental curves.

Table 2: The difference coefficient of model and experimental pore size distribution curves

Sample	$f_{1,DLCA}$, %	$f_{1,RLCA}$, %
1	22	19
2	20	21

The coefficient of difference for the DLCA and RLCA models does not exceed 25 %. As shown from the presented pore size distribution curves, the model structures correspond to the experimental ones. Therefore, the obtained structures can be used in the future both for predicting the properties of silica-resorcinol-formaldehyde aerogels, and for modeling the structure of silica-carbon aerogels based on them.
Table 3 shows a comparison of the performance of the two algorithms. The parameter for comparison is the time spent on generating the structure.

Table 3: DLCA and RLCA algorithms performance

Sample	T_{DLCA}, min	T_{RLCA}, min
1	41	250
2	58	370

As can be seen from the table, the generation of structures by the RLCA method takes several times longer. This is due to the fact that in the RLCA method, unlike DLCA, aggregation of particles and clusters does not occur with a 100 % probability and, therefore, the generation of the structure lasts longer, the smaller these probabilities.

5. Conclusions

The generation of structures which adequate to the experimental samples allows modeling the various properties of aerogels in silico, which saves resources on carrying out costly experiments.
In this work two porous structures modeling methods were implemented - DLCA and RLCA. Aggregation probability in RLCA leads to structure branching increasing. Also structure generation time increases too. RLCA structures obtained with suggested aggregation probability calculation method wasn't more adequate than DLCA structures.
On the basis of these methods, a cellular automaton model for the silica-resorcinol-formaldehyde aerogel structures generation was developed. The developed software allows obtaining model structures of silica-resorcinol-formaldehyde aerogels with given structural characteristics adequate to the experimental samples.

Acknowledgments

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