

NANOSTRUCTURED CARBON XEROGEL FOR METHANE STORAGE

S. Filatov¹, M. Dolgikh¹, G. Ahremkova¹, O. Filatova¹, J. Zhang², X. Yi²

¹*A.V. Luikov Heat and Mass Transfer Institute National Academy of Sciences, Belarus*

²*Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan, 250014, P. R. China*

Carbon nanostructured materials such as carbon aerogels and carbon xerogels were obtained by pyrolysis of organic aerogels at temperatures from 250 ° C to 600 ° C from resorcinol-formaldehyde resin in a nitrogen flow, followed by high-temperature activation with carbon dioxide at 900-1000 ° C. Experimental studies aimed at synthesizing the synthesis and improving the structural and adsorption characteristics of carbon aerogels were carried out according to the classical scheme in three stages: sol-gel polymerization of organic oligomers (synthesis of organic aerogels), supercritical drying in a stream of carbon dioxide, and high-temperature carbonization of the resulting organic aerogels.

As a starting material for the production of nanostructured carbon xerogels, a phenol-formaldehyde resin with a given texture, synthesized using various catalysts, was used.

Aerogels are gel materials in which the liquid phase is completely replaced by the gas phase. Carbon aerogels are highly porous materials consisting of a three-dimensional framework formed by various extended forms of carbon nanomaterials, which are characterized by a low density (less than 100 mg / cm³). Among the known methods for the preparation of carbon aerogels, the most widespread are the methods based on the preparation of three-dimensional polymer matrices using the sol-gel technology with their subsequent carbonization. At the same time, organic polymer matrices based on resorcinol-formaldehyde are often used to obtain carbon aerogel at the stage of sol-gel technology. The use of various solvent removal methods (solvent exchange method, subcritical, supercritical and freeze drying) allows the creation of aerogels with the required properties and structure [1-12].

Most often, carbon-based materials are used as sorbents for methane storage - activated carbons and activated coke, as well as carbonated organic materials of plant origin. Recently, carbon-based nanostructured adsorbents obtained by carbonization of mesoporous phenol-formaldehyde resin and belonging to the class of carbon xerogels have begun to be considered as promising adsorbents suitable for storing and transporting methane.

This work is devoted to the study of methane adsorption in the pressure range of 0.1 - 4 MPa and the temperature range of 273-323K on nanoporous carbon xerogels obtained by carbonization of resorcinol-formaldehyde aerogels.

In general, resorcinol-formaldehyde organic gels go through two main stages in the synthesis process. The first stage is associated with the preparation of a mixture of sols and the subsequent gelation and curing of the gel. The second stage is associated with the drying of the wet gel. The important factors affecting the properties of the organic gel in the first stage are the concentration of the catalyst, the initial pH of the gel, and the presence of solids in the ash. The most important factors affecting the properties of the organic gel in the second step are the drying procedure (eg, super- or subcritical drying) and the difference between the surface tension of the solvent before and after drying. Corresponding resorcinol formaldehyde carbon gels are produced from organic gels in a third step, which involves carbonation or activation.

Sol-gel process. In this research resorcinol-formaldehyde polymer was used as a precursor, Fig. 1. For its formation, we used resorcinol (analytical grade, GOST 4352-77) and formaldehyde (analytical grade, GOST 1625-89).

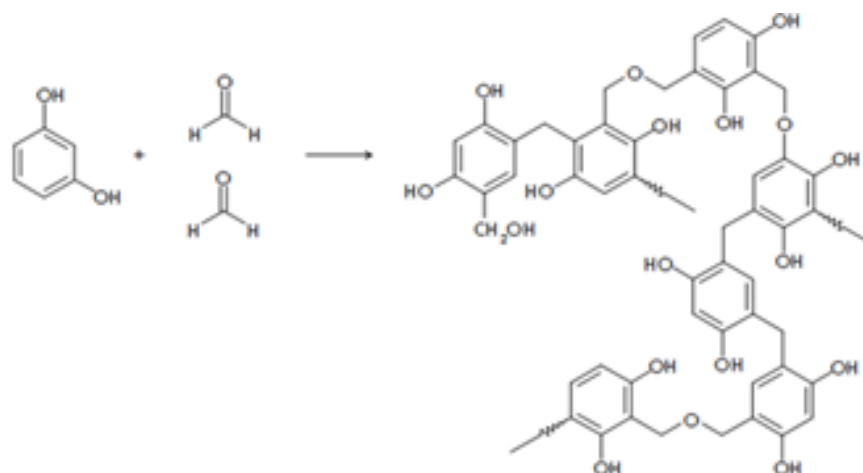


Fig. 1. Typical scheme of polycondensation of resorcinol - formaldehyde precursor of carbon xerogel

Resorcinol-formaldehyde gels were prepared in one step by the sol-gel transition. In the preparation of gels, resorcinol was preliminarily dissolved in acetone, a catalyst (KCl, NaOH, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ was added in a number of experiments) to the resulting solution, and formaldehyde was introduced dropwise with vigorous stirring. The gel was formed within 24-30 hours, after which it was washed five times with acetone to remove unreacted substances and dried in supercritical carbon dioxide at a temperature of 40°C and a pressure of 10 MPa.

As an alternative method, the synthesis of resorcinol-formaldehyde polymer can be carried out by adding a 37% formalin solution to an aqueous solution of resorcinol and potassium hydroxide. As a result of the polymerization reaction, a gel was obtained, which was then washed with a large amount of acetone, filtered and dried to constant weight at $70\text{--}80^\circ\text{C}$, and cured by heat treatment in air for several hours. At high curing temperatures (up to 200°C), a highly crosslinked polymer matrix is formed.

An increase in temperature increases the rate of all reactions occurring during the polycondensation of resorcinol-formaldehyde resins. Depending on the number of active hydrogen atoms in the phenolic nucleus, the molar ratios of the initial reagents, the rate and depth of the reactions, a variety of intermediate and final products can be formed that differ in chemistry, composition and degree of polymerization from monomeric methylophenols to polymethylene- or polydimethyleneoxide phenols.

Supercritical drying process. The final stage in the preparation of a carbon xerogel is the removal of the solvent from the pores of the gel. The main challenge in the solvent removal process is to maintain the highly porous structure. The use of heat or freeze drying in most cases does not ensure the production of an aerogel, since during thermal drying a phase boundary forms inside the pores of the gel, which leads to the appearance of capillary pressure, which destroys the structure of the sample. In this case, the smaller the pore size, the greater the pressure and the greater the change in the structure of the sample. The use of heat drying does not allow obtaining material with a developed surface. During freeze drying, solvent crystals are formed inside the pores, which lead to the formation of macropores, thus reducing the specific surface area. Thus, only drying in the medium of supercritical fluids makes it possible to preserve the initial gel structure unchanged.

It should be noted that one of the key stages in the preparation of mesoporous carbon xerogels with a given pore size distribution is supercritical drying, during which the solvent is removed in the form of a supercritical fluid without changing the gel structure. In this case, the properties of aerogels can vary significantly depending on the supercritical fluid used. Avoiding supercritical drying leads to an increase in pore size.

Pyrolysis process. For the final stage of obtaining materials based on carbon aerogels, the pyrolysis process is used as a post-processing of aerogels based on organic resins (resorcinol-

formaldehyde in our case). Pyrolysis is carried out in a tube furnace in an inert atmosphere (nitrogen, argon) or in a vacuum at high temperatures (up to 1400 °C). Typical values for the formation of carbon sorbents are pyrolysis at a temperature of 680-700 °C in a nitrogen flow (volumetric flow rate 150 ml / min) for 1 hour, heating rate 10 °C / min. To form the transport channels, the temperature is increased to 900 °C at a rate of 5 / min and maintained for 40 minutes, after which it is reduced to room temperature (20 °C) at a rate of 10 / min. These temperatures ensure complete pyrolysis of the xerogel, Fig 2.

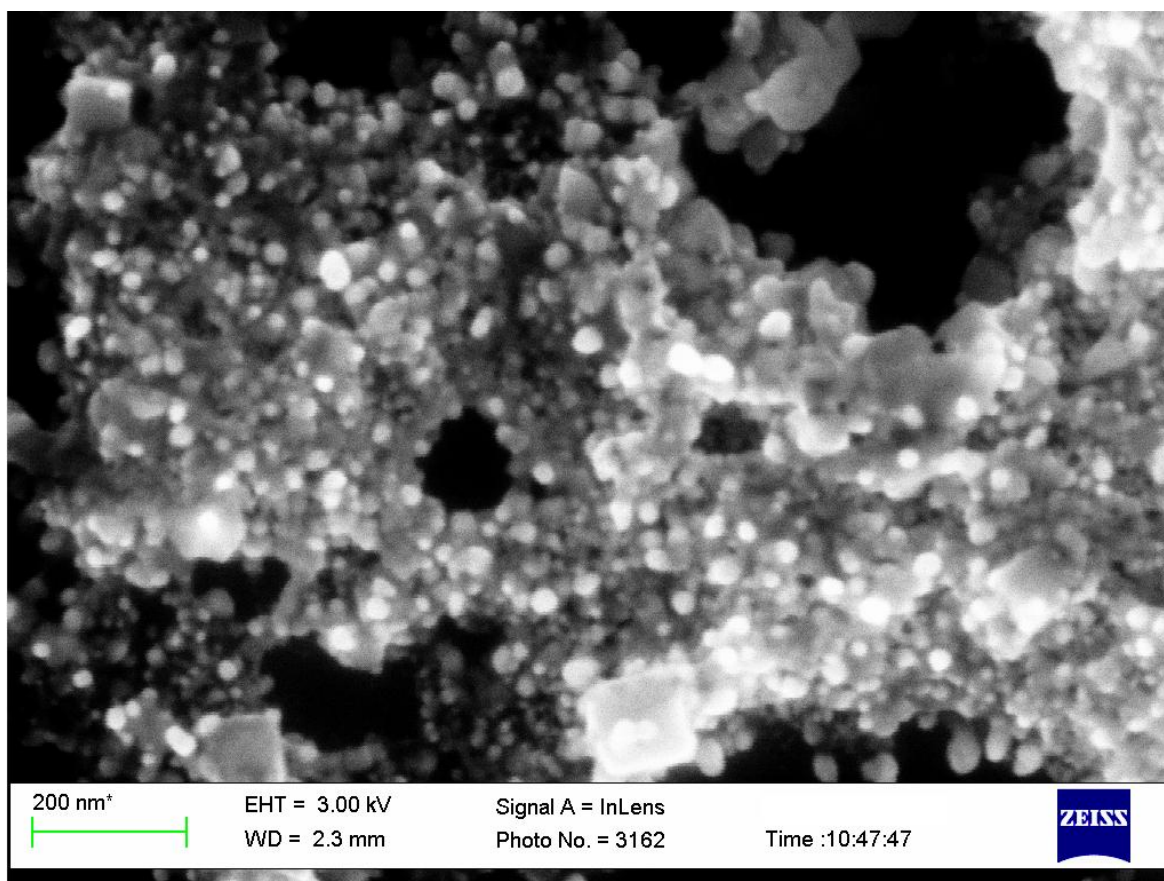


Fig.2. Typical structure of carbon xerogel

During pyrolysis, the organic part of the resorcinol-formaldehyde xerogel is oxidized, leaving only carbon. To carry out the process in vacuum, an additional pump connection is required. To carry out the process in an atmosphere of inert gases, it is necessary to control the gas flow rate and control the absence of impurities in the gas environment.

The relatively simple design of the pyrolysis reactor in the form of an insert into a tubular furnace makes it easy to change samples without waiting for the furnace to cool (this increases the life of the tubular furnace) and somewhat reduces the temperature gradient over the volume of the xerogel, increasing the sample homogeneity. However, relatively high gas flow rates can cause temperature gradients and sample inhomogeneities. In this case, the xerogel yield is less than 5-10% of the initial mass of the resorcinol-formaldehyde polymer.

The analysis of the specific area of carbon sorbents used for the sorption of methane was carried out using an ASAP 2020 system (Micromeritics, USA), fig.6-9. Typical results of the BET specific surface area analysis of sorbents are given on next figures. The carbon sorbent obtained in our work is a porous synthetic carbon material containing the structure of micro-, meso- and macropores, interconnected. Most of the methane is adsorbed in micropores with effective radii of 1.8-2.1 nm. In mesopores with an effective radius of 2-100 nm, adsorption can occur by the mechanism of capillary condensation. The effective radii of macropores are 100-200 nm and the adsorption in them is negligible. As a rule, macropores play the role of transport channels, their sizes significantly exceed the diameter of methane molecules, which makes it

possible to quickly supply and remove methane to micropores, therefore, quickly fill and empty the adsorber. Since the size of micropores is larger than the diameter of methane molecules, the adsorption capacity for methane in them is sufficiently high and the density of the adsorbed gas approaches its density in a liquid one, as a result of which the methane content in a vessel filled with an adsorbent is much higher than in an empty vessel of the same volume at the same pressure. It should be noted that the adsorption capacity for methane increases with increasing pressure up to 4-8 MPa.

Our studies also have shown that the samples under study have a cellular structure with high uniformity. The presence of macropores determines the high total porosity and the ratio between the true and apparent density, which is more than 90%. Based on electron microscopy data, the wall thickness of carbon aerogels was calculated, which varied over a wide range from 10 to 600 nm, fig.3-4.

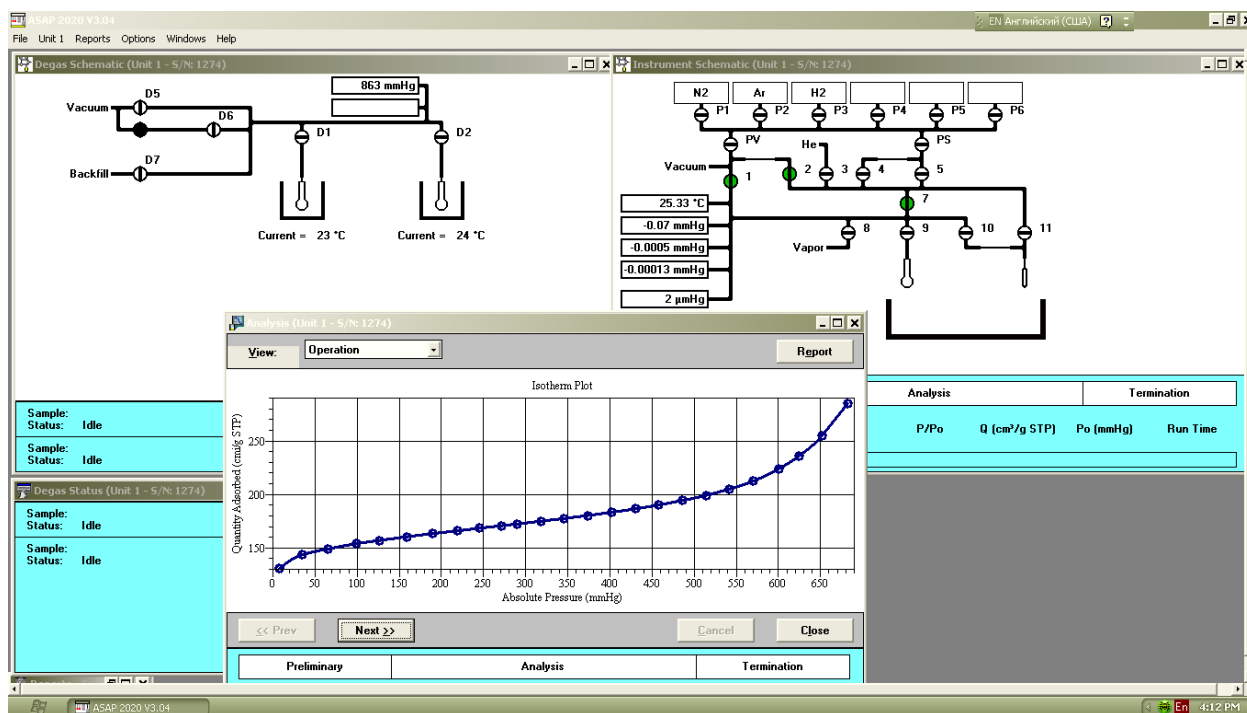


Fig.3. Typical ASAP2020 mnemonic diagram during carbon xerogel sample test

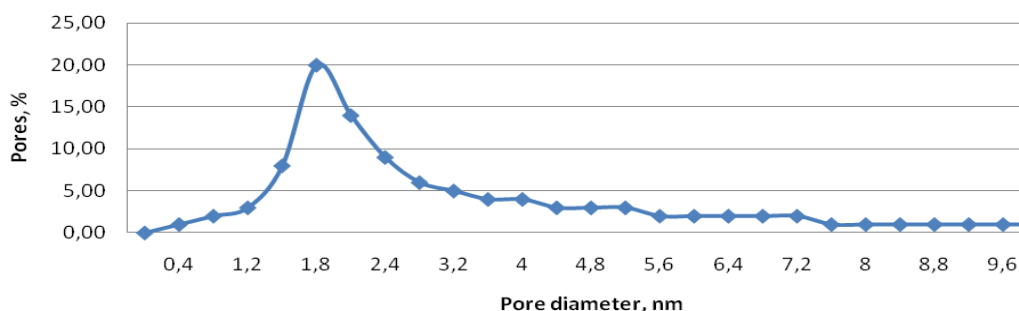


Fig.4. Typical pore size distributions of the carbon xerogel test samples obtained by pyrolysis of resorcinol-formaldehyde gel

Methane storage investigation. For experimental studies, a laboratory tank for adsorbed storage of methane was used in the form of a thin-walled cylindrical cylinder with a volume with a valve, equipped with porous copper block to prevent the movement of the sorbent during sorption-desorption cycles.

The test sample of carbon xerogel was placed in a balloon and the balloon was evacuated at room temperature. After that, the cylinder with xerogel was weighed on an analytical balance and connected to a vacuum line, which was then supplied with methane at a given pressure. After the completion of the adsorption process and the establishment of the initial temperature, the cylinder valve was closed, the cylinder was disconnected from the gas main and weighed again. The amount of adsorbed methane was determined from the change in mass.

To measure heat effects during cyclic sorption and desorption, a system with two 0.3 dm³ cylinders and a pressure sensor connected to a second vessel of the same volume, but not filled by sorbent are used for volumetric measurements, was also used.

Cyclic (multiple) sorption-desorption analysis. To analyze the degradation of the sorbent during repeated adsorption-desorption, we used a setup with electric valves and computer control, which provides cyclic evacuation of a cylinder with xerogel, supply of methane to the cylinder under pressure, and venting gas from the cylinder through a throttle hole.

Experiments carried showed that the amount of adsorbed methane changes by less than 3% and is probably associated with the measurement error more than with the aging processes of the sorbent.

It also should be noted that the results refer to a model gas - high purity methane. Results for multi-component natural gas can be expected to vary slightly.

In addition, the measurements were carried out without taking into account the thermal effects during sorption and desorption. The problem of complete gas extraction from the sorbent was not considered.

Conclusion

The studied adsorbent of a carbon xerogel based on the pyrolysis of a polymer-precursor of resorcinol-formaldehyde has a specific surface area more 2500 m²/g and an average pore size less than 2 nm. The samples under study have a cellular structure with high uniformity. The presence of macropores determines the high total porosity and the ratio between the true and apparent density, which is more than 90%.

References

1. Dubinin M.M. Adsorption in micropores, M. Nauka, 1983. - 186 p.
2. Dubinin M. M., Radushkevich L. V. Dokl. AN SSSR, 55, 331 (1947)
3. Bakaev V. A. Dokl. AN SSSR, 167, 369 (1966).
4. Frolov Yu. G. Course of colloidal chemistry. Surface phenomena and dispersed systems. - M.: Chemistry, 1989. -- 464 p.
5. Keltsev NV Fundamentals of adsorption technology. - M.: Chemistry, 1984 - 592 p.
6. Greg S., Sing K. Adsorption, specific surface, porosity. - M.: Mir, 1984. -- 310 p.
7. R. W. Pekala, J. Mater Sci., 24, No. 9: 3221 (1989).
8. R.W. Pekala, C.T. Alviso, X. Lu, J. Gross, J. Fricke, New organic aerogels based upon a phenolic-furfural reaction / J. Non-Cryst Solids, 1995, 188, 34-40p.
9. M. Petricevic, M. Glora, and J. Fricke, Carbon, 39, No. 6: 857 (2001).
10. J. Yamashita, T. Ojima, H. Hatori, and Y. Yamada, Carbon, 41, No. 2: 285 -2003.
11. Matthew J. Prosniewski, Tyler A. Rash, Ernest W. Knight, Andrew K. Gillespie, David Stalla, Conrad J. Schulz, Peter Pfeifer, Controlled charge and discharge of a 40-L monolithic adsorbed natural gas tank, Adsorption, 10.1007/s10450-018-9961-2, 24, 6, (541-550), (2018).
12. Rui Zang, Zhihong Li, Yiao Xu et al. Proc. of Intern. Conf. on Carbon (15—20 Sept. 2002, Beijing, China). Matthew Beckner, Anne Dailly Hydrogen and methane storage in adsorbent materials for automotive applications //Energy Research, Volume40, January 2016, Pages 91-99.