CARBON MEMBRANES PRODUCED FROM POLYMERIC COMPOSITIONS DEPOSITED ON POROUS CERAMIC SUPPORTS

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Introduction

Carbonization of organic polymeric compounds allows to synthesize various carbon materials including novel carbon nanostructures. Using high-temperature mesoporous supports high-temperature permselective membranes with different gas separation mechanisms can be produced depending on the type of polymers (precursors), the coating method and the carbonization conditions.

Previously we have developed two methods of carbon coating deposition on mesoporous α-Al_2O_3 - based ceramic tubular supports: the gas phase method consisting of preliminary treatment by volatile fluorides followed by hydrocarbon partial cracking [1] and carbonization of the compositions based on ED-20 epoxy resin with fluoroelastomers cured by xylylenediamines [2]. In the first case dispersion of carbon in ceramic structure has been observed. Membrane coatings produced by carbonization consisted of stable carbon structures with good adhesive properties and homogenous porous structure. Several authors have shown that membranes with the surface layer of carbon molecular sieves (CMS) produced by carbonization of thermally or chemically cross-linked polymers have improved selectivity in gas separation. In the present work we investigate the possibility of CMS-membrane preparation by means of carbonization of polymer film pre-deposited on mesoporous ceramic tubular supports.

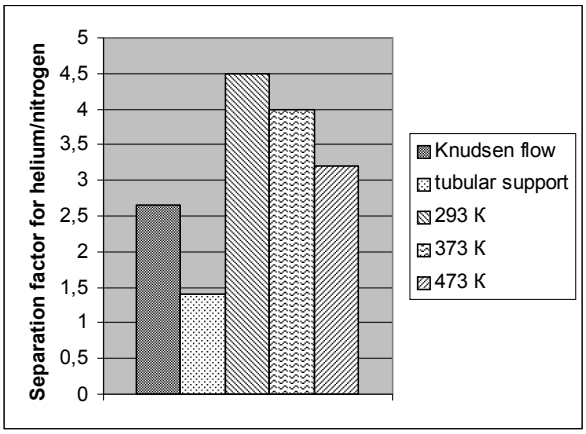
Results and discussion

Commercially available in Russian Federation solutions of LBS-1, RSFF-3010, BZH-3 types based on phenol-formaldehyde resin (PFR) were investigated as possible precursors for CMS-membrane synthesis. Ceramic mesoporous α-Al_2O_3 - based tubes with the outer diameter of 8 to10 mm and the length of 30-60 mm were used as supports.

Polymers were deposited by multiple dipping into solutions with PFR concentration in the range 24-76 mass.%. Before the carbonization the obtained films were cured by heating in air at the temperature of 250^{0}C during 4 hours. Carbonization of precursors was carried out by heating up to 850^{0}C at a rate of 1.6 ^{0}C/min in nitrogen flow of 180-300 ml/min; activation of the produced membrane was carried out according the same scheme but in carbon dioxide flow. Gas separation properties of membranes were tested using nitrogen and helium by volumetric method. The samples were also characterized by means of scanning electron microscopy (S-570 Hitachi).

The quality of coatings was estimated by means of "bubble point" method in water or ethyl alcohol. The detected defects were removed using special sealing material with high adhesive properties.

Temperature dependence of selective properties of produced membranes for He/N_2 is shown as a diagram.



As can be seen carbonization of precursors based on PFR improves selectivity up to three times compared to that of initial commercial support. However for obtaining practically important values of selectivity additional support modification is necessary in order to liquidate defects occurring at experimental-industrial production. Efficiency of membrane activation by carbon dioxide flow under conditions similar to those at carbonization is to a great extent determined by the thickness of carbonized precursor layer.

Uniformity of the porous structure of the obtained carbon coatings was confirmed by "bubble

point" method; few point defects deteriorating membrane selectivity were found.

Conclusions

The influence of gas permeability of supports, concentration of precursor solutions, number of deposited polymer layers on the thickness and structural defects of the selective layer has been studied.

The relationship between multiplicity of the solution deposition on the support, solution concentration and gas permeability of carbonized coatings (initial and activated ones) has been found.

The main stages of synthesis of the composite membrane with selective carbon molecular sieves layer has been developed.

Membranes of this type can also be used for the creation of catalytic membrane reactors by means of catalytically active materials addition into precursors at the stage of polymer coating preparation or at the stage of carbonization [3].

References

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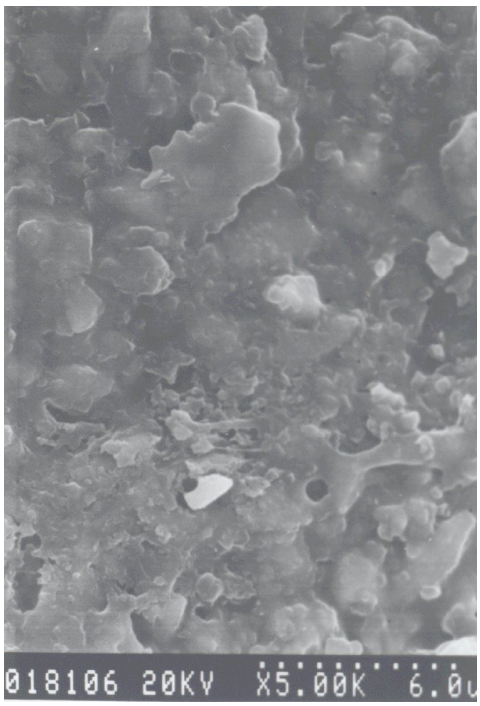

Photo 1. Surface of carbonized membrane.

Photo 2. Surface of carbonized membrane after activation.