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The Impact of the Nanostructure of the Functional Polysiloxane Layer in Planar Ceramic Membranes on Their Sorption Properties

V.V. Tomina[1,*], I.V. Melnyk[1], Yu.L. Zub[1,†]

[1] *Chuiko Institute of Surface Chemistry of NAS of Ukraine, 17, General Naumov Str., Kyiv 03164 Ukraine*

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The paper describes the functionalization of planar ceramic membranes (Al_2O_3) with the active layer containing 3-mercaptopropyl complexing groups. The sol-gel method was used for that. There was analyzed the influence of the ratio of alkoxysilanes and the dilution of the original sol on the nanostructure of the produced surface layer. The work is aimed to develop the techniques for ceramic membranes functionalization by complexing groups, therefore, these membranes can be used for the removal of heavy metal ions from aqueous media in the process of filtration.

Keywords: ceramic membranes, surface functionalization, sol-gel method, 3-mercaptopropyl groups.

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1. INTRODUCTION

Inorganic membranes are a good alternative to polymeric membranes due to their chemical stability and mechanical strength. Therefore, their application in baromembrane processes goes back to the 1970s [1, 2]. They are characterized by high porosity and flux. Since the transport properties and the separating properties of ultra- and microfiltration membranes are mainly determined by the characteristics of their active surface layer, the introduction of functional groups in such layer would significantly increase their selectivity, in particular to heavy metal ions. The sol-gel method based on the hydrolytic co-polycondensation reaction of alkoxysilanes, which allows obtaining a thin active layer on the membrane surface, is the most suitable for such task.

Recently, there has been described the introduction of phenyl and amino groups in the structure of pervaporation and gas separation membranes using the sol-gel method [3, 4]. However, there is almost no data in literature on the receipt of ceramic membranes with complexing groups in the surface layer for baromembrane processes, in particular for selective removal of heavy metal ions from the solutions. In this aspect, alkoxysilane with HS-group attracts attention as functionalizing component. This is due, primarily, to high selectivity of sulfur-containing sorbents towards ions of noble and heavy metals. The use of macroporous supports will maintain high flux inherent to microfiltration membranes. Thus, the application of sol-gel method for creating polysiloxane layer with complexing groups on the surface of macroporous support will make it possible to produce new functionalized ceramic membranes to remove heavy metals in the filtration processes.

2. EXPERIMENTAL PART

2.1 Materials

There were used planar ceramic Al_2O_3 membranes (Anodisc, Whatman) with overall diameter of 25 mm. They are characterized by symmetric porous structure, average pore size of 0.1 microns and a porosity of 25-50%. Chemicals for functionalizing sol preparation: tetraethoxysilane, $Si(OC_2H_5)_4$ (TEOS, Aldrich, 99%), 3-mercaptopropyltrimethoxysilane, $(CH_3O)_3Si(CH_2)_3SH$ (MPTMS, Aldrich, 95%); 0.1 N HCl, ethanol (96%).

2.2 The Technique for the Deposition of the Active Layer on the Surface of a Planar Ceramic Membrane

The active layer deposition technique included the preparation of sol based on alkoxysilanes. For TEOS hydrolysis, 5 cm^3 of it were mixed with the same volume of ethanol (solvent). Then there were added 4.0 cm^3 of HCl acid (0.0024 M) as a catalyst at a constant stirring. This was accompanied with opalescence which disappeared when heated to 70-80°C for 30 min. For MPTMS hydrolysis, it was also mixed at an equal volume ratio with ethanol (in 4.0 cm^3), followed by the addition of 3.6 cm^3 of hydrochloric acid as a catalyst. The mixture was stirred to form a transparent sol (~ 3 min). Preliminary cooled TEOS sol was mixed with MPTMS sol (at TEOS/MPTMS molar ratio of 1/1) and deposited on the surface of the ceramic membrane. The functionalized membrane was dried first in air and then in the oven: for 4 h at 50°C and 8 hours at 80°C. To produce sol with TEOS/MPTMS ratio 2/1, there was performed the hydrolysis of twice smaller amount of MPTMS (2.0 cm^3), in smaller volumes of ethanol (2.0 cm^3) and acid (1.8 cm^3).

2.3 The method of Electron Microscopy

The method of scanning electron microscopy (SEM) was used to investigate the porous structure of the membranes. The images were obtained with an electron microscope JSM 6060 LA (Jeol, Japan) using secondary electrons at accelerating voltage of 30 kV. To prevent the accumulation of the positive charges and to

* v.v.tomina@mail.ru
† zub_yuriy@isc.gov.ua

receive contrasting images, the surface of the samples was covered with thin continues layer of gold or platinum by cathodic sputtering in vacuum.

2.4 The Method of Vibrational Spectroscopy

FT-IR spectra were recorded on a Thermo Nicolet Nexus FTIR spectrometer using diffuse reflection mode "SMART Collector" in the 4000 – 400 cm^{-1} range, with a resolution of 8 or 4 cm^{-1}. The samples were ground with KBr (Fluka, spectranal) at the ratios of sample/KBr = 1/20 and 1/6. There were also recorded the spectra of the initial membranes using mirror as a comparison. The spectra were processed with the software of firm-supplier "OMNIC".

2.5 Method for Determining the Concentration of Silver (I) Ions

Working aqueous silver nitrate solutions were prepared from $AgNO_3$ batches (pH ~ 2). The silver concentration, both in the initial solutions and the collected samples was determined by AAS method using resonance signal 328.1 nm on atomic absorption spectrophotometer C-115-M1 in depleted (oxidative) flame (acetylene/air mixture). The source of resonance radiation was spectral lamp LS-2. The detection limit was 0.01 μg/cm^3.

3. RESULTS AND DISCUSSION

3.1 Functionalization of Planar Ceramic Membranes with 3-mercaptopropyl Groups

Fig. 1 represents the scheme of surface functionalization of planar ceramic membranes. As can be seen, the technique is based on the hydrolytic co-polycondensation reaction of TEOS and MPTMS. Firstly, there was used functionalizing sol with TEOS/MPTMS ratio of 1/1. To produce polisyloxane coatings with optimum properties, the original sol was diluted with ethanol 2, 3, and 4 times. There corresponding volume ratios "sol/alcohol" were 1/1, 1/2, and 1/3, respectively (see Table 1).

According to the Table 1, the increasing dilution of the original sol decreases the degree of membrane functionalization. This decrease is proportional to the degree of original sol dilution. In addition to TEOS/MPTMS ratio of 1/1, there was also used the TEOS/MPTMS ratio of 2/1 for the functionalization of planar ceramic membranes (see examples in Table 2).

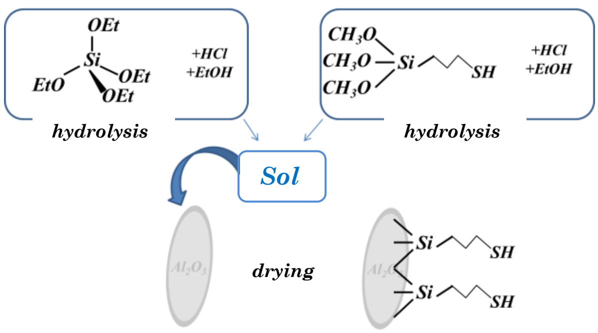

Fig. 1 – Scheme of membrane functionalization

Table 1 – Membranes functionalized with sol at equimolar TEOS/MPTMS ratio

Membrane	sol/ethanol (vol.)	m function. layer, g	functionalization degree, %
VM2	1:0	0.022	54
VM3	1:1	0.012	29
VM4	1:1	0.011	26
VM5	1:2	0.0069	17
VM6	1:2	0.0074	18
VM7	1:3	0.0049	10
VM8	1:3	0.0059	15
VM7a	1:3	0.006	14

However, in this case only at the triple dilution of the initial sol, the degree of membrane functionalization proportionally decreases about 3 times (see sample VM11).

Table 2 – Membranes functionalized with sol at TEOS/MPTMS molar ratio of 2/1

Membrane	m membr before funct., g	sol/ethanol (vol.)	m function. layer, g	functiona-lization degree, %
VM9	0.0414	1:0	0.019	46
VM10	0.0398	1:1	0.0147	37
VM11	0.0427	1:2	0.0059	14
VM12	0.0418	1:3	0.0066	16

3.2 IR Spectral Analysis

The IR spectra of all the functionalized membranes (Fig. 2) clearly recorded sharp low intensity absorption band at ~ 2550 cm^{-1}, referring to the ν (SH) of mercapto groups. There are also bands characteristic of propyl chain vibrations ($\nu_{s,as}$(CH), $\delta_{as}(CH_2)$, $\delta(CH_2)$, and $\omega(CH_2)$) (Fig. 2). A weak band at 1410 cm^{-1} should be mentioned separately, because it is characteristic of vibrations of CH_2 group associated with Si atom. This clearly indicates the introduction of 3-mercaptopropyl functional groups to the surface layer of the membranes.

3.3 Study of the Morphology

According to SEM images, on the surface of planar ceramic membrane (the average pore diameter of which is 1.5-2 microns, Fig. 3a), functionalized with sol at equimolar TEOS/MPTMS ratio, there forms an active layer of nanoparticles from the side of the membrane which contacted with the sol (compare Fig. 3b with Fig. 3c).

When the membrane was functionalized with concentrated sol (Fig. 3d) at equimolar TEOS/MPTMS ratio, there was observed the accumulation of polydisperse particles on its surface, whose sizes range from 30 to 200 nm, although dominated by particles with a diameter of ≈70 nm. In the case of twice diluted (with ethanol) sol, the surface is functionalized more uniform (Fig. 4a), and the average particle diameter is ≈60 nm. When the sol was triply diluted with ethanol (Fig. 4b), there formed a uniform layer of nearly monodisperse spherical particles (d_{av} = 65 nm). With even greater dilution of the initial sol, the active layer is formed with spherical nanoparticles of 55 nm in size (Fig. 4c). The dilution is accompanied with increasing gaps between particles on the membrane surface.

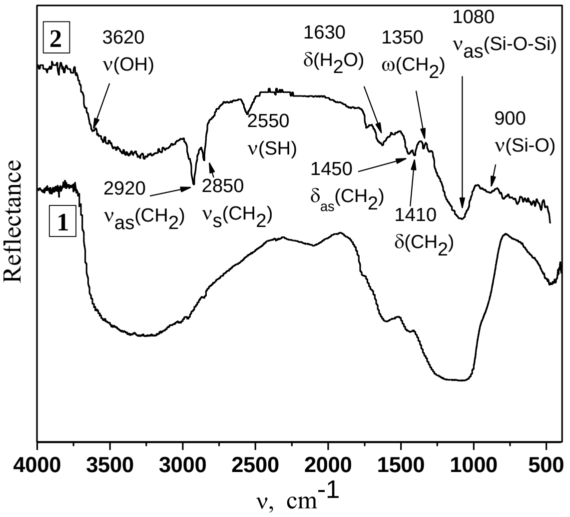

Fig. 2 – IR spectra of the functionalized (2) and non-functionalized (1) ceramic membranes

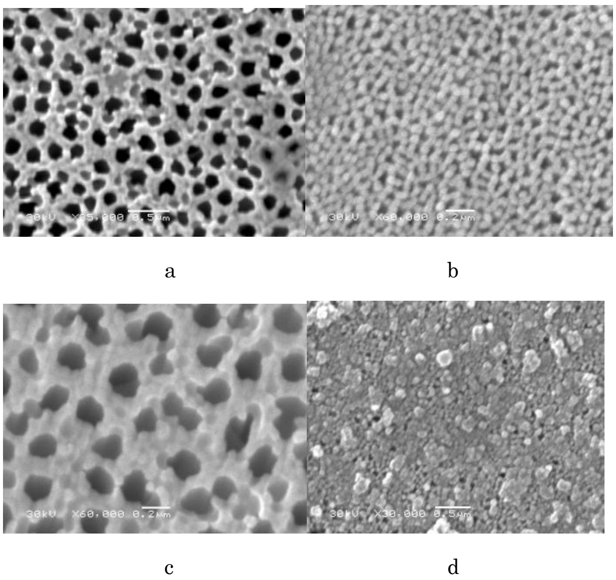

Fig. 3 – SEM images of the original membrane (a); membrane VM3: (b) – side that contacted with sol, (c) – reverse side; (d) – membrane VM2, functionalized with concentrated sol

However, at the ratio of TEOS/MPTMS = 2/1 there is observed the formation of xerogel-like layer on the membrane surface. When using concentrated or twice diluted sol (samples VM9 and VM10, respectively), there formed a solid vitreous layer. This is clearly seen in the image of the cross-section of the membrane (Fig. 4e). This vitreous layer is characterized by a smooth surface (Fig. 4d) and completely covers the membrane. Since the layer is nonporous, it is expected that the functionalized membranes, thus, prove unsuitable for microfiltration. When diluting functionalizing sol, there forms a non-continuous layer (see Fig. 4f), with separate pores blocked by the gel.

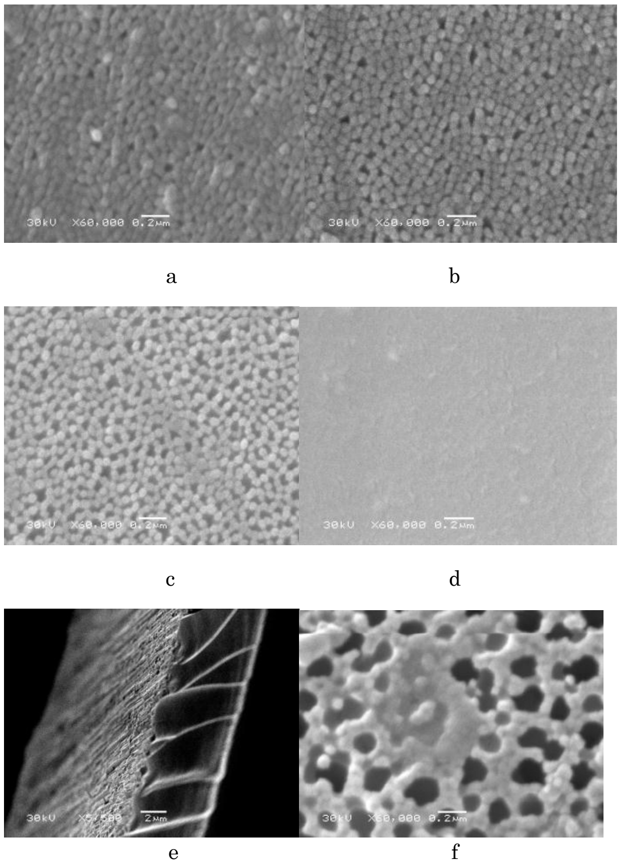

Fig. 4 – SEM images of membranes VM4 (a), VM5 (b), VM8 (c), and VM9: (d) – functionalized surface, (e) – cross-section, VM12 (f)

3.4 Analysis of Sorption Properties of Functionalized Membranes

There has been studied the sorption capacity of the derived membranes towards silver(I) ions (the concentration of silver in the initial solution was 81 mg/l). It was determined, that the initial membrane practically does not absorb silver(I) ions. For functionalized membrane, the sorption of silver(I) ions was higher in the case of a diluted sol. Thus, for a membrane VM11 (sol/ethanol = 1/1) specific sorption of Ag^+ (mol/g) is 0.075, and for membrane VM13 (sol/ethanol = 1/3), it is 0.6. This is apparently due to the formation on the surface of a homogeneous active layer and, consequently, greater availability of functional groups for adsorption. When using concentrated sol, part of the functional groups in the active layer of the membrane is blocked and no longer available for sorption. The same behavior was seen for tubular ceramic membranes [5]. However, in all cases, the amount of adsorbed silver is less than the theoretically calculated amount of groups, considering the mass of the deposited layer. It is clear that some groups remain idle. This is consistent with the data of IR spectroscopy.

4. CONCLUSIONS

It was determined that during functionalization of planar ceramic membranes with $\equiv Si(CH_2)_3SH$ groups using sol-gel method, there is observed the formation of complexing layer on their surface. At the equimolar ratio of TEOS and MPTMS in the initial sol, the formation of layer composed of nanoparticles is observed. Meanwhile the reduction of MPTMS portion produces vitreous coatings. The dilution of the initial sol with ethanol leads to the formation of a homogeneous surface layer, consisting of nearly monodisperse nanoparticles of spherical shape. Such layer is characterized by the highest sorption capacity towards silver(I) ions.

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REFERENCES

1. M.T. Bryk, *Membrane encyclopedia* (Kyiv: "KM Academy": 2005).
2. *Inorganic membranes. Synthesis, Characteristics and Application* (Ed. R.R. Bhave) (New York: Van Nostrand Reinhold: 1991).
3. S. Araki, S. Imasaka, S. Tanaka, Y. Miyake, *J. Membrane Science* **41**, 380 (2011).
4. S. Araki, T. Satoh, H. Doi, H. Yano, Y. Miyake, *Desalin. Water Treat.* **7**, 12 (2009).
5. V.V. Tomina, I.V. Mel'nik, R.P. Pogorilyi, V.M. Kochkodan, Yu.L. Zub, *Protection of Metals and Physical Chemistry of Surfaces* **49**, 386 (2013).