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LDRD Final Report on Nano-Scale Engineering of Smart Membranes

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Douglas A. Loy, Gregory M. Jamison, Roger A. Assink, Rick J. Buss,
C. Jeffrey Brinker, Carol S. Ashley, Jean-Loup Faulon

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Douglas A. Loy, Gregory M. Jamison, Roger A. Assink, Rick J. Buss, C. Jeffrey
Brinker, Carol S. Ashley, Jean-Loup Faulon
Encapsulants and Porous Materials Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-1407

Abstract

A new approach to the fabrication of porous, amorphous inorganic membranes using organic pore templates was investigated. The pore templates were a new family of hybrid organic-inorganic monomers. As background for membrane work, the monomers were polymerized by sol-gel techniques to make crosslinked polymers. Molecular modeling was used to create computer simulations of the materials and provide insight into their architecture and the origins of their porosity. The resulting materials, a class of molecular composites, were then converted into porous silicas using low temperature oxygen plasma techniques. A select few of the monomers were copolymerized with silica monomers to form non-porous thin films on mesoporous substrates. The films were converted into porous silica thin films with thermal oxidations and the resulting membranes were tested for gas selectivities and flux.

CONTENTS

	<u>PAGE</u>
I. Introduction.....	7
II. Results.....	8
III. Presentations and Publications.....	8

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LDRD Final Report on Nano-Scale Engineering of Smart Membranes

Introduction

The purpose of this project was the development of chemically robust inorganic membranes that mimic active biological membranes (i.e., that exhibit molecular recognition capabilities) for uses in gas or liquid separations, sensors, catalysts, selective adsorbents, etc.

In a recent study entitled "Membrane Separation Systems: A Research Needs Assessment" the DOE stressed the critical importance of membranes in developing more energy-efficient technologies. They ranked pervaporation, reverse osmosis, gas separation, and facilitated transport membranes as the four highest-ranking priorities of membrane research. These applications normally require thermally and chemically stable supported thin films with nano-scale pores (0.2-2.0 nm) and extremely narrow pore size distributions. Although inorganic membranes exhibit excellent thermal and chemical stability, there are no U.S. suppliers of inorganic membranes with pores smaller than about 4.0 nm. What's more, the U.S. is falling behind Japan and Europe in advanced inorganic membrane R&D.

Our approach has been to embed designed organic templates in dense sol-gel thin film matrices. The template molecules are copolymerized with tetraethoxysilanes to afford a solution of polymeric silica. Dense, non-porous, thin films are formed from the silica-template solution. The template are removed by heating to 500 °C in air or with an oxygen plasma. The loss of the organic template generates pores in the thin film. The novel elements of this process are 1) to use sol-gel processing to prepare a thin (1000 Å) film that is non-porous and 2) generate porosity by building the silica around an organic template that can be removed to create a pore without disturbing the silica's architecture.

Key points of interest in this research were the size of the pores that form from different sized organic templates and whether or not this method would allow very small pores, capable of molecular sieving, to be formed. The research was carried out in several stages. 1) New hybrid organic-inorganic monomers and materials were synthesized and characterized. 2) Methods for removing organic templates were investigated. 3) Procedures for incorporating the organic templates into the thin films were developed. 4) Prototype membranes were prepared by depositing a thin film of the templated thin film on a mesoporous membrane support and firing the membrane at 500

°C to generate the porosity. 5) The gas selectivities of the resulting membranes were then determined.

Results

This research project was a very productive effort. The project's investigators made significant contributions in the areas of computer modeling, new materials synthesis and characterization, and in the development of an entirely novel approach to fabricating amorphous inorganic membranes. Because of the breadth and volume of the research that was conducted as part of this project, the remainder of the report is a list of publications, including abstracts, in the three areas of research that were impacted by the LDRD: "New Hybrid Organic-Inorganic Materials," "Development Of Templating Techniques," and "Membrane Fabrication And Testing."

Publications and Presentations

1. New Hybrid Organic-Inorganic Materials.

"Arylsilsesquioxane gels and related materials. New hybrids of organic and inorganic networks," Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700-10.

Abstract. Molecular building blocks for the preparation of amorphous hybrid organic-inorganic network materials are prepared. Hydrolysis and condensation of bis(triethoxysilyl)aryl and -ethynyl monomers results in formation of aryl- and ethynyl-bridged silsesquioxanes in the form of xerogels. The gels are glasslike materials composed of uniform aggregates of particles between 50 and 80 nm in diam. Atomic force microscopy is used to examine the fine-grained aggregate characteristics of Phenylene-bridged silsesquioxanes. The aryl-bridged materials are microporous with surface areas as high as 1000 m²/g and thermally stable to 400 °C in air. Solid-state ¹³C- and ²⁹Si-NMR spectroscopies are used to evaluate the integrity of the aryl and ethynyl bridges and to determine the degrees of hydrolysis (semiquantitative) and condensation in the network materials.

"Preparation of aryl-bridged polysilsesquioxane aerogels," Loy, D. A.; Shea, K. J.; Russick, E. M. *Mater. Res. Soc. Symp. Proc.* **1992**, 271, 699-704

Abstract. The authors report the preparation of a new class of organic-inorganic hybrid aerogels from aryl-bridged polysilsesquioxanes. 1,4-Bis(trimethoxysilyl)benzene and 4,4'-bis(trimethoxysilyl)biphenyl were sol-gel processed to form phenyl- and biphenyl-bridged supercritical carbon dioxide extraction. The aryl-bridged pronounced influence on surface area from the reaction conditions used in preparing the initial gels. Specifically, high surface arogels (up to 1750 m²/g) are obtained from gels prepared with either acid or base catalysts. The materials were characterized by nitrogen sorption surface analysis, and by TEM.

"Arylene- and Alkylene-Bridged Polysilsesquioxanes," J. H. Small, K. J. Shea, and D. A. Loy, *J. Non-Crystal. Solids* **1993**, 160, 234-46.

Abstract. Bis(trimethoxysilyl)arylene monomers and the 1,6-bis(trimethoxysilyl)hexylene monomer were hydrolytically condensed under sol-gel conditions using both acid and base catalysts to produce their respective arylene- and alkylene-bridged polysilsesquioxane materials. Polymerization reactions yielded gels within 24 hours. One notable exception was the acid catalyzed polymerization of 2,5-bis(trimethoxysilyl)thiophene which required approximately one month to gel. The gels were processed by extracting with low dielectric solvents or by aqueous extraction. Solid state ¹³C and ²⁹Si CP MAS NMR, infrared spectroscopy, and gas sorption porosimetry were measured on the xerogels. The materials were transparent, glass-like xerogels with surface areas as high as 1100 m²/g and porosity primarily confined to a micropore region <20 Å diameters. Xerogels prepared using the aqueous extraction had surface areas between 500-956 m²/g.

"Alkylene- and Arylene-Bridged Polysiloxane Network Materials," Loy, D. A.; Jamison, G. M.; Assink, R. A.; Zender, G. and Shea, K. J. *Polym. Mater. Sci. Eng.* **1994**, 70, 373.

Abstract. Hexylene- and phenylene-bridged polymethylsiloxane xerogels and aerogels were prepared by sol-gel polymerizations. The materials were prepared by the hydrolysis and condensation of 1,6-bis(diethoxymethylsilyl)hexane and 1,4-bis(diethoxymethylsilyl)benzene under acidic and basic conditions. The polymerizations afforded network polymers in the form of gels within several hours. The gels were dried

to afford both xerogels and aerogels. The materials were characterized by solid state ^{29}Si and ^{13}C CP MAS NMR spectroscopy, nitrogen sorption porosimetry, thermal gravimetric analysis, and scanning electron microscopy.

"Alkylene- and Arylene-Bridged Polysiloxane Network Materials," Jamison, G. M.; Loy, D. A.; Assink, R. A.; Zender, G. and Shea, K. J. *Mater. Res. Soc. Symp. Proc.*, (Better Ceram. Chem. 5) **1994**, in press.

Abstract. Hexylene- and phenylene-bridged polymethylsiloxane xerogels and aerogels were prepared by sol-gel polymerizations. The materials were prepared by the hydrolysis and condensation of 1, 6-bis(diethoxymethylsilyl)hexane and 1, 4-bis(diethoxymethylsilyl)benzene under acidic and basic conditions. The polymerizations afforded network polymers in the form of gels within several hours. The gels were dried to afford both xerogels and aerogels. The materials were characterized by solid state ^{29}Si and ^{13}C CP MAS NMR spectroscopy, nitrogen sorption porosimetry, thermal gravimetric analysis, and scanning electron microscopy.

"Hexylene- and Phenylene-Bridged Polysiloxane Network Materials," Loy, D. A.; Jamison, G. M.; Assink, R. A.; Shea, K. J. and Myers, S. *ACS Symp. Ser.* 585: Washington, D. C., **1995**, p. 264.

Abstract. Hexylene- and phenylene-bridged polymethylsiloxane xerogels and aerogels were prepared by sol-gel polymerizations. The materials were prepared by the hydrolysis and condensation of 1, 6-bis(diethoxymethylsilyl)hexane 1 and 1, 4-bis(diethoxymethylsilyl)benzene 3 under acidic and basic conditions. The polymerizations afforded network polymers in the form of gels within several hours. The gels were dried to afford both xerogels and aerogels. The materials were characterized by solid state ^{29}Si and ^{13}C CP MAS NMR spectroscopy, nitrogen sorption porosimetry, thermal gravimetric analysis, and scanning electron microscopy.

"Alkylene-Bridged Polysilsesquioxane Aerogels. Highly Porous Hybrid Organic-Inorganic Materials," Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Russick, E. M.; Assink, R. A.; Prabakar, S.; Shea, K. J. *J. Non Cryst. Solids* **1995**, 186, 44-53.

Abstract. Alkylene-bridged polysilsesquioxane gels were prepared by sol-gel polymerizations of a, w-bis(triethoxysilyl)alkanes. The gels were extracted with

supercritical carbon dioxide to afford a novel class of hybrid organic-inorganic aerogels. The effect of the length of the alkylene bridging group and catalyst (HCl and NaOH) on structure was examined. Molecular structure was characterized by solid state ^{13}C and ^{29}Si CP MAS NMR spectroscopies. The alkylene bridging groups survived sol-gel polymerization to give materials with average degrees of condensation of 79% and 90% for the acid- and base-catalyzed aerogels, respectively. Scanning electron microscopy was used to examine the macro structure of the gels and nitrogen sorption porosimetry was used to measure their surface areas and pore structures. Most of the alkylene-bridged aerogels were mesoporous, high surface area materials. As with alkylene-bridged polysilsesquioxane xerogels, surface area decreased with increasing alkylene bridging group length. Only the base-catalyzed tetradecylene-bridged aerogel was found to be non-porous.

"Origin of Porosity In Aryl-Bridged Silsesquioxanes." Schaefer, D. W.; Beaucage, Loy, D. A.; Ulibarri, T. A.; Black, E.; Shea, K. J.; Buss, R. J. Better Ceramics through Chemistry VII, 1996.

Abstract. Arylene-bridged polysilsesquioxanes are a novel class of porous materials prepared by sol-gel processing of ethoxysilane monomers in which there are two or more trialkoxysilyl groups positioned about an arylene "bridging" group. The majority of these materials are highly porous with surface areas as high as $1880\text{ m}^2/\text{g}$. In an effort to understand the origins of porosity in these materials, small-angle x-ray and neutron scattering were employed to characterize phenylene-, biphenylene- and terphenylene-bridged polysilsesquioxanes. Phenylene-bridged polysilsesquioxane xerogels and aerogels were also compared to understand the effect of drying protocol on pore structure. The effect of catalyst concentration is reported for the base-catalyzed system.

"Sol-Gel Synthesis of Hybrid Organic-Inorganic Materials. Hexylene- and Phenylene-Bridged Polysiloxanes," Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Assink, R. A.; Myers, S. A.; Shea, K. J. *Chem. Mater.* 1996, 8, 656-663.

Abstract. New highly crosslinked polysiloxanes were prepared by sol-gel polymerization of 1,6-bis(diethoxymethylsilyl)hexane and 1,4-bis(diethoxy-methylsilyl)benzene. Hydrolysis and condensation of the monomers under acidic and basic conditions with four equivalents of water led to the rapid formation of hexylene- and phenylene-bridged polysiloxanes in the form of gels. The dry gels (xerogels) were intractable, insoluble

materials. The materials were noticeably hydrophobic and exhibited no swelling in organic solvents or water. Most of the xerogels were highly porous with surface areas as high as $1025 \text{ m}^2/\text{g}$. The pore size distribution could be manipulated by the choice of the bridging group, but those hexylene-bridged polysiloxanes prepared under acidic conditions were always found to non-porous.

2. Development of Templating Techniques.

“Porous materials by design. Plasma oxidation of hydrocarbon templates in polysilsesquioxanes,” Loy, D. A.; Buss, R. J.; Assink, R. A.; Shea, K. J.; Oviatt, H. *Polym. Prepr.* **1993**, *34*, 244-5.

Abstract. Arylene- and alkylene-bridged polysilsesquioxanes were treated with low temperature oxygen plasmas to remove the hydrocarbon components leaving porous silica behind. Solid state ^{29}Si NMR and IR spectroscopy were used to confirm the loss of the bridging groups. The authors were successful in generating new porosity with the plasma treatment of the non-porous decylene-bridged underway with a series of alkylene-bridged polysilsesquioxanes to determine the effect of bridging group length on the final silica porosity.

“Plasma Oxidation of Hydrocarbon Templates in Bridged Polysilsesquioxanes. Porous Materials by Design.,” Loy, D. A.; Shea, K. J.; Buss, R. J.; and Assink, R. A. in *ACS Symposium Series* **1994**, *572*, 122.

Abstract. Hydrocarbon bridging groups in polysilsesquioxane network polymers were used as templates for porosity. Arylene- and alkylene-bridged polysilsesquioxanes were prepared by the hydrolysis and condensation of bis(triethoxysilyl)aryl monomers and bis(triethoxysilyl)alkane monomers. The bridged polysilsesquioxane xerogels and monolithic gels were treated with inductively coupled oxygen plasmas at low temperature ($\leq 100 \text{ }^\circ\text{C}$). All of the bridged polysilsesquioxane gels save a microporous monolith were quantitatively converted to silica gels. Non-porous alkylene-bridged polysilsesquioxanes were plasma oxidized to porous silica gels whose pore size and shape appeared to be related to the length of the bridging group.

“Engineering of porosity in amorphous materials. Plasma oxidation of hydrocarbon templates in polysilsesquioxanes,” Loy, D. A.; Buss, R. J.; Assink, R. A.; Shea, K. J.; Oviatt, H. *Mater. Res. Soc. Symp. Proc* **1994**, *346*, 825-9.

Abstract. Arylene- and alkylene-bridged polysilsesquioxanes were prepared by sol-gel processing of bis(triethoxysilyl)-arylene monomers, and alkylene monomers. The arylene polysilsesquioxanes were porous materials with surface areas as high as 830 m²/g (BET). Treatment with an inductively coupled oxygen plasma resulted in the near quantitative removal of the arylene bridging groups and a coarsening of the pore structure. Solid state ²⁹Si NMR was used to confirm the conversion of the sesquioxane silicons (T) to silica (Q). The alkylene-bridged polysilsesquioxanes were non-porous. Oxygen plasma treatment afforded silica gels with mesoporosity. The porosity in the silica gels appears to arise entirely from the oxidation of the alkylene spacers.

“Molecular engineering of porous silica using aryl templates,” Loy, D. A.; Shea, K. J. United States Patent No 5,321,102, June 14, 1994.

Abstract. A process for manipulating the porosity of silica using a series of organic template groups covalently incorporated into the silicate matrix. The templates in the bridged polysilsesquioxanes are selectively removed from the material by oxidation with oxygen plasma or other means, leaving engineered voids or pores. The size of these pores is dependent upon the length or size of the template or spacer. The size of the templates is measured in terms of Si-Si distances which range from about 0.67 nm to 1.08 nm. Changes introduced by the loss of the templates result in a narrow range of micropores ~i.e. <~ nm). Both aryl and alkyl template groups are used as spacers. Novel microporous silica materials useful as molecular sieves, dessicants, and catalyst supports are produced.

“Cross-condensation reactions in an organically modified silica sol-gel,” Prabakar, S.; Assink, R. A.; Raman, N. K.; Brinker, C. J. *Mater. Res. Soc. Symp. Proc* **1994**, *346*, 979-84.

Abstract. High resoln. ²⁹Si NMR has been used to study the extent of cross condensation taking place in a hybrid organic-inorganic sol-gel system. Tetraethoxysilane (TEOS) + methyltriethoxysilane (MTEOS) sol-gels were chosen for this purpose. The sols were prepared by acid catalyzed hydrolysis of TEOS and MTEOS with a H₂O/Si ratio of 0.3. ²⁹Si NMR shows signals due to both self-condensation and cross-condensation between

TEOS and MTEOS. Resonance assignments were made by comparing the positions and intensities of peaks in the spectra of single and multicomponent systems. It was found that, within experimental error, the self- and cross-condensation rates are equal and that extensive Molecular level mixing takes place during the early stages of the reaction.

"Computer-aided Structure Elucidation for Arylene-Bridged Polysilsesquioxanes," Faulon, J.-L.; Loy, D. A. ; Carlson, G. A. ; Shea, K. J., *Comp. Matls. Sci.*, **1995**, 3, 334-346.

Abstract. Phenylene- and terphenylene- bridged polysilsesquioxane networks are modeled using computer-aided structure elucidation and molecular dynamics (MD) simulations. The models are matched with analytical results such as elemental analysis, solid state ^{29}Si NMR, and gas sorption porosimetry. Models which are cross-linked in every direction in three-dimensional space do not contain pore volume and are rejected. Models which are cross-linked in only two dimensions fit well with all analytical data. In conclusion, the bridged polysilsesquioxane networks seem to be formed by an aggregation of two dimensional structures covalently or hydrogen bonded together.

3. Membrane Fabrication And Testing

"Sol-gel strategies for controlled porosity inorganic materials," Brinker, C. J.; Sehgal, R.; Hietala, S. L.; Deshpande, R.; Smith, D. M.; Loy, D.; Ashley, C. S. *J. Membr. Sci* **1994**, 94, 85-102.

Abstract. The porosity (i.e., pore vol., pore size, and surface area) of ceramic materials prepared by sol-gel processing depends on the size and structure of primary particles or polymers formed by condensation reactions, the organization of these structures, often by aggregation, to form a gel, and the collapse of the gel by drying. This paper reviews with 41 refs. these ideas in the context of the formation of thin films suitable for inorg. membranes and introduces a number of specific strategies designed to control pore sizes in the range appropriate for gas sepn.: (1) aggregation of fractals; (2) management of capillary pressure, (3) control of condensation rate, and (4) the use of org. or microporous templates in composite thin film structures. These strategies are contrasted with the more traditional particle packing approach to preparing controlled porosity materials.

"Organic template approach to molecular sieving silica membranes," Raman, N. K.; Brinker, C. J., *J. Membr. Sci.* (1995), 105(3), 273-9.

Abstract. We demonstrate a "template" approach to prepare microporous inorganic membranes exhibiting high flux combined with high selectivity, overcoming limitations inherent to both conventional inorganic (sol-gel, CVD) and organic membrane approaches. Hybrid organic-inorganic polymers prepared by co-polymerization of tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTES) were deposited on commercial asymmetric alumina supports. Heat treatments were employed to densify the inorganic matrix and pyrolyze the methyl ligands, creating a continuous network of micropores. Resulting membranes exhibited very high CO₂ permeance values ($2.57 \times 10^{-3} \text{ cm}^3/\text{cm}^2\text{-s-cm Hg}$) combined with moderate CO₂/CH₄ separation factors (71.5) with only a modest reduction in CO₂ permeance ($2.04 \times 10^{-4} \text{ cm}^3/\text{cm}^2\text{-s-cm Hg}$). Combined CO₂/CH₄ selectivity factors and CO₂ fluxes exceeded those of all known organic membranes.

SUMMARY

The research conducted as a part of this LDRD project has made significant impacts in several areas of science and technology. A large group of new template monomers were synthesized and polymerized to afford hybrid organic-inorganic materials. Structure-property, i.e. porosity, relationships were investigated and monomers capable of forming non-porous materials were identified. Materials prepared from these monomers were used to determine methods for template removal; both low temperature, inductively coupled oxygen plasma and thermal oxidation treatments were found to quantitatively remove the organic templates. Chemical formulations were developed that allowed dense thin films of the silica-template copolymer to be prepared. Then, membranes were prepared with the biphenylene and phenylene templates. Selectivity measurements indicate that resulting membranes are mesoporous; separations with these membranes can take place by Knudsen effect, but not molecular sieving. Finally, membranes prepared with an even smaller templates revealed that high flux and selectivity can be obtained in an inorganic membrane material using a template approach.

Acknowledgments

The authors would like to thank Duane Schneider for monomer and polymer synthesis and NMR characterizations, Pam Ward (1812) for assistance with plasma studies, Linda McLaughlin and Brigitta Baugher for their help with nitrogen sorption porosimetry, and Kenneth J Shea's group at UC Irvine for their synthetic contributions. This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

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