SAND2000-1888C

DEVELOPMENT OF NEW HYBRID ORGANIC-INORGANIC MATERIALS FOR HYDROGEN SEPARATION MEMBRANES AT SANDIA NATIONAL LABORATORIES.

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SEP 15 2000
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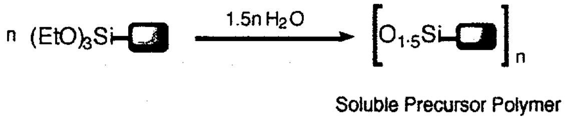
ABSTRACT

We have been developing a new class of hybrid organic-inorganic materials as candidates for hydrogen separation membranes. This type of material shows significant promise for use in membranes due to good thermal and chemical stability, and ease of processing into defect-free thin films. These polysilsesquioxanes are easily prepared from the hydrolysis and condensation of organotrialkoxysilane monomers with reactive organic functionalities, such as maleimide and methacryloxypropyl groups, that are stable to sol-gel conditions but can be "cured" thermally or chemically as a membrane. Introducing highly dispersed catalysts into these materials was realized through the pre-coordination of palladium to a silane monomer before the polymerization. Finally, a new route to inorganic membranes from polysilsesquioxanes with thermally cleavable organic substituents was investigated. This new method circumvents some of the difficulties associated with sol-gel fabrication of silica membranes by using well-defined, processible precursors.

INTRODUCTION

Hybrid organic-inorganic materials are a promising class of materials for hydrogen membrane applications requiring moderate thermal stability and chemical resistance. This project utilizes a new class of hybrid organic-inorganic materials called polysilsesquioxanes (Scheme 1) to meet these requirements while permitting an extraordinary degree of control over physical and chemical properties.[1] There have recently been several reports of hybrid organic-inorganic materials being used for nanofiltration,[2] pervaporation,[3] proton conductors,[4] and gas separations.[5] Many of these utilize hybrid materials derived from tetraalkoxysilanes and physically compatible polymers with functional groups which are reactive with the silica precursor. Guizard has used several hybrid compositions to achieve respectable air separation.[5c] It is this precedent, coupled with the thermal stability of the polysilsesquioxanes that inspired this research. This report describes our preliminary results including the synthesis of a new maleimide-functionalized monomer[6] and a commercial methacryloxypropyl-substituted monomer to prepare membrane precursors that are spun coated onto a mesoporous alumina support, then thermally cured (Scheme 2) to give a glassy thin film membrane. Next we examined chemical methods for introducing palladium nanoparticles into these hybrid materials. And lastly, we prepared three new hybrid materials as precursors for preparing defect free silica membranes through low temperature (< 300 °C) thermolyses. Integral to all of this work is the preparation of well-defined, processible polymeric precursors with inorganic scaffolding and reactive organic groups. Polysilsesquioxanes (Scheme 1) were chosen as these polymeric precursors because of their ease of formation, wide variety of organic substituents, and ready availability.[1]



Scheme 1. Formation of polysilsesquioxanes as precursor polymers for membrane fabrication from the sol-gel polymerization of monomers. Pre-assembly of the polymers before membrane fabrication alleviates the problems associated with condensation products inherent in sol-gel routes to membranes.

Scheme 2. Thermal curing of precursor polymers after deposition on a mesoporous support. Cure chemistry involves a reactive functionality on the organic group. The silsesquioxane network remains relatively unchanged.

DISCUSSION OF CURRENT ACTIVITIES

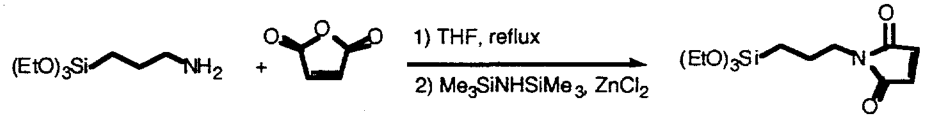
Our current efforts have been focussed on two distinct areas: 1) hybrid organic-inorganic hydrogen membranes and 2) inorganic hydrogen membranes. In both cases we capitalize of the bifunctionality of the selected organotrialkoxysilanes. Monomers are prepared with three alkoxide substituents attached to the single silicon that are hydrolyzed and condensed into a siloxane network polymer. Our studies of the sol-gel chemistry of polysilsesquioxanes has revealed that organotrialkoxysilanes, despite being tri-functional, afford soluble resins or polymers with alkyl groups greater than two carbons in length. This permits well-defined polysilsesquioxanes to be prepared as precursors to membranes. The organic group bears the second functionality that, ideally, survives the aforementioned sol-gel polymerization to react thermally or through radical, Diels-Alder or Alder-ene chemistry to cure the polymer into a glassy, non-porous material suitable for membranes.

MONOMER AND MATERIALS SYNTHESES

Organotrialkoxysilanes with electron deficient groups, such as N-propylmaleimide, methacryloxypropyl-, or styryl-, make ideal candidate monomers to meet the project's requirements of bifunctionality and polymerizability to afford soluble polymers. We selected a maleimide-functionalized trialkoxysilane as the first candidate monomer because of its reactivity towards thermal and radical crosslinking and its propensity to undergo the aforementioned pericyclic reactions. It is also more symmetrical than the methacryloxypropyltrialkoxysilanes making characterization easier. However, because the maleimide-functionalized monomers are new compounds, membranes were also prepared from methacryloxypropyltriethoxysilane.

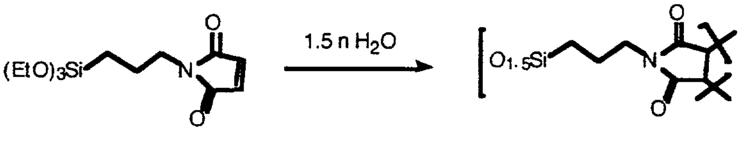
The maleimide-functionalized monomer can be readily prepared from the commercially available aminopropyltriethoxysilane and maleic anhydride (eq 1). The resulting monomer is isolated as a crystalline solid.

(eq 1)



When the maleimide monomer was polymerized under sol-gel conditions only intractable resins were obtained. We discovered that the electrophilic maleimide was reacting to form crosslinks during the sol-gel reaction (eq 2).

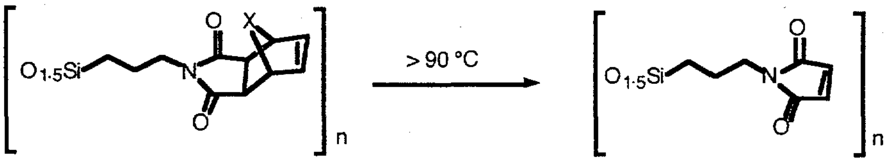
(eq 2)



In order to overcome this lack of chemical selectivity, the maleimide group was "protected" as the Diels-Alder adduct with furan (eq 3). The resulting oxanorabornene group was unreactive to sol-gel conditions, but the maleimide functionality could be readily regenerated with loss of the volatile furan (bp = 35 °C) by heating the material to over 90 °C (eq 4).

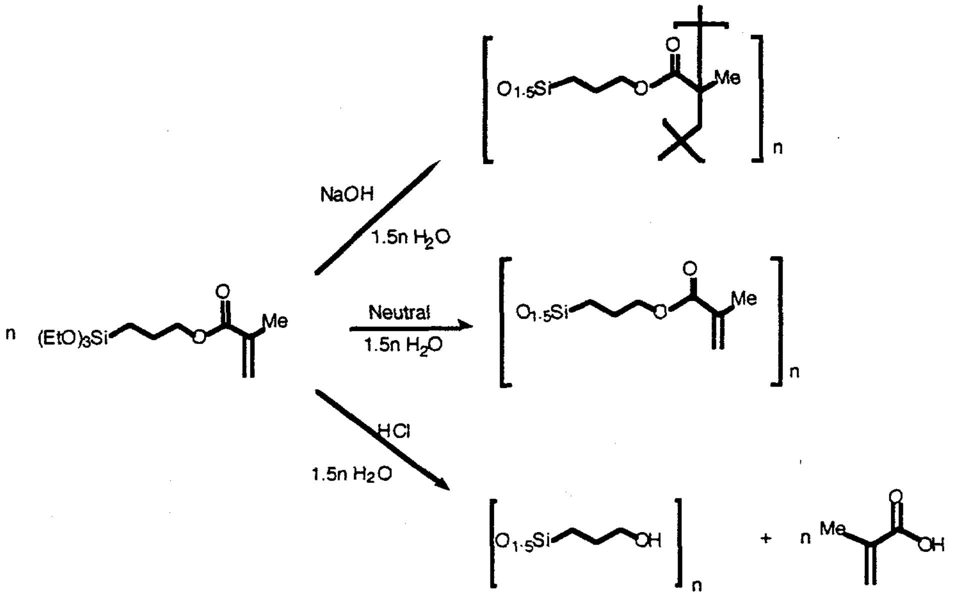
(eq 3)

(eq 4)



The maleimide could then be thermally or free radically crosslinked or reacted with curing agents such as bis(dienes) through Diels-Alder additions or polyenes for Alder-ene chemistry. In practice, the protected polymer is cast as the thin film membrane and curing is concurrent with deprotection. This is the first time this family of protected maleimide-silanemonomers has been prepared. It is also the first time a coupling agent has been prepared with a protected, thermally released reactive functionality of the organic group. This arrangement would be useful not only in constructing hybrid organic-inorganic materials for membrane applications, but also for silane coupling agent applications as well.

Methacryloxypropyltriethoxysilane is a commercially available coupling agent that has been used to prepared hybrid organic-inorganic composites. In this study, the monomer was sol-gel polymerized under acidic, neutral and basic conditions (Scheme 3).



Scheme 3. Polymerization of methacryloxypropyltriethoxysilane under basic, neutral and acidic conditions. Only the neutral conditions afforded the desired material.

It was discovered that base catalysts induced polymerization of the methacrylate carbon-carbon double bond concurrently with the sol-gel reaction at the triethoxysilyl group. Under acidic conditions, the ester linkage between the triethoxysilyl group and methacrylate was hydrolyzed releasing methacrylic acid. Under neutral conditions, only sol-gel polymerization at the triethoxysilyl group was observed and the desired methacryloxypropylsilsesquioxane polymer was obtained.

PREPARATION OF MEMBRANES

Both hybrid organic-inorganic and inorganic membranes described in this study are asymmetric with a thin film of the non-porous membrane deposited on the top of a mesoporous alumina support in the form of a disk. The precursor polymers are dissolved in tetrahydrofuran or ethanol and are spun cast on the disk. The molecular weight must be sufficiently high for the polymer film to remain on the surface of the support without intercalating into the mesoporous structure. We were able to prepare asymmetric membranes composed of both cured maleimide- (Figure 1) and methacryloxypropyl- (Figure 2) functionalized polysilsesquioxanes. It was determined with the maleimide system that a free radical initiator added to the polymer prior to spin coating was useful in curing the resins before the material could sink into the 80 nm pores characteristic of the alumina supports used in this study (Figure 1).

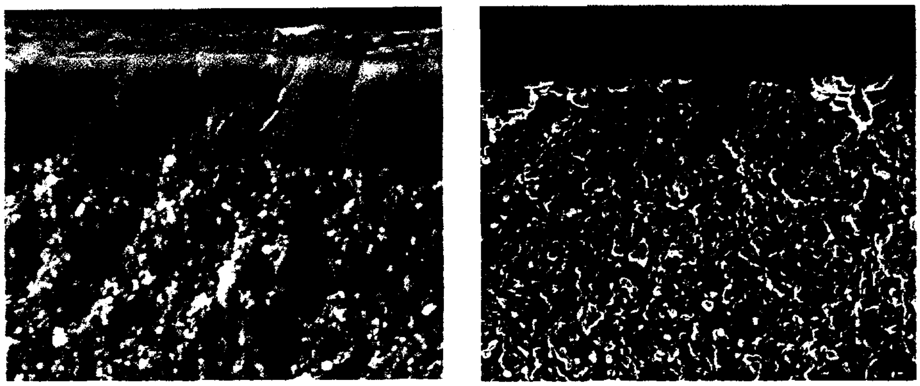


Figure 1. Micrographs of maleimide-functionalized polysilsesquioxane spun cast onto mesoporous alumina supports and thermally cured. The well-oriented polymeric film on the left was cured with a free radical catalyst (AIBN). The polysilsesquioxane spun without the catalyst (shown on the right) melted into the porous support faster than the material could crosslink.

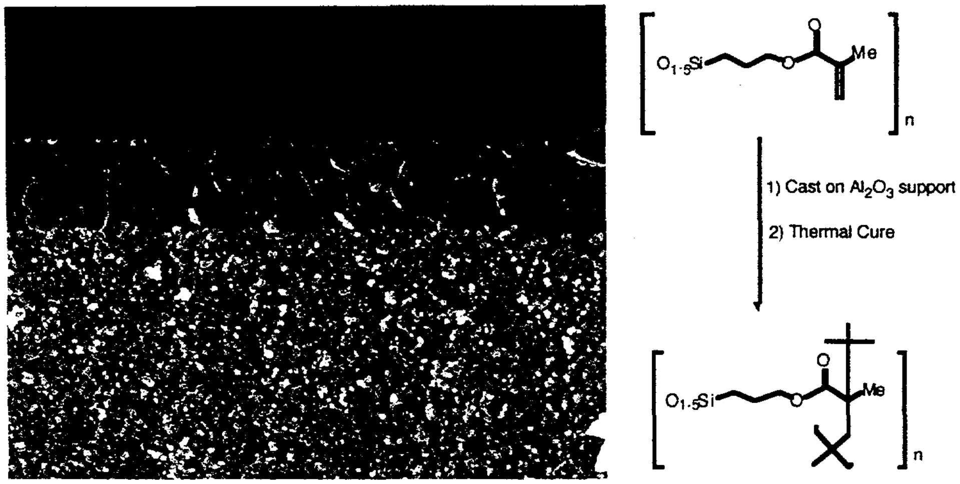


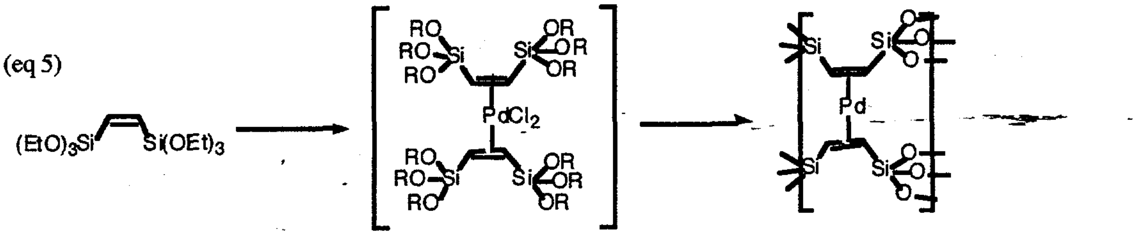
Figure 2. Scanning electron micrograph of hybrid organic-inorganic membranes prepared from the thermal curing methacryloxypropyl-functionalized polysilsesquioxanes.

We were also able to demonstrate that the methacryloxypropyl polysilsesquioxane could be cast and thermally/free radical cured without having to resort to a Diels-Alder protecting group. The methacrylate group is less reactive towards both radical and Michael additions (allowing it to survive the sol-gel process under neutral conditions).

HYBRID ORGANIC-INORGANIC MATERIALS WITH HIGHLY DISPERSED PALLADIUM

In this section of the study, we prepared hybrid organic-inorganic materials with high dispersed palladium. This was accomplished in order to demonstrate that we could prepare these materials without aggregation of the palladium before investigating the thermolytic decomposition of hybrid materials to afford palladium loaded inorganic membranes. The materials were successfully prepared by pre-assembling the hybrid monomer[7] and palladium in a solution, then polymerizing the hybrid monomer to give a highly crosslinked polymeric gel (eq. 5).

(eq 5)



Transmission and scanning electron micrographs and EDS analysis revealed that the palladium was incorporated into the dried gels in a highly dispersed form.

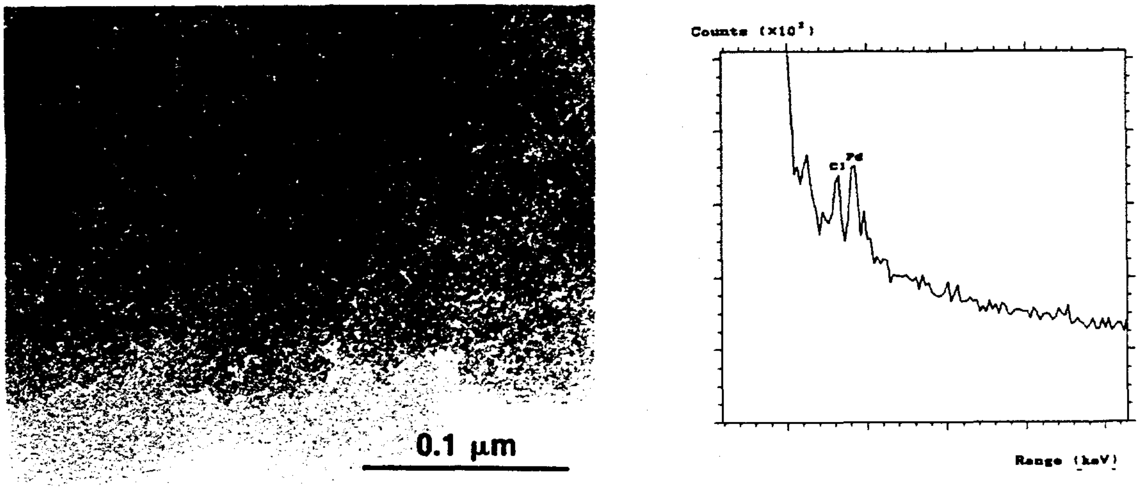
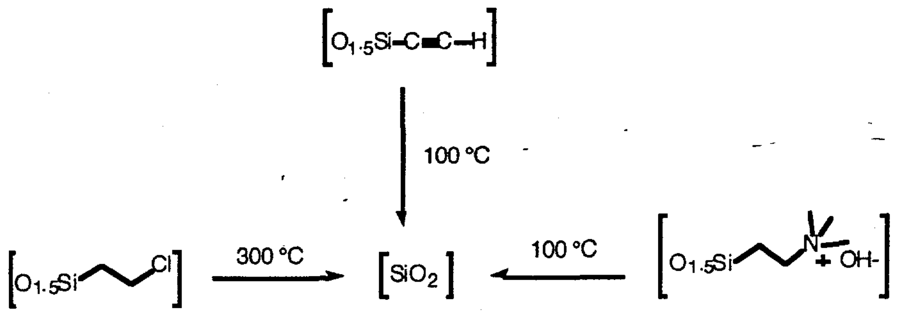


Figure 3. Transmission electron micrograph (left) showing palladium (dark spots) particles less than 5 nm in diameter with minimal aggregation. The EDS graph confirms presence of palladium with some residual chlorine.

The palladium particles could be prepared as small as 5 nm in diameter with little indication of aggregation (Figure 3). The next step was the design and preparation of hybrid polymers to use as processible precursors to inorganic membranes.

HYBRID ORGANIC-INORGANIC MATERIALS AS SILICA MEMBRANE PRECURSORS

Silica membranes are commonly prepared by sol-gel coating a solution of silica pre-polymers onto a mesoporous support in a size exclusion, slip deposition technique. The method can be used to make gas-sieving membranes, but control over the molecular size of the silica precursors is difficult because sol-gel polymerization continues throughout the dip coating process and in stored solutions. This dynamic situation makes membrane reproducibility difficult. We are developing an alternative system (Scheme 4) capitalizing on the ability of silsesquioxanes to form soluble polymers with excellent shelf life. This should make deposition and membrane features more reproducible. To prepare silica membranes, the organic component must be removed during processing. To avoid silicon oxycarbide formation, we have prepared a family of polysilsesquioxanes that will convert to silica at temperatures ranging between 100-300 °C. We have prepared and characterized these materials (Scheme 4) and are presently evaluating their thermal stabilities and film forming properties.



Scheme 4. Thermal decomposition of chloroethyl-, ethynyl, and trimethylammonium hydroxide functionalized polysilsesquioxanes.

CONCLUSIONS

In conclusion, polysilsesquioxanes appear to be an excellent class of materials for hydrogen separation membranes. We have successfully demonstrated that thin films composed of hybrid organic-inorganic materials can be deposited on mesoporous alumina to afford asymmetric membranes. We developed a new family of "protected" maleimide-functionalized silane monomers that can be pre-polymerized to afford the membrane precursor, spin coated, and thermally cured to afford a membrane. We also prepared membranes from the methacryloxypropylsilane monomer. In addition, we demonstrated the preparation of palladium loaded hybrid organic inorganic membrane precursors. The palladium was found to be in the form of highly dispersed nanoparticles in the final gels. And lastly, we have prepared three new hybrid organic-inorganic materials to be thermolyzed at relatively mild temperatures to afford a silica membrane.

ACKNOWLEDGMENTS

I would like to acknowledge the technical contributions of Dr. Raef Shaltout, Dr. Joe Carpenter, McKinzie Minke, Duane Schneider and Brigitta Baugher. I would also like to thank Dr. Kamyar Rahimian for reading and editing the manuscript. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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