Innovative Concepts Phase I: Inorganic Membranes for CO₂/N₂ Separation

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Abstract

Silica membranes were prepared using a novel technique of catalyzed-atomic layer deposition of silica within a mesoporous matrix. Pyridine was used to catalyze the silicon chloride attachment to the hydroxylated silica surface at room temperature. This half-reaction was followed by the hydration of the surface with water regenerating surface hydroxyls and completing one reaction cycle. The technique resulted in the self-limited pore size reduction of the mesoporous matrix to pore sizes near 1 nm. The self-limited reaction was presumed to be the exclusion of the large catalyst molecule from the pore entrance. In addition to pore size reduction, viscous flow defects were repaired without significantly reducing overall porosity of the membrane. In addition, we investigated the ability of amine-functionalization to enhance the CO₂ transport in silica membranes. Specifically, we examined three synthesis techniques for functionalizing silica membranes with amino groups that resulted in different surface chemistries of the silica membranes. These differences were correlated with changes in the CO₂ facilitation characteristics. It was found that high loadings of amino groups where interaction with the silica surface was minimized promoted the highest CO₂ transport.

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Introduction

The objective of our Phase I. Innovative Concepts project was to prepare thermally stable, defect-free inorganic membranes with optimal control of the microstructure and surface functionality. My graduate student and I completed the work at the University of Maine between 9/24/02 to 9/23/03. Membranes were tailored for optimal CO₂/N₂ separation. The project was relevant to CO₂/N₂ Separations and Carbon Sequestration within NETL's University Coal Research program. We reported Phase I results at the NETL Coal Contractors' meeting in June 2003. We also reported results in two published journal articles, [1,2] and one journal article accepted for publication, [3] I also submitted research results to the Department of Energy *Secretary's Weekly* [4]. Research results regarding CO₂/N₂ separation were incorporated into a Ph.D. thesis [5], and were the source of an undergraduate class project for students taking Senior Process Design, CHE 479. Results were also presented at the Annual Coal Contractor's Meeting in Pittsburgh, PA in June 2003 [6] and at the Fall AIChE meeting in San Francisco, CA in November 2003.[7] The results for the project are reported below.

1. Synthesis of surfactant templated mesoporous silica membrane.

The first goal of the project was to synthesize a mesoporous silica membrane to be modified for CO₂/N₂ separation. Mesoporous silica membranes with cubic pore ordering (MCM-48) were synthesized via a hydrothermal process. Templated silica particles were deposited within the pores and on the surface of a macroporous alumina membrane. Figure 1 presents the gas permeation data as a function of average pressure across the membrane for a typical MCM-48 membrane. A positive slope with respect to average pressure indicates the presence of viscous flow defects or pinholes of macroporous

diameter. Figure 1 demonstrates that we were able to successfully deposit a defect free mesoporous layer on the macroporous support.

Figure 1. Gas permeation of several gases as a function of average pressure drop for a hydrothermally deposited silica membrane.

The MCM-48 layers were approximately 7 μm thick as determined by scanning electron microscopy (SEM). A thinner mesoporous layer was developed using a dipping technique. A stable silica sol was synthesized and then mixed with surfactant (cetyltrimethylammoniumbromide). The resulting sol was dip coated on macroporous alumina supports and calcined to remove the surfactant template.

Figure 2 presents gas permeation data as a function of average pressure for a typical dip coated mesoporous silica membrane. The gas permeance, also free of viscous flow, was nearly twice as large for the dip-coated membrane as for the hydrothermal membrane due to a decrease in membrane thickness down to 2 μm. These results are summarized in a paper published in the *Journal of Membrane Science* [1].

Figure 2. Gas permeation of several gases as a function of average pressure drop for a dip coated mesoporous silica membrane.

2. Catalyzed atomic layer deposition for controlled pore size reduction of mesoporous supports

A novel technique known as catalyzed atomic layer deposition (C-ALD) was investigated to reduce the pores of the supports to the microporous range. C-ALD was used to deposit monolayers of silica within the mesoporous layer of a templated membrane. The overall reaction for the membrane modification was:

This reaction was broken down into two successive half reactions, where Si was deposited by SiCl_4 reaction with the surface, followed by oxidation with H_2O :

where * indicates a surface species. Pyridine was used to catalyze reaction A.

Membranes fabricated using C-ALD were generated using a reactor temperature of 80°C.

Figure 3 presents nitrogen permeation data as a function of average pressure drop for a membrane before modification and after 10, 20 and 30 AB cycles. For most membrane supports 20 AB cycles were required to modify the pores to the point that the

pyridine catalyst was excluded from the pore as shown in Figure 3. These measurements confirmed the self-limiting nature of the C-ALD process that provides a built-in mechanism for pore size and porosity control in the microporous region. In addition, it confirmed the use of C-ALD as a general method for defect repair where the deposition reaction is limited to the larger pores and defects, leaving the smaller pores unmodified. This is in contrast to conventional chemical vapor deposition and atomic layer deposition techniques, where smaller pores are completely plugged resulting in significant porosity losses.

Figure 3. Nitrogen permeance with respect to average pressure drop for a mesoporous support before and after 10, 20 and 30 C-ALD modification cycles

Figure 4 presents nitrogen permeance vs. pressure data for a membrane support with viscous flow defects and the same membrane after 10 and 20 AB modification cycles. The support used in this experiment showed a substantial contribution of 3.3% of the total nitrogen flux via viscous flow. After 10 AB cycles the viscous flow contribution of the defects was reduced to less than 1% of the total nitrogen flow. After 20 AB cycles there was no evidence of any viscous flow contribution to the total N_2 permeance.

Figure 4. Nitrogen permeance as a function of average pressure for a defective mesoporous support and after 10 and 20 AB deposition cycles.

These results indicate that as modification progressed, the base catalyst was excluded from smaller pores, but continued to modify larger pores. As the process continued, larger pores were modified until all pores (including small pinholes and micro-crack defects) were small enough to exclude the catalyst. Modification ceased at the point where the catalyst was totally excluded from the pores of the membrane. At this point, a defect free silica membrane with nearly monodisperse pore diameter was obtained.

Defect-free membranes are critical for high performance in gas separation membranes because the gas mixture is forced through the pores, enhancing separation.

Task 2. demonstrated that the catalyst limited the deposition reaction within the mesoporous matrix by reactant exclusion from the pores, providing a method for controlling final pore size and porosity. The self-limited pore size reduction also proved C-ALD as a general method for defect repair in inorganic membranes. New knowledge from Task 2. resulted in two papers submitted for publication: one accepted in *Industrial Engineering and Chemistry Research Journal* [2]. and the other accepted for publication in *Advanced Materials (Chemical Vapor Deposition)* [3] .

3. Surface modification to enhance carbon dioxide permeance

To enhance the diffusion of CO₂ through the C-ALD membranes, a final ALD step was performed to functionalize the pore surface with amino groups. Membranes functionalized with 20 AB cycles were exposed to aminopropyldimethylethoxysilane (APDMES) at a vapor pressure of 200 torr for a period of 1 hr. The resulting ALD reaction is presented in Figure 5. Upon exposure, the APDMES reacted with the surface silanol groups to produce methanol along with a new Si-O-Si bond.

Figure 5. ALD reaction of APDMES with silica surface

The reaction was verified using diffuse reflectance-FTIR on a silica powder sample. The powder was exposed to APDMES for 1 hour at 50°C. The spectra for the powder before and after exposure are presented in Figure 6. The absorbance bands located near 3000 and 1450 cm⁻¹ are attributed to the methyl groups of the APDMES. The FTIR spectrum of the modified powder verifies the surface modification by APDMES. The absorbance band around 3700 cm⁻¹ is due to the SiOH surface species and was present even after exposure. This result indicated an incomplete surface

modification by the APDMES, as expected. As shown in figure 5, the amine quickly formed a hydrogen bond after the Si-O-Si bond was formed.

Figure 6. DRIFT spectra for a silica powder before and after APDMES atomic layer deposition .

Figure 7 presents the data of CO₂ permeance for a membrane modified with 20 C-ALD cycles and for the same membrane after exposure to APDMES for 1 hour at 50°C. The CO₂ permeance was enhanced by the presence of the Aminopropylated surface. In addition to the increase in permeance the increase of activation energy also indicated that surface interactions play a larger role in the modified membrane.

In order to increase the surface concentration of amino groups, membranes were exposed to ethylenediamine (EDA) prior to APDMES. This reaction is presented in Figure 8. It has been shown that the addition of ethylenediamine prior to APDMES catalyzes the reaction reducing necessary exposure times to 10 minutes [5]. The reaction also allows for complete coverage of the surface by APDMES ALD. The ethylenediamine forms a hydrogen bond with the surface hydroxyl group. The ethylenediamine molecules are only displaced by the nucleophilic attack of the surface hydroxyl on the silicon alkoxide, effectively blocking hydrogen bonding of the amine from the APDMES molecule back to the silica surface. Therefore, complete APDMES addition at all available silanols is facilitated.

Figure 7. CO₂ permeance for a 20 cycle C-ALD membrane before and after surface modification by exposure to APDMES.

Figure 8. EDA catalyzed ALD of APDMES at a silica surface.

EDA catalyzed atomic layer deposition of APDMES was performed on a 20 cycle membrane by exposure to EDA for 15 minutes followed by exposure to APDMES for 15 minutes at 50°C. Carbon dioxide permeance data for membranes functionalized with and without EDA treatment is presented in Figure 9.

Figure 9. Carbon dioxide permeance for membranes modified with and without EDA prior to APDMES exposure.

The membrane treated with EDA exhibited a larger CO₂ permeance as well as an increase in activation energy for diffusion.

Results from Task 3 can be summarized with two major points. First, silica membranes functionalized with -NH₂ facilitated transport of CO₂ through the membrane by increasing surface concentration and surface diffusion. Second, the CO₂ transport was sensitive to the functionalization chemistry of the membrane.

Summary

Results from the project indicate that catalyzed-atomic layer deposition of silica within a mesoporous matrix provided pore size control of the silica membranes near 1 nm and repaired viscous flow defects without significantly reducing overall porosity of the membrane. While studies to this point have been limited to using pyridine as a catalyst for controlling pore size, the groundwork has been laid to apply this novel technique for achieving membranes with different pore sizes.

In addition to establishing a novel technique for membrane synthesis, we also established methods for functionalizing the silica surface with amino groups for enhancing CO₂ transport. It was confirmed that CO₂ transport was enhanced with amino functionalization and that care must be taken with the synthesis of this step in order to maximize CO₂ transport.

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