

A New Concept for the Fabrication of Hydrogen Selective Silica Membranes

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Principal Investigator: Michael Tsapatsis

tsapatsi@cems.umn.edu

Phone 612 626 0920

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**University of Minnesota Twin Cities Campus
Department of Chemical Engineering and Materials Science
Institute of Technology
151 Amundson Hall
421 Washington Avenue SE
Minneapolis, MN 55455**

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ABSTRACT

It was proposed to investigate a new concept for the synthesis of molecular sieve hydrogen selective membranes. This concept is based on the use of exfoliated layered zeolite precursors in coating processes to make nanocomposite films with inorganic or polymeric matrices. We discovered that creating exfoliated zeolite layers was much more difficult than anticipated because the methods originally proposed (based on existing literature reports) were not successful in providing exfoliated layers while preserving their porous structure.

Although the original goals of fabricating high-selectivity-high-flux membranes that are stable under conditions present in a water-gas-shift reactor and that are able to selectively permeate hydrogen over all other components of the mixtures present in these reactors were not accomplished fully, significant progress has been made as follows:

1. Proof-of-concept hydrogen-selective nanocomposite membranes have been fabricated
2. Methods to exfoliate layered zeolite precursors preserving the layer structure were identified
3. Unexpectedly, membranes exhibiting high ideal selectivity for carbon dioxide over nitrogen at room temperature were produced.

The findings listed above provide confidence that the proposed novel concept can eventually be realized.

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INTRODUCTION

As stated in the NRC report on Novel Approaches to Carbon Management “*there is a need for novel membranes that can perform the separation of CO₂ and H₂ at high temperature and pressures.*” Extensive efforts over the last several decades have explored high temperature hydrogen(H₂)-selective membranes made of silicon dioxide (SiO₂), other oxides, palladium (Pd) and other metals or alloys, and more recently various zeolites and non-aluminosilicate molecular sieves. Although promising separation results have been reported for many of these technologies they all suffer from high processing costs for membrane fabrication and long term stability limitations. In this project we revisited the objective of high temperature H₂-selective membranes with a fresh look and proposed to explore a new simple concept for the fabrication of ultra-thin, stable molecular sieve H₂-selective membranes.

This proposal was based on the use of thin films of plate-shaped layered silicates to form hydrogen selective membranes. These layered silicates are precursors to certain zeolite frameworks and, in principle, can be exfoliated to produce highly anisotropic exfoliated molecular sieve layers. In fact, literature reports by other groups pointed to the feasibility of the proposed new concept because procedures to prepare, so called, *exfoliated zeolites* have been reported and the use of the corresponding materials as catalysts with superior performance have been documented.

The simple idea of making molecular sieve membranes by using thin anisotropic plate-like zeolite crystals and exfoliated zeolites dispersed in an inorganic (e.g., sol gel silica) or polymeric matrix was attempted for the first time with activities supported by this award. The potential advantages of the proposed approach compared to other technologies that are currently under development include:

- No need to grow (hydrothermally or by chemical vapor/fluid deposition) the selective layer/film on the support. The formation of the selective film is based exclusively on a coating process using pre-made components.
- Potential for high selectivity and flux because in the case of exfoliated layers or high aspect ratio nanocrystals very thin layers (ca. 10 to 1,000nm respectively) can, in principle, be made.
- Potential for high stability since the selective components (zeolite layers) are crystalline and more hydrothermally stable than various amorphous oxides used in similar membrane applications.

The proposed work plan included four interrelated tasks. Although several layered silicates were candidates for the proposed research, these four tasks were mainly concentrated on MCM-22-(P) because a considerable body of reliable literature existed for the synthesis and delamination of this material making it an ideal starting point to benchmark the feasibility of our approach. Two other selected similar materials were proposed to be investigated latter on (Task 5) during the timeframe of this project. The tasks were as follows:

Task 1. Synthesis of MCM-22-(P) and optimization of plate-like morphology

Subtask 1.1. Hydrothermal Synthesis; Subtask 1.2. Delamination

Task 2. Preparation of multilayered coatings of the plate-like particles and microstructural characterization Subtask 2.1. Preparation of suspensions of MCM-22-(P) plate like particles; Subtask 2.2. Covalent assembly; Subtask 2.3. Ionic assembly

Task 3. Determination of membrane separation performance Subtask 3.1. Single component permeation measurements; Subtask 3.2. Mixture permeation measurements

Task 4. Determination of membrane stability in a water gas shift environment

Task 5. Evaluation of the related materials PREFER and MCM-47

At the start of this project, we realized that the exfoliation methods reported in the literature (on which we based our expectation for straightforward preparation of exfoliated zeolite layers) were actually causing severe damage to the zeolitic layers destroying the pore structure and yielding low aspect ratio layers.

For this reason, we formulated an alternative plan to pursue **Tasks 1-3** using highly anisotropic (but not exfoliated) zeolite MCM-22 crystals. These crystals are plate-like with dimensions of about 1 μ m in width and length and less than 100nm in thickness (i.e., aspect ratio of about 10). Along their thin dimension, they have the same transport-limiting pore constrictions (expected to be hydrogen selective) as the exfoliated layers we were planning to use. However, each of these crystals contains about 50-100 single layers as opposed to 1 layer per exfoliated zeolite particle that was the ultimate goal of this project. In the *Results and Discussion, section 1*, we will present results which show that hydrogen selective membranes can be prepared using these thicker building blocks. The membranes were prepared using layer-by-layer deposition based on covalent assembly (ionic assembly was not pursued) to build about 5 layers of MCM-22 and mesoporous silica matrix resulting in 1micrometer thick membranes supported on flat α -alumina discs. These membranes, at 220°C, exhibited H₂/CO₂ and H₂/N₂ ideal selectivities of approximately 10 and 50, respectively, with an activated hydrogen flux of 0.005 to 0.01 mol/m²-s, when they were operated with 1 bar trans-membrane pressure difference. We did not perform mixture permeation measurements but we expect similar selectivities at elevated temperatures. These values serve as proof of concept and indicate that the set targets of selectivity of 100 and hydrogen permeance of 0.1 mol/m²-s-bar at 500°C may be achievable if single exfoliated layers could be used instead of the zeolite crystals. As described in *Results and Discussion, section 3*, only recently we managed to develop the appropriate procedure to isolate structurally intact exfoliated zeolite layers and we did not have the time to repeat Task 3 using these layers.

Due to the difficulties mentioned above, only few tests were performed using tubular membranes. Moreover, the stability experiments described in **Task 4** were not performed because we thought that it will be appropriate to perform these tests only after exfoliated membranes approaching the targets of Task 3 will become available. At this stage, we can only state that the single exfoliated layers appear to be stable after calcination at 550°C.

In **Task 5**, we proposed exploratory work on the alternative (in place of MCM-22(P)) layered silicates PREFER and MCM-47. Instead of these silicates, which have similar transport limited pore constrictions perpendicular to the silicate layer as MCM-22(P), we decided to use the layered silicate AMH-3 and its composites with the high temperature

stable polymer polybenzimidazole. This choice was based on recent progress in our lab to swell and partially exfoliate AMH-3, a layered silicate with larger pore openings than MCM-22(P). This work is described in the *Results and Discussion, section 2.*

An additional Task (**Task 6**) was added to perform a preliminary techno-economic analysis. The findings are described in *Results and Discussion, section 4.*

EXECUTIVE SUMMARY

The goal of this project was to use crystalline layered silicates to form high temperature hydrogen/carbon dioxide selective membranes. It was proposed to:

- a. Synthesize layered silicate materials.
- b. Prepare dispersions of as synthesized or delaminated layered silicates.
- c. Prepare membranes by coating the layered silicates on macro-mesoporous supports
- d. Test the membranes for H₂/CO₂ selectivity at high temperature and pressures and for structural and functional stability at high temperature in the presence of water vapor.

In the original proposal we set very ambitious goals in terms of membrane performance: H₂/CO₂ selectivity of 100 and hydrogen permeance of 0.1 mol/m²-s-bar at 500°C. Our optimism was based on the expectation that exfoliated zeolites can be readily prepared which in turn was based on numerous reports in the literature. However, we quickly realized that exfoliation of zeolite precursors is not a trivial task, especially when one wants to preserve the original crystal structure of the layers. For this reason, for a considerable portion of this study, we concentrated on using anisotropic zeolite nanocrystals (aspect ratio of 10) rather than exfoliated zeolites (aspect ratio >100). The membranes were prepared using layer-by-layer deposition to build about 5 layers of MCM-22 and mesoporous silica matrix resulting in 1micrometer thick membranes supported on flat α -alumina discs. These membranes, at 220°C, exhibited H₂/CO₂ and H₂/N₂ ideal selectivities of approximately 10 and 50, respectively, with an activated (i.e., increasing with temperature) hydrogen flux of approximately 0.005 to 0.01 mol/m²-s, when they were operated with 1 bar trans-membrane pressure difference. These values serve as proof of concept and indicate that the set targets for selectivity and hydrogen permeance may be achievable if single exfoliated layers could be used instead of the zeolite crystals. Moreover, unexpectedly, a certain membrane preparation procedure can give carbon dioxide selective films (room temperature ideal selectivity of carbon dioxide over nitrogen ~ 100). These, with further development, may be of interest for room temperature post-combustion CO₂ recovery.

With respect to the ultimate goal stated in the original proposal, i.e., use of exfoliated zeolite layers, we have concentrated our efforts to two layered zeolite precursors: MCM-22(P) and AMH-3. MCM-22(P) was the focus of the proposal and the performed work. The layered silicate AMH-3 was used for exploratory studies instead of the originally proposed exploratory studies of the layered silicates PREFER and MCM-47 because swollen AMH-3 became available in our lab.

The work on AMH-3 has been concluded and appeared in references 2, 3 and 4. The main conclusion regarding AMH-3 is that while it can be exfoliated and yield hydrogen selective membranes (ideal selectivity for hydrogen over carbon dioxide about 40), the current swelling procedure causes drastic structural changes of the layers which preclude precise determination of the layer structure in the nanocomposites. As a result further systematic improvements of performance become a challenging task. Future work will be directed in preserving the structure of the porous silicate layers of AMH-3. This work will be conducted using other funding sources.

The findings on MCM-22(P) appear very promising. This layered zeolite precursor can be swollen and exfoliated while the structure of single layers is very similar to that in the original layered material. Our findings regarding layered structure preservation using a new procedure developed under this grant and comparisons with the extensively destroyed layers prepared by the procedures previously reported in the literature were described in reference 5. Recent unpublished work, described in this report, lead to isolation of exfoliated zeolite layers at high yield. This is a breakthrough in the area of exfoliated zeolites and an enabling discovery for the realization of the proposed concept. We plan to use these exfoliated layers to form thinner (0.1 instead of 1 micrometer) yet more tortuous for CO₂ permeation and thus more selective membranes. This work will be performed using other funding sources.

EXPERIMENTAL

1. Synthesis of Layered Silicates AMH-3 and MCM-22(P)

The synthesis of the layered silicate materials AMH-3 and MCM-22 are described in detail in references 2 and 5 correspondingly and references therein. A typical procedure is as follows:

First, NaOH (Fisher, 99%) and sodium aluminate (MP Biomedicals, 42% Na₂O and 55% Al₂O₃) were added to deionized (DI) water. Subsequently, hexamethyleneimine (HMI, Aldrich 99%) was mixed with the above solution. Finally, fumed silica (Cab-O-Sil M5, 99.8%) was slowly added under continuous stirring. The mass composition of this mixture was 1 fumed silica: 0.1 NaOH: 0.03 sodium aluminate: 0.8 HMI: 13.1 H₂O. The mixture was stirred vigorously for 5 h. The viscous gel was transferred to 45 mL Teflon liners quickly, and the liners were mounted in autoclaves (Parr Instruments). The autoclaves were positioned and rotated in an oven preheated to 135 °C. After 11 days, the reaction was quenched with tap water and the solid was recovered from the mother liquid and washed by 5 repetitions of centrifugation and decanting. MCM-22 (P) was not dried.

2. Calcination of MCM-22(P) to produce zeolite MCM-22 plate-like nanocrystals.

Calcination of silicate particles without any specific treatment will lead to severe agglomeration. To avoid this problem a polymer-aided calcination method by Yan and co-workers was adapted and described in reference 1 and references therein.

A typical process is as follows:

About 5 g of MCM-22 (P) wet cake was added to 20 mL water in a glass jar. MCM-22 (P) in water was stirred for 2 h and sonicated for 1 h. A Branson 1210 sonicator, 50-60 Hz, was used for sonication unless otherwise indicated. Then, the suspension of MCM-22 (P) was filtered by a syringe equipped with a filter tip (POREX) that has 15 μm retention size. After that, 10 g of acrylamide, 0.1 g of *N,N*2-methylenebisacrylamide, and 0.25 g of (NH₄)₂S₂O₈ were in turn added to a glass beaker while the MCM-22 (P) suspension was stirred. The glass beaker was immersed in a sonication bath and sonicated for 1 h. After sonication, a pudding like polymer was formed, cut to pieces in a crystallization glass, and transferred to a furnace. The polymer, in which MCM-22 (P) was embedded, was dried overnight at 80 °C under a N₂ environment and heated to 550 °C under N₂ flow with a 2 °C/min ramp rate. After it was held for 2 h, the N₂ flow was switched to air flow and the temperature was held for additional 12 h under air followed by slow cooling. After the calcination process, only white powder, i.e., MCM-22, was left and collected.

3. Preparation of nanocomposite zeolite MCM-22/silica films using layer-by-layer deposition

Initial work on this procedure was described in detail in reference 1. The procedure for the deposition of one layer involves sonication assisted covalent attachment of MCM-22 crystals (based on the procedure developed by Yoon and co-workers) followed by evaporation induced self-assembly of mesoporous silica (based on the method of Brinker and co-workers). This procedure is repeated several times to form the stated number of layers. Follow up work lead to the development of improved procedures mainly with respect to the deposition of the silica sol layer. Details on these procedures will be provided in a publication that we will prepare in the near future. However, at this stage we cannot provide these detail recipes since they are under consideration for intellectual

property protection. For the purpose of this report, the two different silica layer deposition procedures used will be referred to as procedures A and B. With the detail on how the mesoporous matrix is prepared omitted, the procedure remains the same as the one described in the original proposal, reference 1 and indicated in the procedure below: Each alumina substrate held by a Teflon holder was first placed vertically in a glass reactor. About 30 mL dry toluene was added to the reactor and the substrate was completely immersed. Then, 3 mL of 3-chloropropyl trimethoxysilane (Aldrich) (3CP-TMS) was added to the solution. The solution was refluxed at 110 °C for 3 h with dry argon purging. Meanwhile, 0.015 g of MCM-22 particles were dispersed into 40 mL of dry toluene by sonication for 1 h. After substrate functionalization with 3CP-TMS was completed, the substrate was sandwiched between two cover glasses. The sandwiched substrate was quickly placed inside the MCM-22 suspension and held by a Teflon holder. The glassware was then placed inside an ultrasonicator (Branson 1210, 50-60 Hz). The sandwiched substrate was first placed vertically and sonicated for 4-10 min. The sandwiched substrates were then positioned horizontally and sonicated for another 2 min. A silica sol was prepared following a method reported by Brinker and co-workers. The silica sol was further 256:1 diluted by ethanol in order to make a thin silica layer. Detailed information about making the silica sol and the dip coating will be described elsewhere. Two different procedures for this step are referred to as A and B. The surface of α -alumina discs was coated by this diluted silica sol before the first MCM-22 particle deposition. Each subsequent silica coating step was followed by a calcination step, heating samples up to 480 °C with a ramp rate of 1°C/min, holding them for 4 h, and cooling them slowly.

4. Swelling of AMH-3 and preparation of nanocomposites

The procedure for the swelling of AMH-3 has been described in detail in reference 4. In an typical preparation to get swollen AMH-3, 2.061 g of dodecylamine was dissolved in 50 mL of deionized water at 60°C with slow stirring for 30 min to make a homogeneous solution. The proton exchange experiment was allowed to proceed until the pH value became ca. 6.4, corresponding to approximately 30 min of exchange reaction. At this point, an aqueous solution of dodecylamine was titrated slowly in order to prevent abrupt pH change of this system. The mixture solution was further reacted at 60°C under reflux with vigorous stirring. After 12 h of reaction, the product was centrifuged to separate the solid product and rinsed with deionized water. The washing procedure was repeated four times to remove the residual amines from the particle surface. Following drying at room temperature for two days under air flow, about 0.1 g of swollen AMH-3 (white powder) was produced. Synthesis of nanocomposites has been described in reference 3. Additional information was given in reference 2. Typically, swollen AMH-3 was dispersed in *N,N*-dimethylacetamide (DMAc), followed by successive addition of the 7.5 wt% PBI solution obtained from Pall Corp. After 2 h of vigorous stirring at 100 °C, a measured amount of 20 wt% PBI solution was added on the basis of mass percentage of inorganic materials desired. The mixture was allowed to be mixed for 2 h at 100 °C and then sonicated for 1 h. The mixture solution was poured on a glass plate and cast using doctor's blade. The glass plate was covered to prevent the inclusion of dust during solvent evaporation. Before permeation measurements, all of the membranes were annealed under vacuum in cyclic manner between 50°C and 280°C four times.

5. Swelling and exfoliation of MCM-22(P) and production of pure layered zeolite

The procedure for the swelling and exfoliation of MCM-22(P) resulting in single highly crystalline layers dispersed in a polymer were described in reference 5. Typically 9.0 g of aqueous slurry of MCM-22-(P) (20 wt % solids) was mixed with 35.0 g of an aqueous solution of 29 wt % cetyl trimethyl ammonium bromide (CTAB) (Aldrich) and 11.0 g of an aqueous solution of 40 wt % tetrapropylammonium hydroxide TPAOH (Alfa Aesar). The pH of the resulting mixture was typically 13.80. The mixture was allowed to stir for 16 h at room temperature, after which the particles were recovered by repeated cycles of centrifugation and water washing (10 min centrifugation at 10,000 rpm, and re-dispersion in fresh water). Nanocomposites were prepared by melt blending in a DACA Mini Compounder vertical, co-rotating twin screw extruder with a recirculation channel. Polystyrene (3.8 g, *Mn* 45 000) and room-temperature swollen MCM-22(P) (0.16 g) were mixed manually and loaded into the compounder preheated to 120 °C. The mixture was blended sequentially at 120 °C for 10 min, 170 °C for 10 min, and 150 °C for 5 min and finally extruded out at 130 °C. A screw speed of 350 rpm and nitrogen environment was used for blending. A circular disc (25 mm × 1 mm) was prepared by compressing the extrudate at 1000 psi and 150 °C for 10 min. However, the isolation of exfoliated zeolite layers was not achieved at this time. Follow up work resulted in a procedure by which single highly crystalline layers can be recovered free of any additive (e.g., polymer, surfactant, solvent, etc.). This procedure will be described in a publication that we will prepare in the near future and is currently being patented.

6. Characterization of Microstructure

X-Ray Diffraction (XRD), Scanning (SEM) and Transmission Electron Microscopy (TEM), and Dynamic Light Scattering (DLS) were used to characterize the silicate powders, thin films and dispersions.

7. Single Gas Permeation Measurements

The permeation set up for flat discs is shown in Figure 1. 200-250 ml/min of single gas (He, H₂, N₂, and O₂) were fed to one side (retentate) of the permeation cell, the other side (permeate) of which was under vacuum. Since the retentate side was open to ambient air, 1 atm pressure difference was maintained between the feed side and the permeate side. The pressure in the permeate side was measured by use of a pressure transducer and continuously recorded in a computer. The ideal gas law was used to estimate the molar flow rate across the membranes from the recorded pressure. The permeance is calculated according to the following equation,

$$P = \frac{dp}{dt} \frac{V}{RT} \frac{1}{A} \frac{1}{\Delta p} \left(\text{in } \frac{\text{mol}}{\text{sec} \cdot \text{m}^2 \cdot \text{Pa}} \right)$$

where dp/dt is the rate of pressure change in the permeate side, V is the volume of the permeate side, R is the ideal gas constant, T is temperature, A is the cross-sectional area of the membrane, and Δp is the pressure difference across the membrane.

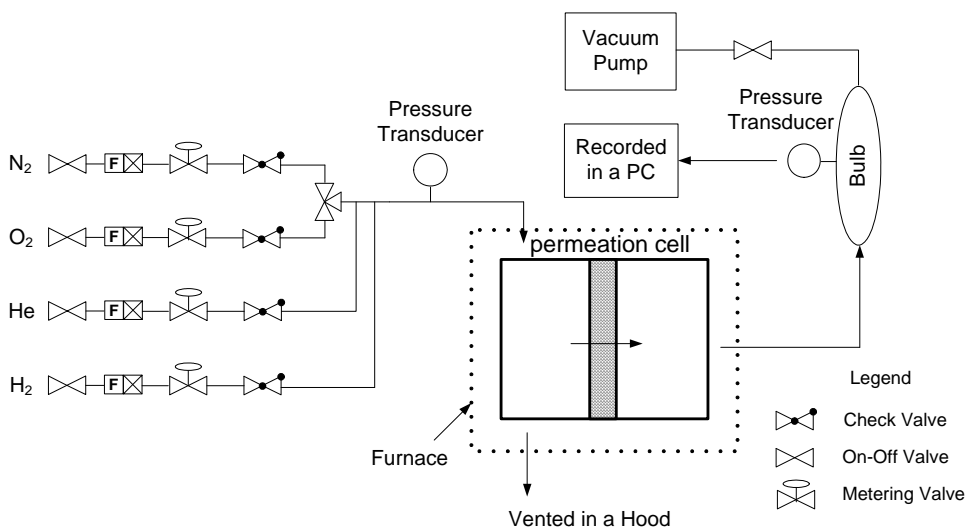


Figure 1. A schematic of single gas permeation measurement set-up.

A different permeation set up was used for SS tubes and is shown in Figure 2. About 2 l/min of a single gas (He, H₂, N₂, and CO₂) were fed to the inside of a SS tube which was pressurized to around 1.2 atm using a back pressure regulator, while the outside of the SS tube was open to ambient air, ~ 1 atm. Accordingly, around ~ 0.2 atm pressure difference was maintained across the SS tubes. The pressure values before and after feeding as well as that in the permeate side were recorded in a computer. The ideal gas law was used to estimate the molar flow rate across the membranes based on the recorded pressure. The permeance was calculated according to the procedure described above.

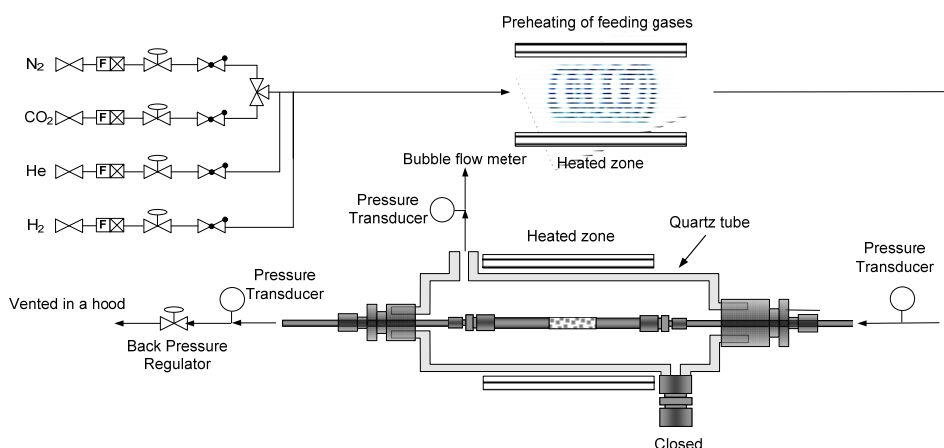


Figure 2. A schematic of single gas permeation measurement set up for mesoporous silica-MCM-22 films on SS tubes.

The majority of this project was performed using home made α -alumina discs. Very few studies were performed using stainless steel tubes and are included in section 1.4.

RESULTS AND DISCUSSION

1. MCM-22 /mesoporous silica nanocomposite films prepared using layer by layer deposition

A typical SEM image of 2-time-coated mesoporous silica/MCM-22 (i.e., a film that contains two layers of MCM-22 crystals and two layers of mesoporous silica prepared using evaporation assisted casting) films is shown in Figure 3.

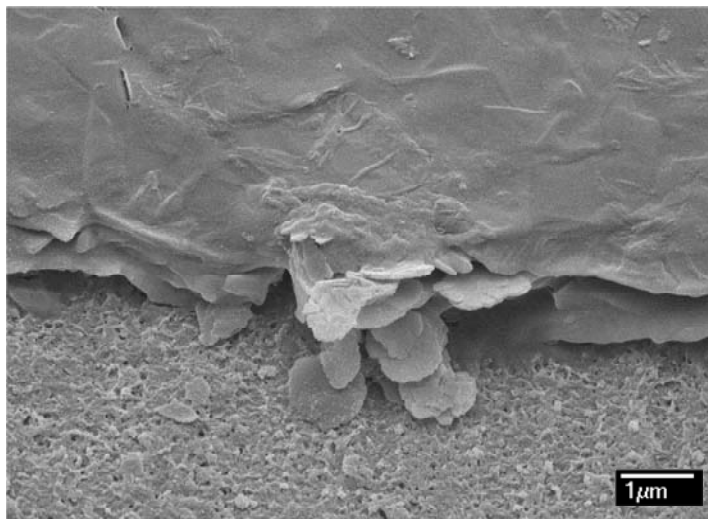


Figure 3. SEM of a 2-time-coated mesoporous silica-MCM-22 film in tilted view.

By repeating this procedure, i.e., successive coating of mesoporous silica and MCM-22 crystals multilayered films can be made. All these films were characterized by SEM (top view and cross section) and XRD followed by permeation tests. As stated in the Experimental Section (part 3) two different procedures for the formation of the silica layer were used referred to as A and B the details of which are not disclosed here since they may be the subject of a patent application.

1.1 Membranes made using procedure-A-for-the-formation-of-silica-layers on α -alumina discs.

Up to five-times-coated films were prepared on alumina supports. Hydrogen selectivity increased monotonically with the number of coatings as shown in Figure 4. More detailed permeation data, for a 5-times-coated membrane, are given in Figure 5. Modest selectivities (below 10 and about 20 for hydrogen over carbon dioxide and nitrogen respectively) can be obtained at 220°C. The hydrogen permeance will provide fluxes on the order of 10^{-3} to 10^{-2} mol/m²-s, i.e., one to two orders of magnitude below the desirable levels. SEM examination of 5-times-coated films indicate film thicknesses of about 1 micrometer suggesting that film thickness reduction by an order of magnitude or more will be needed to achieve desirable levels of flux. At the same time selectivities need to be improved.

1.2 Membranes made using procedure-B-for-the-formation-of-silica-layers on α -alumina discs.

As shown in Figures 6 and 7 comparable moderate performance is obtained for membranes on alumina discs prepared using procedure B. As it is shown next, surprisingly, an interesting and promising behavior was observed when procedures A and B were combined.

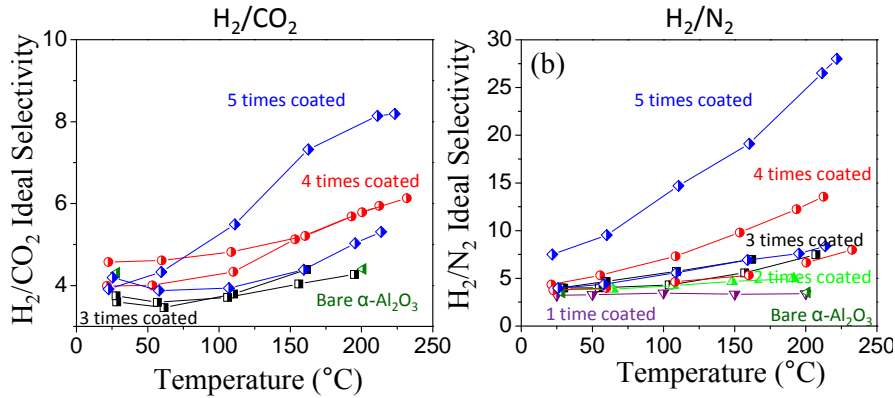
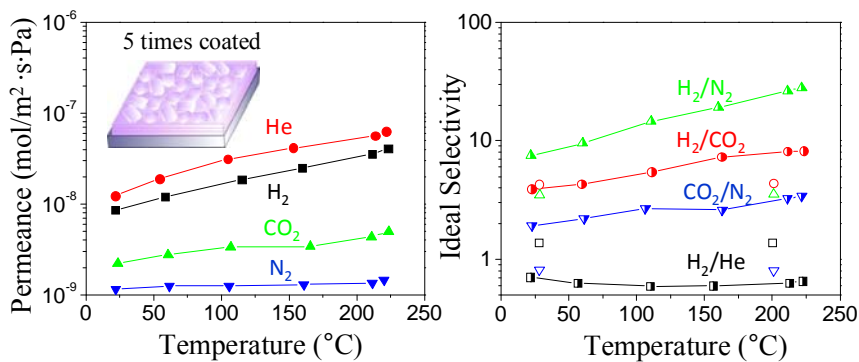


Figure 4. Hydrogen selectivity of membranes prepared using procedure A.



*Open symbols : selectivity through α -Al₂O₃ discs

Figure 5. Permeation data for 5-times-coated membrane using procedure type A.

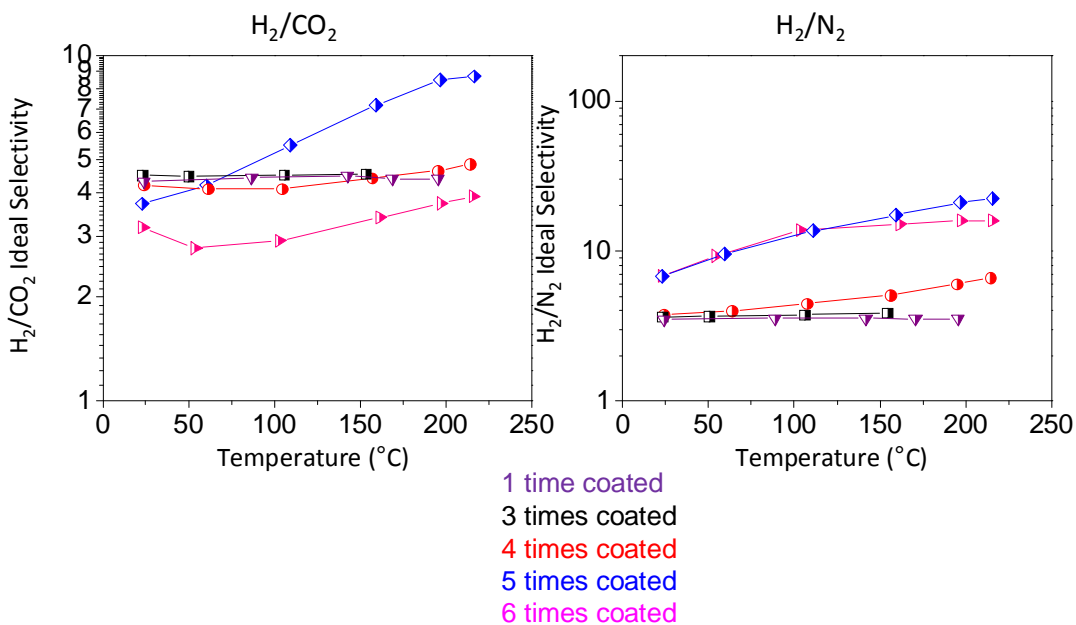


Figure 6. Hydrogen selectivity of membranes prepared using procedure B.

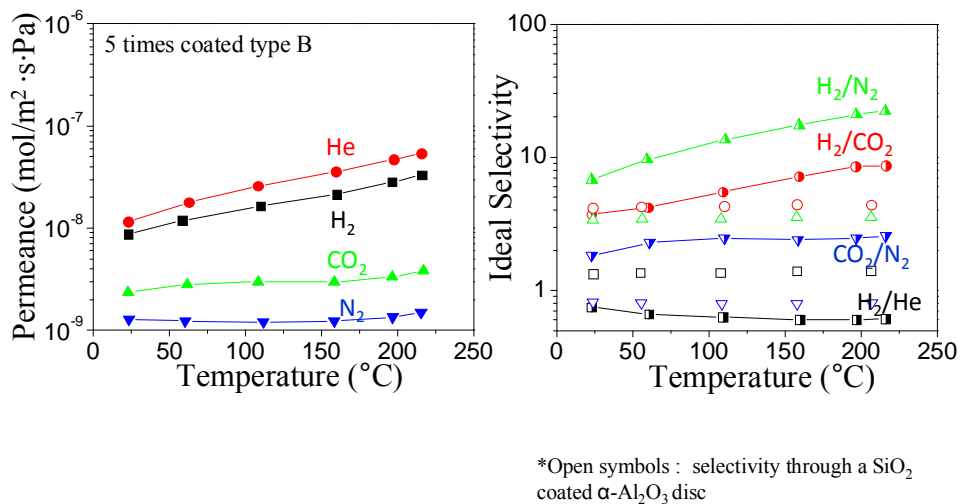


Figure 7. Permeation data for 5-times-coated membrane using procedure type B.

1.3 Membranes made using procedure-A-followed-by-B-for-the-formation-of-silica-layers on α -alumina discs

A distinct behavior was observed when layers of MCM-22 and silica were deposited on alumina discs using a combination of type A and type B procedures for the silica layers. The hydrogen over carbon dioxide selectivity was improved consistently and levels of about 6 to 9 were reached consistently at 220°C. The hydrogen over nitrogen selectivity was also improved and was consistently over 30 (with the exception of one membrane) over the entire range of temperatures tested. For one membrane the hydrogen over nitrogen selectivity exceeded 100 at room temperature. Figure 9 shows detail permeation data for one of the membranes shown in Figure 8. In addition to hydrogen selectivity, this membrane shows good carbon dioxide over nitrogen selectivity. This is the case for almost all of the membranes prepared using 3 coatings by procedure type A followed by coatings type B for silica deposition as shown in Figure 10. The explanation of this behavior requires additional work. However, it is promising for practical applications and underscores the importance of the matrix phase in these nanocomposite films.

The data presented in this section demonstrate that micrometer thick nanocomposite films consisting of MCM-22 plate-like nanocrystal and mesoporous silica layers can be prepared and exhibit molecular sieving behavior. These membranes, at 220°C, exhibited H_2/CO_2 and H_2/N_2 ideal selectivities of approximately 10 and 50, respectively, with an activated (i.e., increasing with temperature) hydrogen flux of approximately 0.005 to 0.01 mol/m²-s, when they were operated with 1 bar trans-membrane pressure difference. Although these values are below (by an order of magnitude) the targets set in the proposal they are a clear demonstration of the proposed concept. Moreover, unexpected high selectivity for carbon dioxide over nitrogen was established and is promising for room temperature separations.

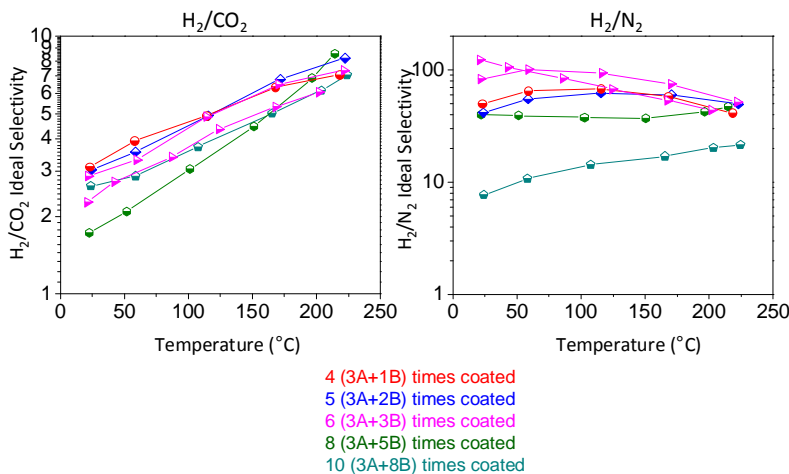
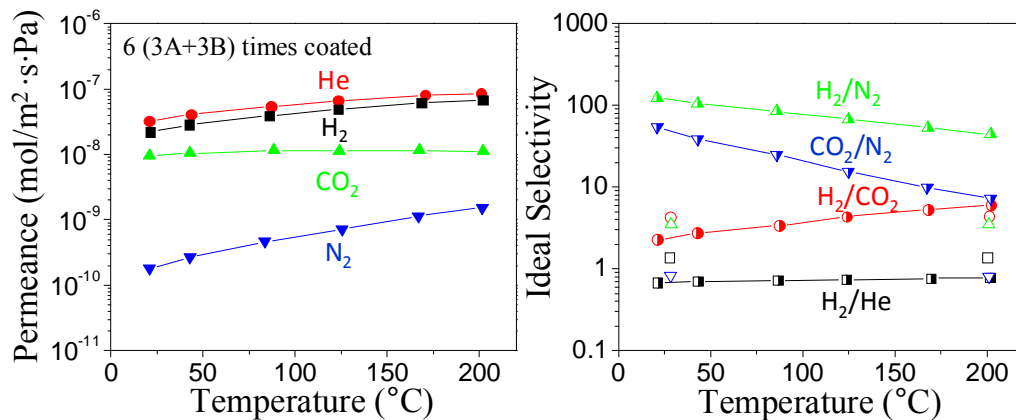


Figure 8. Hydrogen selectivity of membranes prepared using 3 coatings by procedure type A followed by coatings type B.



*Open symbols : selectivity through α -Al₂O₃ discs

Figure 9. Permeation data for 6-times-coated membrane using 3 procedures type A followed by 3 procedures type B.

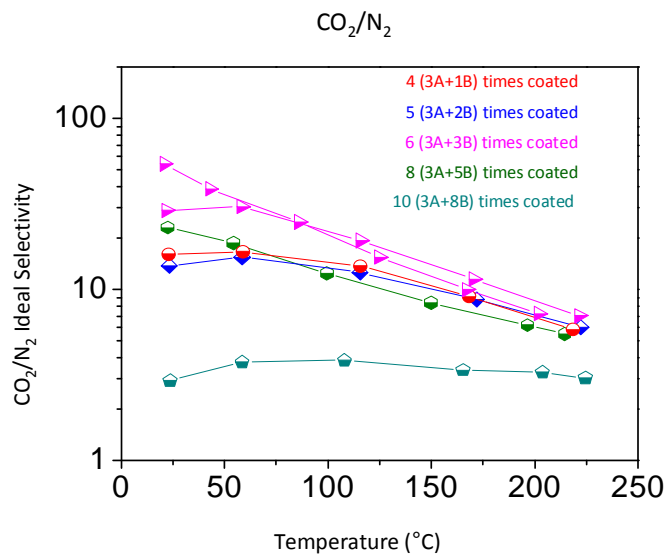


Figure 10. Carbon dioxide over nitrogen selectivity for MCM-22/silica membranes prepared using 3 coatings by procedure type A followed by coatings type B.

1.3 Mesoporous silica-MCM-22 films on Stainless Steel (SS) Tubes

The monotonic increase of ideal selectivity (H_2/N_2 and H_2/CO_2) with temperature looks promising especially if operation at high temperature range (300 ~ 500°C) can be achieved. Measurements at high temperatures using the home-made α -alumina discs cannot be made in our lab due to the rubber o-ring seals used in the permeation system. Since SS tubes come with welded non-porous stainless steel connections that can sustain high temperature and high pressure, we attempted the fabrication of mesoporous silica-MCM-22 films on SS tubes. The change of support from α - Al_2O_3 discs to SS tubes could enable operation at high temperature (300 ~ 500°C), which is a common temperature range for water gas shift reaction. Additionally, the tubular shape of SS tubes is considered as attractive by various industries. Moreover, SS tubes that have large pore size (on the order of 10 μm) are expected to provide higher flux than α - Al_2O_3 discs having ~ 0.1 μm sized pores. The tubes were obtained from Pall Corp. Because they are costly, only a limited number of experiments were performed.

At first, MCM-22 particles were chemically attached on to the surface of zirconia coated SS tubes. It seems that MCM-22 particles were uniformly deposited on the surface. After the MCM-22 particle deposition, SiO_2 coating and calcination followed as was the case for mesoporous silica-MCM-22 film formation on α - Al_2O_3 discs. Single gas permeation result of a 4-time-coated mesoporous silica-MCM-22 film showed that the gas transport through the film was dominantly governed by Knudsen diffusion after four deposition cycles.

Following SEM examination we attributed this finding to failure of the zirconia layer due to brittle fracture during sonication assisted deposition. Therefore, future work should be performed using asymmetric stainless steel supports without a zirconia layer. The main limitation is that these supports are expensive and therefore we cannot perform extensive investigations as with the home made α -alumina supports.

2. AMH-3 nanocomposite films

The swollen derivative of AMH-3 was prepared by intercalation of primary amine molecules (dodecylamine) following proton exchange in the presence of amino acid. In this procedure, an aqueous solution of DL-histidine was employed as buffer and source of protons to exchange the strontium and sodium cations in the original structure. Ion exchange was allowed to proceed at room temperature before the aqueous solution of dodecylamine was added to obtain swollen AMH-3. As described in detail in reference 4, several alternative procedures failed to yield swollen AMH-3.

AMH-3 swelling occurs without disintegration of the silicate layers (see reference 2). However, despite the mild conditions used for ion exchange and swelling, the local order and connectivity of AMH-3 layers is not preserved. It is unclear if this process involves only intralayer condensation preserving the 8 MR pores or more drastic rearrangements that alter the layer porosity. In either case, however, the occurrence of structural changes during this process indicates that swollen AMH-3 should be regarded as a new material rather than an intercalated phase. Although further characterization is needed in order to identify the structure of the layer, we proceeded to incorporate the swollen derivative of AMH-3 in polymer nanocomposites to investigate its potential as a selectivity-enhancing additive.

A low-permeability material, polybenzimidazole (PBI), was chosen as a continuous phase due to its promise for use in membranes for fuel cells and gas separation. In order to enhance the dispersion of swollen AMH-3, a priming technique was used. The microstructure of prepared nanocomposites was characterized by TEM and XRD. Cross-sectional TEM imaging of the nanocomposite films reveals the presence of plate-like particles (Figure 11a). Particles with ~ 100 nm circular contrasts were characterized by tilting to evaluate whether they are from plate-like or globular particles (Figure 11b). The morphology of dark contrast was changed as the tilting angle was increased, indicating plate-like particles. This also suggests that the plate-like particles in the nanocomposites are randomly-oriented within the continuous phase of PBI. Along with the platelets of ca. 100 nm in diameter, TEM images also reveal that a second population of smaller, globular or irregularly-shaped reticular particles is present possibly from the fragmentation of silicate layers. In terms of X-ray diffraction (not given here), the characteristic peaks of swollen AMH-3 disappeared by mixing with PBI. Preliminary interpretation of SAXS data (see reference 3) suggests that the plate-like particles are not completely exfoliated but swollen clusters of few AMH-3 layers.

The performance of swollen AMH-3 nanocomposite membranes was evaluated in terms of the hydrogen/carbon dioxide ideal selectivity. Figure 12 summarizes the single-gas permeation results of a 2 wt% and 3 wt% swollen AMH-3 nanocomposite membrane measured at 35 °C in comparison with those of pure polybenzimidazole membranes and various glassy polymers. Similar to the conventional polymer-layered silicate composites, the swollen AMH-3 nanocomposite membranes exhibit permeability reduction. However, the decrease of carbon dioxide permeability is more pronounced than that of hydrogen. As a result, at room temperature the swollen AMH-3 nanocomposite membranes show

higher H_2/CO_2 ideal selectivity by a factor of two. The improvement of ideal selectivity cannot be attributed to the organic surfactant because a PBI membrane with the same amount of dodecylamine shows similar ideal selectivity with pure polybenzimidazole membranes. It is possibly due to the molecular sieving action of the silicate additives and/or the modification of the polymer properties at the polymer/silicate interfaces. If the former is the dominant factor and considering the morphology of nanoparticles in swollen AMH-3 nanocomposites, there is room for further selectivity improvements if single exfoliated flat layers of swollen AMH-3 can be incorporated as a selective phase. The good dispersion of silicate particles also suggests that these nanoparticles could be applied in the skin layers of hollow fiber membranes fabricated with PBI.

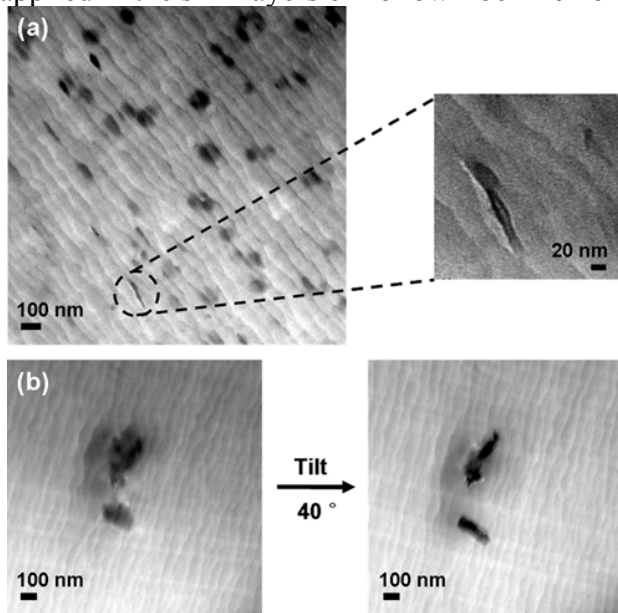


Figure 11. TEM images of cross section from 3 wt% swollen AMH-3 nanocomposite (a) and TEM images from tilting experiments confirming plate-like morphology of silicate particles (b).

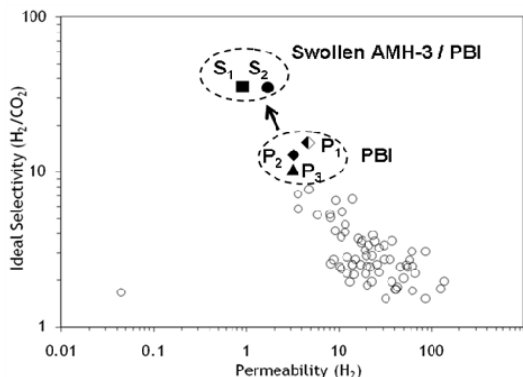


Figure 12. Hydrogen/carbon dioxide ideal selectivity versus hydrogen permeability in Barrer. Pure PBI (P_1) from reference⁹, pure PBI from this work (P_2), PBI with dodecylamine (P_3), 3 wt% (S_1) and 2 wt% (S_2) swollen AMH-3/PBI nanocomposites. The open symbols denote other glassy polymers from the literature⁸.

3. Highly crystalline single layers of the zeolite precursor MCM-22(P)

As originally proposed, we also investigated the exfoliation of MCM-22 (P) to single layers in order to improve the deposition procedure (thinner layers are expected to be easier to coat), reduce the membrane thickness and/or increase the silicate particle overlap, and prepare nanocomposites. Single layers of MCM-22 can be made by exfoliating the layered structure of MCM-22 (P). This exfoliated layer is promising to fabricate multi-layered mesoporous silica-MCM-22 films due to the higher aspect ratio than that of MCM-22 (P) and small thickness ($< 5\text{nm}$) of the exfoliated particles. One of the steps in the process of making exfoliated layers is swelling of the interlayer space using a surfactant. However, we found that the available swelling procedures (e.g., ref. 6 and 7) result in significant destruction of the layer structure. SEM imaging in Figures 13 and 14 shows the dramatic change of morphologies of MCM-22 (P) before and after the swelling step. It appears that the originally sharply edged platelet shaped MCM-22 (P) became blurred around the edge and consisted of agglomerated layered crystals.

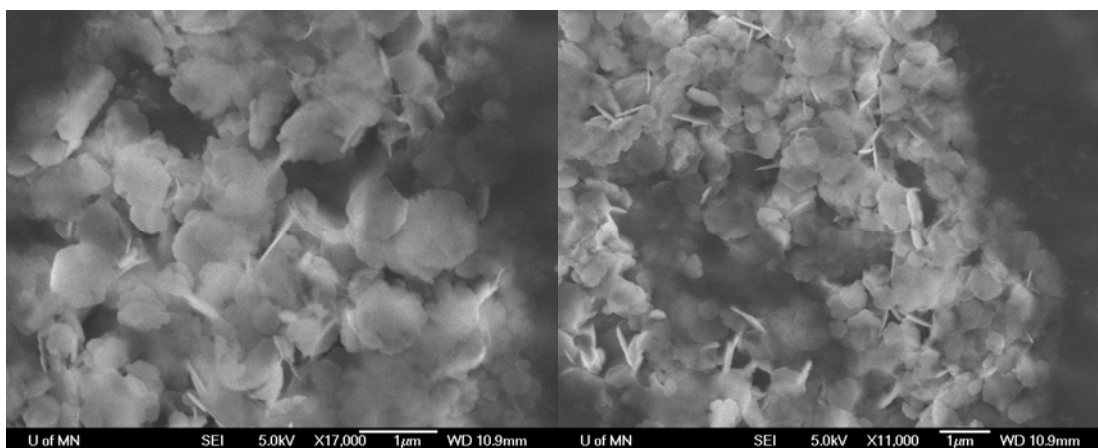


Figure 13. SEM Images of MCM-22 (P) before swelling.

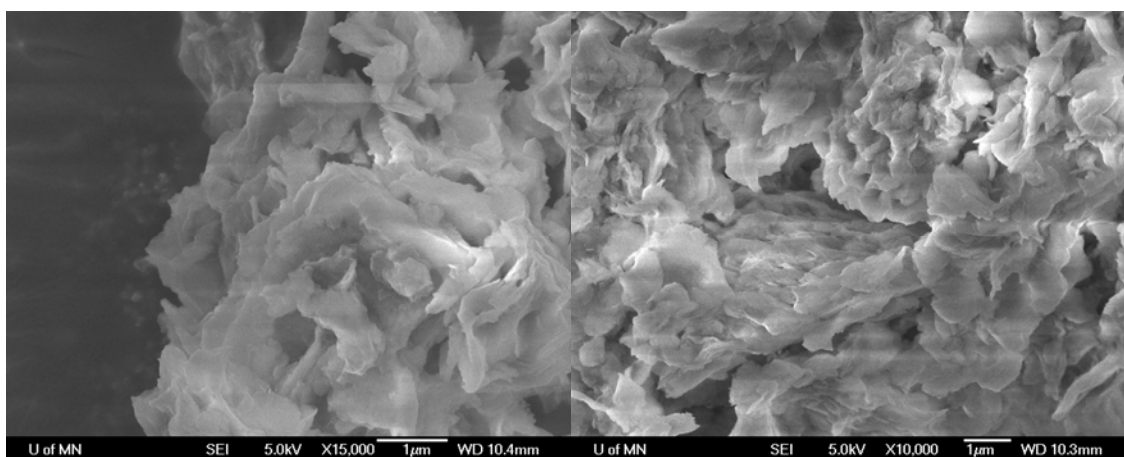


Figure 14. SEM Images of MCM-22 (P) after swelling for 16 h following the literature procedure.

More systematic studies (especially extensive NMR –performed by Professor D. Shantz’s group at Texas A&M- and TEM imaging) showed that the rather aggressive (high pH and high temperature) swelling procedure of the literature (references 6 and 7) leads to considerable damage of the silicate layer (Figure 15). Here, crystals appear to be much more fragmented, with curled layers and amorphous regions. Although this damage may not constitute a significant problem for the catalytic applications which are the target of the literature (6, 7), it may be problematic for our purpose which requires high aspect ratio intact silicate layers. Therefore, we developed an alternative procedure that does not compromise the layer structure (reference 5). Figure 16 shows HRTEM images of the original MCM-22 (P) and the swollen MCM-22 (P) obtained under the new procedure. Structural schematics of MCM-22 (P) have been overlaid on the TEM micrographs in order to guide visualization. MCM-22 (P) shows ~ 2.5 nm thick layers. Each layer appears as two dark bands separated by a bright band. The bright band is attributed to the 10-MR pore system within the layer, while the dark bands appear due to the higher silica density in the remaining parts of the layer (top and bottom). The gallery space between the two layers also appears as a bright band. Swollen MCM-22 (P) under the new procedure displays well ordered layers with expanded interlayer distance relative to MCM-22 (P). As evidenced in Figures 15 and 16, swollen MCM-22 (P) using the swelling procedure of the literature generally lacks the long range ordered stacking obtained for swollen MCM-22 (P) under the new procedure.

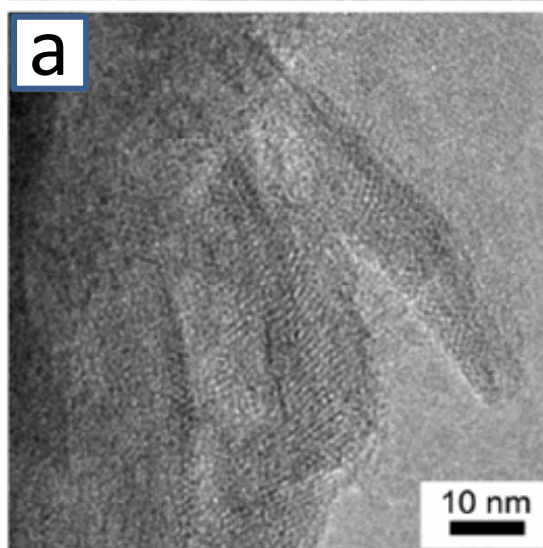


Figure 15. HRTEM image of swollen MCM-22 (P) using the swelling procedure of the literature.

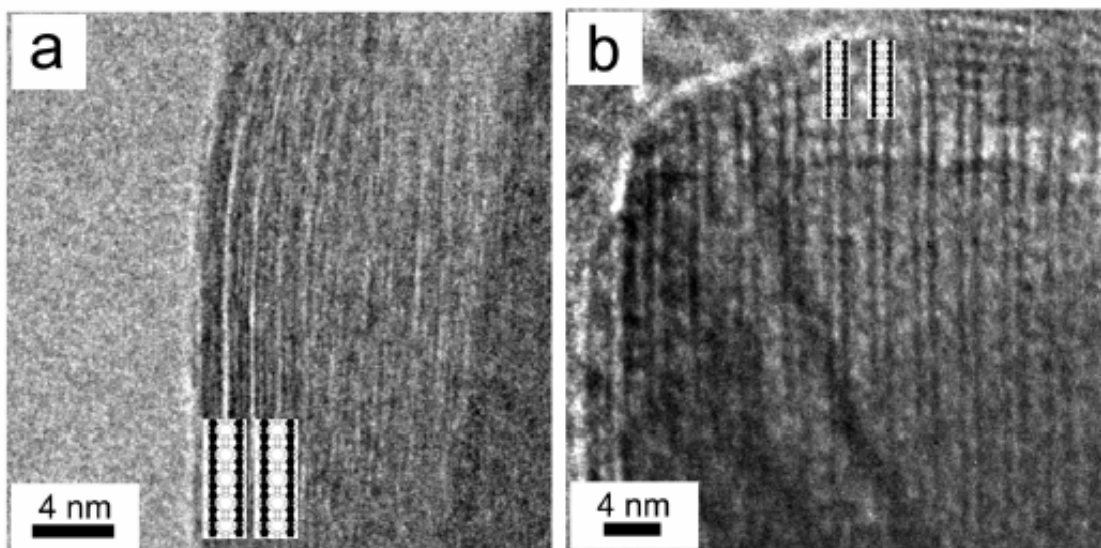


Figure 16. HRTEM images of (a) MCM-22 (P) and (b) swollen MCM-22 (P) under the new procedure. Schematics of single MCM-22 (P) layer have been overlapped on the images to facilitate identification of layers.

The swollen material was then used to prepare exfoliated layers. We obtained best results using a solvent-free method: melt blending with a polymer. The choice of the polymer, temperature and time of melt blending were found to be important parameters for the degree of exfoliation, layer structure preservation and the ability to recover the exfoliated layers in pure form, i.e., free of any additive (polymer, surfactant, solvent, etc.). All of the above parameters were optimized and high-aspect-ratio, high-crystallinity single layers were obtained. Figure 17 shows high aspect ratio single layers embedded in a polymer. High resolution imaging clearly indicates the preservation of the crystal structure in the layers. Figure 18 shows the pure exfoliated zeolite layers obtained after removing the polymer and surfactant. Again, high degree of crystallinity is indicated.

We consider the findings reported in this section to be very significant. As stated above, the difficulties associated with obtaining intact layers of exfoliated zeolites were underestimated. The previous procedures clearly indicated that this is possible, but because of their emphasis in catalytic applications they did not focus in layer structure preservation. We developed new procedures for swelling (under milder conditions), exfoliation (using melt blending) and zeolite layer recovery (not disclosed at this stage due to intellectual property issues) that allowed us to prepare, for the first time, high aspect ratio (100-1,000) intact exfoliated layers in pure powder form. It would have been ideal if these procedures were available at the start of this grant. In that case, all the activities described in *Section 1: MCM-22 /mesoporous silica nanocomposite films prepared using layer by layer deposition* would have been performed using exfoliated layers rather than nanocrystals. At the time of the writing of this final report, the exfoliated layers are used for the fabrication of nanocomposite films using polymers and mesoporous silica as the matrix.

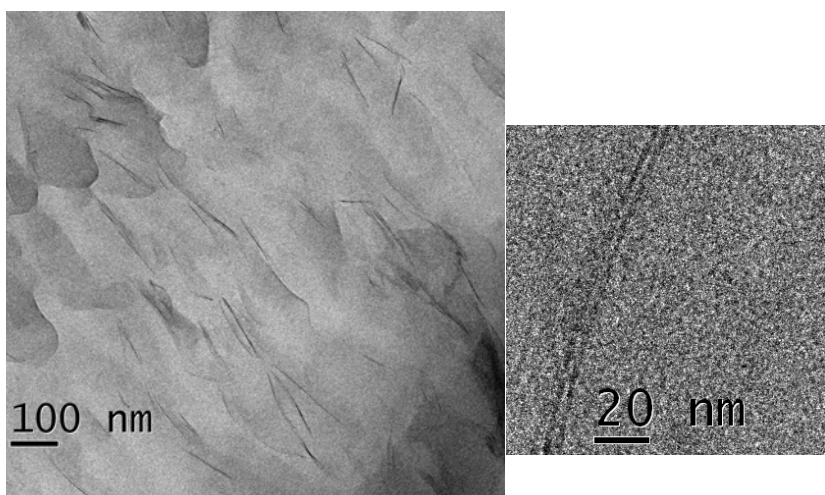


Figure 17. TEM images of MCM-22 exfoliated zeolite layers embedded in a polymer after melt blending. The high resolution image on the right indicates preservation of the original structure.

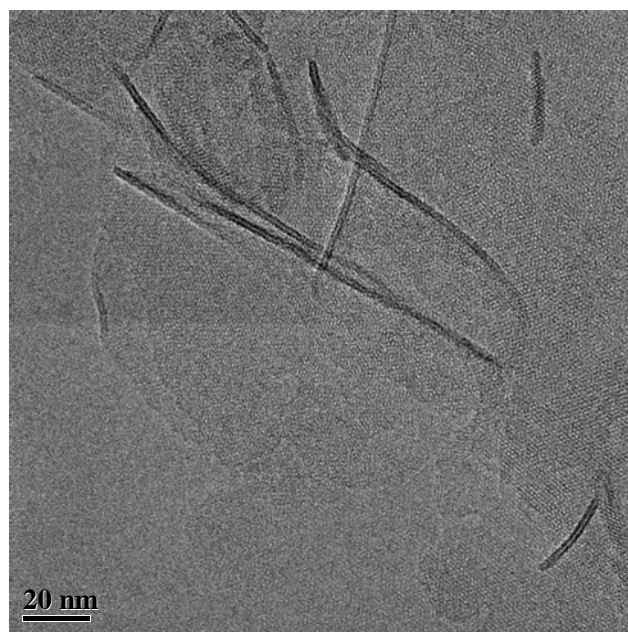


Figure 18. HRTEM images of pure MCM-22 exfoliated zeolite layers.

4. Preliminary Techno-economic Analysis

A preliminary techno-economic analysis was attempted but with no success. We were unable to create a converged flow-sheet for an IGCC plant. Therefore, the preliminary techno-economic analysis was based on literature reports. The intended use of the proposed membranes is in high-temperature membranes or membrane-reactors integrated in an IGCC plant containing water gas shift reactor. We know of few studies that are applicable:

1. A report by Gottlicher and Pruschek (1997)¹⁰ presents a classification and comparison of various proposed carbon dioxide removal approaches, based on calculations of the authors and review of about 300 references. This study states that if coal is to be used the Integrated Gasification Combined Cycle (IGCC) with CO shift conversion and physical absorption is the option of choice based on current (1997) technology status. It is pointed though that further progress in membrane technology could improve efficiency and economy in the long term. More specifically, for 90% CO₂ removal the efficiency reduction for an IGCC can be as low as 4% when a membrane reactor is used for CO shift because of lower steam demand reducing energy losses. However, all the details for the membrane performance characteristics (e.g., selectivity, permeance) used for this estimation are not provided.

2. Another more detail techno-economic feasibility study (Bracht et al., 1997)¹¹ used a set of rather detail simulation and optimization tools for industrial scale membrane reactors (Koukou et al., 1998)¹² including computational fluid dynamics (CFD) along with mass and energy balances. Membrane reactors were shown to be efficient for the water gas shift reaction (WGS) in an IGCC plant with CO₂ emission control. In this study, the WGS reaction is accomplished in a two step adiabatic system. In the first reactor high conversion takes place accompanied with a large temperature rise. After cooling, the gas mixture enters at 325°C and 36 bars a membrane reactor where by hydrogen removal the conversion exceeds the thermodynamic equilibrium limit of the inlet composition. The cooling step is introduced in order to keep the highest temperature in the membrane reactor below 500°C mainly because of membrane stability limitations. The hydrogen is obtained at 21bar. The design is based on a microporous silica membrane (ECN) with hydrogen/carbon dioxide selectivity of 15 and permeance of 0.1 mol/m²-s-bar. It is now known that this membrane is unstable under water gas shift conditions. However the calculations can be used to evaluate the potential of the membranes of this project. It is shown that with this membrane 90% CO conversion, 80% H₂ recovery and 80% carbon recovery can be accomplished in an IGCC with dry gas cleaning with a 3% loss in net electric efficiency compared to the efficiency of the process with no CO₂ removal. This report formed the basis of this project. A selectivity of 15 and proof of stability have not been achieved yet. As stated above these should be the subjects of future work. Improved stability may further allow for higher operation temperatures in the membrane reactor reducing or eliminating the requirements for cooling. Moreover, if increased selectivity (more than 15) can be achieved, it would lead to higher values of CO conversion or to smaller reactor size for the same conversion level because of improved hydrogen removal and higher equilibrium displacement. For example, when the selectivity is 40 instead of 15 half of the reactor length can accomplish the same conversion and hydrogen recovery under certain operating conditions (Koukou et al., 1998)¹². Based on the these references, we can conclude that at least 80% reduction of CO₂ emissions from coal-fuelled power plants will be accomplished by the proposed technology if a selectivity of 15 and permeance of 0.1 mol/m²-s-bar at 500°C could be achieved resulting in residual carbon dioxide emissions of 0.1 KgCO₂/kWhr (see Figure 1 in Gottlicher and Pruschek, 1997). The efficiency of the system with the membrane reactor is higher than that of a system with conventional CO₂ removal and the investment costs are lower.

The following is more detailed summary of the findings in ref. 11.

Membrane operates stable at 500°C
 Membrane H₂/CO₂ selectivity: 15, Membrane permeance: 0.1 mol/m²-s-bar
 Membrane tube length 2 m
 Total membrane surface area 2176 m²
 Total number of membrane tubes 3300
 Membrane tube diameter 10.4 cm
 Total catalyst volume 25.3 m³
 Estimated membrane cost: approximately \$6,000,000

IGCC Configuration	Net electric efficiency [%]	Overall CO₂ recovery[%]¹
No CO ₂ removal	46.7	
Conventional CO ₂ removal ²	40.5	88
WGS-MR + conventional gas cleaning	42.8	80
WGS-MR + dry gas cleaning	43.4	80

1: based on coal input; 2: CO₂ removal by Rectisol wash

IGCC case	base-case	conventional CO₂ removal	WGS-MR CO₂ removal with conventional gas cleaning
CO ₂ recovery ¹		88	80
CO ₂ state		gaseous (1.3 bar, 38 °C)	gaseous (1.0 bar 74 °C)
Net power [MW]	379	355	433
Net efficiency [% LHV]	46.7	40.5	42.8
Specific investment ² [ECU/kW]	1560	1869	1594
COE ³ (6000 h/a) [ECU / kWh]	0.0787	0.0867	0.0835

1: based on coal input; 2: European Currency Unit, 1ECU=.27 US\$, 30 July 1996;
 3: Cost of electricity generation.

Based on the above, the currently available membranes which have fluxes about one order of magnitude less than the ones assumed in the calculation and are 30% less selective are not expected to provide any improvements. Therefore, further work should be directed for the fabrication of improved flux and selectivity membranes to meet or exceed the originally set targets.

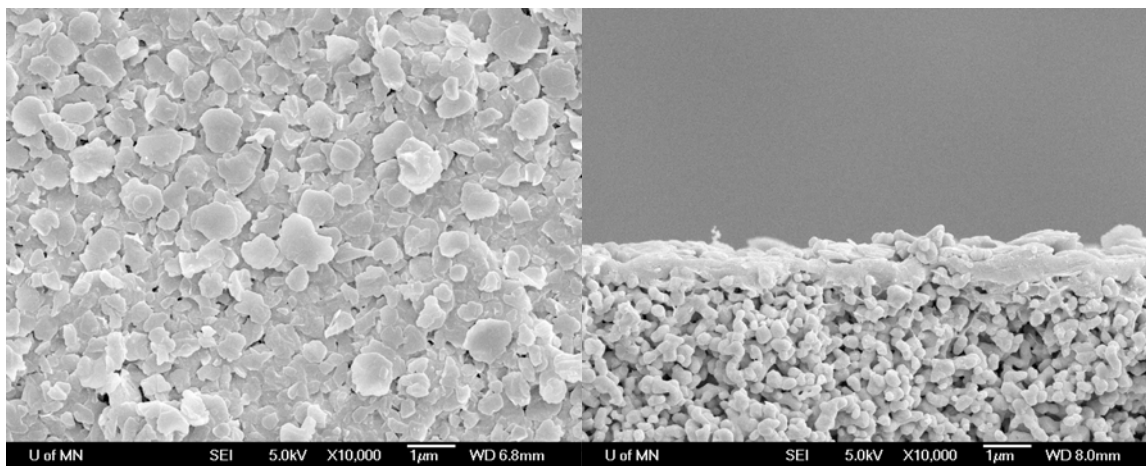
5. Ongoing and Future Work

Ongoing work is directed towards the preparation of nanocomposite films containing oriented exfoliated zeolites obtained, using our new process, from the layered zeolite precursor MCM-22(P). Because the structure of these layers is preserved during swelling and exfoliation and very high aspect ratio layers can be produced in pure form, we consider this material the most promising one for further development of high-flux-high-selectivity membranes. The pore openings perpendicular to the exfoliated zeolite layers are 6-MR and may raise concern regarding allowing hydrogen to permeate. However, the permeation data from nanocomposite films containing oriented MCM-22 nanocrystals indicate hydrogen selectivity.

The current state-of-the-art of MCM-22/silica nanocomposite films is the one discussed in section 1. The multilayered films are approximately 0.5-1 micrometer in thickness and contain less than 10 layers of MCM-22 crystals (Figure 19). We expect that by using the nm-thick exfoliated layers we will be able to prepare films with thickness of 0.1 to 0.5 micrometers that despite their reduced thickness will contain about 50-100 layers of high aspect ratio (100-1,000) exfoliated zeolite and therefore, showing improved flux (due to reduced thickness) and selectivity (due to increased tortuosity from layer overlap), approaching the goals set in the original proposal. The ongoing and future work will be conducted independent of the subject DOE-funded project.

MCM-22/Silica Films

4 (3A+1B) times coated



Continuous, compact, and thin ($< 1\mu\text{m}$) films formed using layer-by-layer deposition.

Figure 19. SEM image of typical film that can be achieved using MCM-22 nanocrystals. This film contains 4 overlapping layers of MCM-22 crystals.

CONCLUSIONS

A major challenge for the utilization of exfoliated zeolites was identified: layered structure preservation upon swelling, exfoliation and formation of nanocomposites.

Typical methods used to swell and exfoliate other layered silicates are not directly applicable to layered zeolite precursors.

New methods were developed for the swelling and exfoliation of two materials: AMH-3 and MCM-22(P). However, only MCM-22(P) can be exfoliated yielding high aspect ratio layers which preserve their original pore structure.

Nanocomposites of MCM-22 nanocrystals with silica matrix can be made using layer-by-layer deposition. Also, nanocomposites of AMH-3 derived layers and a polymer matrix can be prepared. All these materials were hydrogen permselective (over carbon dioxide and nitrogen). However, the permeances and selectivities achieved are not at the level to justify consideration for commercial evaluation.

Order of magnitude improvements in permeance and selectivity are needed and they may be achieved using the recently prepared exfoliated MCM-22 layers.

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LIST of ACRONYMS and ABBREVIATIONS

AMH-3: Abbreviation for a layered silicate with microporous layers

Barrer: Units for membrane permeability (membrane permeance multiplied by membrane thickness); 1 Barrer= 10^{-10} (cm³(STP)-cm)/(cm²-s-cmHg).

DLS: Dynamic Light Scattering

HRTEM: High Resolution Transmission Electron Microscopy

MCM-22(P): Abbreviation for a layered zeolite precursor with microporous layers

MCM-22: Abbreviation for zeolite produced by calcination of MCM-22(P)

8-MR: 8-Member Ring, indicates number (8) of SiO₄ tetrahedra that define the pore openings along the three dimensions in AMH-3

6-MR: 6-Member Ring, indicates number (6) of SiO₄ tetrahedra that define the pore opening perpendicular to the layers of MCM-22(P)

NMR: Nuclear Magnetic Resonance

SAXS: Small Angle X-Ray Scattering

SEM: Scanning Electron Microscopy

SDA: Structure Directing Agent

TEM: Transmission Electron Microscopy

XRD: X-Ray Diffraction