Semi-Annual Progress Report 1

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Recipient: GE Global Research

Project Title: Integrated High Temperature Coal to Hydrogen System with CO2 Separation
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Project Period: June 1, 2005- November 30, 2005

Executive Summary

A significant barrier to the commercialization of coal-to-H_2 technologies is high capital cost. The stringent purity requirements for H_2 fuels are generally met by using a series of unit clean-up operations for residual CO removal, sulfur removal, CO_2 removal and final gas polishing to achieve pure H_2. A substantial reduction in cost can be attained by reducing the number of process operations for H_2 cleanup, and process efficiency can be increased by conducting syngas cleanup at higher temperatures.

The objective of this program is to develop a detailed design for a single high-temperature syngas-cleanup module to produce a pure stream of H_2 from a coal-based system and to develop the new high-temperature membrane materials at the core of that design. The novel "one box" process combines a shift reactor with a high-temperature CO_2-selective membrane to convert CO to CO_2, remove sulfur compounds, and remove CO_2 in a simple, compact, fully integrated system.

The three technical tasks of this program will develop the scientific basis for a one-box system. Task 1 will assess the new design space for a shift reactor that incorporates a high-temperature membrane. Task 2 will develop new high-temperature membrane materials with selectivity for CO_2 and H_2S and evaluate permeability and temperature capability. The design of the integrated module will be completed during Task 3, building on the design concept of Task 1 and using the demonstrated capabilities of the new membrane materials from Task 2. Designs will be developed for both pilot and full-scale systems. Pilot scale demonstration and full-scale membrane development are key steps of technology development that will be conducted after successful completion of this program.

In the first six months of the program, a conceptual design for the one-box system was developed in Task 1 and the performance targets for the system and the membrane were evaluated. In Task 2.1 processes were developed for creating pore architectures in ceramics that are applicable to membrane structures. In Task 2.2, candidate materials were identified that have the potential for facilitated transport of CO_2 and H_2S at high temperatures.

Task 1 Develop detailed system-level design for integrated reactor

Design concepts were specified for the integrated reactor, efficiency and cost analysis was performed for those design concepts, and the best concept was down-selected. The results provided the detailed performance/design targets for membrane development. The integrated reactor design features a reactor with hollow membrane tubes integrated with a sulfur-tolerant shift catalyst. CO_2 and H_2S are captured in

the sweep stream. The membrane reactor design integrates multiple functions, including shift reaction, hydrogen purification, CO_2 separation and acid gas removal, in one reactor module.

Capital cost and efficiency analyses were performed for the case of maximum hydrogen production. An entitlement of about 6% capital cost savings was identified and a 10% increase in the efficiency was calculated for the system using the integrated syngas cleanup module. Membrane performance targets were identified from the system analysis. A membrane permeability target was defined from system cost considerations and selectivity targets were obtained from system efficiency optimization.

Task 2 – Develop high-temperature CO_2 separation materials

In order to enable the "one-box" process, high temperature separation membrane materials must be developed with high CO_2 and H_2S selectivity and high permeability. A model to predict the selectivity of gases relative to H_2 was developed. The model was used to predict the selectivity of a membrane given its pore architecture and adsorption properties. It was also used to set the pore size and adsorption properties targets to reach the target selectivities.

Task 2.1 – Develop mesoporous inorganic membrane structure

Templated synthesis methods were used to fabricate mesoporous ceramics with well-defined pore size and the desired pore organization. The objective of this sub-task was to systematically identify self-assembling structure directing agents (SDAs) and processing conditions for the preparation of defect-free mesoporous silica films on porous alumina supports. To this end, the work was performed in two stages. In the first stage, 37 SDA candidates were screened for their ability to produce structures with the desired pore size. In the second stage, a family of defect-free structures was produced using promising SDAs identified in the first stage. Structures with pore sizes of 2 nm, 5 nm and 10 nm were identified. These samples show good filling and minor defects. Efforts to optimize the processing to produce defect-free structures have begun.

Task 2.2 – Identify functionalization groups for CO_2 and H_2S selectivity

In order to attain the targeted selectivity, materials that enable rapid non-Knudsen diffusion of CO_2 and H_2S were identified. A list of candidate oxides was identified, based on the strengths of their CO_2 and H_2S affinities. Fundamental materials adsorption parameters were measured and determined from literature data. Adsorption isotherms for CO_2 on ceramic powders were measured to benchmark the literature and to evaluate new materials. Three materials were identified that meet the design requirements for reverse selectivity of CO_2 relative to H_2 and one material was down-selected for future work. One material was identified for H_2S selectivity and was down-selected for future work.

In the next six month performance period, work on a component level design will ensue in Task 3. In Task 2.3, fabrication will be initiated for membrane structures that integrate the materials identified with Task 2.2 with the pore structures created in Task 2.1. Initial characterization of the selectivity of those membrane structures will begin in Task 2.4.

Introduction

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Results of work
Task 1. Develop detailed system-level design for integrated reactor
A CO_2-selective membrane reactor design was identified as a candidate design for the high temperature integrated syngas cleanup system with CO_2 separation. This reactor design concept is characterized by a reactor containing hollow membrane ceramic fibers, sulfur-tolerant water-gas-shift (WGS) catalyst and a sweep gas system. Preliminary cost analysis for the design concept was carried out to determine the economic benefits as well as the capital cost sensitivities of various system parameters. These in turn were used to identify the preliminary performance targets for the membrane material development. To understand the impact of the membrane reactor concept on the system efficiency, a base case coal-to-hydrogen system analysis model was constructed using Aspen Plus software. Using the baseline model, the process model for the coal-to-hydrogen using integrated CO_2 membrane reactor was built using a customized membrane reactor module. The preliminary analysis results indicate that the a coal-to-hydrogen system with integrated CO_2 membrane reactor has a lower capital cost as well as a higher system efficiency compared with a conventional coal-to-hydrogen plant. Based on the analyses, the key components of the optimal membrane reactor design were down-selected and the membrane material performance targets identified.

Task 1.1 Develop conceptual designs for the high-temperature membrane reactor
Approach
The conceptual design of the integrated high-temperature membrane reactor was identified based on the conventional coal-to-hydrogen plant process requirements, and it leveraged existing membrane reactor designs for other reaction processes obtained from the literature. The goal was to obtain benefits of process intensification from the integration of several syngas clean-up steps into a single reactor. The features of the CO_2 membrane reactor for processes intensification were identified as:
1. An integrated high temperature shift reactor
2. Selective removal of CO_2
3. Selective removal of H_2S

A wide literature survey was also conducted, which focused on various membrane reactor designs. The preliminary membrane design concept was selected based on the engineering calculations and the critical performance characteristics of the system.

Conclusion
A CO_2 selective water-gas-shift (WGS) membrane reactor design was identified. The design features a membrane reactor with hollow membrane tubes integrated with a sulfur-tolerant WGS catalyst. It provides the potential for an integrated capability of high temperature CO_2 and H_2S removal as well as providing a water gas shift reaction with high conversion.

Task 1.2 Perform efficiency and cost analysis for design concepts identified in Task 1.1
Approach
Estimation of the capital cost of a coal-to-hydrogen plant with the membrane reactor was carried out using the baseline case selected from the coal-to-hydrogen economic analyses published by DOE-NETL [Gray, 2002]. The capital cost of the integrated membrane WGS reactor can be estimated based on the cost of the membrane material and the cost of a conventional WGS system. The total capital cost of a

coal-to-hydrogen plant with integrated membrane reactors was estimated assuming all other equipment cost, labor, taxes, interests and project contingency remain the same as the baseline case.

For the system efficiency analysis, a base case coal-to-hydrogen process model was built with Aspen Plus software. The scope of the system model included all major gasification equipment, syngas cleanup units, hydrogen production/purification units, tail gas combustor/expander and heat recovery steam generators. A customized membrane reactor model was developed and used to replace the syngas cleanup units in the baseline case model. The two system models have the same coal feed rate and are both configured to maximize hydrogen production with minimal electricity output. The plant efficiency can be calculated as

$$E = (H2\ HHV + Net\ Power\ Output) / HHV\ of\ Coal\ Feed \times 100\%$$

Results and Discussion

Capital cost estimates were performed for two coal-to-hydrogen plants, both with 3000TPD coal feed rates. The baseline case (Mitretek Case [Gray, 2002]) uses conventional syngas cleanup units and the other uses the CO_2 membrane reactor. In the membrane reactor case, there is no additional cost of equipment for CO_2 separation since CO_2 is removed through the membrane reactor. Because the hydrogen stream exiting the membrane reactor is already at high concentration, the final hydrogen polishing unit can be much smaller than the conventional H_2 separation & purification unit. The cost of the integrated CO_2 membrane WGS reactor is assumed to be the sum of a conventional water gas shift reactor plus the additional membrane material costs. All remaining equipments and other costs for the membrane reactor case are assumed to be the same as the Mitretek baseline case [Gray, 2002]. Based on that analysis, the total installed plant cost is reduced by about 6.1%.

Table 1 summarizes the results of the system efficiency analysis of a coal-to-hydrogen plant with CO_2 membrane reactor and that of the baseline case published in the Mitretek report [Gray, 2002]. At the same coal feed rate of 3000 TPD, the coal-to-hydrogen plant with a CO_2 membrane reactor can produce 363 TPD of hydrogen while the conventional coal-to-hydrogen plant produces 285 TPD of hydrogen. As a result of the highly efficient hydrogen separation capability of the membrane reactor, the hydrogen loss in the tail gas is greatly reduced which results in a slight decrease in system power output. The conventional syngas cleanup and CO_2 separation units can achieve 87% CO_2 capture rate while the coal-to-hydrogen plant using membrane reactor can reach 93% CO_2 capture rate. The overall efficiency of a coal-to-hydrogen plant with membrane reactor is 69.8% while a conventional coal-to-hydrogen plant has an efficiency of 59%.

Table 1. Coal-to-hydrogen system efficiency analysis

	Mitretek Case 2 - Baseline Coal-to-H_2 w/ CO_2 Seq. [Gray, 2002]	Coal-to-H_2 w/ CO_2 Membrane Reactor
Wet Coal Feed (TPD)	3,000	3,000
Hydrogen Production (TPD)	285.0	363.0
Net Power Output (MW)	26.9	23.2
CO_2 Captured %	87.0%	93.2%
Efficiency %	59.0%	69.8%

Conclusion

The preliminary economic and system efficiency analysis suggest that a coal-to-hydrogen system using a CO_2 selective membrane WGS reactor can reduce the total plant capital cost by 6% while achieving an overall system efficiency of nearly 70% comparing to the 59% efficiency of a baseline coal-to-hydrogen plant with CO_2 separation [Gray, 2002]. The results demonstrate the maximum potential economic benefits and technical advantages of the CO_2 membrane technology.

## Task 1.3 Downselect best design concepts for integrated reactor
Approach

The economic and process model developed for the coal-to-hydrogen system with CO_2 membrane WGS reactor was used as a tool for the membrane system sensitivity analysis and key performance targets identification. For example, the sensitivity of analysis on the system capital cost indicates that it is closely related to the membrane material permeability and thickness. Therefore the economics of the system impose certain minimum performance targets for the membrane material properties.

Results and Discussion

The capital cost is sensitive to the membrane permeability and the membrane thickness – the higher permeability, the lower the capital cost. The economic analysis model was used to determine the break-even values of permeability and membrane thickness and then to determine the targets for membrane permeability and thickness that optimize economic benefit to the system versus the membrane development effort.

Although the membrane selectivity is not a significant factor in the capital cost of the membrane system, the Aspen system analysis model developed in Task 1.2 indicates that it is one of the main membrane properties affecting the coal-to-hydrogen system efficiency. Figure 1 shows the sensitivity analysis of the system efficiency to normalized membrane selectivity.
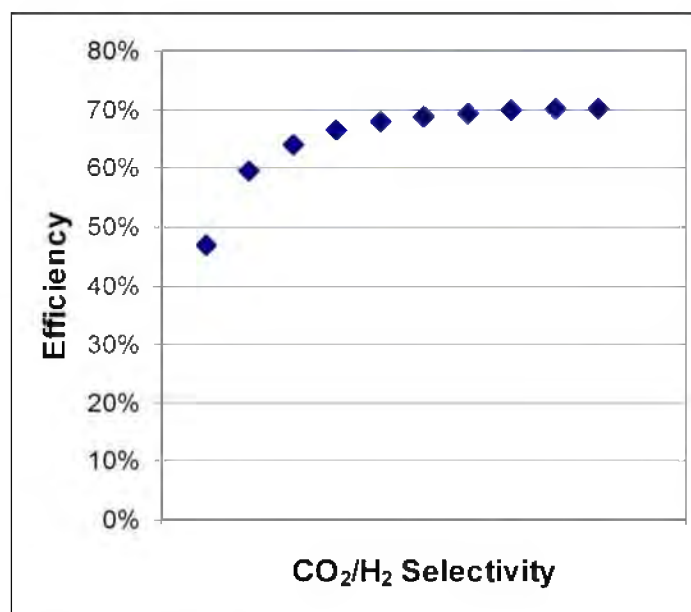
Figure 1. Sensitivity analysis of Coal-to-H_2 system efficiency as a function of normalized membrane selectivity

This analysis shows that system efficiency increases with higher membrane selectivity for CO_2. A selectivity target was selected near the point at which the gain in efficiency leveled off with increasing selectivity

Conclusion

Through the use of economic and system efficiency modeling tools developed during Task 1.2, the major performance targets and their minimum requirements for the membrane material were identified including permeability, thickness and selectivity.

Task 2. Develop high-temperature CO$_2$ separation materials

Introduction

The goal of this task is to demonstrate the feasibility of reverse-selective, high-temperature ceramic membrane materials that separate CO$_2$ and H$_2$S from H$_2$. Reverse selectivity is selectivity in which the heavier gas is enriched relative to the level expected for Knudsen selectivity. For CO$_2$/H$_2$, the Knudsen selectivity is 0.21. Reverse selectivity can be achieved through enhanced CO$_2$ surface transport. Enhanced CO$_2$ transport can be attained by the preferential adsorption and diffusion of CO$_2$ on the pore surface relative to H$_2$. Based on this approach, CO$_2$/N$_2$ selectivities of ~10 have been reported for zeolite, silica, and activated carbon membranes with permeabilities as high as ~10^4 Barrer [Shekhawat, 2003].

Up to this point, efforts to develop membranes with enhanced surface transport have focused on identifying a porous material which itself has suitable surface transport properties. The problem with this approach is the limited number of compositions available that satisfy both the structural requirement (well-defined pores) and the transport requirement (fast surface diffusion of CO$_2$).

This program proposes to decouple the requirements using a functionalized mesoporous membrane consisting of a well-defined mesoporous support and a surface coating that imparts the desired diffusion characteristics. That simplifies the membrane synthesis process into three tasks: preparation of the mesoporous support (Task 2.1), identification of suitable functional groups and coatings (Task 2.2), and functionalization of the mesoporous support (Task 2.3).

Materials Design

To achieve the desired selectivity, surface diffusion must be the dominant mode of CO$_2$ transport with higher fluxes than the bulk Knudsen diffusion of H$_2$. The rate of surface diffusion depends on the amount of CO$_2$ adsorbed and its relative mobility. The surface flux of gas molecules along membrane walls can be expressed as $J = -D\dfrac{d\theta}{dz}$, where D is the surface diffusivity of the gas molecule, and $\dfrac{d\theta}{dz}$ is the concentration gradient of gas molecules in the direction of flow. Diffusivity can be described by an Arrhenius expression, $D = D_0 \exp(-\dfrac{\Delta H}{kT})$, where the heat of adsorption, ΔH represents the maximum activation barrier to surface hopping of the gas molecule. In this picture, surface flux is maximized if the functional coating has a small ΔH. However, small ΔH also means low surface affinity and accordingly, a low adsorbate concentrations on the pore walls, leading to small surface flux. On the other hand, strong surface affinity or large ΔH will make surface hopping unfavorable, and the resulting surface flux will be small. For optimal surface flux, the pore wall surface should be composed of a material having an intermediate ΔH in the operating regime.

With increasing pore radius, it is more difficult to achieve the desired selectivity in structures with larger pores. Physically, this is due to the higher degree of surface diffusion needed to offset the increased Knudsen flow through the larger pores.

The materials design indicates that mesoporous inorganic membrane structures with pore diameters between 2-10 nm are required, and functional materials with the required ΔH must be identified. The development of the former will be described as part of Task 2.1 and the latter as part of Task 2.2.

Task 2.1 Develop mesoporous inorganic membrane structure
Approach
Introduction and objective

Templated synthesis combining self-assembling structure directing agents (SDA) with sol-gel methods can produce mesoporous silica with size tunable, monodisperse, periodically organized pores [Kresge, 1992],[Yang, 1999],[Zhao, 1998], Dabbs, 2000]. Control over the porosity is achieved primarily through suitable choice of SDA, solvent, and processing conditions [Dabbs,2000]. Systematic studies of surfactants and block copolymers as SDAs have been performed [Yang, 1999]. The open literature contains many examples of recipes for the synthesis of particles and supported films [Dabbs, 2000]. Although progress is being made in the hydrothermal deposition of mesoporous silica films onto porous supports, the approach is still plagued by problems with gap defects that allow fluid flow to bypass the mesoporous structure [Nishiyama, 2001].

The objective of this sub-task was to identify systematically a set of SDAs and the processing conditions for the preparation of defect-free mesoporous silica films on porous alumina supports. To this end, the work was performed in two stages. In the first stage, 37 SDA candidates were screened for their ability to produce structures with the desired pore size. In the second stage, a family of defect-free structures was produced using promising SDAs identified in the first stage.
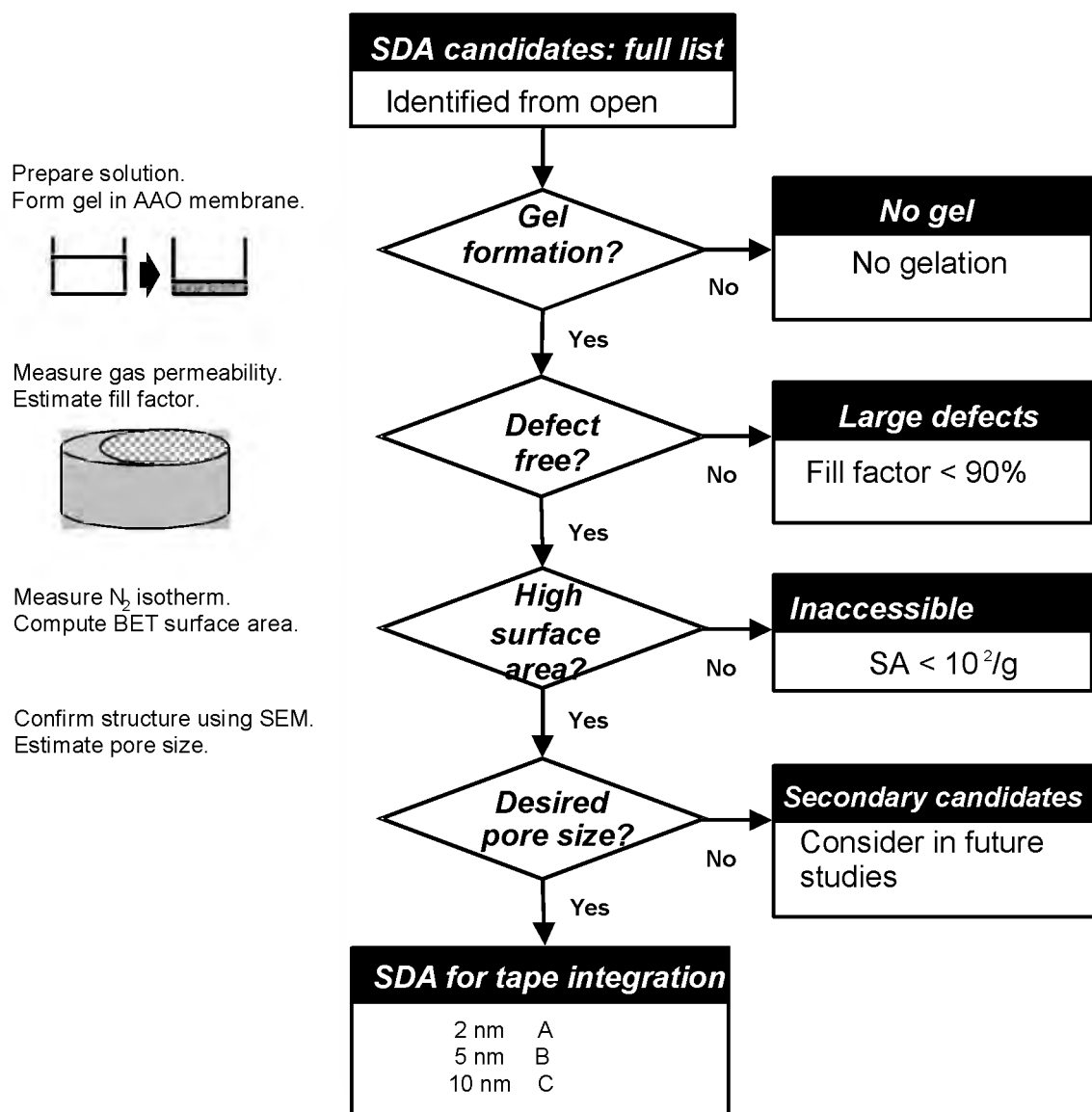
Rationale and selection criteria for SDA

The performance calculations summarized above showed that pore sizes of less than 2 nm are desirable for high selectivity CO_2/H_2 membranes based on the surface transport concept. Porous supports with pore sizes ranging from 2 to 10 nm *before coating* with the surface-active material are needed as membrane supports.

Figure 2 summarizes the criteria and results of the SDA selection process. Since SDAs vary greatly in chemical structure and characteristic size, 37 candidates were chosen on the basis of previous use in the open literature and commercial availability. The primary selection criterion was the ability of the SDA to produce pores of 2, 5 or 10 nm.

Experimental methods

Mesoporous silica/alumina membranes were prepared by depositing a SDA-templated silica gel into a porous anodic alumina (AAO) support [Ku, 2005]. AAO membranes are a model system for study because they possess cylindrical pores with a well-defined pore size which facilitates quantitative estimates of the shrinkage from gas permeability data. Samples were characterized by air permeability, nitrogen adsorption, and electron microscopy to determine the pore size and macroscopic defect rate.

Prepare solution.
Form gel in AAO membrane.

Measure gas permeability.
Estimate fill factor.

Measure N_2 isotherm.
Compute BET surface area.

Confirm structure using SEM.
Estimate pore size.

SDA candidates: full list
Identified from open

Gel formation? → No → **No gel** / No gelation

Yes ↓

Defect free? → No → **Large defects** / Fill factor < 90%

Yes ↓

High surface area? → No → **Inaccessible** / SA < 10^2/g

Yes ↓

Desired pore size? → No → **Secondary candidates** / Consider in future studies

Yes ↓

SDA for tape integration

|	
2 nm	A
5 nm	B
10 nm	C

Figure 2. Flowchart of SDA screening process

Results and Discussion

As shown in Figure 2, SDAs were grouped into 5 categories, according to their effectiveness in producing a desired membrane structure: *no gel, large defects, inaccessible porosity, secondary candidates,* and *SDAs for integration*.

- *No gel*: Three SDAs did not produce gels.

- *Large defects*: Nine SDAs were classified into this group. Defects were inferred from gas permeability measurements.

- *Inaccessible porosity*: Eight SDAs fell into this category. BET surface area measurements of less than 10 m^2/g indicated that very little porosity was accessible.

- *Secondary candidates*: Seventeen SDAs produced high surface area and low permeabilities.

- *SDAs for integration*: Three SDAs, with nominal pore sizes of about 2, 5 and 10 nm, were selected for further study.

Figure 3 shows cross-sectional scanning electron microscope (SEM) images of mesoporous silica inside the AAO supports. Average pore sizes of about 2, 5, and 10 nm were estimated from the images using a line profile method. The porosity appears to be interconnected.
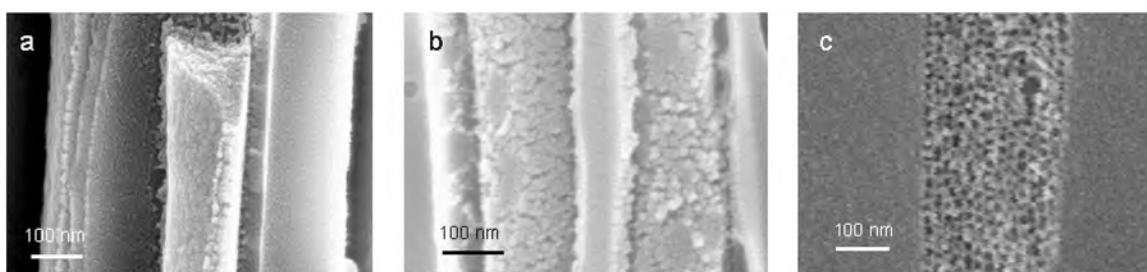
Figure 3. SEM images of porous structures produced using selected SDAs. (a) A (b) B (c) C

Preparation of membrane layers

Mechanically robust membranes were needed to test for CO_2 selectivity. To this end, mesoporous silica structures were fabricated on tape cast alumina membrane supports. Circular (¼" diameter) samples were prepared using each of three SDAs (A, B, and C) identified in Stage 1 to demonstrate the feasibility of mesoporous silica-alumina membranes with pore sizes of 2, 5 and 10 nm.

Experimental approach

Asymmetric alumina membranes were prepared using a tape-casting method. The membranes were dipped into precursor solutions and dried and heat-treated. Cross-sectional SEM imaging was used to examine the local microstructure within the membrane. Gas permeance measurements were used to test for the presence of defects in the mesoporous silica-alumina membranes. All three types of surfactant-templated silica membranes were tested, by measuring flow for differential pressure across the membranes ranging from 7 kPa to 140 kPa. The permeance was computed from the measured flow, test aperture size, the applied pressure gradient.

Results and discussion

The defect density can be inferred from the slope and intercept of a plot of membrane permeance as a function of pressure. The ratio of the slope to the zero pressure permeance or the permeance deviation factor is one measure of defect density. This parameter provides an indication of the relative amount of Knudsen flow relative to viscous flow. Evidence was seen that some defects are present. However, it is not possible to deconvolve the defect size and number fraction of defects without additional information about the microstructure.

Some insight was obtained by comparing the permeance deviation factors of the mesoporous silica-infiltrated supports against an unfilled support. The order of magnitude agreement of these values suggests that defects in the porous support dominate the defect structure of the filled membranes. Efforts to mitigate this problem are under way.

Conclusion
Mesoporous silica/alumina porous membranes with nominal pore sizes of about 2, 5, and 10 nm were produced. These samples show good filling and minor defects. Efforts to optimize the processing to produce defect-free structures have begun.

Task 2.2 Identify functionalization groups for CO_2 and H_2S selectivity

Approach

Introduction and objective

The objective was to identify metal oxide compositions that have rapid surface transport of CO_2 or H_2S. A methodology was developed to identify materials with predicted high CO_2 selectivity based on adsorption measurements. The methodology was extended to identify H_2S-selective materials based on literature measurements. Candidate compositions were selected for each.

When metal oxide surfaces are exposed to CO_2, adsorption takes place by physisorption and chemisorption processes. Chemisorbed CO_2 molecules form monodentate and bidentate surface carbonate species. The surface carbonates can form on metal oxide surfaces even in cases where the metal does not form a stable bulk carbonate phase. That can be rationalized as the result of low coordination of surface atoms and additional configurational degrees of freedom for phase formation. While there is evidence for surface migration of these carbonates on the oxide surfaces [Tsuji, 2003], [Liao, 2002], surface diffusion kinetics have not been extensively quantified. However, near-equilibrium CO_2 adsorption measurements can be used to estimate and compare CO_2 mobility on various oxide surfaces, as outlined below.

Experimental approach: CO_2 adsorption isotherms

ΔH can be calculated from adsorption isotherms for CO_2 adsorption on candidate metal oxide powders. An apparatus for measuring adsorption isotherms (Micromeritics ASAP 2020 Chemi) was brought on line. Isotherms were obtained by measuring the CO_2 uptake of a high surface area sample of known mass, as a function of pressure. The sample was dosed with a known amount of CO_2 (determined by the set point pressure) and the decrease in pressure due to CO_2 adsorption was monitored. Once the pressure was stable, the process was repeated, until the sample surface was saturated and the set point pressure was maintained without a pressure drop. The process was repeated at the next set point pressure. The amount of CO_2 adsorbed on the sample surface at every pressure can be accurately determined by this method. The sample temperature was kept constant during these measurements. The isoteric heat of adsorption, ΔH, was calculated from a series of isotherms as described below. Specific surface areas of the samples were measured by N_2 adsorption.

CO_2 adsorption measurements were made on α-Al_2O_3 and other oxide nanopowders. Isotherms were obtained at temperatures ranging from 100 °C to 500 °C. The sample surfaces were regenerated, between isotherms, by annealing at 600 °C in a He atmosphere to remove remnant adsorbates. These results were benchmarked against adsorption isotherm measurements and analyses have been reported in the literature for γ-Al_2O_3 [Horiuchi, 1998].

Results and Discussion

CO_2 adsorption isotherms for α-Al_2O_3 are plotted in Figure 4a. The plot shows that CO_2 adsorption decreased with increasing temperature. Adsorption isoteres or lines of constant coverage obtained from the adsorption isotherms in Figure 4a are plotted in Arrhenius form (ln P vs. 1/T) in Figure 4b. The isoteric heat of adsorption is related to the slopes of the isoteres by the Van't Hoff equation,
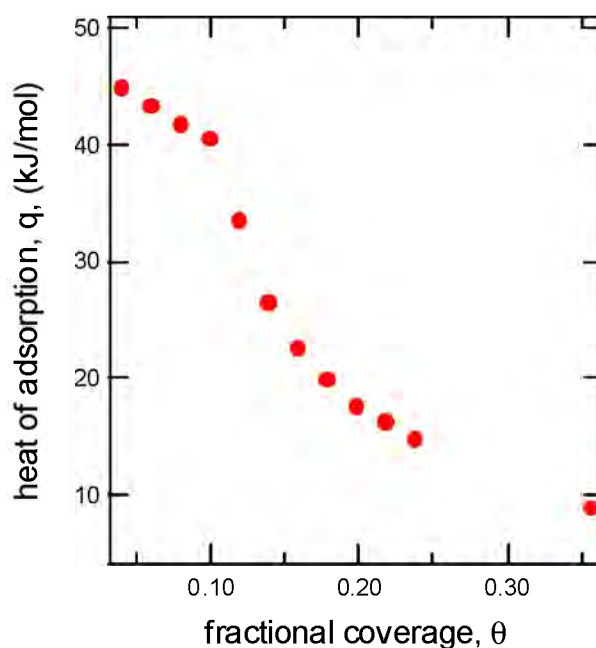
$$\Delta H = -R\frac{d\ln P}{d(1/T)}$$. The heat of adsorption as a function of surface coverage is plotted in Figure 5. At

low surface coverage (θ) the interaction between gas molecules is negligible, and ΔH is dominated by solid-gas interactions. As θ increases there is greater interaction between the CO_2 molecules, and the decrease in ΔH suggests that this interaction is repulsive.
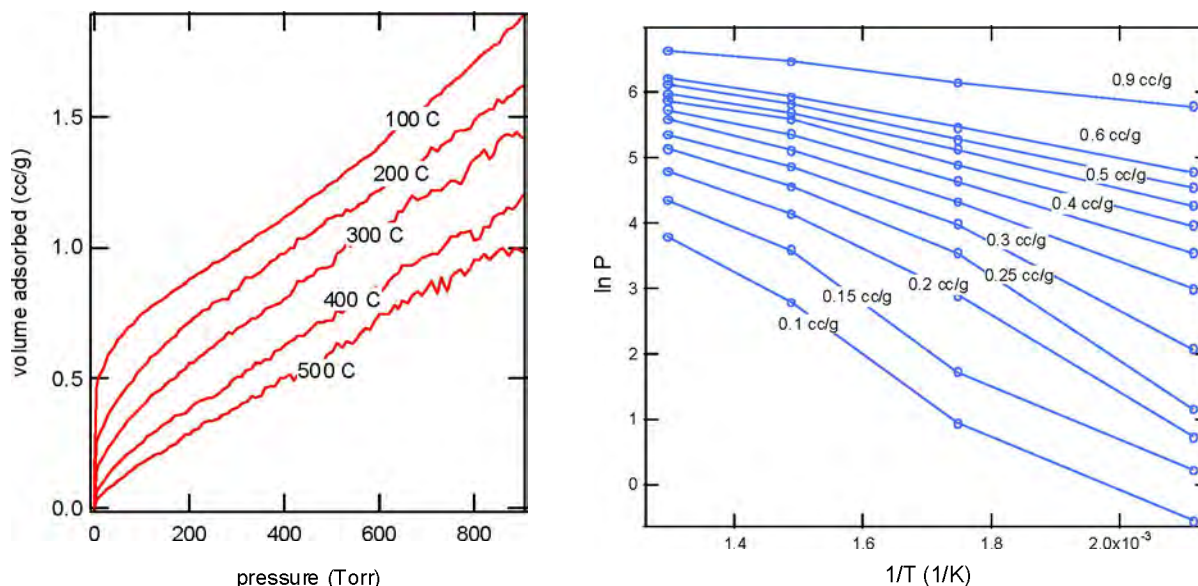
Figure 4 a) CO_2 adsorption isotherms for α-Al_2O_3 b). Isoteres for CO_2 for α-Al_2O_3, calculated from adsorption isotherms

Figure 5. Isoteric heat of adsorption as a function of surface coverage for α-Al_2O_3

The measured heat of adsorption for α-Al_2O_3, about 40 kJ/mol, is in good agreement with values reported in the literature for γ-Al_2O_3 [Horiuchi, 1998]. However, estimates of surface flow indicate that alumina is not a suitable material for CO_2 surface transport.

Adsorption properties including the heat of adsorption were measured and obtained from the literature for other oxide materials. Three oxides were found to be potential candidates to reach the target selectivities determined in Task 1, and one was down-selected. Future work will focus on integrating that surface functional material with the pore structures developed in Task 2.1.

Evaluation of materials for H_2S selectivity

Separation of H_2S from the syngas stream within the high temperature integrated membrane reactor offers advantages of reduction in footprint and consolidation of processes. High temperature absorption processes are being developed as one approach to sour gas removal without gas cooling [Swisher, 1992]. However, large volumes of adsorbents may be required and regeneration of adsorbents can be energy intensive [Burke, 2002].

Membrane separation of H_2S offers potential advantages of compact design, low operating cost, and modular design. However, membrane separation of H_2S from syngas streams is more difficult than membrane separation of CO_2 because the partial pressure driving force for H_2S is significantly lower. The reverse selectivity for H_2S/H_2 must be higher than that for CO_2/H_2.

The same methodology to estimate the selectivity for H_2S vs H_2 was used as was outlined above for CO_2/H_2. H_2S adsorption properties were obtained from the literature for several oxides. One oxide was determined to be a potential candidate to reach target selectivities. Future work will focus on integrating that surface functional material with the pore structures developed in Task 2.1.

Conclusion

The heat of adsorption of CO_2 *(ΔH)* was identified as an important adsorption characteristic, by which the surface diffusion kinetics of CO_2 on metal oxide surfaces can be estimated. That quantity can be calculated from CO_2 adsorption isotherms that were measured and obtained from the literature. One material has been down-selected for further optimization for CO_2 separation and a second material has been down-selected for further optimization for H_2S separation.

Cost Status

Budget period	From	To	Total Approved Budget	DOE Share of Total Approved Budget	Recipient Share of Total Approved Budget	Total Costs	Federal Share of Costs	Recipient Share of Costs
1	6/1/05	11/30/05				115,111	92,089	23,022
1	12/1/05	5/31/06	332,539	266,031	66,508			
2	6/1/06	11/30/06						
2	12/1/06	5/31/07						
Totals								

Schedule Status

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Performance targets for system and membrane	11/30/05		11/30/05	100%	
2.1	Synthesis of inorganic mesoporous membrane structures with varying pore sizes and architectures	11/30/05		11/30/05	100%	
2.2	Identification of functional materials enhancing CO_2 and H_2S transport	11/30/05		11/30/05	100%	
2.3	Synthesis of membrane structure with the functional materials incorporated within them	5/31/07				
2.4	Characterization of membrane selectivity and permeability as a function of temperature	5/31/07				
3	Predicted performance of optimized integrated reactor	5/31/07				
3	Projected capital and operating costs of integrated module	5/31/07				

Summary of accomplishments
Accomplishments attained during the period 6/1/2005-11/30/2005 include the following:
1. A system design concept was down-selected and evaluated.
2. Capital cost and efficiency benefits were quantified for the system design concept.
3. Performance targets for the membrane materials were identified
4. A family of pore structures was obtained that meet the targets.
5. Functional materials with the potential for enchanced CO_2 and H_2S transport were identified and down-selected for further study.

Problems or delays
None to report.

Technology transfer
One provisional patent application was filed during this reporting period U.S. Provisional Patent Application Serial No. 60/721560, filed on September 28, 2005. Two non-provisional patent applications were filed during this reporting period: Docket 162652-2, "Functionalized Inorganic Membranes for Gas Separation" and Docket 162652-3 "Methods and Apparatus for Hydrogen Gas Production," filed on October 31, 2005.

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