TITLE: **DEVELOPMENT OF Pd-Ag COMPOSITE MEMBRANE FOR SEPARATION OF HYDROGEN AT ELEVATED TEMPERATURE**

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1. ANSTRACT

Program Introduction: Rational and Objective

The purpose of this project is to develop hydrogen-selective *Pd-Ag* composite membrane in microporous substrate for use in production and separation of hydrogen at elevated temperature. The objectives of this research are to: (1) Fabricate H_2-selective *Pd-Ag* composite membrane in planar and tubular configurations on microporous porous stainless steel substrate by electroless deposition process; (2) Study the H_2-permeation characteristics of *Pd-Ag* composite membranes using pure hydrogen and mixed gases. Evaluate the membranes for long term integrity and stability under thermal cycling for *Pd-Ag* film adhesion and H_2-permeation properties; (3) Using tubular *Pd-Ag* composite membrane, design and fabricate shell-and-tube structured membrane reactor and conduct steam reforming of methanol experiments to study the equilibrium shifts and permeation characteristics; and (4) Validate the performance of the membrane-reactor using our membrane-reactor model for steam reforming of methanol.

Accomplishment Achieved to Date

Electroless Plating Bath Setup

An electroless plating bath with digital continuous monitoring of temperature is installed in a Fisher Scientific constant temperature water bath under a fume hood. The water bath temperature can be controlled up to 90 °C with a safety factor ± 0.24 °C. The plating bath solution temperature and pH is monitored by an ACUMET AP 061 pH digital meter which has an electrode equipped with K-type thermocouple. A MasterFlex osmotic solution drive pump with flow control 500 ml/min to 4 liter/min is used for circulation of osmotic solution. The new bath can be conveniently used for plating either the inside or outside of the tubular microporous substrate. It can be also used for deposition on planar substrate. As electroless plating is strongly sensitive to in-situ cleaning procedure of substrate, ultrasonic cleaning bath originally custom

modified for tube cleaning is installed under the same fume hood. The new electroless plating bath provides improved safety and stability.

In this work, bi-layered or multi-layered palladium silver growth or continuous Pd-Ag nuclei growth is being determined by XRD or EDS analysis. XRD and EDS analysis is useful to calculate bulk composition of the samples and also to estimate the amount of Pd-Ag deposited with varying plating time. The new composite membranes are characterized by SEM, EDX and XRD analysis. We also studied the effects of surfactants on electroless plating bath stability and rate of deposition of palladium on micro-porous catalytic substrates were investigated. Also to better understand the role of EDTA in bath stability, we studied the Pd^{+2}/EDTA coordination kinetics in typical electroless plating bath conditions.

Permeability Measurement Set-up

To measure the gas permeability through Pd-membranes, we assembled and tested a computer controlled permeability measurement set-up with gas sampling connecting to a gas chromatograph (GC). The set-up will also be used for membrane-reactor study for steam reforming of methanol. We have conducted permeability measurements of hydrogen through Pd-membranes that we fabricated in the lab. We continue to use this Permeability Measurement Setup to test all new membranes that we use for membrane-reactor study.

Modeling of Steam Reforming of Methanol

A Pd-thin film on microprous stainless tubular support deposited by electroless deposition process is used as an H_2-selective membrane. The membrane reactor is configured in a shell and tube design where the reaction takes place in the tube side and hydrogen separation occurs radially in the shell side. We developed a 2-D steady state membrane reactor-separator model to describe the reactive reforming processes with effective radial concentration gradients due to hydrogen permeation across the membrane cylindrical surface. Coupled finite difference equations were formulated based on reaction thermodynamics of different chemical species. Results of the reactor simulation were highlighted based on reactor size, catalytic properties, inlet and outlet fluid flow parameters, operating conditions, space velocity and molar ratio. From parametric study, it was observed membrane reactor provided considerably higher conversion compared to non membrane packed bed reactor. This is attributed to continuous separation of one of the products (hydrogen) as reaction proceeds, which shifts the thermodynamic equilibrium rightward.

Membrane-Reactor Performance Study

Currently, we are running experiments on steam reforming of methanol in a membrane-reactor set-up. We completed the membrane-reactor set-up. In the set-up, temperature, pressure and flow controllers are all computer controlled. Gas compositions are measured by a HP GC.

Plans for Remaining Period of Performance

We plan to complete the membrane-reactor study by the end of this summer. Currently, we are working on several manuscripts. After the membrane-reactor work, we plan to complete these manuscripts and submit to Journals for review/publication. Concurrently, we plan to complete the final technical report for submission to US DOE – NETL.

2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENT RECEIVING SUPPORTS FROM THE GRANT:

Presentations/Proceedings:

1. M.A. Islam, M.H. Akanda, and S. Ilias, "A Study on Steam Reforming of Methanol in a Pd-based Membrane Reactor," Paper No. 1144, Indian Institute of Chemical Engineers (IIChE) - Chemical Engineering Congress 2007 (CHEMCON 2007), Kolkata, India (December 27-30, 2007): Conference Proceedings in CHEMCON 2007 CD, Paper No. 1144, pp 1-6 (2007).
2. M.A. Islam, M.H. Akanda, and S. Ilias, "A Study On Steam Reforming Of Methanol In A Pd-Based Membrane Reactor Fabricated By Surfactant Induced Electroless Plating," Paper No. 361f, 2007 AIChE Annual Meeting, Salt Lake City, Utah (Nov 2-9, 2007)
3. M.A. Islam, and S. Ilias, "Evaluation and Characterization of Pd-based Membrane Fabricated by Surfactant Induced Electroless Plating," Paper No. 362d, 2007 AIChE Annual Meeting, Salt Lake City, Utah (Nov 2-9, 2007)
4. Islam, M.A., Basti, M.M., and Ilias, S., "Synthesis of Pd-Membranes: Pd^{+2}/EDTA Coordination Kinetics in Typical Electroless Plating Bath Conditions," Abstract and Preprint Paper #215 (ACS FUEL Division), ACS 2007 Annual Meeting, August 19-23, Boston, Massachusetts.
5. Akanda, M.H., Islam, M.A., and Ilias, S., "Modeling of Steam-Methanol Reforming in a Pd-based Membrane Reactor," Accepted for presentation at the 2007 NAMS Annual Meeting, June 12-16, 2007, Orlando, Florida.
6. Islam, M.A., and Ilias, S., "Modeling of Steam-Methanol Reforming in a Pd-based Membrane Reactor," Accepted for presentation at the 2007 NAMS Annual Meeting, June 12-16, 2007, Orlando, Florida.
7. Islam, M.A., and Ilias, S., "Effect of Surfactants in Fabrication of Palladium Thin-film Composite Membrane by Electroless Plating Method," Accepted for presentation at the 2007 NAMS Annual Meeting, June 12-16, 2007, Orlando, Florida.
8. Islam, M.A., and Ilias, S., "Modeling of Permeability Enhancement in Presence of Dislocations in α-phase Palladium-Hydrogen Equilibria," Presented at the 9^{th} International Congress on Inorganic Membranes (ICIM9), June 25-29, 2006, Lillehammer, Norway.
9. Islam, M.A., and Ilias, S., "Modeling of Hydrogen Permeability in Presence of Dislocations in α-Phase Palladium-Hydrogen Equilibria," Paper #466, Proc. CHEMCON 2006, December 27-30, 2006, Bharuch, India.

Thesis/Dissertations:

M.H. Akanda, "Modeling of Methanol Reforming in a Pd-based Membrane Reactor," MS Thesis, North Carolina A&T State University, Greensboro, NC (2007).

Students Receiving/Received Supports:

1. E. Dudley (BS Chemical Engineering, May 2008, accepted a job with Shell Research in Houston, Texas).
2. M.A. Rahman (MS in Chemical Engineering, Expected in August 2009).
3. M. A. Islam (PhD candidate in Energy & Environmental Study, Expected in December 2008).
4. M.H. Akanda (MS in Chemical Engineering, August 2007, currently a PhD student at Auburn University, Alabama).