Title: **DEVELOPMENT OF LOW COST MEMBRANES (Ta, Nb & CELLULOSE ACETATE) FOR H_2/CO_2 SEPARATION IN WGS REACTORS**

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ABSTRACT:

Objectives:

The overall objectives of this project are: a) to prepare and optimize nano-bimetallic catalysts supported in mesoporus Al_2O_3 and SiO_2 granules for the WGS reaction, b) a novel low cost metal (Ta/Nb)/ceramic and cellulose acetate membranes to separate H_2/CO_2 and obtain 97% purity and 95% recovery of the hydrogen produced in the WGS reaction at a pressure of approximately 15 bar, c) a WGS reactor that will integrate high temperature (HTS) and low temperature (LTS) water gas shift catalysts and gas separation membranes, and d) to develop and demonstrate an improved process and a reactor for the water gas shift (WGS) reaction that is capable of producing and isolating high purity hydrogen and carbon dioxide for sequestration. This is a collaborative research effort between Grambling State University (GSU) and Louisiana Tech University (LTU) with an industrial collaborator CeraMem Corporation. Two senior faculty, an undergraduate student and two graduate students are working on the project. We have obtained the sputtering targets, ceramic disks, and chemical supplies.

Accomplishments:

We have design a $H_2/CO/CO_2$ permeability testing system consisting of mounting flanges for the ceramic disks and GC step-up. The GC system has been calibrated with known mixture concentrations of H_2, CO, and CO_2, and optimized the flow rates for the GC column. We have conducted a permeability test for plain microporous ceramic dicks and obtained the concentrations of H_2 and CO_2 peaks in the original sample mixture and after passing thorough membrane, and the concentrations were successfully quantified using GC. Our results indicate 100% permeability of H_2 and CO_2 through the bare microporous ceramic dicks. The system is ready to test the permeability of ceramic disks coated with Ta/Nb/cellulose-acetate films.

We have set up the facilities for the preparation of Al_2O_3 granular catalysts using nanoparticle incorporated sol-gel/oil-drop methods. As a first trail, WGS catalyst systems: 1) Cu(7%) and Ce(8%) in alumina, and 2) Cu(5%), Ce(7%) and Ni(8%) in alumina were synthesized using the sol-gel/oil-drop methods. DTA and TGA studies on these catalysts showed that the dehydration temperature is at around 200°C and calcination is complete by heating to 450°C. SEM observations showed that the Cu-Ce catalyst granules are larger with larger pores and have less

mechanical strength compared to Cu-Ce-Ni. A gas flow reactor connected to a Gas Chromatograph (GC) was used with a gas mixture of N_2(80%), CO(16%), and H_2O(4%) to optimize the reaction temperatures for Cu-Ce and Cu-Ce-Ni catalyst and found to be ~ 250°C and 200°C, respectively. A batch reactor with calculated amount of water and CO gas at certain pressure was operated at the optimum reaction temperatures to obtain CO conversion as a function of time. After ~ 1 hr reaction ~43% CO is converted in case of Cu-Ce catalyst and about 62% CO in the case of Cu-Ce-Ni catalyst. The overall CO conversions after 10 hrs reaction were 69% for Cu-Ce catalyst and 83% for Cu-Ce-Ni catalyst. In summary, Cu-Ce-Ni/Al_2O_3 catalyst is a better candidate for WGS reaction to produce hydrogen from CO and H_2O mixture compared to Cu-Ce/Al_2O_3 catalyst.

In the second set of WGS catalysts, we have prepared Ce-promoted Cu and Cu/Ni incorporated alumina granular catalysts using sol-gel/oil-drop nanoparticles method with following compositions: (a) Ni(7%)Ce(8%), (b) Ni(5%)Cu(2%)Ce(8%), (c) Ni(3.5%)Cu(3.5%)Ce(8%), (d) Ni(2%)Cu(5%)Ce(8%), (e) Cu(7%)Ce(8%). PXRD analysis confirmed nanoparticle nature of the metal oxides and their phases on the catalyst granules. BET surface of the five catalyst shows a range of 235-140(m2/mg) surface area and the average pore size distribution of 18 Å. Gas flow reactor study to optimize the reaction temperatures for these five catalysts showed that the catalysts (b), (e) and [(a) are LT-WGS type with optimum temperature range of ~ 200°C, 200°C and 250°C, respectively, while catalysts (d) and (c) are HT-WGS type with optimum temperature range of ~ 340°C and 360°C, respectively. The amount of CO conversion correlates with the surface area of the catalyst obtained from BET analysis. In summary, LT-WGS Cu(7%)Ce(8%)/alumina and HT-WGS Ni(3.5%)Cu(3.5%)Ce(8%)/alumina catalysts sow the best CO conversion.

We have designed a $H_2/CO/CO_2$ permeability testing system consisting of mounting flanges for the ceramic disks and GC step-up. We have conducted a permeability test for plain/bare microporous ceramic dicks and obtained 100% permeability of H_2 and CO_2. Thin films of metallic Nb and Ta were deposited using sputtering techniques (LTU's DC-RF Magnetron Sputter Deposition System - PVD300, Unifilm Technology Inc.) on three ceramic disks each with following dimensions and porosities: 11/8" (OD) and 0.281" thickness; and the porosities: 0.16 um, 0.5um, and 0.8um. The thickness of the coated metal films is ~ 400 nm. Separately, NbO and TaO were also deposited on the surface of ceramic disks and reduced to metallic Nb and Ta using aluminothermic reduction: $M_2O_5(s) + 10/3\ Al\ (s/l) \rightarrow 2\ M + 5/3\ Al_2O_3\ (s)$; (M = Na and Ta) under inert atmosphere/high temperature (1200°C). These membranes were characterized by PXRD and DTA analysis. Then we have investigated the gas permeabilities of the membranes using a GC analysis of CO in the pre/post gas streams. The %CO (mol%) in the post gas stream are analyzed and compared between the sputtered films and the films formed by the aluminothermic method. DTA of M_2O_5 (M = Nb and Ta) and Al mixtures shows reduction of M_2O_5 to M at the temperature ~ 950°C. PXRD of sputtered disks show metallic phases of Nb and Ta films and Al_2O_3 disk. PXRD of chemically coated disks shows mixtures of phases: M, M_2O_5, Al_2O_3 and alloy. Sputtered disks show increasing H_2 permeability with porosity of the ceramic disk. Nb has a higher permeability than Ta at a given disk porosity. Chemically Nb and Ta coated disks showed lower H_2 permeability for Nb, while Ta showed higher H_2 permeability compared to the sputtered films.

Future Plans:

We are planning to prepare Ni and Ce silica supported low temperature catalysts with various compositions and compare to the alumina supported catalysts. We are in the process of designing a stainless steel permeability testing system at higher pressure/temperature.

PUBLICATIONS AND PRESENTATIONS:

"*Development of Low Cost Membranes for H_2/CO_2 Separation for WGS Reactors*", Abstract, University Coal Research/HBCU-MI Contractors Review Conference, Pittsburgh June 5-7, 2007.

"*Nanoscience and Nanotechnology Innovations for Future Advancement*", Naidu V. Seetala, Invited Talk, Northwest Louisiana chapter of the American Association of University Women (AAUW), Ruston, LA, April 19, 2007.

"*Microreactors for Syngas Conversion to Higher Alkanes: Effect of Ruthenium on Silica-Supported Iron-Cobalt Nanocatalysts*" S. Zhao, V. S. Nagineni, Naidu V. Seetala, and D. Kuila, in Print, Industrial & Engineering Chemistry Research 2007.

"*Synthesis, Self-assembly, and Chemical Ordering of FePt Nanoparticles* ", Naidu V. Seetala, Invited Talk, Functional Nanoassemblies Seminar Series, Institute for Micromanufacturing (IfM), Louisiana Tech University, Ruston, LA, April 17, 2007.

"*Synthesis and characterization of non-noble nanocatalysts for hydrogen production in microreactors*", K. Shetty, S. Zhao, W. Cao, U. Siriwardane, Naidu V. Seetala, D. Kuila, J. Power Sources 163 (2007) 630–636.

"*Preparation and characterization of sol-gel alumina supported bimetallic nanocatalysts for WGS reaction",* J. Bass, N.V. Seetala, A.M.R. Jayasingha, R.K. Garudadri, and U. Siriwardane, Louisiana Academy of Sciences Meeting, Northwestern State University, Natchitoches, LA, March 14, 2008.

"*Sol-gel synthesis and characterization of alumina supported Cu-Ni-Ce catalysts for water-gas-shift (WGS) reaction*"**,** Ramakrishna S. Garudadri, Ruwantha A.M. Jayasingha, Naidu V. Seethala and Upali Siriwardane, 235th ACS National Meeting, New Orleans, LA, April 6-10, 2008.

"Preparation and characterization of alumina porous membranes coated with Nb/Ta thin films for the separation of $H_2/CO_2/CO$", Ruwantha A. M. Jayasingha, Ramakrishna S. Garudadri, Naidu V. Seethala and Upali Siriwardane, 235th ACS National Meeting, New Orleans, LA, April 6-10, 2008.

"Sol-gel alumina supported Cu-Ce and Cu-Ce-Ni nanocatalysts", Johnte Bass and Naidu V. Seethala and Upali Siriwardane, Phillip L. Young 16th Annual Research Symposium, Grambling, LA, April 24, 2008.

"Sol-gel Prepared Cu-Ce-Ni Nanoparticle Alumina Catalysts for WGS Hydrogen Production", Naidu V. Seetala, Johnte Bass, A. M. R. Jayasingha, Rama K. Garudadri, and Upali Siriwardane, to be published in Microscopy & Microanalysis 2008.

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