II.I.3 Advanced Water-Gas Shift Membrane Reactor

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Objectives

- Develop a hydrogen separation membrane material suitable for operation in coal gas environments containing minor amounts of trace impurities naturally present in coal gasification products.
- Identify, through atomistic and thermodynamic modeling, a suitable Pd-Cu tri-metallic alloy membrane with high stability and commercially-relevant hydrogen permeation in the presence of carbon monoxide and trace amounts of sulfur.
- Identify and synthesize a water-gas shift (WGS) catalyst with a high operating life that is sulfur and chlorine tolerant at low concentrations (0.004 atm partial pressure at 42 atm total pressure) of these impurities.
- Maximize hydrogen permeability by designing a more stable ternary body cubic center (bcc) PdCuTM phase.

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Introduction

This project is an effort to conduct atomistic and thermodynamic modeling studies to identify a Pd-Cu tri-metallic alloy membrane with high stability to provide commercially-relevant hydrogen permeation rates in the presence of trace amounts of carbon monoxide and sulfur. The project effort will also seek to identify and synthesize a WGS catalyst with a high engineering and operating lifetime, which will also be sulfur and chlorine tolerant at low concentrations of these impurities. The WGS process will be intensified by removing equilibrium limitations and producing more than 99.99% pure H_2. A schematic of the WGS hydrogen separation membrane reactor is shown in Figure 1. Quantum Mechanical Atomistic Modeling for advanced catalyst design will be used in the characterizing process to enhance the predicted models for the performance evaluation.

Approach

- Identify, through a combination of atomistic and thermodynamic modeling, a suitable Pd-Cu tri-metallic alloy membrane that displays high stability and produces a commercially relevant hydrogen permeation rate under 42 atm of H_2, CO, CO_2, and H_2O containing ~8.8 atm partial pressure of carbon monoxide and 0.004 atm partial pressure H_2S (~100 ppm) in the presence of at least 24 atm of steam.
- Identify and develop a WGS catalyst with robust qualities and high operating lifetime through a combination of atomistic modeling to identify target catalyst structures, catalyst synthesis to realize these structures, micro-reactor kinetics determination and >1,000-hour life testing. The target catalyst activity is a projected precious metal turnover frequency of 0.5 moles CO/moles total precious metal/sec at ~400°C after 45,000 hours of operation under 42 atm of cleaned, oxygen-blown coal gas with a H_2O/CO ratio of ~3 and containing about ~100 ppm sulfur species.
- Hydrogen solubility is small and endothermic; the solubility increases with temperature, contrary to H behavior in other Pd alloys. Thus, increased solubility at a fixed diffusivity yields higher permeability.

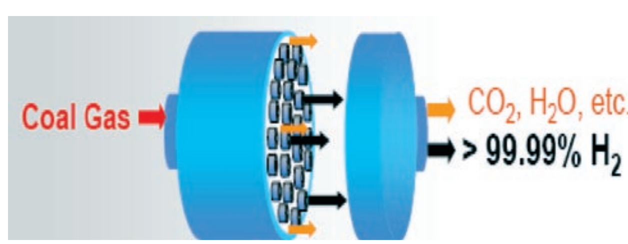

FIGURE 1. Schematic of the WGS Hydrogen Separation Membrane Reactor

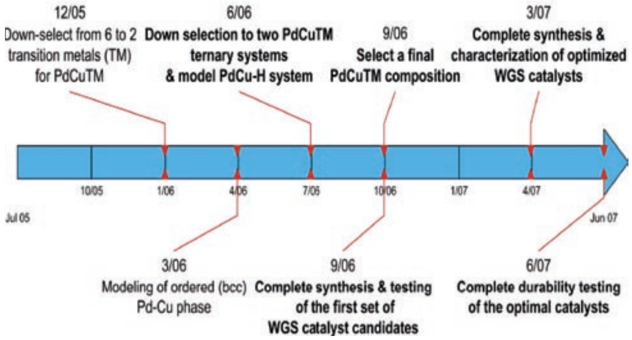

FIGURE 2. Project Timeline and Milestones

Accomplishments

See Figure 2 for the complete project timeline and milestones.

- Completed screening and down-selected from six to two transition metal (TM) substituents for Pd-Cu-TM alloy candidates demonstrating the best potential to enhance stability of the ordered, beta bcc Pd-Cu phase over an extended alloy composition and temperature range.
- Completed modeling of an ordered bcc Pd-Cu phase. Demonstrated that for the bcc Pd-Cu alloy, the hydrogen diffusion activation barriers are lower than those in a Pd-Cu face centered cubic (fcc) alloy.
- Demonstrated that the bulk hydrogen permeability predicted from modeling and experiments are in agreement with values published in the literature.
- Predicted that the ternary alloy will have a sulfur resistance comparable to fcc Pd-Cu alloys with the higher permeability of bcc Pd-Cu alloys.
- Down selection to two PdCuTM ternary systems and modeled PdCu-H system (Figure 3).
- Completed synthesis and testing of the first set of WGS catalyst candidates and selected a final PdCuTM composition.
- Completed durability testing of the optimal catalyst. Showed that the Pd0.47Cu0.52 G50.01 ternary alloy is least susceptible to phase separation with thermal cycling and compositional fluctuations.

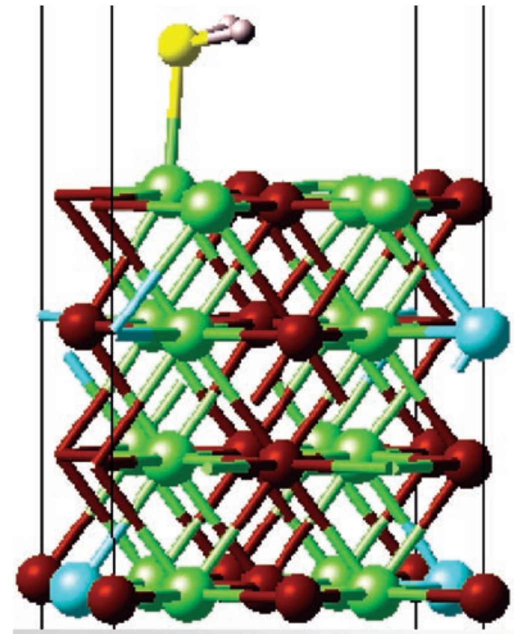

FIGURE 3. Computational Model of H_2S on $Pd_8Cu_7G_5$ (110)

Future Directions

- Complete deployment of atomic and thermodynamic predictions to identify the unique properties of the ordered beta body cubic center Pd-Cu phase that impart high hydrogen permeability.
- Select a final Pd-Cu-TM composition through virtual refinement of phase stability, hydrogen permeability, and resistance to sulfide formation. Complete evaluation of the synthesis and testing of the first set of five WGS catalyst candidates for performance in the presence of 0.004 atm H_2S.
- Complete synthesis and characterization of the optimized sulfur-tolerant WGS catalysts with the desired performance characteristics.
- Complete durability and performance testing and kinetic analysis of the candidate catalysts and characterization of the spent catalysts.
- Complete evaluation and durability test of final set of catalysts and deliver final report.