II.I.7 Production and Storage of Hydrogen from Coal Using C1 Chemistry

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- University of Pittsburgh, Pittsburgh, PA
- Auburn University, Auburn, AL
- University of Utah, Salt Lake City, UT

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Objectives

- Develop novel approaches to produce hydrogen from coal with "breakthrough technology" potential.
- Develop new materials with potential to solve the very difficult problem of hydrogen storage.
- Explore catalytic dehydrogenation of hydrogen-rich carrier liquids as an alternative to reforming.
- Develop novel technology for producing hydrogen from coal, natural gas and biomass using C1 chemistry.
- Develop better methods of producing hydrogen-rich liquids and gases from coal, natural gas, and biomass using C1 chemistry.

Introduction

The CFFLS is a multi-university research consortium with participants from the Universities of Kentucky, Pittsburgh, and Utah, and West Virginia and Auburn Universities. The proposed three-year research project is focused on: 1) developing novel processes for the production of hydrogen using C1 chemistry, 2) developing novel hydrogen storage materials, and 3) synthesis and dehydrogenation of hydrogen-rich carrier liquids. The feedstocks include synthesis gas derived from coal, gaseous and liquid hydrocarbons produced from coal-derived syngas, coal bed methane, and natural gas.

Approach

Experimental results and equilibrium calculations show that a high reaction temperature is favorable for H_2 production, and low temperature improves methane production and selectivity. Among the catalysts we have tested, Cu/MgO exhibits the highest H_2 production but has low methane production and selectivity. Cu/TiO_2 catalyst has high methane production and selectivity but low H_2 production, while Cu/Al_2O_3 catalyst has very low methane production and selectivity with high amounts of di-methyl ether, probably due to the acidic nature of the support. Cu/ZrO_2 is the most effective for co-production of H_2 and methane at temperatures between 240°C and 260°C; this catalyst shows high promise and is being more thoroughly investigated.

In this project, the reforming of methanol is carried out in supercritical water at 276 bar and 700°C to produce H_2 along with CO, CH_4 and CO_2. The reactions are catalyzed by the wall of the tubular reactor made of Inconel 600 which is an alloy of Ni, Cr and Fe. Experiments are conducted to study the effect of pressure, residence time and steam-to-carbon ratio on the H_2 yield. The residence time is varied by changing the length of reactor as well as feed flow rate. Both the experimental results and equilibrium calculations show that as pressure increases, methanation of CO and CO_2 takes place resulting in a loss of H_2. In addition, methane formation is favored at a high residence time and low steam-to-carbon ratio. In this study the following three strategies are proposed for the suppression of methane formation during the production of H_2 from methanol in supercritical water: 1) operation at a low residence time by having small reactor length or high feed flow rate; 2) addition of a small amount of K_2CO_3 or KOH in the feed; and 3) utilization of the surface catalytic activity of the reactor made of Ni-Cu alloy. These three strategies resulted in a significant reduction in methane formation and an enhancement in H_2 production.

Accomplishments

- Developed new continuous methods of producing a high hydrogen content gas by reforming C1 compounds in supercritical water (Figure 1).
- Developed a process to produce hydrogen and chemicals via dehydrogenation of methanol for formaldehyde and subsequent reactions.
- Developed novel bimetallic carbide catalysts for the steam reforming of methanol.
- Catalytic dehydrogenation of alkanes produces pure hydrogen and carbon nanotubes in one step; no carbon oxides are produced. Also, binary Fe-M on various supports exhibit excellent activity and productivity.
- Multi-walled nanotubes are produced at temperatures (T) >600ºC and stacked cone nanotubes at T≤ approximately 500ºC.
- A new Mg(Al)O support has been produced from Mg-Al hydrotalcite precursor. It has high surface area and is easily dissolved in nitric acid, which greatly simplifies nanotube cleaning.
- Fe-Ni nanoparticles of uniform size (10 nm) have been synthesized and dispersed on Mg(Al)O. These catalysts exhibit better activity for hydrogen production than Fe-Ni/Mg(Al)O prepared by the incipient wetness technique.

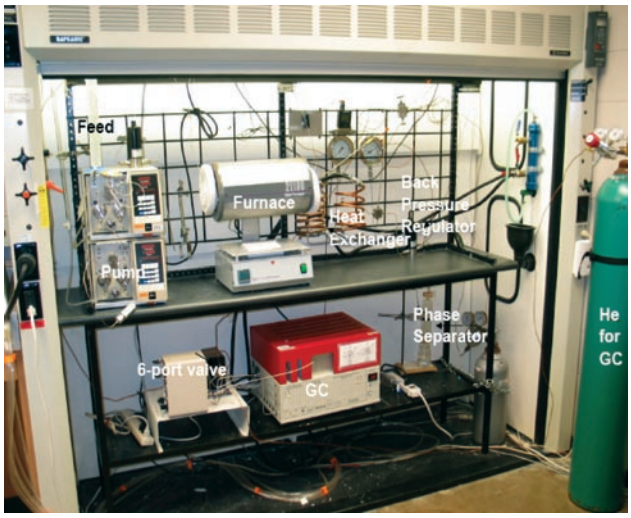

FIGURE 1. Reactor for the Production of Hydrogen by Reforming in Supercritical Water

- Both 4 nm and 12 nm Fe nanoparticles on Mg(Al)O exhibit reasonably good activity for dehydrogenation but not as good as Fe-Ni nanoparticles.
- Hydrogen yield and selectivity for a series of polyols ranging from C_2 to C_6 have been measured using a flow reactor and a variety of experimental conditions. Experiments with glycerol, a by-product of biodiesel manufacture, have shown that it can be converted to hydrogen by splitting the O-H bond using a Pt catalyst or to chemicals by splitting the C-C bond using a Cu catalyst.
- High surface ceria (375 m^2/g) has been synthesized using sol-gel chemistry. The material can be readily doped with precious metals for active WGS catalysts by multiple methods: gas phase incorporation of volatile organometallics and solvent incorporation with suspended, preformed nanoparticles.

Future Directions

- Hold meeting to present research results and obtain program/project direction.
- Build a continuous reactor for the catalytic dehydrogenation of light alkanes to produce pure hydrogen and carbon nanotubes using unsupported, iron-based, nanoparticle catalysts.

Publications/Presentations

1. Gadhe, Jayant B.; Gupta, Ram B., Hydrogen Production from Methanol in Supercritical Water. Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2005), 50(2), 604-605.

2. Gadhe, Jayant B.; Gupta, Ram B., Hydrogen Production by Methanol Reforming in Supercritical Water: Suppression of Methane Formation. Industrial & Engineering Chemistry Research (2005), 44(13), 4577-4585.

3. F. Shi, Y. Zhang, J. W. Tierney and I. Wender, "Co-production of Hydrogen and Chemicals by Vapor Phase Decomposition of Methanol", Am. Chem. Soc., Div. Fuel Chem. 2005, 50 (2).