Novel Preparation and Magneto Chemical Characterization of Nanoparticle Mixed Alcohol Catalysts

PI: Dr. Seetala V. Naidu, Department of Physics, RWE Jones Drive, Carver Hall 81, Grambling State University, Grambling, LA 71245; Telephone: (318) 274-2574, Fax: (318) 274-3281, E-mail: naidusv@gram.edu
Subcontractor/Co-PI: Dr. Upali Siriwardane, Department of Chemistry, Louisiana Tech University, Ruston, LA 71271.
Industrial Collaborator: Hydrocarbon Technologies, Inc
Grant Number: DE-FG26-00NT40836; Performance Period: 02/01/2004 to 02/28/2005)

OBJECTIVE:
Heterogeneous catalysts play an essential role in converting syngas (CO/H_2 mixtures) to fuel. The Fischer–Tropsch (F-T) synthesis is used for several years to produce liquid aliphatic hydrocarbons and oxygenates by the hydrogenation of CO. The significance of synthesis of higher alkanes lies in liquefying natural gas for easy transport, rocket fuel production, and fuel cell production. Nanoscale and well-dispersed fine particle catalysts in sol-gel support offer a large number of advantages such as least diffusion resistance, easy accessibility to reactants, and large number of active sites. The state of the unfilled d-shells and unpaired electrons, morphology and metallic charge distribution of the transition metal (Fe, Co) catalysts are known to govern both their catalytic and magnetic behavior. One of the objectives is to develop methods to prepare effective nanoparticle incorporated heterogeneous F-T catalysts. This objective was achieved through following steps: 1) synthesize nanoparticle precursors- $Fe(acac)_3$, $Co(acac)_2$, and $Cu(acac)_2$, 2) synthesize Fe, Co, Cu nanoparticles using chemical methods, 3) incorporating the nanoparticles into alumina sol-gel and improve metal loading, and 4) prepare the catalyst granules for syngas conversion to yield higher alkanes production.

ACCOMPLISHMENTS:
We have developed effective nanoparticle incorporated heterogeneous F-T catalysts starting with the synthesis of Fe, Co, Cu nanoparticles using $Fe(acac)_3$, $Co(acac)_2$, and $Cu(acac)_2$ precursors and incorporating the nanoparticles into alumina sol-gel to yield higher alkanes production. SEM/EDX, XRD, BET, VSM and SQUID experimental techniques were used to characterize the catalysts, and GC/MS were used for catalytic product analysis.
The nanoparticle oxide method gave the highest metal loading. In case of mixed metals it seems that Co or Cu interferes and reduces Fe metal loading. The XRD pattern for nanoparticle mixed metal oxides show alloy formation between cobalt and iron, and between copper and iron in sol-gel prepared alumina granules. The alloy formation is also supported by DTA and VMS data. The magnetization studies were used to estimate the catalyst activity in pre- and post-catalysts. A lower limit of ~ 40% for the reduction efficiency was obtained due to hydrogenation at 450^0C for 4 hrs. About 85% of the catalyst has become inactive after 25 hrs of catalytic reaction, probably by forming carbides of Fe and Co. The low temperature (300 K to 4.2 K) SQUID magnetometer results indicate a superparamagnetic character of metal nanoparticles with a wide size distribution of < 20 nm nanoparticles.
We have developed an efficient and economical procedure for analyzing the F-T products using low cost GC-TCD system with hydrogen as a carrier gas. Two GC columns DC 200/500 and Supelco Carboxen-1000 column were tested for the separation of higher alkanes and the non-

condensable gases. The Co/Fe on alumina sol-gel catalyst showed the highest yield for methane among Fe, Co, Cu, Co/Fe, Cu/Co, Fe/Cu. The optimization of CO/H_2 ratio indicated that 1:1 ratio gave more alkanes distribution in F-T process with Co/Fe (6% each) impregnated on alumina mesoporous catalyst.

FUTURE WORK:

We plan to prepare Fe/Co nanoparticles loaded in hybrid alumina/silica mesoporous granules. We will vary the alumina/silica and also Fe/Co ratios. We will characterize them using BET, XRD, and SEM/EDX and compare with alumina supported catalysts reported previously. We expect the hybrid alumina/silica catalysts will have higher surface area and different (smaller) pore sizes. We will optimize the catalytic systems for higher alkanes production.

PUBLICATIONS AND PRESENTATIONS:

1. Z. C. Zhong, 2001 JFAP Spring Workshop, Baton Rouge, LA, May 12, 2001.
2. B. Tong, et al., 2nd Louisiana Materials Conference, Baton Rouge, August 25-26, 2001.
3. B. Tong, et al.; Z. C. Zhong, et al., MRS Proc. 704-w9.7, Boston, MA, Nov. 25 – Dec. 1, 2001.
4. Z. C. Zhong, NSF-EPSCoR Meeting, New Orleans, LA, January 25, 2002.
5. Z. C. Zhong, APS Meeting, Indianapolis, IN, March 17-22, 2002.
6. J. Jones, et al., Phillip Young Symposium, Grambling, April 2002.
7. B. Tong, et al., Properties of Metal Nanostructures Conf., *Proc. SPIE* 4810-13, Seattle, WA, July 10, 2002.
8. R. Goduguchinta, et al.; S. N. Vegesna, et al., Louisiana Conf. on Commercial Appl. of Microsystems, Materials and Nanotechnologies, Ruston, Oct. 21-22, 2002.
9. S. V. Naidu, et al., Micro/Nano Technologies for Advaced Physical & chemical Sensors Consortium, Ruston, Dec. 2002.
10. J. Leonard, et al., Louisiana Academy of Science Meeting, Gonzales, LA, March 21, 2003.
11. J. Nwaizugbu, et al.; J. Jones, et al., LAS Meeting, Gonzales, LA, March 21, 2003.
12. U. Siriwardane, et al.; V. Nagineni, et al., ACS Meeting, New Orleans, Mar. 23-27, 2003.
13. S. V. Naidu, et al., MRS Spring Meeting, San Francisco, April 21-25, 2003.
14. S. V. Naidu, et al., Congress on Electron Microscopy, San Antonio, TX, Aug. 3-7, 2003.
15. S. V. Naidu, et al., Microsc. Microanal. 9 (2003) 408.
16. U. Siriwardane, et al.; D. Kuila, et al., ACS Meeting, Anaheim, CA, March 28- April 1, 2004.
17. S. Nagineni, et al.; J. Leonard, et al., La Mater. Res. Conf., Lafayette, Nov. 4-5, 2003.
18. J. Leonard, et al., Phillip Young Symposium, Grambling, April 26, 2004.
19. J. Leonard, et al., LAS Meeting, Lake Charles, LA, March 19, 2004.
20. S. Zhao et al., Accepted, ACS Symposium Series on Microreactors 2004.
21. N.V. Seetala, et al., Proc. Int. Conf. Composites/Nano Eng., Hilton Head, SC, Aug. 8-14, 2004.
22. S. V. Naidu, et al., Congress on Electron Microscopy, Savannah, GA, Aug. 2004
23. S. V. Naidu, et al., Microsc. Microanal. 10 (2004) 484.
24. U. Siriwardane, et al., Submitted, Journal of Catalysis (2004).
25. U. Siriwardane, La Conf. Adv. Mater. & Emerging Tech., New Orleans, Jan. 21-22, 2005.
26. B.P. Zeringue, et al.; D. Kuila, et al, LAS Meeting, Grambling, March 18, 2005.

STUDENTS SUPPORTED:

Post-Doctoral Student: Baiyuen Tong

Graduate Students: Zhengchun Liu, Pallavi Annumwla, Gu Qun, Guo Zhijun, Ramkiran Goduguchinta, Srivani Naga Vegesna, Sireesha Vudatha, Buddy G. Barnett, and Satyendra Vudarapu

Undergraduate Students: Edwin Everett, Karen Luurtsema, Laura Holeman, Andrew Emge, Edward Bruster, Joseph Leonard, Charlene Jones, James Nwizugbu, Sheba Anderson, and Brandon P. Zeringue