Title: **Development of a Catalyst/Support for Methane Reforming**

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ABSTRACT

OBJECTIVE

The overall objective of this project is the development and laboratory demonstration of a unique material which combines a catalyst for reforming methane with a sorbent for the byproduct carbon dioxide. The material has the potential for markedly simplifying the process for reacting steam with methane or carbon monoxide to produce and separate hydrogen in high concentration with an attendant increase in process efficiency.

ACCOMPLISHMENTS TO DATE

The combined catalyst and sorbent under development is designed to increase the rate of reaction of steam with methane or carbon monoxide to produce hydrogen while simultaneously absorbing and separating the by-product carbon dioxide. The catalyst and sorbent are combined into spherical pellets that individually consist of a calcium-based core encased in a porous shell impregnated with a nickel catalyst. Material preparation has been demonstrated on a bench-scale by pelletizing powdered limestone or dolomite to form the cores followed by the application of a coating of alumina and limestone and then calcination to partially sinter the coating. The pellet shells are subsequently impregnated with a nickel salt that is readily converted into elemental nickel by the application of heat and a reducing atmosphere.

The utility of the material has also been demonstrated on a bench-scale by reacting steam with methane or carbon monoxide or a mixture of the two at temperatures in the range of 550 to 650°C in a fixed bed reactor packed with the material. While the by-product carbon dioxide is being absorbed, hydrogen has been produced in concentrations of 95% or more. The sorbent has been regenerated by interrupting the flow of steam and increasing the temperature to 750°C or higher. Since a cyclic process is required for utilizing the material, an important consideration is the effect of cycle repetition on the properties of the material. One effect which has been observed is a gradual decline in absorption capacity as the cycle of absorption and regeneration is repeated. The rate of decline has been found to depend on both the initial calcination conditions and the presence or absence of specific additives. The decline in capacity has been related to a decrease in the surface area and pore volume distribution of the sorbent. The addition of either magnesium oxide or lanthanum oxide to the sorbent has been found to slow the

rate of decline of absorption capacity. This finding is being pursued to determine the optimum concentration of additive and to determine the ultimate absorption capacity of the material after it has undergone a very large number of cycles.

Another important consideration is the physical strength of the shell material. A major component of this material is an activated alumina with a large specific surface area which is affected adversely by calcination at the high temperature required to partially sinter the shell. Various metal oxides have been tested for inclusion in the shell material to reduce the required calcination temperature. The best results have been achieved by the addition of a small amount of lanthanum oxide which greatly improves particle cohesion. This additive has made it possible to calcine the shell material at a much lower temperature than was required when calcium oxide was used.

FUTURE WORK

Combined catalyst and sorbent pellets will be prepared using the most promising formulations for the core and shell. The pellets will be subjected to both physical testing and process evaluation. This evaluation will be conducted by reacting steam with methane and/or carbon monoxide in the presence of the material at different temperatures and pressures. Also limited life cycle testing of the material will be carried out.

LIST OF PAPERS PUBLISHED

J. A. Satrio, B. H. Shanks, and T. D. Wheelock, "Development of a Novel Combined Catalyst and Sorbent for Hydrocarbon Reforming," *Ind. Eng. Chem. Res.*, **44**, 3901-3911 (2005)

J. A. Satrio, B. H. Shanks, and T. D. Wheelock, "A Combined Catalyst and Sorbent for Enhancing Hydrogen Production from Coal or Biomass", *Energy & Fuels*, **21**, 322-326 (2007).

U.S. PATENT

T. D. Wheelock and B. H. Shanks, "Catalyst and Sorbent Material for the Production of Hydrogen," U.S. Patent No. 7,176,159, issued on February 13, 2007.

LIST OF CONFERENCE PRESENTATIONS

J. A. Satrio, B. H. Shanks, and T. D. Wheelock, "A Combined Catalyst and Sorbent for Enhancing Hydrogen Production from Coal," presented at the Clearwater Coal Conference, Clearwater, Florida, April 17-21, 2005.

B. H. Shanks and T. D. Wheelock, "Development of a Catalyst/Sorbent for Methane Reforming," poster presentation at the DOE University Coal Research Contractors Review Meeting, Pittsburgh, PA, June, 2005.

B. H. Shanks and T. D. Wheelock, “Development of a Catalyst/Sorbent for Methane Reforming,” presented at the DOE University Coal Research Contractors Review Meeting, Pittsburgh, PA, June 2006.

K. O. Albrecht, J. A. Satrio, B. H. Shanks and T. D. Wheelock, “Development of a Combined Catalyst and Sorbent for Hydrogen Production,” AIChE National Annual Meeting, San Francisco, CA, November 2006.

STUDENTS SUPPORTED UNDER THIS GRANT

- Karl Albrecht, graduate student in chemical engineering
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