

TITLE: Water Gas Shift Kinetics at Membrane Reactor Conditions

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GRANT NUMBER: DE-FG2699-FT40590

PERIOD OF PERFORMANCE: June 30, 1999 – June 29, 2002

DATE: April 20, 2000

ABSTRACT

The ratio of CO to H₂ produced via the gasification of coal can be adjusted using the water gas shift reaction. This is necessary if the CO/H₂ ratio from the gasifier is not appropriate for subsequent CO hydrogenation to produce fuels and chemicals. It may also be used to generate a pure hydrogen product, with sequestration of the carbon dioxide co-product. In either case, membrane reactors are being considered for this application with the expectation that, among other advantages, using a membrane reactor would not require cooling the gasifier product as much as a conventional shift reactor. Water gas shift is a reversible, exothermic reaction, and consequently the conversion is limited at high temperatures by thermodynamic equilibrium. The use of a highly permselective membrane reactor would avoid this problem, driving the reaction to high conversion at elevated temperatures by selectively removing either H₂ or CO₂. While this conceptually removes the limitation on conversion at high temperature, it is unknown what effect it will have upon the rate of reaction. Water gas shift over commercial, high temperature, iron oxide catalysts is known to be inhibited by the product, CO₂. While the kinetics are not inhibited by the other product, H₂, it isn't known whether the active (Fe₃O₄) state of the catalyst can be maintained in the situation where CO₂ is removed and where an excess of steam is neither needed nor desired. In a membrane reactor an one or the other of these compositional regimes will be encountered.

OBJECTIVES

In this project the kinetics of water gas shift are being studied at conditions that would be expected within a membrane reactor. During this, the initial year of the project, a commercial type iron oxide catalyst is being tested. The emphasis of the kinetics measurements being made is on situations with high concentrations of either CO₂ or H₂ in conjunction with CO/H₂O ratios near the stoichiometric value

of 1. Kinetic measurements are being made at atmospheric pressure and higher. The objective is to develop a microkinetic model for the rate of water gas shift that can accurately describe the kinetics at all conditions and that will also provide insights and guidance in catalyst improvement or design. The resulting kinetic expression will then be used to simulate the performance of membrane reactors and to assess the performance that might be expected (e.g. hydrogen flux). Additional objectives include modification of the catalyst to improve performance as well as identification of new catalytic materials for this application.

RESULTS

An atmospheric pressure reactor system was assembled and kinetic measurements have been made using an iron oxide catalyst. The data collected were combined with the large data set published by Bohlbro (Bohlbro 1969). The following two-step reaction scheme was first fit to the data.



This scheme fits the data quite well, providing a good benchmark for quality of fit. We are now exploring mechanistic models that describe the reaction kinetics and simultaneously offer more insight into the chemistry of the reaction. At the same time, an elevated pressure reactor system has been brought on-line and data are now being collected from that unit and combined with the atmospheric pressure data.

The rate of reaction over the iron oxide catalyst is indeed inhibited by CO_2 . Thus, while elevated pressure kinetic measurements are being made with this catalyst, we have made some preliminary atmospheric pressure kinetic runs using other catalyst materials, in particular supported palladium catalysts.

A simplified, isothermal model for a concentric tube, co-current flow membrane reactor has been developed and is being used in a preliminary assessment of membrane reactor performance. The model assumes Knudsen diffusion through the membrane and ignores the boundary layer at the membrane surface, but it can provide a qualitative indication of how a membrane reactor would perform using a conventional iron oxide catalyst.

PLANS

Our immediate goals are to refine the mechanistic model and complement the kinetic measurements with calorimetry and other characterization methods, to develop a more rigorous membrane reactor model and to use it to perform a meaningful comparison between water gas shift in a membrane reactor and in a conventional reactor system.

REFERENCE

Bohlbro, H. (1969). An Investigation on the Conversion of Carbon Monoxide with Water Vapour over Iron Oxide Based Catalysts. Gjellerup, Copenhagen, Haldor Topsøe.

PUBLICATIONS

none yet.

PRESENTATIONS

none yet.

STUDENT SUPPORTED

Mr. Donghao Ma.

SUBMITTED

“Water-Gas Shift over Fe_3O_4 at Membrane Reactor Conditions,” submitted for presentation at the AIChE Meeting, November 2000, Los Angeles.