R07 #07

Report Title: **Enhancement of Equilibriumshift in Dehydrogenation Reactions Using a Novel Membrane Reactor**

Report Type: Annual	Reporting Period Start Date: 09/01/1999 End Date: 02/29/2000

Principal Author(s): Shamsuddin Ilias
Franklin G. King

Report Issue Date: 03/09/2000	DOE Award No.: DE- FG22 -96PC96222

Submitting Organization(s) Name & Address

North Carolina A&T State University
Department of Chemical Engineering
Greensboro, NC 27411
e-mail: ilias@ncat.edu
Tel: (336) 334-7564

(1)

(2)

(3)

(4)

(5)

DISCLIMER

ABSTRACT

In our previous report we reported technical difficulties encountered in the fabrication of tubular membrane reactor using our Pd-ceramic composite membranes. Although the membrane is highly selective to hydrogen but in test runs we observed leakage of hydrogen from the end-seals and metallic fittings. This was a serious problem. An attempt to improve the seal by tightening was not helpful but resulted in cracks and breakage of the ceramic tube. To test the equilibrium conversion and equilibrium shift effect on dehydrogenation of cyclohexane to benzene and hydrogen in membrane reactor, we used Pd-ceramic discs in our diffusion cell as reactor packed with Pt-catalyst pellets. Test results show that by manipulating the feed (cyclohexane) flow rate and sweep gas flow rate (permeate side) we can have over 55% conversion as opposed to 18.7% equilibrium conversion under identical conditions. This demonstrates the usefulness of the new membrane in H_2 separation and also in membrane-reactor configurations for equilibrium limited decomposition and dehydrogenation reactions.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

To demonstrate the usefulness of our Pd-ceramic composite membranes in membrane-reactor configuration, we studied the dehydrogenation of cyclohexane using planar Pd-ceramic discs. The reactor was packed with Pt-catalyst pellets. The Pd-ceramic membrane discs were fabricated by electroless deposition method. The experimental results suggest that by using our new membrane in membrane reactor, we can achieve a conversion of over 55% against the equilibrium conversion of 18.7% under identical operating conditions. Thus, it possible to shift the equilibrium significantly to the right by recovering hydrogen simultaneously as permeate product from the reactor using of H_2-selective Pd-ceramic membrane.

INTRODUCTION

The overall objective of this project is to develop inorganic and composite membranes for in-situ separation of hydrogen and equilibrium shift in catalytic membrane reactors. The specific objectives of this research are to:

1. Design and fabrication of catalytic membrane reactor using thin film palladium-composite membrane for dehydrogenation of cyclohexane to benzene
2. Conduct dehydrogenation reaction experiments to study the equilibrium shifts and hydrogen permeation characteristics
3. Develop a theoretical foundation for equilibrium shifts and hydrogen transport in the membrane reactor

Membrane Reactor-Separator in Planar Configuration

In our previous report, we reported technical difficulties encountered in fabricating membrane reactor-separator in tubular configuration. The leakage of light gases from the end-seals and through fittings was a major problem. Tightening of fittings and seals resulted in cracks and failure of the reactor assembly.

To test the concept of equilibrium shift, we used Pd-ceramic discs in our diffusion cell as membrane reactor. The reactor side was packed with Pt-catalyst pellets and we used cyclohexane diluted with inert argon as feed. On the permeate side, argon was also used as sweep gas.

RESULTS AND DISCUSSIONS

The dehydrogenation of cyclohexane under atmospheric pressure and 200 ^{o}C were carried out in a planar membrane-reactor. A 39 mm $\times$ 2 mm ceramic disc was used for Pd-film deposition by electroless method. The membrane had an effective surface area of 12 cm^2 for diffusion. In Figure 1, test results are reported for two feed flow rates at 200 ^{o}C and 1 atm pressure. The results are shown as conversion of cyclohexane as a function of sweep gas flow rate. With increasing sweep gas flow rate, the conversion increases and reaches an asymptotic value with further increase in sweep gas flow rate. The flow rate of the feed gas had significant effect on conversion. With increasing feed flow rate, conversion of cyclohexane to benzene and hydrogen decreases. This due to decreased residence time of the reactant in the reactor. With reduced feed flow rate, one obtains higher conversion. At a feed flow rate 8.9E-07 mol/s, we can get over 55%

conversion while the corresponding equilibrium conversion is 18.7%. This implies that we can attain a three-fold increase in conversion using this membrane-reactor by equilibrium shift.

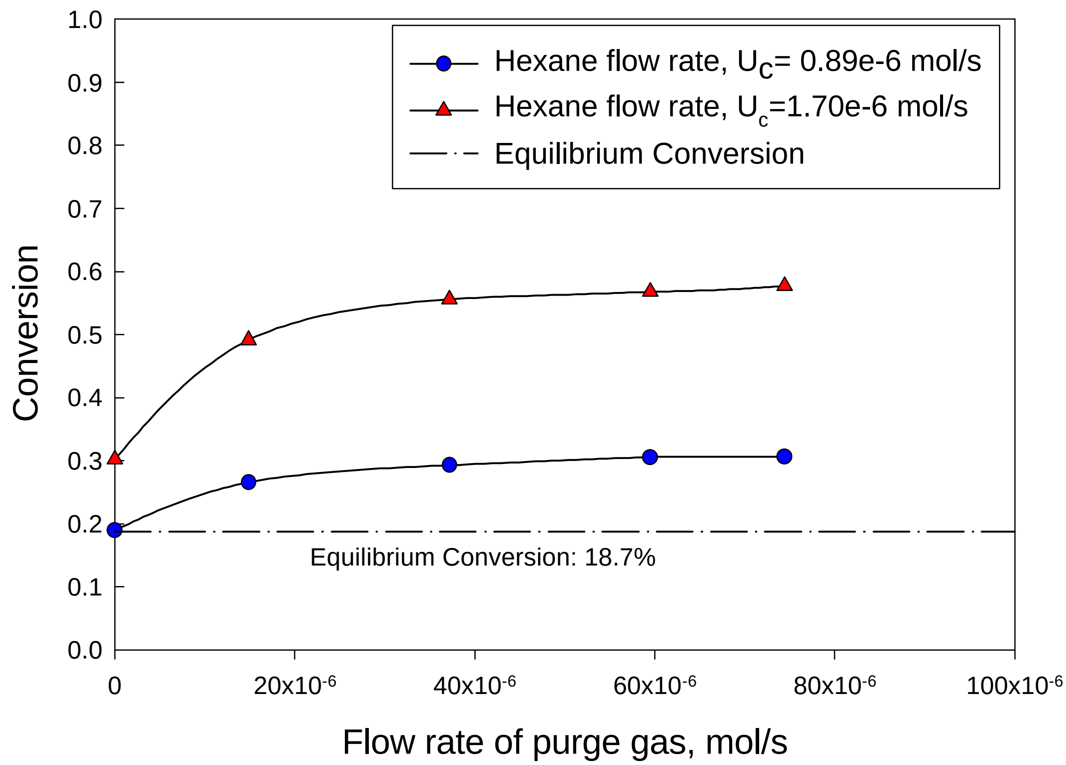

Figure 1: Dehydrogenation of cyclohexane in Pd-ceramic membrane reactor

CONCLUSION

Using our newly developed Pd-ceramic membrane in planar configuration, we demonstrated that it can be used in membrane-reactor configuration to enhance productivity by equilibrium shift of equilibrium limited dehydrogenation and decomposition reactions. We used dehydrogenation of cyclohexane as an example reaction to make point.