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Catalytic Dehydrogenation of Propane and Isobutane in Hydrogen Permselective Membrane Reactors

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Abstract

The dehydrogenation of propane and isobutane was studied in hydrogen permselective packed bed membrane reactors and conventional packed bed reactors. Two different types of developmental membranes were investigated: sol-gel derived silica-based membranes and a pure palladium thin film supported by a porous ceramic substrate. The palladium membranes deactivated and eventually failed when exposed to both isobutane and propane dehydrogenation temperatures above 773 K. Moderate improvements in propylene and isobutylene yields were obtained with the silica-based membrane reactors. An isobutylene yield of 48 mole percent was obtained at a liquid hourly space velocity (LHSV) of 1.8 and temperature of 798 K compared to a yield of 39 percent in a conventional reactor operated with the same flow rate. Similar improvements in propylene yield were obtained when the silica-based membranes were tested in propane dehydrogenation experiments. There was no significant difference in the reaction selectivities for the desired olefin products when the membrane and conventional reactors were operated with the same LHSV. However, for a constant value of the olefin yield, the membrane reactors had a higher reaction selectivity since the desired yield was achieved at a higher LHSV where there was less time for side products to form. Catalyst deactivation rates were generally greater in the membrane reactors, especially when the reactors were operated with high hydrogen removal rates at temperatures of 773 K and above.

Introduction

Catalytic dehydrogenation is a potential method for obtaining alkenes for polymerization and other organic syntheses from low-cost saturated carbon feed stocks. Two examples are the selective production of propylene from propane, and

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isobutylene from isobutane. Thermodynamic limitations on conversion are a significant problem when conventional packed bed reactors are used in both propane and isobutane dehydrogenation. While the propane and isobutane conversion may be increased by operating at higher temperatures, this results in an increase in the rate of catalyst deactivation, and a decrease in the reaction selectivity for the desired olefin products. Catalytic dehydrogenation in hydrogen permselective membrane reactors may be a potential method for increasing the olefin yield while maintaining an acceptable catalyst deactivation rate and reaction selectivity.

There have been several previous studies on both propane and isobutane dehydrogenation in packed bed membrane reactors. Ziaka and coworkers (1993a, 1993b) utilized commercially available porous ceramic membranes with Knudsen diffusion permselectivity to study propane dehydrogenation, while Sheintuch and Dessau (1996) studied this reaction with commercially available thick-walled palladium-ruthenium and palladium-silver alloy tubes. Isobutane dehydrogenation has been studied by Matsuda and coworkers (1993) with a supported pure palladium thin film, Ioannides and Gavalas (1993) with a dense silica membrane, and Sheintuch and Dessau (1996) with the thick-walled palladium alloy tubes. The difference between our study and previous studies is that we are investigating the use of porous silica-based membranes with molecular sieving capabilities as opposed to dense membranes or porous membranes with Knudsen diffusion permselectivity. The porous silica-based membranes have a higher hydrogen permeance than the dense-silica and palladium alloy membranes, and a higher hydrogen permselectitivy than the Knudsen diffusion membranes. Therefore, they are a promising candidate for both isobutane and propane dehydrogenation. In addition, we have also performed tests with a supported pure palladium thin film membrane in order to compare the performance of two different types of developmental membranes in the same experimental system. Another objective of the study was to evaluate the membrane reactor performance at space velocities similar to those used in commercial conventional reactors (LHSV ≈ 1 to 2) so that any improvement in performance was obtained at a practical flow rate.

Experimental

Membrane Preparation

Both the silica-based and palladium-ceramic membranes consisted of silica or palladium films deposited on the inside surface of Membralox® T-170 alumina support tubes obtained from U.S. Filter Corporation. For the palladium-ceramic membranes, the top layer of the asymmetric support tube was composed of α-alumina with a pore diameter of 200 nm. In the case of the silica-based membranes, the top layer of the support tube was composed of γ-alumina with a pore diameter of 5 nm. For ease of handling and testing, the membrane supports (supplied by U.S. Filter in lengths of 25 and 75 cm) were cut into 6 cm sections using a diamond wafering saw.

Electroless plating was used to fabricate the palladium membranes. The plating conditions for membranes tested in propane dehydrogenation experiments were similar to those described by Collins and Way (1993). For the membrane tested in isobutane dehydrogenation experiments, the electroless plating/osmotic pressure procedure developed by Yeung and Varma (1995) was used to deposit the palladium film. In this process, the outside of the membrane support tube was immersed in a 5.8 Molal sucrose bath at 60°C while plating solution was pumped through the inside of the tube.

A polymeric silica sol was used to fabricate the silica-based membranes. The silica films were deposited on the support tubes by a sol-gel process that combines the features of slip casting and dip coating. The supports were calcined at 823 or 873 K following deposition of the silica film. Additional information regarding the sol preparation and membrane coating procedures is presented by Sehgal and coworkers (1994) and Sehgal (1996).

Membrane and Conventional Reactor Experiments

Propane and isobutane dehydrogenation experiments were conducted in packed bed membrane reactors and conventional packed bed reactors operated under the same conditions. The conventional reactor design was similar to the membrane reactor design except the membrane was replaced by a quartz tube with the same inside diameter (0.7 cm). The reactors were packed with a platinum-loaded aluminosilicate molecular sieve catalyst developed by Amoco Corporation. Catalyst preparation procedures were similar to those described by Kaminsky and coworkers (1993).

The experimental system was similar to the one used by Collins and Way (1993, 1994). A shell and tube type design consisting of a single membrane tube inside a quartz tube was used for the membrane module. The ends of the membrane were connected to nonporous alumina tubes using Swaglok® compression fittings with seals (ferrules) made from GRAFOIL® ribbon.

Membrane reactor experiments were conducted at temperatures ranging from 723 to 798 K for isobutane dehydrogenation and 773 to 848 K for propane dehydrogenation. The reactor feed composition was either pure isobutane or propane, or mixtures of isobutane or propane with hydrogen. The total pressure on the reaction side was approximately 1 atmosphere with a sweep side pressure of approximately 0.9 atmospheres. (Note that atmospheric pressure in Albuquerque, New Mexico is approximately 0.84 atmospheres). A nitrogen sweep gas was used to obtain the partial pressure driving force for hydrogen permeation. The ratio of the inlet sweep gas to inlet reactor feed gas flow rates (FR) was varied from 2 to 10. Additional information regarding the experimental conditions and procedures is presented by Collins and coworkers (1996).

Catalyst deactivation occurred to varying degrees in both the membrane and conventional reactor experiments. The catalyst was reactivated by passing air through the system at 723 K or 748 K. Following catalyst reactivation, the same time schedule was followed for the membrane and conventional reactor experiments in order to compare their performance.

Results and Discussion

Results of Gas Permeation Experiments

Gas permeation experiments were performed during the course of the membrane reactor studies to evaluate the membrane performance. Prior to initiating the reactor experiments, pure gas permeation experiments were conducted with hydrogen and nitrogen at 723 K or 773 K. Results of these experiments are summarized in Table 1.

Table 1
Results of Initial Pure Gas Permeation Experiments[1]

	Pd Memb. #1[2]	Pd Memb. #2[2]	Silica Memb. #1	Silica Memb. #2	Silica Memb. #3	Silica Memb. #4	Silica Memb. #5
P_H	0.0024	0.0071	0.0016	0.0031	0.0032	0.0026	0.0013
$\alpha_{H2/N2}$	770	1920	10.2	12.8	18.8	15.2	11.6

[1] Units for the hydrogen permeance (P_H) are cm^3 (STP)/s•cm^2•cm Hg.

[2] Hydrogen permeance values for the palladium membranes are listed in units of cm^3 (STP)/s•cm^2•cm Hg instead of cm^3 (STP)/s•cm^2•cm $Hg^{1/2}$ so that they may be compared to the silica membranes. The listed hydrogen permeance values for the palladium membranes are applicable for a tube side hydrogen pressure of 115 cm Hg and permeate side hydrogen pressure of 64 cm Hg.

The palladium membranes had the best initial performance because their hydrogen permeance and hydrogen/nitrogen permselectivity were higher than those obtained for the silica-based membranes. The small amount of hydrogen permeation observed is attributable to defects in the palladium film and/or leakage through the GRAFOIL® seals used in the membrane module. Palladium Membrane #1 was prepared using the standard electroless plating procedure while Palladium Membrane #2 was prepared with the electroless plating/osmotic pressure procedure. Palladium film thicknesses for the two membranes were approximately 12 μm for Palladium Membrane #1 and 7.5 μm for Palladium Membrane #2. Nitrogen permeances for the two membranes were similar which indicates that the application of osmotic pressure reduces the film thickness required to fabricate palladium membranes with high hydrogen permselectivities. Although the hydrogen/nitrogen permselectivities observed for the silica-based membranes were lower than those obtained for the palladium membranes, the selectivities were significantly higher than the Knudsen diffusion value of 3.74 which indicates that gas permeation was occurring via the molecular sieving transport mechanism.

Hydrogen permeation rates were also monitored during the membrane reactor experiments to evaluate membrane performance under reaction conditions. Hydrogen permeation rates measured during isobutane dehydrogenation experiments conducted at 450°C over an 8 hour time period with Palladium Membrane #2 and Silica Membrane #4 are shown in Figure 1. As shown in Figure 1, the palladium membrane deactivated when it was exposed to reaction conditions. The hydrogen permeation rate decreased significantly with time on stream while at the same time, the hydrogen partial pressure in the effluent (residue) stream from reaction side increased. Therefore, hydrogen was still being generated on the reaction side, but it was not being removed through the palladium membrane. It was possible to reactivate the palladium membrane by flowing hydrogen through the system after the membrane reactor experiments were completed. The hydrogen permeance was generally restored to about half of its original value by flowing hydrogen through the system overnight. The original permeance could then be restored by passing air through the system for 5 minutes at 723 K.

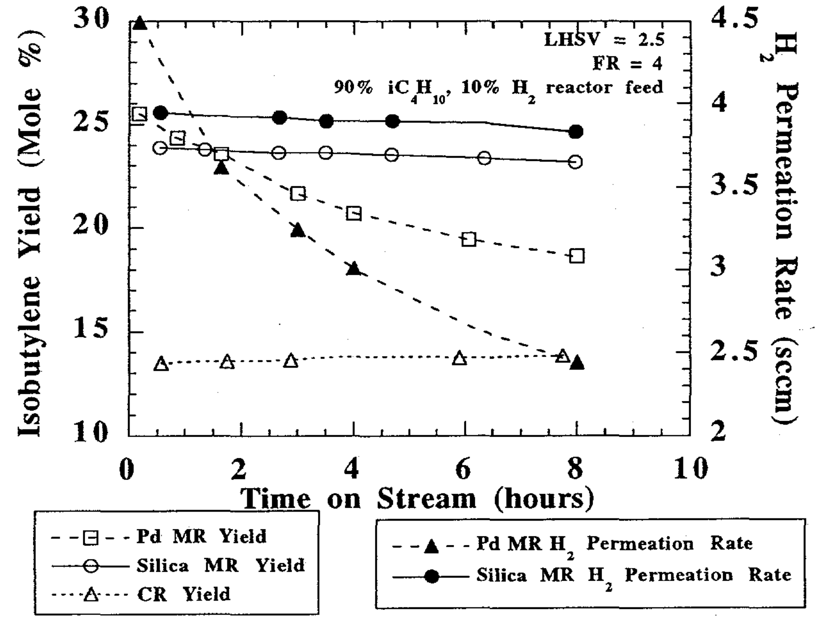

Figure 1 Isobutylene Yields and Hydrogen Permeation Rates Measured in Isobutane Dehydrogenation Experiments Conducted with Silica Membrane #4 and Palladium Membrane #2 at 723 K.

The palladium membranes were also tested for propane and isobutane dehydrogenation at temperatures of 773 K and above. At 773 K, the hydrogen permeation rates decreased with time on stream but permeation rates of the other gases were approximately constant. When the temperature was increased to 798 K, hydrogen permeation rates continued to decrease but permeation rates of the other gases increased with time. This increase in gas permeation rates occurred because defects developed in the palladium film when the membranes were exposed to reaction temperatures above 773 K. Therefore, it appears that a temperature range of 773 to 798 K is the upper limit when palladium membranes fabricated using the conditions employed in this study are used for either isobutane dehydrogenation or propane dehydrogenation.

Although the hydrogen permeance of the silica-based membranes was relatively constant when exposed to reaction conditions compared to the palladium membranes, the permeance of all of the silica-based membranes tested in this study decreased over time. For example, the hydrogen permeance of Silica Membrane #2 decreased by 34 percent after 100 hours of testing while the hydrogen/nitrogen permselectivity remained approximately constant. Similar behavior was observed with the other silica-based membranes. The drop in hydrogen permeance does not result from deactivation/coking due to exposure to reaction conditions because the hydrogen permeance was not recovered when the catalyst was reactivated. Alternative fabrication procedures designed to improve the stability of the silica-based membranes are under investigation in our laboratories.

Results of Membrane Reactor Experiments

Isobutylene yields obtained in the membrane and conventional reactor experiments conducted at 723 K are shown in Figure 1 along with the observed hydrogen permeation rates. The isobutylene yields for the palladium membrane decreased with time while those for the silica-based membrane were relatively constant which indicates that membrane deactivation rather than catalyst deactivation is responsible for the reduction in palladium membrane reactor yields at this temperature. In their study of isobutane dehydrogenation in a palladium-ceramic membrane reactor, Matsuda and coworkers (1993) concluded that catalyst deactivation rather than membrane deactivation (hydrogen permeance) was the limiting factor. There are several differences between the present study and the study performed by Matsuda and coworker's which may account for the discrepancy in results and conclusions. First, the catalysts used in the two studies were different so catalyst deactivation rates are expected to be different. The space velocities used by Matsuda and coworkers were also approximately 5 times lower than those reported in Figure 1, and the hydrogen permeation rate is more sensitive to changes in hydrogen permeance when higher space velocities are used. In addition, Matsuda and coworkers only performed experiments over a one hour time period. As shown in Figure 1, the hydrogen permeance continues to decrease with time on stream after one hour. Finally, the procedure used by Matsuda and coworkers to determine hydrogen permeances following exposure to reaction conditions is not clear. In our study, we were not able to obtain a value for the hydrogen permeance directly following the conclusion of membrane reactor experiments because it increased as soon as the membrane was exposed to hydrogen.

Isobutylene yields and isobutylene reaction selectivities obtained with Silica Membrane #5 are shown in Figure 2 as a function of the LHSV. An isobutylene yield of 56 mole percent was obtained in the membrane reactor at an LHSV of 0.9 (catalyst volume = 2 cm^3, catalyst wt. = 1 g, inlet isobutane flow rate = 6.9 cm^3 (STP)/min) compared to a yield of approximately 40 percent in a conventional reactor operated with the same LHSV. The difference between membrane and conventional reactor yields decreased as the LHSV increased. At the more practical LHSV of 1.8, the membrane reactor yield was only 48 mole percent compared to a yield of 39 percent in the conventional reactor.

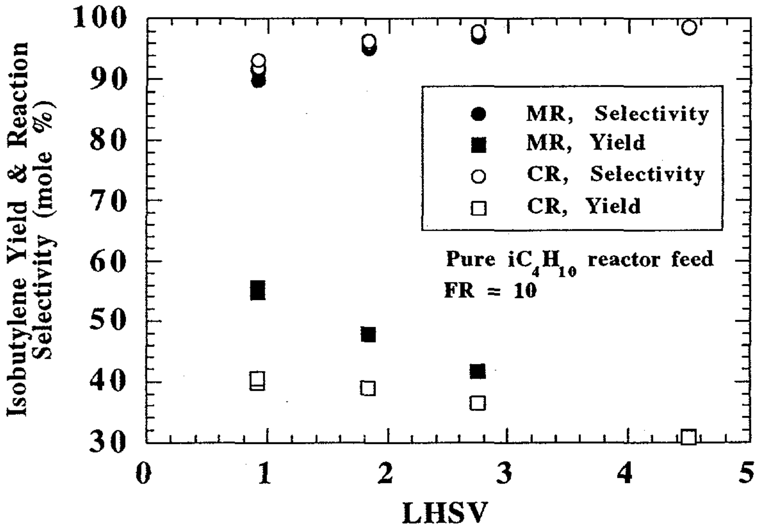

Figure 2 Isobutylene Yield and Reaction Selectivity Versus LHSV For Dehydrogenation Experiments Conducted at 798 K with Silica Membrane #5 and Conventional Reactor.

As shown in Figure 2, there was no significant difference in the isobutylene reaction selectivities between the membrane and conventional reactors at any particular LHSV. However, for a constant value of the isobutylene yield, the membrane reactor had a higher isobutylene reaction selectivity since the desired yield was achieved at a higher LHSV where there was less residence time for undesired side products to form. For example, an isobutylene yield of 42 mole percent and reaction selectivity of 97 mole percent was achieved in the membrane reactor at an LHSV of 2.75 compared to a yield of 40.5 mole percent and reaction selectivity of 93 mole percent in the conventional reactor operated with an LHSV of 0.9. Therefore, a membrane reactor can achieve a desired value of the isobutylene yield with a smaller reactor volume and higher reaction selectivity than a conventional reactor.

Isobutylene yields obtained in experiments conducted at 773 K with Silica Membranes #4 and #5 are shown in Figure 3 as a function of time on stream. Due to its greater hydrogen permeance, the isobutylene yields for Silica Membrane #4 were expected to be higher than those for Silica Membrane #5. However, the yields for Silica Membrane #5 were unexpectedly higher than those obtained with Silica Membrane #4 because catalyst deactivation was a significant problem when Silica Membrane #4 was tested at this temperature. Apparently, the greater hydrogen removal obtained with this membrane was offset by the increased rate of catalyst deactivation which resulted from the reduced hydrogen concentration in the catalyst bed. Therefore, for any given catalyst, the best membrane is not necessarily the membrane with the greatest hydrogen permeance. The effect of hydrogen removal on catalyst deactivation rates must also be considered. Sheintuch and Dessau (1996) have also noted that isobutylene yields in experiments conducted with a palladium-ruthenium alloy tube passed through a maximum with increasing hydrogen concentration in the catalyst bed.

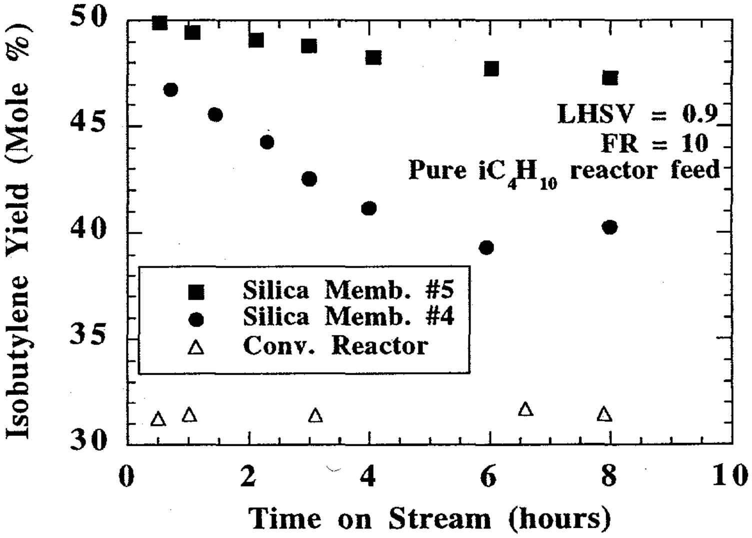

Figure 3 Isobutylene Yield Versus Time on Stream For Dehydrogenation Experiments Conducted at 773 K with Silica Membranes #4 and #5.

Propane dehydrogenation experiments were also performed with Silica Membranes #1, 2, and 3. Detailed information regarding the results of these experiments is presented by Collins and coworkers (1996). Results of the propane dehydrogenation study were similar to those obtained in isobutane dehydrogenation in that only moderate improvements in propylene yields were obtained when the membrane reactors were operated at a practical LHSV. Catalyst deactivation was a significant problem because higher temperatures than those employed in the isobutane dehydrogenation study were required to obtain reasonable propylene yields.

Improvements in the hydrogen permselectivity of the silica-based membranes are needed in order to reduce the amount of isobutane and propane that permeate through the membrane and reduce back permeation of the sweep gas. Permeation losses of the reactants ranged from approximately 5 to 20 percent depending on the specific membrane tested and the LHSV. The permeation of reactants reduces the yield to olefins since the dehydrogenation reactions do not occur on the permeate side. Nitrogen concentrations in the outlet (residue) stream from the membrane reactor ranged from approximately 5 to 35 mole percent which would create a downstream separations problem if improvements in the hydrogen permselectivity are not made.

Conclusions

Pure palladium thin films are not a promising membrane candidate for either isobutane or propane dehydrogenation membrane reactors because the palladium deactivates when exposed to reaction conditions. Future research should focus on the identification and preparation of thin film palladium alloy materials which have a greater resistance to deactivation than pure palladium and sufficient hydrogen permeance. Silica-based membranes appear to be a promising candidate for these reactions provided their long term stability can be improved and their hydrogen permselectivity can be increased without a significant reduction in hydrogen permeance. Improvements in catalyst stability are also required in order to operate the catalyst bed under the lower hydrogen and higher olefin concentrations of the membrane reactor with acceptable catalyst deactivation rates.

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