The Dehydrogenation of Cyclohexane by the Use of a Porous-glass Reactor††

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The dehydrogenation of cyclohexane was studied by the use of a double tubular reactor; the inner tube was made of porous glass, and the outer tube, of non-porous glass. The Pt/Al_2O_3 catalyst was placed inside the inner tube. It was demonstrated that dehydrogenation proceeded beyond the equilibrium conversion to be expected in the absence of a porous tube, by separating the hydrogen produced from the central reaction zone through the porous tube. When the reaction rate was so high that the reactant gas reached equilibrium near the inlet of the reactor, the dehydrogenation conversion became greater (more than twice the equilibrium conversion) as the flow rate in the inner path decreased and the flow rate in the outer path increased. The experimental data obtained by using the porous reactor were well reproduced by a computer simulation based on a simple model, in which such parameters as the flow rate, the gas permeability, and the reaction rate, were considered. The potential application of the present porous-reactor system was also discussed.

The dehydrogenation reaction, which usually requires a high reaction temperature because of the restriction caused by equilibrium, can be expected to proceed seemingly beyond equilibrium if the hydrogen produced by the reaction is removed selectively. Based on this idea, a palladium-alloy membrane was successfully applied to hydrogenation and dehydrogenation reactions.[1,2] Palladium acts as a barrier through which only hydrogen penetrates, and also as a catalyst. However, this membrane may not be used when palladium causes undesirable side-reactions and when poisons to palladium like sulfur are present. In these cases, porous glass[3] is sometimes very useful as the separation medium, since porous glass is fairly inert against chemicals and still has considerable physical strength. The permeability of gases can be controlled to some extent by changing the size and number of pores. Because of these advantages, the permeability of gases through porous glass has already been studied,[4] and application to isotope separation has been attempted.[5] Recently a porous-glass reactor was used to increase the hydrogen yield in the thermal decomposition of hydrogen sulfide.[6,7]

In the present study, a porous-glass reactor was constructed and the effectiveness of the reactor was experimentally examined by applying it to the dehydrogenation of cyclohexane. To confirm the effectiveness, the observed results were semi-quantitatively compared with the results of a computer simulation. On the basis of this comparison, the desirable properties of porous glass and the operation conditions are discussed.

Experimental

The porous reactor used in the present study was a double tubular reactor, as is illustrated in Fig. 1. The inner tube was made of porous Vycor glass (Corning Code No. 7930, outer diameter: 17.3 mm, wall thickness: 1.4 mm), with a mean pore size of 40 Å. The outer tube was ordinary non-porous Pyrex glass. Additional non-porous glass tubes were inserted tightly inside the upper and lower parts of the inner tube in order to minimize the permeation of gases outside the reaction zone (catalyst bed). By the insertion of these two tubes, the gas permeation outside the reaction zone was made negligible. 11 g of a Pt/Al_2O_3 catalyst (Pt: 0.38 wt%) in the form of 1.6 mm beads were packed in the inner tube (the length of the catalyst bed was 14 cm). Prior to the reaction, the catalyst was treated at 400 °C in an oxygen stream for 1 h and then reduced in a hydrogen stream for 1 h. No change in the catalytic activity during the reaction was detectable. Nitrogen, to which 16.0 ± 0.5 mol% cyclohexane was mixed by passing it through an evaporator-saturator kept at 31 °C, was fed into the inner tube (inner path), and pure nitrogen into the outer path (path between the two tubes). The reaction temperature, as measured by an iron-constantan thermocouple, was 215—218 °C at the center of the catalyst bed. The outlet gases of the inner and outer paths were sampled by operating the valves and analyzed by two gas chromatographs directly connected to the valves. The material balance of the reaction was above 90%. The total pressures in the inner and outer paths were both close to 1 atm. A non-porous reactor, both tubes of which were non-porous glass of the same sizes as those of the porous reactor, was also used for purposes of comparison.

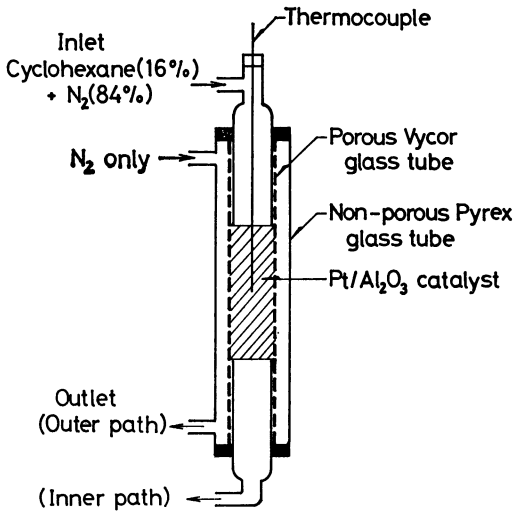

Fig. 1. Schematic diagram of porous reactor.

Results and Discussion

Permeability of Gases. If the diffusion of gases through the porous glass tube is effusion (Knudsen

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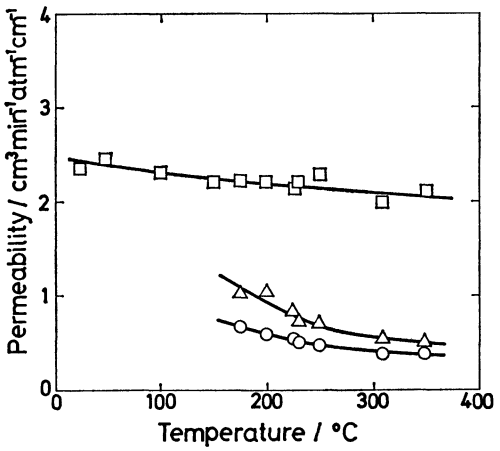

Fig. 2. Gas permeability of the porous tube as a function of temperature.
○: Cyclohexane, △: benzene, □: hydrogen.

flow), the rate of gas permeation can be described by:[4,5,8]

$$N_i = Q_i(P_i - p_i) \quad (1)$$

where N_i is the molar flow rate of the i component per unit of length of the porous glass tube, Q_i is the permeability of the i component, and P_i and p_i are the partial pressures of the inner and outer paths respectively. The permeability, Q_i, depends on the molecular weight, M_i, as in Eq. 2:

$$Q_i = \frac{a}{\sqrt{M_i T}}, \quad (2)$$

where T is the absolute temperature and a is a constant which depends on the properties of the porous barrier. The permeabilities, Q_i, of cyclohexane, benzene, and hydrogen for the porous glass tube used in the present work were measured in the following way. Mixtures of the three gases diluted with nitrogen were conducted into the inner tube loaded with glass beads in the same form as the catalyst, and then the outlet compositions of the reactor were analyzed. The Q_i value was calculated by means of Eq. 3:

$$f_{iL} = Q_i\left(\frac{P_{i0}+P_{iL}}{2} - \frac{p_{iL}}{2}\right)L, \quad (3)$$

where f_{iL} is the flow rate of the i component in the outlet gas of the outer path. The suffixes 0 and L indicate the inlet and outlet respectively, and L is the length of the reactor zone (catalyst bed). By increasing the flow rates in both paths, the changes in the flow rates along the reactor caused by gas permeation were made negligible. In this case, Eq. 3 is readily obtained by integrating Eq. 1 from l (the distance from the inlet of the catalyst bed)=0 to L.

Figure 2 shows the temperature dependence of the permeability. The permeation of hydrogen was obviously dominant, and hydrogen was effectively separated from the other two gases at higher temperatures. The Q_i ratio, as calculated from the molecular weight by means of Eq. 2, is cyclohexane:benzene:hydrogen= 1.00:1.04:6.48, while the observed ratio at 230 °C was 1.0:1.4:4.4. Hydrogen permeation was less preferential than was expected from Eq. 2. Moreover, the permeabilities of cyclohexane and benzene increased rapidly at low temperatures, indicating that diffusion processes other than effusion (probably surface diffusion[4]) increase for cyclohexane and benzene at lower temperatures.

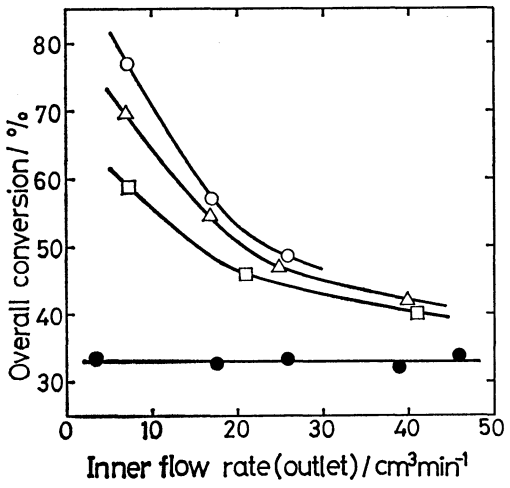

Fig. 3. Comparison of porous and non-porous reactors as applied to dehydrogenation of cyclohexane at 215 °C.
Open symbols: porous reactor [outer flow rate (outlet) was ○: 110 cm³ min⁻¹, △: 60 cm³ min⁻¹, and □: 20 cm³ min⁻¹]. ●: Non-porous reactor.

Dehydrogenation of Cyclohexane by the Use of a Porous Reactor. Comparison of Porous and Non-porous Reaction: The overall conversions obtained with the porous and non-porous reactors are compared in Fig. 3 as functions of the inner and outer flow rates. The overall conversion, X, for the porous reactor is defined and calculated by means of:

$$X = \frac{F_L P_{BL} + f_L p_{BL}}{F_L(P_{CL}+P_{BL}) + f_L(p_{CL}+p_{BL})}, \quad (4)$$

where F and f are the inner and outer flow rates respectively. The suffixes C and B denote cyclohexane and benzene components respectively, while the suffix L indicates the values at the outlet. The relation of the conversion *vs.* W/F obtained with the non-porous reactor showed that the catalytic activity was so high that the reactant gas reached equilibrium within 2 cm from the inlet of the catalyst bed. Consequently, the conversion for the non-porous reactor was constant in Fig. 3 and independent of the inner flow rate. Figure 3 shows clearly that the conversion for the porous reactor was higher than that for the non-porous reactor, which gave an equilibrium conversion. The lower the inner flow rate was, and the higher the outer flow rate was, the greater the overall conversion became. The highest conversion was more than twice the equilibrium conversion which would be expected in the absence of the preferential separation of hydrogen.

Effects of Inner and Outer Flow Rates. The outlet-gas compositions in the inner and outer paths are plotted against the inner flow rate in Fig. 4, together with the conversion. In these experiments, the outer

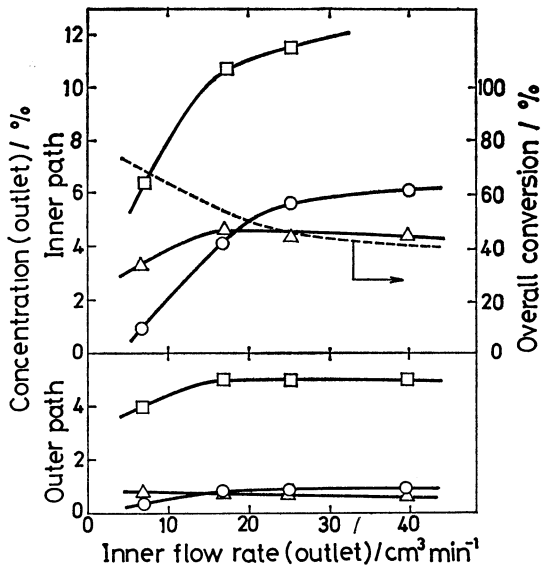

Fig. 4. Effects of inner flow rate on the composition at outlet and overall conversion.
Temperature: 215 °C, outer flow rate (outlet): 60 $cm^3\ min^{-1}$. ——: Composition, - - -: overall conversion, ○: cyclohexane, △: benzene, □: hydrogen.

flow rate was kept constant at 60 $cm^3\ min^{-1}$. The following things may be noted in this figure: (i) The hydrogen concentration in the outer path was much higher than the concentrations of cyclohexane and benzene in the outer path. This dominant permeation of hydrogen into the outer path is the reason why higher conversions were obtained for the porous reactor. (ii) At low inner flow rates, the conversion was high, and the concentrations of hydrogen and cyclohexane in the inner path were very low. The residence time of the reactant gas was probably so high as to remove sufficiently the produced hydrogen from the reaction zone, resulting in the marked increase in the conversion. (iii) The hydrogen concentration in the outer path decreased at a low inner flow rate, in spite of the sufficient removal of hydrogen from the inner path to the outer. This was, however, due to the insufficient supply of the reactant; therefore, it is not contradictory.

The higher conversions at high outer flow rates shown in Fig. 3 are apparently caused by the dilution of hydrogen in the outer path; hydrogen permeation is accelerated by the greater difference in the partial pressure of hydrogen between the inner and outer paths (see Eq. 1). In fact, the hydrogen concentration in the outer path decreased constantly with an increase in the outer flow rate.

Effectiveness of Porous Reactor when the Catalytic Activity is Low. Another experiment was carried out in which the apparent reaction rate was reduced by diluting the Pt/Al_2O_3 catalyst with glass beads of the same size as the catalyst. At 230 °C, the conversion for the porous reactor was 65% (inner flow rate: 7.0 $cm^3\ min^{-1}$, outer flow rate: 90 $cm^3\ min^{-1}$, while that for the non-porous was 40% (flow rate: 7.0 $cm^3\ min^{-1}$). Those results demonstrate that dehydrogenation, even in the case of a low catalytic activity,

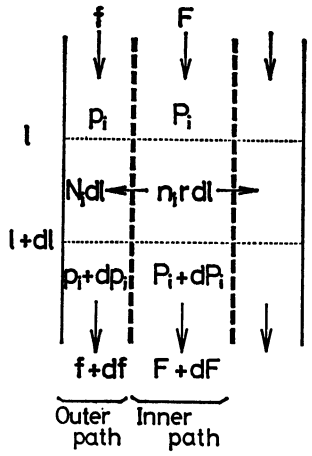

Fig. 5. Material balance in differential length of reactor, l—$l+dl$. F, f, *etc.*: See text.

proceeds beyond the equilibrium conversion (50% at 230 °C) which is to be expected in the absence of the hydrogen permeation, when the porous reactor is used.

Simulation of Reaction with Porous Reactor. A computer simulation was attempted to clarify further the characteristics of the porous reactor obtained experimentally, as has been described in the preceding sections.

Method of Calculation. (i) The rate equation for dehydrogenation was empirically approximated by:

$$r = k\left(P_C - \frac{P^2_{H,e}}{K} P_B P_H\right), \tag{5}$$

where r is the rate of benzene produced; P_i, the partial pressures of cyclohexane (C), benzene (B), and hydrogen (H) respectively; K, the pressure equilibrium constant; $P_{H,e}$, the partial pressure of hydrogen at equilibrium, and k, the rate constant. The k value was experimentally determined as a function of the temperature by the use of the non-porous reactor. The values of K were calculated as a function of the temperature and were experimentally justified in the present temperature region. The conversion calculated by Eq. 5 agreed well with those observed in the W/F range from 0.004 to 0.06 g min cm^{-3} at 200—230 °C. Because the total mass in the inner path changes along the catalyst bed, $P_{H,e}$ was calculated from the gas composition and the K value at every position of the reactor. (ii) The temperature distribution along the catalyst bed was measured (see Fig. 7) and approximated by a biquadratic function of l, the distance from the inlet of the catalyst bed. (iii) The permeation of the three gases was calculated by means of Eq. 1, where the permeabilities, Q_i, measured at 230 °C were used. The permeation of nitrogen was neglected because the reactant gases were very dilute. (iv) By assuming a plug flow in the reactor, a set of equations are obtained from the material balance for the three components in a differential length of the reactor, dl (see Fig. 5). For the inner path,

$$FP_i = (F+dF)(P_i+dP_i) + N_i dl + n_i r dl, \tag{6}$$

where $n_i = 1$, -1, and -3 for i=C, B, and H respec-

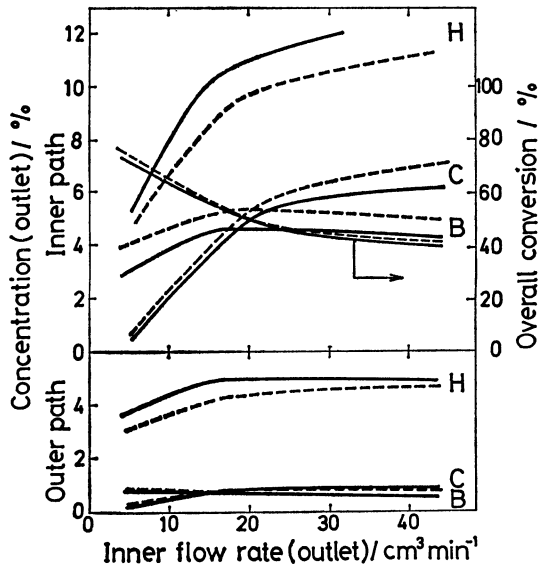

Fig. 6. Comparison of the experimental and simulated results for dehydrogenation of cyclohexane with the porous reactor.
Temperature: 215 °C, outer flow rate (outlet): 60 $cm^3\ min^{-1}$. ——: Experimental, - - -: simulated, C: cyclohexane, B: benzene, H: hydrogen.

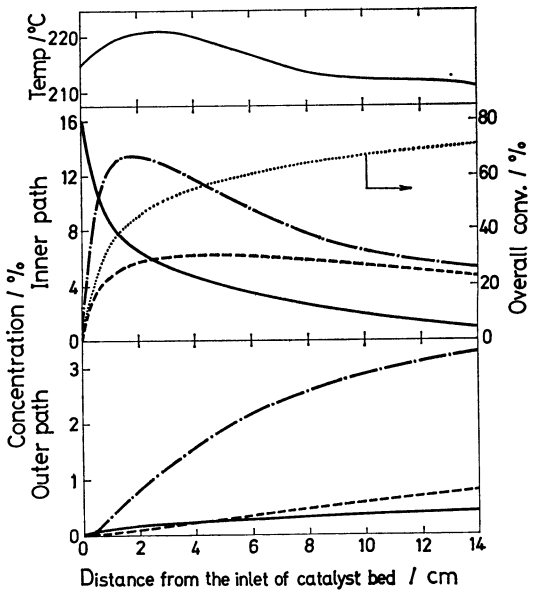

Fig. 7. Change of compositions and overall conversion along the catalyst bed for the porous reactor (simulated).
Inner flow rate (inlet): 7.0 $cm^3\ min^{-1}$, outer flow rate (inlet) 60 $cm^3\ min^{-1}$.
——: Cyclohexane, - - -: benzene, —·—: hydrogen, ·····: overall conversion.

tively. For the outer path,

$$fp_i = (f+df)(p_i+dp_i) - N_i dl \quad (i=C, B, H,). \qquad (7)$$

The flow rates, F and f, in Eqs. 6 and 7 are described in terms of P_i and p_i:

$$F = \frac{F_N}{1-\Sigma P_i} \text{ and } f = \frac{f_N}{1-\Sigma p_i} \quad (i=C, B, H,), \qquad (8)$$

where F_N and f_N are the flow rates of nitrogen (constant) in the inner and outer paths respectively. Equations 6, 7, and 8 are rewritten into six simultaneous differential equations in terms of P_i and p_i (i=C, B, and H); they were solved numerically by the Runge-Kutta method.

Results of Calculation. The calculated results are compared with the observed data in Fig. 6. A good agreement is seen in conversion, and the trend of the outlet compositions is essentially reproduced by the simulation. The simulation data given in Fig. 7 show how the compositions change in the reactor from the inlet to the outlet. Equilibrium is reached within 2 cm from the inlet of the catalyst bed. The hydrogen concentration decreases in the inner path, and increases in the outer path, along the reactor, as expected.

Conclusion

Both the experiments and the simulation proved that the dehydrogenation of cyclohexane proceeds beyond the equilibrium (expected in the absence of a porous tube) by means of the selective separation of hydrogen from the reaction zone by the use of a porous reactor. For example, the conversion for the porous reactor was 80% at 215 °C as compared with the equilibrium conversion of 35% for the non-porous reactor. Since the 80% conversion corresponds to the equilibrium conversion at 255 °C, the porous reactor reduces the reaction temperature by 40 °C. However, a low inner flow rate and a high outer flow rate are necessary to obtain a high conversion. The former is disadvantageous for the reaction efficiency, and the latter for the recovery of hydrogen, because of its low concentration. Thus, the efficiency of the porous reactor is significantly dependent on the permeation rate. It is, therefore, important, for the improvement of efficiency, to select a material with a high and highly selective permeability and to design a reactor with a large area for gas permeation. When such factors as the reaction rate, the permeability, *etc.* are once known, a computer simulation such as is shown in this study may be helpful for the design of a more efficient reactor and the optimization of the operation conditions.

With the aid of a porous reactor, characterized by simultaneous reaction and separation, the reaction temperature can be lowered. By taking advantage of this, the porous reactor may be used for the conversion of low-temperature thermal energy to hydrogen or other chemical energies. The reduction of the reaction temperature is also suitable for reactions that use thermally unstable catalysts or reactants.

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References

1) V. M. Gryaznov, V. S. Smirnov, and M. G. Slinko, "Proc. 5th Int. Congr. Catal., Miami Beach, 1972," North-Holland, Amsterdam (1973), p. 1139; "Proc. 7th Int. Congr. Catal., Tokyo, 1980," Kodansha, Tokyo, and Elsevier, Amsterdam (1981), p. 224.

2) B. J. Wood, *J. Catal.*, **11**, 30 (1968).

3) T. Kyono and A. Makishima, *Zairyo Kagaku*, **12**, 33 (1975).

4) S-T. Hwang and K. Kammermeyer, *Separation Science*, **1**, 629 (1966); *Can. J. Chem. Eng.*, **44**, 82 (1966).

5) K. Higashi, H. Ito, and J. Oishi, *J. Nucl. Sci. Technol.*, **1**, 298 (1964); K. Higashi, A. Oya, and J. Oishi, *ibid.*, **3**, 51 (1966).

6) M. E. D. Raymont, *Hydrocarbon Process.*, **54**, 139 (1975).

7) M. Dokiya, T. Kameyama, and K. Fukuda, *Denki Kagaku*, **45**, 701 (1977).

8) J. Shacter, E. Von Halle, and R. L. Hoglund, "Diffusion Separation Methods," in "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd ed, ed by A. Standen, Interscience, New York (1965), Vol. 7, p. 91.