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Membrane Reactor Using Microporous Glass-supported Thin Film of Palladium.[1) Application to the Water Gas Shift Reaction

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A composite membrane consisting of palladium thin film and a microporous-glass tube was applied to a membrane reactor. In the water gas shift reaction, the membrane reactor gave the conversion level exceeding the equilibrium one for the closed system as a result of the separation of hydrogen produced.

Equilibrium of reversible chemical reactions can be shifted toward the product side by changing reaction conditions such as temperature and pressure. It is also possible to accomplish a similar shift of chemical equilibrium by separating any of the products selectively using a membrane incorporated with the reactor. On the basis of this concept, ceramic and metallic membranes having a function of hydrogen separation have been applied to the membrane reactor.2-5) Ceramic membranes such as porous Vycor glass are fairly inert against chemicals and have considerable mechanical strength, so that they are useful as the separation media. As the separation mechanism by ceramic membranes is based upon the Knudsen diffusion, however, any reactants and products can pass through the membrane. Thus, there is a limitation to the attainable level of reaction, when the ceramic membrane reactor is used. In contrast, metallic membranes, especially palladium exhibit extremely high selectivity for hydrogen separation. Because of this property, palladium membranes have been applied to separation and purification of hydrogen for semiconductor and metallurgical industries. It was shown by Itoh5) that the equilibrium in dehydrogenation of cyclohexane was shifted to the product side by use of a palladium membrane reactor. It was suggested on the basis of a computer simulation that the shift of equilibrium in his reactor system was strongly related to the rate of hydrogen permeation due to a relatively thick membrane used.6) Although the decrease in the thickness of palladium film increases the rate of hydrogen permeation, however, it is difficult to make a thin palladium film because of the small mechanical strength.

In order to overcome this disadvantage, we have developed a composite membrane (Pd/MPG) consisting of palladium and a microporous-glass tube. We reported in a previous paper7) that the Pd/MPG exhibited a high permeability to hydrogen compared with commercial palladium membranes. The purpose of the present work was to study the applicability of the Pd/MPG to a membrane reactor, in which the water gas shift reaction (WGSR) was carried out as a model reaction.

Microporous-glass tubes (o.d. 10 mm, thickness ca 0.8 mm) with an average pore size of 300 nm were supplied by Ise Chemical Industry Co. The outer surface of the tube was wholly covered with palladium by the electroless-plating method, which was previously shown in detail.[7)] The average thickness of palladium film was determined to be 20 μm from the plated amount and the density of palladium.

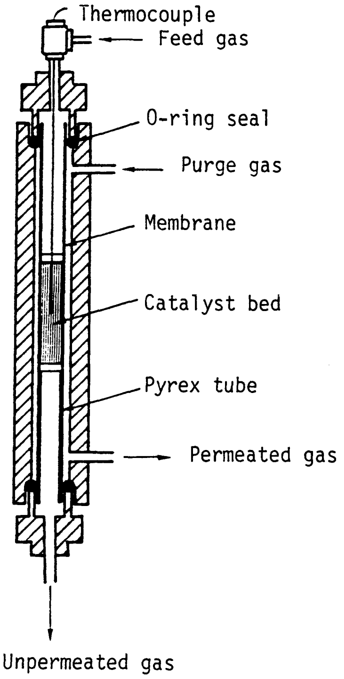

Fig. 1. Pd/MPG membrane reactor.

Reactions were carried out in a continuous flow reactor with a fixed bed of catalyst. Figure 1 shows the detailed structure of the Pd/MPG membrane reactor used in this study. The Pd/MPG was fixed with O-rings at both ends of the tube. A commercial Fe_2O_3-Cr_2O_3 catalyst designated as Girdler G-3 was used in this study and was packed in 8 cm height inside the membrane. To allow the permeation of hydrogen solely in the zone of catalyst bed, a nonporous glass tube was set under the catalyst bed to prevent the contact of reaction mixtures with the membrane. Reactions were carried out at 673 K. The catalyst was heated in a stream of argon and reduced at 673 K for 2 h in a stream of hydrogen diluted with steam prior to reaction. The mixture of carbon monoxide and steam in a molar ratio of 1 was fed to the catalyst bed and argon was introduced to the outside of the membrane in order to sweep the permeated hydrogen. The composition of product gases was determined by means of gas chromatography after the measurement of volumetric flow rates.

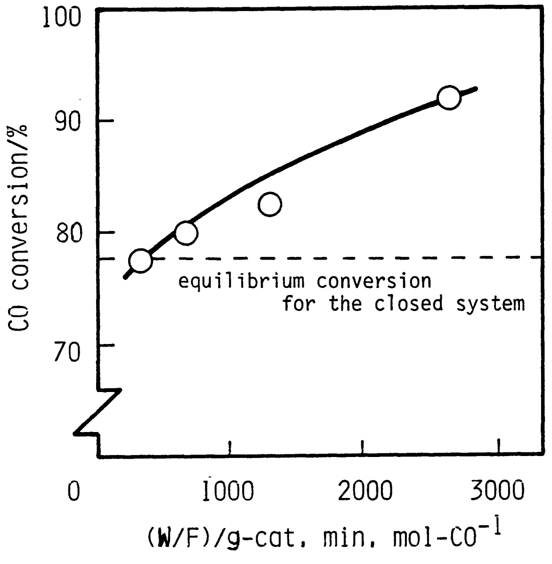

Fig. 2. Acceleration of the water gas shift reaction at atmospheric pressure by use of the Pd/MPG membrane reactor. Reaction conditions: catalyst (Girdler G-3) 3.0 g; temperature, 400°C; H_2O/CO ratio, 1. Sweep argon: flow rate, 400 ml min^{-1}; pressure, 1 atm.

Figure 2 illustrates %conversion of carbon monoxide as a function of time factor (W/F). The equilibrium conversion of carbon monoxide for the closed system was attained at W/F = 330 g-cat min mol-CO^{-1} under these conditions. At higher W/F, the

Pd/MPG membrane reactor gave the conversion level exceeding the equilibrium one and increased with increasing time factor. Concurrently, the molar fraction of hydrogen in unpermeated gases decreased with increasing W/F. This means that the relative rate of hydrogen permeation to hydrogen formation increased with increasing W/F as a result of increased contact between hydrogen and the membrane.

The equilibrium conversion of carbon monoxide is a function of the molar fraction of hydrogen in the reaction system. On the other hand, the permeation of hydrogen is related to the difference in the partial pressure of hydrogen between inside and outside of the membrane. Thus, the pressure difference between inside and outside of the membrane will markedly influence the position of equilibrium as a result of the change in the molar fraction of unpermeated hydrogen. Figure 3 shows the effect of reaction pressure inside the membrane on the conversion level

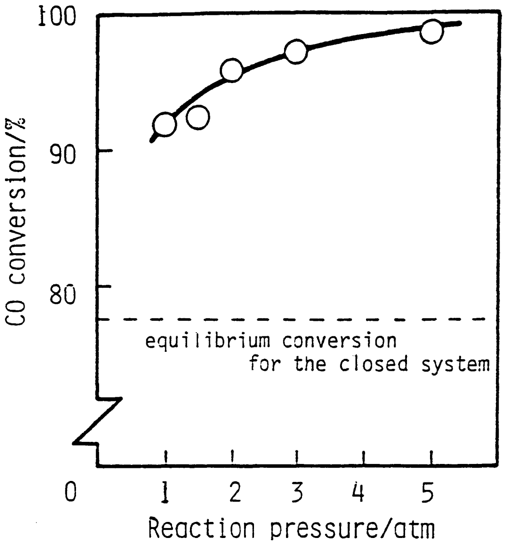

Fig. 3. Effect of reaction pressure on conversion of carbon monoxide. Reaction conditions: catalyst (Girdler G-3), 3.0 g; temperature, 400°C; H_2O/CO ratio, 1; feed rate of carbon monoxide, 25 ml min^{-1}. Sweep argon: flow rate, 400 ml min^{-1}; pressure, 1 atm.

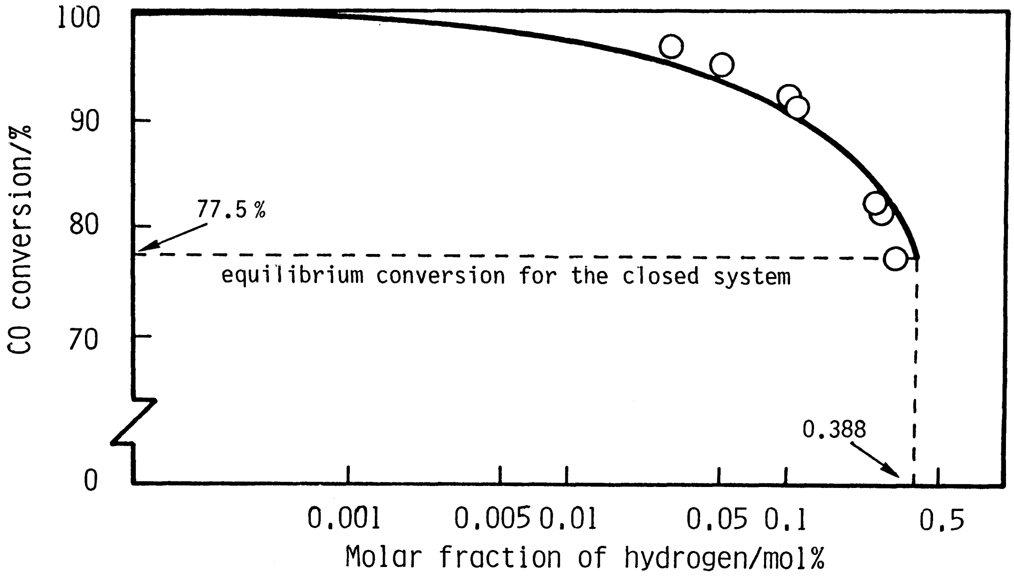

Fig. 4. Conversion of carbon monoxide as a function of the molar fraction of hydrogen at 400°C. ○, experimental results; solid line represents the theoretical values on the assumption of the chemical equilibrium (Kp = 11.92).

of carbon monoxide. The conversion level increased with reaction pressure, and finally reached about 100% at 5 atm. As shown in Fig. 4, the experimentally obtained conversion data overlapped on the theoretical curve calculated as a function of the molar fraction of hydrogen. It is implied that equilibrium is accomplished for this reaction system under these conditions. The partial pressure of hydrogen in unpermeated gases was found to be almost constant at 0.1 atm for every cases, and there was no appreciable difference in the partial pressure of hydrogen between permeated and unpermeated gases. These results mean that the permeation of hydrogen was fast enough in the present case, compared with the production of hydrogen by the WGSR.

The effectiveness of membrane reactor is influenced by the relative rate of hydrogen permeation to reaction. The catalyst used in this study gave the initial rate of reaction in the order of 1×10^{-2} mol g-cat^{-1} min^{-1}. On the other hand, the rate of hydrogen permeation was determined to be 6×10^{-4} mol cm^{-2} min^{-1} at the pressure difference of 0.5 atm. If the effective area (25.1 cm^2) for hydrogen separation in the present membrane reactor is taken into consideration, the rate of hydrogen permeation is evaluated to be almost of the same order as the rate of reaction. This relation allows the Pd/MPG membrane reactor to attain high conversion levels of carbon monoxide in the WGSR.

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