

CHAPTER III

THEORY

Membrane separation processes have been in practice for a few cascades. Now new applications are being explored on a broad horizon. One of the frontier technology areas is membrane reactor which is sometimes referred as membrane catalyst or catalyst membrane system. It presents a variety of reactor. The technology combines the permselectivity of a membrane with a reaction, particularly a heterogeneous catalytic reactions such as dehydrogenation of alkanes, methane steam reforming, oxidation and hydrogenation. The integration of two unit operation offers advantage not only in terms of system simplification and lower capital cost but also yield improvement and selectivity enhancement. This new technology uses the membrane as catalysts or catalyst support and, at the same time, as a physical means for separating reactants and products, controlled addition of a very active reactant or selectively removing undesirable intermediate reaction product to affect the increased yield and selectivity.

In this chapter, the basic knowledge on inorganic membranes is provided as it is an important component of membrane reactor. The characteristics of gas removal and addition through the membrane can be reflected by its transport mechanism. Finally the concept of membrane reactor including its application areas is described, particular interest is on use of palladium membrane as a barrier to remove hydrogen species through membrane in the dehydrogenation reaction system.

3.1 Membrane definition

A membrane is an interphase between two bulk phases and it controls the exchange of mass transfer between them with differing chemical and physical properties. The membrane phase can be one or a combination of the following: non-porous solid, microporous or macroporous solid with a fluid in the pores.

The exchange between the two bulk phases across the membrane is caused from the presence of a driving force. The most common ones are chemical potential such as pressure and concentration gradients and electrical potential. In typical membrane separation, both organic and inorganic membranes are used for separation operation; however, the membranes have not been used in catalytic reactors to enhance the production of some chemicals. There are a limited number of reactor applications for polymer membranes because of their low operating temperature; hence, inorganic membranes may offer more opportunities over a wider range of operating temperatures.

3.1.1 Type of inorganic membrane

Inorganic membrane can be divided into porous and dense membranes as described in details as followed.

1. Porous membrane

Examples of commercial porous inorganic membrane are ceramic membranes such as alumina, silica and titania, glass membrane and porous materials, such as stainless steel and silver. These membranes are characterized by high permeability but low selectivity.

2. Dense membrane

Palladium and its alloys with ruthenium, nickel or other metals from group VI to VIII, Silver, Zirconia are examples of dense membranes. Palladium-based membranes are found to be permeable only to hydrogen while silver and zirconia are permeable only to oxygen. These membranes have high selectivity but low permeability.

Pd-based membranes have been studied extensively due to their extremely high hydrogen permselectivity. Palladium and other noble metal membranes also retain their thermal and corrosive resistance even at elevated temperature. Pd alloys are preferred over pure Pd as the membrane materials because of several considerations. Firstly, pure palladium can become embrittled after repeated cycles of hydrogen sorption and desorption. Secondly, the hydrogen permeabilities of certain Pd-alloys are higher than those of pure palladium. Thirdly, the catalytic activities of the alloy membranes, in many cases, exceed that of palladium alone. Finally, palladium is very expensive.

3.2 Composite membrane

The general approach in the production of thinner membranes is the provision of mechanical stability without compromising flux. While the use of polymeric supports has been extensively explored because of their smooth pore free surface, the use of ceramic, metal and glass supports seem to be the more preferred option due to their excellent thermomechanical stability. Thin film deposition techniques have made it possible to manufacture composite membranes with excellent mechanical and permselectivity characteristics.

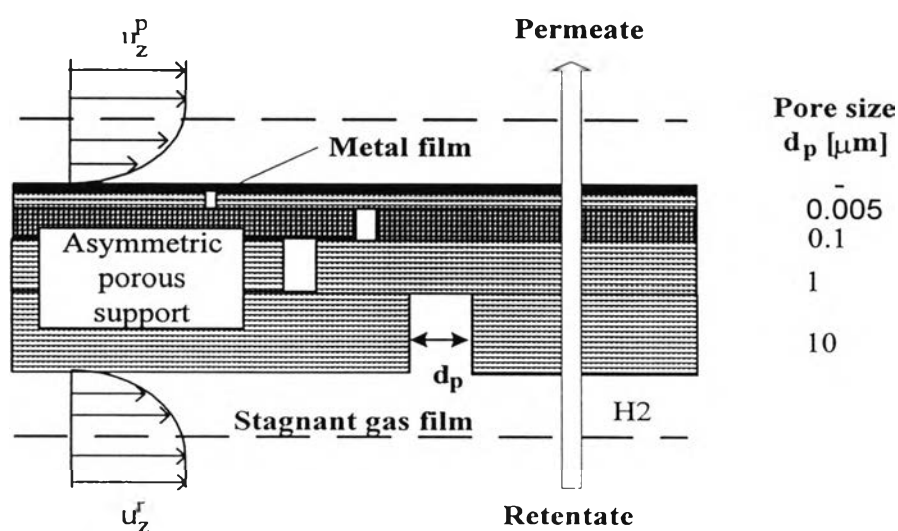


Figure 3.1 Schematic diagram of Pd composite membrane.

3.2.1 Transport mechanism through composite membrane

In general a quantification of the mass transfer through composites of a porous support and a dense separation layer has to take into account the properties of the two materials of porous and dense membranes.

1. Mechanisms of gas transport through porous membranes

Gas permeation across porous membranes takes place by the combination of many flow mechanisms: viscous bulk flow, Knudsen flow, surface diffusion, capillary condensation and molecular sieving. However, in practice only one or a few mechanisms predominate the total transport. Details of each gas permeation mechanism are as follows.

1.1 Viscous flow

Viscous flow takes place when the membrane pore are larger than the mean free path of the permeating gas molecules. Momentum is exchanged among gas molecules during the collision of the gas molecules. As a result, all molecules pass the pores with the average velocity independent of their sizes, shape or masses. This transport is non-separative mechanism.

1.2 Knudsen flow

Knudsen flow regime occurs when pore diameters are smaller than the mean free path of gas to be separated. The collision frequency among gas molecules is negligible compared with that of the gas molecules to pore walls. Thus, each molecule passes the pore at their own velocity. This flow is selective; however, the selectivity of separation in this regime is not high.

1.3 Surface diffusion

This phenomena occurs when there exists the interaction between gases and pore wall. The gases, therefore, are adsorbed on the pore surface, and the migration of the adsorbed film causes an extra flow moving parallel to the gas phase flow. In separation of a gas mixture, some gases are preferentially adsorbed on the pore surface while the other gases are not. The high selectivity is accomplished because of the enhancement of the higher flow rate of adsorbed species in the adsorbed phase.

1.4 Capillary condensation

In porous membrane, capillary condensation occurs when the temperature decreases and/or pressure increases. The adsorbed in both monolayer and multilayer are gradually replaced by the capillary condensed phase. The transport of capillary condensation can be regarded as Poiseuille flow of a viscous liquid filling the pores of the porous media caused by the gradient of capillary force.

1.5 Molecular sieving

Selectivity based on this mechanism is very high because the separation is caused by the size selection. The pore sizes are very small, usually slightly bigger than the size of the diffusion molecule. The smaller molecules in a gas mixture are allowed to pass through the membrane while the larger molecules are obstructed.

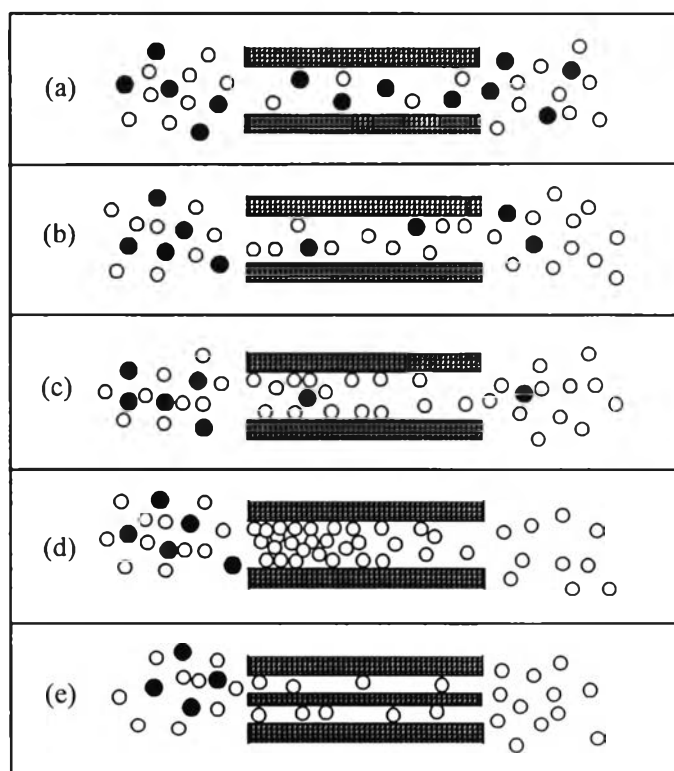


Figure 3.2 Transport mechanisms of gases mixtures through a porous membrane: (a) viscous flow; (b) Knudsen diffusion; (c) surface diffusion; (d) capillary condensation; and (f) molecular sieving [Saracco and Specchia, 1994]

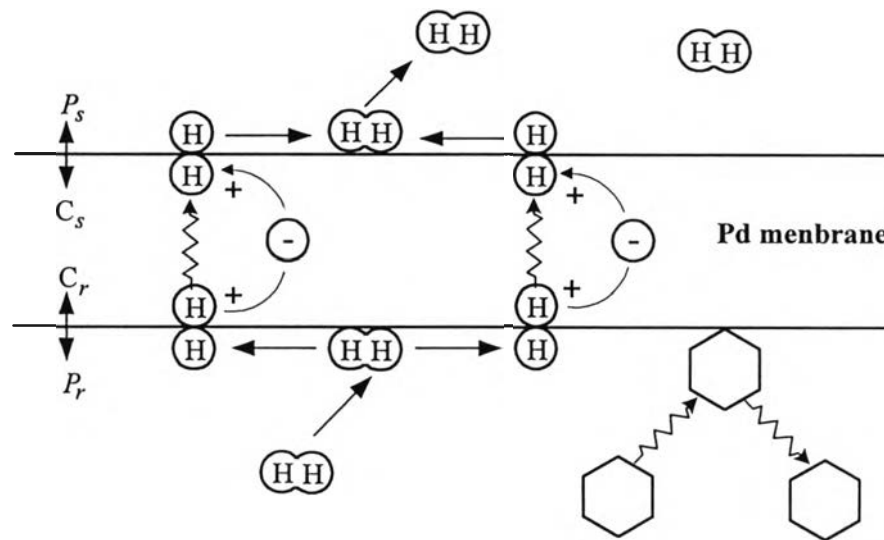


Figure 3.3 Transport mechanism of hydrogen through palladium membrane [Itoh, 1990].

2. Mechanism of gas transport through dense membranes

Since Thomas Graham (1866) discovered that metallic palladium absorbs a large amount of hydrogen, the metal hydride system of which palladium is an important example has been extensively studied. Hydrogen dissolved in a metal hydride system (according to the mechanism to be described below) is considered to behave in an atomic or ionic form which is more reactive than molecular hydrogen in gas phase.

Barrer (1951) proposed that the permeation of hydrogen through a metal (such as palladium) entails three processes, i.e.; 1) dissociative chemisorption of hydrogen on the membrane surface followed by dissolution of the atomic hydrogen in the structural lattice of the metal; 2) diffusion of the dissolved hydrogen in the membrane; and 3) desorption of combined hydrogen atoms as molecules. This can be illustrated in Figure 3.3 where it is shown that only hydrogen undergoes the above solution-diffusion type transport while other molecules are rejected right at the surface of the membrane. The driving force for the difference across the dense palladium membrane is the concentration difference of the dissolved hydrogen in the atomic form. The rate-limiting step is often the bulk diffusion as in the case of palladium membranes.

The transport of oxygen through dense metal (e.g. silver) membrane also follows the same process and generally can be described by solution-diffusion type in term of Fick's first law.

$$J = P[P_1^n - P_2^n] / L \quad (3.1)$$

where J is the permeate flux, P the permeability, L is the membrane thickness and P_i is the gas pressure on the membrane surface, i ($i=1$ or 2 representing the upstream or downstream side). The constant n in Eq. 3.1 is often accepted to be 0.5 assuming that the diffusion through the bulk of the palladium membrane is rate-limiting step compared to hydrogen dissociation and that the concentration of dissolved hydrogen is proportional to the square root of hydrogen pressure. The square root expression in the above equation (Sieverts law) reflects the atomic nature of gas species in the membrane. Considerable experimental evidence, however, suggests a higher value than 0.5 for the exponent n in Eq. 3.1. Hydrogen permeation flux through a palladium membrane may be better correlated to an exponent of $0.68-0.8$ of hydrogen pressures across the membrane (Uemiya.,1991).

3.3 Concepts of membrane reactor

Membrane reactor has the capability of combining reaction and separation in a single unit operation.

3.3.1. Yield-enhancement of equilibrium-limited reactions.

The most common application opportunity of membrane reactor lies in the circumvention of a chemical equilibrium so as to achieve higher per-pass conversions by selective permeation of at least one of the reaction products, through the membrane, as showed in figure 3.4 a,b.

The major potential candidates for such application of inorganic membrane reactors are on dehydrogenation reaction. Since these reactions are endothermic, conversion is favored at high temperatures at the price of significant occurrence of side reactions, which reduce selectivity and lead to catalyst deactivation by coking. By using a membrane reactor, the equivalent conversion could be obtained at lower temperatures thereby suppressing undesired reactions and catalyst deactivation. In addition, since dehydrogenation involves an increase of the over all number of gas molecules of the system, they can be forced to high conversion by reducing the operating pressure, which entails comparatively high reactor volume. As the membrane reactor provides better conversion than conventional reactor higher operating pressures in membrane reactor could be operated with same level of conversion in conventional reactors.

Figure 3.4b showed the coupling of reactions at the opposite membrane sides. This case is the contemporary handling of a dehydrogenation (endothermic) and a hydrogenation (exothermic) at the two sides of a membrane this operation mode could enhance the per-pass conversion of both reaction. Furthermore, the exothermic reaction could in principle supply the heat required for the endothermic one.

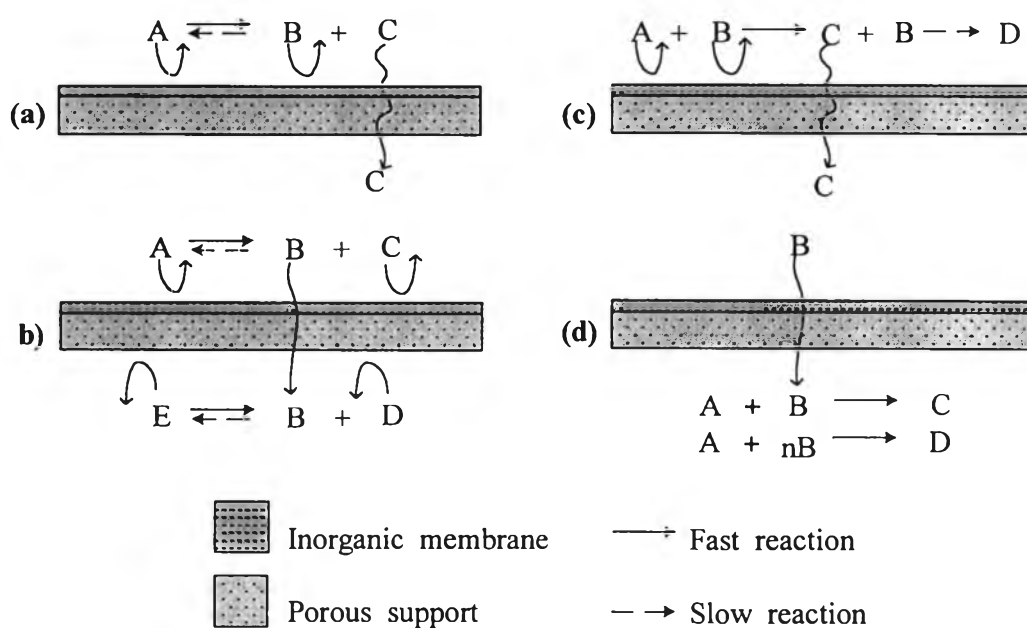


Figure 3.4 Application opportunities of inorganic membrane reactor. Conversion enhancement with catalyst membrane reactors: (a) selective permeation of a reaction product of an equilibrium limited reaction; (b) coupling of reaction. Selectivity enhancement with catalytic membrane reactor: (c) selective permeation of an intermediate, desired product; (d) dosing a reactant through the membrane.

3.3.2. Selectivity enhancement.

The improvement of reaction selectivity is a second field of application of membrane reactors on which most attention of the scientific community is nowadays addressed. In this context, considering consecutive reaction pathways, a permselective membrane could allow permeation of an intermediate product while rejecting either reactants or other undesired products (Figure 3.4c). However, intermediate products (e.g. partially oxidized hydrocarbons) are larger than the complete reaction products (e.g. CO₂) or the reactants themselves (e.g. O₂). This requires the imaginative use of some unconventional permeation mechanisms (e.g. capillary condensation, surface diffusion or multi-layer diffusion), which is rather complex and strongly depends on the particular reaction and membrane considered.

Another opportunity for increase of reaction selectivity lies in the controlled addition of a reactant along the reactor, through either a permselective or a non-permselective membrane as showed in Figure 3.4d. In fact, low oxygen or hydrogen concentrations in the reacting mixture are known to drive certain partial oxidations or hydrogenations to higher selectivities towards intermediate products.

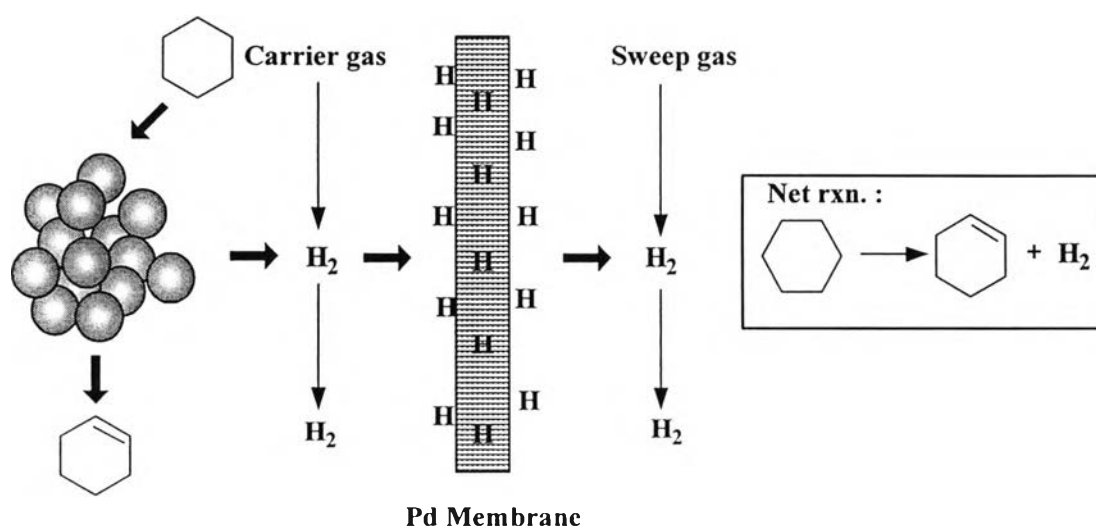


Figure 3.5 Transportation of reaction mixture in dehydrogenation reaction.

3.4 Dehydrogenation in membrane reactor.

Figure 3.5 shows the system of dehydrogenation. When reaction occurs, the reactant must first get to the surface of the catalyst particle, then some adsorption and dissociation must occur on the surface of the catalyst particle. Reaction on the catalyst can proceed producing a permeating product such as H_2 . Now the hydrogen desorbs from the surface of the catalyst, flow past other catalyst particle (or other adsorbing surface) and arrives at the membrane surface. In the case of H_2 on Pd metal, the molecular H_2 must dissociate on the surface and permeates through the Pd layer, then re-associates on the permeate side as H_2 where it is then collected as a pure product. Dissociation on the membrane surface and permeation of the H_2 occur at a feed rate, which permits sufficient time for this permeation to occur. Thus, one sees that operation of a membrane reactor can become mass transfer limited if one does not have a membrane with sufficient flux to satisfy the productivity of the catalyst.