CHAPTER III

THEORY

3.1 Dehydrogenation of ethylbenzene

3.1.1 Nature of ethylbenzene dehydrogenation

Styrene is one of the most important monomers for the manufacture of thermoplastics. The industrial operating conditions of conventional ethylbenzene dehydrogenation reactor are characterized by temperature of 823-923 K, atmospheric or sub-atmospheric pressure, a weight hourly velocity (WHSV) of 0.5-1.2 hr^{-1}, and a molar steam to oil ratio of 6-12. The Fe_2O_3-catalysts doped with K_2O and several metal oxides. Figure 3.1 shows a simplified reaction scheme. Beside the main products styrene and hydrogen, toluene and benzene are formed as side products accompanied by methane, C_2-hydrocarbons, and carbon oxides which are due to oxidation of e.g. carbon and tar deposits by steam.
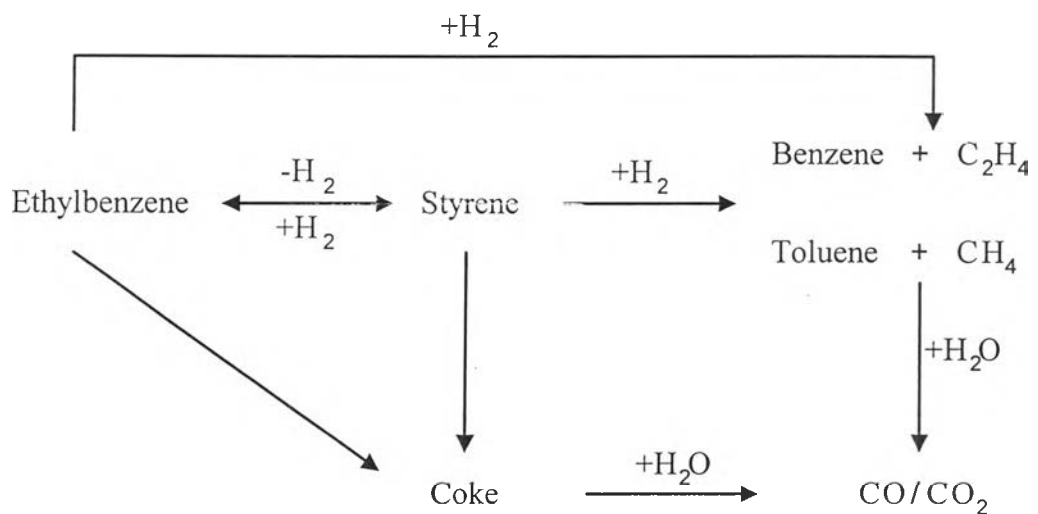
Figure 3.1 Simplified reaction scheme of ethylbenzene dehydrogenation

3.1.2 Catalyst compositions

The different types of catalysts compositions have been used in ethylbenzene dehydrogenation. Several catalysts including oxides of aluminum, cobalt, zinc and manganese have been utilized for this large volume process with the industrial catalyst of choice being potassium-promoted iron oxide operated in steam. The K promoted iron oxide catalyst exhibits an order of magnitude higher activity and stability compared to all other types of catalysts(Coulter *et al.* 1995).

3.1.3 The role of steam

Steam is present in excess with respect to ethylbenzene in all commercial process. The overall effect of the increase of the steam-to-hydrocarbon ratio is to increase the activity, the lifetime and stability of catalyst.

The important roles of the steam in the dehydrogenation of ethylbenzene are summarized as follows:

1. shift of the equilibrium towards higher conversions of ethylbenzene through a decrease of the partial pressure of ethylbenzene;
2. supply of the heat to the endothermic dehydrogenation;
3. decrease of the amount of coke or coke precursors by steam-reforming reactions.

3.1.4 Dehydrogenation of ethylbenzene and oxidation of hydrogen

Dehydrogenation/oxidation process are characterized by the injection of a gas containing oxygen either in the effluent or in the feed of a conventional reactor. Figure 3.2 exemplifies the process chemistry for the case of ethylbenzene dehydrogenation.
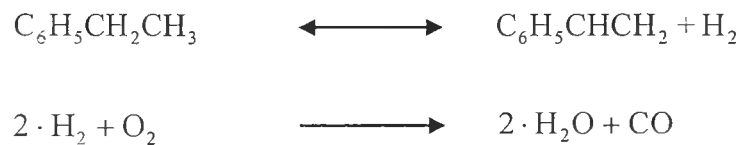
$$C_6H_5CH_2CH_3 \quad \longleftrightarrow \quad C_6H_5CHCH_2 + H_2$$

$$2 \cdot H_2 + O_2 \quad \longrightarrow \quad 2 \cdot H_2O + CO$$

Figure 3.2 Process chemistry for the ethylbenzene dehydrogenation and hydrogen oxidation

The advantages of the hydrogen oxidation coupled to the hydrocarbon dehydrogenation are:

1. the internal supply of the heat for the endothermic reaction;
2. the shift of the dehydrogenation equilibrium by consuming hydrogen, so achieving higher product yields. Higher yields are obtained both by increasing the conversion and by increasing the selectivity.

Membrane reactor has been proposed to modify dehydrogenation and oxidative dehydrogenation process. Membrane is used to separate hydrogen from the product stream and to make it react on the other side of the membrane with an oxygen-containing gas by exothermic reactions. This will provide heat transfer across the membrane to facilitate the endothermic dehydrogenation on the other side of membrane.

3.2 Inorganic membranes

A membrane is an interphase between two bulk phases and it controls the exchange of mass transfer between them. In typical membrane separation, both organic and inorganic membranes are used for separation operation. However, the disadvantages of organic membranes are their low thermal stability, poor mechanical strength, problems of compacting and swelling and poor chemical resistance. As a result, development of membrane made of inorganic materials is considered in this section. Inorganic membranes can be divided into two groups; dense (nonporous) membranes and porous membranes.

3.2.1 Dense membranes

Typical dense membranes are mainly made of thin metal films such as palladium and its alloys, silver and nickel. Membranes prepared with palladium and its alloys can selectively separate hydrogen from other gases. Therefore, palladium membranes have been used in almost all the reaction processes that involved hydrogen such as dehydrogenation of alkanes and steam reforming of methane. All the above mention reactions can exceed the thermodynamic limitation when the reaction are carried out in the palladium membrane reactor. However, the application of palladium membrane is limited by its high cost, difficulty in fabrication, and low permeability as result of thickness required for mechanical durability.

3.2.2 Porous membranes

Porous membranes are superior to dense membranes from the point of view of their permeabilities; nevertheless, the selectivities of the porous membrane are not as

3.2.3 Composite membranes

Composite membranes are used to combine the advantages of the other two types, that is, the high permselectivity of dense membrane and the high permeability of the porous support. Palladium composite membranes, made by deposition of thin palladium layers on a porous support, appear to be the most attractive for used in this application due to their superior permeability and permselectivity.

3.3 Transport mechanisms through dense membranes

The principle property of membranes used in separation applications is the ability to control the permeation of different species. A transport mechanism for gases through dense membrane is explained using the solution-diffusion model.

3.3.1 Solution-diffusion model

The solution-diffusion model, in which permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. A separation is achieved between different permeants because of difference in the amount of material that dissolves in the membrane and the rate at which the material diffuses through the membrane.

The driving forces of gases through dense membranes are pressure, temperature and concentration gradient. The overall driving force producing movement of permeant is the gradient in its chemical potential. Thus, the flux, J_i, of a component, i , is described by the simple equation

$$J_i = -k \frac{d\mu_i}{dx} \qquad (3.1)$$

where $\dfrac{d\mu}{dx}$ is the gradient in chemical potential of component i;

k is a coefficient of proportionality linking this chemical potential driving force with flux.

The chemical potential resulting from the concentration, pressure and temperature can be expressed as

$$d\mu_i = RTd(ln\gamma_ic_i) + v_idP \qquad (3.2)$$

where c_i is molar concentration of component i,

γ_i is activity coefficient linking concentration

P is the pressure

v_i is the molar volume of component i.

In compressible gases, the molar volume changes with pressure; using the ideal gas laws in integrating Eq.(3.2) gives:

$$\mu_i = \mu_i^0 + RTd(ln\gamma_ic_i) + RT\,ln\dfrac{P}{P_{i,sat}} \qquad (3.3)$$

Assumption governing transports through dense membrane by using solution-diffusion model are:

1. fluids on either side of membrane are in equilibrium: that mean there is a continuous gradient in chemical potential form one side of the membrane to the other

2. pressure within a membrane is uniform: that the chemical potential gradient across the membrane is expressed only as a concentration gradient.

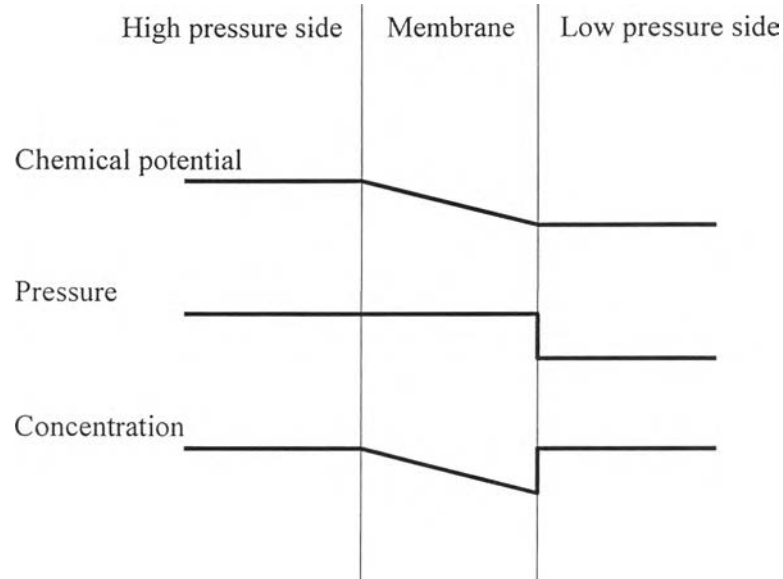The consequence of these assumptions are illustrated Figure 3.3

Figure 3.3 Pressure-driven permeation of a one-component solution through a
membrane according to solution-diffusion transport model.

In these models, the difference in pressure across the membrane does not
produce a gradient in chemical potential. Thus, when a pressure is applied across a
dense membrane, the pressure everywhere within the membrane is constant at the
high-pressure value. Consequently, the major driving force can be expressed as a
concentration gradient within the membrane. The flow that occurs down this gradient
is again express by Eq.(3.1), but, because no pressure gradient exists within the
membrane, Eq.(3.1) can be written, by combining Eq.(3.1) and (3.2) as:

$$J_i = -\frac{RTL_i}{c_i}\frac{dc_i}{dx} \qquad (3.4)$$

This has the same form as Fick's law where term $\frac{RTL_i}{c_i}$ can be replaces by the

diffusion coefficient D_i. Thus:

$$J_i = -Di\frac{dc_i}{dx} \qquad\qquad (3.5)$$

3.3.2 Hydrogen transport through palladium membrane

A widely accepted transport mechanism for hydrogen through palladium membrane is the solution-diffusion model.
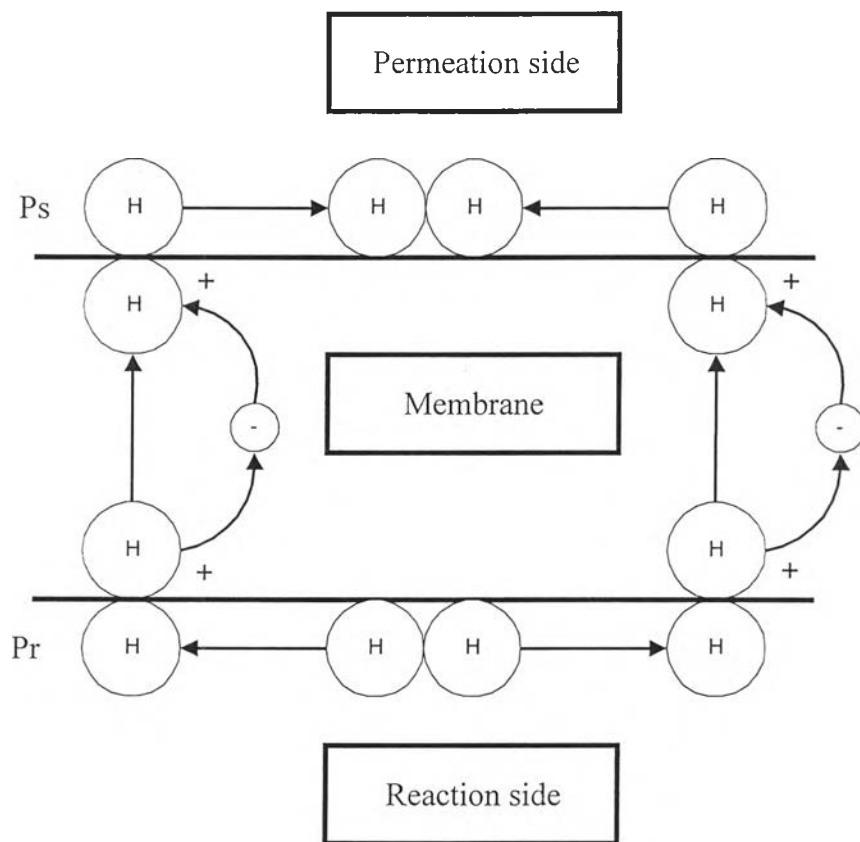

Figure 3.4 Transport mechanism of hydrogen through palladium

The permeation of hydrogen through palladium membrane entails three processes:

1. dissociative chemisorption of hydrogen on the membrane surface followed by dissolution of the atomic hydrogen in the structural a lactic of the metal
2. diffusion of the dissolved hydrogen in the membrane

3. desorption of combined hydrogen atoms as molecules.

This can be illustrated in Figure 3.4 where it is shown that only hydrogen undergoes that above solution-diffusion model while other molecules are rejected at the surface of the membrane. The driving force for the diffusion of hydrogen across the palladium membrane is the concentration difference of the dissolved hydrogen in the atomic form. The transport of hydrogen can be described by solution-diffusion model in term Fick's law:

$$J_i = -\frac{P}{L}\left(P_r^n - P_s^n\right) \tag{3.6}$$

where P is the permeability;

L is the thickness of membrane;

P_{rxn}^n is the pressure on the reaction side;

P_{sep}^n is the pressure on the permeation side.

Finally, Sieverts's law is used to describe the hydrogen transport through the palladium membrane. Consequently, the constant, n, in Eq.(3.6) is 0.5. Thus, the hydrogen flux through the membrane is:

$$J_i = -\frac{P}{L}\left(P_r^{0.5} - P_s^{0.5}\right) \tag{3.7}$$

3.4 Applications of inorganic membrane reactors

The applications of a membrane reactor to heterogeneous gas phase reactions usually employ thermally stable inorganic membranes. Two major areas of applications will be addressed, namely:

1. yield-enhancement of equilibrium-limited reactions: a reaction product is selectively permeating through the membrane, thereby enhancing the per-pass conversion compared to conventional fixed-bed reactors (e.g. dehydrogenations, Figure 3.5a); coupling of reactions at opposite membrane sides(Figure 3.5b);

2. selectivity enhancement: accomplished by selective permeation (Figure 3.5c) or controlled addition(Figure 3.5d) of a reactant through the membrane.
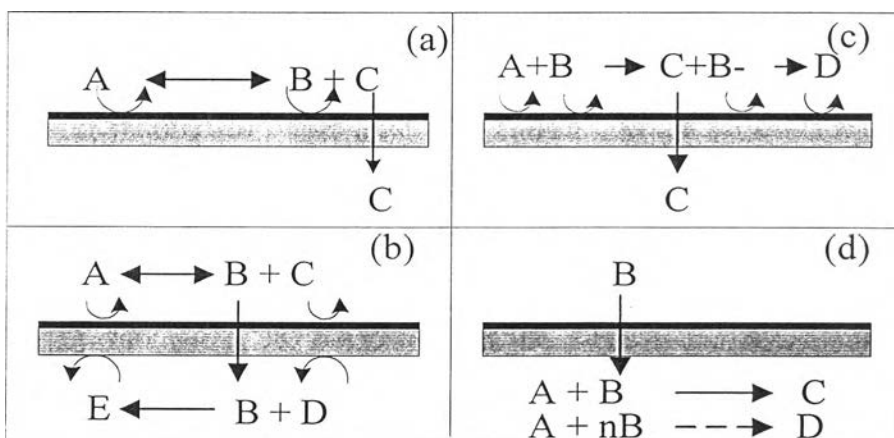

Figure 3.5 Application of inorganic membrane reactors. Conversion enhancement with the membrane reactor: (a) selective permeation of a reaction product of an equilibrium limited reaction; (b) coupling of reaction. Selectivity enhancement with he membrane reactor: (c) selective permeation of an intermediate, desired product; (d) dosing a reactant through the membrane.

3.4.1 Yield enhancement for equilibrium-limited reactions

The most common application opportunity of membrane reactors lies on the yield enhancement for equilibrium-limited reactions. Reactions, which suffer from chemical equilibrium, can achieve higher per-pass conversions by selective permeation, through the membrane, of at least one of the reaction products (Figure 3.5a).

The major potential candidates for such application of inorganic membrane reactors are dehydrogenations. Since these reactions are endothermic, conversion is favoured at high temperatures with the presence of side reactions, which reduce selectivity and lead to catalyst deactivation by coking. By using a membrane reactor, the same conversions could be obtained at lower temperatures thereby suppressing undesired reactions. Further, since dehydrogenations imply an increase of the overall number of gas molecules of the system, they can be forced to high conversions by reducing the operating pressure, which entails comparatively high reactor volume. Such volume could be reduced using a membrane reactor, since equivalent conversion can be operated using higher operating pressures.

Another advantage of the membrane reactor is that the permeated reaction product can be recovered in a quite pure form. However, if the membrane is not permselective enough, the increase of conversion remains limited by the permeability of the reactants, which also affects the purity of the product.

Figure 3.5b shows a further intriguing application opportunity: the coupling of reactions at the opposite membrane sides. A typical case study is the contemporary handling of a dehydrogenation (endothermic) and an oxidation (exothermic) at the two sides of a palladium membrane permeated by hydrogen; this operation mode could enhance the per-pass conversion of the both reactions. Furthermore, the exothermic reaction could be supply the heat required for the endothermic reaction.

3.4.2 Selectivity enhancement

The improvement of reaction selectivity is a second field of application of inorganic membrane reactors. 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 3.5c).

Another opportunity for the increase of the reaction selectivity is based on controlled addition of a reactant along the reactor through a membrane (Figure 3.5d). In fact, low oxygen or hydrogen concentration in the reacting mixture is known to drive partial oxidations or hydrogenations to higher selectivities towards intermediate products.