CHAPTER II

LITERATURE REVIEWS

A membrane reactor has the capability of combining reaction and separation in a single unit operation while a reaction proceeds, a reaction product is selectively removed through the membrane. As a result, the reaction that is limited by equilibrium can exceed the equilibrium conversion found in conventional reactors. The membrane reactor can also be useful in term of selectivity enhancement which can be carried out by selective removal of intermediate product or controlled dosing a reactant through the membrane. There are a number of excellent reviews on catalytic membrane reactors (e.g. Armor, 1998; Gryaznov, 1999; Saracco, *et al.*, 1999; Shu, *et al.*, 1991 and Zaman, *et al.*, 1994). This literature reviews will provide information on types of membranes used in membrane reactor studies and types of membrane reactors.

2.1 Types of membrane

Membranes can be classified broadly into organic and inorganic membranes. In industry, membrane separation has been practiced for a few decades in which most of membranes are organic membranes, mainly polymeric ones. Major applications of the organic membranes are such as microfiltration, ultrafiltration, reverse osmosis and gas separation. However, disadvantages of the organic membranes arise from their low thermal stability, poor mechanical strength and problems on compacting, swelling, and cleaning. As a result, development of inorganic membranes such as metal, ceramic and metal-ceramic composite membranes has been recognized to improve the properties of membranes for harsh conditions.

Both inorganic and polymer membranes are generally used for separation purpose; however, only some of them are applied in catalytic membrane reactors to enhance production of some chemicals. There are a limited number of reactor applications for polymer membranes because of their low upper limit temperature, hence, this review will focus on a variety of inorganic membranes which may offer more opportunities over a wider range of operating temperature.

Inorganic membranes can be categorized into two groups, namely dense (nonporous) and porous inorganic membranes. Dense membranes are mainly made of thin metal films such as palladium and its alloys with silver, zirconia, ruthenium, nickel or other metals from group VI to VIII. Palladium based membranes are permeable only to hydrogen while silver and zirconia are well known to be permeable only to oxygen. Most of the nonporous metallic membranes are known to provide high selectivity but low permeability. Porous membranes are superior to dense membranes from the point of view of their permeability, nevertheless, the selectivity of the porous membranes are not as good as that of the dense membranes.

There are four major fields being studied for improvement of permselectivity, stability and permeability of the porous membranes, i.e.; 1) modification of currently available membranes by imposing permselective top layers by sol-gel method, CVD technique, etc; 2) synthesis of zeolite membranes; 3) development of membranes based on ion conductors; and 4) synthesis of thinner metal film on top of the membranes.

In the last area of studies Pd-alloy membranes have always been the most studied dense membrane, due to high hydrogen permselctivity. However, it suffers from brittleness after repeated thermal cycling owing to the transition between its α- and β-phases, which are stable at low and high temperatures, respectively (Armor *et al.*, 1995). This problem can be overcome or reduced by the use of some alloying elements (i.e.; Ag; Ru; Rh), which stabilize the β-phase against the α-phase. Poisoning by CO and sulfur compounds, which are present in a feed stream, causes a serious problems on both the permeability and catalytic properties. Consequently, this limits their ranges of practical applicability. Most researches in this area are devoted to the reduction of the thickness of the supported Pd-alloy film so as to enable high permeabilities (Shu *et al.*, 1991). However, the penalty of doing that is to have more pinholes, cracks or other defects which would considerably lower membrane permselectivity. It should be noted that the permeation mechanism of hydrogen through Pd involves dissociative adsorption and recombinative desorption at the surface, as well as diffusion. For the relatively thick Pd layer, diffusion is apparently the rate-limitting step, and flux is found to be inversely proportional to layer thickness an approximately square root dependence on H_2 partial pressure. Such behavior is called Sievert's law. As the membrane becomes thinner, the solid-state diffusion will become rapid enough that other rate processes will begin to take part in the permeation rate (Ward *et al.*, 1999).

2.2 Membrane reactor

Membrane reactors can be categorized into three types: namely 1) inert membrane reactor, 2) catalytically active membrane reactor and 3) catalytically barrier membrane reactor. For the inert membrane reactor, catalyst pellets are confined in the membrane and the membrane acts only as a separator. The catalytically active membrane reactor takes advantage of the high surface area of the membrane to deposit active catalysts on the membrane. Reactions take place in the membrane while the membrane also behaves as a separator. In both cases the membranes can be applied as a separator to separate some products from a mixture in one side to the other side. The last case is different from the previous ones. A membrane is catalytically active but not necessary to be selective. It acts as a barrier to separate two streams of reactants. Its applications are, for example, a case where, a reaction is highly exothermic (Hsieh *et al.*, 1996).

The major application areas of membrane reactor can be categorized into two types; selectivity enhancement and yield improvement. Selectivity enhancement can be accomplished by selective removal of products or controlled addition of a reactant though the membrane. Considering consecutive reaction pathways, a permselective membrane could allow permeation of an intermediate product while rejecting either reactant or other undesired product. Another opportunity in this area for the increase of the reaction selectivity lies in the controlled addition of a reactant along the reactor. Partial oxidation or partial hydrogenation are examples. Low oxygen or hydrogen concentration in the reaction mixture drives the reaction to higher selectivities towards intermediate products (Ten Elshof *et al.*, 1995). Such low concentration can be attained by dosing the key reactant (i.e. oxygen or hydrogen) at a desired rate through the membrane.

In the second major area of application, yield-enhancement of equilibrium-limited reactions, a reaction product is selectively removal through the membrane thereby enhancing the per-pass conversion compared to conventional fixed bed reactors. Dehydrogenation reactions are major reactions for application of membrane reactor in this area. 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 same conversion could be obtained at lower operating temperature thereby suppressing undesired reactions. Furthermore, since dehydrogenation reaction imply an increase of the overall of gas molecules the system, they can be forced to high conversion by reducing operating pressure, which entails comparatively high reactor volume. Such volume could be reduced using a membrane reactor (Saracco *et al.*, 1999).

2.2.1 Membrane reactor for selectivity enhancement

The applications of membrane reactors for selectivity enhancement of most partial oxidation reactions (methane oxidation to syngas, oxidative coupling of methane, oxidative dehydrogenation, etc.) have been frequently investigated. Methane to syngas is difficult to control because of the presence of over oxidation of CH_4 to CO_x at high temperature. Thus, a number of researches have groups studyied the use of O_2 selective membranes for assisting this reaction. Balachan *et al.*, (1997) studied this reaction by using perovskite type oxide membranes to control O_2 addition to reaction zone. They found that oxides in the system Sr-Fe-Co-O provided high oxygen permeability. In addition, the membranes were evaluated in a reactor operating at about 1123 K for direct conversion of methane to syngas in the presence of a reforming catalyst. Methane conversion efficiencies of > 99% were observed. Galuszka *et al.*, (1997), also studied this reaction using a 10 μm thick Pd coating on a Al_2O_3 tubular membrane filled with 5% Pd/Al_2O_3 catalyst. A feed of 3:1:4 $CH_4/O_2/N_2$ was passed through the catalyst at 773 K with an argon sweep gas on the permeate side. The argon assisted in the transport of H_2 away from the catalyst bed, resulting in an increase of H_2 yield from 18% to 36%.

Oxidative coupling of methane is another interesting reaction for membrane reactor in the field of selectivity enhancement. Lafarga *et al.*, (1994) applied a membrane reactor concept to supply oxygen in a controlled manner to a fixed bed of catalyst (Li/MgO) so as to drive methane oxidation to higher C_2 selectivity. Competing reactions, deeper oxidation, are hindered by keeping rather low oxygen average concentration along the entire reactor length. The membrane developed was microporous alumina membrane having an average pore size of about 10 μm. The obtained result showed yield (cp to 23% in oxidative coupling product; Coronas *et al.*,1994a) very close to the limits required to achieve commercialization (i.e. 25-30%). Nozaki *et al.*, (1994); Guo *et al.*, (1997) and Sherman *et al.*, (1997) studied this reaction using solid oxide dense membrane both experiment and computer simulation. They found that permeability of this materials appeared to be limited by high oxygen ion recombination rate in perovskite membrane, this also indicated that oxygen fluxes are not limited by diffusion, but by surface exchange rate.

Oxidative dehydrogenation of hydrocarbons is another example of membrane reactor applications. Coronas *et al.* (1995) applied the same reactor used for methane oxidative coupling (a fixed bed of Li/MgO catalyst encompassed by a porous membrane ; Coronas *et al.*, 1994a,b) to the oxidative dehydrogenation of ethane to ethylene. Oxygen was permeated through the membrane whereas ethane was fed axially. Ethane conversion higher than that of conventional pre-mixed feed reactors could be obtained, with good selectivity to ethylene (overall yield equal to 57%).

Pantazidis, (1994) studied this reaction with propane as the reactant. The catalytic performances of various membrane materials having macroporous, mesoporous and microporous structure were evaluated and compared. Two different active phases were used, i.e.; V-Mg-O or Ni based catalyst deposit on catalyst pellets or on zeolite membrane. The V-Mg-O based membrane were found less active but more selective than the nickel based membrane and at temperature above 773 K. The best performance was achieved with the zeolite hybrid reactor when separate feeding configuration was used at high oxygen partial pressure. In this reaction, Tonkovich *et al.*, (1996b) found that the yield of reaction of membrane reactor comparatively higher than a conventional fixed-bed reactor with premixed feed of reactant. This is due to lower oxygen partial pressure in the reaction side of the membrane reactor. In addition, it was found that the operation with the membrane reactor is safer compared to that of concentration reactors with pre-mixing of reactants due to avoidance of the occurrence of explosive mixture.

Several researchers have investigated the use of membrane reactor for partial hydrogenation reaction. Dense metal membranes have been studied for the partial hydrogenation of acetylene at 373 K. These include a Pd/Ni (Gryaznov *et al.*, 1982) and Pd, Pd/Ru and Pd/Ag membrane (Itoh *et al.*, 1993). Both studies found that the permeate hydrogen was very active to hydrogenation of acetylene in which ethylene was the main product. They were also interested in the addition of hydrogen to one double bound of diene. The selective hydrogenation of butadiene in crude 1-butene was performed using a catalytic hollow fiber membrane reactor at 313 K (Liu *et al.*, 1998). The catalyst consisted of polymer-anchored palladium on the inside wall of cellulose acetate or polysulfone fibers. The selectivity of nearly 100% to 1-butene under mild reaction condition was obtained. Lambert *et al.* (1999) studied this reaction in a Pd/γ-Al_2O_3 catalytic membrane of acetylene and 1,3-butadiene. The hydrogenation reaction performed by flowing a premixed feed through the Pd/Al_2O_3 membrane wall provided the highest selectivity to partially hydrogenated product while maintained a high conversion without any loss of hydrocarbon species.

2.2.2 Membrane reactor for yield improvement

The most common application opportunity of membrane reactors lies in the circumvention of chemical equilibrium so as to achieve higher per-pass conversions by selective permeation, through the membrane, of at least one of the reaction products. The dehydrogenation of hydrocarbons is the most widely studied class of reaction in membrane reactors. The motivation for the study of these reactions has been the possibility of enhanced conversions, improved selectivity, decreased downstream separation load and milder operating conditions. The milder operating conditions are percieved to be beneficial not only as energy saving technology but also they might be a remedy for coking and catalyst deactivation problem inherent in many commercial processes. The recent applications are discussed in this review.

Classical works of Itoh *et al.*, (1987) and Gryanov *et al.*, (1986) led the way for others to build small membrane reactors for the dehydrogenation of alkanes. Itoh's work with a 0.05 in thick Pd/Ag membrane tube containing a 0.5% Pt/Al_2O_3 catalyst was able to achieve 99% conversion for the dehydrogenation of cyclohexane to benzene. Their work used an argon sweep to carry away the H_2 permeating the Pd membrane. The reaction over the catalyst was operated at 473 K and 1 atmosphere pressure using an argon stream saturated with cyclohexane vapor. Kikuchi and coworkers (1993, 1995) extended this work into a number of other reactions. The membranes were made of a Pd alloy coated onto a mesoporous membrane support. Isobutane was passed over a Pt/Al_2O_3 catalyst, the yield of isobutylene rose from the equilibrium value of 6% to 23% at 673 K with the presence of membrane. They found that the rate of H_2 production was limited by catalyst activity.

Stream methane reforming is the major route to industry's production of syn gas (CO and H_2) on a world wide scale. Uemiya *et al.*, (1991) studied a membrane reactor which consisted of a thin palladium film supported on porous glass cylinder. The level of methane conversion exceeded equilibrium value in a closed system and the temperature range of 623-773 K due to selective removal of hydrogen from reaction system. Barbieri *et al.*, (1997) also considered this reaction using mathematical model simulation. The effects of various operating parameters such as temperature. They also found that the counter flow configuration at high temperature is advantage over the parallel flow configuration.

Collins *et al.*(1996) studied the dehydrogenation of propane using a Pd film coated on a mesoporous Al_2O_3 support in a device containing a commercial Amoco dehydrogenation catalyst. Propylene yields increased from the equilibrium value of 30% (in the absence of a membrane) to 40% at 823 K. They also reported catalyst deactivation due to carbon deposition on the catalyst. Weyten *et al.*(1997) studied catalyst activity, catalyst deactivation and process performance of the same reaction using a commercial silica membrane which has a moderate H_2 permeance. It was found that a high H_2 transport through the membrane is necessary if a high propane flow rate is to be used. In addition, it is necessary to have a high H_2 selectivity so that almost no reactant or reaction products can diffuse through the membrane to separation side and be lost. In membrane reactor, H_2 is continuously removed from the reaction mixture. The deactivation of the catalyst is very fast because of coking. Two membrane categories (porous and dense) and three types of composite membrane systems (Pd/Ag, silica and Pd-dispersed porous) were studied and their performance were compared with Yildirim *et al.*(1997)'s works. They found that the dense Pd /Ag composite system provided higher performance levels in the range of operating temperature.

Another dehydrogenation reaction of interest in the petrochemical industry is the ethylbenzene dehydrogenation to styrene. Liu *et al.*, (1993) studied this reaction in a two stage packed bed reactor followed by a membrane reactor and a reactor without a membrane unit. A tubular alumina mesoporous membrane with pore size of 40 °A was packed with a commercial K promoted iron oxide catalyst for styrene production. They observed a 4% yield enhancement to styrene with the membrane in the system. Unfortunately, carbon deposition rapidly reduced H_2 permeability even with the presence of a co-feed of stream in the reaction feed.

The studies on dehydrogenation bring out some important factors which were not highlighted in earlier remarks about membrane and device limitations. With dehydrogenation, there are two serious process issues emerged: carbon deposition and catalyst activity. Raich and Foley, (1995) studied dehydrogenation of alkanes in a membrane reactor and concluded that these devices were very limited by the availability of dehydrogenation catalysts with high reactivity. Most commercially available dehydrogenation catalyst do not have high turnover number; further, they are limited by excessive carbon formation which accumulates on the catalyst. Dehydrogenation reactions are endothermic reactions, their high demand for heat means that products of the reaction can be trapped within the pores of the catalyst. The reaction rates are slow which means that the olefinic products will tend to polymerize before permeating away from the catalyst particles. In commercial dehydrogenation operation, the generation of H_2 actually serves to reduce carbon formation. In a membrane reactor, one is trying to remove the H_2 as soon as it forms which only activates the formation of carbon. Carbon formed during dehydrogenation can damage in at least three ways, i.e.; 1) it can block the surface of the catalyst; 2) it can foul the reactor and plug the unit; or 3) it can coat the membrane layer and thus block further H_2 permeation through the membrane layer.

Gobina (1996) studied the influence of inert and reactive sweep gases on the conversion of n-butane in a catalytic membrane reactor. Hydrogen produced from the catalytic dehydrogenation permeated through a Pd/Ag membrane with 6 μm thickness and was removed by the sweep gas. The use of inert (N_2) and reactive sweep gases (N_2/CO and N_2/O_2) enhanced the conversion well above the equilibrium value of 5% to 13.5%, 26% and 40% in N_2, 11%CO/N_2 and 21%O_2/N_2, respectively. Govind *et al.* (1990) also studied these influences. The experiments were conducted under isothermal and adiabatic condition with air passing on the permeation side. Wherein the oxygen reacts exothermically with the permeating hydrogen to decrease its partial pressure in separation side, thereby increasing its flux, and providing heat for the endothermic dehydrogenation reaction.

The comparison of microporous and dense membrane systems was studied by Gobina *et al.*, (1995). A mathematical model was developed and used in the simulation. The catalytic dehydrogenation of ethylbenzene to styrene using two types of membrane reactor systems; i.e. a composite membrane consisting of a thin Pd-Ag alloy deposited on the outside surface of a porous ceramic substrate and a microporous membrane tube. The uses of Pd-Ag composite membrane provided higher conversions for the same contact time than the porous system. They also found that lean feed operations were desirable in the Pd-Ag membrane system while rich feed streams would be appropriate for porous membrane system. This result corresponded to the work done by Schramm *et al.* (1999).

The effect of radial diffusion on the hydrogen separation was studied by Itoh *et al.*, (1994). Low-flowrate gas mixture containing hydrogen was examined under atmospheric pressure at 473 K using an annular packed-bed type of Pd membrane reactor. The radial diffusion model could successfully simulate the profile of hydrogen partial pressure formed along the packed bed of palladium membrane reactor. It was found that a radial distribution of hydrogen partial pressure formed in the packed bed, which is caused by its permeation, led to a lowering in the hydrogen partial pressure near the membrane surface and thereby the virtual flux of hydrogen permeation through the membrane. The efficiency of hydrogen separation is decreased. Koukou *et al.*, (1996) studied the dispersion effects on membrane reactor performance, two membrane types in tubular form were studied ; a selective porous glass with low gas permeabilities and a porous media with very high gas permeabilities. They found that for a low-permeability membrane, the use of the plug-flow model was proved to be a good simulation choice for the membrane reactor. As the permeabilities increased and the process became intensive, dispersion phenomena became important and simulation should be based on more complex dispersion models.

Several investigators have faced the problem on modeling on membrane reactor to achieve interpretation of their experimental data or to assess the role of the various operating parameters (temperature, membrane permeability and permselectivity, feed flow rate and concentrations, etc.) on the performance of membrane reactors. Bindjouli *et al.*,(1994) developed a new reactor model able to perform both catalytic activity and separation simultaneously. These works analysed the influence of gas diffusion through the membrane on mass transfer in the catalytic reactor with an inert membrane wall. A mathematical described that, the present of the membrane has no influence on the radial diffusion phenomena. Casanave *et al.* (1998) simulated the isobuthane dehydrogenation. The simulation predicted the optimal configuration and the influence of the reacting mixture ratio in order to enhance yield of reaction.