

CHAPTER II

LITERATURE REVIEWS

In modern technology, membrane reactors are considered as an alternative to conventional reactors when separation during reaction enhances the reaction efficiency. These devices combine reaction and separation in a single unit operation. They also make it possible to achieve significant enhancement over equilibrium conversion, by continuous removal of one or more products of reaction through the membrane during the reaction. During a few decades, there have been intensive researches in membrane reactors. Review articles by Gryaznov (1999); Quicker *et al.* (2000); Saracco *et al.* (1999); Kikuchi, (1995); Zarman *et al.* (1994); Soria (1995) and Armor (1995) discuss the basic principles and potential applications for membrane reactors.

These literature reviews will provide information on types of membranes, types of membrane reactors and development of mathematical modeling in membrane reactors.

2.1 Types of membrane

Based on the materials used for the manufacture of membranes, they can be broadly classified as organic and inorganic membranes. The first generation of organic membranes is organic cellulose acetate membranes that found commercial application in reverse osmosis and ultrafiltration. However, cellulose acetate membranes have limited pH, temperature and chlorine tolerance range. This led to the development of second generation of organic membranes of polymeric materials such as polyamide, polysulfone, polyvinylidene fluoride and polytetrafluoroethylene. These membranes are more resistant to pH, temperature and chlorine than the cellulose acetate membranes. Major applications of these membranes are found in

reverse osmosis, ultrafiltration and microfiltration operations. However, disadvantages of the organic membranes arise from their low chemical and thermal stability, poor mechanical strength and problems on compacting, swelling, and cleaning.

The potential applications of membranes in reaction engineering and high temperature gas separation are being recognized. The success of membranes in these applications largely depend on the availability of membranes with acceptable permselectivity and thermal stability. Currently available organic membranes are not suitable for high temperature applications because of thermal degradation. As a result, development of inorganic membranes has been recognized to improve the properties of membranes. Inorganic-material-based membranes such as ceramic or metallic, porous or dense membranes are particularly attractive for many high-temperature separations and for heterogeneous or homogeneous reactions; due to their inherent thermal, structural, and chemical stability. Hence, this review will focus on a variety of inorganic membranes.

Inorganic membranes can be classified into two groups according to the separation mechanisms, namely dense (nonporous) and porous inorganic membranes.

Porous membranes such as alumina, carbon molecular sieves, zirconia, titania vycor glass have been used to study the catalytic dehydrogenation of hydrocarbons (e.g. Koukou *et al.* 1996; Gobina *et al.* 1995; Liu *et al.* 1999) and the conversions were found to be higher than the equilibrium limit. Although these membranes can withstand the high operating temperatures required for most dehydrogenation reactions, they show a high permeability but a poor permselectivity. Instead, the separation behavior is governed by Knudsen diffusion, which is affected by molecular weight only, leading to significant loss of reactants.

On the other hand, dense metallic membranes, such as Pt, Ru and Rh, Pd and their alloys membranes have always been the most studied dense membranes, due to their comparatively high hydrogen permselectivity. The separation behavior of the

dense membranes is governed by solution-diffusion transport mechanism. However, H₂ fluxes are low as a result of rather thick membrane required for mechanical stability. If these membranes are made very thin, they become fragile and difficult to incorporate into permeation devices. The introduction of alloying elements into the palladium membranes such as silver, Ru and Rh has been used to impose their resistance to hydrogen embrittlement. Jaward *et al.* (1995) observed that the permeability of hydrogen through the membrane varies dramatically with the alloy composition Pd/Ag > Pd/Ru > Pd.

As a compromise, developments moved to the employment of composite membranes in which the palladium or palladium alloy is deposited as a thin film onto a porous ceramic or metal substrate (Li *et al.* 2000; Quicker *et al.* 2000). Several techniques were developed aiming at depositing a small amount of palladium over porous supports through chemical vapor deposition (Morooka *et al.* 1995), electroless plating (Shu *et al.* 1993), sputtering (Gobina *et al.* 1995), solvated metal atoms deposition (Capannelli *et al.* 1993; Basile *et al.* 1996) and magnetron deposition (Yildirim *et al.* 1997). Such composite membranes based on a thin palladium film on a porous substrate have high permeability and high selectivity with sufficient thermal, mechanical and chemical stability.

Electroless plating was recently employed by Yeung *et al.* (1995) to synthesize Pd and Pd-Ag thin membranes on various supports (e.g. porous alumina, Vycor glass). These membranes were a few microns thick and showed good mechanical and thermal stability. Bauxbaum *et al.* (1996) employed the electroless plating technique to form thin Pd layers on tantalum and niobium tubes. Jeema *et al.* (1996) deposited Pd membranes over a metal support made from stainless steel which is cheaper than tantalum or niobium. The use of the metal support entails lower problems of thermal expansion mismatch between membrane and support and avoids brittleness. These authors could keep membrane thickness at just 6 μm with no defects affecting hydrogen permeability. Higher thickness (8.5-12 μm.) and, consequently, lower permeability were obtained once again by electroless plating by Ilias *et al.* (1997) over α-Al₂O₃ supports.

Another interesting technique for the deposition of ultrathin ($< 500 \text{ }\mu\text{m}$.) Pd membranes on ceramic supports are magnetron sputtering. Jayaraman *et al.* (1995) found that two main parameters are the most critical in the context: surface roughness of the substrate and deposition temperature. Gryzanov *et al.* (1993) successfully used the magnetron sputtering technique to produce films as thin as $0.1 \text{ }\mu\text{m}$ on a variety of substrates and obtained good hydrogen permselectivity and high thermal stability. Thin Pd/Ag films were produced by Yan *et al.* (1994) and Li *et al.* (1993) who applied the metal-organic chemical vapour deposition and spray pyrolysis methods, respectively, to successfully produce films of Pd/Ag as thin as $1\text{-}2 \text{ }\mu\text{m}$ on porous alumina substrates. They also showed that their composite membranes were thermally stable and resistant to thermocycling.

2.2 Membrane reactor

Membrane reactors offer advantages over conventional packed-bed reactors of combining separation and chemical reaction into a single unit operation. Membrane reactor can be classified into two types, namely:

- 1) inert membrane reactor and
- 2) catalytically active membrane reactor.

For the inert membrane reactor, membrane provides a medium for separation of product(s) formed within the catalyst pellets. The catalytically active membrane has catalyst attached to the membrane surface or membrane pores. Deposition of catalyst in the membrane pores or on the membrane surface can be carried out using various techniques such as impregnation and adsorption techniques which are commonly used for conventional catalyst preparation. Therefore, the membranes serve as both a separator and catalyst.

The application of inorganic membrane can be categorized into two fields, namely:

- 1) selectivity enhancement and
- 2) yield-enhancement of equilibrium-limited reactions.

The improvement of reaction selectivity is a first field of application of inorganic membrane reactors. Selective removal of products or controlled addition of a reactant through the membrane can accomplish selectivity enhancement. Considering consecutive reaction pathways, a permselective membrane could allow permeation of an intermediate product while rejecting either reactants or other undesired products. Another opportunity for the increase of the reaction selectivity lies in the controlled addition of a reactant along the reactor, through the membrane. For example, low oxygen or hydrogen concentration in the reaction mixture is known to drive certain partial oxidation or hydrogenation to higher selectivity towards intermediate products (Elshof *et al.* 1995). Dosing the key reactant through the membrane (i.e. oxygen or hydrogen) can attain such low concentrations at a desired level along the reactor length (Coronas *et al.* 1995).

In the second field of application, the yield-enhancement of equilibrium-limited reactions, a reaction product selectively permeates through the membrane, thereby enhancing conversion compared to conventional packed-bed reactors. The major potential candidates for such application of inorganic membrane reactors are dehydrogenation reactions. Since these reactions are reversible reactions, the continuous and selective hydrogen removal through the membrane will improve the yield.

2.2.1 Selectivity enhancement

Major applications on selectivity enhancement in partial oxidation (methane oxidation to syngas), oxidative coupling of methane and oxidative dehydrogenation were investigated. In partial oxidation of methane, porous membranes were used to control oxygen addition to reaction mixture. The selectivity toward desired products were favored if low oxygen concentrations was controlled. Armor (1998) and Balachandran *et al.* (1997) studied this reaction using perovskite typed oxide membranes to control O₂ addition to reaction zone. They found that oxides of perovskite membrane in these systems Sr-Fe-Co-O provided high oxygen permeability. Methane conversion efficiencies of >99% were observed. Yang *et al.*

(1998) investigated this reaction using a microporous zirconia/ α -alumina membrane reactor packed with a Mo-Co-B-O/SiO₂ catalyst. In comparison with the conventional fixed-bed reactor, the membrane reactor could result in a higher selectivity to the desired product.

Oxidative coupling of methane was another of interesting reaction for membrane reactor. Lafarga *et al.* (1994) employed a microporous alumina membrane to supply oxygen in a controlled way to a fixed bed of catalyst (Li/MgO) so as to drive methane oxidation to higher C₂-selectivities. The obtained results showed yield up to 23% in oxidative coupling product which was very close to the limits required to achieve commercialization (i.e. 25-30%)(Coronas *et al.* 1994a). Lin *et al.* (1996) and Ten Elshof *et al.* (1995) used perovskite membranes and detected up to 70% selectivity toward C₂.

Oxidative dehydrogenation of hydrocarbons were studied by a number of research. Coronas *et al.* (1994) and Tonkavich *et al.* (1996b) used porous membrane packed with Li/MgO catalyst for investigating the oxidative dehydrogenation of ethane to ethylene. Oxygen permeated through the membrane. As a result, ethane conversion higher than that of conventional reactors could be obtained with good selectivities of ethylene. Ramos *et al.* (2000) compared the performance of a conventional packed-bed reactor with a catalytic membrane reactor with separate feed of reactants using in handling the oxidative dehydrogenation of propane on a V/MgO catalyst. The membrane reactor gave superior ethylene selectivity. Tellez *et al.* (1997) studied the oxidative dehydrogenation of butane. The membrane reactor was found to be more efficient than a fixed-bed reactor under the same conditions. In addition, it was found that the operation with membrane reactor is safer compared to traditional reactors owing to the avoidance explosive mixture.

2.2.2 Yield enhancement for equilibrium-limited reactions

The most common application opportunity of membrane reactors lies in circumvention of a chemical equilibrium so as to achieve higher per-pass conversion by selective permeation, through the membrane, of one or more of the reaction products. The applications of membrane reactors to yield enhancement are on steam reforming of methane, water gas shift and dehydrogenation of alkanes.

Steam methane reforming technology was the major route to industry's production of syngas (CO and H₂) on the worldwide scale. In 1991 Uemiya and coworkers showed that steam methane reforming can be enhanced using an alumina supported Ni catalyst contained within a Pd on Pd/23%Ag alloy membrane coated onto a porous glass tube. Increasing the sweep gas flow rate enhanced the hydrogen productivity but the rate was limited by the permeability of the membrane. The level of methane conversion exceeded equilibrium value in a closed system with a temperature range of 623-773 K, due to selective removal of hydrogen from reaction mixture. Barbieri *et al.* (1997) also considered this reaction using mathematical model simulation. The effects of various operating parameters such as temperature were considered. They found that the counter flow configuration at high temperature is advantage over the parallel flow configuration.

The water gas shift reaction was another valuable process operation within a refinery. It was used to convert CO to H₂ and CO₂. There had been a few membrane reactor studies on enhancing water gas shift reaction. Kikuchi *et al.* (1991) used a 20 μm layer of Pd coated onto a porous glass tube to enhance CO conversion and H₂ production using a commercial catalyst at 673 K and 1 atm with steam/CO ratio of 2/1.

The major potential candidates for the yield enhancement applications were dehydrogenation reactions. Since these reactions were endothermic, conversion favoured at high temperatures at the price of significant occurrence of side reactions, which reduced selectivity and led to catalyst deactivation by coking. By using a

membrane reactor, equal conversion could be obtained at lower temperature thereby suppressing undesired reactions. The permeated reaction product can be recovered in a rather pure form. However, if the membrane was not permselective enough, the conversion increased remains limited by the permeability of the reactants, which also affected the purity of the product. More details of this application were provided in the next section.

2.3 Applications of membrane reactors on dehydrogenation reactions

The classical works of Itoh (1987) and Gryaznov *et al.* (1986) led the way for others to build small membrane reactors for dehydrogenation of alkanes. Itoh described the use of a 0.05 mm. palladium membrane containing a 0.5% Pt/alumina catalyst for the dehydrogenation of cyclohexane to benzene at 473 K and atmospheric pressure using argon sweep to carry away hydrogen permeating through the membrane. Essentially complete conversion of cyclohexane was achieved (versus the equilibrium value of 18.7% without the membrane reactor). In 1991, Itoh developed the simultaneous ordinary differential equations to compare the maximum conversion in two flow modes (co-current and countercurrent). The study compared the maximum conversion in the palladium membrane reactors with the conventional reactor. The maximum conversion of the co-current reactor was determined by thermodynamics. The countercurrent reactor realized perfect conversion.

Matsuda *et al.* (1993) studied the dehydrogenation of isobutene with chromia/alumina catalyst within a palladium coated on alumina tube. At 623-723 K and atmospheric total pressure, a 16.7% isobutene was achieved in a conventional reactor while a membrane reactor gave a 28.5% conversion at 673 K. This experimental value was higher than the calculated equilibrium value 10.5% for a membrane reactor and 6% for a conventional reactor, with the same amount of catalyst. Kikuchi *et al.* (1993, 1995) extended this work into a number of other reactions. A 20 μm Pd film was deposited on a mesoporous Al_2O_3 tubular membrane.

Isobutane was passed over Pt/Al₂O₃ catalyst contained within the membrane. The yield of isobutylene enhanced from the equilibrium value of 6% to 23% at 673 K with the presence of membrane.

Conllins *et al.* (1996) studied the dehydrogenation of propane using a Pd film coated on a Al₂O₃ support in a device containing a commercial Amoco dehydrogenation catalyst. Propylene yield increased from the equilibrium value of 30% to 40% at 823 K. Ziaka *et al.* (1993a and 1993b) reported the employment of porous alumina membranes with a nominal pore sized of 4 nm. The investigations were carried out at 2×10^4 Pa pressure difference between both sides of the membrane, without sweep gas on the permeate side. Using a propane-hydrogen feed (molar ratio 4:1), a relative increase of propylene yield of 26% was obtained at 637 K. Silica membranes were also investigated by Weyten *et al.* (1997). The membrane reactor was loaded with a chromia/alumina catalyst. The propane yield was at least twice as high as the value obtained at thermodynamic equilibrium in a conventional reactor.

Another type of dehydrogenation reaction is reforming via dehydrocyclization of heptane. Ali and baiker (1996) described a system of two-plug-flow reactors equipped with an interstaged tubular palladium-silver membrane for hydrogen separation. A commercial Pt/Al₂O₃ catalyst was employed for the heptane reforming. This system afforded a 65% higher toluene yield at 673 K and 1.7×10^6 Pa than the same system without interstage membrane.

Another dehydrogenation reaction of interest in the petrochemical industry is the ethylbenzene dehydrogenation to styrene. Wu *et al.* (1992) studied a mathematical model employed to evaluate the performance of a ceramic membrane reactor for the catalytic dehydrogenation of ethylbenzene to styrene. The tubular alumina mesoporous membrane was packed with a commercial K promoted iron oxide catalyst. They observed in a selected case study that an increase more than 5% in styrene yield over the thermodynamic limit was achieved by a hybrid system (a fixed bed reactor in conjunction with a membrane reactor). Use of this system minimizes

the amount of reactant passing through the membrane near the entrance of the membrane reactor. Becker *et al.* (1993) performed a two-dimensional and isothermal mathematical model for the ceramic membrane reactor. The model was compared with the experimental results of the dehydrogenation of ethylbenzene to styrene. Because the membrane reactor performance was highly sensitive to the operating temperature, the simulation results did not fully predicted the experimental results.

Yang *et al.* (1995) investigated two types of membrane reactors to evaluate the influence of membrane reactor configuration on the performance of the ethylbenzene dehydrogenation in a porous alumina membrane reactor. Type I construction combined reaction with separation in the same space. Type II configuration comprised three parts, i.e., reaction prior to separation, reaction and separation, and reaction after separation. The results showed that the overall yield of styrene in type I was only 4% higher than that of the fixed bed reactor at 893 K while 11% enhancement in yield to styrene was obtained with type II. Tiscareno-Lechuga and Hill (1993) were able to reach the equilibrium conversion of ethylbenzene by employing a porous membrane.

The coupling of reaction between dehydrogenation (endothermic) and hydrogenation (exothermic) at the two sides of a Pd membrane is another approach to improve the reactor's performance. The exothermic reaction could supply heat required for the endothermic reaction. Gobina and Hughes (1995) carried out experiment and model for the dehydrogenation of ethane to ethylene in a catalytic membrane reactor, with and without reaction on the permeate side. Later, they (1996) studied the catalytic dehydrogenation of n-butane. The use of nitrogen, CO/N₂ and O₂/CO₂ as a sweep gas at the opposite membrane side increased conversion up to 5-8 times of the equilibrium value. The largest value occurred with the coupling reaction of the permeated hydrogen with O₂ and CO. Itoh and Wu (1997) focused on the thermal sustainment by coupling of reaction on the other side of the membrane.

The comparison of microporous and dense membrane system was studied by Yildirim *et al.* (1997). Experiments were performed by using a high temperature membrane reactor to evaluate the performance of various membranes. Two membrane

categories (porous and dense) and three types of composite membrane systems (Pd/Ag, Silica and Pd-dispersed porous) were studied. They found that the dense Pd-Ag composite system had higher performance in the temperature range of study. However, metal-dispersed porous systems had more advantages due to their significant higher contact surface per unit volume. This result corresponded to those works done by Gobina *et al.* (1995).

2.4 Mathematical model development

The research on membrane reactor has been increased tremendously during the past decade. Besides the experimental work, some efforts have been focused on numerical simulation of these processes. The basic assumptions are isothermal, isobaric and plug flow conditions within the membrane reactor. The simple model fairly explain the reactor behavior. However, Itoh *et al.*, 1992, who studied the dehydrogenation of cyclohexane in the membrane reator, found that the deviation between the experimental and predicted results became larger with increasing flow rate of sweep gas. Wu *et al.* (1992) performed a mathematical model to evaluate the performance of a ceramic membrane reactor for the catalytic dehydrogenation of ethylbenzene to styrene. Membrane reactors demonstrated the possibility of improving the product selectivity along with the increase in conversion. The product yield exceeded the equilibrium limitation for the fixed-bed reactor. However, their study did not verify the simulation results with experimental data.

A two-dimensional model considering both radial and axial directions is necessary for such reactor; however, only a few investigators have developed the two-dimensional models. In 1994, Itoh *et al.* investigated the effect of radial diffusion on the hydrogen separation from a low-flow rate gas mixture containing hydrogen under atmospheric pressure at 473 K using an annular packed-bed type of palladium membrane reactor. The ideal flow model could not explain the experimental results very well but the radial diffusion model could successfully simulate the profiles of hydrogen partial pressure along the packed bed of Pd membrane reactor. They concluded that there existed a gradient of hydrogen partial pressure in the radial

direction in the packed bed. Koukou *et al.* (1996) studied the dispersion effects on membrane reactor performance. Two types of tubular membranes were studied: a selective porous glass with low gas permeabilities and porous alumina with very high gas permeabilities. They observed 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. The simulation should therefore be based on more complex models because radial concentration profiles did not correspond to those obtained with the plug-flow model.

In most studies the problem of heat balance was not well described. The majorities of the mathematical models were studied, assuming isothermal condition inside the reactor. This assumption may lead to unrealistic simulation of the reactor operation. Becker *et al.* (1993) performed a two-dimensional and isothermal mathematical model for the ceramic membrane reactor. The model was compared with the experimental results of the dehydrogenation of ethylbenzene to styrene. Because the membrane reactor performance was highly sensitive to the operating temperature, the simulation results could not perfectly predict the experimental results. Itoh *et al.* (1997) performed a simple mathematical model assuming plug flow and isothermal condition for analyzing the reaction process. They found from the experiment that the axial temperature profile significantly deviated from the isothermal case and, hence, concluded that more strict mathematical analyses taking the heat effects into account was required in a further study. Koukou *et al.* (1997) studied the development of a mathematical model to investigate the performance of the packed-bed membrane reactor for dehydrogenation of the cyclohexane reaction under the non-isothermal condition. They found that the heat effect taking place inside the reactor had to be taken into account because the possible omission induced an overestimation in the predicted temperature field and the calculated reactor conversion. Omorjan *et al.* (1998) studied the performance of a non-isothermal two-membrane reactor for reversible chemical reactions by numerical simulation. It was shown that it was possible to enhance reactant conversion above that of a conventional membrane reactor, for both endothermic and exothermic reversible

reactions by using a two-membrane reactor. Considerable lowering of feed temperature was enable for an endothermic reaction.