SEPARATION AND REACTION USING POROUS AND PALLADIUM MEMBRANES

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ABSTRACT

Two different types of inorganic membranes were prepared in this study, porous-silica/γ-alumina membranes and palladium/α-alumina composite membranes.

Porous silica/γ-alumina membranes were prepared by dip coating, characterized by gas permeation at elevated temperatures and different pressure differences. This membrane was then used to investigate the influence of diffusion direction on gas permeation through it. The results obtained showed that a combination of Knudsen and viscous flow transport mechanisms occurred during the experiments at the working conditions of pressure and temperature with Knudsen flow dominating. The results also showed that the average pore size of the silica layer coated was 1 nm. The diffusion direction was found to influence the gas permeation through this membrane. Higher permeation rates were obtained when the diffusion direction was from layers of largest pore size towards layers of the smallest pore size. A maximum difference of 4% was calculated.

Dense palladium composite membranes were prepared using the electroless plating technique with α-alumina tubes as substrates. The electroless plating technique employed consisted of the conventional two step sensitization-activation method and a hydrazine-based plating bath. Vacuum was used at the initial stages of the procedure to help improve the palladium film quality and once the pores of the substrate were partially plugged, osmotic pressure was introduced through the osmotic 2M NaCl
solution. The palladium film obtained was 7.0 \mu m thick and possessed high selectivity towards hydrogen with a H_2/N_2 ratio of over 1600.

The electroless plating technique was used to plate \( \gamma \)-alumina tube using a modified activation procedure that employs a chloroform solution in palladium acetate. The fabricated palladium film appeared not to adhere to the very smooth outer surface of the \( \gamma \)-alumina.

The composite palladium membrane obtained was used to investigate the influence of reactive and inert sweep gases on hydrogen flux through such membranes and was used to study their usefulness in propane dehydrogenation. Results obtained showed that inert sweep gas used (N_2) improved the hydrogen flux and hydrogen flux improvement was even bigger when a reactive sweep gas (air) was utilized.

The results also showed that the concept of catalytic membrane reactors works. Propane conversions obtained using a catalytic membrane reactor were higher than those obtained using both fixed bed reactor and certainly higher than equilibrium values at the same working conditions.
Chapter I  General Introduction

Membranes have come a long way since pioneers such as Thomas Graham first tried to understand the new membrane phenomenon some 200 years or so (Dittmeyer et al. 2001). Membranes are nowadays an integral part in all major industries. These industries include among others water desalination, petrochemical, pharmaceutical, food processing (Baker 2000; Mulder 1996; Noble and Stern 1995) and their use is steadily expanding thanks to increasing interest from the industrial sector and researchers working worldwide.

The ever expanding employment of membranes as separation tools, albeit slower in some fields than others, is a direct result of the advantages membranes have over conventional separation processes such as pressure swing adsorption and cryogenic distillation. These conventional separation processes are energy intensive and more complex (Asaeda and Yamasaki 2001; Sircar and Golden 2000). The advantages membranes hold over other separation processes have been reported in literature, they include in addition to the advantages mentioned above, the continuity of the separation operation, the easiness of scaling up, the ability of membranes to be combined with other separation processes (hybrid processing) and the ability to carry out working under mild operations (Mulder 1996).

Membranes can be classified in a number of ways. The one based on the material from which membrane is synthesized, subdivides them into organic and inorganic membranes. The organic membranes, mainly polymers, are widely used in
industry and are made of materials such as polysulfone, polyimide, cellulose acetate, silicone rubber and polyphenylene oxide. They are employed in a number of industrial applications such as microfiltration, ultrafiltration, reverse osmosis and gas separation. They are easy to make, cheap and have good quality control (relatively easy to control the structure in terms of its pore size distribution, thickness and shape) but generally are structurally weak, susceptible to contamination, intolerant to high temperature, and have a short life. On the other, hand the inorganic membranes, which are made of a variety of materials, have superior qualities to those of polymeric membranes, which include high thermal, mechanical and chemical stability, but they are brittle and generally more expensive (Armor 1992). The present study deals with inorganic microporous and dense composite palladium membranes, in particular their preparation, modification, characterization, their separation properties and potential in catalytic membrane reactors.

Thesis organization

Chapter II gives a literature review on membranes, their historic background, classification, preparation and transport. A literature review is also given on catalytic membrane reactors and their potential in dehydrogenation reactions.

Chapter III describes in detail the experimental part of the work carried out in this study, including materials and equipments used. Also a detailed description of the dip coating method used to coat γ-alumina tubes with silica and the electroless plating technique to prepare palladium composite membranes by coating α-alumina tubes with thin palladium films. Experimental rigs and methodology are also described in detail.
Chapter IV covers microporous silica membranes, their characterization in particular the transport mechanisms taking place through such membranes and the effects of various variables on transport mechanisms are discussed.

Chapter V discusses the characterization results obtained form the composite palladium membrane and the effect of sweep gas effects on hydrogen permeation through this type of membrane.

Chapter VI gives results for the propane catalytic dehydrogenation reaction using the composite palladium membrane using both a packed bed reactor and a membrane reactor. The performance of both membranes is compared to each other and to the equilibrium conversion of this thermodynamically limited reaction. The effects of temperature and residence time on the propane dehydrogenation reaction are also discussed.

Chapter VII gives the conclusions from this study and recommendations for future work.
Chapter II Literature review of inorganic membranes

2.1 Introduction

The earliest recorded study performed on membranes was carried out over 250 years ago by the French cleric Jean Nollet (Mason 1991), who observed the osmotic pressure and its effect on liquid phase separation. Although membranes continued to be of interest, this interest was confined to lab observations rather than industrial use. At those early days observations made in laboratories helped researchers understand and formulate theories regarding transport phenomenon through membranes. The use of inorganic membranes in gas separation started in the 1940s on a large scale when the United States government used inorganic membranes to separate UF₆ isotopes for nuclear fuel enrichment by Knudsen diffusion (Noble and Stern 1995).

2.2 Polymeric membranes

It was not until the early 1960s that membranes found a meaningful industrial use when Loeb-Sourirajan developed a process to make reverse osmosis membranes from polymeric material that were defect free and had high fluxes. Membranes fabricated from polymers still constitute the larger bulk of membranes employed in commercial gas separation industries. Some of the typical industrial implementations of such membranes are separation of hydrogen from the product stream of ammonia synthesis (Koros and Fleming 1993), separation of air into its constituents (Alexander Stern 1994) and separation of CO₂ from natural gas. Polymeric membranes are relatively cheaper than inorganic membranes due to their ability to be easily spun into hollow asymmetric fibers or spiral wound modules, as a result of their segmental
flexibility and solution processability. However, they have little resistance to high
temperatures and chemicals. The lack of thermal resistance of polymeric membranes
has restricted their use to applications with mild working conditions.

The huge potential of membranes as separating tools has driven both the
industrial and research sector to develop new materials and work on solving ongoing
problems. Nowadays, as a result of advances in inorganic materials, the use range of
membranes has expanded to areas where working conditions (of high temperature and
harsh environments) are more extreme than those that the material that composes
polymeric membranes can tolerate, e.g. high temperature catalytic membrane reactors.

2.3 Classifications of inorganic membranes

There are a variety of classifications for membranes depending on the category
chosen. Based on their structure, inorganic membranes may be classified as symmetric,
asymmetric and composite.

Asymmetric membranes are such that their pore cross section does not vary
across the membrane’s thickness. Asymmetric membranes, however, possess pores with
varying cross section along the membrane thickness. A composite membrane is an
asymmetric membrane skinned with ultra thin dense layer. Figure 2.1 illustrates the
structure of such membranes.
Inorganic membranes are no different in that respect. The most common category of inorganic membranes classification is pore size distribution defined as the distribution of the specific area versus the pore size. It is an important textural parameter for the determination of morphology and pore structure of a porous solid. Based on pore size distribution, inorganic membranes may be classified as porous or dense membranes.

2.3.1 Porous membranes

Porous membranes are classified further into three subcategories;

1. Macroporous.

According to IUPAC, macroporous membranes are those that have a pore size bigger than 50 nm. Those membranes that have a pore size that lies between 2 nm and 50 nm
are termed mesoporous and those whose pore size is smaller than 2 nm are called microporous membranes.

Most of the inorganic membranes commercially available nowadays are asymmetrical in that they consist of a number of layers varying in size starting with a layer of relatively large pore radius and ending with either a mesoporous or a microporous layer which is very thin. This layer can be located on any side of the membrane and it is the gas separation layer. Most of the commercially available porous membranes do not possess both the desirable characteristics of performance and efficiency that membranes are measured by, namely a required selectivity towards mixtures or a high flux through the membrane. This makes it necessary to modify the membrane in order to improve either the membrane selectivity or flux through the membrane or both. The classification of porous inorganic membranes in terms of their pore size, selectivities and permeabilities, is given in Table 2.1.

Table 2.1 Classification of inorganic membranes (Coronas and Santamaria 1999)

<table>
<thead>
<tr>
<th>porous membrane</th>
<th>Pore size, nm</th>
<th>Permeability</th>
<th>Selectivity</th>
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<tbody>
<tr>
<td>Macroporous</td>
<td>&gt; 50</td>
<td>High</td>
<td>Non-selective</td>
</tr>
<tr>
<td>Mesoporous</td>
<td>Between 2 and 50</td>
<td>Moderate to high</td>
<td>Low to moderate</td>
</tr>
<tr>
<td>Microporous</td>
<td>&lt; 2</td>
<td>Moderate</td>
<td>Can be very selective</td>
</tr>
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</table>
2.3.2 Dense membranes

Dense inorganic membranes have no pores in the conventional sense and are either made of polycrystalline ceramic, metals such as palladium, silver and their alloys or solid electrolytes such as zirconia in addition to other metals of groups 3-5 of the periodic table (Soria 1995). These materials are permeable only to few gases, namely hydrogen and oxygen (Schramm and Seidel-Morgenstern 1999). Whereas silver is permeable to oxygen palladium, other metals such as nickel and platinum, as well as other metals, are permeable to hydrogen (Barrer 1941). These membranes are characterized by their high selectivities towards hydrogen and oxygen which can be as high as 100% (Mottern et al.). Palladium based membranes are better suited to working at high temperatures and offer higher resistance to oxidisation and embrittlement than other hydrogen permeable metals (Li et al. 1998). Although self supporting palladium based membranes are commercially available, their thickness is relatively large 50-100 μm (Dittmeyer et al. 2001). These large thicknesses are necessary to make them mechanically stronger. This results in higher costs due to the larger amounts of palladium used to fabricate them and meant lower hydrogen permeability through these membranes since hydrogen permeability is inversely proportional to the film thickness for such membranes (Coronas and Santamaria 1999; Ismail and David 2001; Shu et al. 1991; Ward and Dao 1999). An ideal membrane should be thin enough so as not to impede hydrogen flux and strong enough to withstand the high stresses it is subjected to during its working life.
2.3.3 Composite membranes

Composite membranes are a compromise between porous and dense membranes and are fabricated from different materials. A composite membrane is one that combines the mechanical strength and the high permeation rates of porous membranes with the high selectivity of dense membranes. They usually consist of a dense top layer (metal, zeolites, etc.) on top of a porous substrate (ceramic, stainless steel, etc.). Different techniques are used to coat porous supports with very thin layers. A composite palladium membrane was used in the present study. Composite palladium membranes offer an attractive alternative economically and in terms of performance. A thin palladium or a palladium alloy film is fabricated onto the surface of a porous substrate thus enabling it to be mechanically strong and have a high hydrogen flux.

2.4 Transport mechanisms through inorganic membranes

2.4.1 Porous inorganic membranes

Gas transport through inorganic porous membranes may be one or a combination of a number of mechanisms (Saracco and Specchia 1994). The gas transport mechanisms across the porous media are dictated by factors such as membrane pore size and pore size distribution and material as well as chemical interaction between the chemical species. These mechanisms are strongly related to the ratio of pore size and mean free path of the gas molecule (Burggraaf 1996). The main transport mechanisms are;
2.4.1.1 Poiseuille flow (viscous flow)

This flow mechanism, also known as viscous and molecular flow, occurs when the mean free path of the gas molecule is smaller than the pore size of the porous medium. In such a flow mechanism (Figure 2.2), the gas molecules tend to collide with each other more than they do with the pore walls. In such conditions no separation takes place.

The molar flux of such transport mechanism can be developed from the Hagen Poiseuille equation (Mulder 1996);

\[
J_v = \frac{r^4P}{8\eta RT} \frac{dP}{dz}
\]  

Where \( J_v \) is the gas flux through the membrane (mol/m².s) resulting from the driving force \( \frac{dP}{dz} \), \( r \) is the pore radius (m), \( P \) is the total pressure (Pa), \( \eta \) is the dynamic viscosity (Pa.s), \( R \) is the universal gas constant (8.314 kJ/mol) and \( T \) is the absolute temperature (K).

Figure 2.2 Schematic diagram of Poiseuille flow (viscous flow)
When porosity $\varepsilon$ defined as the fractional pore area, the pore radius $r$ (m) and the tortuosity factor $\tau$, which is an empirical term that reflects the random orientation of the pore network (dimensionless), are introduced into the above equation it becomes;

$$J_v = \frac{\varepsilon r^2 P}{8\eta \tau RT} \frac{dP}{dz} \quad (2.2)$$

Upon the integration of equation 2.2 across the length of the pores and at constant pressure, the permeance is defined as, $F_v$,

$$F_v = \frac{J_v}{\Delta P} = \frac{\varepsilon r^2}{8\eta \tau RT L} P_m \quad (2.3)$$

where $F_v$ is the permeance across the membrane (mol/m$^2$.s.Pa), $L$ is the thickness of porous membrane (m), $R$ is the universal gas constant 8.314 kJ/mol, $P_m = (P_p + P_r)/2$ is the mean pressure across the membrane (Pa) and $P_p$, $P_r$ are the pressure on the permeate side and retentate side respectively (Pa).

2.4.1.2 Knudsen diffusion

This flow mechanism takes place when the mean free path of the gas molecule is significantly greater than the pore size of the porous medium. Knudsen separation mechanism is mostly dominant in porous media having pore diameters ranging from 2-20 nm Mulder (1996). In this flow regime, gas molecules tend to collide more with the pore walls than they do with each other (Figure 2.3). Gas flux due to this mechanism is inversely proportional to the square root of the molecular weight. The mean free path of
the gas molecules can be increased either by increasing the temperature or by lowering the pressure.

Knudsen flow is described by equation (2.4);

\[ J_k = \frac{2v}{3} \frac{dc}{dz} \]  \hspace{1cm} (2.4)

Knudsen flow

Figure 2.3 Schematic diagram of Knudsen flow

\[ J_k = \frac{2v}{3RT} \frac{dp}{dz} \]  \hspace{1cm} (2.5)

where \( v \) is gas velocity (m/s) and is given by the following equation (2.6);

\[ v = \left[ \frac{8RT}{\pi M} \right]^{0.5} \]  \hspace{1cm} (2.6)
where, $M$ is the molar mass

Integration of equation (2.5) over the membrane thickness and incorporating factors such as the porosity of the membrane and the shape complexity of the pores affords the permeance is given by the following equation;

$$F_k = \frac{J_k}{\Delta P} = \frac{2\varepsilon rv}{3\pi R TL}$$  \hspace{1cm} (2.7)

A number of observations may be made. Firstly, both Knudsen and viscous flow are affected by temperature in that as temperature increases the contribution of each one of them decreases. Secondly, the Knudsen diffusion coefficient is a function of the square root of the molecular weight of the gas, but it is independent of mean pressure.

2.4.1.3 Slip flow

Slip flow occurs when gas transport is intermediate between viscous flow and Knudsen flow. Figure 2.4 illustrates slip flow region compared with Knudsen and viscous flow. When the capillary dimensions are smaller or in the same order of the mean free path, slip flow occurs. In this case, molecule-molecule collisions are gradually negligible and molecule-wall collisions occur.
Slip flow is calculated using equation (2.8),

\[ G = \frac{r}{MvL} \left( \frac{P_u - P_L}{2} \right) \]  

(2.8)

where \( G \) is the molar flux, \( P_u \) and \( P_L \) are the upstream and downstream pressure.

The existence of a single transport mechanism across the membrane occurs somewhat seldom; instead a combination of two or more transport mechanisms usually coexist with one particular transport mechanism being the predominant one.
Of particular interest is the intermediate flow region combining both Knudsen and viscous flows. For this kind of flow mechanism, Burggraaf (1996) proposed that the overall (total) permeance of Knudsen and viscous flows is given by the equation (2.9) that combines both mechanisms;

\[ F_i = F_k + F_v \]  

(2.9)

where \( F_i \) is the total permeance resulting from the combination of both Knudsen and viscous flows; \( F_k \) is the Knudsen flow, \( F_v \) is the viscous flow.

\[ F_i = \frac{2\varepsilon rv}{3\tau R TL} + \frac{\varepsilon r^2}{8\eta \tau R TL} \]  

(2.10)

If we take \( B_0 \) to be equal to

\[ B_0 = \frac{\varepsilon r^2}{8\eta \tau R TL} \]  

(2.11)

and take \( K_0 \) to be equal to

\[ K_0 = \frac{2\varepsilon rv}{3\tau R TL} \]  

(2.12)

then equation (2.9) becomes

\[ F_i = k_o + B_o P_m \]  

(2.13)
Equation (2.13) is particularly useful for pore radius calculations although it is not very accurate as it does not account for the 'slip' at the pore walls.

### 2.4.1.4 Surface diffusion

When the interactions between gas molecules and the pore walls become significant, new additional flow mechanisms appear to take place (Uhlhorn et al. 1989). Surface diffusion is such a transport mechanism which occurs when gas molecules have a strong affinity to adsorb on the pore walls. In such a transport mechanism, the preferentially adsorbed molecules diffuse on the surface due to a concentration gradient in the adsorbed phase.

### 2.4.1.5 Capillary condensation

This flow regime takes place at low temperatures when pores are blocked by condensate which evaporates at the permeate side as a result of imposed low pressure. A meniscus is formed at the feed side that promotes further condensation due to decrease in vapour pressure. This flow mechanism can achieve high selectivities as a result of the condensable gas blocking the noncondensable gas (Uhlhorn et al. 1992), (Sotirchos and Burganos 1999).

### 2.4.1.6 Molecular sieving

This mechanism occurs when the pore size of the porous medium approaches that of the diffusing gas species. Here only gas molecules smaller than pore size are allowed to travel through them, any other molecules are blocked. Some of the materials that can be fabricated to promote this flow mechanism are silica and zeolites (Fuertes
and Centeno 1998). Figure 2.5 is a schematic diagram of gas transport mechanisms through porous membranes.

### 2.4.1.7 Configuration diffusion

This transport mechanism takes place when the pore size of the membrane decreases to the dimensions of the gas molecules such as in zeolites. In such a transport mechanism, very small changes in molecule/pore size induce very large changes in the diffusion coefficient resulting in strong shape selectivity (Ramoa Ribeiro et al. 1995)

### 2.4.2 Dense inorganic membranes

Hydrogen transport through palladium is believed to follow the solution diffusion mechanism (Hughes 2001). If the hydrogen transport through the palladium bulk is the rate limiting step then the process of hydrogen diffusion through such membranes is a multi step process that starts with the

1. Molecular hydrogen is adsorbed on the bulk surface.
2. Dissociation of the hydrogen molecules into atoms.
3. Hydrogen atoms dissolve into the palladium.
4. Hydrogen atoms diffuse into the palladium.
5. Hydrogen atoms arrive at the low pressure side of bulk metal.
6. Hydrogen atoms recombine into molecules.
7. Hydrogen molecules desorb away from the bulk metal.
Figure 2.5 Transport mechanisms through porous inorganic membranes

a) viscous flow; b) Knudsen flow; c) surface flow; d) intermediate flow

e) capillary condensation flow; f) molecular sieving flow (Saracco and Specchia, 1994)
In such a mechanism, hydrogen flux is calculated using Fick's law;

\[ j = \frac{Q}{\delta} \left( P_h^n - P_i^n \right) \]  

(2.13)

where \( J \) is flux (cm\(^3\)/cm\(^2\).s), \( Q/\delta \) is the permeance (cm\(^3\).cm/s.bar\(^n\)), \( Q \) is the permeability (cm\(^3\).cm/cm\(^2\).s.bar\(^n\)), \( \delta \) is the membrane layer thickness, \( P_h^n \), \( P_i^n \) are the hydrogen partial pressures on the feed side and the permeate side respectively and \( n \) is the hydrogen pressure exponent, which is equal to 0.5 when the rate limiting step is the bulk metal diffusion of the atomic hydrogen (Sieverts and Kumbhaar 1910).

2.5 Fabrication methods of inorganic membranes

Several methods are used to fabricate inorganic membranes; the methods used depend largely on the objective of the membranes to be fabricated. Some of the most common methods used for membrane fabrications are listed below.

2.5.1 Porous inorganic membranes

2.5.1.1 Phase inversion

There are two variants of this process the more common one involves the preparation of a concentrated solution of a polymer in a solvent. The solution is then spread into a thin film, and then precipitated through the addition of a non-solvent such as water.
2.5.1.2 Anodic oxidation

This method is used to fabricate alumina membranes. The method involves the oxidation anodically of one side of a thin aluminium foil sheet at a moderate voltage in an acid electrolyte such as phosphoric, sulfuric, oxalic or chromic acid or their mixtures at low to moderate temperatures (0-60 °C). The resulting porous oxide film obtained contains a regular array of hexagonal packed cells formed perpendicular to the surface of the metal. Each cell is composed of a cylindrical pore open at one end but closed at the other where a thin aluminium film still blocks the formed pores. In order to open the closed end the metal sheet needs to be removed, this is done by dissolving the metal sheet in hydrochloric acid, cupric chloride or bromide solution.

2.5.1.3 Sol gel

This process involves the preparation of a so called gelatinous substance called a gel by two different routes, a colloidal suspension route and polymeric gel route. In both routes, a precursor, either an inorganic salt or a metal organic compound, is hydrolysed with simultaneous condensation or polymerization reaction. Once a stable sol (a colloidal dispersion of particles in a liquid) is obtained, a few organic chemicals to promote adhesion and modify viscosity are added to the sol. This sol is then cast on a dry porous support and, as a result of capillary forces, water is drawn inside the support leaving gel particles at the pore openings in the support.

2.5.1.4 Pyrolysis

Inorganic porous membranes such as silica and carbon molecular sieves can be made from organic polymers such as silicone rubbers and thermosetting polymers by
degrading the organic polymers by pyrolysis under an inert atmosphere followed by sintering in air.

2.5.1.5 Phase separation and leaching

Porous glass membranes are produced using this process. This process manipulates heat and chemical leaching. Glass making materials such as silica and boron sands along with sodium compounds and alumina are first melted into a homogeneous glass then moulded into the required shape. Under certain conditions of time and temperatures the glass separates into two separate phases. One of the phases consists mainly of silica while the other consists of boric acid. The boric acid phase is then dissolved out of the heterogeneous glass with mineral acid leaving behind a porous glass.

2.5.2 Dense composite membranes

A number of methods are used to modify membranes; this can be done by either coating methods, where the surface of the membrane is coated as the name implies by a thin film, or by modifying its surface to reduce its pore size.

Some common methods used in coating inorganic membranes with a thin dense layer are briefly reviewed below.

2.5.2.1 Magnetron sputtering technique

In this process a plate of material to be deposited is bombarded inside a vacuum chamber with high energy argon ions causing the ejection of both ions and atoms from
the target followed by deposition under condensation of these atoms on an adjacent substrate in the form of a continuous film. This method has been successful in coating different substrate materials. (Checchetto et al. 2004; Nam and Lee 2000; Yildirim et al. 1997) used the magnetron sputtering technique to coat stainless steel substrates with thin palladium films. The former coated commercially available mesoporous composite stainless steel disks with a palladium layer having a thickness of less than 2 μm, and the latter used this method to partially fill the pores and coat the surface of the substrate with a polymeric layer with the aim of fabricating a suitable surface morphology for the palladium film they deposited on the polymeric layer. Yildirim et al.(1997) used this method to coat a Vycor glass tube with a 4 μm Pd/Ag film. Zhao et al.(2000) used this method to coat a commercially available microfiltration ceramic membrane after appropriate preparation; the γ-Al2O3 was coated with a 24% wt. Pd/Ag film having a thickness of 1 μm.

2.5.2.2 Spray pyrolysis

This method involves spraying a slurry solution containing metal salts into a heated gas stream where it is pyrolysed. Li et al (1993) used this technique to deposit Pd/Ag alloy films 1-2 μm thick onto the porous alumina surfaces by spraying Pd(NO3)2 and AgNO3 solution in a H2–O2 flame. However, H2/N2 selectivity obtained by this membrane was only 24 at 500°C which suggests the presence of pinholes.

2.5.2.3 Chemical vapour deposition

This method involves the reaction inside the pores of a membrane of vaporized metal organic components (carried by gas) and other reactants. The reaction product is
deposited inside and onto the membrane pores. This method can be used to coat membrane substrates such as porous Vycor glass (Daub et al. 2001; Nakao et al. 2000; Prabhu and Oyama 2000), porous alumina (Daub et al. 2001; Uemiya et al. 2001).

2.5.2.4 Dip coating

This technique was used in the present study to modify the outer surface of γ-alumina tubes with silica. Scriven (1988) divided the this process into five stages; i.e. the immersion, start-up, deposition, drainage and evaporation stages. The slip casting mechanism is dominant in the initial stage. At this stage, capillary forces draw the fluid into the porous support. As the support is withdrawn from the solution, further deposition takes place by dip-coating. At this stage, the solution entrained on the surface of the support is concentrated by evaporation leading to gelation and finally the collapse of the gel network by capillary of forces accompanying the drying stage. The evaporation takes place during all stages as a result of using a volatile solvent. Several factors affect the resulting film fabricated; such as the structure of the inorganic polymer (condensation and aggregation rates), the time scale of the deposition (related to substrate withdrawal rate and film thickness) and the magnitude of the shear force and capillary effects that accompany the membrane deposition (related to surface tension and gradients in mixed solvents) (Brinker et al. 1990).

2.6 Influence of diffusion direction on gas permeation through porous membranes

A few studies have been undertaken on the effect of diffusion direction on gas permeation through porous media (Schramm and Seidel-Morgenstern 1999; Thomas et al. 2001). In their work, the diffusion direction across asymmetrical membranes
consisting of several layers of $\alpha$-alumina and $\gamma$-alumina layers and a top silica layer were investigated. The results obtained revealed that the flux obtained by gas diffusion direction from the largest pore size layer towards the smallest layer was larger by 6% than that obtained when the diffusion was from the smallest pore size layer towards the largest pore size.

This phenomenon could be significant and therefore it has been investigated in the present work using silica/$\gamma$-alumina membrane prepared by the dip coating method.

2.7 Preparation of composite palladium membranes

Several methods are used to deposit palladium or palladium alloy films on porous substrate. These include among others;

1. Electroless plating.
2. Chemical vapour deposition.
3. Physical vapour deposition.
4. Magnetron sputtering.
5. Sol gel process.

2.8 Preparation of membranes for catalytic reactors using the electroless plating technique

The electroless plating technique is still relatively young; a lot has still to be learned about it. Researchers worldwide are still experimenting and trying to understand the process. The ongoing research covers all aspects of this technique, such as its
suitability to plate certain materials, plating bath compositions, sensitization and activation solutions, working conditions, deposited metal film quality.

2.8.1 Electroless plating technique

This method is commonly used to deposit metallic films onto porous supports. Because of its simplicity in terms of equipments used, low cost and the highly uniform dense films it usually produces on almost any shape of many different materials, it has attracted great attention. Some of its drawbacks are;

1. Difficult to control thickness of deposited film.
2. Difficult to control composition of the plating solution.
3. Deposited film may contain impurities.
4. Difficult control rate of palladium decomposition.

Electroless plating is based on the reduction of a solution containing an EDTA stabilised palladium salt complexes using an appropriate reducer such as hydrazine (in a hydrazine based plating solution) onto an activated surface (preseeded with palladium nuclei using sensitisation activation methods). Ammonia is usually used to stabilise the plating bath. The deposited palladium particles catalyze further reaction and, as a result, a uniform film on the activated surface is obtained. In present work, two different activation methods were employed to activate the α-alumina tubes used as supports.

The conventional substrate surface sensitization activation method using Sn (II) takes place according to the following equation

\[ \text{Pd}^{2+} + \text{Sn}^{2+} \rightarrow \text{Pd}^{2+} + \text{Sn}^{4+} \]
and the palladium deposition takes place according to the following equation:

\[ 2Pd^{2+} + N_2H_4 + 4OH^- \rightarrow 2Pd + N_2 + 4H_2O \]

Some of the aspects researched include improving the quality of the palladium films obtained using this method. Yeung et al. (1998) introduced two different ways of improving the quality of palladium films deposited onto porous Vycor glass tubes using the electroless plating technique. Plating bath modification was one way and incorporation osmosis into electroless plating procedure was the other. The electroless plating solution modification way involved the addition of formaldehyde to the otherwise hydrazine-based plating solution. The results showed that the use of both the modified plating solution and the incorporation of osmosis into the plating procedure resulted in thinner and denser palladium films (0.8 μm for the modified plating solution and 0.9 μm for the osmosis assisted electroless plating compared to that of 3.5 μm obtained by the conventional hydrazine-based electroless plating solution).

Electroless plating assisted with osmosis was used successfully to plate a porous alumina membrane (Zhao et al. 2000). The electroless plating procedure involved activating the membrane with a sol gel of a Pd(II)-modified boehmite sol followed by electrolessly plating the activated support with the assistance of osmosis. The resulting palladium thickness was 1 μm. The membrane was stable at high temperatures up to 450°C and produced H₂/N₂ selectivity of 20-130, and a hydrogen flux of 1.8-87 m³/m².h, depending on the operation conditions.
The electroless plating technique has been used to deposit palladium and palladium and its alloys onto stainless steel surfaces. Li et al. (1998) employed the electroless plating technique combined with osmosis to deposit a palladium film onto the outer surface of stainless steel tubes. The thickness of the palladium film obtained was estimated to be around 10 μm. It was noted that the palladium film obtained was dense with small palladium particles deposited among the larger particles which was attributed to the employment of both techniques. This procedure gave a hydrogen flux of 12 cm$^3$/cm$^2$ min and a hydrogen to nitrogen selectivity ratio exceeding 1000 at temperatures above 400°C.

Reducing the pore size of relatively large pore size supports makes them more suited to palladium deposition using the electroless plating technique. A palladium membrane was prepared by Wang et al. (2004) on the surface of a porous stainless steel filter tube using electroless plating. The large pores of the stainless steel tube were first reduced by placing colloidal zirconium oxide particles inside the stainless steel pores followed by heat treatment. Electroless plating then followed in a hydrazine-based plating bath. The thickness of the palladium film obtained was 10 μm. The hydrogen flux through this membrane and the activation energy were lower than those obtained by a palladium membrane on porous glass which was attributed to the zirconium oxide resistance to hydrogen diffusion inside the pores.

Hydrogen fluxes were shown to be significantly higher at elevated temperatures through the palladium and palladium silver composite membranes prepared by the
sequential plating of palladium followed by silver onto tubular stainless steel supports (Lin and Chang 2004).

A diffusion barrier is usually placed between the membrane substrate and plated film if an intermetallic diffusion between the plated film and the substrate is expected. The reason for this is such diffusion may cause the hydrogen flux through palladium composite membranes to decrease especially at elevated temperature. Gao et al.(Gao et al. 2005) electrolessly plated two groups of membranes with different Pd/Cu ratios. The two membranes prepared were Pd_{84}Cu_{16} and Pd_{46}Cu_{54}. Zirconia was used as a diffusion barrier between the Pd/Cu and the substrate and the palladium alloy films obtained using this method were homogenous and gave infinite H\textsubscript{2}/N\textsubscript{2} selectivities.

The effect of tin chloride used to sensitize substrates on the quality of palladium films produced using the electroless plating method was investigated by Paglieri et al (1999). Palladium films obtained using tin chlorides of various amounts were compared to that obtained using a modified sensitization activation method that uses palladium acetate in chloroform solutions as a sensitizer and does not involve tin chloride. For this purpose, symmetrical α-Al\textsubscript{2}O\textsubscript{3} tubes were used as substrates. They reported that, as the mount of Sn used in the sensitization stage decreased, the hydrogen to nitrogen selectivity was stable for longer; it did not, however, eliminate the problem. This was explained by four possible reasons; the entrapment and adsorption of Sn or chlorine at the interface between the palladium and the substrate surface, the diffusion of Sn along the grain boundaries, which enlarged channels for the diffusion of gases, the different thermal expansion coefficient between the palladium and the substrate and finally the
transformation of porosity originated during plating into the pores. The performance of the composite palladium film fabricated using the modified sensitization activation method gave a constant nitrogen flux for at least a week at 700°C.

A good palladium film is one that is very dense. A novel hydrothermal method was reported by Zheng and Wu (2000) to coat a porous α-Al₂O₃ disc with a palladium film using electroless plating. The purpose of this method was to control the systematic pressure of the plating process in order to improve the density of the palladium film obtained through pore size shrinkage. This method involved controlling the pore size of the substrate by dip coating it first with a boehmite sol, followed by calcination at 900°C for 5 hours which lead to substrate pore size decrease from 3.60 μm to 0.8 μm. This was followed then by coating the substrate with a 0.44 μm palladium film which was smaller than the 0.55 μm palladium film obtained using the conventional electroless plating method.

Various issues related to electroless plating technique such as the influence of osmosis on metal grains size and penetration into substrate were investigated by Souleimanova et al. (2000). They also claimed the development of a new substrate activation procedure. The workers chose a porous polished Vycor glass disc as substrate. A comparison was made between the plated palladium grain size obtained when osmosis was used during the activation step and electroless plating on palladium films obtained when osmosis was only used at the electroless plating procedure or when not used at all. The results obtained showed that the smallest palladium grain size was obtained when osmosis was applied at both stages of activation and electroless plating.
and the second smallest palladium grain size was obtained when osmosis was only implemented during the electroless plating procedure and the largest palladium grain size was obtained when no osmosis was employed at all. The results also showed that the higher the osmotic pressure used the smaller the palladium particle sizes were.

The electroless plating was successfully used to repair palladium films possessing defects. Li et al. (2000) initially found the palladium film plated onto the outer surface of Pd/ α-alumina membranes fabricated using the conventional electroless plating technique had defects and only gave a H₂/N₂ selectivity ratio of 10. Electroless plating combined with osmosis was used to repair a composite palladium membrane. The osmotic pressure was provided by 3 M NaCl solution. The palladium film obtained after repair was defect free within the temperature range from 320-577°C and had a thickness of 10.3 μm. The hydrogen permeation was found to diverge a little from Sievert’s law and both sweep gas and total feed flow rate improved the hydrogen permeation with a final H₂/N₂ ratio of 1000.

Electroless plating can be used to plate metals other than palladium and its alloys such as Ni. Xue et al. (2001) fabricated a Ni–B alloy onto α-Al₂O₃ tubes using this technique. The α-Al₂O₃ was first dipped into a boehmite γ-Al₂O₃ sol (0.5 M) followed by drying and calcining then brushed with a metal paste consisting mainly PdCl₂ and followed by activation in air at 600°C. Finally, it was plated with Ni-B alloy with the help of vacuum which helped give smaller and more homogenous Ni–B clusters as a result of better contact between the plating solution and the activated substrate and the absence of entrapped air and gases which otherwise would have created pinholes and
defects. Combinations of Knudsen and solution diffusion mechanism were reported to take place through these membranes.

One of the advantages of electroless plating method is its ability to plate materials of all shapes. Pan et al. (2003) used electroless plating to deposit palladium films onto $\alpha$-$\text{Al}_2\text{O}_3$ hollow fibers. The preparation step involved coating an intermediate Pd pre-seeded $\gamma$-$\text{Al}_2\text{O}_3$ layer on the outer surface of the macroporous hollow fibers using the sol gel process followed by drying and calcining at 750°C in air and then activation in a 10% $\text{H}_2+\text{N}_2$ atmosphere. The plating bath was hydrazine-based. Characterization of the membrane showed the thickness of the palladium film obtained to be 2-3 $\mu$m. The membrane gave hydrogen to nitrogen selectivity of over 1000 and was stable and durable at 430°C for over 800 h.

Lin and Chang (2005) prepared Pd and Pd/Ag membranes of different palladium and silver loadings using the electroless plating technique, deposited onto the inside of a stainless steel support tube with an average pore size of 4 $\mu$m. The procedure consisted of cleaning and a two step activation method in acidic SnCl$_2$ followed by acidic PdCl$_2$. A number of issues were investigated such as the surface morphology, effect of calcinations and permselectivity of the membranes. A correlation between the skin layer roughness and deposition rate was identified. Roughness of the Pd/Ag film was found to increase with palladium loading and the sequential process followed by calcining produced a homogenous Pd/Ag film. The gas characterization of the composite membranes prepared in this study showed that overall gas flow was the result of a combination of viscous and Knudsen mechanisms.
Volpe et al. (2006) used a modified plating bath to electrolessly plate an anodic alumina tube. The constituents of the modified plating bath were chosen to give a pH of 8.3 rather than the 9-11 values of conventional hydrazine-based plating baths. The use of pH 8.3 was to ensure the prevention of the dissolution of the anodic alumina support and to give the best compromise between the rate of Pd deposition and the rate of alumina dissolution in the plating solution. For this plating bath, a 30 min plating duration was found to be the optimum time to avoid extensive damage to the membrane. The palladium deposited did not seal the pore mouths of the membrane and was located exclusively on the membrane surface.

Membranes made of ceramic materials are well suited to working in very harsh conditions of temperature and pressure due to their thermal and chemical stability as well as their mechanical strength as mentioned elsewhere. For the above mentioned reasons, electroless plating was the method chosen in the present work to fabricate palladium composite membranes with $\alpha$-alumina tubes as substrates. Vacuum was initially employed to help give smaller palladium clusters and better contact between palladium and the activated substrate. Then, at a later stage osmosis was introduced to further densify the plated film. No diffusion barrier was used as intermetallic diffusion was not anticipated at the relatively low temperatures used in the present work, and reducing pore radius prior to electroless plating was not necessary as the palladium films plated on the $\alpha$-alumina tubes were of acceptable quality.

The palladium composite membranes fabricated were used as catalytic membrane reactors for the dehydrogenation of propane at elevated temperatures. Their
gas separation properties were also investigated. The reaction takes place inside the catalyst packed interior of a tubular reactor and one reaction product namely, hydrogen is removed from the reaction zone thorough the palladium film located on the outside of the composite palladium membrane.

2.9 Catalytic membrane reactors

The demand for alkenes such as ethylene, propylene and isobutene is on the increase as a result of their use as raw materials for a number of chemical industries such as plastics, fibers and other chemicals. These chemicals are obtained industrially from fluid catalytic crackers and steam cracking the yield of which is low due to thermodynamic limitations. Another problem with the present production methods of olefins is the possible depletion of the natural resources (hydrocarbons) (Bobrov et al. 2005). One possible way of improving the yield is the catalytic dehydrogenation of alkanes using catalytic membrane reactors. The removal of hydrogen from the thermodynamically limited reaction promotes conversion and lower working temperature, and also provides $\text{H}_2$ as a useful by product.

The concept of catalytic membranes have been studied and researched for quite some time now and interest in them has been on the increase for their potential in a number of chemical reactions. Two different unit operations namely reaction and separation can be combined and carried out inside a catalytic membrane reactor, which is of considerable economic significance. Two of most common functions of catalytic membrane reactors are;

2. Control and addition of one or more reactants.

The membrane reactor preferentially separates and removes one of the reaction products. In the case of thermodynamically limited reactions, the removal of one or more of the reaction products shifts the equilibrium to the right which means higher conversions.

In the case of the controlled addition of one or more reactants, a reactant is fed through the membrane along the length of the reactor. In some applications where the use of oxygen is necessary, for instance such as in some oxidation processes, it is found that the introduction of low pressure oxygen favours the selective oxidation over the deep oxidation to give CO and CO₂ (Coronas and Santamaria 1999).

2.10 Membrane/catalyst configuration

A number of catalysis/membrane configurations exist depending on where the catalyst is located. Figure 2.6 is a schematic diagram of the three different catalyst/membrane configurations.

The first one is a packed bed reactor in which the reactor itself is inert and the catalyst is separate from the membrane. This is the typical arrangement of the first function mentioned above. In the second arrangement, the catalyst is located within the membrane pores. This kind of configuration facilitates easier access of the reactants to the catalyst. In the third configuration the membrane itself is a catalyst and a separator.
Bed of catalyst on an inert membrane

Catalyst is dispersed in an inert membrane

Inherently catalytic membrane

Figure 2.6 Catalyst/membrane combinations
Catalytic membrane reactors have been studied for many dehydrogenation reactions such as the oxidative dehydrogenation of methanol (Brinkmann et al. 2001), (Ermilova et al. 2006), decomposition of ammonia (Abashar et al. 2002), the oxidative coupling of methane, (Mleczko et al. 1996; Ostrowski et al. 1998), the oxidative dehydrogenation of isobutane (de Jesus Diaz Velasquez et al. 2006), the dehydrogenation of isobutane (Liang and Hughes 2005a), the dehydrogenation of ethylbenzene (Li et al. 2007), the dehydrogenation of cyclohexane (Abashar and Al-Rabiah 2005; Jeong et al. 2003)

2.11 The use of sweep gas in catalytic membrane reactors

Either inert or reactive sweep gases can be utilized in catalytic membrane reactors to reduce the pressure difference across the membrane. This results in a pressure difference increase across the membrane which in turn increases the gas flux across the membrane. Schramm and Seidel-Morgenstern (1999) compared cyclohexanol conversions obtained using an inert sweep gas (N2) to those using a reactive sweep gas (air) in a porous glass membrane. The conversions obtained using air as a sweep gas were higher than those obtained using nitrogen which was the result of hydrogen consumption by oxygen in air. This further enhanced the diffusion of hydrogen through the membrane as a result of the bigger pressure difference. All this resulted in further shift of equilibrium conversion.

The influence of inert and reactive sweep gases on the propane dehydrogenation were also studied by Yildirim et al. (Yildirim et al. 1997) who compared propane conversion obtained using reactive sweep gases (CO and air) to those conversions
obtained using nitrogen employing a Pd/Ag composite membrane. The propane conversion obtained using nitrogen sweep was about 17.5% at 400°C compared to the much higher propane conversion of 51% obtained using air and 38% using 11% CO/N₂.

Another study where the influence of reactive sweep on a n-butane conversion was investigated by Gobina and Hughes (1996b). The obtained results showed that reaction coupling of the permeated gas using reactive sweeps for the Pd/Ag membrane gave higher conversions than those obtained using non reactive sweep gases. While the n-butane conversion obtained using nitrogen in co-current mode nitrogen was 13.5%, it increased to 20% under counter-current mode. The use of 11% CO in N₂ gave a conversion of 21% and 21% O₂ in N₂ gave an n-butane conversion of 40%. In a later study (Gobina et al. 1995), it was reported that only concentrations of 5% O₂ and 2% of CO were needed to obtain maximum n-butane conversion.

Gobina and Hughes (1996a) used a composite palladium membrane consisting of palladium film plated on top of a porous Vycor glass tube using magnetron sputtering to study the effect of reactive sweep gas (air (21% vol% O₂)) and inert sweep gas (N₂) on ethane dehydrogenation. Higher ethane conversions were obtained when using the reactive sweep gas than when using nitrogen.

The sweep gas is said to be co-current if its flow direction is the same as that of the gas feed flow and counter-current if the flow direction of the sweep gas is in opposite direction to that of the gas feed mixture. The pressure difference across the membrane is constant over the length of the membrane when the sweep gas flows.
counter-currently to the feed gas, however, it is not the case when the sweep gas flows co-currently. In the latter case, the pressure difference is highest at the membrane inlet and decreases gradually over the membrane length making the counter-current mode the better of the two.

2.12 Propane dehydrogenation reactors

Propylene is an important raw material for many petrochemical products such as polypropylene, acrylonitrile (Andy and Davis 2004), propylene oxide, cumene, phenol, isopropyl alcohol and many others. As a result of global demand for just polypropylene, it is projected that by year 2010 the propylene production will grow to 84 million tonnes (Corma et al. 2005).

2.13 Propylene production route by catalytic membrane reactors

1. Oxidative propane dehydrogenation.
2. Non oxidative propane dehydrogenation.

Oxidative propane dehydrogenation involves feeding the reactor with oxygen either pure or in air at high temperatures which when mixed with the hydrocarbon in the feed could lead to the formation of dangerous explosive mixtures. Non-oxidative propane dehydrogenation on the other hand does not pose such a problem and was chosen to be the case study of the present work
2.14 Literature review on propane dehydrogenation using catalytic membrane reactors

Ziaka et al. (1993a) utilized a commercially available membrane under the trade name of Membrox to study propane dehydrogenation. The membrane used was an asymmetric composite porous alumina tube with an inner diameter of 7 mm, an outer diameter of 10 mm, and a length of 250 mm. The membrane consisted of three layers of 4 nm, 200 nm, and 800 nm supported by a macroporous layer with a pore diameter of 15 μm. The membrane had an internal volume of about 10 cm$^3$ and was packed with 14 mesh commercial 0.5 % Pt/$\gamma$-Al$_2$O$_3$ impregnated with Mg by a wet impregnation technique to improve its sintering and coking characteristics. The experiments were carried out in the temperature range of 520-600°C. Experiments were made with different feed mixtures, the first composed of propane, propylene and hydrogen with molar ration of 1:0.25:0.25 and a residence time of 2 seconds and a tube-side pressure of ~14-21 kPa and a shell side pressure of ~0-7 kPa and no sweep. They observed that propylene yield increased with temperature and that at 600°C the membrane gave a propylene yield of 52.23% as compared to 30.72% obtained by the conventional reactor. This was attributed to the improved conversion and selectivity which was 10% better than that of the conventional reactor. By-products of this reaction included methane, ethylene and small traces of ethane. The effect of propylene to propane ratio in the feed was also investigated. It turned out that as this ratio increased, propylene yield decreased in both reactors and, in all experiments, the membrane reactor performed better than a conventional reactor.
In another study, (1993b) a similar membrane to the one mentioned above was used for propane dehydrogenation. For the propane dehydrogenation experiments in the packed bed membrane reactor, a similar catalyst to the one used in their previous study was used together with a feed gas mixture composed of 80 mol.% propane and 20 mol.% hydrogen and no sweep gas. The experiments were carried out at temperatures ranging from 480°C to 625°C. They observed that for both reactors, propylene yield and propane conversion increased with increasing temperature and residence time but selectivity decreased with both increasing temperature and residence time. The membrane reactor always gave higher propylene yields and propane conversions than the conventional reactor.

Two different membranes were utilized by Collins et al. (1996) in their study of propane dehydrogenation. A silica based membrane with the silica layer on the top of γ-alumina layer having a pore diameter of 5 nm was located on the inside of the asymmetric ceramic support. The support was fabricated by depositing silica layers from a polymeric silica sol using a sol-gel process that involved a combination of slip-casting and dip coating. The other membrane consisted of a ceramic tube with a palladium film coated on top of an α-alumina layer having a pore diameter of 200 nm. The palladium film was fabricated using the electroless plating technique. The reactors, both conventional and membrane, were loaded with a platinum aluminosilicate molecular sieve developed by Amoco Crop. The propane conversions using both membranes were higher than those obtained using a conventional packed bed reactor at the same temperatures and with the same conditions of feed flow rate and composition. The silica based membrane gave a propane conversion of 39.6% at 550°C compared to
the 29.6% of the packed bed reactor, but the downside was the accelerated drop of the propylene yield as a result of catalyst deactivation. The composite palladium membrane gave small propylene yields at low temperatures and even smaller yields at the high temperature of 560°C. This was attributed to the instability of the palladium membrane.

Sheintuch and Dessau (1996) studied propane dehydrogenation by means of two different membranes namely, a 2% Ru/Pd alloy tube with a wall thickness of 254 μm and a 25% Pd/Ag membrane metal tube with a wall thickness of 76.2 μm. Several experimental runs were carried out using different catalyst loadings (0.5, 0.75, and 1.0 g) of supported Pt (0.52%) packed inside the membranes and a sweep gas. They reported a propylene yield of 70% obtained by the Ru/Pd membrane at 550°C compared to 32% at equilibrium, but this was only achievable at the extremely low flow rate of 1 cc/min. It was observed that the rate of propylene yield decline was faster in the thinner Pd/Ag membrane. This was attributed to the higher rate of hydrogen removal from this membrane. The initial propylene yield obtained using the Pd/Ag membrane at 550°C was 47.5% which was less than the 70% obtained using the Ru/Pd membrane at the same temperature. This was explained by the inhibition of the reaction rate at minute concentrations of hydrogen. At much higher flow rates, the propylene yield declined to levels below equilibrium. The much thinner Pd/Ag composite membrane was the reason behind the much faster catalyst deactivation of the catalyst which gave a lower propylene yield than that obtained by the Ru/Pd membrane at the same temperature of 550°C. This was attributed to the higher rate of hydrogen removal from this membrane.
The performance of differently prepared membranes for propane dehydrogenation using Pt/Al$_2$O$_3$ as catalyst was investigated by Yildirim et al. (1997). These included: a dense Pd/Ag composite membrane prepared by magnetron sputtering with a porous Vycor glass tube as substrate, an asymmetric porous γ-alumina Pd-impregnated membrane, and a Pd/Ag composite membrane prepared by magnetron sputtering with an asymmetric porous γ-alumina tube as a substrate and identical to the one used for the Pd-impregnated membrane. The propane dehydrogenation experiments showed that the performance of the dense Pd/Ag composite membrane was superior to the palladium impregnated membrane. The Pd-impregnated membrane could only give measurable propane conversions at temperatures higher than 500°C at which temperature cracking reactions and coke formation started to take place. Although this membrane gave a conversion of 21%, similar to that of equilibrium at 517°C, the dense Pd/Ag gave the same conversion but at the lower temperature of 400°C which is a four times higher than that of equilibrium value. The effect of sweep gas (N$_2$, CO/N$_2$, air) on the propane conversion was also investigated for both membranes. It was found that the use of sweep gas, rather than improving the propane conversion for the impregnated palladium membrane, had the opposite effect due to propane loss. However, although the propane conversion was a little above equilibrium when not using sweep gas, the use of sweep gas did improve the propane conversion for the dense palladium composite membrane. The employment of nitrogen at 400°C increased the conversion by 17.5%, the use of 11% CO/N$_2$ by 38% and air by 51%. These values could only be reached at the much higher temperature of 500°C for the porous palladium impregnated membrane.
Direct propane dehydrogenation was investigated by Weyten et al. (1997) using a commercially available tubular silica based alumina membrane fabricated using chemical vapour infiltration (CVI) acquired from Media and Process Technology Inc. (MPT). This particular membrane is temperature resistant and quite stable. The tube had an inner diameter of 7 mm and an outer diameter of 10 mm and a length of 250 mm with glass coatings at both ends of the tube to ensure gas tight sealing. Three catalysts were used for this study, namely; the standard Cr2O3/Al2O3, a chromia/alumina with potassium promoter and chromia/alumina with cesium and zirconium. All were supported on γ-Al2O3. The activity and the deactivation of the three catalysts were tested at three different temperatures of 450°C, 500°C, and 600°C in the packed bed reactor with a feed mixture of 0.25 vol.% C3H8 in argon. The results showed that at 400°C, coking was not a problem as these catalysts were stable giving propylene yields ranging from 3-5%. These low yields compared to the theoretical yields, were attributed to the high WHSV rate of 0.07 h⁻¹. Deactivation was a big problem at 600°C and propylene yields dropped very quickly. Propylene yields were stable at 17-18% for more than 12 hrs at a temperature of 500°C before they started to decline with coking. As a result of the test carried out on the three different catalysts, the standard chromia/alumina catalyst was chosen for the catalytic membrane reactor study. The effect of hydrogen concentration on the catalyst deactivation was also investigated. The results showed that the addition of hydrogen at 500°C to the feed did not affect the deactivation of the catalyst and hence it was decided that 500°C was the temperature at which the catalytic membrane reactor was to be operated. Pure propane was used as the feed mixture for propane dehydrogenation reaction and the experiments were carried out by packing the membrane with 7.5 g of Cr2O3/Al2O3 at 500°C and atmospheric
pressure. Nitrogen sweep gas in co-current mode was utilized to provide an additional driving force. Regular catalyst regenerations were carried out to burn off coke formed using a mixture of 4 vol.% O₂ in N₂. For their calculations, the authors chose not to take hydrogen and nitrogen into account and, for the yield and selectivity of reaction, only products in the retentate were considered. The propane conversion they obtained using a membrane reactor was 23.8% which was higher than that of equilibrium by 34%. The selectivity obtained was 89% which was a little higher than that obtained using a plug flow reactor. The experiments showed that propane conversions could be improved to almost double the equilibrium conversion but propane conversions were only significant at weight-hourly-spaced-velocities higher than 0.25 hr⁻¹.

Quicker et al. (2000) compared alumina and stainless steel substrate performance for propane dehydrogenation following Pd deposition. A combination of electroless plating technique and chemical vapour deposition was used to plate asymmetric alumina tubes having a thin layer of 0.5 μm pore radius on the inside, with palladium films having a thickness of 2.3 μm. A combination of electroless plating, electroplating, physical vapour deposition and high velocity oxy-fuel spraying were employed for coating the stainless steel tubes with palladium films having a thickness of 8 μm on the outside. The results obtained showed that the propane conversion obtained using the palladium-ceramic membrane were higher than those obtained using the conventional packed bed reactor, the propane conversion increased from 29% for the packed bed reactor to 35.4% for the palladium ceramic membrane. On the other hand, the conversions obtained using the palladium stainless steel membranes were even higher due to the higher hydrogen amount removed through this membrane.
A comparison between the performance of two differently prepared membranes was carried out by Weyten et al. (2000). The performance of a commercially available Pd/Ag membrane having a 7.5 μm thick palladium layer coated onto the outer surface of an Al₂O₃ tube of 200 mm in length and an outer diameter of 25 mm using chemical plating was compared with that of CVI-silica membrane having a length of 250 mm and an inner and outer diameter of 7 and 10 mm respectively. The same catalyst Cr₂O₃/Al₂O₃ was employed for both experiments, but 21 g was used for the Pd/Ag membrane and 7.5 g for the CVI-silica membrane. The experiments were carried out at 773 K and atmospheric pressure. The results obtained from both reactors used showed the concept of the membrane reactor really worked for both membranes but that the Pd/Ag membrane was superior to the CVI-silica membrane since it gave higher propylene yields, the reason being the higher hydrogen selectivity of the Pd/Ag membrane.

A comparison between the performance of a palladium composite membrane reactor and a microporous membrane reactor was made by Hou and Hughes (2002) for the catalytic dehydrogenation of propane. Both membrane reactors were packed with 3 g of an identical 0.5 Pt/alumina catalyst. A feed gas mixture of 50% propane and 50% nitrogen was used. Measurements were taken over a temperature range of 437°C up to 477°C. A mathematical model was then derived to predict performance of both membrane reactors. The results showed that at low residence times, the propane conversions of both the composite palladium reactor and the microporous membrane reactor were marginally higher than those obtained by the fixed bed reactor. It however, at high residence times, the composite membrane reactor gave a propane conversion
double that of the fixed bed reactor and the porous membrane reactor gave a propane conversion 50% higher than that obtained by the fixed bed reactor. The employment of nitrogen as sweep gas for the composite membrane reactor improved propane conversion to 20% at a 10 cm³/ min flow of sweep gas and improved the propane conversion to 33% at 150 cm³/ min of sweep flow. However, the influence of sweep gas for the porous catalytic membrane reactor was very marginal as the propane increase was of only 2-3%, which was due to this membrane’s lack of hydrogen permselectivity. The effect of pressure was also studied. The results showed that although propane conversions obtained by the composite membrane reactor did not decrease when low sweep gas flow rates were used, they did actually improve the conversion when high sweep flow rates were used. Sweep gas co-current and counter-current flow patterns were also compared for both membranes. The simulation showed that the sweep gas counter-current flow pattern increased the propane conversion for the composite membrane reactor, but both sweep gas flow patterns of co-current and counter-current had little effect on the porous membrane reactor.

A sol-gel technique was used by Schafer et al. (2001) to deposit silica layers onto commercially available tubular alumina filter membranes having a length of 300 mm and with an inside diameter of 7 mm and outer diameter of 10 mm. The silica layer obtained using this technique was less or equal to 1 nm. The propane dehydrogenation reaction was carried out at 535°C and the catalyst employed was Cr₂O₃/Al₂O₃. Nitrogen was used as sweep gas on the shell side of the reactor. It was found that using the membrane reactor gave higher propylene yields than fixed bed reactor.
A composite palladium membrane was prepared by Jong-San et al. (2002) by coating the inner surface of a $\gamma$-Al$_2$O$_3$ tube with palladium using electroless plating method. The tube was 100 mm in length and with a 7 and 10 mm inner and outer diameter respectively. The inside of the tube was packed with a catalyst (K/Sn/$\gamma$-Al$_2$O$_3$) and the membrane area was 22 cm$^2$/g$_{cat}$. The experiment consisted of allowing a gas feed mixture of propane of 20 mol. % in nitrogen with argon as sweep gas at temperatures ranging from 350-550°C and a pressure difference of 1 psi. The propane conversions obtained were above equilibrium at this temperature range. For instance, the propane conversion was 52.0% at 500°C, almost twice as much as that at equilibrium.

Bobrov et al. (2005) coated 75 mm long $\alpha$-alumina tubes having outer diameters of 7 mm and carbon tubes having outer diameters of 10 mm and identical length with catalytically active molybdenum selective layers using chemical vapour deposition. The obtained selective layers had an average pore size of 10 nm for the $\alpha$-alumina tubes and 12 nm for the carbon tubes. They reported a propane conversion of 17% at 580°C for the molybdenum coated ceramic membranes and a propane conversion as high as 28% at 580°C for the molybdenum coated carbon membranes.

2.15 Conclusions

In spite of its young age, the electroless plating technique has great potential and has proved to be a very useful and versatile method of fabricating thin palladium and palladium alloy composite membranes by depositing metals such as palladium and its
alloys onto substrates of differing shapes and fabricated from a large number of different materials.

The electroless plating technique has been used in the present study to prepare palladium composite membranes. Thin palladium films were deposited onto the outer surfaces of α-alumina tubes. A two step sensitization-activation and a modified method were used to activate the substrates prior to plating. Hydrazine-based plating baths were used to plate the porous tubes. In order to enhance the quality of the palladium films prepared, mild vacuum was initially used then at a later stage, osmosis was implemented to densify the palladium films. Reducing the pore size of the substrate tubes was not necessary as the palladium film prepared were of acceptable quality. No diffusion barrier layer was used as intermetallic diffusion was not anticipated at the temperatures employed.

The prepared composite palladium membranes were used to investigate the influence of inert and reactive sweep gases on hydrogen permeation through these membranes as well as their usefulness in dehydrogenation reactions with propane dehydrogenation as a study case.
Chapter III Experimental

3.1 Introduction

This chapter covers in some detail all aspects of experimental related procedures. This includes all chemicals and apparatus utilized and it is divided into two parts; the first one discusses the experimental part related to the preparation and characterization of silica coated porous \( \gamma \)-alumina membrane while the second part deals with the experimental side of fabrication and characterization of composite Pd/\( \alpha \)-alumina membranes. The latter was employed for the catalytic dehydrogenation of propane.

3.2 Silica coated \( \gamma \)-alumina ceramic membranes

In this part of the present work, porous \( \gamma \)-alumina ceramic tubes, provided by ECN in the Netherlands, were coated twice with silica using the dip-coating technique to modify their outer surface in order to enhance their ability to separate gases. The coated tubes were then characterized by gas permeation measurements and subsequently were used to study the effect of diffusion direction on gas permeation rates. The \( \gamma \)-alumina ceramic tubes were 200 mm long and had an outside diameter of 14 mm and an inside diameter of 7 mm. The tubes were fabricated in 2 layers, the \( \gamma \) layer being deposited on the surface of an \( \alpha \)-alumina supporting layer. Other physical properties of the tubes are listed in Table 3.1.
Table 3.1 γ-tube specifications

<table>
<thead>
<tr>
<th>Layer</th>
<th>Pore size</th>
<th>Thickness μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-alumina support layer</td>
<td>160 nm</td>
<td>-</td>
</tr>
<tr>
<td>γ-layer</td>
<td>4 nm</td>
<td>2</td>
</tr>
</tbody>
</table>

3.2.1 Dip-coating method

A silica solution, the composition of which is listed in Table 3.2, was used to deposit silica on the outer surface of the porous γ-alumina tubes using the dip-coating method with the aim of reducing their pore size and as a result enhance their gas separation characteristics.

Table 3.2 Chemicals used for the modifications of γ-alumina supports

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sylgard 184 base</td>
<td>Dow Corning</td>
</tr>
<tr>
<td>Sylgard 184 curing agent</td>
<td>Dow Corning</td>
</tr>
<tr>
<td>Iso-pentane</td>
<td>BDH</td>
</tr>
</tbody>
</table>

The dip-coating procedure consists of several steps as follows:

3.2.1.1 Cleaning

Prior to modification of the porous tubes, they were blown clean with nitrogen to remove any dust or packing material; they were then flushed with ethanol and dried for
24 hours at 70°C. Great care was taken to ensure that the tubes were not touched with bare hands so as to prevent contamination and to prevent scratching the outside layer.

3.2.1.2 Silica solution preparation method

The following steps were taken to prepare the silica solution used in the dip-coating method.

1- 90 ml of iso-pentane were poured into a clean 150 ml beaker.
2- 10 ml of Sylgard 184 base were added to the beaker containing the iso-pentane.
3- The solution was stirred for a few minutes in order to obtain a homogenous solution (colourless).
4- 1 ml of Sylgard 184 curing agent was added to the mixture and the beaker was capped to prevent the solution evaporating.

3.2.2 Dip coating procedure

Having cleaned the tube, both ends of the to be dip coated ceramic support were plugged by rubber stoppers of appropriate size. The silica solution was then poured into a 100 ml test tube and the already plugged ceramic tube was dipped into the silica solution for about 20 minutes. To prevent the silica solution from evaporating the test tube was plugged. Finally, the tube was carefully and slowly withdrawn from the solution, dried at 60°C for 24 hours and then calcined at 450°C for 6 hrs. The tube was then characterized at room temperature to determine if there has been any improvement of its gas separation properties as a result of the outer surface modification. The dip-coating procedure was repeated until a separative flow mechanism was obtained. In this
study, two coatings were carried out. Figure 3.1 illustrates the various steps involved in the dip-coating technique.

3.2.3 Experimental equipment

The experimental equipment used in this part of the present study consisted of a membrane module, a gas delivery system, a heating system, and flow rate measuring devices. Two modules were used to house the membrane, a glass permeator and a stainless steel permeator.

The glass permeator was initially used to assess gas permeation at room temperature and used relatively low pressure differences to determine the effect of surface modification on the performance of the membranes with regard to its separation properties.

Figure 3.2 is a schematic diagram of this permeator. It consists of a glass housing that is tightened against a metal plate by bolts with a rubber sheet in-between. This provides sealing between the glass housing and the metal plates and prevents damaging the glass when tightening. Sealing between the stainless steel tubes connected to the membrane and the metal plates was achieved by pliable rubber “O” rings secured in place by screws.

The glass permeator has four ports; two of these ports are on the shell side of the membrane and the other two are on the membrane’s tube side. The two output ports on
Figure 3.1 Schematic diagram of the various steps involved in the dip-coating (from the outside) of \(\gamma\)-alumina tubes
the tube side of the membrane are made of two different materials, namely plastic and steel, glued together with strong adhesive with the plastic side connected to the membrane. Sealing between these tubes and the membrane was achieved by screw clips. The module also has appropriate fittings to install pressure measuring equipment consisting of a pressure transducer (Digitron model P445) having a pressure range 0-10 bar G, and some gate valves. Owing to the fact that this module comprises a glass housing and other parts made of rubber and plastic, it can only be operated at low pressure differences and room temperature.

The other membrane module used was a stainless steel permeator, this was the main module used for housing the membranes to be studied at high temperatures and pressures. This was originally supplied by ECN in the Netherlands. Figure 3.3 is a simple schematic diagram of this module, while Figure 3.4 is a more detailed schematic diagram of the same module. This module is made of stainless steel and contains four ports, two on the shell side of the membrane and the other two on the tube side of the membrane. These ports can be manipulated in a number of ways depending on the gas flow direction required and whether a sweep gas is to be used.

Due to the very narrow space between the outer surface of the membrane and the bore of the stainless steel shell, it was quite difficult to mount the membrane inside this module without contaminating or scratching it. To prevent damaging the membrane's surface, the membrane was carefully wrapped inside a thin and very clean sheet of paper and then mounted inside the module. Once it was in place, the membrane was secured by tightening one of its ends and the paper sheet was gently pulled out the other
end. Moulded Gee Graaf graphite rings acquired from Gee Graphite having the properties and physical dimensions listed in Table 3.3 were used for sealing.

![Diagram of glass permeator](image)

**Figure 3.2 Schematic diagram of the glass permeator**

![Diagram of stainless steel permeator](image)

**Figure 3.3 Simplified schematic diagram of the stainless steel permeator**

One graphite ring was slid over each end of the membrane and then the module was tightened.
When tightening took place, the graphite rings placed between the end caps and the stainless steel shell are squeezed and elongated perpendicular to both the module inner wall and the membrane outer surface providing the sealing required. Tightening the stainless steel module to get adequate sealing proved to be problematic; if excessive torque was used when tightening, one risked crushing the membrane. However, too small a torque was used, the sealing required is not obtained. ECN states that the tubes used in the present study can withstand torques as high as 15 Nm. An especially designed torque wrench that can exert a torque as high as 62 Nm was used for tightening and only a torque of 8 Nm was required to obtain adequate sealing.

Table 3.3 Physical dimensions and properties of the moulded graphite rings used for sealing the stainless steel permeator

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm3)</td>
<td>1.96</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>98</td>
</tr>
<tr>
<td>Outside diameter (mm)</td>
<td>18</td>
</tr>
<tr>
<td>Inside diameter (mm)</td>
<td>14.3</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Figure 3.4. Detailed schematic diagram of the stainless steel module
3.2.4 Experimental setup

The experimental rig used to initially assess the quality of the silica coating at room temperature is schematically illustrated in Figure 3.5. It consisted of the glass permeator connected to gas cylinder/cylinders by plastic tubing of appropriate size. Permeation rates were measured by a soap-bubble flow meter connected to the module by a combination of rubber and plastic tubing. The pressure was sensed by pressure transducers RS 256-736 connected to a Digitron read out model P445 which has a pressure range of 0-10 bar G, and temperature was recorded by a sheathed Chromel-Alumel thermocouple of diameter 1 mm.

For membrane calcination and characterization at higher temperatures, the experimental rig was assembled differently. Figure 3.6 is a schematic diagram for the experimental set up for characterization of the γ-alumina coated with silica at higher temperatures. In addition to all systems mentioned above for the characterization of the same membrane at room temperature, the membrane here was housed inside the stainless steel module and heat was provided by a programmable furnace [Carbolite type 3TF/15/75/450] that was used to heat and cool the membrane system at preset ramp rates.

3.2.5 Methodology

Once the experimental rig was assembled either as in Figure 3.5 or Figure 3.6, a gas leak test was performed. This was done by gradually pressurizing the experimental system up to 2 bars gauge and applying a soap solution to all fittings and observing if gas bubbles evolved from any of the fittings. If gas bubbles were observed indicating the presence of a gas leak, the fitting or fittings where the leak originated were
retightened until the gas bubbles ceased to evolve. Once the gas leak test had been carried out and no leaks were detected the experimental runs were started.

3.2.5.1 The experimental runs

If the experiment was to be carried out at a high temperature, the system was heated by the furnace at a ramp rate of 2°C/min up to the required temperature. The pressure then was gradually increased up to the desired pressure. Once steady state conditions were attained, flow rates of the permeating gas were measured using a soap-bubble flow meter. Table 3.4 lists all gases used in the characterization, and later on to study the effect of gas direction of the on gas permeation

Table 3.4. Gases used in the characterization of the silica/γ-alumina membrane, and in the study of the effect of gas direction on gas diffusion

<table>
<thead>
<tr>
<th>Gas</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen 99.99% purity</td>
<td>BOC</td>
</tr>
<tr>
<td>Hydrogen 99.999% purity</td>
<td>BOC</td>
</tr>
<tr>
<td>Helium 99.999% purity</td>
<td>BOC</td>
</tr>
</tbody>
</table>
Figure 3.5 Schematic diagram of the experimental rig with the glass permeator as the module holding the membrane.
Figure 3.6 Schematic diagram of the experimental set up for silica coated membrane at higher temperature
3.3 Pd/α-alumina membranes

The α-alumina tubes were provided by ECN in Petten in the Netherlands and their physical properties are presented in Table 3.5. These were used in this part of the present work to prepare composite Pd/α-alumina membranes. The electroless plating technique was used to plate thin palladium films on the outside surface α-alumina ceramic tubes. The porous ceramic α-alumina tubes used as supports for the palladium films were 200 mm long, had an outside diameter of 14 mm, and an inside diameter of 7 mm.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (mm)</th>
<th>( r_p ) (μm)</th>
<th>Porosity (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_0 )</td>
<td>3.0</td>
<td>2.5</td>
<td>0.4</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>0.05</td>
<td>0.14</td>
<td>0.35</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>0.05</td>
<td>0.09</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The palladium films obtained were then characterized by gas measurements and subsequently used for gas separation measurements and to study the propane dehydrogenation reaction over a Pt/alumina catalyst.

3.3.1 Chemicals used in the electroless plating technique

The chemicals used in this part of the study and their suppliers are listed in Table 3.6 and gases used in the gas separation measurements are listed in Table 3.7.
Table 3.6 Chemicals used to for the fabrication of Pd/ α-alumina composite membrane

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 37%</td>
<td>Fisher Scientific International company</td>
</tr>
<tr>
<td>H$_2$NNH$_2$, 35 wt% solution in water</td>
<td>Aldrich Chemical Company, Inc</td>
</tr>
<tr>
<td>NH$_4$OH 35%, analytical reagent grade</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA), 99+, A.C.S.</td>
<td>Sigma Aldrich Company</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sigma Aldrich Company</td>
</tr>
<tr>
<td>Palladium (II) chloride hydrate 99.9%</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Deionized water</td>
<td>Lab</td>
</tr>
<tr>
<td>Palladium (II) acetate 98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Chloroform</td>
<td>BDH</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>

Table 3.7 Gases used for the separation measurements and their supplier

<table>
<thead>
<tr>
<th>Gas</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen 99.99% purity</td>
<td>BOC</td>
</tr>
<tr>
<td>Hydrogen 99.999% purity</td>
<td>BOC</td>
</tr>
<tr>
<td>Carbon dioxide 99.99% purity</td>
<td>BOC</td>
</tr>
<tr>
<td>Air</td>
<td>BOC</td>
</tr>
</tbody>
</table>
3.3.2 Pd/α-alumina composite membrane fabrication using electroless plating technique

Prior to applying the electroless plating technique to fabricate palladium composite membranes, the tubes onto which the palladium film is to be coated had to be cleaned, sensitized and activated.

Cleaning: this is critical for substrate tubes intended to be coated with palladium using the electroless plating technique if a successful adhesion between the palladium film fabricated and the substrate is to be realized. All dirt and organic contaminants had to be removed. Figure 3.7 illustrates the cleaning cycle applied in order to remove all contaminants from the substrates.

Two different methods of sensitization and activation methods were employed in present work; the conventional sensitization and activation method and the modified sensitization and activation method.

![Cleaning cycle diagram]

Figure 3.7 Cleaning cycle for removing all contaminants from substrates intended to be coated with palladium
In the conventional sensitization and activation method, following cleaning of the tubes to be sensitized, both ends of the support are plugged with rubber caps with a small PVC tube going through the top cap to help hold the tube into place when activating and sensitizing. The sensitization and activation solutions, the constituents of which are listed in Table 3.8 and Table 3.9, were both then poured into two different 100 ml test tubes. A cycle of steps starting with immersing the clean tube into the sensitization solution for 5 minutes, then rinsing with deionized water followed by immersing the tube into the activating solution for 5 minutes then again rinsing with deionized water, was repeated 10 times to ensure that palladium nuclei are spread evenly onto the whole support surface. Figure 3.8 is a schematic diagram illustrating the sensitization activation procedure.

Table 3.8 Composition of sensitization solution of the conventional method

<table>
<thead>
<tr>
<th>Sensitization solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₂·2H₂O</td>
<td>5 g/l</td>
</tr>
<tr>
<td>HCl (37%)</td>
<td>1 ml/l</td>
</tr>
<tr>
<td>Temperature</td>
<td>20°C</td>
</tr>
</tbody>
</table>

Table 3.9 Activation solution composition

<table>
<thead>
<tr>
<th>Activation solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(NH₃)₄Cl₂</td>
<td>5×10⁻⁴ mol/l</td>
</tr>
<tr>
<td>HCl (37%)</td>
<td>1 ml/l</td>
</tr>
<tr>
<td>Temperature</td>
<td>20°C</td>
</tr>
</tbody>
</table>
The other method used to sensitize and activate some α-alumina tubes prior to electrolessly plating them with palladium was the modified sensitization activation method (1999). The palladium films obtained as a result were initially of good quality in terms of palladium film thickness and selectivity, however, later on in the experiments, they were found to be unstable and developed pinholes and cracks as a result of the heat and pressure cycling. The composition of the sensitization solution is listed in Table 3.10.
Table 3.10 Constituents of the sensitization solution of the modified method

<table>
<thead>
<tr>
<th>Sensitization solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium acetate</td>
<td>2-4 g/l in chloroform</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Duration</td>
<td>120 min</td>
</tr>
</tbody>
</table>

This method involves the immersion of the clean tube into the palladium acetate-chloroform solution for about 2 hours followed by a heat treatment to activate the support. The heat treatment consists of heating the substrate in nitrogen from room temperature up to 400°C at a ramp rate of 2°C/min then from 400°C up to 450°C under air for about half an hour to get the palladium acetate transformed into palladium oxide. Then, prior to introducing hydrogen into the system, nitrogen was used to purge air from the system. This was followed with hydrogen introduction into the system for 1 hour to reduce the palladium oxide into palladium atoms. Finally, the tube was cooled to room temperature under nitrogen and at the same ramp rate of 2°C/min and by that time the tubes were ready for plating.

3.3.2.1. Conventional electroless plating procedure

Conventional and osmosis assisted electroless plating techniques were used in this study. The conventional method was applied first and was assisted in the later stages with osmosis. In the conventional electroless plating, the support was plugged from both ends by rubber stoppers to prevent the plating solution from getting into the inside the tube, then the tube was immersed into the plating solution which was already
in a heating bath at a constant temperature of 60°C. The composition of the plating bath is shown in Table 3.11. Due to the rapid decomposition of hydrazine when in contact with palladium, only 0.5 ml of 0.1 M hydrazine was added to the plating solution about every half hour. The substrate was occasionally gently shaken (using the holder) to get rid of evolving ammonia and nitrogen gas bubbles resulting from the reaction as some of these gas bubbles got adsorbed on the outer surface of the substrate which affects the quality of the palladium film plated.

Plating baths quantities depend on the size of the glass tube containing it. In the present study, each plating bath contained about 50 ml of plating solution. Once a plating solution was thought to have been depleted of palladium (gases ceased to evolve as a result of the reaction), plating solution baths were replaced with fresh ones. Vacuum supplied by a water pump was used to give an indication of the plating progress. The vacuum was not used straight from the start due to the relatively large pores of the substrate. As more and more pores were plugged by palladium, a mild vacuum was introduced slowly to help direct the palladium towards those spots that were still uncoated. The amount of vacuum increased with time as there were less and less pores yet to be coated with palladium. Once the tube was judged to have been coated with the right palladium film thickness based initially on the amount of plating solution consumed and confirmed by its weight gain, the coated tube was withdrawn from the plating bath, flushed with tap water (inside and outside) and then cleaned with boiling deionized water for 2 hours. The composite membrane was then dried in an oven for 24 hours at 130°C. The composite membrane was now ready to be tested. Figure 3.9 illustrates the apparatus used for this purpose.
Table 3.11 Plating bath constituents

<table>
<thead>
<tr>
<th>Component</th>
<th>composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl₂</td>
<td>4 g/l</td>
</tr>
<tr>
<td>EDTA 2Na</td>
<td>67.2 g/l</td>
</tr>
<tr>
<td>NH₃·H₂O (28%)</td>
<td>350 ml/l</td>
</tr>
<tr>
<td>N₂H₂·H₂O (0.5 mol/l)</td>
<td>10 ml/l</td>
</tr>
<tr>
<td>pH</td>
<td>11.2</td>
</tr>
<tr>
<td>Temperature</td>
<td>60°C</td>
</tr>
</tbody>
</table>

Figure 3.9 Schematic diagram of conventional electroless bath
3.3.2.2 Modified electroless plating procedure

Electroless plating coupled with osmosis can be used in a number of ways depending on the substrates' pore size. If the tube’s pore size is small enough, simultaneous electroless plating coupled with osmosis may be employed right from the start. However, if the pore size of the tubes is relatively large, as was in the case of the α-alumina tubes used in the present study, simultaneous electroless plating with osmosis right from the start would be counterproductive as most of the plating solution would end inside the tube being plated from the outside. For that reason, osmosis was only introduced at the latter stages of plating when most of the pores were partially or completely plugged with palladium. In this procedure, a 2 M NaCl solution was circulated inside the tube while the tube was immersed in the plating solution. Figure 3.10 is an illustration of the apparatus used for this procedure.

Figure 3.10 Schematic diagram of conventional electroless bath assisted with osmosis
3.3.2.3 Palladium film quality testing

The composite membrane was now ready to be tested for palladium film quality. This was done by mounting the composite palladium membrane into the glass permeator and measuring nitrogen permeation flow rates at room temperature and under various pressure differentials. A good membrane with no pinholes or defects should be impermeable to nitrogen. However, if there was an indication that the tube possessed pinholes or defects, the membrane would then be taken back to the plating solution to plate it further, this time with the help of osmosis.

3.3.3 Experimental setup

The experimental setup used for the palladium composite membrane separation measurements is similar to that used for the silica coated γ-alumina membrane but is different from that used for propane dehydrogenation reaction. Figure 3.11 is a schematic diagram of the experimental setup used for the propane dehydrogenation reaction. Here again it comprises of a feed system, a heating system, a membrane module system, and a gas chromatograph. The feed system consists of gas cylinder/cylinders, mass flow controllers (Brooks mass flow controllers model 5850TR/DA182DI) and a 0152 Control box) to blend gases so as to give the required gas mixture composition, and a mixing chamber where the gases were mixed. A programmable furnace [Carbolite type 3TF/15/75/450] was used to heat and cool the membrane at a ramp rate not exceeding 2°C/min to prevent palladium film from cracking as a result of the difference between the thermal expansion coefficients of palladium and the alumina substrate.
Sealing the palladium membrane inside the stainless steel permeator was a major problem. The difficulty arose from the fact that the palladium film is very fragile, so deciding the right amount of torque that should be applied when tightening was very critical. Applying too much torque may damage the palladium film and not necessarily the alumina substrate and applying too little torque may result in not obtaining gas tight sealing. Although as mentioned earlier, the supports should withstand torques as high as 15 Nm as ECN claim, it was found in the present study that supports coated with palladium could only withstand as high a torque as 9 Nm.

Prior to carrying out any experiments, all mass flow controllers to be used for providing specific and steady gas flow rates had to be calibrated. This was done by setting a number of set points and measuring the corresponding actual gas flow rates using soap-bubble flow meters. A calibration graph was then obtained relating the set points to the actual gas flow rates. The experimental setup was also gas leak tested exactly in the same manner as was done with the porous membrane.

Following the mounting up of the membrane inside the stainless steel permeator and the experimental rig was assembled as in either figure 3.5 or figure 3.6 depending on the type of measurement to be carried out, the membrane system was heated up to 450°C under nitrogen. Annealing then took place by flowing hydrogen for 24 hours at 450°C to plug the very fine pores that the palladium film may still have possessed.
3.3.4 Gas separation measurements

Once the required temperature was reached, hydrogen was allowed to flow to the tube side and permeating hydrogen flow rates measured on the shell side. Permeating hydrogen flow rates through the palladium film without sweep gas were compared to those with sweep gas. Sweep gases used were air, nitrogen and carbon dioxide and gas mixtures made of these gases. Gas mixing was done with the help of Brooks mass flow controllers model 5850TR/DA182DI and a mixing chamber. These experiments were carried out at a temperature range of 400-470°C and a pressure difference range of 0.05-0.15 bar gauge.

3.3.5 Propane dehydrogenation analysis

Two modes of operation; namely fixed mode and membrane mode for the dehydrogenation reaction were used in the present study. Initially, a gas mixture of 50% propane-50% nitrogen was used as the feed gas, this was found to be prone to coking. Hydrogen was found to suppress coking and for that reason a gas mixture of 20% hydrogen to propane was used as the feed gas. The Pd/α-alumina membrane tube was carefully packed with 3 g of 0.5% Pt on alumina provided by Johnson Matthey, in the form of 3mm equant cylindrical pellets with the Pt deposited on the outer surface.

Figure 3.11 is a schematic diagram of the experimental rig used for the propane dehydrogenation analysis. The experiment was carried out at temperatures ranging from 400°C to 440°C and a feed pressure of 1.1 bars and atmospheric outlet pressure. Composition of reaction products was analyzed using a Varian CP-3800 chromatograph equipped with two detectors; a thermal conductivity detector TCD on which a 2 m long
and 3 mm OD column packed with 5 Å molecular sieve acquired from Alltech was mounted. This was used to separate hydrogen and nitrogen. The other detector was a flame ionization detector FID on which an AT-Alumina capillary column acquired from Altech having a length of 50 m and an inside diameter of 0.5 mm was mounted to separated propane and propylene. A computer connected to the chromatograph acquired analysis data and the result of calculations were printed out.

The TCD detector was used to separate hydrogen produced as a result of the reaction and nitrogen which was one of the feed gas mixture components when using a 50% propane – 50% nitrogen. Both columns had to be conditioned first; this was done overnight under helium and at 200°C, and then were both calibrated using known gas mixture compositions. Tables 3.12 through to Table 3.14 list parameters for both detectors and columns used in the analysis.

Table 3.12 Operating conditions for the TCD detector

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>120°C</td>
</tr>
<tr>
<td>Range</td>
<td>0.05</td>
</tr>
<tr>
<td>Filament temperature</td>
<td>190°C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>20 ml/min</td>
</tr>
<tr>
<td>Reference flow rate</td>
<td>20 ml/min</td>
</tr>
</tbody>
</table>
Table 3.13 Operating conditions for the FID detector

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Electronics</td>
<td>On</td>
</tr>
<tr>
<td>Range</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 3.14 Flow rates of carrier and detector gases for the gas chromatograph

<table>
<thead>
<tr>
<th>Detector</th>
<th>Carrier gas</th>
<th>Carrier gas flow rate (ml/min)</th>
<th>Makeup gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCD</td>
<td>Helium</td>
<td>20</td>
<td>Helium</td>
</tr>
<tr>
<td>FID</td>
<td>Hydrogen</td>
<td>15</td>
<td>air</td>
</tr>
</tbody>
</table>

Gases used inside and operating conditions of the capillary column for the dehydrogenation reaction are listed in table 3.15.

Table 3.15 Operating conditions for capillary column

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>15 ml/min</td>
</tr>
<tr>
<td>Make-up gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Makeup gas flow rate</td>
<td>20 ml/min</td>
</tr>
</tbody>
</table>

Gas mixtures used in the calibration of the capillary column are listed in Table 3.16.
Table 3.16 Gases used in the calibration of the capillary column

<table>
<thead>
<tr>
<th>Gas</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>propane</td>
<td>2</td>
</tr>
<tr>
<td>propylene</td>
<td>2</td>
</tr>
<tr>
<td>Nitrogen (balance)</td>
<td>96</td>
</tr>
</tbody>
</table>

3.3.6 Catalyst activation

Following assembling the experimental setup as in figure 3.11, testing it for any gas leaks, and calibrating the mass flow controllers, the membrane module was heated to the required temperature from room temperature at a ramp rate of 2°C/min under nitrogen. Once the required temperature was reached, hydrogen was introduced into the system in order to activate the catalyst. This lasted for 2 hours at 400°C.

3.3.7 Dehydrogenation methodology

The membrane module was heated using the furnace mentioned earlier to the required temperature at a ramp rate of 2°C/min. Once the required temperature was reached, a certain propane/hydrogen flow rates provided by a mass flow controller were introduced into the inner side to the membrane, and the pressure at this reaction side of the membrane was gradually increased up to the working pressure of 0.1 bar gauge. Once steady state conditions were attained, analysis of the propane dehydrogenation reaction commenced. Samples of the reaction products were withdrawn from the system using a gas tight syringe (10 μl Hamilton, microlitre syringe). These samples were then injected into the capillary column injector mounted on the capillary column. A PC-based GC workstation interfaced with the gas chromatograph was used to analyze the
dehydrogenation gas products. The TCD detector was employed when using a feed gas mixture of 50% propane-50% nitrogen to separate any hydrogen or nitrogen permeating through the membrane.

Different propane flow rates provided by mass flow controllers were used in the present study starting from 80 ml/min up to 176 ml/min at the feed pressure applied of 0.1 bar gauge. Higher pressures were not used so as to avoid peeling off the palladium film. Sweep gas effect on the propane conversion was studied; nitrogen sweeps of 100, and 700 ml/min were used in the present study. Temperature effect on propane conversion was also studied. Propane dehydrogenation was carried out at 400 440 470°C.
Figure 3.11 Schematic diagram of the experimental rig for the propane dehydrogenation analysis
Chapter IV  Silica coated γ alumina membrane; its characterization and the
effect of gas diffusion direction on gas permeation rate thorough it.

4.1 Introduction

In this chapter, the characteristics of the gamma alumina membrane coated with silica, the effect of multilayer silica deposition on the gas separation, and the effect of gas diffusion direction on the gas permeation rate were investigated at various pressures and temperatures.

4.2 Types of alumina membranes

There are several phases. Any alumina phase is determined by the temperature it has been subjected to and the chemical path it has taken. The most common alumina membranes used commercially are alpha and gamma membranes. Whereas the α-alumina membranes have a very high thermal and hydrothermal stability beyond 1000°C, the γ-alumina membranes are subject to structural changes beyond 600 °C. Water promotes phase changes of the γ-alumina membranes at elevated temperatures. Heating γ-alumina membranes to a higher temperature converts them into α-alumina membranes with decreased pore diameter and increased porosity.

4.3 Membrane preparation

A γ-alumina tube with the specifications listed in Table 3.1 provided by ECN in the Netherlands and with pore diameter determined by thermoporometry using liquid was coated with silica solution as described in Chapter III and then characterized by gas permeation measurements.
The outer surface of the fresh gamma alumina tube had to be coated with two layers of silica using the dip coating technique described in Chapter III as the pore radius of the original $\gamma$-tube was too large to give any gas separation. As a consequence of the deposition of silica onto the outer surface of the tube resulting in plugging of the pores, the permeation of gases used decreased and gas selectivity increased, but care had to be taken to avoid over coating the tube, which would cause the membrane to be non-selective. The methodology would involve coating the tube with the first layer, calcining it and then characterizing it by gas permeation measurements to find out if the membrane has any selectivity. If no selectivity was observed, or too small a selectivity was obtained, another coating was carried out. In the present study two coatings were found to be adequate. A powder X-ray diffraction pattern was recorded, but only peaks due to $\gamma$-alumina could be observed suggesting that the silica layer was amorphous.

4.4 Flow mechanisms through microporous membranes

A single or a combination of several flow mechanisms may take place inside microporous media. These include viscous flow (Poiseuille flow), surface diffusion and Knudsen diffusion. In order to narrow down the flow mechanisms that may be taking place inside the silica coated membrane, the membrane was characterized by gas permeation measurements at various working conditions of temperature and pressure.

When plotting gas permeation versus mean pressure, a straight line should be obtained where slope gives the value of $B_o$ of equation (2.13) and intercept the value of $K_o$ of equation (2.13). The pore radius is given by;
Another useful application to the equations above is determining the membrane average pore radius.

The average pore size values for the \( \gamma \)-alumina membrane coated twice was obtained using equation (4.1) and are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Average pore radius ( r ) (nm) from ( H_2 ) permeance</th>
<th>Average pore radius ( r ) (nm) from ( N_2 ) permeance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>1.05</td>
</tr>
</tbody>
</table>

4.5 Silica membrane characterisation

Characterization of the silica membrane was carried out by gas permeation measurements at various pressures and temperatures.

4.6 Effect of number of depositions on gas permeance

The number of coatings needed in order to achieve the separation required depends on the pore radius of the substrate. For instance the \( \alpha \)-alumina tube used in the propane dehydrogenation reaction has a larger pore radius than the \( \gamma \)-alumina hence it needs more dip coatings than \( \alpha \)-alumina tubes. Figure 4.1 shows the effect of number of
coatings on gas permeance for an α-alumina tube at room temperature. The graph indicates that both Knudsen and viscous flow mechanisms co-exist, although the Knudsen mechanism is predominant. It is worth mentioning that a single coating had too high a flow to be experimentally determined with the equipment available.

Figure 4.2 shows the effect of number of silica coatings on the hydrogen to nitrogen permeance ratio at room temperature. It should be noted that the single coating had too high a flow to be experimentally determined with the equipment available. It appears that number of coating helps increase the permeance ratio up to a point after which further coatings do not necessarily enhance gas permeance ratio. This is not quite unexpected and it could probably be explained by the fact that after the reduction of the pore radius below a certain point, other processes, such as surface diffusion, take place.

Figure 4.3 shows the permeance of hydrogen, nitrogen and helium for the γ-membrane coated with silica once at room temperature as function of the mean pressure using the glass permeator. Table 4.2 compares between the ideal Knudsen separation factor for a few gases and their permeance ratio measured experimentally at room temperature for the single coated membrane.

The permeance ratio measured experimentally for H₂/N₂ was 3.62, which is close to the Knudsen separation factor of 3.74, and the measured permeance ratio of the He/N₂ was 2.18, which again is close to the ideal separation factor of 2.65.
The permeance ratio of H₂/He was 1.49 which is very close to the ideal Knudsen separation factor.

Table 4.2 Ideal Knudsen separation factors and measured separation factors

<table>
<thead>
<tr>
<th>Gases</th>
<th>Ideal Knudsen separation factor</th>
<th>Permeance ratio measured experimentally*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/N₂</td>
<td>3.74</td>
<td>3.26</td>
</tr>
<tr>
<td>He/N₂</td>
<td>2.65</td>
<td>2.18</td>
</tr>
<tr>
<td>H₂/He</td>
<td>1.41</td>
<td>1.49</td>
</tr>
</tbody>
</table>

* Single silica coated membrane at room temperature.

Looking at Figure 4.3, it is observed that the gas permeances are independent of pressure, which suggests that that the majority of flow is Knudsen.

The single silica coated γ-alumina membrane was coated once more to find out if further coatings would improve the hydrogen to nitrogen separation factor. Figure 4.4 illustrates the gas permeance versus the mean pressure. Again a combined Knudsen and viscous flow appears to take place with the majority of the flow contributed by Knudsen flow. The average permeance ratio of hydrogen to nitrogen obtained by the twice coated silica membrane was 3.34, which is a slight improvement on the ratio obtained using the once coated silica membrane of 3.26. This is a direct result of the reduction of pore size upon silica dipping. Both ratios are in fair agreement with the ideal Knudsen separation factor of 3.74 for hydrogen and nitrogen. As was mentioned above, it was decided no further coatings are needed and that two coatings are adequate for the purpose of the investigation.
Figure 4.5 and Figure 4.6 illustrate the effect of the number of silica layers on the permeance of gases through the membrane. Figure 4.1 shows the effect of the number of silica coatings on gas permeance for the α-alumina membrane at room temperature. Figure 4.2 illustrates the effect of the number of silica coatings on the H₂/N₂ permeance ratio for the α-alumina membrane at room temperature.
Figure 4.3 Gas permeance versus mean pressure at room temperature for the γ-alumina membrane coated once with silica.

Figure 4.4 Gas permeance versus mean pressure at room temperature for the γ-alumina membrane coated twice with silica.
Figure 4.5 Silica deposition effect on hydrogen permeance across the γ-alumina membrane at room temperature.

Figure 4.6 Silica deposition effect on nitrogen permeance across the γ-alumina membrane at room temperature.
gas permeance at room temperature. As expected, both permeances of hydrogen and nitrogen decreased as a result of further silica deposition which can be explained by the fact that further pore plugging by silica is occurring.

4.7 Membrane characterization at elevated temperatures

The performance of the twice silica coated γ-alumina membrane was investigated at temperatures ranging from 400°C up to 470°C in the stainless steel permeator. Figures 4.7 and 4.8 show the effect of temperature increase on hydrogen and nitrogen permeance at temperatures ranging from 400 to 470°C. It is quite clear that temperature increase has led to a slight permeance decrease for both gases. Although this could mean that the transport mechanism(s) contributing to the overall gas permeation through the silica coated was either Knudsen or viscous or both combined, it is apparent that the majority of the flow is contributed by a Knudsen mechanism.

Figure 4.9 illustrates a comparison between the hydrogen and nitrogen permeances at 400°C for the γ-alumina membrane coated twice with silica. The Knudsen flow appears to be the major contributor with a small viscous flow contribution, the ratio of hydrogen to nitrogen permeances was 3.7 at 400°C, close to ideal Knudsen separation factor of 3.74.

Plotting hydrogen, nitrogen, and helium permeances versus the reciprocal of the square root of the gas molecular weight Figure 4.10, gives a straight line passing through the origin. This again goes to show that dominant transport mechanism is
Figure 4.7 Effect of temperature on hydrogen permeance across the γ-alumina membrane coated twice with silica

Figure 4.8 Effect of temperature on nitrogen permeance for the γ-alumina membrane coated twice with silica
Figure 4.9 Gas permeance versus transmembrane pressure at 400°C temperature for the γ-alumina membrane coated twice silica

Figure 4.10 Gas flux vs molecular weight of gas for the γ-alumina membrane coated with silica at room temperature
Knudsen flow, since this transport mechanism is proportional to the square root of molecular weight.

4.8 Diffusion direction effect on gas permeation

A few measurements have been carried out to study the effect of diffusion direction on gas permeation. Some workers focused their work on palladium composite membranes (Dittmeyer et al. 2001; Goto et al. 2000; Liang and Hughes 2005b; Ryi et al. 2006). Other workers, however, investigated porous membranes (Schramm and Seidel-Morgenstern 1999; Thomas et al. 2001).

In the present study, gas diffusion direction was investigated at various temperatures and a comparison made between the gas permeance for each gas direction.

Figures 4.11 and 4.12 illustrate a comparison between the hydrogen permeance with the hydrogen diffusion direction from shell to tube and the same gas permeance, but with the hydrogen diffusion from tube to shell, at temperatures of 450 °C and 470°C respectively. The hydrogen permeance across the membrane obtained with the hydrogen flow direction from the tube side to the shell side was higher than that obtained when hydrogen flow direction was from the shell side to the tube side. The hydrogen permeance improvement was about 2% for both temperatures.

Figures 4.13, 4.14 and 4.15 illustrate another comparison, but this time it is for nitrogen gas at 430°C, 450°C and 470°C. In each graph, a comparison is made between nitrogen permeances obtained with flow from shell to tube and that from tube to
Figure 4.11 Hydrogen permeance versus mean pressure at 450°C for the γ-alumina membrane coated twice

Figure 4.12 Hydrogen permeance versus mean pressure at 470°C for the γ-alumina membrane coated twice with silica
Figure 4.13 Nitrogen permeance versus mean pressure at 430°C for the γ-alumina membrane coated twice with silica

Figure 4.14 Nitrogen permeance versus mean pressure at 450°C for the γ-alumina membrane coated twice with silica
shell. Here again the nitrogen permeance with the flow direction from tube to shell was higher than that obtained with the flow direction from shell to tube. The nitrogen flux improvement was as high as 4%.

In all figures, for single gases, the transport mechanisms prevailing in this membrane are a combination of viscous and Knudsen flows, with Knudsen flow dominating. The tube to shell diffusion direction gave higher gas permeances than those when the gas diffusion direction was from shell to tube at all temperatures investigated.

The permeances of the gases when diffusion direction was from the tube to shell was more by an average of about 4% than that when diffusion direction was from tube to shell. This phenomenon can be explained by the pressure profile existing between
layers. If the membrane used in this study is considered to consist of three layers (the \(\alpha\)-alumina layer on the tube side with largest pore radius, then the \(\gamma\) layer in the middle with the medium pore radius and finally, the silica layer on the shell side with the smallest pore radius) then its schematic diagram would look something like that depicted in figure 4.16. When the gas flow direction is from shell side (silica layer), the applied pressure, upstream pressure is \(P_{1s}\) and when it is from the shell side (the \(\alpha\)-alumina layer) the upstream pressure is \(P_{1a}\). When \(P_{1s}=P_{1a}\), then the pressure profile would be similar to what is depicted in Figure 4.16. The \(\alpha\)-alumina layer having the largest pore radius, followed by the \(\gamma\) layer, and last the silica layer.

In both gas flow directions, the pressure has to overcome three barriers, namely the layers. The difference though is that when the flow direction is from the \(\alpha\)-alumina layer towards the silica layer, the overall pressure difference is less than that when gas flow direction is the opposite. The pressure drop across \(\alpha\)-alumina layer is less than that across the silica layer owing to the larger pore radius of the layer. This results in the interfacial pressure \(P_{3a}\) being bigger than \(P_{3s}\) and, as a consequence, the overall gas flow rate across the membrane when the gas flow direction is from the \(\alpha\)-alumina layer towards the silica layer is relatively bigger than that if the flow direction is the other way around.

The permeance improvement obtained as a result of altering the flow direction is not significant in this study (about 4%). Other workers (Thomas et al. 2001) used \(\alpha\)-alumina supports with a thickness of 1.5 mm onto which there were three different \(\alpha\)-alumina layers and a \(\gamma\)-alumina layer with various radii. On top of all these layers they
deposited a silica layer using the sol-gel technique. They observed a flow rate difference of 6% when altering flow directions. The reason the flow difference obtained in this work was lower than that reported by Thomas et al. (Thomas et al. 2001) becomes clear when the structure of the two membranes used by Thomas et al. (Thomas et al. 2001) and the one used in this work are compared. Table 4.3 lists the membrane structure used by Thomas et al. (2000) and the silica coated membrane used in this work.

The first observation made is the number of layers that constitute each membrane. Whereas Thomas et al. (2000) used an asymmetric porous membrane having 4 layers with the $\gamma$ layer having the least pore size of 6 nm; the silica membrane used in the present study has only three layers on the silica layer having the least pore size of 1 nm. The smaller pore size of the silica layer in this work exerts more resistance to gas flow and hence any subsequent pressure would be less than that of the 6 nm layer of the other work.

Table 4.3. Comparison of membrane structure

<table>
<thead>
<tr>
<th>Layer</th>
<th>Composition</th>
<th>Pore radius</th>
<th>Thickness</th>
<th>Layer</th>
<th>Composition</th>
<th>Pore radius</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse</td>
<td>$\alpha$-Al$_2$O$_3$</td>
<td>3 $\mu$m</td>
<td>1.5 mm</td>
<td>$1^{st}$</td>
<td>$\alpha$-Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>200 nm</td>
<td>25 $\mu$m</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-Al$_2$O$_3$</td>
<td>60 nm</td>
<td>25 $\mu$m</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>6 nm</td>
<td>2-3 $\mu$m</td>
<td></td>
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<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.9 Conclusions

Depositing silica onto the outer surface of the gamma alumina membrane by means of dip coating helped plug the pore radius of the membrane. Successive silica deposition will not always improve the gas selectivity. The silica membrane obtained showed that both Knudsen and viscous flow were present and contributed to the overall flow of gases permeating through the membrane, but Knudsen flow is predominant at both room and elevated temperatures.

Both transport mechanisms were also present when gas diffusion direction was changed from tube to shell. The diffusion direction did have an effect in that gas permeances were relatively higher when the gas flow direction was from the tube to shell than when it was from shell to the tube. The main reason for that was the higher interfacial pressure between layers caused by the different pore capacities of the respective layers.
5.1 Introduction

Composite Pd/α-alumina membranes fabricated by electroless plating porous α-alumina tubes with a palladium film were first characterized by gas permeation measurements and then their usefulness in gas separation and dehydrogenation reactions was investigated. Propane dehydrogenation was subsequently used as a case study to investigate the membrane performance under reaction conditions.

5.2 Electroless plating critical issues

Although the electroless plating technique is an attractive method of plating palladium films onto different substrates, and has many advantages over other methods of plating, it nevertheless has its own problems. Some of these problems are related to the substrates being plated and a few other problems to the procedure itself.

One of the problems attributed to the support is degree of surface smoothness. This problem was apparent when attempts were made in this study to plate γ-alumina tubes using this technique and using identical sensitization, activation and plating solutions and the same temperature to those used to plate the α-alumina tubes. Due to the very smooth surface of the γ-tube, the resulting palladium films peeled off quite quickly and, after several trials, this type of substrate was abandoned. Previous work (Li et al. 2000) had established that the rougher surface of the α-alumina tubes enabled the palladium layer to ‘key’ into the substrate more easily.
Two of the biggest obstacles encountered in this study were mounting the composite palladium membrane inside the stainless steel permeator and removing it from the permeator. This was due to the very small space existing between the outer surface of the composite membrane and the inside shell of the stainless steel permeator which made the mounting and dismounting from the stainless steel permeator without damaging the very fragile palladium surface layer very difficult. As a result, and in spite of all care taken to mount and dismount the membranes inside the stainless steel permeator, a few of these membranes were damaged and had to be discarded.

Another problem associated with the physical properties of the support was the imperfect roundness of the tubes, due to their manufacture by extrusion. This led to leakage problems later on when the composite palladium membranes were mounted inside the stainless steel permeator. This problem was not as critical when the composite membrane was mounted inside the glass permeator for initial assessment. The reason for this (in the case of the glass permeator) was the fact that the plated tube is connected to the inlet and outlet ports by flexible plastic tubing, so that when tightening, the plastic tube would as a result of its flexibility take the shape of the plated tube. It was different when using the stainless steel permeator. The graphite rings are perfectly round and, when compressed, they would contact the same distance towards the composite membrane. As a result, if the tube was not perfectly round, some areas would not be as leak-tight as others and some points of the outer surface of the composite membrane would be under more stress than others. Applying more torque to obtain better sealing will cause the tube to crush. It is worth mentioning that the
imperfect roundness was not apparent at first, and only after many trials and close inspection of the tubes was this discovered.

Palladium film consistency in terms of thickness and density is another problem. No two palladium films obtained as a result of electroless plating were identical in terms of thickness or hydrogen to nitrogen selectivity. This may be due to impurities that are difficult to get rid off or even control. The palladium films have a tendency to develop pinholes and cracks as a result of temperature cycling, pressure cycling and long exposure to gases.

As a result of all these problems mentioned above, many tubes had to be discarded either right after plating (peeling off), or while sealing inside the stainless steel permeator, or even after a few hours of characterization at higher pressures and temperatures. Table 5.1 lists some of the tubes that were damaged as a result of the pressure and temperature cycling.

Table 5.1 Properties of some of the tubes that were tested and characterized and then were damaged at 450°C and ΔP = 0.5 bar

<table>
<thead>
<tr>
<th>Tube</th>
<th>H₂</th>
<th>N₂</th>
<th>H₂/N₂ ratio</th>
<th>Pd layer thickness, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5.6</td>
<td>0.0089</td>
<td>627.9</td>
<td>7</td>
</tr>
<tr>
<td>II</td>
<td>9.4</td>
<td>0.0055</td>
<td>1709</td>
<td>9</td>
</tr>
<tr>
<td>III</td>
<td>2.7</td>
<td>0.0040</td>
<td>675</td>
<td>12</td>
</tr>
<tr>
<td>IV*</td>
<td>7.6</td>
<td>0.0046</td>
<td>1652</td>
<td>7.7</td>
</tr>
</tbody>
</table>

* Tube IV was used to investigate the effect of sweep gas on hydrogen permeation through palladium
5.3 Composite Pd/α-alumina membranes characterization

A palladium/composite membrane with the physical properties listed in Table 5.2 was plated onto the outer surface of α-alumina tubes. The physical properties are listed in Table 3.5, the membrane obtained by using the electroless plating method described earlier in Chapter 3.

Table 5.2 Physical properties of the α-alumina tube and palladium film obtained

<table>
<thead>
<tr>
<th>Tube</th>
<th>α-alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh weight, (g)</td>
<td>55.9</td>
</tr>
<tr>
<td>weight after plating, (g)</td>
<td>56.7</td>
</tr>
<tr>
<td>weight gain, (g)</td>
<td>0.8</td>
</tr>
<tr>
<td>membrane area, (cm²)</td>
<td>79.1</td>
</tr>
<tr>
<td>approx. film thickness, (μm)</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Annealing in hydrogen was found to enhance the membrane's hydrogen to nitrogen selectivity. The obtained membrane was first characterized by nitrogen and hydrogen permeation measurements at 450°C. Figure 5.1 shows the hydrogen and nitrogen permeation flux as a function of differential pressure at 450°C of the membrane prior to annealing.
The selectivity of hydrogen to nitrogen for this membrane at 450°C is illustrated in Figure 5.2. The H₂/N₂ selectivity decreased with increasing ΔP. The reason for this is the different pressure dependence of hydrogen and nitrogen. Hydrogen is believed to follow Sievert’s law when diffusing in palladium with the pressure raised to the power 0.5. Palladium, however, is impermeable to nitrogen, and nitrogen flow measured here is the result of pinhole and cracks where the pressure effect is to the power 1.

Upon annealing the membrane in hydrogen for 4 hours at 400°C, the membrane selectivity improved dramatically. Figure 5.3 illustrates the hydrogen and nitrogen permeation fluxes through the annealed membrane versus the trans-membrane pressure difference at 450°C. As a result of annealing in hydrogen, the selectivity of hydrogen to nitrogen over the pressure difference depicted in the graph was improved by an average of ≈ 180%. The improved hydrogen permeance across the palladium film may
be attributed to change of palladium film either the micro structure or phase structure (Yeung et al. 1999), or to small pinholes being sealed (Jarosch and de Lasa 2001).

As a result of the different dependence of hydrogen flux across palladium films compared to other gases, the selectivity of hydrogen to nitrogen is pressure difference dependent as shown in Figure 5.2.

![Figure 5.2 Pressure dependence of hydrogen to nitrogen selectivity of Pd/α-alumina membrane at 450°C](image-url)
A comparison between the selectivity without annealing in hydrogen and that after annealing is illustrated in the Figure 5.4. The annealing appears to plug any pinholes existing in the palladium film hence the selectivity improvement.
Hydrogen permeation through dense palladium films is given typically by equation (5.1)

\[ J = \frac{Q}{\delta} \left( P_h^n - P_i^n \right) \]  

(5.1)

where, \( J \) is hydrogen flux (cm\(^3\)/cm.min), \( Q \) is the pure palladium permeability coefficient (cm\(^3\)/cm.min.bar\(^n\)), \( \delta \) is the palladium membrane thickness (cm), \( P_h, P_i \) are hydrogen feed pressure and hydrogen permeate pressure respectively (bar\(^n\)) and \( n \) is the hydrogen pressure exponent which is equal to 0.5 when the rate limiting step is the bulk metal diffusion of atomic hydrogen (Sieverts and Kumbhaar 1910).

Experimental values of \( n \) range between 0.5 and 1 (Zhao et al. 1998). Values greater than 0.5 may be the result of pinholes within the palladium film or other transport processes taking place such as surface processes which are generally first order (Morreale et al. 2003). As shown in Figure 5.5, the exponent in the present work was 0.5 indicating control was by diffusion of H atom through the Pd film.
The permeability coefficient $Q$ is a function of temperature and can be expressed mathematically as follows

$$Q = Q_{HO} \exp\left(\frac{E_a}{RT}\right)$$

(5.2)

where, $Q_{HO}$ is the pre-exponential factor in the Arrhenius relationship, $E_a$ is the apparent activation energy of hydrogen permeation, $R$ is the universal gas constant, and $T$ is the absolute temperature. The apparent activation energy may be calculated from the Arrhenius plot of hydrogen permeation flux vs. $1/T$ as shown in Figure 5.6.
The activation energy for this type of membrane reported in literature lies anywhere between 10 kJ/mol and 48.50 kJ/mol, however, the activation energy for the membrane in this study was 12.7 kJ/mol ±1% comparable to the value of 12.9 kJ/mol, (Zhang et al. 2006), 12.48 kJ/mol (Souleimanova et al. 2001), and 11.36 kJ/mol (Cheng et al. 2002).

5.4 Hydrogen permeation through the membrane assisted with sweep gas

Different sweep gases were used to investigate their effect on hydrogen permeation through the palladium composite membrane at 400°C. Gases used were oxygen, nitrogen and carbon dioxide. It is worth mentioning that as gas flow direction was from tube side to shell side and sweep gas flow was on the shell side of the membrane, a different set of smaller pressure differences was applied in this part of the investigation to prevent the palladium films from being separated from the substrate by
the internal pressure in the tube side. Whereas Figure 5-7 illustrates the effect of N₂ and CO₂ on the hydrogen permeation, Figure 5.8 shows the effect of oxygen on the hydrogen permeation. One can see that the introduction of sweep gas improved the hydrogen flux, but there was little difference in hydrogen flux improvement between nitrogen and carbon dioxide. This is due to the fact that the only contribution they made was in reducing the pressure difference as opposed to oxygen which, in addition to increasing the pressure difference across the membrane, reacted with permeating hydrogen increasing the pressure difference further.

It is observed that of all sweep gases mentioned earlier, air gave the better hydrogen flow rate through the membrane. The improvements in hydrogen flow rates across the membranes were not by large. This slight improvement may be explained by the fact that when using a sweep gas such as nitrogen, for instance, the improved flow rate of hydrogen across the membrane results from increasing the pressure difference across the membrane. However, when using air, there is an added influence that contributes to the increased hydrogen flow rates and that is the reaction that takes place between hydrogen permeating through the membrane and oxygen present in air, since a by-product of that reaction (water) was observed on the permeate side.
Figure 5.7 Effect of $\text{N}_2$ and $\text{CO}_2$ sweep on hydrogen flux across the membrane at 400°C.

Figure 5.8 illustrates the effect of oxygen increase on the hydrogen permeation through the composite palladium membrane.

Figure 5.8 Hydrogen permeation through the composite palladium membrane versus pressure difference at 400°C.
5.5 Conclusions

The implementation of sweep gas on the shell side of the composite palladium membrane improves the hydrogen flux by increasing the trans-membrane pressure difference, thus increasing the driving force. There was not much difference in hydrogen flux obtained when nitrogen and carbon dioxide were used as sweep gases. However, using air did improve the hydrogen as the pressure difference increase was higher due to the combined effect of sweep and reaction.
6.1 Introduction

Composite Pd/α-alumina membranes fabricated by electrolessly plating porous α-alumina tube with a palladium film were used to investigate their usefulness in dehydrogenation reactions. In the present work, propane dehydrogenation was used as a case study.

The obtained membrane was characterized by nitrogen and hydrogen permeation measurements at 450°C as described in Chapter V.

6.2 External mass transfer effects

The rate of propane disappearance at steady state may be expressed in terms of mass transfer from the bulk phase to the catalyst surface or in terms of the reaction rate on the catalyst.

\[ r_A = k_m a_m (C_{AB} - C_{As}) \]  \hspace{1cm} (6.1)

and

\[ r_A = \frac{F_{C_3H_8} X_{C_3H_6}}{W_{cat}} \]  \hspace{1cm} (6.2)

where

- \( r_A \) is the propane reaction rate expressed in unit mass of catalyst,
- \( a_m \) is the outer catalyst surface per unit mass,
- \( C_{AB} \) and \( C_{As} \) are the propane concentrations in the bulk phase and in the catalyst phase respectively,
- \( F_{C_3H_8} \) is the molar flow rate of propane,
- \( X_{C_3H_6} \) is the propane conversion,
- \( W_{cat} \) is weight of catalyst and
- \( k_m \) is the mass transfer
which is a function of Reynolds number $dpG/\mu$ and Schmidt number $\mu/\rho D_{AM}$ The following relationship (Satterfield 1970) has been chosen for the determination of interphase mass transfer:

$$\frac{K_g d_p}{D_{AB}} = 2.0 + 0.63 (Re)^{1/2} (Sc)^{1/3}$$

(6.3)

Where

$K_g$ is the mass transfer coefficient

$d_p$ is diameter of particle

$D_{AM}$ is the molecular diffusivity of component A being transferred in the mixed gases

$G$ is the mass velocity based on total cross-sectional area of reactor

$\mu$ is the viscosity of the fluid

Re is Reynolds number

$Sc$ is Schmidt number

$\rho$ is density of fluid

Combining equations (6.1), (6.2) and (6.3) at steady state one obtains:

$$\frac{C_{AB} - C_{Ar}}{C_{AB}} = \frac{F_{C_{l1}} X_{C_{l1}}}{K_m a_m W_{cat}}$$

(6.4)
If the rate of reaction becomes entirely rate-controlling, then the value of $C_{AB}$ should approach that of $C_A$, and $\frac{C_{AB} - C_A}{C_{AB}}$ should be very small. In such a condition, the resistance of the external mass transfer can be neglected.

The values of $\frac{C_{AB} - C_A}{C_{AB}}$ were calculated directly from propane dehydrogenation experimental data. Results obtained using equation (6.4) are only valid for experimental data collected on a conventional fixed bed reactor. The reaction rate values calculated using equation (6.1) are average values for the reaction over the total reactor so equation (6.4) is only roughly valid for the present case. The values $\frac{C_{AB} - C_A}{C_{AB}}$ calculated are extremely small which indicates that the interface mass transfer effects should be negligible under the present experimental conditions. The detailed calculation procedure is given in Appendix B.

6.3 Propane conversion definition

The propane conversion may be calculated using the following equation;

$$x = \left(\frac{F_n Y_i}{} - \frac{(F_t Y_{2i})}{(F_n Y_i)}\right)$$

(6.5)

where $F_n$ is the total flow rate of feed mixture, $Y_i$ is the mole fraction of propane in the feed, $F_t$ is the total flow rate in the tube and $Y_{2i}$ is the mole fraction of propane in the tube side.
6.4 Equilibrium constant for propane dehydrogenation reaction

The equilibrium constant value for the reversible propane dehydrogenation reaction at any given temperature was calculated from standard Gibbs free energy and standard enthalpy of formation at 298 K and a total pressure of 1 atm for ideal gases using thermodynamic data ($\Delta H$ and $\Delta S^0$) provided by Stull et al. (1996) and is plotted in Figure 6.1. The equilibrium constant is temperature dependent and may be calculated using the following equation (6.2).

$$\ln K_p = \frac{1}{R} \left( \frac{-\Delta H}{T} + \Delta S^0 \right)$$  

(6.6)

and for any given temperature $K_p$ may be calculated as follows:

$$K_p = 1.59 \times 10^7 \exp\left(-\frac{15526.04}{T}\right)$$  

(6.6)

6.5 Gas feed mixture

A gas mixture of propane–hydrogen (80 vol. %/20 vol. %) was used as the feed gas for the propane dehydrogenation study. Hydrogen was added to the mixture in order to suppress coke formation, a problem associated with the thermodynamically limited process which results in either low yield to propene at low temperatures or catalyst deactivation at high temperatures (Bobrov et al. 2005).
6.6 Propane conversion estimation

Propane equilibrium may be expressed in terms of pressure units as shown in equation (6.7);

\[ K_p = \frac{P_{C_3H_6} P_{H_2}}{P_{C_3H_8}} \]  

(6.7)

where, \( K_p \) is the equilibrium constant of the propane dehydrogenation reaction (Pa), \( P_{C_3H_6} \), \( P_{C_3H_8} \) and \( P_{H_2} \) are the partial pressure of propane, propylene and hydrogen respectively.

\( K_p \) may alternatively be expressed in terms of the propane equilibrium conversion, \( x_e \) as in equation (6.8);

\[ K_p = \frac{x_e}{1 + \alpha + x_e} \frac{x_e}{1 + \alpha + x_e} \frac{1 - x_e}{1 + \alpha + x_e} P_T \]

(6.8)

where, \( x_e \) is propane equilibrium conversion, \( \alpha \) is the mole ratio of the diluent gas (hydrogen) to propane in the feed gas mixture, and \( P_T \) is the total pressure (Pa). Table 6.1 lists equilibrium constants for the propane dehydrogenation reaction at given temperatures and their respected equilibrium conversions for the present dehydrogenation system.
Table 6.1 Equilibrium constants and their respective equilibrium conversions at given temperatures for the dehydrogenation reaction system

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Equilibrium constant $K_p$ (Pa)</th>
<th>Equilibrium conversion $x_e$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>154.27</td>
<td>4.3</td>
</tr>
<tr>
<td>440</td>
<td>562.56</td>
<td>8.24</td>
</tr>
<tr>
<td>470</td>
<td>1354.86</td>
<td>12.68</td>
</tr>
</tbody>
</table>

6.7 Fixed bed mode

Packed bed reactor operation was carried out by carefully packing the inner side of the membrane coated α-alumina with 3 g of Pt/Al$_2$O$_3$ catalyst provided by Johnson Matthey and then closing both ports located on shell side of the membrane and flowing the propane/hydrogen mixture through the tube at various flow rates starting from 80 up to 210 cm$^3$/min at different temperatures ranging from 400 up to 470°C.

6.8 Activation energy of propane dehydrogenation estimation

The activation energy of the propane dehydrogenation reaction was estimated by first calculating the reaction rate constant $k$ from a kinetics study of the fixed bed reactor using the integral analysis method of (Froment and Bischoff 1990) described in Appendix (A). The results obtained were used to plot an Arrhenius graph of $\ln k$ against $1/T$ shown in Figure 6.2. The activation energy of the reaction was obtained from the slope of the line and was found to be 135 J/mol compared to 148 kJ/mol reported by Yildirim et al.(1997).
6.9 Fixed bed to equilibrium conversions comparisons

Figures 6.3 through 6.5 show comparisons between the conversions obtained by the fixed bed reactor and the equilibrium conversions at similar temperatures and varying residence times. Temperatures used ranged from 400°C up to 470°C.

In Figure 6.3, where the data was obtained using working temperature 400°C, shows the propane conversion obtained by the fixed bed reactor exhibits an increase above equilibrium of 138% at the highest residence time and by 42% at the lowest residence time.

\[ \ln K_p = 16.58 - [15526.05 \times (1/T)] \]

Figure 6.1 Plot of \( \ln K_p \) against \( 1/T \)
In Figure 6.4 the data show again that the fixed bed reactor mode gave better propane conversions than those of equilibrium at 440°C, illustrating an increase by about 170% at the highest residence time and by 114.8% at the lowest residence time over the equilibrium conversion.

Figure 6.5 compares the propane conversion obtained by the fixed bed reactor to the equilibrium conversion at 470°C. At this temperature, the propane conversion obtained by the fixed bed reactor was higher by 96% at the highest residence time and by 65.6% at the lowest residence time.

As expected, residence time increases as the propane has more time in contact with the catalyst increasing conversion.
Table 6.2 gives a comparison between propane conversions obtained as a result of fixed bed reactor and equilibrium conversion.

Table 6.2 A comparison between propane conversions obtained as a result of fixed bed reactor and equilibrium conversion

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Propane equilibrium conversion</th>
<th>Average $C_3H_8$ conversion obtained using fixed bed reactor</th>
<th>$C_3H_8$ Average % increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.3</td>
<td>10.3</td>
<td>139.5</td>
</tr>
<tr>
<td>440</td>
<td>8.24</td>
<td>17.6</td>
<td>113</td>
</tr>
<tr>
<td>470</td>
<td>12.68</td>
<td>23.5</td>
<td>85.3</td>
</tr>
</tbody>
</table>

Figure 6.3 Propane conversion (fixed bed) versus residence time at 400°C
Figure 6.4 Propane conversion (fixed bed) versus residence time at 440°C

Figure 6.5 Propane conversion (fixed bed) versus residence time at 470°C
It should be noted that for all three temperatures used in this work, the fixed bed reactor gave a higher conversion of propane compared to the equilibrium level. This is due to the highly active Pt/alumina catalyst producing coke and hence leading to an apparent higher conversion of propane.

6.10 Membrane reactor

The membrane reactor was operated by flowing the same feed gas mixture used in fixed bed mode study at certain operating conditions of flow rate and temperature and a pressure difference of 1.1 bars. Figures 6.6 through to Figure 6.8 compare propane conversions obtained by membrane reactor mode compared to equilibrium conversion at the same temperatures.

Figure 6.6 shows that the propane conversion obtained at 400°C using the membrane reactor is higher than that of equilibrium as expected. The propane conversion increase was about 214% at the highest residence time and by 132% at the lowest residence time used.

Figure 6.7 illustrates a comparison between the performances of the membrane reactor compared with the equilibrium value at 440°C. Here again, propane conversion obtained by the membrane reactor is higher than that of equilibrium. The propane conversion increase ranged from 118% at the lowest residence time to about 181% at the highest residence time used.
In Figure 6.8 the data show propane conversion increase obtained using the membrane reactor to equilibrium conversion at 470°C ranged from 60% at the lowest residence time to 100% at the highest residence time used. One observation is made and that is the flatter shapes of the curves obtained using membrane reactors that those using fixed
Figure 6.7 Propane conversion (membrane mode) versus residence time at 440°C

Figure 6.8 Propane conversion versus residence time at 470°C
bed reactor. This may be explained by coke formation and possible membrane effect on the catalyst activity and hydrogen separation.

6.11 Membrane reactor against fixed bed reactor

Propane conversions obtained using membrane reactors are higher than those obtained by a fixed bed reactors. This was a direct consequence of continuously removing the hydrogen produced by the reaction.

Figure 6.9 shows propane conversions obtained by using fixed bed reactor mode and membrane reactor mode at 400°C. The membrane reactor mode gave better propane conversions throughout the residence time range used in this experiment. The propane conversion obtained by the membrane reactor improved on that obtained by fixed bed reactor by an average of 59.6% over the residence time used.

Figure 6.10 shows another comparison between propane conversions obtained by a fixed bed reactor and a membrane reactor at 440°C. Here, the improvement was by 12.9% at the highest residence time used and 60.9% at the lowest residence time used contrary to expectations. This may be explained by catalyst instability, the formation of coke and a membrane affect should not be excluded.

Figure 6.11 illustrates another comparison between the propane conversion obtained by the fixed bed reactor and that obtained by a membrane reactor at the same temperature of 470°C. There was no apparent improvement in propane conversion at
Figure 6.9 Propane conversion (membrane - fixed bed) versus residence time at 400°C

Figure 6.10 Propane conversions obtained by fixed bed and membrane reactor
this temperature for larger residence times. This again is probably due to coke formation.

The relatively low propane conversion increase in membrane reactor compared to fixed bed may be explained by the continuous removal of hydrogen (feed+reaction) from the tube-side in the membrane reactor which leads to more coke forming compared to the fixed bed reactor

6.12 Effect of sweep gas on propane conversion

Sweep gas affects the hydrogen permeation rate through the palladium film by reducing the pressure on the permeate side of the membrane hence increasing the trans-membrane pressure difference. Nitrogen sweep was used to investigate the sweep gas effect on propane dehydrogenation. It flowed on the shell side of the membrane. Nitrogen flow rates of 100 and 700 cm$^3$/min were used. The sweep gas effect on the propane dehydrogenation is illustrated in Figures 6.12 through 6.14.

In Figure 6.12 one can see that sweep gas improved the propane conversion at 400$^\circ$C and this improvement is proportional to the sweep gas flow rate. At the lowest flow rate used, the propane conversion improvement over a non-swept membrane reactor using a sweep gas flow rate of 100 cm$^3$/min was approximately 34.5% and by as much as 89% using a sweep gas flow rate of 700 cm$^3$/min.

At 440$^\circ$C, as shown in Figure 6.13, there is an apparent improvement of propane conversion of the membrane assisted with sweep gas over that obtained by membrane
mode without sweep gas, however, it is clear that the propane conversion obtained using a 700 cm³/min sweep gas is not much higher than that obtained by using a 100 cm³/min.

At 470°C, both sweep gas flow rates of 100 and 700 cm³/min gave better propane conversions than those obtained by membrane without sweep gas but here there was no difference in propane conversions between those obtained by using 100 and 700 cm³/min.

6.13 Effect of temperature on membrane reactor conversion

Figure 6.15 illustrates the effect of temperature on the propane conversion of the membrane reactor. The graph further illustrates that the reaction is temperature activated. As temperature increased from 400°C to 440°C, the propane conversion obtained using a membrane reactor improved by 64.7% and as the temperature was increased to 470°C the propane conversion of the membrane increased by 84.1%.

![Figure 6.15 Propane conversion obtained by fixed bed and membrane reactor at 470°C](image)
Figure 6.12 Comparison between performance of fixed bed, membrane and sweep gas at 400°C

Figure 6.13 Performance comparison between fixed bed, membrane and sweep gas at 440°C
Figure 6.14 Performance comparison between fixed bed, membrane and membrane with sweep gas at 470°C

Figure 6.15 Effect of temperature on membrane performance
6.14 Conclusions

A composite Pd/α-alumina membrane was used to study its performance in dehydrogenation reactions. Propane dehydrogenation was chosen as a case study using 3 g of Pt/Al₂O₃ provided by Johnson Matthey were used as a catalyst.

The investigation was carried out at various temperatures and propane feed flow rates. A non reactive sweep gas (N₂) was used to study its effect on propane dehydrogenation.

The catalyst used appears to be quite active as propane conversions obtained by fixed bed reactor mode were higher than equilibrium conversions for the same temperature. The membrane reactor mode gave better still propane conversions than those of equilibrium and fixed bed reactor mode.

Coke started forming at the relatively high temperature of 440°C but its true effect could only be felt at 470°C. The introduction of non reactive sweep gas helped improve propane conversion, but it had a certain limit as to the extent of propane conversion improvement.

The membrane concept proved to be a feasible way of carrying out some thermodynamically limited reactions such as dehydrogenation reactions.
Aspects of porous inorganic membranes and composite palladium membranes were investigated in the present work. Silica membranes were fabricated by the dip coating method onto the outer surface of γ-alumina tubes. The silica γ-alumina membranes obtained were characterized by gas permeation measurements at elevated temperatures and different pressure differences. The effect of gas diffusion direction on gas permeance was also investigated.

Composite palladium membranes were fabricated onto the outer surface of α-alumina membranes using the electroless plating technique assisted with osmosis. The obtained membranes were characterized by gas permeation measurements at elevated temperatures and different pressure differences. The gas separation properties of such membranes were also studied. These membranes were later used to investigate the concept of catalytic membrane reactors. Propane dehydrogenation was chosen as a case study.

7.1 Conclusions concerning composite palladium membranes

1. The electroless plating technique is a simple and a much cheaper way of plating continuous thin palladium films onto α-Al₂O₃ support tubes than other common methods.

2. Plating γ-Al₂O₃ employing the electroless plating was unsuccessful in the present work the reason behind which was the ultra smoothness of its surface.
which made it very difficult for the plated palladium film to adhere to the $\gamma$-$\text{Al}_2\text{O}_3$ surface.

3. Although sensitization and activation method used by Paglieri et al. (1999) is an improvement on the conventional two step sensitization-activation method as it is less time consuming and there is no tin involved, it does, however, involve heat treatment. This involves mounting the treated support into the stainless steel module and sealing it using graphite rings (in the present work). This almost certainly contaminated the surface which affects the quality of the palladium film obtained later using electroless plating, especially the areas where the tube is sealed.

4. It is quite difficult to reproduce palladium films of identical physical properties using this electroless plating technique.

5. Composite palladium films may develop pinholes as a result of impurities in palladium plating baths.

6. Osmosis can be utilized to repair palladium films that possesses pinholes, and defects or just to densify them.

7. Palladium films obtained had a short life. Temperature and pressure cycling caused them to crack and develop pinholes.
8. Composite palladium membranes are very fragile and need to be handled with the utmost care when sealing and mounting them inside reactor modules.

9. Gas-tight sealing of composite palladium membranes proved to be almost impossible because of their fragility. To get a gas tight seal, one needs to exert a larger torque than the membranes can tolerate.

10. The hydrogen to nitrogen selectivity of composite palladium membranes is much superior to that of silica γ-alumina membranes. Hydrogen to nitrogen selectivity was well over 1500 at 400°C compared to 3.7 for silica γ-alumina membranes at the same temperature.

11. Pressure dependence of the hydrogen flux for the palladium composite membrane was found to be to the power 0.5 and the hydrogen diffusion through the palladium is activated by temperature which is described by the Arrhenius equation. The activation energy $E_a$ was 12.7 kJ/mol.

12. Sweep gas improves the hydrogen flux thorough this membrane as it increases the pressure difference across the membrane. The hydrogen flux is improved further when the sweep gas is reactive. In such a case, the pressure difference is increased as a result of sweep plus reactive nature of the sweep.
7.2 Conclusions concerning silica $\gamma$-alumina membrane

1. Silica deposited $\gamma$-alumina membranes can be fabricated using the dip coating method. They are superior to composite palladium membranes in terms of mechanical strength and thermal stability.

2. Sealing of these silica membranes is relatively easier than sealing composite palladium membrane due to their mechanical strength. The silica coated membranes can withstand torques of up to 15 Nm whereas the composite palladium membrane can only withstand a torque of around 8.2 Nm.

3. A combination of Knudsen and Poiseuille flow coexists in this membrane at the temperature range used with Knudsen diffusion dominating. Hydrogen to nitrogen selectivity is close to the Knudsen separation factor.

4. Pore size distribution has an effect on gas permeance. Higher gas permeance is obtained when gas flow direction if from larger pore size layers towards smaller pore size layers and vice versa which is attributed to the pressure profile inside the structure of the porous membrane.

7.3 Conclusions concerning catalytic membrane reactors for the propane dehydrogenation study

1. The concept of a membrane reactor proved to be feasible and
2. The catalytic membrane reactor increased the propane conversion beyond that of the equilibrium value which is the result of selectively removing a reaction product (hydrogen) through the membrane.

3. A direct result of equilibrium shift by the membrane reactor is obtaining higher conversions at lower temperatures than those predicted thermodynamically. This has technical and economic implications.

4. The conversion of membrane reactors could be improved further by using sweep gases and even further still by using reactive sweep gases.

7.4 Recommendations for future study

Inorganic membranes porous and dense have great potential in separation processes but they are complex and their complexity arises from the vast number of different factors involved in materials they are produced from and other parameters. It is an understatement to say that a lot of work needs to be done in order to better understand membranes and how they work and the effect of the various parameter's. Some of the areas that need to further study and investigation are mentioned below;

1. The fragility of composite palladium membranes is one of their biggest disadvantages; further work needs to be done to find ways to enhance the mechanical strength of such membranes without compromising their outstanding permselectivity and hydrogen flux properties.
2. The two step sensitization activation method is tedious and time consuming. Different ways of preparation and activation methods should be sought that would get rid of tin which is not environmentally friendly and detrimentally affects the quality of the palladium film fabricated.

3. Ways of reducing impurities that are incorporated within the palladium film fabricated during plating procedure require further study. Such impurities are one of the main reasons behind the palladium film developing pinholes and cracks at elevated temperatures.

4. Gas-tight sealing is a major contributor to better membrane performance. Although graphite seals used in this work were thermally stable they however were also a source of membrane contamination during activation and membrane permeation testing. Less contaminating seals fabricated from different materials should be used.

5. Ways of suppressing coke formation should be looked at. Adding hydrogen to the feed gas (propane) did not prevent coke forming although it may have suppressed it somewhat.

6. The effect of gas diffusion direction through porous membranes should be studied further as it may have significant economic implications.
LIST OF SYMBOLS

\( a_m \) \quad \text{Specific catalyst surface are, m}^2/\text{kg-cat}

\( C_{AB} \) \quad \text{Concentration of propane in the bulk phase, kmol/cm}^3

\( C_{AS} \) \quad \text{Concentration of propane at the catalyst surface, kmol/cm}^3

\( J_v \) \quad \text{gas flux through the membrane (mol/m}^2.\text{s) for viscous flow}

\( D_{AB} \) \quad \text{Effective diffusivity of component A in B, m}^2/\text{s}

\( d_p \) \quad \text{Diameter of catalyst particle, m}

\( E \) \quad \text{Activation energy, kJ/mol}

\( dp \) \quad \text{Membrane pore diameter, cm, m}

\( dz \) \quad \text{Distance difference, cm, m}

\( E_a \) \quad \text{Apparent activation energy of hydrogen permeation, kJ/mol}

\( F \) \quad \text{Permeance, cm}^3/\text{cm}^2.\text{s.bar, m}^3/\text{m}^2.\text{s.Pa}

\( F_{C_3H_8} \) \quad \text{Molar flow rate of propane, mol/s}

\( G \) \quad \text{Mass velocity of mixture gas, kg/m}^2.\text{s}

\( j \) \quad \text{Permeation flux, cm}^3/\text{cm}^2.\text{s, or m}^3/\text{m}^2.\text{s}

\( j_d \) \quad \text{Mass transfer j factor}

\( k_g \) \quad \text{Mass transfer coefficient, kmol/m}^2.\text{kPa.s}

\( k \) \quad \text{Reaction rate constant, kmol/kg-cat.Pa}

\( K_p \) \quad \text{Equilibrium constant for propane dehydrogenation, Pa}

\( L \) \quad \text{Membrane length, cm, m}

\( M \) \quad \text{Gas molecular weight}
\( M_{ave} \)  
Average mixture molecular weight

\( P_m \)  
Mean pressure across the membrane, bar

\( Q \)  
Pure palladium permeability coefficient, \((\text{cm}^3/\text{cm.min.bar})^n\)

\( Q_{HO} \)  
Pre-exponential factor in the Arrhenius relationship

\( r \)  
Pore radius, nm

\( r_A \)  
Propane reaction rate, \(\text{kmol/kg-cat.s}\)

\( R \)  
Universal gas constant, 8.314 kJ/mol

Re  
Reynolds number, dimensionless

\( Sc \)  
Shmidt number, dimensionless

\( T \)  
Temperature, K

\( W_{cat} \)  
Catalyst weight, kg

\( X_{C_3H_6} \)  
Conversion of propane

\( x_e \)  
Equilibrium conversion of propane

\( Y \)  
Molar fraction

\( Z \)  
Reactor length, m
GREEK SYMBOLS

\( \alpha \)  
Dilution ratio of propane in equation (6.8)

\( \eta \)  
Viscosity of gas, kg/m.s

\( \mu_m \)  
Viscosity of mixture gas, kg/m.s

\( \rho \)  
Density, kg/m\(^3\)

\( \varepsilon \)  
porosity

\( \sigma_{AB} \)  
Collision diameter, Å

\( \Omega_{AB} \)  
Collision integral

\( \tau \)  
tortousity

\( \delta \)  
Palladium film thickness, cm

SUBSCRIPTS

\( A \)  
Component A

\( B \)  
Component B

\( h \)  
High pressure side

\( l \)  
Low pressure side

\( k \)  
Knudsen

\( t \)  
total

\( v \)  
Viscous
REFERENCES


dehydrogenation on nanostructured composite membranes." *Desalination*, 200(1-3), 692-694.


APPENDIX A: Integral analysis of Packed bed Reactor, Kinetics Calculations

The reaction rate is calculated according to the method of Froment and Bischoff (1990). The reaction rate $r$ (kmol/kg.cat.s) may be calculated in terms of pressure from the following equation;

$$r = k \left( \frac{P_{C_3H_8}}{P_{C_3H_6}} - \frac{P_{C_3H_8} P_{H_2}}{K_p} \right)$$

Where $P_{C_3H_8}$ is the partial pressure of propane in (Pa) $P_{C_3H_6}$ is the partial pressure of propylene (Pa), $P_{H_2}$ is the partial pressure of hydrogen (Pa), $K_p$ is the equilibrium constant obtained from thermodynamic data (Pa) and $k$ is the reaction rate constant (kmol/s.kg cat. Pa).

The partial pressures of propane, propylene and hydrogen are presented in Table. A.1.

<table>
<thead>
<tr>
<th>Specie</th>
<th>No. of moles initially in</th>
<th>Number of moles out</th>
<th>Partial pressure of specie</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3H_8$</td>
<td>1</td>
<td>$1 - x$</td>
<td>$(\frac{1 - x}{1.25 + x}) \cdot p$</td>
</tr>
<tr>
<td>$C_3H_6$</td>
<td>-</td>
<td>$x$</td>
<td>$(\frac{x}{1.25 + x}) \cdot p$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>-</td>
<td>$x$</td>
<td>$(\frac{x}{1.25 + x}) \cdot p$</td>
</tr>
<tr>
<td>$H_2^*$</td>
<td>0.25</td>
<td>0.25</td>
<td>$(\frac{0.25}{1.25 + x}) \cdot p$</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1.25 + $x$</td>
<td>$p$</td>
</tr>
</tbody>
</table>
The reaction rate equation above is alternatively presented in terms of conversion as follows;

\[ r_A = k \left( \frac{1 - x}{1.25 + x} \right) \frac{x}{K_p} \left( \frac{x}{1.25 + x} \right)^2 \]

The design equation for a packed bed reactor is given by the following equation;

If a species A enters the reactor schematically drawn below, the molar balance of species A would be,

\[ F_{A0} - F_A + r_A \Delta W = 0 \]

Where \( F_{A0} \) is the initial inlet molar flow rate (mole/s) of species A, \( F_A \) is the molar flow rate of species A leaving and \( W \) is the catalyst weight.

It follows that by dividing the above equation by \( \Delta W \) and taking the limit as \( \Delta W \to 0 \).

\[ - \frac{dF_A}{dW} = - r_A \]

Substituting for \( F_A \) in terms of the conversion and the molar feed rate entering the reactor, \( F_{A0} \)

\[ F_{A0} \frac{dX}{dW} = - r_A \]
If the pressure drop and catalyst decay are neglected, the integral form of the packed-catalyst bed design equation is

\[ W = F_{AO} \int_0^x \frac{dx}{-r} \]

The reaction rate can be

\[ kW = \int_0^x \frac{dx}{P} \left( \frac{1 - x}{1.25 + x} \right) \left( \frac{x}{1.25 + x} \right) \left( \frac{x}{1.25 + x} \right) P \]

The above equation can be solved numerically using Simpson's rule \[3/8\]. The temperature and molar flow rate are varied and for each set of temperature and molar flow rate a value of \( k \) is obtained. \( Lnk \) is then plotted against \( 1/T \) and the activation energy of the reaction is calculated from the slope of the line obtained.

\[ Lnk = LnA \exp\left(-E/RT\right) \]

The activation energy calculated was 135 kJ/mole, and the pre exponential factor \( (A) = 4.4 \times 10^5 \)
APPENDIX B: Calculation of mass transfer effects

B.1 External mass transfer calculations

Feed composition

\[ Y_{\text{propane}} = 0.8 \]
\[ Y_{\text{hydrogen}} = 0.2 \]

Temperature \( T = 470^\circ C = 743 \text{ K} \)

Catalyst used Pt/Al\(_2\)O\(_3\)

Catalyst particle size \( d_p = 3 \times 3 \text{ mm cylindrical pellets} \)

Reaction rate \( r = 2.329 \times 10^{-6} \text{ kmol/kg-cat.s} \)

\[ a = 0.419 \text{ m}^2/\text{kg-cat}. \]

Average feed gas mixture molecular weight \( M_{\text{ave}} \) can be obtained utilizing the following equation

\[
M_{\text{ave}} = \sum_{i} Y_i M_i
\]

\[
M_{\text{ave}} = (0.8 \times 44.096) + (0.2 \times 2)
\]

\[
M_{\text{ave}} = 35.68
\]

Total feed flow rate = \( 1.67 \times 10^{-6} \text{ m}^3/\text{s} \)

Tube cross section area = \( 1.5 \times 10^{-4} \text{ m}^2 \)

The molar flow rate = \( 2.9 \times 10^{-8} \text{ kmol/s} \)

Molar flow rate per unit area = \( 1.93 \times 10^{-4} \text{ kmol/m}^2.\text{s} \)

Mass flow rate = \( G_m \times M \)

Mass flow rate \( G = 6.89 \times 10^{-3} \text{ kg/ m}^2.\text{s} \)
B.2 Density of bulk phase

The density of the bulk phase may be calculated using

\[ \rho_m = \frac{M_{\text{ave}}}{22.4} \frac{273}{T} \frac{P_i}{100} \]

\[ \rho_m = 0.643 \text{ kg/m}^3 \]

B.3 Mixture viscosity

Viscosity of propane and hydrogen were obtained from CRC handbook of chemistry and physics.

\[ \mu \text{ of propane @ 743 K} = 1.943 \times 10^{-5} \text{ kg/m.s} \]

\[ \mu \text{ of hydrogen @ 743 K} = 1.761 \times 10^{-5} \text{ kg/m.s} \]

Mixture viscosity was calculated using the following equation:

\[ \mu_m = \frac{y_1 \mu_{H_2} (M_{H_2})^{0.5} + y_2 \mu_{C_3H_8} (M_{C_3H_8})^{0.5}}{y_1 (M_{H_2})^{0.5} + y_2 (M_{C_3H_8})^{0.5}} \]

\[ \mu_m = 1.934 \times 10^{-5} \text{ kg/m.s} \]

B.4 Calculation of diffusion coefficient

The diffusion coefficient was calculated using the following equation quoted by Satterfield (1970)
\[
D_{AB} = 0.001858 \frac{T^{3/2}}{P} \left[ \frac{(M_A + M_B)}{M_AM_B} \right]^{0.5} \Omega_D
\]

Where

\( D_{AB} \) is the diffusivity, \( m^2/s \)

\( T \) is temperature, \( K \)

\( M_A \) is the molecular weight of A

\( M_B \) is the molecular weight of B

\( P \) is pressure \( kPa \)

\( \sigma \) is collision diameter, \( Å \)

\( \Omega \) is the collision integral based on the Lennard-Jones potential

<table>
<thead>
<tr>
<th>Functions</th>
<th>hydrogen (B)</th>
<th>Propane (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon/k ), ( K )</td>
<td>59.7</td>
<td>237.1</td>
</tr>
<tr>
<td>( \sigma ), ( Å )</td>
<td>2.827</td>
<td>5.118</td>
</tr>
</tbody>
</table>

\[
\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}
\]

\[
\sigma_{AB} = 3.973 \ Å
\]

\[
\frac{k}{\varepsilon_{AB}} = \sqrt{\frac{\varepsilon_A \cdot k}{\varepsilon_A \cdot \varepsilon_B}}
\]
\[ \frac{k}{\varepsilon_{AB}} = 8.41 \times 10^{-3} \text{ K} \]

At 743 K, \( \frac{k}{\varepsilon_{AB}} = 6.245 \) so from Table 1.2 page 14, Satterfield 1970, \( \Omega = 0.7648 \)

\[ D_{AB} = 0.00021 \text{ m}^2/\text{s} \]

B.5 Schmidt number calculation

\[ N_{Sc} = \frac{\mu_m}{\rho_m D_{AB}} \]

\[ N_{Sc} = 0.1432 \]

B.6 Reynolds number calculation

\[ N_{Re} = \frac{d_{p} G}{\mu} \]

\[ N_{Re} = 1.0688 \]

For 0.01 \( < N_{Re} < 50 \)

\[ j_d = \frac{0.84}{N_{Re}^{0.51}} \left( \frac{k_g \rho_m}{G} \left( \frac{\mu_m}{\rho_m D_{AB}} \right) \right)^{2/3} \]

\[ k_g = 0.0318 \text{ kmol/m}^2\text{kPa.s} \]

\[ P_A - P_B = \frac{r}{k_g a_m} \]

\[ P_A - P_B = 0.0001748 \text{ kPa} \]
\[ P_B = \gamma_{C,H_4} \times P_i \]

\[ P_B = 88 \text{ kPa} \]

The percentage depletion of propane across the film is

\[ \left( \frac{\Delta P}{P_B} \right) \% = 0.0001986\% \]

As seen, the value obtained is negligible and it may be concluded that the reaction measured during the kinetic experiments was free of external diffusion effects.