Chapter 1

Introduction

The production of hydrogen is of great importance due to its use in the chemical and fuel industries [1-3]. Currently, the dominant method of hydrogen production is the catalytic reforming of CH_4 with steam ($CH_4 + H_2O$ z $CO + 3H_2$). In industry, the reaction is carried out at high temperatures (1073 – 1103 K) and high pressures (20 – 40 bar) to obtain high yields of the products [1]. The uses of hydrogen are numerous and varied. As a pure product, hydrogen has many uses, such as in refinery processes, ammonia synthesis, hydrogenation, and fuel cells. As a mixture with CO, hydrogen also has extensive uses, such as in methanol synthesis, hydroformylation, and long-chain hydrocarbon synthesis via Fisher-Tropsch reaction.

In recent years, the reforming of CH_4 with CO_2 ($CH_4 + CO_2$ z $2\ CO + 2\ H_2$) has attracted great attention as an alternative method for hydrogen production since this reaction utilizes an environmentally problematic greenhouse gas, CO_2 [4]. However, the CH_4 reforming reactions are energy extensive, because they are endothermic in nature and must be carried out at high temperatures to obtain high conversions (high yield of H_2). Another way to achieve high H_2 yield is to carry out the reactions in a hydrogen separation membrane reactor. Membrane reactors are advanced chemical reactors in which reaction and separation can be carried out simultaneously. Concurrent and selective removal of the product hydrogen from the reforming reactions can enhance the yield of H_2 by providing a continuous thermodynamic driving force for the reactions.

In this work, two important subjects were studied. The first subject was the development of hydrogen separation silica membranes. The preparation, characterization, and gas transport mechanism of the silica membranes are presented. The second subject was membrane reactors. The catalytic reforming of CH_4 with CO_2 was carried out in a hydrogen separation membrane reactor, and these results are also presented.

1.1. Literature Review

1.1.1. Hydrogen Selective Membranes

In the last decade much research has been directed to the development of hydrogen selective membranes with particular emphasis on inorganic silica membranes [5-19] and metallic palladium membranes [20-24]. The main reason for this was that these membranes can be utilized at high temperatures where chemical reactions occur. The objective of the efforts was to obtain membranes of high hydrogen permeability and selectivity. While the silica and palladium membranes offer high hydrogen permeability, excluding transport of other gases, the rate of hydrogen permeation largely depends on the thickness of the membranes. In order to achieve high hydrogen permeance and selectivity, the membranes should be thin and defect-free. However, thin membrane films are not mechanically strong for industrial applications. The methodology used to overcome this problem was to form thin silica or palladium membrane layers on mechanically strong porous supports such as leached Vycor, alumina, or stainless steel. A schematic of the preparation of the supported membranes is shown in Figure 1.1.

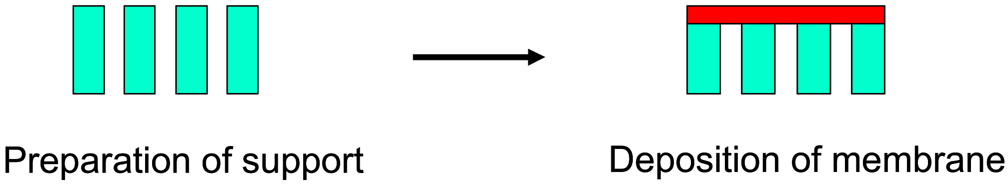

Figure 1.1. Typical processing of the supported membranes

In most of the studies, the membrane layer deposition was carried out by chemical vapor deposition (CVD), sol-gel, or electroless plating techniques at various conditions. These membranes displayed high hydrogen permeability and selectivity over other gases. The preparation method and performance of the membranes are summarized in Table 1.1.

Table 1.1. Performance of hydrogen separation membranes

Method	Support	H_2 permeance 10^{-8} mol m^{-2} s^{-1} Pa^{-1}	H_2 Selectivity	Reference
CVD ($SiCl_4 + H_2O$)	Porous Vycor	5.0 at 873 K	H_2/N_2 = 500 - 1000	5
CVD ($SiCl_4 + H_2O$)	Porous glass	3.6 at 873 K	H_2/N_2 = 200 - 300	6
CVD ($SiCl_4 + H_2O$)	Porous Vycor	5.0 at 873 K	$H_2/N_2 > 500$	7
CVD ($SiCl_4 + H_2O$)	Porous Vycor	8.8 at 873 K	H_2/N_2 = 350	8
CVD ($SiH_4 + O_2$)	Porous Vycor	3.2 at 873 K	H_2/N_2 = 2000 - 3000	9
CVD (TEOS + O_2)	Porous Vycor	0.9 at 473 K	He/O_2 = 6	10,11
CVD (TEOS, $SiCl_4$ + O2)	Porous glass	6.6 at 973 K	H_2/N_2 = 500 - 3000	12
CVD (TEOS)	Porous Vycor	2.2 at 873 K	H_2/ CH_4 = 27000	19
CVD (TEOS)	Alumina	9.0 at 873 K	H_2/N_2 = 100 - 1000	13
CVD (TEOS)	Alumina	2.2 at 873 K	H_2/N_2 = 1000	14
CVD (TEOS)	Alumina	2-22 at 873 K	$H_2/N_2 > 1000$	15
Sol-gel and CVD	Alumina	12 at 500 K	$H_2/N_2 > 300$	16
Sol-gel (silica)	Alumina	336 at 373 K	H_2/CH_4 = 40 - 200	16
Sol-gel (silica)	Alumina	112 at 473 K	H_2/CH_4 = 5000	18
CVD (Pd)	Alumina	300 at 773 K	$H_2/N_2 > 500$	22
Electrodeposition (Pd)	S. Steel	250 at 723 K	H_2/N_2 =3000	20

For potential industrial applications like high-temperature hydrogen separation and simultaneous reaction and separation, inorganic silica membranes offer unique advantages (excellent thermal and chemical stability) while palladium suffer from some drawbacks (embrittlement, chemical poisoning, and high material cost) [25,26]. Many studies have been reported in the synthesis of supported silica membranes [5-16,18,19]. The hydrogen permeance of these membranes varies over a wide range ($10^{-7} – 10^{-9}$ mol m^{-2} s^{-1} Pa^{-1}) showing a trade off with the selectivity over N_2 which ranges from 100 to 3000. It is likely that the results in these studies are due to gas transport through defects or pinholes in the membranes which gives rise to an increase in the permeance of hydrogen and concomitant decrease in the selectivity because of the transport of other gas molecules.

Recently our research group reported the preparation of a novel silica membrane, referred to as Nanosil, which shows high hydrogen permeance (10^{-8} mol m^{-2} s^{-1} Pa^{-1}) and unprecedented selectivity (100 % with respect to CH_4, CO, and CO_2) [19]. The silica layer was deposited on porous Vycor glass by thermal decomposition of tetraethylorthosilicate (TEOS) in argon flow at atmospheric pressure. The CVD method used differed form that of previous work reported in the literature. In the early studies the silica was usually formed by the oxidation of SiH_4 or $SiCl_4$ with molecular oxygen or water vapor. This resulted in only moderate hydrogen selectivities and poor stabilities. There have been a few reports of the synthesis of silica membranes by TEOS decomposition. The membranes in those studies were prepared in vacuum by flowing high concentrations of TEOS, and this resulted in also moderate hydrogen selectivity. The results of these previous investigations indicate that the silica layer deposited was not uniform, but had defects.

1.1.2. Membrane Reactors for the CH_4 Reforming Reactions

A characteristic feature of membrane reactors is that reaction and separation can be carried out simultaneously in the same system. The selective and concurrent removal of products of a reaction can offer not only increased yields, but also enhanced selectivities for the products of interest. These advantages have been shown in a number of studies with hydrogen separation membrane reactors for various dehydrogenation reactions [27-49]. Among the studies, of particular interest was the catalytic reforming of methane with either steam [27-34] or carbon dioxide [35-40].

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^0 = 225 \text{ kJ mol}^{-1} \qquad (1.1)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^0 = 247 \text{ kJ mol}^{-1} \qquad (1.2)$$

Many of the above membrane reactor studies have shown that improved yields could be achieved, at times even exceeding equilibrium levels, by removing the product hydrogen from the reactions [27-29,31,35,37-39]. Such results are obtained when the rate of hydrogen removal is comparable to that of hydrogen production by reaction [50]. Enhanced separation rates can be achieved either by using a membrane of high permeability, or optimizing reactor configurations (ratio of membrane area to reactor volume) or varying operating conditions (residence time, flow direction of reactants and sweep gas, sweep gas flow rates, etc.). These factors were discussed in many of the above membrane reactor studies. One factor that has not been treated in detail is the effect of pressure in enhancing hydrogen production. From an industrial point of view, the reforming reactions are preferred to be operated at high pressures in order to obtain high product yields in a given reactor volume

1.2. Scope of the Present Work

As summarized in the preceding section, the Nanosil membrane developed in our group showed high hydrogen permeance with unprecedented hydrogen selectivity over other gases. In Chapter 2, the structure and gas permeation properties of the Nanosil membrane and fresh porous Vycor membrane are presented. The membranes were characterized applying atomic force microscopy (AFM). This work was the first application of AFM to this system and revealed the surface structures of the porous Vycor and the silica membrane.

In Chapter 3, a study on the mechanism of gas transport through the porous Vycor support and the Nanosil membrane is presented. While there have been a number of reports in the literature for synthesis of silica membranes, mechanisms of gas transport through these membranes have not been studied in detail. In this chapter, the characteristics of gas permeation through the silica membrane are presented, and mechanism of gas transport is reported as by applying existing diffusion theories and a newly developed treatment

In Chapter 4, the synthesis, characterization, and gas permeation properties of a highly hydrogen permeable silica membrane, supported on porous alumina, are presented. The CVD method applied in the preparation of the Nanosil membrane was extended to the porous alumina support in this work. The silica/alumina composite membrane obtained showed one order of magnitude higher hydrogen permeance (10^{-7} mol m^{-2} s^{-1} Pa^{-1}) than the permeance of the Nanosil membrane. The membrane was characterized using field emission- scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). The gas permeation properties of the membrane were also discussed.

In Chapter 5, a membrane reactor study for the catalytic reforming of CH_4 with CO_2 is presented. The reforming reaction was carried out in a hydrogen separation membrane reactor at various pressures (1-20 atm) and temperatures (873 K and 923 K), and the results were compared to those obtained in a packed bed reactor of the same geometry in order to asses performance of the membrane reactor for the reaction. It was found that the concurrent separation of hydrogen from the reaction in the membrane reactor resulted in increased yields of the reaction products (CO and H_2) above the yields obtained in the packed bed reactor. Effect of pressure in the membrane reactor was studied for the reforming reaction which produces a net increase in moles and is not favored thermodynamically with increasing pressure The reforming reaction was conducted at non-equilibrium conditions at various pressures and temperatures, and a tradeoff in hydrogen production due to the effect of pressure on thermodynamic equilibrium and permeation rate was experimentally demonstrated.

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