Inorganic Membranes and Membrane Reactors

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Abstract—The inorganic membrane reactor is a combined unit operation of chemical reactions and membrane separations. By having a membrane reactor, the downstream separation load can be reduced. Also, the yields can be increased and conversion can be improved for equilibrium limited reactions. However, many of the industrial chemical reactions take place at high temperature that the conventional polymeric membranes cannot withstand. A great deal of research has been done recently to develop ion-conducting ceramic membranes. Many of these have been successfully employed to form membrane reactors for many industrially relevant chemical reactions, such as hydrogenation, dehydrogenation, oxidation, coupled reactions, and decomposition reactions. An overview is given for the area of inorganic membrane preparations and membrane reactors. Many examples of petrochemical interests are presented, including hydrocarbon conversions and fuel cell applications.

Key words: Inorganic Membranes, Inorganic Membrane Reactions, Ceramic Membranes, Palladium Membranes, Fuel Cells

INTRODUCTION

The interest in inorganic membranes goes beyond the scientific curiosity. The long history of hydrogen purification with palladium foils, helium separation with fused quartz, and oxygen separation with silver represents the successful industrial applications of inorganic membranes. However, since the gas permeability through these metals is much lower than that through polymeric membranes, attention has largely been focused on polymer membranes for practical applications. The progress of inorganic membranes had been relatively dormant until the development of thin composite metal membranes and ion-conducting ceramic membranes. These membranes, unlike the polymeric membranes, offer virtually complete separation. Since the inorganic membranes can withstand high temperatures and hostile environments, their applications to membrane reactors for many industrial processes attracted considerable attention. The concept of a membrane reactor was first successfully proven in bioreactor applications with polymeric membranes and appropriate enzymes as catalysts. In this review paper, the recent development of inorganic membranes and their use in membrane reactor applications will be discussed with relevant references. For further details, readers are referred to other recent review papers in the field [Armor, 1998; Saracco et al., 1994, 1999; Saracco and Specchia, 1994; Drioli, 2001; Boddeker et al., 2001; Stoukides, 2000; Zaman and Chakma, 1994].

ADVANTAGES AND DISADVANTAGES

Inorganic membranes offer the following advantages:

• Ability to withstand high temperatures for a long time
• Resistance to hostile environments (organic solvents, large pH changes, detergents, steam, etc.)
• High mechanical strength (stable at high pressure and high pres-

sure drop)
• Resistance to microbial attacks
• High flux (throughput)
• Easy cleaning (steam or backflushes)
• Long life
• Easy modification to add catalytic activity

While there are so many advantages for inorganic membranes, some disadvantages are very critical and serious enough to hamper the progress of industrial application of inorganic membranes, as listed below:

• Brittleness (easy to crack)
• Difficult sealing problems at high temperature applications
• Low surface-to-volume ratio
• Few membranes with high selectivity
• Expensive capital and repair costs

METALLIC MEMBRANES

1. Palladium-Based Composite Membranes

The palladium-based membranes are the most frequently used metal membranes owing to their very high hydrogen selectivity [Nagamoto and Inoue, 1981, 1985, 1986]. They have been used for hydrogenation, dehydrogenation, dehydrogenation-oxidation and steam reforming reactions. The exclusive transport mechanism toward hydrogen is generally believed to be due to the interaction of hydrogen atoms and palladium metal. Molecular hydrogen is dissociated and chemisorbed on one side of the membrane and dissolved in the palladium matrix. The atomic hydrogen then diffuses to the other side of the membrane. There, the hydrogen atoms recombine and desorb as molecular hydrogen. Therefore the driving force for the permeation becomes the difference in the square root of pressures at both sides of the membrane [Hwang and Kammermeyer, 1975; Shu et al., 1991]. Only hydrogen gas can go through, while no other gas molecules are allowed to transfer through the dense palladium membrane.

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There are several problems with palladium membranes. The first is hydrogen embrittlement [Armor, 1992]. This is caused by the large distortion in lattice structure due to the alpha-beta phase transformation. When the cyclic stress is present by adsorption and desorption of hydrogen, the palladium becomes very brittle.

Another big problem with palladium membrane is its sensitivity to poisoning in the presence of CO, H_2S, SO_2, sulfur, arsenic, chlorine, mercury, zinc, and unsaturated hydrocarbons, etc. The mechanical instability problem (hydrogen embrittlement) may be somewhat eased by making alloys with other metals such as Ag, Ru, Rh, or other rare earths [Armor, 1992]. Some alloy elements from the VI, VII, and VIII groups in the periodic table are also known to increase palladium membrane permeability [Gryaznov et al., 1987; Gryaznov, 1992].

In practice, it is a difficult challenge to select the best alloying metals and their amounts in order to achieve the high permeability, catalytic activity, and resistance to poisoning and hydrogen embrittlement.

Another major hurdle with palladium alloy membranes is the reduction of membrane thickness. The flux will increase as the membrane gets thinner, therefore the costs will decrease because of the reduced operating and material costs. Many methods have been developed to prepare a thin palladium-coated composite membrane, some of which will be briefly outlined and reviewed below.

1-1. Electroless Plating

One can produce thin palladium-based composite membranes by dipping porous support materials such as ceramic, metal, or glass in a bath of palladium salt complex solution. For uniform coating, the support material must be cleaned, sensitized, and activated before dipping. Palladium deposition takes place on the support surface by autocatalyzed reduction reaction of metastable metallic complexes. Uemiya et al. [1988, 1991a, b] and Kikuchi et al. [1989a, b] used porous glass tubes while Govind and Atnoor [1991] employed porous silver as supports. Shu et al. [1993] were successful in depositing palladium and silver on porous stainless steel. Also, alumina [Uemiya et al., 1990, 1991c, d, e; Matsuda et al., 1993] and stainless steel were coated with thin palladium layers by electroless plating.

1-2. Sputtering

This process removes atoms from a suitable target and deposits on the support surface in the form of a thin film by means of rapid ion bombardment from a high-energy plasma [Konno et al., 1988; Gryaznov et al., 1993; Jayaraman et al., 1995; Xomeritakis and Lin, 1997]. Thin films of binary and ternary alloys of palladium with manganese, cobalt, ruthenium, tin, and lead were deposited on polymeric, porous stainless steel and oxide supports by Gryaznov et al. [1993]. Sputter deposition on polymer membranes usually produces very fragile and defective membranes, which cannot function at high temperatures. Metallized porous ceramic membranes may allow operation at elevated temperatures if the adhesion of metal on the substrate is gas-tight.

1-3. Spray Pyrolysis

A solution of metal salts is sprayed into a heated gas stream and pyrolyzed. Li et al. [1993] produced palladium-silver alloy membrane by using spray pyrolysis of a palladium nitrate and silver nitrate solution in a hydrogen-oxygen flame. They obtained an alloy membrane with a thickness of less than $2\,\mu m$, but the separation

factor between hydrogen and nitrogen gases was too low compared with those of membranes obtained by other methods.

1-4. Chemical Vapor Deposition (CVD)

The successful physical vapor deposition techniques used for the electronic industry do not offer gas-tight composite membranes. It is believed that in those methods film formation takes place on top of the support. It is difficult to control and produce uniformly thin metal films and good adhesion on the support materials. Also, they require cumbersome and time-consuming pretreatment steps. Thus, attention is growing for vapor phase processes such as reactive CVD producing good film quality and fast film growth. Yan et al. [1994], Morooka et al. [1995], Uemiya et al. [1994], and Xomeritakis and Lin [1996, 1997] used thermal decompositions of volatile metal-lorganic palladium precursors for fabrication of composite membranes. Dense palladium was deposited inside pores of ceramic support (α-alumina tubes) by CVD employing thermal decomposition of a metallorganic precursor (palladium acetate or palladium acetylacetonate).

2. Silver Alloy Membranes

The only other metal membrane that has been studied in membrane reactors is silver alloy, which permits oxygen permeation [Anshits et al., 1989; Gryaznov et al., 1986, 1989]. Based on the poor performance, the silver alloy membranes have not been actively pursued for use in membrane reactors or separation devices.

SOLID ELECTROLYTE MEMBRANES

Although some novel solid electrolytes can selectively transfer specific elements such as F, C, N, S, etc., most of the recent studies have only focused on two types of solid electrolytes: one for oxygen-conducting and the other for hydrogen-conducting ceramics. The reasons are that these new ceramic materials offer very high permeabilities toward oxygen and hydrogen, respectively; with infinite separation factors. Thus, they are very suitable not only for gas separations but also for membrane reactors involving oxygenation, oxidative coupling of methane, hydrogenation, dehydrogenation, etc. If the as shown in Figs. 1 and 2. The impurities or dopants incorporated into these oxides during preparation may cause oxygen vacancies. Through these vacancies the oxygen anions are passed from one site to the next. Also, electrons may be transmitted by either n-electron conductivity is low, that particular ceramic material can be used for fuel cell application.
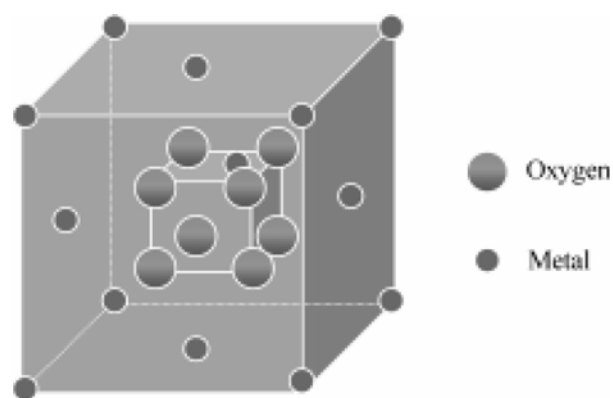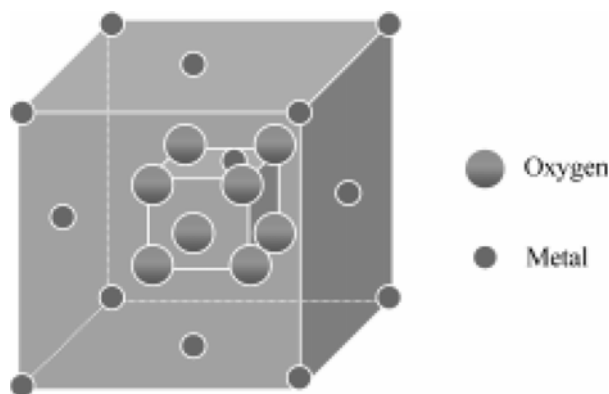

Fig. 1. Fluorite type structure.
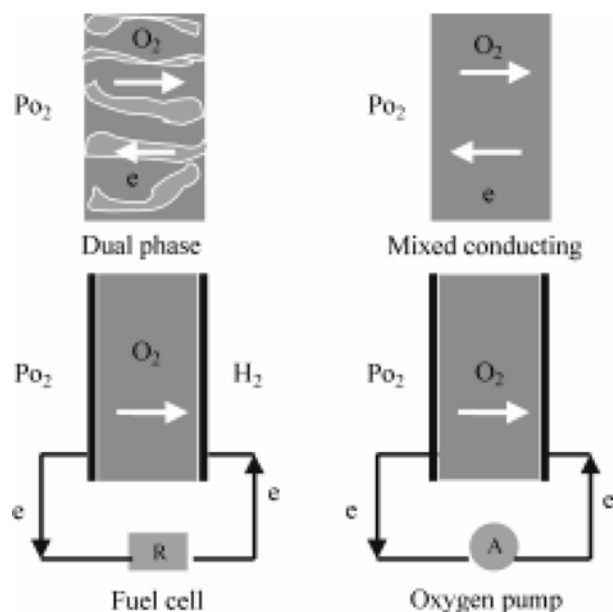
Fig. 2. Perovskite-type structure.

Fig. 3. Four ways of making oxygen ion-conducting ceramic membranes.

1. Oxygen Ion-Electron Conducting Ceramics

The most widely studied materials as ion-conducting membranes are fluorite- and perovskite-type ceramics. Metal oxides in the form of fluorite and perovskite have crystalline structures with a simple cubic lattice type conduction or p-type conduction.

Four different ways of making oxygen ion-conducting membranes are illustrated in Fig. 3. The top left picture is the dual phase membrane. The top right picture shows the oxygen permeation by a mixed oxygen ion-electron conducting membrane. In both of these processes, the driving force for overall oxygen permeation is the difference of oxygen partial pressure raised some power across the membrane. The bottom left picture shows how an air-hydrogen fuel cell works with the oxide membrane sandwiched by two electrodes. It generates electric power as oxygen permeates to react with hydrogen. The bottom right picture depicts an oxygen pump. This arrangement requires external power to drive the oxygen from one side to the other.

1-1. Fluorite Type

The two most commonly studied oxygen ion-electron conduct-

ing ceramics of fluorite-type are based on yttria stabilized zirconia (YSZ) as shown by Dou et al. [1985] and Kim and Lin [1998], and δ-phase Bi_2O_3 as reported by Jurado et al. [1988] and Bouwmeester et al. [1992]. In spite to a of their high oxygen ion conductivity, their oxygen flux through dense membranes are still limited very low level due to the low electronic conductivity. Doping multivalent metal oxides can increase the electronic conductivity [Arashi and Naito, 1992; Nigara et al., 1995; Han and Worrell, 1995; Han et al., 1997]. A similar result was obtained by preparing dual-phase membrane [Chen et al., 1996; Kim and Lin, 2000]. Ceria has the highest oxygen-ion mobility, a large solubility for acceptor doping, a variable-valent cation, and an extensive range of nonstoichiometry. Pure CeO_2 exhibits n-type electronic conduction. Tuller [1992] showed that doping with acceptor Y_2O_3 increases the ionic conductivity at the expense of electronic conductivity. Thus, the doped ceria ceramics are good candidates for solid electrolytes for a fuel cell.

1-2. Perovskite Type

The oxygen flux attained by various fluorite type ceria membranes is still too low to be applicable for membrane reactors. Teraoka et al. [1985, 1988] first demonstrated that $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ based perovskite-type ceramic membranes possess considerably high oxygen fluxes at high temperatures suitable for membrane reactors. Since then there have been many re- ports [Kruidhof et al., 1993; Qiu et al., 1995; Stevenson et al., 1996; Tsai et al., 1998; Xu and Thomson, 1998; Zhang et al., 1999] on the same subject, but the oxygen flux hardly improved. Oxygen conducting perovskite-type membranes were used in membrane reactor for oxidative coupling of methane by Hamakawa et al. [1993], Teymouri et al. [1993], Zeng et al. [1998], and Zeng and Lin [2000].

Qi et al. [2000] summarized four different methods of preparing $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_{3-\delta}$ powders to produce dense ceramic membranes: citrate method, solid-state method, spray-pyrolysis method, and co-precipitation method. Each method offered different compositions that changed the oxygen permeability and electronic conductivity. In general, perovskite-type membranes show higher oxygen flux, electronic conductivity, and mechanical strength than fluorite-type materials, because perovskite is capable of achieving high degree of doping while retaining good phase stability.

2. Proton-Electron Conducting Ceramics

Certain perovskite-type materials can transport hydrogen readily since they can host large amount of protons in their lattice structure.

2-1. Perovskite Type

Proton-conducting perovskite-type membranes were used in hydrogen separation from gas mixtures by Hamakawa et al. [1994] and Iwahara et al. [1986], and in hydrogen sensors by Yajima et al. [1995]. Qi and Lin [2000] reported two methods of preparing perovskite-type materials, the citrate method and the oxalic acid method.

2-2. Terbium Doped Strontium Cerate

Terbium doped strontium cerate ($SrCeO_3$), SCTb, showed high electrical and proton conductivity in hydrogen atmosphere. Also, Kreuer [1997], Iwahara et al. [1986], and Iwahara et al. [1990] reported that $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (SCYb) and $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ (BCNd) have very high proton conductivity at $900\,^{\circ}C$ in pure hydrogen. Since both SCYb and BCNd possess significant amount of oxygen vacancy, they exhibit high oxygen ion conductivity as much as proton

conductivity. It is interesting to note that SCYb is essentially a non-oxygen ionic conductor. The electronic conductivity of SCTb in oxygen is several orders of magnitude smaller than that of SCYb, allowing it to be an ideal proton-conducting electrolyte for fuel cell and sensor applications [Qi and Lin, 1999].

POROUS MEMBRANES

The majority of inorganic membranes that are being employed by industry now are porous metals and ceramic membranes such as alumina, silica, titania, zirconia, glass, etc. Since these materials have been known and used for a long time, there is abundant literature. In this review paper, hence, mainly the new types of ceramic membranes will be discussed.

TRANSPORT MECHANISMS

Since the transport mechanisms in conventional porous inorganic membranes are well described by viscous flow, Knudsen flow, surface diffusion, capillary condensate flow, and molecular sieving flow [Hwang and Kammermeyer, 1975], it will be omitted here. The hydrogen flux J_{H_2} through a thick palladium membrane is known to obey:

$$J_H = Q_H\left(\frac{(P''_{H_2})^{1/2} - (P'_{H_2})^{1/2}}{l}\right) \tag{1}$$

where l is membrane thickness and Q_{H_2} is hydrogen permeability, which can be expressed as a product of diffusivity and solubility. The upstream and downstream partial pressures of hydrogen are P''_{H_2} and P'_{H_2}, respectively. The square root dependency of flux on

gas pressure is due to surface dissociation of hydrogen molecule. However, the hydrogen permeation rate is in general determined by the surface exchange rates and the proton ion diffusion rate through the bulk membrane [Hamakawa et al., 1994; Qi and Lin, 1999, 2000].

The oxygen permeation rate is in general determined by the surface exchange rates and the oxygen ion diffusion rate through the bulk membrane [Teraoka et al., 1985, 1988; Kruidhof et al., 1993; Qiu et al., 1995; Stevenson et al., 1996]. For a thick membrane, the surface exchange step may be ignored and the bulk diffusion becomes the controlling rate. In this case, the oxygen permeation flux through oxygen ion conducting ceramic membranes is expressed as:

$$J_x = Q_{O_2}\left(\frac{(P''_{O_2})^{-n} - (P'_{O_2})^{-n}}{l}\right) \tag{2}$$

where n is the power coefficient, which depends on the creation speed of oxygen vacancy with the change of ambient oxygen partial pressure, l is membrane thickness, and Q_{O_2} is oxygen permeability, which can be expressed as a product of diffusivity and solubility. The upstream and downstream partial pressures of oxygen are P''_{O_2} and P'_{O_2}, respectively. As the membrane thickness decreases, the oxygen permeation rate will depend not only on the bulk diffusion but also on the surface kinetics.

MEMBRANE REACTORS
(CATALYTIC MEMBRANE REACTORS)

Membrane reactors are chemical reactors in which membranes are used to combine two unit operations, namely reaction and separation, into a single one. When Michaels [1968] originally suggested

Table 1. Types of chemical reactions

Equilibrium shift reactions:	
Hydrogenation, Dehydrogenation, Oxidation, Coupling Reactions, and Decomposition.	
$H_2S \rightarrow H_2 + S$,	$CO + H_2O \rightarrow CO_2 + H_2$,
$CH_4 + H_2O \rightarrow CO; CO_2; H_2; \cdots$,	$CH_3OH \rightarrow CH_2O + H_2$,
$CH_3OH + Toluene \rightarrow Ethylbenzene; Propene$,	
$C_2H_6 \rightarrow C_2H_4 + H_2$,	Propane $\rightarrow$ Propene,
Propene $+ H_2O \rightarrow$ Acetone,	Butane $\rightarrow$ Butene,
Isobutane $\rightarrow$ Isobutene,	2-Butene $+ H_2 \rightarrow$ Butane,
Hexane $\rightarrow$ Ethane; Propene	Cyclohexane $\rightarrow$ Benzene,
Hydrogenation (gas phase):	
$CO + H_2 \rightarrow$ Hydrocarbons,	$CO_2 + H_2 \rightarrow$ Hydrocarbons,
$C_2H_2 + H_2 \rightarrow C_2H_4$,	$C_2H_4 + H_2 \rightarrow C_2H_6$,
1-Butene $\rightarrow$ Butane,	Cyclohexene $\rightarrow$ Cyclohexane,
Benzene $\rightarrow$ Cyclohexane,	Nitrobenzene $\rightarrow$ Aniline,
Furfural $\rightarrow$ Furfuril Alcohol.	
Hydrogenation (liquid phase):	
Acetone $+ H_2 \rightarrow$ 2-Methylpentanone-4,	
Acetone $+ H_2 \rightarrow$ 2-Methylpenten-2-one-4,	
2-Butyne-1,4-diol $+ H_2 \rightarrow$ cis trans-Butenediol,	
cis trans-butene-1,4-diol $+ H_2 \rightarrow$ cis trans-Butanediol,	
Quinone $+$ Acetic Anhydride $\rightarrow$ Vitamin K,	
Dehydrolinalool $+ H_2 \rightarrow$ Linalool.	

Table 1. Continued

Dehydrogenation (gas phase):	
$H_2S \Rightarrow H_2+S$, $CH_4+H_2O \Rightarrow CO+3H_2$, Propane $\rightarrow$ Aromatics, Butene $\rightarrow$ Butadiene, n-Hexane $\Rightarrow$ Cyclic Hydrocarbons.	$CO+H_2O \Rightarrow CO_2+H_2$, $CH_3OH+H_2O \rightarrow 3H_2+CO_2$, Isopropanol $\rightarrow$ Acetone, n-Hexane $\Rightarrow$ Benzene,

Dehydrogenation (liquid phase):	

$CH_3OH \rightarrow HCOOCH_3$;
 (Nafion) $CH_2(OCH_3)_2$;
   Methylformate;
   Methylal; H_2; H_2O
	$CH_3OH \Rightarrow CH_3OCH_2OH$; H_2; $\cdots$
	 (H_3PO_4; Heteropolyacids, Pt)

Oxydation:	
$CH_4+O_2 \Rightarrow C_2+\cdots$, Propylene$+O_2 \Rightarrow$ Propylene Oxide, Propylene$+O_2 \Rightarrow$ Hexadiene; Benzene$+\cdots$, Benzylic and Allylic Compounds$+O_2 \Rightarrow \cdots$, $SO_2+\frac{1}{2}O_2 \rightarrow SO_3$, $CH_4+O_2 \Rightarrow C_2+\cdots$, $CH_3OH+O_2 \rightarrow H_2CO$; CO; CH_4; $\cdots$, Ethylbenzene$+O_2 \rightarrow$ Styrene; CO_2; $\cdots$,	$C_2H_4+O_2 \rightarrow$ Ethylene Oxide, Butene$+O_2 \Rightarrow$ Butadiene, $CO+\frac{1}{2}O_2 \rightarrow CO_2$, $CH_4+O_2 \Rightarrow CO_2+H_2O$, $C_2H_4+\frac{1}{2}O_2 \rightarrow C_2H_4O$; CO_2; O_2, $C_3H_6+O_2 \rightarrow C_3H_4O$; CO_2; H_2O.

Coupling of reactions:
$C_2H_6 \rightarrow C_2H_4+H_2$ and $H_2+\frac{1}{2}O_2 \Rightarrow H_2O$, $2CH_4 \rightarrow C_2H_6+H_2$ and $H_2+\frac{1}{2}O_2 \Rightarrow H_2O$,   Butane $\rightarrow$ Butenes and $H_2+\frac{1}{2}O_2 \Rightarrow H_2O$,   Cyclohexanol $\rightarrow$ Cyclohexanone and Phenol $\Rightarrow$ Cyclohexanol,   2-Butene $\Rightarrow$ Butadiene and Toluene $\Rightarrow$ Benzene,   Cyclohexane $\rightarrow$ Benzene and o-Xylene $\Rightarrow$ Benzene; Methane,   Cyclohexene $\Rightarrow$ Benzene and Cyclohexene $\rightarrow$ Cyclohexane,   Cyclohexane $\Rightarrow$ Benzene and Toluene $\rightarrow$ Benzene; Methane.

Liquid phase homogeneous and heterogeneous catalysis on porous membranes:	
$NO+H_2S+O_2 \rightarrow 2 HNO_3+S$, $C_2H_4+H_2+CO \Rightarrow CH_3CH_2CHO$, Methyl-$t$-butylether $\rightarrow$ Iso-butene Methanol, Oleic Acid$+$Ethanol $\Rightarrow$ Ester$+H_2O$.	$C_2H_4+O_2 \rightarrow CH_3CHO$, CH_4, C_2H_6, $C_3H_6+H_2O_2 \Rightarrow \cdots$, Nitrobenzoic Acid$+H_2 \Rightarrow \cdots$,

More reactions:
Dehydrogenation of Ethane; Propane; n-Butane; Cyclohexane; Ethylbenzene; Methanol,   Reduction of Nitrogen Oxide with Ammonia,   Steam Reforming of Methane.

Fuel cell applications:
Membranes: Oxygen Conductors (Low Electrical Conductivity),   Fuels: H_2, CO, CH_4, CH_3OH, C_2H_5OH, and NH_3,   Temperature Range: 627-1,094 °C.

this to achieve greater conversion by shifting the equilibrium limited reactions through selective elimination of one of the products, only polymeric membranes were available for separations. A couple of drawbacks with polymer membranes have retarded wide usage of membrane reactors for industrial applications. Polymers exhibit only partial selectivity and cannot withstand high temperatures. Since then various inorganic membranes have been developed to overcome these shortcomings as discussed above. At present, only two

kinds of inorganic membranes attract most of the attention: one for hydrogen and the other for oxygen. For hydrogen separation membranes, metallic palladium and proton-permeating ceramics hold promise. For oxygen separation membranes, only oxygen ion-conducting ceramics have been considered as practical candidates for membrane reactor materials.

There are several different ways to construct a membrane reactor. A vessel of an inert membrane with permselectivity can be packed

with catalyst or the catalyst may be fluidized. Another method is to employ a catalytic membrane, which may be made of either the catalyst itself or an inert membrane impregnated with catalyst. This type is called a catalytic membrane reactor. The catalytic membrane reactor can be packed with catalysts or contain fluidized catalyst. Both tubular and flat disk membranes have been used for membrane reactors in laboratory in parallel or cross flow mode. For industrial reactors, the shell-and-tube type may be more feasible.

1. Types of Chemical Reactions

Table 1 lists some examples of typical chemical reactions that have been studied using various inorganic membranes in membrane reactor arrangement. Some potential candidates for industrial membrane reactor applications include: water-gas shift reaction, methane steam reforming, dehydrogenation of ethane, propane, butane, cyclohexane, ethylbenzene, etc. By using a membrane reactor, the selectivity towards desired products can be enhanced for many oxidative reactions. Also, numerous coupling reactions can take advantage of membrane reactor configuration. The role of membrane reactors is not limited to practical applications. Catalysis of many reactions and some oxidation reactions can be better understood, thus resulting in improved reaction mechanisms for those reactions.

2. Equilibrium Shift Using Membrane Reactors

As illustrated in Table 2, many of the equilibrium-limited reac-

tions were the favorite subjects of earlier studies applied to membrane reactors. Many of these reactions attracted a great deal of interest from the petrochemical industry [Armor, 1998]. In a membrane reactor, one of the products can be eliminated continuously, thus yielding a shift of equilibrium in a thermodynamically limited reaction. Even a small percentage of equilibrium conversion can result in a huge economic gain for industrial processes. If hydrogen is involved as one of the species in the equilibrium-limited reaction, the proton-conducting membrane can be effectively employed as the membrane that can supply or eliminate hydrogen to and from the reaction zone.

3. Palladium-Based Membrane Reactors

The palladium membranes are highly selective to hydrogen, and therefore have been widely used for hydrogenation, dehydrogenation, and steam reforming reactions. Decomposition of hydrogen sulfide was tested by both palladium membrane [Edlund and Pledger, 1993] and proton-conducting ceramic membrane [Peterson and Winnick, 1996]. Water-gas shift reaction and methane steam reforming were studied by using palladium-based membranes. Many dehydrogenations of hydrocarbons were also the subject of research by the palladium-based membranes as shown in Table 3, in which examples of other reactions are also given. The palladium membranes have several drawbacks that include hydrogen embrittlement, cor-

Table 2. Equilibrium shift using membrane reactors

Type of chemical reactions	References
$CO + H_2O \rightarrow CO_2 + H_2$	Champagnie et al., 1992; Edlund et al., 1992; Kikuchi et al., 1989a; Seok and Hwang, 1990; Uemiya et al., 1991b.
$CH_4 + H_2O \rightarrow CO; CO_2; H_2; \cdots$	Adris et al., 1991; Guy, 1992; Oertel et al., 1987; Tsotsis et al., 1992, 1993; Uemiya et al., 1991a; Vayenas et al., 1992.
$CH_3OH \rightarrow CH_2O + H_2$	Song and Hwang, 1991.
$C_2H_6 \rightarrow C_2H_4 + H_2$	Bitter, 1988; Guy, 1992; Champagnie et al., 1992; Chan and Brownstein, 1991; Tsotsis et al., 1993; Ziaka et al., 1993.
$C_3H_8 \rightarrow C_3H_6 + H_2$	Bitter, 1988; Roth, 1988; Tsotsis et al., 1993; Ziaka et al., 1993.
$C_2H_6 \rightarrow C_2H_4; C_4H_8$	Seok and Hwang, 1990.
$C_4H_{10} \rightarrow C_4H_8$	Zaspalis et al., 1991.
Isobutane $\rightarrow$ Isobutene	Ioannides and Gavalas, 1993.
Cyclohexane $\rightarrow$ Dehydrogenation	Guy, 1992; Itoh, 1987; Okubo et al., 1991.
Ethyl Benzene $\rightarrow$ Dehydrogenation	Michaels and Vayenas, 1984; Moser et al., 1992; Gallaher et al., 1993; Tiscareno-Lechuga et al., 1993.

Table 3. Palladium-based membrane reactors

Type of chemical reactions	References
$H_2S \rightarrow H_2 + S$	Edlund and Pledger, 1993; Peterson and Winnick, 1996.
$CO + H_2O \rightarrow CO_2 + H_2$	Kikuchi et al., 1989a; Uemiya et al., 1991b.
$CH_4 + H_2O \rightarrow CO; CO_2; H_2; \cdots$	Uemiya et al., 1991a.
Propane $\rightarrow$ Aromatics	Uemiya et al., 1990; Uemiya et al., 1991a.
Isobutane $\rightarrow$ Isobutene	Matsuda et al, 1993.
Isobutene Dehydrogenation	Raich and Foley, 1995.
1,3-Pentadien $\rightarrow$ Cyclopentane; Cyclopentene	Gryaznov et al., 1993.
$CO + H_2O \rightarrow$ Hydrocarbons	Gryaznov et al., 1993.
Paraffin, Olefin, Cyclohexane, Toluene Dehydrogenation	Armor et al., 1993; Farris and Armor, 1993; Raich and Foley, 1995; Gryaznov et al., 2001.
Ethanol $\rightarrow$ Acetaldehyde	Raich and Foley, 1998.

Table 4. Oxygen-conducting ceramic membrane reactors

Type of chemical reactions	References
$H_2S \rightarrow H_2 + S$	Alqahtany et al., 1992.
$CH_4 + O_2 \rightarrow C_2 + \cdots$	Eng and Stoukides, 1991a, b; Chiang et al., 1993; Eng et al., 1995; Jin et al., 2000; Lin and Zeng, 1996, 1997; Zeng et al., 1998; Zeng and Lin, 2000, 2001.
$CH_4 + H_2O \rightarrow CO; CO_2; H_2; \cdots$	Alqahtany et al., 1993a, b.
$CH_4 + O_2 \rightarrow H_2CO$	Bafas et al., 2001.
$CH_4 + O_2 \rightarrow H_2; CO$	Hibino et al., 1995.
$CH_4 + O_2 \rightarrow C_2H_4; C_2 + \cdots$	Jiang et al., 1994; Hibino et al., 1996.
$C_2H_6 + O_2 \rightarrow CO_2; H_2O$	Kaloyannis and Vayenas, 1997.
$C_3H_4 + O_2 \rightarrow CO_2; H_2O$	Petrolekas et al., 1998; Beatrice et al., 2000.
$C_3H_6 + O_2 \rightarrow CO_2; H_2O$	Beatrice et al., 2000.
$CH_3OH + O_2 \rightarrow H_2CO; CO_2$	Cavalca et al., 1993.
$NO + C_3H_6 + O_2 \rightarrow N_2; CO_2; H_2O; \cdots$	Pliangos et al., 2000.
$CO_2 \rightarrow O_2; C; CO$	Itoh et al., 1993.
$NO_x \rightarrow N_2; O_2$	Cicero and Jarr, 1990.
$SO_y \rightarrow S; O_2$	Cicero and Jarr, 1990.
$H_2O \rightarrow H_2; O_2$	Nigara et al., 1997

Table 5. Proton-conducting ceramic membrane reactors

Type of chemical reactions	References
$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	Iwahara et al., 2000.
$NO + H_2 \rightarrow N_2; N_2O$ (low current density); NH_3 (high current density)	Kobayashi et al., 1996, 2000a, b, c.
$N_2 + 3 H_2 \rightarrow 2 NH_3$	Marnellos et al., 2000; Panagos et al., 1996; Yiokari et al., 2000.
CH_3OH synthesis	Panagos et al, 1996.
$CH_4 \rightarrow C_2H_6; C_2H_4$	Chiang et al., 1992.
$CH_4 + O_2 \rightarrow C_2 + \cdots$	Langguth et al., 1997a, b.
$H_2S + O_2 \rightarrow SO_2; H_2$	Peterson and Winnick, 1996.

rosion by sulfur compounds, and high cost. Composite palladium membranes have recently been synthesized and tested using many different techniques [Ziegler et al., 2001; Goto et al., 2000; Nam et al., 1999; Jun and Lee, 1999, 2000; Souleimanova et al., 2000; Li et al., 2000; Yeung et al., 1999; Cheng and Yeung, 1999].

4. Oxygen Conducting Ceramic Membrane Reactors

As mentioned earlier, membrane reactors for oxygenation reactions can be constructed by using oxygen ion-conducting ceramic membranes. Table 4 lists some of the popular oxygenation reactions reported in the literature that have been carried out in various dense ceramic membrane reactors. Cicero and Jarr [1990] reported the U.S. Department of Energy's demonstration and feasibility study of using high-temperature ceramic membranes to remove sulfur and nitrogen contaminants found in gas streams of coal-based power generation systems. Eng, Stoukides, and their coworkers published many papers on ceramic membrane reactors, as shown in the references. Their studies on the oxidation of methane and methane steam reforming are especially noteworthy and very relevant in applications to fuel cells and sensors. Itoh et al. [1993] applied an yttria stabilized zirconia (YSZ) membrane reactor system to enhance the direct thermal decomposition of carbon dioxide at high temperature. Nigara et al. [1997] split water to generate oxygen and separated it through a high temperature oxygen permeation membrane: calucia-stabilized zirconia doped with cerium oxide. Bafas et al.

[2001] studied the partial oxidation of methane to formaldehyde in a continuous gas recycle membrane reactor/separator. They achieved 56% selectivity with 89% methane conversion.

5. Proton-Conducting Ceramic Membrane Reactors

The proton-conducting ceramic membrane reactors have been investigated for many industrially attractive chemical reactions. Table 5 lists some examples: hydrogen generation by water splitting, hydrogenation of NO, ammonia synthesis, methanol synthesis, hydrogenation and dehydrogenation of alkanes and alkenes, dimerization of methane, and oxidation of hydrogen sulfide.

6. Fuel Cell Applications

The recent flurry of activities in fuel cell research and the advent of inorganic membranes created a perfect environment conducive to developing efficient fuel cells. All kinds of hydrocarbons as well as hydrogen were studied as the fuel and some examples are shown in Table 6. Both oxygen ion- and proton-conducting ceramic membranes have been employed in fuel cell research. The yttria stabilized zirconia (YSZ) membranes received considerable attention among many researchers for carrying out oxidation reactions.

7. Porous Membrane Reactors

Porous inorganic membranes were among the first inorganic materials that were made into reactors and tested. In the early days, no ion-conducting ceramic membranes were available. These included porous Vycor glass, which is an intermediate product of Vycor brand

Table 6. Fuel cell applications

Chemical reactions	Membranes	References
$H_2+O_2 \rightarrow H_2O$	Zirconia Cermet; Ceria-based	Bieberle et al., 2001.
$CH_4+O_2 \rightarrow CO; H_2; \cdots$	YSZ; BaCeY	Alqahtany et al., 1993a; Asano et al., 1995.
$CH_4+H_2O \rightarrow CO; H_2; \cdots$	YSZ	Alqahtany et al., 1993b.
$CH_4+NH_3+O_2 \rightarrow HCN; \cdots$	YSZ	McKenna et al., 1993.
Oxidation of n-Hexane; Benzene; Toluene	YSZ	Yamanaka and Otsuka, 1993a, b.
Oxidation of Alkanes; Alkenes; Benzene	YSZ	Otsuka and Yamanaka, 1998.
Oxidation of Toluene; n-Decane; Synthetic Diesel Fuel	YSZ	Kim et al., 2001.
Oxidation of CH_3OH	YSZ	Jiang and Virkar, 2001.
Oxidation of CH_3OH	Zirconium sulfoarylphosphonate	Alberti et al., 2000.
Oxidation of $C_2H_5OH+H_2O$	YSZ	Jiang and Virkar, 2001.
$C_4H_8+O_2 \rightarrow CO; H_2; CH_4 \cdots$	SmSrCo	Hibino et al., 2001.
Toluene+$O_2 \rightarrow$ Cresol	YSZ	Otsuka et al., 1992.
$H_2S+O_2 \rightarrow SO_2; H_2$	Lithium sulfate	Peterson and Winnick, 1996.

Table 7. Porous membrane reactors

Chemical reactions	Membranes	References
$CO+H_2O \rightarrow CO_2+H_2$	Porous Vycor Glass	Seok and Hwang, 1990.
$CH_4+H_2O \rightarrow CO; CO_2; H_2;$	Alumina	Tsotsis et al., 1992, 1993.
$CH_4+O_2 \rightarrow CO_2+H_2O$	Pt/gamma-Alumina	Neomagus et al., 2000.
$CH_3OH \rightarrow CH_2O+H_2$	Porous Vycor Glass	Song and Hwang, 1991.
$C_2H_6 \rightarrow C_2H_4+H_2$	Pt/Alumina	Champagnie et al., 1992; Tsotsis et al., 1993.
$C_3H_8 \rightarrow C_3H_6+H_2$	Alumina	Bitter, 1988; Tsotsis et al., 1993; Ziaka et al., 1993.
$C_3H_6 \rightarrow C_2H_4; C_4H_8$	Porous Vycor Glass	Seok and Hwang, 1990.
$C_4H_{10} \rightarrow C_4H_8$	Alumina; Pt-SiO$_2$	Zaspalis et al., 1991.
Isobutane $\rightarrow$ Isobutene	Dense SiO$_2$ on Vycor	Ioannides and Gavalas, 1993.
Oxidation of H_2S	Sintered Stainless Steel	Neomagus et al., 1998.
Hydrogenation of nitrate in water	Pd/Alumina; Tin/Alumina	Daub et al., 2001.
Reduction of aqueous nitrate	Pd-Cu/Alumina	Ilinitch et al., 2000.
Cinnamaldehyde hydrogenation	Cu-Pt/gamma-Alumina	Pan et al., 2000.
Dehydrogenation of ethylbenzene to styrene	Fluidized Bed in Metal Reactor	Abdalla and Elnashaie, 1995.
Dehydrogenation of ethylbenzene to styrene	Pd/Porous Stainless Steel	She et al., 2001.

glass by Corning Glass, porous alumina (both alpha and gamma), porous stainless steel, and their modified or composite membranes. Although membrane selectivity was generally poor, permeation flux was adequate enough to test the very concept of membrane reactor for many of the industrial chemical reactions as shown in Table 7.

8. Other Applications (Sensors and Separation Devices)

Besides the industrial membrane reactors, many of the membrane reactor concepts (cited references in this review) can be utilized in producing oxygen and hydrogen gases as well as manufacturing chemical sensors, but they will not be discussed here since it is beyond the scope of the present review.

CONCLUSIONS

The concept of the membrane reactor is a novel idea. By combining the chemical reaction with the separation process in a single unit operation, many advantages over the conventional reactor/separator can be realized. At the same time, there are still many obstacles before this new device can become fully operational in industry. Most of the research published so far deals with laboratory scale

experiments. The potential applications involve high-temperature industrial reactions, separations of oxygen and hydrogen gases, fuel cells, and sensors. The latest developments of ion-conducting ceramic membranes raise much hope of future success. However, more efforts should be made to address sealing problems, high cost, low permeability, membrane defects, stability of membranes, and long-term performance data.

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