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Fundamentals of Membrane Reactors

1.1 INTRODUCTION

A membrane reactor (MR) is a device integrating a membrane with a reactor in which the membrane serves as a product separator, a reactant distributor, or a catalyst support. The combination of chemical reactions with the membrane functions in a single step exhibits many advantages, such as preferentially removing an intermediate (or final) product, controlling the addition of a reactant, controlling the way for gases to contact catalysts, and combining different reactions in the same system. As a result, the conversion and yield can be improved (even beyond the equilibrium values), the reaction conditions can be alleviated, and the capital and operational costs can be reduced significantly. Different reactions usually require different types of membranes. Membrane reactors are also operated in different modes. The purpose of this chapter is to introduce readers to the main concepts of membranes and membrane reactors. The principles, structure, and operation of inorganic membrane reactors are presented below.

1.2 MEMBRANE AND MEMBRANE SEPARATION

A membrane is defined as a region of discontinuity interposed between two phases [1]. It restricts the transport of certain chemical species in a specific manner. In most cases, the membrane is a permeable or semi-permeable
medium and is characterized by permeation and perm-selectivity. In other words, the membrane may have the ability to transport one component more readily than others due to the differences in physical and/or chemical properties between the membrane and the permeating components.

### 1.2.1 Membrane Structure

Membranes can be classified according to different viewpoints – for example, membrane materials, morphology and structure of the membranes, preparation methods, separation principles, or application areas. In general, the most illustrative means of classifying membranes is by their morphology or structure, because the membrane structure determines the separation mechanism and the membrane application. Accordingly, two types of membranes may be distinguished: symmetric and asymmetric membranes. **Symmetric membranes** have a uniform structure in all directions, which may be either porous or non-porous (dense). A special form of symmetric membrane is the liquid immobilized membrane (LIM) that consists of a porous support filled with a semi-permeable liquid or a molten salt solution. **Asymmetric membranes** are characterized by a non-uniform structure comprising a selective top layer supported by a porous substrate of the same material. If the selective layer is made of a different material from the porous substrate, we have a **composite membrane**. Figure 1.1 shows schematically the principal types of membranes.

Sometimes, the porous support itself may also possess different pores and exhibit an asymmetric structure. Figure 1.2 depicts the cross-section of an asymmetric membrane where the structural asymmetry is clearly observed [2]. The asymmetric membranes usually have a thin selective

![Figure 1.1](image_url)  
**Figure 1.1** Schematic diagrams of the principal types of membranes: (a) porous symmetric membrane; (b) non-porous/dense symmetric membrane; (c) liquid immobilized membrane; (d) asymmetric membrane with porous separation layer; (e) asymmetric membrane with dense separation layer.
to obtain high permeation flux and a thick porous support to provide high mechanical strength. The resistance of the membrane to mass transfer is largely determined by the thin top layer.

Based on the membrane structure and separation principle, membranes can also be classified into porous and dense (non-porous) membranes, as depicted schematically in Figure 1.3. The porous membranes have a porous separation layer and induce separation by discriminating between particle (molecular) sizes (Figure 1.3(a)). The separation characteristics (i.e., flux and selectivity) are determined by the dimensions of the pores in the separation layer. The membrane material is of crucial importance for
chemical, thermal, and mechanical stability but not for flux and rejection. The non-porous/dense membranes have a dense separation layer, and separation is achieved through differences in solubility or reactivity and the mobility of various species in the membrane. Therefore, the intrinsic properties of the membrane material determine the extent of selectivity and permeability. The LIMs can be considered as a special dense membrane since separation takes place via the filled liquid semi-permeable phase, although a porous structure is contained within the membrane.

1.2.2 Membrane Separation

The membrane separation process is characterized by the use of a membrane to accomplish a particular separation. Figure 1.4 shows the concept of a membrane separation process. By controlling the relative transport rates of various species, the membrane separates the feed into two streams: the retentate and the permeate. Either the retentate or the permeate can be the product of the separation process.

The performance of a membrane in separation can be described in terms of permeation rate or permeation flux (mol m⁻² s⁻¹) and permselectivity. The permeation flux is usually normalized per unit of pressure (mol m⁻² s⁻¹ Pa⁻¹), called the permeance, or is further normalized per unit of thickness (mol m⁻³ m⁻² s⁻¹ Pa⁻¹), called the permeability, if the thickness of the separation layer is known. In many cases only a part of the separation layer is active, and the use of permeability gives rise to larger values than the real intrinsic ones. Therefore, in case of doubt, the flux values should always be given together with the (partial) pressure of the relevant components at the high-pressure (feed) and low-pressure (permeate) sides of the membrane as well as the apparent membrane thickness.

![Figure 1.4 Schematic drawing of the membrane separation process.](image-url)
The permeation flux is defined as the molar (or volumetric or mass) flow rate of the fluid permeating through the membrane per unit membrane area. It is determined by the driving force acting on an individual component and the mechanism by which the component is transported. In general cases, the permeation flux ($J$) through a membrane is proportional to the driving force; that is, the flux–force relationship can be described by a linear phenomenological equation:

$$J = -L \cdot \frac{dX}{dx}$$  \hspace{1cm} (1.1)

where $L$ is called the phenomenological coefficient and $dX/dx$ is the driving force, expressed as the gradient of $X$ (temperature, concentration, pressure, etc.) along the coordinate ($x$) perpendicular to the transport barrier. The mass transport through a membrane may be caused by convection or by diffusion of an individual molecule – induced by a concentration, pressure, or temperature gradient – or by an electric field. The driving force for membrane permeation may be the chemical potential gradient ($\Delta\mu$) or the electrical potential gradient ($\Delta\phi$) or both (the electrochemical potential is the sum of the chemical potential and the electrical potential). In case the concentration gradient serves as the driving force, the transport equation can be described by Fick’s law:

$$J_A = -D_{Am} \cdot \frac{dc_A}{dx}$$  \hspace{1cm} (1.2)

where $D_{Am}$ (m$^2$ s$^{-1}$) is the diffusion coefficient of component A within the membrane. It is a measure of the mobility of the individual molecules in the membrane and its value depends on the properties of the species, the chemical compatibility of the species, the membrane material, and the membrane structure as well. In practical diffusion-controlled separation processes, useful fluxes across the membrane are achieved by making the membranes very thin and creating large concentration gradients across the membrane.

For the pressure-driven convective flow, which is most commonly used to describe flow in a capillary or porous medium, the transport equation may be described by Darcy’s law:

$$J_A = -Kc_A \cdot \frac{dp}{dx}$$  \hspace{1cm} (1.3)
where $dp/dx$ is the pressure gradient existing in the porous medium, $c_A$ is the concentration of component A in the medium, and $K$ is a coefficient reflecting the nature of the medium. In general, convective-pressure-driven membrane fluxes are high compared with those obtained by simple diffusion. More details of the transport mechanisms in membranes can be found elsewhere [3].

The perm-selectivity of a membrane toward a mixture is generally expressed by one of two parameters: the separation factor and retention. The separation factor is defined by

$$
\alpha_{A/B} = \frac{y_A y_B}{x_A x_B}
$$

(1.4)

where $y_A$ and $y_B$, $x_A$ and $x_B$ are the mole fractions of components A and B in the permeate and the retentate streams, respectively.

The retention is defined as the fraction of solute in the feed retained by the membrane, which is expressed by

$$
R = \left(1 - \frac{c_p}{c_f}\right) \times 100\%
$$

(1.5)

where $c_f$ and $c_p$ are the solute concentrations in the feed and the permeate, respectively. For a selective membrane, the separation factors have values of 1 or greater whereas values of the retention are 1 or less.

Membrane separations are driven by pressure, concentration, or electric field across the membrane and can be differentiated according to type of driving force, molecular size, or type of operation. Common membrane processes include microfiltration, ultrafiltration, nanofiltration/reverse osmosis, gas separation, pervaporation, and dialysis/electrodialysis [3, 4]. Some processes have been applied extensively for separation and purification of gas and liquid mixtures in industry.

1.2.3 Membrane Performance

The membrane performance can be evaluated using permeability, selectivity, and stability. Ideally, a membrane with both high selectivity and permeability is required, but the attempt to maximize one factor will usually compromise the other. Comparatively, selectivity is a more important characteristic of a membrane because low permeability can be compensated to a certain extent by an increase in membrane surface area, whereas low selectivity leads to multi-stage processes which in most cases are not economical compared with established conventional processes.
The permeability and selectivity of a membrane are determined by the material and the structure of the membrane, which essentially determine the separation mechanism and application. Asymmetric membranes are mostly applied in practical applications because they have a thin selective layer to obtain high permeation fluxes and a thick porous support to provide high mechanical strength. For a certain mass separation, the type of membrane and the driving force required depend on the specific properties of the chemical species in the mixture.

In addition to permeability and selectivity, the following membrane stabilities are also required in various industrial applications:

- chemical resistance
- mechanical stability
- thermal stability
- stable operation.

Although the stability of a membrane depends on the membrane structure to some extent, it is mainly determined by the nature of the membrane material. For example, the upper temperature limit of polymeric membranes never exceeds 500°C, but inorganic materials can withstand very high temperatures and are inherently more stable at high temperatures and with various chemicals such as aggressive organic compounds and liquids with extreme pH values.

1.3 INORGANIC MEMBRANES

1.3.1 Types of Inorganic Membranes

Inorganic membranes are made of inorganic materials such as metals, ceramics, zeolites, glasses, carbon, and so on. Actually, inorganic membranes usually consist of several layers from one or more different inorganic materials. Details of inorganic membranes with respect to their syntheses, characterizations, transport theories, and scaling-up problems have been well reviewed and summarized by several authors [5, 6].

Inorganic membranes may be of either symmetric or asymmetric structure. Symmetric membranes often have considerable thickness to obtain sufficient mechanical strength. This is unfavorable for obtaining large fluxes, which usually require thin separation layers. In order to obtain high fluxes, most applicable inorganic membranes possess a multi-layered asymmetric structure as shown in Figure 1.5(a). A porous substrate with large pores (1–15 µm for low flow resistance) but sufficient mechanical...
strength is used to support a thin selective layer for separation. Commonly used materials for the macroporous support include Al₂O₃, ZrO₂, TiO₂, Si₃N₄, carbon, glass, stainless steel, and so on. Figure 1.5(b) shows the pore structure of a silica membrane supported on a cylindrical α-Al₂O₃ porous tube (outer diameter (OD) 10 mm; thickness 2 mm; average pore size 1 µm) [7].

In general, it is difficult to produce a thin separation layer directly on top of a support with large pores because the precursor system from which the separation layer is made will penetrate significantly into the pores of the support (e.g., the small particles from which small-pore membranes are made will penetrate much larger pores), leading to an increase in flow resistance. Furthermore, the thin layers covering large pores are mechanically unstable and would crack or peel off easily. A practical solution is to produce a graded structure by adding one or more intermediate layers with gradually decreasing layer thickness and pore size between the bulk support and the separation layer. An intermediate layer is also applied to
match the thermal expansion difference of the membrane with the substrate, and as a buffer zone in case of chemical incompatibility during the membrane preparation process.

The separation layer may be dense (non-porous), such as Pd or Pd-alloy membranes for hydrogen separation and mixed (electronic, ionic) conducting oxide membranes for oxygen separation, or porous, such as metal oxides, silicalite, or zeolite membranes. Inorganic membranes are generally named for this separation layer, since it determines the properties and application of the membrane. The flux and selectivity of inorganic membranes are mainly determined by the quality of the separation layer, which is required to be defect-free and as thin as possible.

In addition to the planar geometry, inorganic membranes can also be produced in flat disk, tubular (dead-end or not), monolithic multi-channel, or hollow fiber configurations as shown in Figure 1.6. Disk membranes are often used in the laboratory because they can easily be fabricated by the conventional pressing method. In the case of tubes, they can be assembled in a module containing a number of tubes connected to a single manifold system.

The multi-channel monolithic form is developed to increase the mechanical robustness and the surface area-to-volume ratio, which gives more separation area per unit volume of membrane element. In the monolithic membranes, the monolith bulk is a porous support and the separation layer is produced on the inner surface of the channels. Therefore, feed is introduced in the channels and the permeate is obtained from the membrane wall, as shown in Figure 1.7. The surface area-to-volume ratio of the multi-channel monolithic membrane ranges from 130–400 m² m⁻³ compared with 30–250 m² m⁻³ for tubes. Honeycomb multi-channel monolithic membranes can even reach up to 800 m² m⁻³ of surface area-to-volume ratio.

Figure 1.6 Tubular (a), monolithic (b), and hollow fiber (c) inorganic membranes.
It is possible to increase the surface area-to-volume ratio of tubular membranes by decreasing their diameter. If the diameter of the membrane tube is reduced to a certain level, it is then called a hollow fiber membrane. Such hollow fiber membranes usually have an internal diameter ranging from 40–300 µm and wall thicknesses of 10–100 µm, and can provide surface area-to-volume ratios of more than 3000 m² m⁻³ [4].

A variety of inorganic membranes are summarized in Table 1.1. The metal membranes mainly include palladium-based membranes for hydrogen permeation and silver-based membranes for oxygen permeation. Currently, the commercially available inorganic membranes are porous membranes made from alumina, silica and titania, glass, and stainless
steel. These membranes are characterized by high permeability, but low selectivity. ZrO$_2$- or CeO$_2$-based membranes are solid oxide electrolytes and their permeability depends on their ionic conductivity.

### 1.3.2 Fabrication of Inorganic Membranes

As inorganic membranes have a multi-layered asymmetric structure consisting of porous support, intermediate layers and a selective separation layer, the fabrication of inorganic membranes is a multi-step process, as illustrated in Figure 1.8.

The fabrication starts with the preparation of porous substrates, with which the shape and configuration of the final membrane products can be determined. The porous substrate is critical for the quality of the membrane itself, because it not only provides sufficient mechanical strength but also takes effect on the permeability and selectivity of the membrane. Therefore, the commercial availability of high-quality substrates is a critical issue in the further development of membrane separation units.

Porous substrates are mostly made from ceramics like $\alpha$-Al$_2$O$_3$, but also from other materials such as metal or glass. They are formed by shaping inorganic powders and consolidation of the green body by

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**Figure 1.8** Fabrication process of inorganic membranes.
sintering. Four main stages are included in the fabrication process: choice of inorganic powder, paste/slurry preparation, shaping into green body, and firing into a porous substrate at high temperature. The particle size and morphology of the inorganic powders, the composition and homogeneity of the powder suspension, and the drying and firing conditions have considerable influence on the quality of the porous substrates [8]. Depending on the tubular or flat sheet (or disk) configuration, porous substrates can be prepared by the well-established techniques of slip casting, tape casting, pressing, or extrusion [4]. Figure 1.9 shows schematically the extrusion apparatus for shaping mono- or multi-channel tubular substrates. Different shapes are obtained by changing the geometry of the die (e.g., number of channels, diameter of channels, and external diameter of tubes).

Porous substrates should have a smooth surface with constant and homogeneous characteristics (wettability) and a narrow pore size distribution. Pores much larger than average and grains broken out of the surface, or irregularities in the porous substrate, may result in defects in the separation layer applied on it. Therefore, surface modification or formation of intermediate layer(s) is necessary to prepare a thin and defect-free membrane.

The preparation of intermediate layers is actually a process to produce a porous layer with smaller pores than those in the bulk support. Since

![Figure 1.9](image-url) Schematic view of the extrusion apparatus for the fabrication of tubular membranes (porous substrates): (1) endless screw; (2) paste inlet; (3) compression; (4) vacuum; (5) pressure gauge; (6) vacuum chamber; (7) die. Reproduced from [8]. With permission from Elsevier.
Inorganic membranes are difficult to have thermostable powder particles smaller than 5–6 nm, an intermediate layer with pore diameters below 2 nm cannot be produced by packing of spherical or plate-shaped particles. Sometimes, more than one intermediate layer has to be produced to form a graded structure with gradually decreasing layer thickness and pore size between the bulk support and the separation layer.

The separation layer, either porous or dense, can be formed using different methods such as sol-gel and template routes, hydrothermal synthesis, chemical vapor deposition (CVD), or physical sputtering, depending on the membrane material and its application. These membrane preparation methods will be described in the following chapters of this book for different membranes and membrane reactors. We note that the preparation of inorganic membranes involves a multi-step high-temperature treatment process. Therefore, inorganic membranes are much more expensive than polymeric ones.

1.3.3 Characterization of Inorganic Membranes

Inorganic membrane performances are determined by the membrane structure and the material properties. Information on pore size, shape, distribution, connectivity, and porosity for porous membranes and gas tightness, crystal structure, and surface properties for dense ceramic membranes is of importance to predict the separation performances of the membranes. The membranes developed have to undergo a series of characterization tests using techniques based on adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and so on. The characterization of inorganic membranes generally refers to three aspects: evaluation of porous features (porosity, pore size and distribution, tortuosity, etc.); microstructure and morphology (pore shape, surface, cross-section); and transport or reaction properties (permeability, selectivity, reactivity). Table 1.2 summarizes the common characterization methods for inorganic membranes.

1.3.4 Applications of Inorganic Membranes

Compared with their polymeric counterparts, inorganic membranes are characterized by high chemical and thermal resistances and high mechanical stability, and thus can be applied in a harsh environment. However, inorganic membranes also exhibit the shortcoming of high cost, because
of their long and complicated production route in which multi-step high-temperature treatment is required. Therefore, inorganic membrane applications should preferably be found in areas where polymer membranes cannot or do not perform well. The application areas of inorganic membranes mainly include [8]:

- separation in food, beverage, and biotechnology fields;
- purification in environmental protection;
- energy conversion in solid oxide fuel cells;
- separation and reaction in petroleum and chemical industries.

### 1.4 INORGANIC MEMBRANE REACTORS

#### 1.4.1 Basic Principles of Membrane Reactors

In a conventional design of chemical production process, the reaction and separation functions are carried out by two different processing units, as illustrated in Figure 1.10(a), where a membrane separator is used for product separation. If the membrane is placed inside the reactor to carry out the separation function as shown in Figure 1.10(b), it then becomes a membrane reactor. Since the reaction and separation proceed simultaneously, the separation of products can be accomplished in the reactor unit itself, or at least the downstream separation load can be
Inorganic Membrane Reactors

reduced. As a result, the chemical process will become much simpler and the operational costs will thereby be reduced drastically. Moreover, the reaction can be enhanced significantly due to the combination of membrane functions. Based on the above discussions, an MR is a device integrating a membrane with a reactor in which the membrane functions as a separator or a reaction interface to enhance the reaction process.

Both organic (polymeric) and inorganic membranes have been used in MRs. Since organic membranes cannot withstand high temperature, organic MRs are applied mainly in biochemical processes (thus called membrane bioreactors), such as for the production of fine chemicals via the use of enzymes and for large-scale biogas production from waste and environmental clean-up. Most chemical reactions of interest operate at temperatures well in excess of the limitation of polymeric membranes; inorganic membranes with inherent high-temperature structural and chemical stability are appropriate candidates for use in catalytic MRs. The main requirement is to produce membranes with the desired properties of good separation and selectivity and enough robustness to withstand the severe operating conditions often encountered in industrial practice.

Membrane reactors promote a reaction process based on the following three routes, with the membranes having different effects:

1. The membrane serves as a product extractor (Figure 1.11(a,b)). For thermodynamically limited equilibrium reactions, the removal of at least one of the products by the membrane from the reaction zone makes the reaction equilibrium shift to the product side with the single-pass conversion increased (Figure 1.11(a)). On the contrary, if the intermediate product is taken out through the membrane, the
undesired side-reactions or the secondary reaction of products can be suppressed, leading to improved selectivity (Figure 1.11(b)).

2. The membrane serves as a reactant distributor (Figure 1.11(c,d)). A reactant is added to the reaction zone in a controlled manner through the membrane. As a consequence, the side reactions are limited, leading to increased selectivity and yield. In addition, it is
possible to use low-purity feed instead of pure reactant to obtain higher selectivity and reduce capital investment and operation costs.

3. The membrane serves as an active contactor (Figure 1.11(e,f)). Reactants are supplied to the catalyst by the controlled diffusion in the membrane, hence a well-defined reaction interface (or region) between two reactant streams is created. The reactants can be provided from one side or from opposite sides of the membrane. Furthermore, more reactive sites can be provided due to the easy access of reactants to the catalyst, and thus the catalyst’s efficiency can be increased greatly.

A synergy may be created due to the use of MRs. Since the chemical reaction can be enhanced by membrane separation, it is possible to attain a given conversion at less severe conditions of temperature and pressure. This implies that hot spots may be avoided and the MR may be energy-efficient and relatively safe in operation. Furthermore, the reduction in temperature leads to a decrease in catalytic deactivation from coke deposition and sintering, and thus provides improved catalyst life and/or less frequent regeneration requirements. In addition, the MR may also allow hot separation of products and eliminate the need for quenching a reaction to prevent back-reactions.

1.4.2 Incorporation of Catalyst in Membrane Reactors

Most chemical reactions take place in the presence of a catalyst. There are four ways to incorporate catalysts in the membranes of MRs, as illustrated in Figure 1.12 [9].

(a) **Catalyst physically separated from an inert membrane**

In this case, the membrane compartmentalizes the reactor and functions for separation but is not involved directly in the catalytic reaction (called an “inert membrane”). The catalyst pellets are usually packed or fluidized on the inert membrane (Figure 1.12(a)), which acts as an extractor for fractionation of products and/or as a distributor for controlled addition of reactants. This incorporation of catalyst is most popular in practical use and can easily be operated. Since the catalyst is physically separated from the membrane, the separation function of the membrane and the activity of the catalyst can be modulated independently. Catalysts are generally placed on the separation layer
(b) Catalyst coated on the membrane surface
In this case, the catalyst is coated on the membrane surface using a catalyst paste (Figure 1.12(b)). The catalyst layer is generally porous and is integrated with the membrane into a single body.
If the catalyst is reactive with the separation layer of the membrane, direct contact between them must be avoided.

(c) **Catalyst dispersed in the membrane porous structure**
In Figure 1.12(c), the catalyst is dispersed in the porous substrate of the membrane to form a membrane catalyst. One of the reactants or products traverses through the membrane into or out of the reaction zone. In classical reactors, the reaction conversion is often limited by the diffusion of reactants into the pores of the catalyst or catalyst carrier pellets. If the catalyst is inside the pores of the membrane, the combination of the open pore path and transmembrane pressure provides easier access of the reactants to the catalyst as shown in Figure 1.13. As a result, the access of reactants to the catalyst is improved and the catalytic efficiency can be increased greatly. If the membrane thickness and porous texture, as well as the quantity and location of the catalyst in the membrane, are adapted to the kinetics of the reaction, the membrane catalyst can be 10 times more active than that in the form of pellets [10, 11].

(d) **Inherently catalytic membranes**
In some cases, the membrane material is inherently catalytic and the membrane serves as both catalyst and separator, controlling the two important functions of the reactor simultaneously as shown in Figure 1.12(d). A number of meso- and microporous inorganic membrane materials have catalytic properties, such as titania and zeolites with acid sites. As an example, mesoporous TiO$_2$

![Figure 1.13](image-url)  
*Figure 1.13* Comparison of the contact of the reactant with the catalyst in (a) a catalyst-supported pellet and (b) a catalyst-loaded membrane. Reproduced from [10]. With permission from Elsevier.
photocatalytic membranes prepared by the sol-gel process are used for the continuous degradation of volatile organic compounds (VOCs) in water [12]. Most perovskite membranes for oxygen permeation also exhibit good catalytic activity toward the oxidation of hydrocarbons [13].

In general, the membranes modified by coating a catalyst on the membrane surface or loading a catalyst inside the membrane’s porous structure are called “catalytic membranes.” In most cases, catalytic membranes do not need to be perm-selective but are required to be highly active for the reactions considered and to have a sufficiently low overall permeability so that they are operated in the diffusion-controlling regime. For catalytic membranes, the catalytic composition and activity as well as the porous texture have to be optimized for the reactions considered and kept stable in use. However, it is difficult to modulate these properties of catalytic membranes. Therefore, very few studies have been performed on catalytic MRs in application. It is noteworthy that in some cases extra catalysts will be applied in the catalytic MRs to promote the reactions considered.

1.4.3 Configuration of Membrane Reactors

Unlike conventional reactors, MRs have two compartments separated by the membrane and thus are characteristic of at least three inlets/outlets for the feed and product streams. They are designed and fabricated based on the membrane configuration and the application conditions.

Tubular MRs are applied mostly in laboratory studies and industrial applications. Figure 1.14 shows schematically the structure of a tubular MR. The catalyst may be placed on either the tube side or the shell side. Two feed streams are introduced concurrently or countercurrently on opposite sides of the membrane. Usually, a sweep gas (feed 2) is employed on the permeate side to reduce the build-up of products and therefore reduce the potential rise in film mass transfer resistance on the permeate side of the membrane. The ends of the membranes are sealed by glazing or by very fine powders. The membrane tube is sealed by carbon or graphite strings pressed against Swagelok-type compression fittings. In industrial reactors, a shell and tube configuration with an assembly of single tubes or multi-channel monoliths may be incorporated into a large shell.

Disk/flat sheet MRs are applied mostly in research work because they can be fabricated easily in the laboratory with a small amount of
membrane material. Figure 1.15 shows the structure of a disk/flat sheet MR. The membrane disk is mounted between two vertical ceramic or quartz tubes. Pyrex or gold gaskets are used to obtain effective seals between the disk and the walls of the tubes at high temperatures by placing the assembly in compression with the use of spring clamps. The catalyst is usually packed on the membrane or coated on the membrane surface.

In general, hollow fiber membranes can be assembled into reactors following the same procedures as for tubular MRs. Hollow fibers offer a much greater packing density, but suffer from poor mechanical strength. Figure 1.16 illustrates schematically the configuration of a hollow fiber MR [13, 14]. A quartz shell is used to house the hollow fibers. Two pairs of gas inlet/outlet fittings and alumina thermocouple sleeve assemblies are housed in quartz end-caps that fit closely to the inner wall of the shell tubing. The hollow fiber membranes are placed in a pair of quartz tubes
with flexible silicone tubes to connect to the lumen-side gas inlet/outlet of the reactor and to offset the thermal expansion of the hollow fibers occurring during operation. A seal is achieved by using high-temperature water-based glass/ceramic sealant. A thermocouple that can be moved along the length of the module is inserted inside an alumina sleeve, the tip of which is positioned close to the center of the hollow fibers, allowing...
the temperature profile to be recorded during operation. A custom-made furnace with a short can be used to heat the reactor so that the sealing points are kept away from the high-temperature zone. The catalyst, if used, is usually packed in the fiber lumen for convenient operation.

In addition to the above-mentioned MR configurations, other MRs including catalyst fluidized bed membrane reactors (CFBMRs), electrolyte membrane reactors (EMRs), and membrane microreactors (MMRs) have also been developed and investigated. Figure 1.17 shows a typical representation of the fluidized bed MR for hydrogen production [15]. Hydrogen-permeable membranes are placed vertically in a catalyst bed. A mixture of steam and hydrocarbon gas is fed into the bottom of the reactor to fluidize the particulate catalyst. Hydrogen is separated through perm-selective membranes. Details of these special MRs will be given in the following chapters of this book.

1.4.4 Classification of Membrane Reactors

So far, MRs have been investigated extensively in the literature. These MRs can be categorized based on the properties of the membrane or the reactor itself. A summary of different types of MRs is given in Table 1.3.
The packed bed membrane reactor (PBMR) is by far the most commonly referred to reactor in which the reaction function is provided by a packed bed of catalysts in contact with the membrane. The membrane itself is not catalytic or at least not intentionally so, but is used to add or remove certain species from the reactor. If the membrane is highly perm-selective, this configuration appears ideal for situations where two complementary reactions take place on either side of the membrane – the product of the reaction on one side acting as a reactant on the other side, while the endothermicity of one reaction is compensated by the exothermicity of the other. When the catalysts at work are present in a fluidized mode, the reactor is then called a fluidized bed membrane reactor (FBMR).

In catalytic membrane reactors (CMRs), the reactions take place directly on the membrane and the membrane functions as both a catalyst and a separator/distributor. This requires that the membrane material has intrinsic catalytic activity or that it is modified by the addition of active components. Some of the commonly utilized inorganic (such as metal oxide and zeolite) and metal membranes are intrinsically catalytically active. In other cases, the catalysts can be integrated with the membrane into a single body by being coated on the membrane surface or deposited inside the membrane porous structure. In case the membrane does not participate in the reaction directly, but is used to add or remove certain species from the reactor, this is called an inert membrane reactor (IMR).

Table 1.3 Types of membrane reactors

<table>
<thead>
<tr>
<th>Membrane reactor type</th>
<th>Description</th>
<th>Acronym</th>
</tr>
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<tbody>
<tr>
<td>Packed-bed membrane reactor</td>
<td>Additional catalysts are packed in the membrane reactor</td>
<td>PBMR</td>
</tr>
<tr>
<td>Fluidized-bed membrane reactor</td>
<td>Catalysts in the reactor are present in a fluidized mode</td>
<td>FBMR</td>
</tr>
<tr>
<td>Inert membrane reactor</td>
<td>The membrane does not participate directly in the reaction</td>
<td>IMR</td>
</tr>
<tr>
<td>Catalytic membrane reactor</td>
<td>The membrane functions as both catalyst and separator</td>
<td>CMR</td>
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<tr>
<td>Catalytic non-selective</td>
<td>The membrane is not selective but serves as a catalytic site for reactions</td>
<td>CNMR</td>
</tr>
<tr>
<td>membrane reactor</td>
<td></td>
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</tr>
<tr>
<td>Flow-through catalytic</td>
<td>Catalytic reactions take place while the reactants flow through the membrane</td>
<td>FTCMR</td>
</tr>
<tr>
<td>membrane reactor</td>
<td>Membrane is integrated with the microreactor having a characteristic length</td>
<td>MMR</td>
</tr>
<tr>
<td>Electrolyte membrane reactor</td>
<td>An external electrical circuit is applied to complete reactions</td>
<td>EMR</td>
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In some applications the membrane is not required to be perm-selective but only to provide reactive sites. Such devices are called catalytic non-perm-selective membrane reactors (CNMRs). The reactants can flow into the membrane from opposite sides, and the membrane’s role is to provide a controlled reactive interface. If the reactants flow through the membrane from one side to the other while the reaction takes place instantly, such a reactor is also called a flow-through catalytic membrane reactor (FTCMR).

When the membrane is integrated in a microreactor having a characteristic length of <1 mm, it is called an MMR. For EMRs, an external electrical circuit is necessary for reactions to proceed. Electrical power can be co-generated with the production of chemicals in the EMRs.

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