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HYDROGEN RECOVERY USING INORGANIC MEMBRANES

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Introduction

Global annual production and utilization of hydrogen now total some 6×10^{11} Nm^3. Of this amount, approximately 50% is produced by steam reforming or partial oxidation of natural gas. Other sources include electrolysis of water and recovery from refinery off-gases. The main use of bulk hydrogen includes synthesis of ammonia, hydrotreating of heavy petroleum feedstocks, hydrogenation of vegetable oils and manufacture of transformer steels and other metallurgical heat treatment operations. More recent applications where high purity hydrogen is required include semiconductor processing and fuel cells. To obtain high purity several methods may be adopted, such as pressure swing adsorption and cryogenic technology. However, both these methods have disadvantages, including cost and degree of purity obtained; the cryogenic method gives purities ranging from 90 to 98% only.

Membranes can provide an efficient low cost means of separation and purification for hydrogen. Although polymeric membranes are well proven for gas separation, they are limited to temperatures not much greater than 250°C whereas, in many applications, high temperature processing is required. Inorganic membranes have shown considerable development in recent years and, apart from their high temperature stability, they have in general much higher fluxes than polymeric membranes.

Inorganic membranes suitable for the recovery and purification of hydrogen may be divided into two classes, namely, porous and dense membranes. The former includes materials such as alumina, silica, zirconia and porous metals, for example, stainless steel. The dense membranes include palladium and its alloys, in which the unique permeation properties of palladium to hydrogen are utilized.

Porous Membranes

To achieve appropriate separations with this type of membrane, the pore size needs to be small. However, to achieve a suitable gas permeation rate through the membrane, the membrane should be as thin as possible. To meet this requirement, a composite structure is usually adopted in which a thin finely microporous separation layer is supported on a thicker more open microporous material. Such structures have now been developed by a number of procedures.

The various possible gas permeation mechanisms applicable to porous membranes are illustrated in **Figure 1**.

In this figure, the progression from Knudsen diffusion to molecular sieving is in parallel with increasing permselectivities (it should be noted that viscous flow gives no separation). The separation factor for all the processes depends strongly on the pore size and its distribution, the temperature, pressure and the

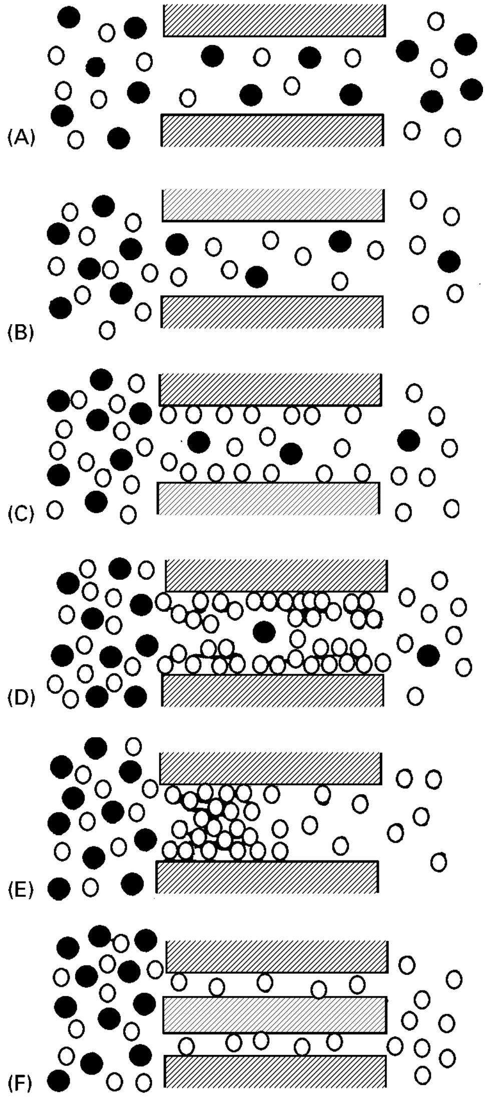

Figure 1 Transport mechansim in porous membranes. (A) Viscous flow. Pore diameter is greater than gas mean free path – no separation. (B) Knudsen flow. Pore diameter is smaller than gas mean free path – separation is proportional to the square root of Ma/mB. (C) Surface diffusion. Absorbed gas on the pore water contributes to total gas flow. Transport of condensable vapour is enhanced. (D) Multilayer diffusion. Transport of absorbed gases is dominant and so condensable vapours have high transport rates. (E) Capillary condensation. Absorbed gas completely blocks pores. There is no transport of nonabsorbed gas. (F) Molecular sieving. Pores are so small that they begin to filter small molecules from large ones. Transport of small molecules is preferred. Modified with permission from Saracco G and Specchia V (1994) Catalytic inorganic membrane reactors: present experience and future opportunities. *Catalysis Review, Science and Engineering* 36: 305.

nature of the membrane and the permeating molecules. Because of these factors, porous membranes are more versatile in their applications compared with dense metal membranes, because they can be used for separation of gases other than just hydrogen and oxygen only. Conversely, porous membranes show significantly lower selectivities compared with dense membranes.

Viscous flow occurs when the mean free path of the gaseous molecules is much less than the pore diameter. Under these conditions, molecule–molecule collisions are much more frequent than collisions between the molecules and the walls of the pores. The mean free path, λ, of a gas molecule is given by:

$$\lambda = kT/(2\sigma p) \qquad [1]$$

where k is the Boltzmann constant, T the absolute temperature, p the absolute pressure and σ the collision diameter of the molecule. Thus, λ will increase with increase in temperature and with decrease in pressure. Calculated values of λ are shown in **Table 1** for a number of gases. Since the pore diameter of many separation membranes is of the order of 1–4 nm it can be seen that mean free paths under conditions often encountered in many catalytic processes are greater than the pore diameter and therefore Knudsen diffusion can be the operating mechanism for many current membranes.

In Knudsen flow, as shown in Figure 1B, the molecules collide on average more frequently with the pore walls than with one another when the mean free path becomes much greater than the pore diameter and absolute pressure does not affect the flux if this flow is fully developed. With a binary mixture, the highest separation factor achievable is given by the ratio of the inverse of the square roots of the molecular weights. Hence, small molecules are preferentially transported across the membrane and the greatest potential is for separation of hydrogen from other gases. Even in this case, however, separation is limited: that for a hydrogen–nitrogen mixture is only 3.74 at best.

Table 1 Mean free paths for representative gases (nm)

Gas	*Gas diameter (nm) σ*	*Temperature 500 K*		*Temperature 800 K*	
		0.1 MPa	*1.0 MPa*	*0.1 MPa*	*1.0 MPa*
H_2	0.29	183	18.3	293	2.9
CO	0.37	113	11.3	181	18.1
N_2	0.37	111	11.1	177	17.7
CO_2	0.39	102	10.2	164	16.4
C_4H_{10}	0.50	62	6.2	100	10.0
C_6H_{12}	0.61	42	4.2	67	6.7

Surface flow occurs (Figure 1C) when one of the permeating molecules can be preferentially physisorbed or chemisorbed on the pore walls and migrates along the surface. Surface diffusion increases the flux of the more strongly adsorbed components while reducing the contribution of the gas phase diffusion to total gas transport by decreasing pore diameter. Surface flow becomes more important as the pore size is reduced. Also, the effective pore diameter is further decreased by adsorption of the relevant species on the walls of the pores and thus obstructing the transfer of the other species through the free volume of the pores. As the temperature increases, most species will desorb from the surface and surface diffusion becomes less important.

Multilayer diffusion has been postulated to occur when molecule–surface interactions are very strong. The process is shown diagrammatically in Figure 1D. It may be regarded as an intermediate flow regime between surface flow and capillary condensation.

When the pores are small enough and one of the components of the gaseous mixture to be separated is a condensable vapour, absorbed vapour on the surface of the pore walls may be sufficient for the condensate to block gas-phase diffusion through the pore (Figure 1E). The condensate fills the pores and then evaporates at the permeate side, which has to be maintained at low pressure. In this case, only the condensed vapour permeates the membrane and nonabsorbed gases are almost totally retained by the membrane.

Molecular sieve transport occurs when pore diameters are small enough to permit only smaller molecules to permeate, while larger ones are excluded from entering these molecular-sized pores (Figure 1F). This type of process is frequently referred to as shape-selective diffusion. A necessary condition for effective separation by this means is that the pore size distribution is monodisperse and that the pores are very small – of the order of 0.5–1.0 nm.

From the above considerations it can be seen that a small pore size is necessary to obtain adequate separations. Since very finely porous membranes must necessarily have low permeabilities, useful fluxes are only obtained if the separating layer is made very thin. This has led to the evolution of asymmetric membranes in which the thin separation layer is supported on a wide pore matrix of similar material. Composite membranes have been developed in which different materials are used for the separation and support layers of the membrane. Molecular sieve membranes have been produced in this manner. An interesting development is the use of nanoporous carbon membranes for gas separation. These membranes, which are produced by carbonization of polymers, have pore sizes in the molecular sieve range 0.5–0.6 nm) and operate by a combination of selective adsorption and surface flow. Rao and Sircar have shown that these nanoporous membranes can separate hydrogen from carbon dioxide and hydrocarbons with high selectivity. Experiments with silicalite zeolite for the separation of hydrogen and butane mixtures by Moulijn's group at Delft have shown that butane excludes hydrogen from the pores of the silicalite at room temperature by butane adsorption. However, at high temperature where adsorption effects are reduced, hydrogen permeation now predominates. These examples show that there is considerable scope for hydrogen separation from gas mixtures by using membranes with very small pore sizes and utilizing the adsorption and surface diffusion behaviour of the species involved.

Dense Membranes

A second type of hydrogen-separating membrane is the dense membranes made from various metals, metal alloys and metal oxides. Hydrogen permeates a number of metals at high temperatures, including tantalum, niobium, vanadium nickel, iron, copper, cobalt and platinum. Alloys of these and other metals also possess high permeation rates for hydrogen together with certain metal oxides such as perovskites, which permeate hydrogen ions at temperatures in excess of 700°C. However, the main materials developed for hydrogen permeation are palladium and its alloys. This is because of the very high level of hydrogen absorption possible with these materials. Pure palladium absorbs 600 times its volume of hydrogen at room temperature, with the various palladium alloys absorbing comparable quantities. Although metals such as niobium and tantalum, also possess the ability to absorb large quantities of hydrogen, the formation of surface oxide films inhibits the ingress of hydrogen into the bulk metal and consequently these metals cannot be used to permeate hydrogen as such. Attempts have been made to overcome this problem by deposition of thin layers of platinum or palladium but the results have not been entirely successful, due in part of the formation of intermetallic compounds.

Consequently, palladium and/or palladium alloys represent the main dense metals currently favoured for membranes for selective permeation of hydrogen because of the high hydrogen permeation rates achievable at temperatures less than 500°C. However, below a critical temperature of 300°C and a critical pressure of 20 bars, the hydrogen–palladium system exhibits two-phase behaviour. Early experiments with palladium membranes resulted in mechanical failure due to the expansion and contraction of the metal lattice as hydrogen was absorbed and released. Alloying palladium with other elements such as silver, yttrium or cerium enables this difficulty to be overcome and an alloy of palladium with, for example, about 23% silver has been shown to be stable and have the optimum permeation rate for hydrogen.

Hydrogen Transport in Metal Membranes

Hydrogen transport through metal membranes is a multi-step process, as illustrated in **Figure 2**. Hydrogen molecules in the feed gas are adsorbed on to the metal surface where they dissociate into atoms. These atoms then diffuse through the metal to the downstream (permeate) side of the membrane where they recombine to form hydrogen molecules on the surface. These molecules are finally desorbed into the permeate gas stream. The process is selective, in that only hydrogen is transported through the membrane; other gases are excluded, so that in theory the membranes should have infinite selectivity. However, due to a number of factors, this does not occur, although very high selectivities can be attained.

Depending on which of the above steps is controlling, the exponent of the pressure driving force for the overall permeation will change. For diffusion control by hydrogen atoms, which process is normally attained at high temperatures, the overall hydrogen flux (J) will be given by:

$$J = K(p_{\mathrm{h}}^{0.5} - p_{\mathrm{l}}^{0.5}) \qquad [2]$$

where p_{h} and p_{l} are the feed and permeate side pressures of hydrogen respectively.

However, if adsorption and/or dissociation of hydrogen into atoms is the controlling step then the pressure exponents will tend to a value close to unity.

Metal Composite Membranes

Palladium–silver alloys have been used for a number of years for preparation of ultra-pure hydrogen for laboratory use. In recent years larger units have been made for the electronics industry. These membrane modules typically contain a number of small diameter alloy tubes with a metal wall thickness of about 50 μm. Sheet palladium alloys have also been used successfully for separation of hydrogen in reaction systems by Gryaznov and co-workers in Russia. However, the use of metal membranes alone has two serious disadvantages. If the permeation rate of hydrogen through the metal is diffusion-controlled, then the hydrogen flux is inversely proportional to metal thickness; most pure metal–alloy systems require a finite thickness to withstand the necessary pressure differential inherent in the separation process. Associated with this increased metal thickness is the material cost of palladium and its alloys.

Because of these factors, a number of methods have been proposed to overcome this problem, but essentially the common feature is to deposit the palladium on to a porous support material. The aim has been to obtain thin films of thickness ranging from 1 to 10 μm, but much thinner films have been produced by some investigators. The danger is that, with very thin films, the likelihood of pinholes being present increases considerably. Thin films in the micron range will give greatly increased fluxes, but the main difficulty is to produce films without cracks and to have good adherence to the support material. Substrates which have been used include porous glass, aluminas, silica, zirconia and stainless steel, although other porous materials have also been tried. The main

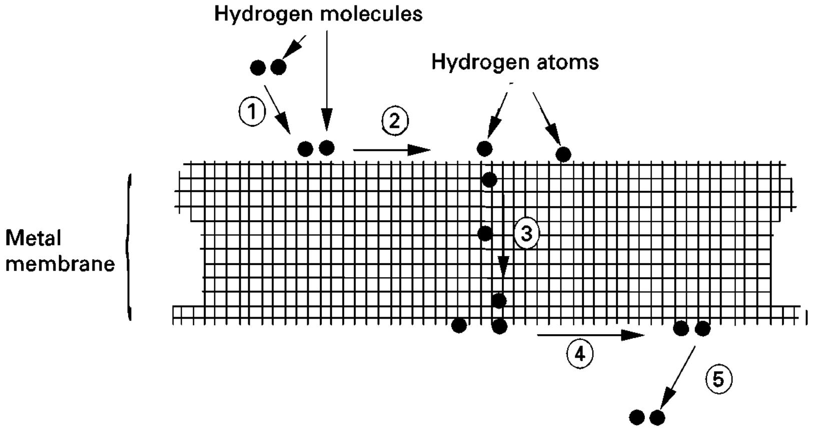

Figure 2 Permeation of hydrogen through metal membranes. 1, Sorption; 2, dissociation; 3, diffusion; 4, reassociation; 5, desorption.

techniques which have been developed for the deposition of thin films of palladium and palladium alloys on to porous substrates include:

1. magnetron sputtering
2. electroless plating
3. chemical vapour deposition
4. physical vapour deposition (thermal evaporation)
5. flame pyrolysis

There is some distinction in the way which palladium is deposited by these methods. The magnetron sputtering and vapour deposition methods tend to produce surface films whereas the chemical process of electroless plating can also act as a pore-plugging process. It has been found by a number of investigators, including the present author, that in comparing the suitability of α- and γ-alumina substrates for electroless plating, the wider pore α-alumina gives a more pinhole-free deposition. This has been attributed to the tendency of the electroless plating process to plug the pores; the more accessible wider pore mouths of the α-alumina facilitate entry of the depositing palladium.

In recent years the use of porous stainless steel as a support medium has been investigated since, although the pore sizes of stainless steel are currently larger than those of ceramic materials, this is compensated for by the robustness of the stainless steel and its potentially easier fabrication into an appropriate membrane module.

Use of composite membranes based on either ceramic or stainless steel supports is able to provide hydrogen permeation fluxes of $10^{-6}\,\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$ or better with hydrogen–nitrogen selectivities in the range of 1000–5000. These results are suitable for a number of processes for hydrogen recovery, which are currently under evaluation.

Technical Challenges to the Use of Membranes for Hydrogen Recovery

Membranes used for separation of hydrogen from other gases at high temperature should possess the following features:

1. thermal and chemical resistance
2. crack-free
3. small pore diameters (porous membranes)
4. large surface areas for membrane modules
5. require high temperature seals
6. composite membranes must retain adherence of the separation layer under thermal cycling
7. fouling of the membranes must be avoided

Some of these problems are being overcome currently. A major problem is that of sealing the individual membrane units into a module. If cylindrical tubes are to be used as membranes, then a shell-and-tube configuration as in conventional heat exchangers would seem to be the most favourable configuration, with the individual membrane tubes sealed into the end-plates of the shell. A stainless steel supported membrane tube would clearly have advantages in this case and would be preferable in terms of robustness compared to ceramic tubes.

Cost is a further factor. Although palladium is frequently cited as a major cost, it should be pointed out that, at present, the costs of porous ceramic or stainless steel support tubes are significant. No doubt these costs will decrease with increased production, but these represent a current constraint on applications.

Present Status and Potential Developments

Because of the increased demand for hydrogen as a clean fuel and for newer applications where very high purity is required (current semiconductor processing requires hydrogen with impurities of 10 p.p.b. or less), there will be a continued demand for processes to fill this need. Membrane technology can provide a significant input into this demand. Both porous and dense membranes can be utilized to provide recovery of hydrogen from process streams, but dense membranes are necessary at present to provide hydrogen of high purity. Although palladium and palladium alloys have been used almost entirely for production of pure hydrogen, other metals such as niobium, tantalum and vanadium possess, in theory, good permeating properties and are less expensive than palladium. The problem of the surface oxide layer inhibiting permeation of hydrogen is being tackled with some success and further efforts will undoubtedly lead to better performance from these materials.

With porous membranes, perhaps the most important developments are likely to occur with zeolite membranes. The development of these, either as individual membranes or in composite form on another support material, will undoubtedly open up a new area of application for inorganic membranes for hydrogen recovery and purification.

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IMMOBILIZED BORONIC ACIDS: EXTRACTION

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Introduction

With the exceptions of antibody and molecular imprint-based methods, most solid-phase extractions rely on relatively nonspecific nonpolar van der Waals or ionic interactions. Another exception to the use of nonspecific interactions involves the use of reversible covalent bond formation with vicinal diols, or similar structures, in the target analyte with immobilized boronic acids. Clearly, the potential to exploit this type of interaction is limited but, where it can be exploited, highly specific solid-phase extraction (SPE) methods can result. Such methods, based on the use of boronic acids immobilized on materials, such as sepharose gels or phenylboronic acid (PBA) covalently linked to silica gel, have provided the basis for a number of SPE methods, as described below.

Mechanism of Interaction of Analytes with Immobilized PBA

The extraction mechanism that results in the formation of cyclic boronates is illustrated in **Figure 1**. In order for the reaction to proceed, the boronate must be in the reactive $-B(OH)_3^-$ form, which is readily obtained by equilibrating the phase with an alkaline buffer. When the sample is applied, the covalent bond forms only with analytes possessing suitable functional groups, e.g. vicinal diols, found in sugars or catechols. Other functional groups which can form covalent bonds with boronic acids include α-hydroxy acids, aromatic *O*-hydroxyacids and amides, 1,3-dihydroxy-, diketo-, triketo- and aminoalcohol-containing compounds. With formation of the covalent bond, the analyte is strongly bound to the phase, which may then be washed with strongly eluotropic solvents to remove nonspecifically retained contaminants (an alkaline pH must be maintained). Analytes can then be recovered using an acidic buffer/solvent, which hydrolyses the covalent bonds to liberate retained compounds and return the PBA to the $-B(OH)_2$ form.

As well as these specific interactions with PBA, a number of nonspecific interactions can also occur with residual silanols, the aminopropyl group via which the PBA is attached to the silica, and the phenyl ring itself, which offers the opportunity for π–π interactions. In addition, the boronic acid can act as a hydrogen bond donor, cations can also bind to the boronic acid, and there is the potential for the formation of charge-transfer complexes with unprotonated amines. All of these interactions may happen when performing an extraction, and care must be taken to ensure that the extraction scheme is optimized to the required boronate retention mechanism if the maximum specificity is to be obtained.

Buffer Selection

The first criterion to ensure a good extraction efficiency is to select a buffer for extraction on to