Separation Technology R&D Needs for Hydrogen Production in the Chemical and Petrochemical



Industries

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Separation Technology R&D Needs for Hydrogen Production in the Chemical and Petrochemical Industries

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Hydrogen Production: Chemical and Petrochemical Industries

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Foreword

The Vision2020 Technology Partnership, an industry-led organization for accelerated innovation and technology development, formed a committee to identify research and development needs for separation technology to drive equilibrium processes for the Chemical and Petrochemical Industry. This committee was established in June 2004 and chartered with the responsibility to define the drivers and R&D requirements of the chemical and petrochemical industries for equilibrium separations. Several chemical production processes were selected for review and two topics, hydrogen and carbon dioxide separations, were developed into full studies. This report, the first of two, is directed to commercial, industrial hydrogen production. The report on CO_2 equilibrium separations processes is expected to be published in the future.

Executive Summary

The goal of this study is to identify research and development needs for separation technology to drive equilibrium processes for the Chemical and Petrochemical Industry. The growing requirements for hydrogen in chemical manufacturing, petroleum refining and the new emerging clean energy concepts will place greater demands on sourcing, production capacity and supplies.

A review was conducted of the current state of the art and emerging literature concepts on both adsorption and membrane separation technology applicable to H_2 production. Recommendations for future R&D needs are discussed. An emphasis is placed on flow sheet design modification with adsorption or membrane units being added to existing plants for near term impact, and on new designs for new adsorption or membrane reactor/separators for a longer term sustainable impact.

About 41 MM tons/yr of H_2 is produced worldwide, with 80% of it being produced from natural gas by steam reforming, partial oxidation or autothermal reforming. H_2 is used commercially to produce CO, syngas, ammonia, methanol and higher alcohols, urea and hydrochloric acid. It is also used in Fischer Tropsch reactions, as a reducing agent (metallurgy), and to upgrade petroleum products and oils (hydrogenation). Current industrial practices are summarized in terms of the key reforming and shift reactions and reactor conditions, with the four most widely used separations techniques --absorption, adsorption, membrane and cryogenic. As all of these reactions are reversible, the H_2 or CO or syngas production from natural gas and hydrocarbon feedstocks is equilibrium limited, and consequently provides opportunities for process improvement.

It has been estimated that the reforming of natural gas to produce H_2 consumes about 31,800 Btu/lb of H_2 produced. It is further estimated that 450 trillion Btu/yr could be saved with a 20% improvement in just the H_2 separation and purification train after the H_2 reformer. This potential for energy savings is a major driver for future R&D and for implementation of adsorption or membrane separation technology.

Recommendations for future separations R&D are set forth in 5 areas – adsorbent materials development (both long term and short term), membrane development (both long term and short term) and plant design modification with additional separations systems. Targets for these areas are listed below (See the full report for detailed performance requirements).

Adsorbent Development – short term goals:

- High capacity CO₂ and CO selective adsorbents, and
- New pressure swing adsorption (PSA) cycle designs.

Membrane Development – short term goals:

- High temperature membranes that are selective only to O₂, or H₂, or CO₂,
- Low temperature O_2 selective membranes with permeance > 100 x 10⁻⁸ mole/s/m²/Pa,
- Stable, functional hydrogen permselective dense membrane based on Pd,
- Hydrogen permselective membranes based on Knudsen transport, with a selectivity of \sim

100 or more, and are stable to water vapor,

- CO₂ permselective polymer or inorganic membranes with selectivity of > 15-20,
- Develop high temperature membranes that are selective to H_2 , > 15-20, and
- High temperature stable membranes with selectivity to CO or H₂O.

Adsorbent Development - longer term goals:

- Develop advanced structured adsorbent materials to include materials development for rapid cycle PSA,
- Develop a PSA hybrid separation system,
- CO₂ removal via temperature swing adsorption (TSA),
- Improved hydrogen separations with sorption enhanced reaction processes,
- CO selective adsorbents, and
- Improved hydrogen selective adsorbents.

Membrane Development - longer term goals:

- In general, next generation membrane materials,
- Develop high-integrity, H₂ selective mixed matrix membranes,
- Develop organic-inorganic hybrid membrane materials; and
- Improved hydrogen selective inorganic microporous membrane materials to include:
 - Molecular transport hydrogen selective membranes,
 - o Atomic transport/dense metallic membranes,
 - Ion transport membranes, and
 - Improved polymeric membrane materials.

Current Commercial Practices

Overview of Hydrogen Production and Uses

Worldwide, industrial hydrogen is currently produced at over 41 MM tons/yr with 80% of production coming from the steam reforming of natural gas [1]. Globally, hydrogen produced "on-purpose", i.e., not as part of a petrochemical processing, is about 16 trillion scf/year; and refinery by-product hydrogen is about 14 trillion scf/yr, or about half the global total. The growing demand for hydrogen in chemical manufacturing, petroleum refining, and the new emerging clean energy concepts will place greater demands on supply and will most certainly impact pricing.

This Vision2020 sponsored study was undertaken to provide research and development guidance for the planning and development of new separation technologies to drive the unfavorable equilibrium thermodynamics for improved H_2 production. A starting point for this assessment is to define current technology and operating conditions. Following this introductory information, specific recommendations are set forth to provide the performance improvements needed to enhance efficiencies and achieve energy savings.

Hydrogen is used commercially in petroleum and chemical processing for hydrodesulfurization, and the production of syngas, ammonia, methanol, higher alcohols, urea and hydrochloric acid [2-6]. It is also used in Fischer Tropsch reactions, as a reducing agent (metallurgy), and to upgrade petroleum products and oils (hydrogenation, hydrocracking) [2-6]. Due to increased demand, H_2 is increasingly being produced from natural gas by steam reforming, partial oxidation and autothermal reforming.

The reforming of natural gas to produce H_2 consumes about 31,800 Btu/lb of H_2 produced at 331 psig based on 35.5 MM tons/yr production [7]. It is estimated that 450 trillion Btu/yr could be saved with a 20% improvement in just the H_2 separation and purification train after the hydrogen reformer [7]. Clearly, improved separation technology can offer substantial dividends [8].

Reforming reactions and typical operating conditions are summarized below. The four most widely used separations methods, i.e., absorption, adsorption, membrane and cryogenic, are also summarized. These chemical reactions are reversible, and the hydrogen productivity is equilibrium limited. It is the intent of this study to focus on the use of adsorption and membrane processes to drive these equilibrium limited production technologies.

H₂ Production

Figure 1.1a displays a flow sheet of a typical, commercial large-scale hydrogen or syngas production plant incorporating a pre-reformer, a steam reformer, high and or low temperature water gas shift reactors, and H_2 purification units such as 1) absorption with methanation, 2) pressure swing adsorption, or 3) membrane with methanation. Figure 1.1b displays a flow sheet of a typical, commercial ammonia production plant incorporating a steam reformer and possibly a secondary reformer or a partial oxidation reactor, high and or low temperature water gas shift reactors, and a H_2 purification unit such as absorption with methanation. Figure 1.1c displays a

flow sheet of a typical, commercial syngas production plant incorporating a pre-reformer, a steam reformer and possibly a secondary reformer or an autothermal reformer, and absorption based H_2 purification unit [1-6,9]. The symbol F in these figures defines the flow rate in arbitrary units with the feed flow rate being 1.0. The numbers to the right of the molecular symbols in these figures are stream composition numbers in mol or vol%.

Tables 1.1 to 1.4 provide a technology summary for commercial hydrogen production. These tables include the types of hydrogen, ammonia, methanol and syngas plants in operation. They also provide the licensor, production capacity and the numbers of units operating worldwide [3,4].

The feedstock to a **steam methane reformer (SMR)** is first desulfurized to reduce the sulfur levels to below 2 ppmv to protect the SMR catalyst. This desulfurization step is accomplished with a Co-Mo or zinc oxide hydrogenation catalyst, employed at 360 to 400° C, to convert the sulfur into H₂S, which is later removed from the gas via a downstream absorption or adsorption step.

Absorption is the most widely practiced separation technique for removing H_2S from natural gas. The three absorption processes most commonly utilized are the monoethanolamine (MEAprocess, the methyldiethanolamine (MDEA)-process, and the Purisol-process. However, because of the relatively low operating temperatures of these absorption processes, their use in desulfurization is limited to gas streams containing primarily light hydrocarbons.

The use of adsorption for H₂S removal is a more novel approach. Activated carbon (via PSA) and ZnO have been particularly successful. In the latter case, a ZnO cartridge is used to trap the H₂S (ZnO + H₂S \rightarrow ZnS + H₂O) at about 350-450 °C. Because of the high operating temperature, this approach offers the advantage of being able to process gases containing heavier hydrocarbons. Once the ZnO becomes saturated, air at 700 °C is used to regenerate the cartridge to form SO₂, which is subsequently removed via absorption.

After desulfurization, steam methane reforming is then carried out at 780 to 900°C and 25 to 35 atm using an alkali-promoted Ni catalyst supported on alumina. The reaction is:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 (endothermic: $\Delta H = 227 \text{ kJ/mol}$) (1)

This reaction is highly endothermic and hence requires a substantial energy input. However, SMR produces the greatest number of hydrogen molecules per molecule of methane and some of the needed energy can be obtained from combustion of recycled product gases, CO and H_2 , and unconverted CH_4 .

In some cases, a pre-reformer is used, as shown in Figures 1.1a and 1.1c. The pre-reformer is basically a reformer unit located up stream of the main (or primary) reformer that operates at a much lower temperature (400-500 $^{\circ}$ C) to convert mostly ethane and heavier hydrocarbons into methane. As an ancillary bonus, it also reforms some of the methane into CO and H₂.

In other cases, a secondary reformer is used, as shown in Figures 1.1b and 1.1c. The secondary reformer is basically a partial oxidation (POX) unit located downstream of the primary reformer to achieve maximum methane conversion. It uses oxygen (or air in the case of ammonia production) and operates at about 1000 °C.

The **partial oxidation (POX) of methane** can be carried out with or without a catalyst. When a catalyst is not used the flame temperature ranges between 1300 and 1400°C at a pressure of 55 to 80 atm. The reactions that occur include:

$CH_4 + O_2 \rightarrow CO_2 + 2H_2$	(exothermic and rapid: $\Delta H = -318 \text{ kJ/mol}$)	(2)
$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	(exothermic and rapid: $\Delta H = -36 \text{ kJ/mol}$)	(3)
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	(exothermic and rapid: $\Delta H = -802 \text{ kJ/mol}$)	(4)
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	(endothermic and slow: $\Delta H = 247 \text{ kJ/mol}$)	(5)
$CH_4 + H_2O \rightarrow CO + 3H_2$	(endothermic and slow: $\Delta H = 227 \text{ kJ/mol}$)	(6)

with the resulting H to CO ratio being 1.6 to 1.8. The oxygen to carbon ratio is carefully controlled in this process to minimize soot formation, while maximizing H₂ production. This process takes advantage of the heat given off by reactions (2), (3), and (4). These reactions use a small fraction of O₂ (usually pure) in the feed to initiate and drive this process. Reaction (5) is environmentally attractive as it uses CO₂ as the reactant. It produces, however, the smallest number of hydrogen molecules per molecule of methane. It is affected by the reverse water gas shift (RWGS) reaction, consuming product H₂ with reactant CO₂ according to:

$$CO_2 + H_2 \rightarrow CO + H_2O$$
 (endothermic: $\Delta H_{298}^o = 41 \text{ kJ/mol}$) (7)

For the catalytic partial oxidation process, the flame temperature is lower, i.e., between 780 and 900°C, and the pressure is reduced to between 25 and 35 atm. The catalyst is generally similar to or the same as the SMR catalyst, being comprised of supported nickel. In this case, the resulting H to CO ratio is 1.8 to 3.0.

The POX process does not require a desulfurization step (an economic advantage). However, POX commonly employs an oxygen plant to provide enriched or pure O_2 to avoid processing N_2 downstream (an economic disadvantage). In some cases, such as ammonia production, some N_2 is desirable, as it is needed in the syngas to provide the correct composition to the ammonia production unit.

When steam and oxygen (possibly as air) are mixed with methane and fed to a reactor, the process is generally referred to as **autothermal reforming (ATR).** In practical terms, ATR utilizes the highly exothermic combustion process of POX through reaction (4) to supply the energy needed for the endothermic SMR reactions in the same reactor. Combustion takes place in the first zone of the reactor, with the product gases carrying the energy needed to initiate and

sustain the SMR reactions in the second zone. ATR not only has the same control issues associated with the ratio of carbon to oxygen as POX does, but it also has to consider the effects of this ratio on conversion in the SMR zone.

SMR is more common for industrial hydrogen production and maintains an economic edge over ATR and POX, except for very large installations where ATR becomes more cost effective. A key factor is the air separation unit for POX and ATR. However, POX, and to a lesser extent ATR, are more effective for handling diverse hydrocarbon feedstocks, such as naphthas. Natural gas is still the preferred feedstock at today's cost of methane relative to crude oil [1]. As can be seen from the data in Tables 1.1 to 1.4, typical hydrogen plants use steam reforming (SMR), whereas methanol production plants tend to use ATR, and syngas production plants use either ATR or POX, with ammonia production plants using steam reforming or ATR. Typical flow sheets are provided in Figures 1.1a, 1.1b and 1.1c.

Depending on the application, a water gas shift reactor (WGS) may be needed downstream of the reformer or partial oxidation unit to decrease the CO concentration in the reformer and to improve H_2 production and purity (refer to Figures 1.1a and 1.1b). For example, a typical equilibrium limited SMR converts from 70 to 80% of the CH₄ with a product composition given in Figure 1.1a [10, 11]. Note the high concentration of CO at around 8 vol%. After the WGS reactors, the CO concentration is reduced to around 0.5 vol%. Both high temperature (HT) and low temperature (LT) WGS reactions are commercially practiced. The HT WGS reaction uses iron/chrome oxide catalyst and operates in the range of 350 to 500 °C. The LT WGS reaction proceeds as:

$$CO + H_2O \rightarrow CO_2 + H_2$$
 (exothermic: $\Delta H_{298}^o = -41 \text{ kJ/mol}$) (8)

In some cases the LT WGS can be eliminated. For example, both HT and LT WGS reactors are used in the reformer/wet scrubbing process, whereas only the HT WGS reaction is used in the reformer/PSA process (see below) [5].

H₂ Purification

The separation technology used in H₂ production depends on the application, the desired H₂ purity and the downstream impact of CO or N₂. Four different H₂ purification technologies are widely practiced in industry; these include 1) absorption, both chemical and physical, 2) adsorption, 3) membranes and 4) cryogenic processes [9]. Prior to 1980 [5], the CH₄ reforming step was followed by both a high and low temperature shift process to convert CO to H₂. Wet scrubbing, with a weak base such as potassium carbonate or an amine, ethanolamine, was then used to remove CO₂. Typical feed compositions to the wet scrubber are provided in Figure 1.1. The remaining CO and CO₂ are sent to a methanation reactor (the opposite of reforming) to reduce the carbon oxides to around 50 ppmv. This wet scrubbing process, which is still in operation today, produces a product stream containing 95-97 vol% H₂, 2-4 vol% CH₄ and 0-2 vol% N₂. In general, wet scrubbing is commonly used in the production of ammonia, as high purity H₂ is not needed (Table 1.4).

In the early 1980s, new hydrogen plants were being built with PSA units as the main H_2 purification process. This eliminated the CO₂ scrubber, the low temperature CO shift reactor and the methanation reactor. PSA is able to produce very pure H₂ by removing relatively high concentrations of CO and CO₂ [12,13]. A typical feed composition to the PSA unit is provided in Figure 1.1a. The PSA unit offers advantages of improved product purity (99-99.99 vol% H₂, 100 ppmv CH₄, 10-50 ppmv carbon oxides, and 0.1-1.0 vol% N₂) with capital and operating costs comparable to those for wet scrubbing. Modern PSA plants for H₂ purification generally utilize layered beds containing 3 to 4 adsorbents (silica gel/alumina for water, activated carbon for CO₂ and 5A zeolite for CH₄, CO and N₂ removal). Depending on the production volume requirements, anywhere from four to sixteen columns all operate in tandem. A typical 10-bed PSA unit can produce 120 MMscfd H₂ at high purity and a recovery of 90%. The PSA unit is operated at ambient temperature with a feed pressure ranging between 20 and 60 atm. The hydrogen recovery depends on the desired purity, but ranges between 60 and 90%, with the tail gas (i.e., the desorbed gas containing H₂O, N₂, CO₂, CH₄, CO and H₂) generally being used as fuel for the reformer. In general, PSA is used in the production of high purity H₂, with purities in some cases exceeding 99.9999+ vol%. A list of companies with PSA H₂ plants in operation and their corresponding capacities is provided in Tables 1.1 and 1.2.

Membrane processes, such as the Polysep membrane systems developed by UOP and the PRISM membrane systems developed by Monsanto, and now sold by Air Products and Chemicals, Inc., [3] recover H₂ from various refinery, petrochemical, and chemical process streams. Both are based on polymeric asymmetric membrane materials composed of a single polymer or layers of at least two different polymers, with the active polymer layer being a polyimide. The Prism system is based on a hollow fiber design and Polysep is spiral wound sheet type contactors. Both are used to recover H₂ from refinery streams at purities ranging from 70 to 99 vol% and recoveries ranging from 70 to 95%. Figure 1.1a depicts one example where a membrane separation unit is used commercially in a hydrogen production plant. Relatively pure H₂ containing a very low concentration of CO₂ leaves this unit in the low pressure permeate stream. This stream can be sent to a methanator for CO₂ removal and further purification. The high pressure retentate stream, consisting of H₂ and CO₂ with low concentrations of CO and CH₄, can be used as fuel. Table 1.1 provides some information on the number of membrane plants and their H₂ production capacities.

Standard condensation processes are used to remove excess water in hydrogen production, (Figures 1.1a, 1.1b and 1.1c). Cryogenic separation processes are generally used in the production of high purity CO and moderately pure H_2 from syngas. This process is also used to adjust the composition of the syngas for a chemical feedstock unit, especially in the production of ammonia [14]. Cryogenic systems are applied to recover high purity H_2 from refinery off gas streams containing C_2 + liquid products. A list of companies that utilize cryogenic H_2 purification is provided Table 1.4.

A detailed understanding of these commercial H_2 production processes provides an essential basis for guiding future R&D to achieve improvements and breakthroughs in adsorption and membrane technology. The goal is to achieve energy savings and improved process performance and economics. To set forth recommendations for future R&D on hydrogen production, key factors must be considered: 1) The large scale of industrial production, 2) materials requirements, 3) economic goals and drivers and 4) purity demands. Emerging literature concepts in adsorption and membrane technology for H_2 production and purification are reviewed and then recommendations are set forth for future R&D. It is anticipated that this review involving 25 industrial scientists active in the filed and seven leading academic scientists will provide valuable guidance to funding agencies, and useful suggestions for industrial and academic researchers, to facilitate the development of applicable, new technologies.

Emerging Literature Concepts

For this review, a focus has been placed on emerging concepts in the separation sciences to overcome the equilibrium limitations for H_2 production and purification. The potential for novel adsorbents and membranes, and associated processes, particularly for high temperature operations are outlined. There are two major thrusts to this approach: 1) To use new adsorption and or membrane technologies to drive reversible reactions in the reformer, shift or partial oxidation reactors, and 2) to facilitate the purification of H_2 downstream from the reactors. Many opportunities are identified, including hybrid systems that can afford significant improvement.

Adsorption

The emerging literature concepts on the use of adsorbents and adsorption processes in the production of H_2 by SMR, POX and ATR have been rather focused since the commercial implementation of PSA for downstream H_2 purification about 20 years ago. The ongoing research includes 1) PSA process refinements, 2) sorption enhanced reaction processes (SERP) or periodic adsorptive separating reactors, and 3) selective adsorbents for CO_2 and CO. These studies have the potential for both near term and longer term impact on the adsorptive applications for H_2 production. Adsorbent/membrane hybrid technologies are also being explored for sequential operation. A brief summary of each of these emerging areas is provided below.

PSA Process Refinements

The major breakthrough in PSA technology for large-scale H_2 purification came in the early 1970's with the development of a 4-bed, multi-layer PSA process (discussed above). Since that time modifications have added additional beds, typically 7 to 10 beds [15], as many as 16 beds [16], and sometimes tanks for storing intermediate process streams between cycle stages. Along with more beds and tanks came more complex cycle sequencing to achieve higher throughputs with the same or even less volume of adsorbent distributed in the additional beds. Each bed undergoes several adsorption and regeneration cycle steps including 1) pressurization, 2) high pressure feed, 3) co-current depressurization, 4) counter-current depressurization, 5) counter-current purge, and 6) several equalization (pressurization/depressurization) steps between two beds. Potential for improvements can be realized by further refinement of these complex cycle steps and their sequencing to create a separation process.

For H_2 PSA technology, as with many other commercial processes, what initially appeared to be a rather trivial evolutionary process improvement, has had the impact of a revolution. New PSA cycling strategies have had this effect. As an example, Whysall and Wagermans of UOP [16] recently demonstrated that the duration of the purge step does not have to be equal to or less than the duration of the adsorption step, and by extending the purge step, the production capacity of a PSA H₂ plant, for the first time, could exceed 110 Nm³/hr using 16 beds. Baksh et al. of Praxair Technology, Inc. [17,18] decreased the number of PSA beds with the judicious use of storage tanks to collect and reuse gas during cycle steps, and to increase H₂ production per unit adsorbent. Baksh et al. [19] also show that the PSA process performance can be improved significantly by first removing N₂ from the feed stream using modified (via cation exchange) Xtype zeolite adsorbents, which also advantageously remove CO₂. Xu et al. of Air Products and Chemicals, Inc. [20] modified the pressure equalization steps by using four steps with just six beds, and decreasing the cycle time for pressure equalization between beds [21]. Chen et al. of The BOC Group, Inc. [22,23] show how to recover CO from a typical SMR plant using a unique two-phase PSA cycle sequence, by using a CO selective adsorbent impregnated with Cu(I) for complexation with CO. Kapoor et al., also of The BOC Group, Inc. [24], show how to augment an existing H₂ plant to produce CO from syngas more effectively by using an additional PSA unit containing a CO selective adsorbent.

Sircar and Golden [25] describe several other novel, rather complex, approaches to PSA cycle sequencing not only for H_2 purification, but also for simultaneous H_2 and CO₂ purification. The latter PSA cycle involves two interconnected cascades of PSA beds each operating with their own unique cycle sequence and number of beds. It is clear that there are numerous ways to arrange and operate PSA processes. Many improved novel PSA cycle sequences are anticipated for use in H_2 production plants, based on continued industrial and academic research.

Another way to improve the performance of a PSA process is to decrease the cycle time, which allows more gas to be processed using less adsorbent. This is referred to as rapid cycle PSA. For example, QuestAir has recently announced improved H_2 purification technology with a rapid cycle PSA unit with a rotary valve. This technology is planned for installation in the largest liquid H_2 plant in Asia to be fabricated in Japan. Rapid cycle PSA is not a new concept. However, the process required major innovations in process design for handling the gas streams before commercialization became feasible. This innovation has been reported in a series of patents by Keefer et al. of QuestAir Technologies Inc. [26-28] which describe the rotary valve and multi-bed cycle sequencing approaches.

Adsorbent attrition and intraparticle mass transfer effects still limit how rapid the cycle sequencing can be carried out. This problem has been partly alleviated with the recent development of novel structured adsorbents, incorporating very small commercially available adsorbent particles or crystals, like activated carbons and zeolites, in a support material like a sheet of paper. In this way, the effects of mass transfer and adsorbent attrition are minimized. Structured adsorbent materials are described in the recent patents by Golden et al of Air Products and Chemicals, Inc. [29-31], and by Keefer et al [32]. A second generation, ultra rapid cycle PSA H₂ purification system was developed recently by researchers at QuestAir. In this system a rotary adsorbent bed concept has supplanted the rotary valve concept, with the rotary adsorbent bed being comprised of multiple beds within one cylindrical adsorber unit [33]. This unique configuration has resulted in a very compact PSA unit that can be operated at very short cycle times and thus very high H₂ production rates. Further improvements in this technology will require the continued development of new structured, multilayered adsorbents, with each layer containing an adsorbent that is selective to one or more of the gases to be separated.

Over the past decade, academic researchers have also focused on the development, understanding and optimization of new PSA cycle configurations for H_2 purification. Zhou et al. [34] recently explored novel PSA cycle configurations for H_2 purification to decrease the required feed pressure and minimize the number of beds by using storage tanks. Biegler et al.

[35] are developing important optimization tools for multi-bed PSA processes, especially for H_2 purification, that when perfected should allow for significant improvements in the PSA process performance by simple process tuning. Finally, Warmuzinski et al. [36,37], and Lee et al. [38-41] are attempting to design a multi-layered adsorbent bed through mathematical simulation and bench scale experimentation. The complexity between the different cycle steps in a H_2 purification PSA unit has recently been reported by Waldron and Sircar [42]. Continuing R&D in this important area is recommended.

Sorption Enhanced Reaction (Periodic Adsorptive Separating Reactors)

Conducting reaction and adsorptive separation in a single fixed bed reactor configuration dates back at least to 1987, beginning with the work of Kadlec et al. [43-45]. The general idea is to use the adsorbent to selectively remove one or more of the products formed from an equilibrium limited reaction to shift the equilibrium in favor of increased conversion. The adsorbent is then regenerated with a pressure or temperature swing. Improved adsorbents with greater selectivity, larger working capacity, more rapid adsorption and desorption kinetics, reduced sensitivity to moisture and other poisons are required for this approach to become of commercial interest. Finally, all these characteristics are required at elevated temperatures that are optimum for the reaction. These higher temperatures are typical of the regeneration conditions for most commercial adsorbents like zeolites, activated carbons, activated aluminas or silica gels. Hence, for many applications operation at the high reactor temperatures requires the development of new adsorbents.

A team at Air Products and Chemicals, Inc. has developed Adsorptive Separating Reactors using what they refer to as a sorption enhanced reaction process (SERP). SERP is a fixed bed process with the reactor containing a mixture of a conventional catalyst and a high temperature adsorbent that is selective to one of the products produced during the catalytic reaction. For an equilibrium limited reaction, the adsorbent shifts the equilibrium in favor of higher conversion through Le Chatlier's principal. When the adsorbent becomes saturated with the product, a simple pressure swing in the bed can be used to regenerate it. In a series of patents [11,46-49] and three publications [50-52], this group shows a redesign of the methane reforming operation. For this approach a high temperature CO₂ selective adsorbent is mixed with a typical reforming catalyst to conduct the SMR and WGS reactions in one unit and at lower temperatures than used in SMR. Reforming can be practiced at these lower temperatures because of the in situ removal of CO₂ [46,49]. Medium purity H₂ production (~ 95%) was achieved by conducting this SERP process in a WGS reactor using a shift catalyst and at least two, CO₂ selective adsorbents. The feed for this unit was obtained from a conventional SMR [53].

For CO production, the SERP concept was modified by using a conventional SMR with a CO-Vacuum Swing Adsorption (VSA) unit containing a CO-selective adsorbent, with the tail gas being sent to a reverse WGS (RWGS) Sorption Enhanced Reaction (SER) unit [11,47]. This RWGS SER unit was used to convert CO₂ and H₂ into more CO and H₂O using a typical shift catalyst mixed with an H₂O-selective adsorbent to remove H₂O from the product gas, again to shift the equilibrium in favor of CO production. The CO stream was then sent to the CO-VSA for purification, and some fuel was produced. By integrating a CO₂ TSA unit with commercially available CO₂ selective adsorbents such as 5A and 13X zeolites and aluminas, and a RWGS SER unit, the production of high purity CO was improved [48].

In a more general patent, three uses of the SERP concept are discussed [54]. In the first case SMR is driven using CO_2 and or CO selective adsorbents. In the second case, methane reforming with CO_2 can be revamped by using CO or H₂ selective adsorbents. In the third case, H₂O selective adsorbents are used in the production of CO using a RWGS reactor. An emphasis is placed on the judicious use of these different adsorptive reactors to optimize the production of H₂, CO or syngas from the reforming of methane. There appears to be significant potential for new adsorbents, and development of additional applications of the SERP concept.

The success of the SERP relied on CO_2 , H_2O and even H_2 selective adsorbents. A CO selective adsorbent such as Cu(I) or Ag(I) on silica-alumina was also utilized in a VSA unit for producing a pure CO stream as the heavy product. The preferred CO_2 adsorbents include: K-promoted hydrotalcite (HTlc), modified double layer hydroxides, spinels and modified spinels, with metal oxides and mixed metal oxides of Mg, Mn, La and Ca, and clay minerals such as sepiolite and dolomite [46,48,49,53,54]. The preferred H₂O adsorbents include commercially available A, X and Y zeolites, mordenites and aluminas and silica gel [11,47,54]. The preferred H₂ adsorbents include metal hydrides such as Pd, PdAg, MgNi, FeTi and LaNi [54]. The preferred CO adsorbents include Cu(I) or Ag(I) on silica-alumina [54]. Examples of novel, yet relevant, uses of metal hydrides for H₂ purification and separation include: 1) the purification of H₂ by PSA [55]; 2) a PSA/TSA process for the methanation of carbon oxides using fluorinated metal hydrides [56]; and 3) analysis of a novel PSA cycle for H₂ purification and concentration that relies on the shape of the metal hydride H₂ adsorption isotherm to be unfavorable (i.e., an inverted Langmuir isotherm) [57]. Clearly, a wide range of commercially available and developmental adsorbent materials can be used within the confines of the SERP concept.

Harrison et al. [58-60] have been researching the SERP for the steam reforming of methane in a single unit using a TSA cycle to remove CO_2 reversibly from the reaction product gas with CaO. Rodrigues et al. [61-66], and also Alpay et al. [67, 68], have been studying the performance of the SERP for the steam reforming of methane (SMR) in a single unit using a PSA cycle to remove CO_2 reversibly from the reaction product gas using a K-promoted HTlc. The continued experimental validation of modeling analyses, coupled with the study of various PSA cycle sequences, should contribute to the understanding of this type of adsorptive reactor system, and to optimizing its performance.

It is clear that these SERPs allow SMR, WGS and or RWGS reactors to operate at reduced temperatures or pressures, and can reduce or eliminate downstream separation and purification units, while producing high purity H_2 , CO, or syngas. Although the SERP concept seems to work well, industrial acceptance of this technology has been limited. Again, further implementation of this SERP would be fostered with the development of improved adsorbents, especially high temperature adsorbents.

Selective Adsorbents

There are many opportunities other than SERP for new selective adsorbents in the H_2 production plant. The areas with the most active research involve: 1) CO₂ selective adsorbents at ambient,

and especially elevated, temperatures for selective CO_2 removal from reaction products, and 2) CO selective adsorbents to remove CO from streams containing CO_2 . Other adsorbents that may contribute to improved processes include 1) commercially available H_2O selective adsorbents such as A, X and Y type zeolites, mordenites, aluminas and silica gels, and 2) H_2 selective adsorbents such as metal hydrides, e.g. Pd, PdAg, MgNi, FeTi and LaNi.

It is worth pointing out that the H_2 capacity of literally thousands of metal hydrides and their alloys have been studied for years. Typical capacities range from A) 1 to 2 wt% H_2 for the LaNi and FeTi hydrides at ambient temperatures and pressures of around 100 to 200 psia, to B) MgH₂ exhibiting the highest known H_2 capacity of around 7 wt% at 200 °C and similar pressures [69,70]. However, most metal hydrides are O_2 and H_2O sensitive, and some are CO sensitive Thus, the development of improved and stabilized metal hydrides is recommended.

In the section below, only high temperature CO_2 selective adsorbent development and ambient temperature CO selective adsorbent development are considered. Other applications with commercially available adsorbents have a successful track record in industrial applications. Table 1.5 summarizes the typical capacities of commercial and developmental CO_2 and CO selective adsorbents.

A recent review on CO_2 absorbents, by Yong et al. [71], covered activated carbons, zeolites, metal oxides and hydrotalcite compounds (HTlcs) for reversible adsorption. The overall conclusion is that activated carbons and zeolites are superior to metal oxides and HTlcs for ambient temperature applications, and yet for high temperature applications metal oxides and HTlcs are preferred over activated carbons and zeolites. Typical activated carbons exhibit 1.5 to 2.0 mol/kg CO_2 adsorption at 25 °C and 500 torr, which decreases to 0.1 to 0.2 mol/kg at 250 to 300 °C and 500 torr. Similarly, 5A zeolite exhibits ~ 3.0 mol/kg at 25 °C and 500 torr, and 0.2 mol/kg at 250 °C and 500 torr. Clearly, the capacities of these materials would be less than 0.1 mol/kg at the temperatures associated with the SMR, WGS and RWGS reactive adsorbers.

For selective adsorbents, the K-promoted hydrotalcite (HTlc) materials exhibit a high and pressure-reversible CO₂ capacity at temperatures compatible with SMR and WGS and RWGS applications [72,73]. Mayorga et al. [73] at Air Products and Chemicals report synthesis procedures and operational capacities for both HTlcs and double layer hydroxides. Rodriques et al. [74-76] have characterized HTlcs for CO₂ adsorption at ambient and elevated temperatures, as has Alpay et al. [67,68]. Overall, the reversible CO₂ capacities typically range between 0.4 and 0.7 mol/kg at 300 and 400 °C and 200 and 700 torr, even in the presence of steam. This performance is highly dependent on the synthesis and pretreatment conditions. Double layer hydroxides exhibit even higher reversible capacities in the presence of steam, typically of around 1.5 mol/kg at 375 °C and 230 torr [73]. These adsorbents are attractive not only for sorption enhanced reaction processes (SERPs), but also for high temperature PSA processes, as shown recently by Ritter et al. [77].

Several teams are also exploring alumina as a high temperature and pressure-reversible CO_2 adsorbent for use in a PSA cycle [71,78]. The CO_2 capacity of aluminas undoped and doped with metal oxides and carbonates ranges from 0.06 (undoped) to 0.52 (doped with 9 wt% Li₂O) mol/kg at 400 °C and 500 Torr [78], which is similar to that reported by Yong et al. [71] for

commercially available basic aluminas, (~ 0.3 mol/kg at 300 °C and 500 torr).

Lithium zirconate and CaO can function as high-temperature, selective CO_2 adsorbents with temperature-reversibility. Lin et al. are exploring the zirconates [79-81], as is Nair [82] in Japan. Typical CO_2 adsorption capacities are high at 3.4 to 4.5 mol/kg at 500 °C and 760 torr, with reasonable regeneration rates exhibited at 780 °C that improve with CO_2 free purge gas [80]. The sensitivity of these materials to H₂O vapor has not been reported.

CaO adsorbents are being investigating by Fan [83-85], Harrison [56-58], Kuramoto [86] in Japan, and Abanades [87] in Spain. These materials are also showing high CO₂ capacities at high temperatures with reasonable regeneration rates. For example, typical reversible CO₂ capacities range between 4 to 8 mol/kg at 500 °C and 150 torr, with regeneration carried out at 900 °C in N₂ [86]. A similarly high CO₂ capacity of 7 mol/kg resulted for a CaO exposed to 76 torr of CO₂ and cycled over 50 times at 700 °C using N₂ for purge. This is a large reversible CO₂ capacity. These CaO adsorbents are very sensitive to sulfur but the sensitivity to H₂O vapor has not been reported [83]. The operating temperature range of this material may be too high for most SMR, WGS and RWGS reactors, however.

 π -complexation adsorbents for CO have been known since 1977, based on the patent literature [88, 89]. These adsorbents generally consist of a high surface area support (i.e., silica, alumina or zeolite) that contains a monolayer of a transition metal salt such as Cu(I) or Ag(I). Variations of these initial CO-selective materials are under development for selective CO removal from gas streams that contain CO₂. Peng et al. at Air Products and Chemicals [90-92] developed a supported Cu(CO)Cl complex for CO adsorption. Lin et al. [93] have also developed a CO adsorbent utilizing supported CuCl on mesoporous alumina via a sol-gel process. Similarly, Hirai et al. [94,95] have been developing CO selective adsorbents based on complexing Cu(I) halide, such as Cu(I)-ethanediamine supported on silica gel.

The capacity of these Cu(I) π -complexation adsorbents for CO is reported as 0.8 and 1.2 mol/kg at 25 to 30 °C and 760 torr, with a reasonable working capacity of 1.2 mol/kg over 76 to 760 torr at 30 °C [92]. A similar working capacity of 0.8 mol/kg between 0.6 and 760 torr at 30 °C, has been reported by Hirai and coworkers [94,95]. Examples on the use of such CO-selective adsorbents can be found in the recent patents by the BOC Group Inc. [22,24] for production of high purity CO from typical SMR streams using VSA cycles.

In general, the use of these Cu(I) π -complexation adsorbents for CO is limited because the gas stream must first be dried to avoid poisoning of the active metal ion. Improved moisture sensitivity is needed. For the high temperature CO₂ selective adsorbents, improvements in capacity should be the focus of future work. Clearly, additional research and development on CO₂ and CO selective adsorbents are recommended for use at ambient and elevated temperatures, and in combination with PSA and TSA cycle development.

Membranes

Over 430 patents have been issued since 2000 for hydrogen selective membranes. Table 1.6 provides an accounting summary of the patent literature. Three classes of membranes dominate:

 O_2 permeable membranes, H_2 permeable membranes, and CO_2 permeable membranes. Table 1.7 provides a list of researchers working on O_2 selective membranes. Tables 1.8 to 1.13 provide lists of researchers working on H_2 selective membranes. Table 1.14 provides a list of researchers working on CO_2 selective membranes. Tables 1.15 and 1.16 provide detailed information about the selectivities and permeances of the membrane materials. A review of each of these emerging membrane areas is provided below.

Oxygen Permselective Membranes

The development of improved oxygen permselective membranes is essential for the commercial implementation of syngas production via partial oxidation (POX). POX is an exothermic process, which produces a lower H_2 /CO ratio (=2) than steam reforming, and provides advantages in syngas production, Fischer-Tropsch chemistry and other gas to liquid processes. POX processes can operate at lower temperatures and pressures providing energy savings. However, there are several issues that still make this technology unattractive.

A key issue for POX implementation is the use of pure O_2 , which adds the capital cost of a large O_2 plant. The use of air is generally avoided, because N_2 requires expensive downstream separation. This is not an issue for ammonia production plants where downstream N_2 separation is not required. Here air is the preferred oxidant. A second issue is the need for a uniform distribution of oxygen in catalytic reactors to avoid hot spots or deep oxidation that reduces efficiency. Oxygen selective membranes would help resolve both of these problems: air would be fed to the shell side of a catalytic membrane reactor so the oxidation (POX) can be conducted with greater control. Enriched nitrogen would be produced as a by-product.

Modified perovskites of the general formula ABO₃ are being developed as O₂ permselective membranes. For ABO₃, A is an alkali metal and B is commonly a lanthanide or a first row transition metal. Modifications $A_xA_{1-x}B_yB_{1-y}O_{3-\delta}$ using heterovalent elements A' and B' to create local defects and oxygen vacancies in the crystal structure, afford an enhanced material that is both an electronic and an ionic conductor – known as a mixed conductor. The presence of vacancies is represented by the generic letter δ , to indicate that the valence of $A_xA_{1-x} + B_yB_{1-y}$ becomes less than six. The O²⁻ anion conductivity is achieved by replacing cations A and B with acceptor cations A' or B' of lower charge. Thus, the perovskite structure affords fertile ground for modifications to tailor properties.

Modified perovskite membranes such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [96-98], $La_{0.2}Sr_{0.5}Fe_{0.2}Co_{0.8}O_x$ [99], $La_{0.3}Sr_{0.7}Co_{0.8}Ga_{0.2}O_{3-\delta}$ [100], $SrFe_{0.7}Al_{0.3}O_{3-\delta}$ [100], $SrCo_{0.5}FeO_x$ [97.99,101] have been investigated in tandem with a packed catalyst beds (normally Ni based). Catalytic membranes such as La_2NiO_4 [102], can eliminate the need for packed catalyst beds. It has been hypothesized [96] that part of the gas hydrocarbons fully combust at the reactor side surface of the perovskite membrane, and then the resulting CO_2 and H_2O reform the remaining hydrocarbons into H_2 and CO. Both $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [96-98] and $SrCo_{0.5}FeO_x$ [97,99,101] membranes have shown high throughput rates (i.e., > 15 and 5 ml(STP)/min/cm², respectively) of feed gas with high methane conversion and CO selectivities > 95%. These flux rates are approaching projected commercialization targets [103]. Although these results are promising, they have not been widely used commercially.

The high temperature stability, 850° C, of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃₋₈ membrane was demonstrated by Shao et al. [97] up to 1000 hr. At lower temperatures, however, a decrease in oxygen permeability was observed. Apparently, this deterioration is not caused by the H₂O or CO₂ as observed elsewhere [9], but by a decomposition and segregation of the perovskite into two phases. In general, methane conversions and CO selectivities larger than 95% can be achieved if the membrane thickness (0.2-1.5 mm), the feed gas residence time (< 0.1 s), and the temperature (750-950°C) are tuned such that the oxygen flux through the membrane ensures a CH₄/O₂ ratio of around 2. Attempts to achieve thinner membranes, longer residence times or higher temperatures diminish the CO selectivity. Changes in the opposite direction diminish methane conversion. A broad summary on these membranes is provided in the work of Thursfield and Metcalfe [104].

Hydrogen Permselective Membranes

Using H_2 selective membranes to enhance hydrocarbon conversions for hydrogen and syngas production is receiving considerable attention. Selective separation of hydrogen at high temperatures is appealing for hydrogen and ammonia production plants, as it lowers CO content, which subsequently reduces operational and capital costs for PSA units and methanators. These cost reductions are further maximized if H_2 selective membranes are incorporated into hybrid SMR, POX or WGS reactors. This approach will benefit industrial H_2 and ammonia production, as well as the manufacture of syngas for methanol production and Fischer Tropsch synthesis.

A hybrid H_2 -selective membrane reactor for steam reforming would enhance methane conversions at lower operational temperatures and cut steam consumption. A restricted amount of H_2O may also help reduce the production of CO_2 in the reformer, which is an important goal for gas to liquid syngas systems. Also, the ability to operate at lower temperatures in both syngas production units and WGS reactors would reduce coke formation, which is significantly suppressed at temperatures below 450 °C. Less coking would reduce the frequency of catalyst regeneration yielding less downtime, increased productivity.

Hydrogen selective membranes such as metallic and dense ceramics, as well as less selective porous inorganic and organic membranes, have been evaluated for commercial hydrogen separation. Because hydrogen is transported in dissociated form, both metallic and dense ceramic membranes can be 100% selective towards hydrogen. This particular ability allows for ultra pure hydrogen, containing little (< 1 ppm) or no carbon oxides. However, no porous (Knudsen based) membrane has been able to meet hydrogen separation purity and economic requirements. Despite this, porous membranes can still be useful to drive the reaction. More work is needed to explore practical opportunities in this area.

To overcome the relatively low permeance and high cost of dense and metallic membranes researchers are exploring the utility of high permeance, less costly and less selective inorganic porous membranes. Enhanced conversions can be realized with these membrane systems. Because of the relatively large content of carbon oxides (>> 100 ppm) and possibly methane, hydrogen streams produced through these membranes are limited to fuel use or are sent to a PSA train for further purification. Inorganic and organic, particularly glassy ($T_g > 100^{\circ}C$)

membranes, can also be used for hydrogen recovery from tail gas streams of PSA units, which normally operate at around room temperature. For improved purity, these H₂ streams can be sent back to a PSA unit for further processing.

Among hydrogen selective membranes, Pd membranes remain the most promising. These Pd based membranes have limitations that have restricted commercial use. Key limitations include embrittlement, thin films that are free of cracks or pinholes (hillocks), delamination, and sulfur poisoning. The current state of Pd membrane research is summarized by Collot [9], Uemiya [106], Kikuchi [106,107], Paglieri and Way [108] and Armor [109]. In addition, Rothenberger et al. [110] provides an extensive summary on the performance of Pd membranes.

Hydrogen selective membrane systems that can function with high flux are needed for the huge H_2 flows of a typical steam reformer or WGS reactor. The flux levels of state-of-the-art Pd membranes are inadequate and need improvement by a factor of 2-4 times to become economically attractive. As a result, current research is focused on the consistent preparation of thinner Pd films, i.e., ~ 5 µm, that can still afford high selectivity. This approach is designed to address flux and economic issues.

Thin Pd membranes deposited on a porous support, such as porous alumina or porous metal, are able to withstand operating conditions typical of H₂ manufacture processes. Typical Pd film deposition has been carried out via chemical vapor deposition (CVD) [106,107,111], electroless plating [106,107,112-117], a sol-gel method [118], spray pyrolysis, sputtering [119], and solvated metal atom deposition [111] on inert porous supports (Inconel, Stainless Steel or alumina). Among these techniques, electroless deposition currently appears to be the most reliable. For example, Pan et al. [112] prepared 2-3 µm thick films of Pd impregnated alumina that show stable permeances of 125 mol m⁻² s⁻¹ Pa⁻¹ with H₂/N₂ selectivities of 1000 for about 800 hr of continuous operation.

Membranes of palladium and its alloys are also promising for hybrid membrane reactor systems. Palladium membranes have been used in lab scale catalytic POX [117,120-122], SMR [106,107,111,114-117,123-129], CO₂ reforming [130,131], and WGS [132-137] reactors to drive methane conversions. Modeling analyses of these systems can be found in the works of Aasberg et al. [133], Barieri et al. [138], Marigliano et al. [125,126], Lin et al. [114,115], Roy et al. [127], Abashar [139] and Hou et al. [140]. In general, hybrid reactors based on Pd or Pd alloy membranes do show promise, but much work is needed before a realistic demonstration project is warranted.

Both dense ceramic (perovskites) and mixed ceramic-metal (cermets) membranes are receiving increased R&D attention for the selective separation of H_2 at high temperatures. Key accomplishments have been summarized in the work of Collot [9] and Siriwardane et al. [141]. However, detailed structural performance information is lacking. There are several principal research groups investigating these materials including: 1) the Argonne National Laboratory (ANL)/National Engineering Technology Laboratory (NETL) (Balachandran and Rothenberger) in a collaborative effort, 2) Eltron Research Inc. (Roark and Sammels), 3) Ceramatec Inc. (Elangovan), 4) the University of Cincinnati (Lin), and 5) the ITN Energy Systems Inc/INEEL/ANL/Nexant with Praxair as a consulting partner. Although there have been reports

indicating that high H₂ fluxes have been achieved, more work is needed to address issues including: 1) thermal stability, 2) controlled film thicknesses (> 30 μ m), 3) ability to function under high pressures for extended periods of time, and 4) to operate at temperatures below 800°C.

High temperature porous membranes (e.g., silica, silicalites and zeolite) have also been investigated for application with 1) SMR [142-144], 2) CO₂ (dry) reforming [145-153] and 3) WGS [154-156]. These materials have the advantage of lower price and higher permeance than Pd-based membranes. In general, microporous silicas show the highest H₂ selectivities [142-148, 150, 153, 155, 156], with the best H₂/N₂ selectivities exceeding 10,000 for membranes prepared with chemical vapor deposition [145-147]. A literature summary is given in the work of Prabhu and Oyama [147], and is reproduced in Tables 1.15 and 1.16.

To date, the most promising results for a membrane separation with steam reforming were achieved with a silica-zirconia composite membrane prepared via sol-gel coating [142]. This system exhibited H_2/CO_2 selectivities of >20 for fluxes >100 mol cm⁻² s⁻¹ Pa⁻¹. However, the presence of water vapor may significantly affect the performance of these silica membranes over time, particularly if operated at relatively low temperatures, such as in a WGS reactor. Silanol groups within the silica structure react with water leading to structural densification which reduces performance. Detailed information on these materials is provided in Tables 1.15 and 1.16. Potential for improvement here appears to be promising.

Polymeric Hydrogen Permselective Membranes

Hydrogen permselective polymeric membranes are widely used for H_2 recovery from refinery streams at low temperatures. As indicated earlier, polymeric membranes that are selective towards H_2 over heavier gases, like CO₂, can be used for hydrogen recovery in tail streams of PSA units. Diffusion selectivity and solubility selectivity, along with permeance (the absolute magnitude of permeability), are the key factors governing performance of a polymeric membrane for H_2 separation [9,157]. Diffusion selectivity favors smaller molecules and solubility selectivity favors larger molecules.

In general, the selectivity of glassy polymers (i.e., polymers with glass transition temperatures above the operating temperature) is dominated by diffusion selectivity, which is governed primarily by the size difference between the gas molecules and the size sieving ability of the polymer material. Membranes made of glassy polymers are used for removing lighter gases like H₂. The selectivity of rubbery polymers (i.e., polymers with glass transition temperature below the operating temperature) is dominated by solubility selectivity. These membranes are used for removing heavier gases from a mixture. Temperature affects these selectivities in different ways. For a given polymer, within its glassy or rubbery range, diffusion selectivity generally becomes more important as temperature increases, while the opposite is generally true for solubility selectivity, particularly for temperatures below room temperature. Freeman [157] showed in a typical H_2/N_2 vs. H_2 permeability plot why glassy polymers are preferred over rubbery membrane materials for most H_2 separation applications, where high selectivity is needed to meet permeate purity specifications. Important exceptions are the rubbery membranes (e.g., MTR VaporSep) that are used to recover H_2 from refinery streams. Here the high

permeability of the rubbery polymer membrane is more important than H₂ purity in driving the system economics.

While selectivity is the key to purity, it is the membrane area that drives capital cost. Hydrogen is not very soluble in most glassy polymers, and permeance is governed by the diffusion rate. Since diffusion rates go up with temperature, higher temperatures (staying 15-20°C below the glass transition temperature) are usually favored for H_2 separations using glassy polymer membranes.

Information on polymeric membranes that selectively permeate H_2 over CO_2 is limited. Due to the high permeability of CO_2 , the selectivity of H_2 in the presence of CO_2 is typically low for organic polymers. Orme et al. [158] showed that for a wide range of polymers the H_2/CO_2 selectivities varied between 0.5-2.5. The H_2 permeabilities and selectivities for other polymeric membranes are shown in Tables 1.15 and 1.16. For these polymers the H_2/CO_2 selectivity varied between 2 and 15. Of particular interest are the results provided by Hradil et al. [159] with alumina supported styrene-divinylbenzene membranes. High permeabilities (i.e., 500-4000 Barrers) were reported for H_2 , but H_2/CO_2 selectivity data is lacking. Achieving high H_2 permeability with high H_2/CO_2 selectivity remains an important technical challenge. However, a polymer membrane that selectively permeates both H_2 and CO_2 relative to CO could still be used to drive the unfavorable equilibrium of the water gas shift reaction, though downstream scrubbing of the CO_2 might be required.

Carbon Dioxide Permselective Membranes

 CO_2 is a highly permeable gas; generally, only H_2 and He are more permeable. In fact, at low temperatures, the solubility selectivity of CO_2/H_2 dominates the diffusivity advantages of H_2 and membranes have been developed with selectivity towards CO_2 . Rubber type membranes would be preferred for CO_2/H_2 separation. Orme et al. (2001) have reported that rubbery polyphazenes (Tg << 0°C) show interestingly high CO_2/H_2 selectivities of ~ 10 with modest CO_2 permeabilities of ~ 250 barrers. In recent years, the group directed by Spontak [160-162] has shown similar CO_2/H_2 selectivities, (i.e., 6-10), using crosslinked poly(ethylene glycol) (PEG) membranes, but with reduced CO_2 permeabilities of 40-70 barrers. Further work is needed.

There are a few glassy polymer membranes that show large selectivities towards heavier gases. The groups directed by Freeman [163] and Pinnau [164-166] have been working with these glassy polymers with high molecular free volume to separate light hydrocarbons (C3+) from light (or permanent) gases. These polymers, which consist of substituted polyacetylenes (e.g., Poly(1-trimethylsilyl-1-propyne), PTMSP; Poly(1-methyl-1-pentyne), PMP; Poly(tert-butylacetylene), PTBA) have shown high permeabilities and favorable selectivities for CO₂ over H₂. Initial permeabilities in these membranes decrease with time [164]. Kuraoka et al. [167] have shown that glassy organosilanes with long organic pendant groups (i.e., C18) and very small porosity (~ 1.7%) can also be very selective towards CO₂ (CO₂/He ~5 at 300°K). Table 1.16 displays some of the results obtained for these types of membranes. This is an area where the fundamental science suggests a breakthrough may be possible.

Selective surface flow (SSF) adsorbent membranes function as a result of the affinity that CO_2 has over H_2 in adsorbing to the membrane surface. An example of such a membrane is a high surface area carbonaceous material where the pores are uniform and in the upper end of the molecular sieving size range. In this way, the heavier gas (e.g., CO_2) readily adsorbs over the light gas (e.g., H_2) on the wall of the pore, which decreases the effective diameter of the pore and excludes the light gas from entering the pore. The heavy component then simply diffuses along the surface of the walls down a concentration gradient through the SSF adsorbent membrane material. However, the selectivity is not very high for these systems (Table 1.16).

The first SSF membranes were developed by Air Products and Chemicals. They consisted of a carbonized resin supported on a porous alumina or a metal tube [10,55,168,169]. Recently, Way et al. [170,171] have reported on new types of SSF membranes made of modified porous Vycor glass. The selectivities of these membranes are provided in Table 1.16. Though invented by industrial researchers, industrial interest in SSF membranes appears to have waned. To move this separations technology forward would require a commercial scale demonstration. None have been announced.

 CO_2 selective membranes have been prepared from promoted hydrotalcites and modified zirconates. Here CO_2 is selectively complexed with the membrane material at high temperatures. The concept of these solubility-based separations has been suggested in the literature [9,172]. However, much more work is needed to demonstrate both feasibility and economic reliability.

Conclusions from the Background Survey

This survey identified several areas where major improvements or even breakthroughs may be achieved in hydrogen production with the judicious use of adsorption and membrane processes. In several other areas, fundamental limits seem to place big hurdles in the path forward. In the next section, recommendations are presented for support of future work in the more promising areas to reduce energy consumption, the environmental impact, and feedstock requirements, all while improving the process economics.

Recommendations for Future R&D

Recommendations are set-forth for future hydrogen separations R&D in the following two sections of this report. These recommendations are set-forth for near term, 0 - 5 years, and longer range research developments, 7 - 15 years. The near term developments in separation technology for equilibrium driven processes are divided into three categories:

- Near Term Adsorbent Development
- Near Term Membrane Development
- Near Term Adsorption Process Development

The long range developments in separations technology for equilibrium driven processes are also divided into three categories:

- Long Term H₂ Flow Sheet Augmentation with Adsorption and Membrane Processes
- Long Term Advanced Adsorbent Materials and Process Development for H₂ Production
- Long Term Advanced Membrane Materials for H₂ Production

Existing flow sheets and conceptual flow sheets to foster ideas for near and long term H_2 production plant modifications with adsorption and membrane technologies are provided in Figures 1-3 for guidance.

Flow Sheets for Guidance

Figures 1.1a, 1.1b and 1.1c display flow sheets depicting the current state-of-the-art for industrial H_2 production technology. In these figures, the operating conditions associated with each unit operation are provided. The three major separations processes are identified: 1) condensation for water removal; 2) CO₂ scrubbing with MEA or MDEA; and 3) PSA for CO₂, CO and CH₄ removal. Hydrogen selective polymeric membranes are just beginning to find industrial applications in hydrogen production as indicated.

For the near term, hypothetical hydrogen production plant flow sheets, indicating where adsorption and or membrane processes might be able to augment existing plants in the near term are shown in Figure 1.2a. Figure 1.2b shows a hypothetical near term syngas production plant flow sheet, indicating where adsorption and or membrane processes might be able to augment existing plants in the near term.

For the long term, hypothetical hydrogen production plant flow sheets of the reformer section, indicating where adsorption and or membrane processes might be able to augment existing plants are shown in Figure 1.3a. Figure 1.3b shows hypothetical longer term hydrogen production plant flow sheets of the water gas shift section, indicating where adsorption and or membrane processes might be able to augment existing plants. Similarly, Figure 1.3c shows a hypothetical longer term hydrogen production plant flow sheet of the purification section, indicating where adsorption and or membrane processes might be able to augment existing plants. Finally, hypothetical longer term syngas production plant flow sheets, indicating where adsorption and or

membrane processes might be able to augment existing plants are shown in Figure 1.3d.

A) Near Term Adsorbent Development

Overarching Goal: develop high capacity adsorbents with rapid adsorption-desorption kinetics, improved selectivity and operational stability at elevated temperature in the present of steam and other reaction components.

Recommendations:

- 1) Develop high capacity CO_2 and CO selective adsorbents that can operate in the presence of hydrogen and steam at elevated temperatures. Working capacities similar to commercial low temperature adsorbents like 5A zeolite for CO_2 (at elevated temperatures in the range of 3-4 mol/kg) are desirable.
- 2) Develop new Pressure Swing Adsorption (PSA) cycle designs at either ambient or elevated temperatures that take advantage of these new adsorbents. Possibly a TSA or a PSA/TSA hybrid cycle design could be envisioned.

As a guide, the classes of materials being studied today include:

- low temperature activated carbons, carbon molecular sieves, and zeolites for CO₂,
- high temperature hydrotalcites, CaOs and zirconates for CO₂,
- ambient temperature Cu and Ag impregnated alumina and silica adsorbents for CO,
- metal hydrides and their alloys for H₂, and
- structured adsorbents for rapid PSA, or PSA/TSA processes, e.g., carbon fiber molecular sieves.

In general, these materials have a potential for commercial use in H_2 production. However, all materials suffer from one or more of the following deficiencies:

- too expensive
- insufficient working capacity,
- insufficient selectivity,
- slow adsorption or desorption or mass transfer kinetics,
- moisture sensitivity,
- vulnerability to poisons like CO or S,
- too rectangular of an adsorption isotherm shape making regeneration difficult with pressure,
- too strong of a physiochemical interaction requiring regeneration with relatively high temperature instead of pressure, and
- limited rapid cycling capability because commercial pellet materials tend to crumble if the cycling is too fast.

Overall, the typical process conditions (Figure 1.1) and flow rates (Tables 1.1 to 1.4) that will be

encountered in a H_2 production plant are included for reference and guidance. Table 1.5 provides some insight into the numbers now being achieved. Any improvement in these numbers will be highly desirable as most of these adsorbent materials are not yet commercially viable as a result of their performance, as discussed above.

B) Near Term Membrane Development

Overarching goal: develop high temperature membranes that are selective only to O_2 , H_2 or CO_2 , that exhibit high permeability, are robust and resistant to fouling and degradation, and that exhibit good mechanical stability under high differential pressures.

Recommendations:

1) Develop low temperature functioning O_2 selective membranes with higher permeance, > $100 \times 10^{-8} \text{ mole/s/m}^2/\text{Pa}$:

The current oxygen permselective membranes of the perovskite type operate at too high of a temperature (> 800° C), and offer too low of a permeance. Improvements are sorely needed.

2) Develop a high flux membrane for hydrogen permselective dense membrane based on Pd that is not subject to embrittlement with increased stability without forming defects, such as hillocks, in the Pd or alloy film.

To ensure large fluxes, Pd membranes must be very thin ($\leq 20 \ \mu m$); this has not been achieved to date without having serious flaws, like diminished mechanical stability.

To provide mechanical stability, Pd has been supported on porous materials such as aluminas, or alternatively, over lower cost dense metals, e.g., V, Zr, Nb, Ti. In the latter case, it may be possible to grow Pd films as thin as 3 to 5 μ m, which also protects Ti from forming passive layers. The goal is to develop these thin membranes without forming defects, such as hillocks, in the Pd thin film.

When operating below 650° C, the adsorption of H₂ results in the embrittlement of the Pd films. To avoid this, Pd is being alloyed with, for example, 20 to 60 wt% Cu or Ag. Better methods are needed.

State-of-the-art Pd membrane films suffer from being too brittle, and avoid peeling and hillock formation, i.e., cracks and pinholes in the deposited metal films, which possibly occur due to surface irregularities in porous support with the thinner films ($\delta < 10 \mu m$). New synthesis methods are needed that circumvent these serious flaws.

3) Develop hydrogen permselective membranes based on Knudsen transport, e.g., porous materials such as molecular sieve silica, with a selectivity of more than 100, and that are stable to water vapor.

Current hydrogen selectivities with various gases are generally < 20 (see Tables 1.15 and 1.16).

Improvement to around 100 is needed. This necessarily implies inorganic high temp materials need to be developed for this purpose.

Porous hydrophilic membranes are known to deteriorate in water vapor at intermediate temperatures. These membranes need to be more water tolerant.

Develop additives that improve moisture stability and do not adversely affect performance.

- 4) Develop CO₂ permselective polymer membranes with H₂/CO₂ selectivity of >15-20, with at least 2 times higher CO₂ flux than current commercial membranes, and with higher stability to syngas production conditions of 200°C or higher.
- 5) Develop CO_2 permselective inorganic membranes with selectivity of > 15-20 or higher as these systems provide the desirable temperature stability.

In general these membranes show commercial potential with energy saving impact in hydrogen production. However, each membrane suffers from one or more of the following deficiencies:

- each membrane generally suffers from low selectivities of CO₂ to H₂ (see Tables 1.15 and 1.16),
- the membranes are not stable under the conditions of H₂ and syngas production, 200 °C,
- polymer membranes need separations selectivities of >15-20 or higher to justify temperature management cost, and
- inorganic membranes need to be more stable when exposed to water, to minimize changes in the performance of hydrophilic inorganic membranes.

Innovative ways to add agents to complex CO_2 for high up take of CO_2 in the membrane should be developed.

New approaches are needed in the development of polymeric membranes that have higher selectivity to CO_2 .

Can promoted hydrotalcite, modified zirconate or other inorganic membrane materials resolve some of these issues with polymeric membranes?

6) Develop high temperature membranes that are selective for H_2/CO at 200°C, with higher selectivity that exceeds the range (15-20) for current commercial membranes.

7) High temperature stable membranes with selectivity to CO are needed for improved H₂ production.

Overall, the typical process conditions (Figure 1.1) and flow rates (Tables 1.1 to 1.4) that will be encountered in a H_2 production plant are included for reference and guidance. Tables 1.15 and 1.16 provide some insight into the numbers now being achieved. Any improvement in these numbers will be highly desirable, as most of these membrane materials are not yet commercially viable as a result of their performance.

C) Near Term Adsorption Process Development

Overarching goal: develop new or modify existing adsorption process technology that offers increased energy savings, lower capital and operating costs, affords higher reliability and reduces footprint and environmental impact.

Recommendations:

1) Need an improved way of operating a conventional PSA unit with increased energy efficiency.

State-of-the-art PSA processes suffer from the following: the feed pressures tend to be very high (see Figure 1.1), the beds tend to be very large, and the operation tends to be very complex because of the relative high number of beds. Some ideas for improvement include:

- rethink the use of the PSA tail gas,
- revamp the existing PSA plant through cycle modification or relaxing the H_2 purity constraint,
- using, lower or even higher, purge gas pressure,
- replace one or more of the adsorbents with more efficient ones,
- increase, or even decrease, the number of adsorbent vessels, and
- add storage tanks to replace some of the adsorbent beds.

2) Need H₂, CO or CO₂ selective PSA process with cycle sequencing modifications.

Collaboration with external research teams, Academic or National Labs, could accelerate this development. Some ideas include:

- develop new PSA cycles that take advantage of the heavy reflux concept, where a pure heavy product (like CO₂) is more desirable than pure light product (like H₂). Note that a H₂ selective metal hydride adsorbent makes the H₂ the heavy component, and
- foster a clear understanding of the design of such a PSA cycle, which appears to be lacking compared to the commercial light reflux PSA processes. Hence, the application of the heavy reflux PSA concept for H₂ production is a desirable near term target.

3) Need improved efficiency for thermal management in the design of H₂ TSA and PSA/TSA hybrid cycles. Some ideas include:

- rethink bed designs for rapid heating and cooling because the long times required to heat conventional beds for regeneration and then cool them to the feed temperature give rise to long cycle times and thus exceedingly large columns, and
- take advantage of the many heat sources that are available throughout a H₂ production plant that may lend themselves to a TSA or a PSA/TSA hybrid cycle configuration for selective CO₂ or CO removal from a process stream. Figure 1.2 therefore includes PSA,

TSA and, other adsorption cycles that could be used for hydrogen separation.

D) Long Term H_2 Flow Sheet Augmentation with Adsorption and Membrane Processes

Overarching goal: develop new hydrogen adsorption and membrane process technology that offers lower capital and operating costs and affords higher reliability and up-time with improved energy savings.

Recommendations:

1) Develop hybrid technology for H₂ production. For example, develop a multi-Functional hybrid reactor for Steam Methane Reforming (SMR) by combining the reactor with a CO₂ selective adsorbent and an H₂ permeable membrane.

Driving equilibrium processes in this way can greatly improve manufacturing process efficiencies. This design would not only shift the equilibrium favorably of the reforming reaction, but it would also facilitate the WGS reaction.

Recommended approach: develop new adsorbent and membrane separation materials.

It appears that highly selective and highly permeable membranes will always be very difficult to fabricate. However, with hybrid multi-reactive, multi-separation designs, the criteria for selectivity or permeability may be relaxed, so a less selective membrane with a high flux may suffice. The information provided in Figure 1.3 could serve as a base for modification.

E) Long Term Advanced Adsorbent Materials and Process Development for H₂ Production

Overarching goal: develop new adsorbent materials and hydrogen process technology that offers increased energy savings, lower capital and operating costs, affords higher reliability and reduces footprint and environmental impact.

Recommendations:

- 1) Develop advanced structured adsorbent materials for use in rapid cycle Pressure Swing Adsorption (PSA).
- 2) Further develop the design of rapid cycle PSA for hydrogen production.
- 3) Minimize the cycle time in rapid PSA to improve its throughput and hence efficiency by investigating the limiting relationship between adsorbent particle size, surface properties and accelerated cycle times.
- 4) Develop a PSA hybrid separation system, e.g. with a structurally integrated permeable membrane. Investment in these kinds of novel hybrid unit operation concepts is recommended.

5) CO₂ removal via TSA: develop Temperature Swing Adsorption (TSA) and or PSA/TSA hybrid cycles with improved materials for use in H₂ separation technology.

6) Improved hydrogen separations with Sorption Enhanced Reaction Processes using thermal swing regeneration and new materials.

Consider novel approaches such as incorporating a high temperature reversible metal hydride as a H_2 selective adsorbent in a Sorption Enhanced Reaction Processes to drive the equilibrium.

7) CO selective adsorbents: research on novel CO selective adsorbents is needed.

8) Improved hydrogen selective adsorbents are important for the next advances in design options for H₂ production technology.

The challenges here are substantial, especially for selectivity and for durability at moderate temperatures and tolerance for containments such as CO or sulfur.

Overall, this would rely on the development of structured adsorbent materials for rapid cycle PSA. Recently, with the introduction of QuestAir's H₂ purification technology, based on rotary valve or rotary beds, as discussed above, there appear to be many opportunities for this new approach. Any improvement in a conventional PSA cycle can most likely be used with the rapid cycle PSA systems. Although, QuestAir and Air Products and Chemicals have developed proprietary structured adsorbent materials (see above), continued research and development in this area is needed for both near and longer terms.

F) Long Term Advanced Membrane Materials for H₂ Production

Overarching goal: develop new membrane materials that offer increased energy savings, lower capital and operating costs, affords higher reliability and reduces footprint and environmental impact.

Recommendations:

1) Next generation membrane materials are needed that offer high selectivity for hydrogen (>100), while resisting fouling and cracking or embrittlement, and while withstanding high temperatures and pressures. Such membranes could save substantial energy by replacing hydrogen PSA plants.

2) Develop high-integrity, mixed matrix membranes, which are scalable and offer a wide variety of separation characteristics for industrial H₂ production:

Additional research is recommended on selective mixed matrix membranes: Improve performance by improving compatibility between the mixed-matrix materials. Desirable properties include:

- high mechanical strength, adaptable to manufacturing process, inertness to chemical attack, and plasticization for use in membrane reactor technology,
- high H₂ flux and H₂/CO₂, H₂/CO selectivity at high temperatures,
- high CO₂ flux and CO₂/H₂ selectivity at high temperatures,
- high CO flux and CO/H₂ selectivity at high temperatures,
- high O_2 flux and O_2/N_2 selectivity at high temperatures, and
- high H_2O flux and high H_2O/H_2 , H_2O/CO_2 selectivity at high temperatures.

3) Develop organic-inorganic hybrid membrane materials for high temperature membrane reactor technology: New materials that may serve as selective high temperature membranes for H₂, CO or syngas production are needed.

Design concepts could be based on biomimetic materials to be applied for H_2 separation membranes that can function at higher temperatures.

4) Improved inorganic and microporous membrane materials:

A) Molecular Transport Hydrogen Selective Membranes: i.e., microporous membranes to separate hydrogen:

- improved materials: uniform membranes,
- robustness to steam and common petroleum contaminants,
- improved permeance,
- examples of materials include zirconia, alumina, classical zeolites, ZSM-5, Ti-Si zeolites, carbon zeolites, porous SiC, carbon molecualr sieves, etc.,
- micropores: < 1 nm, but prefer < 0.5 nm,
- target selectivity: > 80-100 for H₂/CO₂,
- address hydrolytic stability of silica based microporous materials, for improved durability,
- need low-cost fabrication of the microporous membranes with high flux and high separation factors,
- incorporation of the shift catalyst into the membrane unit,
- higher quality support materials with a more uniform pore size and less surface roughness,
- improve membrane fabrication for controlling pore size and pore size distribution,
- long-term testing under industrial conditions,
- improved metal to ceramic seals,
- improved sealants for membranes to modules, and to end seals, and
- improved synthesis needed for these materials, e.g., for zeolites, etc.

B) Atomic Transport/Dense Metallic Membranes: e.g., Pd alloys and Pd coated metals:

- durability,
- sealing and joining technology,
- operate at lower pressure without hydrogen embrittlement,

- resistance to sulfur poisoning,
- improved plating methods $< 1-3 \mu m$,
- Pd–Cu alloys and other new alloys, and
- address issues of hillock formation (membrane defects formed during operation).

C) Ion Transport Membranes:

- new ceramic materials and process development, and
- need improved flux, selectivity, and stability-robustness to water and ammonia.

D) Mixed Matrix Membranes:

- high potential,
- wide variety of separation characteristics, but
- joining technology is needed.

5) Improved polymeric membrane materials

A) Hydrogen Selective Polymer Membranes:

- Increase the operating temperature for H₂ separation membranes to 400°C, and
- polyimide and polysulphone function well at 200°C; need membranes that can operate at 400°C.

B) CO₂ Permselective Membranes:

• Need CO_2 selectivity over H_2 so H_2 is retained on high pressure side.
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Figure 1.1a. Flow sheet of a typical, state-of-the-art, large-scale hydrogen or syngas production plant incorporating a pre-reformer, a steam reformer, high and or low temperature water gas shift reactors, and H_2 purification units such as absorption with methanation, pressure swing adsorption, or membrane with methanation. The F is a flow rate defined in arbitrary units with the feed flow rate being 1.0. The numbers to the right of the molecular symbols are stream composition numbers in mol or vol%.



Figure 1.1b. Flow sheet of a typical, state-of-the-art, large-scale ammonia production plant incorporating a steam reformer and possibly a secondary reformer or a partial oxidation reactor, high and or low temperature water gas shift reactors, and a H_2 purification unit such as absorption with methanation. The F is a flow rate defined in arbitrary units with the feed flow rate being 1.0. The numbers to the right of the molecular symbols are stream composition numbers in mol or vol%.



Figure 1.1c. Flow sheet of a typical, state-of-the-art, large-scale syngas production plant incorporating a pre-reformer, a steam reformer and possibly a secondary reformer or an autothermal reformer, and absorption based H_2 purification unit. The F is a flow rate defined in arbitrary units with the feed flow rate being 1.0. The numbers to the right of the molecular symbols are stream composition numbers in mol or vol%.



Figure 1.2a. Hypothetical near term hydrogen production plant flow sheets, indicating where adsorption and or membrane processes might be able to augment existing plants in the near term. Tag Indicators: 1a: dense (highly selective) high T membranes: Pd, ion (proton) and electron conductive perovskites (ceramic and cermets); 1b: porous high T membranes: hydrogen selective Inorganic membranes (silica molecular sieves, silicalite zeolites); 1c: porous low T membranes: hydrogen selective organic and Inorganic membranes; 1d: metal hydrides for high T hydrogen concentration via PSA or TSA; 1e: PSA for hydrogen purification or CO_2 concentration; 2a: high

T CO₂ adsorption (hydrotalcites, CaO); 2b: high T CO₂ selective membranes (hydrotalcites); 2c: low T CO₂ selective membranes (surface flow membranes, organic membranes); 3a: low T PSA for CO concentration (π -complexation adsorbents); 4a: high T oxygen dense membranes (ion and electron conductive perovskites).



Figure 1.2b. Hypothetical near term syngas production plant flow sheet, indicating where adsorption and or membrane processes might be able to augment existing plants in the near term. Tag Indicators: 1a: dense (highly selective) high T membranes: Pd, ion (proton) and electron conductive perovskites (ceramic and cermets); 1b: porous high T membranes: hydrogen selective Inorganic membranes (silica molecular sieves, silicalite zeolites); 1c: porous low T membranes: hydrogen selective organic and Inorganic membranes; 1d: metal hydrides for high T hydrogen concentration via PSA or TSA; 1e: PSA for hydrogen purification or CO₂ concentration; 2a: high T CO₂ adsorption (hydrotalcites, CaO); 2b: high T CO₂ selective membranes); 3a: low T PSA for CO concentration (π -complexation adsorbents); 4a: high T oxygen dense membranes (ion and electron conductive perovskites).



Figure 1.3a. Hypothetical longer term hydrogen production plant flow sheets of the reformer section, indicating where adsorption and or membrane processes might be able to augment existing plants in the longer term. Tag Indicators: 1a: dense (highly selective) high T membranes: Pd, ion (proton) and electron conductive perovskites (ceramic and cermets); 1b:

porous high T membranes: hydrogen selective Inorganic membranes (silica molecular sieves, silicalite zeolites); 1c: porous low T membranes: hydrogen selective organic and Inorganic membranes; 1d: metal hydrides for high T hydrogen concentration via PSA or TSA; 1e: PSA for hydrogen purification or CO₂ concentration; 2a: high T CO₂ adsorption (hydrotalcites, CaO); 2b: high T CO₂ selective membranes (hydrotalcites); 2c: low T CO₂ selective membranes (surface flow membranes, organic membranes); 3a: low T PSA for CO concentration (π -complexation adsorbents); 4a: high T oxygen dense membranes (ion and electron conductive perovskites).



Figure 1.3b. Hypothetical longer term hydrogen production plant flow sheets of the water gas shift section, indicating where adsorption and or membrane processes might be able to augment existing plants in the longer term. Tag Indicators: 1a: dense (highly selective) high T membranes: Pd, ion (proton) and electron conductive perovskites (ceramic and cermets); 1b: porous high T membranes: hydrogen selective Inorganic membranes (silica molecular sieves, silicalite zeolites); 1c: porous low T membranes: hydrogen selective organic and Inorganic membranes; 1d: metal hydrides for high T hydrogen concentration via PSA or TSA; 1e: PSA for hydrogen purification or CO₂ concentration; 2a: high T CO₂ selective membranes (surface flow membranes); 3a: low T PSA for CO concentration (π -complexation adsorbents); 4a: high T oxygen dense membranes (ion and electron conductive perovskites).



Figure 1.3c. Hypothetical longer term hydrogen production plant flow sheets of the purification section, indicating where adsorption and or membrane processes might be able to augment existing plants in the longer term. Tag Indicators: 1a: dense (highly selective) high T membranes: Pd, ion (proton) and electron conductive perovskites (ceramic and cermets); 1b: porous high T membranes: hydrogen selective Inorganic membranes (silica molecular sieves, silicalite zeolites); 1c: porous low T membranes: hydrogen selective organic and Inorganic membranes; 1d: metal hydrides for high T hydrogen concentration via PSA or TSA; 1e: PSA for hydrogen purification or CO₂ concentration; 2a: high T CO₂ adsorption (hydrotalcites, CaO); 2b: high T CO₂ selective membranes (hydrotalcites); 2c: low T CO₂ selective membranes (surface flow membranes, organic membranes); 3a: low T PSA for CO concentration (π -complexation adsorbents); 4a: high T oxygen dense membranes (ion and electron conductive perovskites).



Figure 1.3d. Hypothetical longer term syngas production plant flow sheets, indicating where adsorption and or membrane processes might be able to augment existing plants in the longer term. Tag Indicators: 1a: dense (highly selective) high T membranes: Pd, ion (proton) and electron conductive perovskites (ceramic and cermets); 1b: porous high T membranes: hydrogen selective Inorganic membranes (silica molecular sieves, silicalite zeolites); 1c: porous low T membranes: hydrogen selective organic and Inorganic membranes; 1d: metal hydrides for high T hydrogen concentration via PSA or TSA; 1e: PSA for hydrogen purification or CO₂ concentration; 2a: high T CO₂ adsorption (hydrotalcites, CaO); 2b: high T CO₂ selective membranes (surface flow membranes, organic membranes); 3a: low T PSA for CO concentration (π -complexation adsorbents); 4a: high T oxygen dense membranes (ion and electron conductive perovskites).

Licensor H ₂ Plants	System	Sizes (MMsfd)	Plants worldwide
Linde AG	SR-WGS(HT)-PSA	1-100	250
Technip	SR-WGS(HT)-PSA	-	220
Uhde	SR-WGS(HT)-PSA	-130	56
Haldor Topsøe	SR-WGS(HT)-PSA	0.2-200	21
UOP LLC	PSA (Polybed)	-200	700
UOP LLC	membrane (Polysep)	-320	50
Howe-Baker Engineers	SR-WGS(HT)-PSA	1-90	170
Foster Wheeler	SR-WGS(HT)-PSA	1-95	100
Lurgi Oel-Gas-Chemie	SR-WGS(HT)-PSA	1-200	105
Haldor Topsøe	Methanol SR-PSA	- 1	10
Air Products	Membrane (PRISM)	-	270
Air Products	PSA (PRISM)	15-120	270

 Table 1.1.
 Licensors of hydrogen plants, type of plant, production rate, and number of plants worldwide.

Reference: Hydrocarbon Processing, Gas Processes 2002, Gulf Publishing Co. SR = steam reforming, WGS = water gas shift, HT = High temperature, PSA = Pressure Swing Adsorption

Table 1.2. Licensors of ammonia plants, type of plant, production rate, and number of plants worldwide.

Licensor Ammonia Plants	System	Sizes (mtpd)	Plants worldwide
Linde AG	SR-WGS(HT)-PSA	230-1350	3
Uhde	SR-2R-WGS (HT-LT) -	500-1800	14
	CO ₂ Scrubber-M		
Haldor Topsøe	SR-2R-WGS (HT-LT)-	650-2050	60
	CO ₂ Scrubber-M		
Kellogg Brown & Root, Inc	ATR-WGS (HT-LT)-	-1850	200
	CO ₂ Scrubber-M		

Reference: Hydrocarbon Processing, Petrochemical Processes 2003, Gulf Publishing Co. SR = steam reforming, 2R = Secondary Reformer WGS = water gas shift, HT = High temperature, LT = Low Temperature, PSA = Pressure Swing Adsorption, M = methanator

Table 1.3. Licensors of methanol plants, type of plant, production rate, and number of plants worldwide.

Licensor Methanol Plants	System	Sizes (mtpd)	Plants worldwide
Davy Process Technology	PR-SR	2000-3000	55
Uhde	SR	-1250	11
Haldor Topsøe	PR-ATR	-	-
Haldor Topsøe	PR-SR	-3030	-
Lurgi Oel-Gas-Chemie	PR-ATR	-5000	37

Reference: Hydrocarbon Processing, Petrochemical Processes 2003, Gulf Publishing Co. PR = Prereformer, SR = steam reforming, ATR = authothermal reformer

Table 1.4.	Licensors of syngas	plants, type	of plant,	production	rate, and	number (of plants
	worldwide.						

Licensor Syngas Plants	System	Sizes (MMsfd)	Plants worldwide
Davy Process Technology	PR-SR	_	_
Conoco	POX	-500	-
Uhde	SR	-130	56
Haldor Topsøe	PR-ATR	-	21
Haldor Topsøe	SR	-	-
Howe-Baker Engineers	ATR	-	-
Syntroleum	ATR	25-1000	-
Air Products	POX (ACORN)-	-	11
Air Products	cryogenic SR (ACORN)-cryogenic	-	6

Reference: Hydrocarbon Processing, Gas Processes 2002, Gulf Publishing Co. R = Pre-reformer, SR = steam reforming, POX = partial oxidation, ATR = authothermal reformer

Adsorbent	Adsorbate	<u>T (°C)</u>	P (torr)	Loading (mol/kg)	Mode
act. carbon	CO_2	25	500	1.5-2.0	PSA
act. carbon	CO ₂	250-300	500	0.1-0.2	PSA
5A zeolite	CO ₂	25	500	~ 3.0	PSA
5A zeolite	CO ₂	250	500	0.2	PSA
HTlc (K-promoted)	CO ₂	300-400	200-700	0.4-0.7	PSA
double-layer hydroxides	CO ₂	375	230	1.5	PSA
alumina (un-doped)	CO ₂	400	500	0.06	PSA
alumina (doped w/Li ₂ (CO ₂ D)	400	500	0.52	PSA
alumina (basic)	CO ₂	300	500	0.3	PSA
Li zirconate	CO ₂	500	760	3.4-4.5	TSA
CaO	CO ₂	500	150	4-8	TSA
CaO	CO ₂	700	76	7	TSA
Cu(I) (alumina)	СО	25-30	760	0.8-1.2	PSA
Cu(I) (alumina)	СО	30	760	0.8	PSA

 Table 1.5.
 Typical capacities of commercial and developmental CO2 and CO selective adsorbents.

	Total	Pd based	Inorganic	Organic
Total	431	127	113	287
Membrane Technology and Research Inc	22	0	1	11
Praxair Technology Inc	17	1	3	2
Idatech I I C	13	6	0	1
The Regents of the University of California	15	2	2	5
Symyx Technologies Inc	8	0	0	4
UOPIIC	9	3	3	2
Air Products and Chemicals Inc	7	1	0	3
Plug Power Inc	8	0	1	3
ATI Properties Inc	5	1	0	0
Lynntech Inc	7	2	3	4
Walter Juda Associates Inc	5	5	0	0
Worcester Polytechnic Institute	5	5	0	0
Proton Energy Systems	6	1	0	2
Texaco Development Corporation	4	0	0	1
Battelle Memorial Institute	4	1	1	3
California Institute of Technology	7	0	3	6
Conoco Inc	3	1	1	1
Eltron Research Inc	3	2	2	1
Ford Global Technologies Inc	3	3	0	0 0
Siemens Westinghouse Power Corporation	3	2	1	1
The C & M Group Llc	3	2	2	2
The University of Chicago	3	0	2	0
University of Wyoming	3	3	0	1
Boc Group Inc	2	0	1	1
Borst Inc	2	0	0	0
BP Amoco Corporation	2	0	0	0
Conocophillips Company	2	0	0	1
Corning Incorporated	2	0	2	1
Engelhard Corporation	2	0	1	0
General Motors Corp	2	1	2	0
Honda Motor Co Ltd	2	0	0	2
Honeywell International Inc	2	0	0	1
HRL Laboratories Llc	2	0	0	0
HY9 Corporation	2	2	1	0
International Fuel Cells Llc	2	1	0	1
Johnson Electro Mechanical Systems LLC	2	0	0	0
Massachusetts Institute of Technology	2	1	1	0
Microcoating Technologies Inc	2	0	0	1
Millennium Cell Inc	2	1	0	1
Nanoset LLC	2	1	0	1
Niagara Mohawk Power Corporation	2	0	0	1
Northwest Power Systems LLC	2	2	0	0
Perkinelmer Instruments LLC	2	0	0	2
Quantum Group Inc	2	1	1	1
Rensselaer Polytechnic Institute	2	0	0	2
The BOC Group Inc	2	0	1	0
The Gillette Company	2	1	0	0
The Regents of the University of Colorado	2	0	2	1
Ztek Corporation	2	0	0	1

Table 1.6. Number of patents issued since 2000 on hydrogen selective membranes.

Table 1.7. Top investigators with more than three peer-reviewed publications on dense perovskite oxygen selective membranes for partial oxidation of methane (POX) and oxidative dehydrogenation of paraffins (ODP) since 1995 and their publications in these areas since 2003.

		Investigators	Organization	1995			2003		Τ	Т
		8		Total	POX	ODP	Total	РОХ	ODP	•
	1	W. Yang, G. Xiong	State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, P.R. China	36	20	7	10	6	3	
	2	V.V. Kharton, A.A. Yaremchenko, J.R Frade	Department of Ceramics and Glass Engineering, University of Aveiro, Aveiro, Portugal	32	7	0	16	6	0	
	3	Y.S. Lin	Department of Chemical Engineering, University of Cincinnati, Cincinnati, OH, USA	28	11	2	4	1	0	
	4	N. Xu	Membrane Science and Technology Research Center, Nanjing University of Technology, Nanjing, P.R. China	23	19	0	1	5	0	
	5	U. Balachandran	Energy Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA	14	13	0	1	1	0	
	6	H.J.M. Bouwmeester	Laboratory for Inorganic Materials Science, Department of Science and Technology & MESA+ Research Institute, University of Twente, Enschede, The Netherlands	13	3	1	3	2	0	
	7	C.S. Chen	Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui, PR China	13	2	0	7	2	0	
	8	T Ishihara	Department of Applied Chemistry, Faculty of Engineering, Oita University, Oita, Japan	8	3	0	3	0	0	
	9	Y.H. Ma	Center for Inorganic Membrane Studies, Dept. of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA, USA	7	7	0	10	0	0	
	10	A. C. van Veen, D. Farrusseng, C. Mirodatos	CNRS-IRC, Villeurbanne, France	6	0	3	4	3	0	
	11	A.J. Jacobson	Department of Chemistry, University of Houston, Houston, TX, USA	6	2	0	1	0	0	
	12	N. Yang	College of Materials Science and Engineering, Nanjing University of Technology, Nanjing, P.R. China	5	2	0	2	0	0	
	13	S. Diethelm	Laboratoire d'Energétique Industrielle, Lausanne, Switzerland	4	2	2	3	0	0	
	14	K.S. Lee	Energy Materials Research Team, Korea Institute of Energy Research, Yusong, Daejeon, South Korea	4	0	0	3	0	0	
	15	A. Atkinson	Department of Materials, Imperial College London, Exhibition Road, London SW7 2BP, UK	3	0	0	1	0	0	
	16	Z. Chen	Department of Chemical Engineering, Auburn University, Auburn, AL, USA	3	2	0	0	3	0	
	17	F.T. Ciacchi	CSIRO Manufacturing Science and Technology, Victoria, Australia	3	3	0	1	0	0	
	18	A. Bose	U.S. Department of Energy, NETL, Pittsburgh, PA, USA	3	0	0	0	0	0	
	19	C. Guizard, A. Julbe, C. Levy	Institut Européen des Membranes (CNRS UMR 5635), Montpellier, France	3	0	1	1	0	0	
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Table 1.8. Investigators with the largest number of peer-reviewed publications in palladium based hydrogen selective membranes since 1995 and their publications since 2003.

	Investigators	Organization	1995	2003
1	N. Itoh	National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan	20	1
2	R. Hughes	Chemical Engineering Unit, University of Salford, Manchester, UK	20	1
3	A. Basile	Institute on Membrane Technology, University of Calabria, Rende, Italy	17	4
4	E Kikuchi	Department of Applied Chemistry, School of Science and Engineering, Waseda University, Tokyo, Japan	14	1
5	BPA Grandjean	Department of Chemical Engineering and CERPIC, Laval University, St. Foy, Quebec, Canada	12	1
6	S. Uemiya	Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Tokyo, Japan	12	1
7	V. Violante, S. Tosti A. Adrover	ENEA, Centro Ricerche di Frascati, Frascati, Rome, Italy	12	5
8	S Morooka, K. Kusakabe	Department of Applied Chemistry, Kyushu University, Fukuoka, Japan	11	1
9	F.A. Lewis	School of Chemistry, Queen's University, Belfast, North Ireland, UK	10	0
10	X.Q. Tong	Department of Material Sciences, Tsinghua University, Beijing, China	10	0
11	C. Nishimura, Y Zhang	National Institute for Materials Science, Tsukuba, Japan	9	4
12	H. Amandusson, L.G. Ekedahl, H. Dannetun	Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden	8	0
13	H.I. Chen, T.C. Huang	Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan	8	4
14	K Kandasamy	Physics Department, University of Jaffna, Jaffna, Sri Lanka	8	0
15	K.H. Lee	Membranes and Separation Center, Korea Research Institute of Chemical Technology, Yusung, South Korea	7	1
16	S.I. Pyun	Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Yusong-Gu, South Korea	7	0
17	J.D. Way	Colorado School of Mines, Department of Chemical Engineering, Golden, CO, USA	9	3
18	P. Zoltowski	Institute of Physical Chemistry of Polish Academy of Sciences, Warsaw, Poland	7	2
19	Y.S. Lin	Chemical Engineering Department, University of Cincinnati, Cincinnati, OH, USA	6	1
20	J.K Ali	Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, Zürich, Switzerland	6	0

Table 1.9. Investigators with the largest number of peer-reviewed publications in palladium based hydrogen selective membranes since 2003.

	Investigators	Organization	2003	
1	H.I. Chen, T.C. Huang	Department of Chemical Engineering, National Cheng Kung	5	
		University, Tainan, Taiwan		
2	V. Violante, S. Tosti, A. Adrover	ENEA, Centro Ricerche di Frascati, Frascati, Rome, Italy	5	
3	H.D. Tong	MESA+ Research Institute, University of Twente, Enschede, The Netherlands	4	
4	A. Basile	Institute on Membrane Technology, University of Calabria, Rende, Italy	4	
5	C. Nishimura, Y. Zhang	National Institute for Materials Science, Tsukuba, Japan	4	
6	F.C. Gielens	Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands	3	
7	S.I. Yamaura	Institute for Materials Research, Tohoku University, Katahira, Japan	3	
8	J. Munera, L.M. Cornaglia, E.A. Lombardo	Instituto de Investigaciones en Catálisis y Petroquímica, Santiago del Estero, Argentina	3	
9	Y.H. Ma	Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA, USA	3	
10	J.D. Way	Colorado School of Mines, Department of Chemical Engineering, Golden, CO, USA	3	
11	K.S. Rothenberger	National Energy Technology Laboratory (NETL), US Department of Energy, Pittsburgh, PA, USA	2	
12	M.R. Rahimpour	Department of Chemical Engineering, Shiraz University, P.O. Box 71345, Shiraz, Iran	2	
13	P. Zoltowski	Institute of Physical Chemistry of Polish Academy of Sciences, Warsaw, Poland	2	
14	M.P. Harold	Department of Chemical Engineering, University of Houston, Houston, TX, USA	2	
15	L. Wang	National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan	2	
16	C. Ramesh	Indira Gandhi Centre of Atomis Research, Materails and Chemistry Division, Kalpakkam, Tamil Nadu, India	2	
17	S. Yamaguchi	Research Institute, Chiba Institute of Technology, Narashino, Japan	2	
18	S. Uemiya	Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Tokyo, Japan	1	
19	K.H. Lee	Membranes and Separation Center, Korea Research Institute of Chemical Technology, Yusung, South Korea	1	
20	Y.S. Lin	Chemical Engineering Department, University of Cincinnati, Cincinnati, OH, USA	1	

Table 1.10. Top investigators with more than two peer-reviewed publications on the use of hydrogen selective membranes for steam reforming since 2000 and their publications since 2003.

	Investigators	Organization	2000	2003	
1	Z.X. Chen, S.S.E.H.	Department of Chemical Engineering, Auburn University,	12	9	
2	A Basile	Institute on Membrane Technology University of Calabria	8	5	
		Rende, Italy	0	5	
3	J. Munera, L.M. Cornaglia E.A. Lombardo	Instituto de Investigaciones en Catálisis y Petroquímica, Santiago del Estero, Argentina	5	5	
4	T. Tsuru	Department of Chemical Engineering, Hiroshima University, Higashi-Hiroshima, Japan	4	1	
5	Y.M. Lin	Center for Environmental, Safety and Health Technology Development, Industrial Technology Research Institute, Chutung, Taiwan	4	2	
6	M.E.E. Abashar	Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia	3	1	
7	G. Barbieri	Research Institute on Membrane Technology, University of Calabria, Rende, Italy	3	0	
8	C.S. Chen	Laboratory of Advanced Functional Materials and Devices, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, P. R. China	3	0	
9	G. Xiong	State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, P.R. of China	3	0	
10	S.T. Oyama	Environmental Catalysis and Materials Laboratory, Department of Chemical Engineering, Virginia Tech., Blacksburg, Virginia	3	1	
11	T.T. Tsotsis	Department of Chemical Engineering, University of Southern California, Los Angeles, California	3	1	
12	C.T. Au	Department of Chemistry, Centre for Surface Analysis and Research, Hong Kong Baptist University, Hong Kong, China	2	0	
13	H.I. de Lasa	Chemical Reactor Engineering Centre, University of Western Ontario, London, Ontario, Canada	2	0	
14	J.R. Grace	Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC, Canada	2	1	
15	S. Uemiya	Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Tokyo, Japan	2	1	
16	T. Yamaguchi	Department of Chemical System Engineering, The University of Tokyo, Tokyo, Japan	2	1	
17	Y. Matsumura	Research Institute of Innovative Technology for the Earth, Kizu-cho, Soraku-gun, Kyoto, Japan	2	2	

	Investigators	Organization	2000	
1	A. Basile	Institute on Membrane Technology, University of Calabria, Rende, Italy	6	
2	V. Violante, S. Tosti, A. Adrover	ENEA, Centro Ricerche di Frascati, Frascati, Rome, Italy	4	
3	E. Drioli	Department of Chemical Engineering and Materials, University of Calabria, Rende, Italy	3	
4	J.D. Way	Colorado School of Mines, Department of Chemical Engineering, Golden, Colorado	2	
5	J.C.D. da Costa	Australian Research Council (ARC) Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane, Qld 4072, Australia	2	

Table 1.11. Top investigators with more than two peer-reviewed publications on the use of hydrogen selective membranes for water gas shift reaction since 2000.

Table 1.12. Top investigators with more than three peer-reviewed publications on the use of porous inorganic hydrogen selective membranes since 1995, divided into silica, zeolite or other oxide (zirconia or titania) membranes.

	Investigators	Organization	Total	SiO ₂	Zeolite	ZrO ₂ or TiO ₂
1	K. Kukasabe	Department of Applied Chemistry, Kyushu	24	13	11	4
	S. Morooka	University, Fukuoka, Japan				
2	K.H. Lee	Membrane and Separation Research Center,	11	11	0	0
		Korea Research Institute of Chemical				
		Technology, Yuseong, Daejeon, South Korea				
3	H Ohya	Department of Material Science and Chemical	9	7	0	4
	TTakeuchi	Engineering, Yokohama National University,				
—		Yokohama, Japan		0		
4	S. T. Oyama	Department of Chemical Engineering, Virginia	9	8	0	0
		Polytechnic Institute and State University,				
-	O L H	Blacksburg, VA, USA	0	0	0	0
5	G.J. Hwang	Hydrogen Energy Research Center, Korea	8	8	0	0
		Institute of Energy Research, Daejeon, South				
- 6	M Accada	Noted	6	6	0	5
0	M. Asaeua	Lirochimo University Higoshi, Hirochimo	0	0	0	3
	1. 15010	Japan				
7	V S L in	Department of Chemical Engineering	6	3	5	2
,	1.5. Em	University of Cincinnati Cincinnati OH USA	0	5	5	2
8	M. Nomura	Department of Advanced Nuclear Heat	6	6	1	0
Ũ	101. 1 (0111414	Technology, Japan Atomic Energy Research	0	Ũ	-	° °
		Institute, Ibaraki, Japan;				
9	R. Hughes	Chemical Engineering Unit, University of	5	3	0	0
	C	Salford, Manchester, UK				
10	M Watanabe	Laboratory of Electrochemical Energy	5	4	1	1
		Conversion, Faculty of Engineering, Yamanashi				
		University, Takeda, Kofu, Japan				
11	J.A. Dalmon	Institut de Recherches sur la Catalyse, Centre	4	0	4	0
		National de la Recherche Scientifique,				
		Villeurbanne Cedex, France				
12	S. Yamaura	Institute for Materials Research, Tohoku	3	0	0	0
		University, Katahira, Japan				
13	H Verweij	Laboratory for Inorganic Materials Science,	3	3	0	0
		Faculty of Chemical Technology, University of				
		Twente, P.O. Box 217 7500 AE Enschede The				
I		Netherlands				

Table 1.13. Top investigators with more than two peer-reviewed publications on the use of porous inorganic hydrogen selective membranes since 2003, divided silica, zeolite or other oxide (zirconia or titania) membranes.

	Investigators	Organization	Total	SiO ₂	Zeolite	ZrO ₂ or TiO ₂
1	K.H. Lee	Membrane and Separation Research Center,	7	7	0	0
		Korea Research Institute of Chemical				
_		Technology, Yuseong, Daejeon, South Korea				
2	K. Kukasabe	Department of Applied Chemistry, Kyushu	6	2	4	2
_		University, Fukuoka, Japan				
3	M. Nomura	Department of Advanced Nuclear Heat	5	5	0	0
		Technology, Japan Atomic Energy Research				
		Institute, Ibaraki, Japan;				
4	G.J. Hwang	Hydrogen Energy Research Center, Korea	4	4	0	0
		Institute of Energy Research, Daejeon, South				
_		Korea				
5	S. T. Oyama	Department of Chemical Engineering, Virginia	9	3	0	0
		Polytechnic Institute and State University,				
_		Blacksburg, VA, USA				
6	S. Yamaura	Institute for Materials Research, Tohoku	3	0	0	0
		University, Katahira, Japan				
7	N.E. Benes	Laboratory of Inorganic Materials Science,	2	2	0	0
		Faculty of Chemical Technology and MESA ⁺				
		Research Institute, University of Twente,				
		Enschede, The Netherlands				
8	D. Fritsch	Institut für Chemie, GKSS Forschungszentrum	2	1	0	1
		Geesthacht, Geesthacht, Germany				
9	Q. Wei	University of Science and Technology of China,	2	2	0	1
		Departmet of Materials Science and				
_		Engineering, Hefei, PR China				
10	J. Yan	Tongji University, Shanghai, PR China	2	0	2	0

Table 1.14. Top investigators involved on CO_2 selective membranes useful for H_2/CO_2 separation since 1995 and their publications since 1995 and 2002.

	Investigators	Organization	Туре	1995	2002
1	R. J. Spontak & N. P. Patel	Department of Chemical and Biomolecular Engineering, North Carolina State University, Relaigh NC USA	Dense Polymeric	8	6
2	I. Pinnau & R. W. Baker	Membrane Technology and Research, Inc., Menlo Park, CA, USA	Dense Polymeric	8	4
3	B. D. Freeman	Department of Chemical Engineering, University of Texas at Austin Austin TX USA	Dense Polymeric	13	2
4	K. I. Okamoto	Department of Advanced Materials Science & Engineering, Faculty of Engineering, Yamaguchi University Libe, Yamaguchi, Japan	Dense Polymeric	5	3
5	L. S. Teo	Department of Chemical Engineering, National Cheng Kung University Tainan Taiwan	Dense Polymeric	3	0
6	K. K. Sirkar	Department of Chemical Engineering, Center for Membrane Technologies, New Jersey Institute of Technology Newark NI USA	Facilitated Transport & Capillary Contactor	14	4
7	K. H. Lee	Membranes and Separation Research Center, Korea Research Institute of Chemical Technology, Taejon, S. Korea	Capillary Contactor, Facilitated Transport	13	8
8	Z. Wang	Chemical Engineering Research Center, Tianjin University, Tianjin, Peop. Rep. China. Chinese	Facilitated Transport	5	5
9	H. Matsuyama & M. Teramoto	Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-	Dense Polymeric Capillary Contactor, Facilitated Transport	21	4
10	Q. Yuan	Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Peop, Rep. China	Facilitated Transport	3	3
11	R. Noble	Department of Chemical Engineering, University of Colorado, Boulder, CO, USA.	Facilitated Transport	5	2
12	R Quinn	Corporate Science and Technology Center, Air Products and Chemicals, Inc., Allentown, PA, USA	Facilitated Transport	5	1
13	J. D. Way	Department of Chemical Engineering, University of Colorado, Boulder, CO, USA	Surface Flow	2	1
14	S. Sircar	Air Products and Chemicals, Inc., Allentown, PA, USA	Surface Flow	4	0
15	G. F. Versteeg & V. Y. Dindore	Institute for Kjemisk Processteknologi, NTNU, Trondheim, Norway	Capillary Contactor	8	8
16	P. H. M. Feron	TNO Institute of Environmental Sciences, The Netherlands	Capillary Contactor	10	6
17	J Sanchez	Institut Europeen des Membranes-UM2, Montpellier, Fr.	Capillary Contactor, Dense Polymeric	5	5
18	O. Falk-Pedersen	Kvaerner Process Systems, Sandefiord, Norway	Capillary Contactor	7	4
19	S.T. Hwang	Department Chemical Engineering, University Cincinnati, Cincinnati, OH, USA	Capillary Contactor	3	3
20	B. L. Knutson	Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY, USA	Capillary Contactor	5	2
21	R. Wang	Institute of Materials Research and Engineering, Singapore, Singapore	Capillary Contactor	2	2
22	Z. K. Xu	Institute of Polymer Science, Zhejiang University, Hangzhou, Peop. Rep. China	Capillary Contactor	2	2

Support	Method	x	X/N ₂	Selectivity K/CO ₂	X/CH₄	X permeability (barrers) ^a	X permeance (10-8 mol/s/m2/Pa)	Reference
Mullite	no treatment	H_2	~ 2.5-4.0 at 823 K	~ 3.0-5.0 at 823 K	~ 2.0-3.0 at 823 K		720 at 823 K	[153,154]
Mullite	TEOS, sol-gel/coating	H_2	~ 2.7-3.7 at 823 K	~ 3.2-4.7 at 823 K	~ 2.0-2.8 at 823 K		250-430 at 823 K	[153,154]
γ-alumina	no treatment	H_2			~ 2.2 at 873-923 K		2100-2200 at 873-923 K	[150]
γ-alumina	TEOS, CVD for 2h at 873 K	H_2		~ 8.0 at 873 K	~ 8.0 at 873 K		100 at 873 K	[150]
γ-alumina	TEOS, CVD for 4h at 873 K	H_2		~ 55.0 at 873 K	~ 85.0 at 873 K		50 at 873 K	[150]
γ-alumina	TEOS, CVD for 4.5h at 873 K	H_2		~ 180.0 at 873 K	~ 300.0 at 873 K		30 at 873 K	[150]
γ-alumina	TEOS, CVD for 1h at 923 K	H_2		~ 14.0 at 923 K	~ 14.0 at 923 K		120 at 923 K	[150]
γ-alumina	TEOS, CVD for 1.7h at 923 K	H_2		~ 180.0 at 923 K	~ 280.0at923K		30 at 923 K	[150]
γ-alumina	Zeolite, SiO ₂ :Al ₂ O ₃ :Na ₂ O (9:10:22.5), sol gel	H_2			~ 2.0-1.7 at 573-973 K		-	[152]
Vycor glass	no treatment	H_2		~ 4.26 at 873 K	~ 2.76 at 873 K		4 at 873 K	[147,148]
γ-alumina	Zeolite, SiO ₂ :Al ₂ O ₃ :Na ₂ O (9:10:22.5), sol gel	H_2		5.5-3.5 at 298-973 K	9.5-4 at 298-973 K		55-20 at 298-973 K	[151]
γ-alumina	Ru, 1 deposited layer	H_2	~ 2.8 at 773 K				3490 at 773 K	[175]
γ-alumina	Ru, 2 deposited layers	H_2	~ 2.4 at 773 K				1800 at 773 K	[175]
alumina	TEOS+MTES, hydrophobic, sol-gel/coating	H ₂		~ 3.0-6.0 at 298-473 K			90-130 at 298-473 K	[157]
alumina	TEOS+MTES, hydrophilic, sol-gel/coating	H ₂		~ 2.0-3.0 at 298-473 K			0.37-0.15 at 298-473 K	[157]
γ-alumina	TEOS. sol-gel/coating	H ₂	~ 20 at 473 K	~ 5 at 473 K			5 at 473 K	[176]
γ-alumina	TEOS+organic surfactant. sol-gel/coating	H ₂	~ 15 at 473 K	~ 5 at 473 K			2 at 473 K	[176]
α-alumina	TEOS. sol-gel/coating	H ₂	~ 3.9-2.7 at 673 K				89-120 at 673 K	[177]
α-alumina	TEOS. sol-gel/coating+1 to 5 times Pd acetate soaking and VD	H ₂	~ 4.0-11.0 at 673 K				~ 2.7-6 at 673 K	[177]
Si ₃ N ₄	Polysilizane (PSZ), coating	H ₂	~ 83-141 at 423-573 K	~55-93 at 423-573 K	~ 205-325 at 423-573 K		0.35-1.3 at 423-573 K	[178]
α-alumina	TEOS, CVD for 2-3h at 600 oC, sol-gel/coating	H ₂	~ 40-50 at 673 K				40-50 at 673 K	[179]
α-alumina	TEOS. CVD for 2.5h at 600 °C, sol-gel/coating+ evacuation	H _a	~ 4 at 673 K				1.3 at 673 K	[179]
Stainless Steel	TEOS, sol-gel/coating	H _a	> 110 at 523 K	> 101 at 523 K			~200 at 523 K	[180]
α-alumina	Polydimethylsilane+aluminum acetylacetonate, coating+Pyrolisis at 573K	H _a	~ 13-4 at 298-473 K		~ 10-4 at 298-473 K		0.5-1.0 at 298-473 K	[181]
α-alumina	Polydimethylsilane+aluminum acetylacetonate, coating+Pyrolisis at 773K	H _a	~ 5 at 298-473 K		~ 5-4 at 298-473 K		0.2-0.65 at 298-473 K	[181]
α-alumina	Polydimethylsilane+aluminum acetylacetonate, coating+Pyrolisis at 973K	H _a	~ 6-2 at 298-473 K		~ 6-2 at 298-473 K		0.08-0.11 at 298-473 K	[181]
Carbon Molecular Sieve	no treatment	Н.	~ 16 5 at 473-673 K		~ 2-4 at 473-673 K		~8.0-9.0 at 473-673 K	[182]
α-alumina	PdEDTA ²⁻ dispersed in v-alumina, sol-gel/coating	н.	>1000 at 703 K		2 141 110 010 11		~86-124 at 703 K	[114]
Vycor-4nm	no-treatment	H.	3.9 at 523 K		2.9 at 523 K		1.62 at 523 K	[153,154]
a-alumina	TEOS sol-gol costing, catalutic membranes	2	0.0 41 020 11		17-27 at 573-773 K		20-30 at 573-773 K	[145]
a-alumina a-alumina		П ₂		45 at 570 770 K	~ 17-27 at 573-773 K		20-30 at 573-773 K	[145]
α-alumina	TEOS, sol-gel coating, catalytic membranes	H ₂		15 at 573-773 K	4/ at 5/3-//3 K		200 at 573-773 K	[158]
	TEOS+ZTBO, sol-gel coaling	n ₂	~83-70 at 573-773 K	~7-23 at 573-773 K	~27-35 at 573-773 K		700-500 at 573-773 K	[144]
	TEOS+21BO, sol-gel coaling+ horotreatment	n ₂	50-200 at 573-773 K	50-200 at 573-773 K	50-200 at 573-773 K	12 10 at 522 K	170-50 at 573-773 K	[144]
Polybenzimidazole		H ₂		~ 6-20 at 523 K		~ 13-18 at 523 K		[183]
alumina	Ru, CVD	H_2	6.5 at 773 K				345 at 773 K	[109,110]
alumina	Pt, CVD	H_2	280 at 773 K				286 at 773 K	[109,110]
alumina	Pd, CVD	H_2	13 at 773 K				325 at 773 K	[109,110]
alumina	Pd (8 μm), electroless-plating	H_2	inf.				345 at 773 K	[109,110]
α-alumina	Pd-Cu, electroless deposition, 4 µm	H_2	11-63 at 723 K				28-110 at 723 K	[184]
Polyimide	N2 Pyrolysis at 973 K for 3.6 min	H_2	~ 100 at 353 K	~ 6 at 353 K	~ 130 at 353 K		~33.4-54 at 353 K	[185]
Polyimide	N2 Pyrolysis at 1123 K for 3.6 min	H_2	~ 215 at 353 K	~ 14 at 353 K	~ 630 at 353 K		~6 -10 at 353 K	[185]
Polyimide	Pyrolysis, vacuum	H_2	~ 64-110 at 823 K				12.5-15.8 at 823 K	[186]
Polyimide	Pyrolysis, Ar, He or CO2	H_2	~ 7.0-35.0 at 823 K				13.5-25 at 823 K	[186]
α-alumina	γ-alumina+polycarbosilane pyrolyzed at 823	H_2	~ 2.5 at 283 K	~ 1.0 at 283 K			~130 at 283 K	[187]
α-alumina	γ-alumina+polycarbosilane pyrolyzed at823	H_2	~ 4.5 at 573 K	~ 2.7 at 573 K			~ 80 at 573 K	[187]
α-alumina	γ-alumina+polycarbosilane pyrolyzed at 673	H_2	~ 14.5 at 573 K	~ 4 at 573 K			~ 8 at 573 K	[187]

Table 1.15. Performance of various state-of-the-art hydrogen selective membranes in terms of selectivity and permeability.

Hydrogen Production: Chemical and Petrochemical Industries

^aA 1 µm thick membrane with a permeability of 1 barrer will present a permeance of 3.346x10-10 mol s⁻¹ m⁻² Pa⁻¹.

Table 1.16.	Performance of various state-of-the-art hydrogen and carbon dioxide selective (in gray) membranes in terms of
	selectivity and permeability.

Support	Method	х		Selectivity		X permeability	X permeance	Reference
			X/N ₂	X/CO ₂	X/CH ₄	(barrers)	(10-8 mol/s/m2/Pa)	
Polyimide	casting	He	95.4 at 308 K	2.49 at 308 K	3.03 at 308 K	20.8 at 308 K		[188]
Polyimide	Polyimide/2,4,6-triaminopyrimidine mixed-matrix, casting	He	1281.2 at 308 K	14.79 at 308 K	1242.4 at 308 K	2.87at 308 K		[188]
Polyimide	Polyimide/4A zeolite mixed-matrix, casting	He	44 at 308 K	2.14 at 308 K	4.77 at 308 K	20 at 308 K		[188]
Polyimide	Polyimide/13X zeolite mixed matrix, casting	He	39.7 at 308 K	1.6 at 308 K	11 at 308 K	53.5 at 308 K		[188]
Polyimide	Polyimide/4A zeolite/2,4,6-triaminopyrimidine mixed-matrix,casting	He	1281.8 at 308 K	12.54 at 308 K	7733.33 at 308 K	2.32 at 308 K		[188]
Polyimide	Polyimide/13X zeolite/2,4,6-triaminopyrimidine mixed-matrix, casting	He	563 at 308 K	7.77 at 308 K	1012.5 at 308 K	4.87 at 308 K		[188]
Polysulfone	Silicone, coating for 6-10 min	H_2	~20-51 at 323 K				0.89-1.39 at 323 K	[189]
alumina	Polyimide/silica(AprTMOS) mixed matrix w/wo TMOS sol-gel coating	H ₂	~4-9 at 363 K	~6-7 at 363 K		~11-18 at 363 K		[190]
alumina	Polyimide/silica(AprTMOS) mixed matrix w/wo TMOS sol-gel coating	H_2	~10-17 at 463 K	~6-12 at 463 K		~21-45 at 463 K		[190]
alumina	Polyimide/silica(AprMDEOS) mixed matrix w/wo TMOS sol-gel coating	H_2	~14-23 at 363 K	~3-5 at 363 K		~52-63 at 363 K		[190]
alumina	Polyimide/silica(AprTMOS) mixed matrix w/wo TMOS sol-gel coating	H_2	~21-28 at 463 K	~4-8 at 463 K		~100-160 at 463 K		[190]
Polyethersulfone	no treatment	H_2	~7.5-21 at 303 K				~8.5-2.1 at 303 K	[191]
alumina	styrene-divinylbenzene(Amberlite) in PPO+Chloroform	H_2			~6.5 at 333 K	450-600 at 333 K		[161]
alumina	styrene-divinylbenzene(Lewatit) in PPO+Chloroform	H_2			~10-40 at 333 K	1800-3900 at 333 K		[161]
alumina	ethylene dimethacrylate (Poly(EDMA) in PPO+Chloroform	H_2			~10-20 at 333 K	300 at 333 K		[161]
alumina	styrene-divinylbenzene(Hyp-St-DVB) in PPO+Chloroform	H_2			~66-300 at 333 K	1200-1800 at 333 K		[161]
Poly(aryl ether ketone), PEK-C	casting	H_2	~80-50 at 298-373K	~4-8 at 298-373K	~146-71 at 298-373K	~11-32 at 298-373K		[192]
Poly(aryl ether ketone), DMPEK-C	casting	H_2	~91-54 at 298-373K	~4-8 at 298-373K	~125-81 at 298-373K	~10-30 at 298-373K		[192]
Poly(aryl ether ketone), TMPEK-C	casting	H_2	~117-64 at 298-373K	~4-5 at 298-373K	~130-75 at 298-373K	~21-45 at 298-373K		[192]
Poly(aryl ether ketone), IMPEK-C	casting	H_2	~38-30 at 298-373K	~2-4 at 298-373K	~45-35 at 298-373K	~42-70 at 298-373K		[192]
PolyAmide-Imides	mPda/DAM, various ratios (1-8)	He	~452-76 at 303K	~14-2 at 303K		~3-37 at 303K		[193]
PolyAmide-Imides	1.5NaPda/DAM, various ratios (1-8)	He	~162-75 at 303K	~5-2 at 303K		~8-37 at 303K		[193]
PolyAmide-Imides	1.5NaPda/DETDA, various ratios (1-8)	He	~200-30 at 303K	~7-1 at 303K		~7-34 at 303K		[193]
Polysulfone	casting	H_2	~46 at 298K	~1.8 at 298K	~50 at 298K	11 at 298 K		[193]
PolyAmide-Imides	mPda/DAM (1-1)+LiCI (various contents)	He	~130-387 at 303K	~4-15 at 303K		~16-5 at 303K		[166]
ZSM-5-18A	sol-gel	H ₂		0.83 at 298K			24 at 298K	[194]
ZSM-5-21A	sol-gel	H_2	1.45 at 298K	0.53 at 298K	1.70 at 298K		26 at 298K	[194]
ZSM-5-22A	sol-gel	H ₂	1.43 at 298K	0.34 at 298K	3.20 at 298K		20 at 298K	[194]
ZSM-5-22B	sol-gel	H_2		0.59 at 298K			29 at 298K	[194]
ZSM-5-28*A	sol-gel	H_2	1.2 at 298K	0.37 at 298K	2.60 at 298K		19 at 298K	[194]
Poly(1-trimethylsilyl-1-propyne), PTMSP	casting	H_2	.92 at 298K	0.45 at 298K		~19000 at 298 K		[167]
Poly(1-methyl-1-pentyne), PMP	casting	H_2	2.43 at 298K	0.54 at 298K	2 at 298K	5800 at 298 K		[166]
Poly(tert-butylacetylene), PTBA	casting	H_2	7 at 298K	0.53 at 298K	3.52 at 298K	300 at 298 K		[166]
α-alumina	γ -alumina+polycarbosilane pyrolyzed at 673	H_2	~ 6 at 283 K	~ 0.6 at 283 K			~ 6 at 283 K	[187]
Teflon	casting	H ₂	4.2 at 298K	0.92 at 298K	5.2 at 298K	3300 at 298 K		[195]
TFE-BDD copolymer	casting	H_2	4.3 at 298K	0.79-0.95 at 298K	5.3-6.4 at 298K	2100-3400 at 298 K		[165]
Vycor	HDFS, sol-gel coating	H_2	1.51 at 293K	0.24 at 293K	0.92 at 293K			[172]
γ-alumina	ODS, sol-gel coating	H_2	3.4 at 293K	0.67 at 293K	1.4 at 293K		1.3 at 293K	[173]
Air products SSF membrane		H_2		0.2 at 293K		3.5 at 293K		[171]

^aA 1 µm thick membrane with a permeability of 1 barrer will present a permeance of 3.346x10-10 mol s⁻¹ m⁻² Pa⁻¹.
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Glossary

ANL, Argonne National Laboratory atm, Atmosphere ATR, Autothermal Reformer btu, British Thermal Unit cm, centimeter CVD, Chemical Vapor Deposition hr, hour HT, High Temperature HTIcs, Hydrotalcite compounds KJ, kilojoule LT, Low Temperature MDEA, methyldiethanolamine MEA, monoethanolamine MM, Million (10^6) m, meter ml, milliliter mm, millimeter NETL, National Engineering Testing Laboratory µm, micron Pa, Pascal POX, Partial Oxidation ppmy, parts per million by volume PSA, Pressure Swing Adsorption psia, pounds per square inch, atmosphere psig, pounds per square inch, gauge RWGS, Reverse Water Gas Shift s, second scf, standard cubic feet scfd, standard cubic feet day SER, Sorption Enhanced Reaction SERP, Sorption Enhanced Reaction Process SMR, Steam Methane Reformer SSF, Selective Surface Flow STP, Standard Temperature and Pressure TSA, Temperature Swing Adsorption vol %, volume per cent VSA. Vacuum swing adsorption WGS. Water Gas Shift Reactor